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EP-A- 385 522	**EP-A- 0 151 884**
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EP-A- 0 346 995	**EP-A- 0 415 698**
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Description

The present invention is concerned with aqueous liquid detergent compositions which contain sufficient detergent-active material and, optionally, sufficiently dissolved electrolyte to result in a structure of lamellar droplets dispersed in a continuous aqueous phase.

Lamellar droplets are a particular class of surfactant structures which, inter alia, are already known from a variety of references, e.g. H.A.Barnes, 'Detergents', Ch.2. in K.Walters (Ed), 'Rheometry: Industrial Applications', J. Wiley & Sons, Letchworth 1980, FR-A-2426731, GB-A-2023637, GB-A-2031941 and EP-A-301884.

Such lamellar dispersions are used to endow properties such as consumer-preferred flow behaviour and/or turbid appearance. Many are also capable of suspending particulate solids such as detergency builders or abrasive particles. Examples of such structured liquids without suspended solids are given in US patent 4 244 840, whilst examples where solid particles are suspended are disclosed in specifications EP-A-160 342; EP-A-38 101; EP-A-104 452 and also in the aforementioned US patent 4 244 840. Others are disclosed in European Patent Specification EP-A-151 884, where the lamellar droplet are called 'spherulites'.

The presence of lamellar droplets in a liquid detergent product may be detected by means known to those skilled in the art, for example optical techniques, various rheometrical measurements, X-ray or neutron diffraction, and electron microscopy.

Non pre-published EP-A-346 995 describes structured liquids comprising a deflocculating polymer. Formulation 12 comprises also triethanolamine.

Non pre-published EP-A-415 698 describes structured fabric softening liquids comprising a deflocculating polymer. These compositions have a pH of less than 6.0 and an electrolyte/isopropanol ratio lower than 1:1.

The droplets consist of an onion-like configuration of concentric bi-layers of surfactant molecules, between which is trapped water or electrolyte solution (aqueous phase). Systems in which such droplets are close-packed provide a very desirable combination of physical stability and solid-suspending properties with useful flow properties.

The viscosity and stability of the product depend on the volume fraction of the liquid which is occupied by the droplets. Generally speaking, when the volume fraction is around 0.6, the droplets are just touching (space-filling). This allows reasonable stability with an acceptable viscosity (say no more than 2.5 Pas, preferably no more than 2.0 Pas, more preferably no more than 1 Pas at a shear rate of $21s^{-1}$). This volume fraction also endows useful solid-suspending properties.

A problem in the formulation of liquid detergent compositions is to have a relatively high volume fraction of lamellar droplets without the occurence of flocculation of the droplets. When flocculation occurs between the lamellar droplets at a given volume fraction, the viscosity of the corresponding product will increase due to the formation of a network throughout the liquid. Flocculation may also lead to instability reflected in phase separation of the product.

It is an object of the invention to minimise the physical instability of liquid detergent compositions of the lamellar droplet type. Surprisingly it has now been found that active-structured detergent compositions which are physically unstable due to the above described flocculation effect and/or a low volume fraction of lamellar droplets, can be made more stable by the incorporation of low levels of hydrotroping agents.

A second aspect of the present invention is the discovery that low levels of hydrotroping agents can be used for the stabilisation of active structured liquid detergent compositions.

In formulating liquid detergent compositions, it is sometimes desirable to include hydrotroping materials; these materials may for example be included for providing secondary benefits, for example anti-wrinkling properties or perfume benefits or for providing other benefits such as a decrease in solubility of certain ingredients which may be prone to decomposition in solubilised form.

It is well-known in the art to incorporate high levels, typically about 5 % by weight or more of hydrotroping materials in aqueous liquid detergent compositions. The obtained compositions are of isotropic nature, i.e. all detergent active materials are homogeneously dispersed. These liquid do not comprise a dispersion of lamellar droplets in an aqueous phase. Also these liquids do generally not have solid suspending properties. Thus up till now it has been believed that the incorporation of relatively high levels of hydrotroping materials in liquid detergent compositions inevitably results in the formation of an isotropic product at the expense of many advantages, including solid suspending properties.

Therefore a problem in using hydrotroping materials in liquid detergent compositions of the lamellar droplet type is that the hydrotroping materials tend to "dissolve" the detergent active materials from the lamellar droplets into the aqueous phase, therewith possibly reducing the physical stability and/or solid suspending properties.

It has now been found that the use of relatively high levels of hydrotroping materials in liquid detergent compositions of the lamellar droplet type is possible, when the hydrotroping materials are used in combination with an effective amount of a salting-out electrolyte.

Accordingly, the present invention relates to a physically stable liquid detergent composition comprising a dispersion of lamellar droplets of detergent active materials in an aqueous continuous phase, with solid-suspending properties, said composition comprising a salting-out electrolyte and from 0.05 to 20 % by weight of a hydrotroping material, other than glycerol and triethanolamine, the weight ratio of salting out electrolyte to hydrotrope being from 20:1 to 1:1, said composition providing a pH within the range of 7.5 to 12.5.

Compositions of the invention are physically stable. Furthermore compositions according to the invention which contain low levels of hydrotroping materials are preferably physically unstable in the absence of hydrotropes. 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 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.

Liquid detergent compositions according to the invention are preferably volume stable in that they show less than 25 %, preferably less than 10 %, more preferably less than 5 % volume increase during storage at a temperature between 20 and 37°C for a period for three months after preparation.

For the purpose of this invention a hydrotroping material is a component, which, when added to a standard lamellar droplet type liquid detergent compositions, in a large amount (say 5% by weight) without the addition of an effective amount of salting-out electrolyte, destabilises the dispersed lamellar phase, therewith causing the -at least partly-breaking down of this phase into an L_2, active rich L_1 or isotropic micellar structure. L_2 and L_1 phases are for example described by G.J.T. Tiddy, in Physical Reports 57, No 1 (1980) 1-46. The presence of such an isotropic micellar structure may in some instances be evidenced by the forming of a separate isotropic phase; also possible is that the micellar structure is present in the continuous aqueous base of the product, then the presence may be evidenced by the fact that the aqueous phase -when isolated-contains more than 1% by weight of surfactant materials.

For the purpose of the present invention the preferred standard composition for distinguishing between hydrotroping materials and non-hydrotroping materials has the following formulation:

Ingredient	wt parts
Na Las	28
Synperonic A7	12
Na-Citrate	5-10
Water	60

The level of Na-Citrate in the standard composition is at least 5 parts by weight, more preferably however the level of Na-Citrate is 10 parts by weight.

Suitable hydrotroping materials for use in compositions of the present invention may for example be selected from the class of hydrotroping materials which have hitherto been suggested for use in isotropic detergent compositions. Examples of suitable materials are:

(i) the alkali metal aryl sulphonates, preferably the sodium aryl sulphonates for example sodium xylene sulphonate, sodium toluene sulphonate, sodium cumene sulphonate, sodium tetralin sulphonate, sodium naphtalene sulphonate and the short chain alkyl derivatives thereof;
(ii) mono- or di-hydric alcohols or derivatives thereof such as lower alcohols such as ethanol or isopropanol, propyleneglycol, ethylene glycol; alcohol derivatives such as mono- or triethanolamine or 1,2 propylene glycol dibuthyl ether; and higher alcohols, such as C3-10 alcohols preferably having a carbon chain length which is at least 4 carbon atoms shorter than the average chain length of the hydrocarbyl chain of the surfactant materials used in the composition;
(iii) hydrocarbon materials such as for example C_{8-12} parafins (e.g. SHELL SOLT ex SHELL), preferably for these materials the carbon chain length of the hydrocarbon chain being at least 2 carbon atoms shorter than the average chain length of the hydrocarbyl chain of the surfactants used in the composition;
(iv) organic solvent materials such as limonene, linalool, benzyl alcohol, diglyme, dibuthyl phtalate and terpene.

Also mixtures of two or more hydrotroping agents may be used. For the purpose of this invention glycerol is not a hydrotroping agent. Preferred hydrotroping materials are the lower alcohols such as ethanol.

The level of hydrotroping material in compositions of the present invention can be varied as described hereinbefore within a range of from 0.5 - 200% by weight. At low electrolyte levels the preferred levels of hydrotroping materials are in the range from 0.05 to 4.0 % by weight of the composition, more preferably up to 1.0 %. For use in combination with relatively high levels of salting-out electrolytes, the preferred level of hydrotroping materials is at least 1.0 % by weight, more preferably at least 4.0%.

Compositions of the invention also comprise detergent active materials, preferably at a level of from 1 to 70% by weight of the composition, more preferably from 5 to 50 % by weight, most preferably from 10 to 40 % by weight.

In the case of blends of surfactants, the precise proportions of each component which will result in such stability and viscosity 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 detergent-active 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, subclasses and specific materials described in 'Surface Active Agents' Vol.1, 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 alkylene 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 ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

Also possible is the use of salting-out resistant active materials, such as for example described in EP-A-328 177, especially the use of alkyl polyglycoside surfactants, such as for example disclosed in EP-A-70 074.

Preferably the level of nonionic surfactants is more than 1 % of the composition, more preferably from 2.0 to 20.0% by weight of the composition, most preferably from 3.0 to 6.0 %. Especially preferred nonionic materials for use in compositions of the present invention are ethoxylated alcohols comprising from 2 to 10 EO groups. Advantageous materials are for instance Synperonic A7, Synperonic AS and Synperonic A3 (ex ICI) or mixtures thereof.

Compositions of the present invention preferably contain 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 8 to 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent 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 glyceryl 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-C_{20}) with sodium bisulphite and those derived from reacting paraffins with SO_2 and Cl_2 and then hydrolyzing with a base to produce a random sulponate; 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 hydrolyzing the reaction product. The preferred anionic detergent compounds are sodium (C_{11}-C_{15}) alkyl benzene sulphonates and sodium and potassium primary (C_{10}-C_{18}) alkyl sulphates.

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, 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.

The compositions also contain a salting-out electrolyte.

In a preferred embodiment of the invention the salting-out electrolyte is present in an effective amount. This effective amount can be determined by adjusting the amount of electrolyte while keeping the relative amounts of the other ingredients constant. The effective amount of electrolyte in the level wherein the detergent active materials are predominantly present in the lamellar droplets and not in micellar form and wherein the composition is preferably physically stable. Preferably the level of electrolyte is chosen such that after centrifuging the composition for 17 h at 750 G the level of surfactant in the aqueous phase is less than 5% by weight, more preferably less than 2%, most preferably less than 1%.

The level of salting-out electrolytes is preferably from 1 to 50 % by weight. More preferably the level of salting-out electrolytes is from 5 to 45%, most preferably from 10 to 35 % by weight. Salting-out electrolyte has the meaning ascribed to in specification EP-A-79 646, that is those materials having a lyotropic number of less than 9.5. Optionally, some salting-in electrolyte (as defined in the latter specification) may also be included.

Preferred salting-out electrolytes are for example citrates, borates, formates and tripolyphosphates. Preferred salting-in electrolytes are NaCl and No-acetate. 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.

Examples of phosphorus-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.

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.

It has been found that the stabilising effect of the hydrotroping agent is especially noticeable in compositions containing zeolite builders, especially in compositions containing high levels of zeolite builders, for example of from 10 to 30 % by weight of the compositions, more preferred from 15 to 20%.

In the context of inorganic builders, we prefer to include electrolytes which promote the solubility of other electrolytes, for example use of potassium salts to promote the solubility of sodium salts. Thereby, the amount of dissolved electrolyte can be increased considerably (crystal dissolution) as described in UK patent specification GB 1 302 543.

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, tartrate mono succinate, tartrate disuccinate and citric acid.

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-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. Surprisingly it has been found that the effectiveness of these polymer builder polymers is enhanced due to the presence of low levels of hydrotroping materials as presently claimed.

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 100ml 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 301,883. Typical levels are from 0.5 to 4.5% by weight.

The viscosity of compositions according to the present is preferably less than 2500 mPas, especially preferred less than 2000 mPas, more preferred less than 1500 mPas, most preferred between 30 and 1000 mPas at 21 s^{-1}.

One way of regulating the viscosity and stability of compositions according to the present invention is to include viscosity regulating polymeric materials.

Viscosity and/or stability regulating polymers which are preferred for incorporation in compositions according to the invention include deflocculating polymers having a hydrophilic backbone and at least one hydrophobic side chain. Such polymers are for instance described in our copending European application 89201530.6. (EP-A-346 995).

The compositions of the invention have solid suspending properties, preferably they do not yield any visible sedimentation after storage for 3 weeks at 21°C when 10% of a solid particulate material e.g. calcite or zeolite is incorporated.

Compositions of the invention preferably contain from 10-80% by weight of water, more preferably 15-60%, most preferably 20-50%.

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, fabric softeners such as clays, amines and amine oxides, 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), germicides and colourants.

An especially preferred embodiment of the present invention relates to the combined use of bleach ingredients and hydrotroping materials in liquid detergent compositions of the lamellar droplet type. Surprisingly it has been found that the use of relatively high levels of hydrotroping materials enhances the stability of the bleach ingredient, especially when partially insoluble bleaches such as sodium perborate are used. Preferably the level of bleach material, especially of peroxygen bleach material, more preferably of perborate or percarbonate bleach material is from 1- 25 % by weight of the composition, more preferred from 3- 20 %, most preferred from 5 - 15 %.

Preferably when bleach materials are used in combination with hydrotroping materials, the following provisos apply:

(a) if the hydrotroping material is a C_{1-5} polyhydric alcohol used at a level of from 1-20 % of the composition, then the composition does not comprise a bleach material in combination with a metaborate electrolyte; and
(b) if the composition comprises minor amounts of hydrotrope other than water-miscible solvents, then the composition does not comprise a peroxygen bleach compound and shows less than 25 % volume increase when stored at 20-37°C for three months.

In another preferred embodiment of the invention, compositions comprise salting-out electrolyte, water and hydrotrope, wherein the weight ratio of water to hydrotrope is between 20:1 and 1:1, more preferably between 10:1 and 3:1. The weight ratio of salting-out electrolyte to hydrotrope is from 20:1 to 1:1, preferably from 10:1 to 2:1, more preferably from 8:1 to 4:1. The weight ratio of water to electrolyte is preferably from 10:1 to 1:1, more preferably 8:1 to 2:1, most preferably 6:1 to 4:1.

Compositions of the invention may be prepared by any conventional method for the preparation of liquid detergent compositions. A preferred method involves the dispersing of the electrolyte ingredient together with the minor ingredients except for the temperature sensitive ingredients -if any- in water of elevated temperature, followed by the addition of the builder material, the hydrotroping material and the detergent active material under light stirring and finally cooling the mixture and adding any temperature sensitive minor ingredients such as enzymes, perfumes etc.

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.

To ensure effective detergency, the liquid detergent compositions should be alkaline, and it is preferred that they should provide a pH within the range of 8.5 to 12, preferably 9 to 11, when used in aqueous solutions of the composition at the recommended concentration. To meet this requirement, the undiluted liquid composition should also be of a pH above 7, for example pH 7.5 to 12.5. It should be noted that an excessively high pH, e.g. over pH 13, is less desirable for domestic safety. If hydrogen peroxide is present in the liquid composition, then the pH is generally from 7.5 to 10.5, preferably 8 to 10, and especially 8.5 to 10, to ensure the combined effect of good detergency and good physical and chemical stability. The ingredients in any such highly alkaline detergent composition should, of course, be chosen for alkaline stability, especially for pH-sensitive materials such as enzymes, and a particularly suitable proteolytic enzyme. The pH may be adjusted by addition of a suitable alkaline material. The invention will now be illustrated by way of the following Examples. In all Examples, unless stated to the contrary, all percentages are by weight.

Synperonic, Shell Solt, Sokalan, bequest and Tinopal are trade marks.

EXAMPLE I

Liquid detergent compositions of the following formulation were prepared by heating the water to 50°C and mixing the fluorescer, the calcium chloride, Dequest, silicone, glycerol, borax and the hydroxide into the liquid, followed by the addition of the zeolite material and the SXS material. A premix of the ABS material and the Synperonic material is added to the system under stirring. The pH of the product is adjusted to about 7.5. Finally the product is cooled to ambient temperature and the remaining ingredients are added and the product is stored for three weeks at 25°C.

Ingredient % wt	formulation	
	A	B
ABS*)	7.2	7.2
Synperonic 7EO	4.8	4.8
Zeolite**)	20.0	20.0
Sokolan CPT***)	2.5	2.5
polyacrylate PA 50	0.2	0.2
Glycerol	8.0	8.0
Borax	5.7	5.7
$CaCl_2$	0.15	0.15
enzymes	0.48	0.48

*)linear alkyl benzene sulphonate (SIRENE X12 L)
**) Wessalith P
***) ex BASF

(continued)

Ingredient % wt	formulation	
	A	B
Dequest 2060S	0.6	0.6
fluorescer	0.05	0.05
Silicone Q2 3300	0.35	0.35
NaOH	2.0	2.0
Perfume	0.3	0.3
SXS****)	---	0.4

****) sodium xylene sulphonate

Compositions A and B were both lamellar structured liquid detergent compositions having solid suspending properties. Composition A, outside the scope of the present invention, had direct after preparation a viscosity of 1270 mPas at 21 s^{-1}. After three weeks storage at 25 C the compositions showed 10 % by volume phase separation. Composition B according to the invention had an initial viscosity of 890 mPas at 21 s^{-1} and showed no visible phase separation after storage for three weeks at 25°C.

EXAMPLE II

The following compositions were prepared as in Example 1.

Ingredient	% wt	
Tap water	Balance	
fluorescer	0.05	0.05
Ca chloride	0.3	0.3
Sodium hydroxide	3.7	3.7
Citric acid 1aq	2.5	2.5
Dequest 2060 S	1.2	1.2
Glycerol	5.0	6.5
Borax	4.0	4.0
Silicone Q 23300	0.35	0.35
Zeolite (wessalith P)	25.0	25.0
SXS	0.45	0.9
ABS	7.0	7.0
Synperonic 3EO	1.2	1.2
Synperonic 7EO	3.6	3.6
Savinase	0.5	0.3
Amylase	0.2	0.2
Perfume	0.3	0.3
Sokalan PA50	0.3	0.5

Both compositions were stable liquid detergents having a lamellar structure. The corresponding compositions minus the hydrotroping material were physically unstable (some phase separation upon storage).

Example III

The following compositions were made by mixing the ingredients in the order as indicated.

Component	Composition (in parts by weight)			
	1	2	3	4
ABS	<-------------28-------------->			

(continued)

Component	Composition (in parts by weight)			
	1	2	3	4
Synperionic A7	<-------------12-------------->			
Water	<-------------60-------------->			
Na-citrate	<-------------10-------------->			
Ethanol physical Stability	0 unstable	2.5 stable	5.0 unstable	10 unstable

This example illustrates that low levels of hydrotroping materials can have a stabilising effect on liquid detergent compositions of the lamellar droplet type, while higher levels of hydrotroping material may cause physical instability due to the breaking of the lamellar structure.

Example IV

The following formulation was prepared by adding the ingredients to water in the order listed.

Ingredient (wt parts)	A	B	1	2
Na LAS	28	28	28	28
Synperonic A7	12	12	12	12
water	60	60	60	60
Na-citrate	10	10	20	20
polymer[1])	-	-	1	1
ethanol	-	5	5	10
physically stable ?	just unstable	no	yes	just stable
Isotropic active rich phase present?	no	yes	no	no

[1]) polymer A-11 as described in EP-A-346 995.

Example V

The following compositions were made by adding the ingredients in the listed order to water under stirring.

Ingredient (% wt)	1	2
Na LAS	28	28
Synperonic A7	12	12
Na-citrate	10	10
borax	3.5	3.5
Glycerol	5	5
monoethanolamine	2	4
triethanolamine	2	4
savinase	0.3	0.3
Tinopal CBS-X	0.1	0.1
polymer[1])	1	1
water	<----balance---->	
stable ?	yes	yes
Isotropic active rich phase present ?	no	no

1) Polymer A-11 as described in EP-A-346 995

Example VI

The following compositions were prepared by adding the electrolyte together with the minor ingredients except for the perfume and the enzymes to water of elevated temperature, followed by the addition of the detergent active material as a premix under stirring and thereafter cooling the mixture and adding the enzymes, perfumes and the bleach.

INGREDIENT (% WT)	A	B
Na-Dobs	21	21
Synperonic 7	9	9
Glycerol	--	3.5
Metaborate	2.6	2.6
Nacitrate/ Citric acid[1])	9.8	9.8
Dequest 2060S (as 100%)	0.4	0.4
Na-perborate tetrahydrate[3])	20	20
Enzyme, Alcalase	0.8	0.8
$CaCl_2.2H_2O$	0.2	0.2
Fluorescer, Tinopal CBSX	0.1	0.1
Silicon, Dow Corning DB100	0.3	0.3
Perfume	0.3	0.3
deflocculating polymer[4])	1	1
ethanol	2.5	2.5
water	balance	
pH	9	9

[1]) This mixture is used to adjust the final pH.

[2]) Expressed as % of analyzed enzyme level in the fresh sample.

[3]) As 100 % perborate, added as a dispersion (Proxsol ex ICI, approximate 65% perborate dispersion in water with an average perborate particle size of 40 micrometer).

[4]) Deflocculating polymer of formula I of EP-A-346 995, wherein x=50, y=0, R^5=H, R^6=CH_3, R^1= -CO-O, R^2 and R^3 are absent, R^4= $-C_{12}H_{25}$, mW= 7,500.

5) wt% -approximate- of total perborate, obtained by removal of the undissolved bleach particles by mild centrifugation.

6) Not measured

The obtained products had the following characteristics:

	A	B
Volume stability (% volume increase, 3 months 25 °C)	0	0
clear layer separation (3 weeks 37 °C)	no	no
solid sedimentation (3 weeks 37 °C)	no	no
Viscosity 21 s^{-1}	800	850
dissolved perborates[5])	1.5	3
bleach activity (2 months ambient T)	98	98
enzyme activity (2 months ambient T)[2])	83	70

[2]) Expressed as % of analyzed enzyme level in the fresh sample.

5) wt% -approximate- of total perborate, obtained by removal of the undissolved bleach particles by mild centrifugation.

Comparative examples

A composition as described in example IX of EP-A-293 040 (P&G) was prepared by adding the following ingredients in the order listed under stirring:

Ingredient	% wt
Water	32
Ethanol	5
butyldiglycolether	5

(continued)

Ingredient	% wt
Linear DOBS	13
Nonionic	3.5
Sodium cocoylsulfate	3.0
coconut fatty acid	1
oleic acid	2
EDTA	1
STP	15
sodium perborate.H_2O	13
sodium formate	1
protease	0.5
sodium hydroxide to pH	11
perfume/minors	balance

When the composition was made under normal stirring conditions, the resulting product was pasty to very viscous, while the bleach ingredient caused an unacceptable degree of moussing; when the composition was made under gentle stirring conditions, the viscosity of the final product was 2370 mPas at 21 s^{-1} and the product was volume instable (20-25 % volume increase after storage for 1 week at 37°C) and physically unstable (7 % phase separation after storage for 1 week at 37°C, some phase separation after storage for 1 week at ambient temperature). This example illustrates that compositions as disclosed in EP-A-293 040 are difficult to reproduce and suffer from an unacceptable high viscosity and/or volume instability and/or physical instability.

A composition according to example 70 of US-A-4,618,446 (A&W) was prepared by adding the NaOH to the water at ambient temperature, followed by the addition of the surfactants, the remaining electrolytes and the remaining ingredients.

Ingredient	% wt
coconut diethanolamide	3.3
sodium carbonate	2.4
STP[1])	14.8
Zeolite A	9.9
Optical brighteners	0.16
C_{12-18}. 8EO	3.1
C_{16-18} phosphate	1.7
oleic acid	9.1
sodium hydroxide	0.9
SXS	0.5
water	balance

[1]) anhydrous STP

The same composition was prepared wherein the SXS was omitted. Both compositions were stored for 21 and 42 days at 25°C.

The composition without the SXS ingredient was physically stable (no phase separation after storage), the composition with SXS was physically stable after 21 days of storage, but unstable after 6 weeks. The viscosity of the composition without SXS was 2,750 mPas at 21 s^{-1}, the viscosity of the composition with SXS was 3,800 mPas.

This example illustrates that compositions as disclosed in US-A-4,618,446 do not comprise SXS as a stabiliser; furthermore compositions according to this patent appear of high viscosity.

Claims

1. A physically stable liquid detergent composition comprising a dispersion of lamellar droplets of detergent active materials in an aqueous continuous phase, with solid-suspending properties said composition comprising a salting-

out electrolyte and from 0.05 to 20 % by weight of a hydrotroping material, other than glycerol and triethanolamine, the weight ratio of salting-out electrolyte to hydrotrope being from 20:1 to 1:1, said composition providing a pH within the range of 7.5 to 12.5.

2. A liquid detergent composition according to claim 1 comprising from 1 to 35 % of a salting-out electrolyte and at least 1.0 % by weight of a hydrotropic material.

3. Composition according to claims 1-2. wherein the hydrotroping material is selected from the group of:

(i) alkali metal aryl sulphonates. selected from sodium xylene sulphonate, sodium toluene sulphonate, sodium cumene sulphonate, sodium tetralin sulphonate, sodium naphtalene sulphonate. and the short chain alkyl derivatives thereof;
(ii) mono- and dihydric alcohols and derivatives thereof, selected from lower alcohols such as ethanol. isopropanol, propyleneglycol and ethylene glycol, monoethanolamine and 1,2 propylene glycol dibutyl ether, and higher alcohols having 3-10 carbon atoms, wherein the carbon chain length is at least 4 carbon atoms shorter than the average chain length of the hydrocarbyl chain of the surfactant materials used in the composition;
(iii) hydrocarbons materials, selected from C_8-C_{12} paraffins, wherein the hydrocarbon chain of the hydrocarbon chain is at least 2 carbon atoms shorter than the average chain length of the hydrocarbyl chain of the surfactants used in the composition; and
(iv) organic solvent materials, selected from limonene, linalool, benzyl alcohol, diglyme, dibutyl phthalate and terpene;

and mixtures thereof.

4. The use of from 0.05 to 20 % by weight based on the total composition, of a hydrotroping material, other than glycerol, as a stabiliser for liquid detergent compositions comprising a dispersion of lamellar droplets of detergent active materials in an aqueous continuous phase and a salting-out electrolyte.

5. Use according to claim 4, wherein the hydrotroping material is selected from the group of:

(i) alkali metal aryl sulphonates, selected from sodium xylene sulphonate, sodium toluene sulphonate, sodium cumene sulphonate, sodium tetralin sulphonate, sodium naphtalene sulphonate, and the short chain alkyl derivatives thereof;
(ii) mono- and dihydric alcohols and derivatives thereof. selected from lower alcohols such as ethanol, isopropanol, propyleneglycol and ethylene glycol, monoethanolamine, triethanolamine and 1,2 propylene glycol dibutyl ether, and higher alcohols having 3-10 carbon atoms, wherein the carbon chain length is at least 4 carbon atoms shorter than the average chain length of the hydrocarbyl chain of the surfactant materials used in the composition;
(iii) hydrocarbons materials, selected from C_8-C_{12} paraffins, wherein the hydrocarbon chain of the hydrocarbon chain is at least 2 carbon atoms shorter than the average chain length of the hydrocarbyl chain of the surfactants used in the composition; and
(iv) organic solvent materials, selected from limonene, linalool, benzyl alcohol, diglyme, dibutyl phthalate and terpene;

and mixtures thereof.

Patentansprüche

1. Physikalisch stabile flüssige Detergent-Zusammensetzungen, enthaltend eine Dispersion von lamellaren Tröpfchen von detergentaktiven Materialien in einer wässerigen kontinuierlichen Phase mit Feststoff-suspendierenden Eigenschaften, wobei die Zusammensetzung einen Aussalz-Elektrolyt und von 0,05 bis 20 Gewichtsprozent eines hydrotropierenden Materials, das nicht Glycerin und Triethanolamin ist, enthält, wobei das Gewichtsverhältnis des Aussalz-Elektrolyts zum Hydrotrop im Bereich von 20 : 1 bis 1 : 1 liegt, und die Zusammensetzung einen pH-Wert innerhalb des Bereichs von 7,5 bis 12,5 vorsieht.

2. Flüssige Detergent-Zusammensetzung gemäß Anspruch 1, **dadurch gekennzeichnet**, daß sie von 1 bis 35 % eines Aussalz-Elektrolyts und zumindest 1,0 Gewichtsprozent eines hydrotropen Materials enthält.

3. Zusammensetzung gemäß den Ansprüchen 1 bis 2, worin das hydrotropierende Material ausgewählt ist aus der Gruppe:

(i) Alkalimetallarylsulfonate, ausgewählt aus Natriumxylolsulfonat, Natriumtoluolsulfonat, Natriumcumolsulfonat, Natriumtetralinsulfonat, Natriumnaphthalinsulfonat, und die kurzkettigen Alkyl-Derivate derselben,
(ii) einwertige und zweiwertige Alkohole und Derivate derselben, ausgewählt aus niederen Alkoholen, wie Ethanol, Isopropanol, Propylenglykol und Ethylenglykol, Monoethanolamin und 1,2-Propylenglykoldibutylether, und höhere Alkohole mit 3 bis 10 Kohlenstoffatomen, worin die Kohlenstoffkettenlänge zumindest 4 Kohlenstoffatome kürzer ist als die durchschnittliche Kettenlänge der Hydrocarbylkette der in der Zusammensetzung verwendeten Surfactantmaterialien,
(iii) Kohlenwasserstoffmaterialien, ausgewählt aus C_{8-12}-Paraffinen, worin die Kohlenwasserstoffkette der Kohlenwasserstoffkette zumindest 2 Kohlenstoffatome kürzer ist als die durchschnittliche Kettenlänge der Hydrocarbylkette der in der Zusammensetzung verwendeten Surfactants, und
(iv) organische Lösungsmittelmaterialien, ausgewählt aus Limonen, Linalool, Benzylalkohol, Diglyme, Dibutylphthalat und Terpen,

und Mischungen derselben.

4. Verwendung von 0,05 bis 20 Gewichtsprozent auf Basis der gesamten Zusammensetzung eines hydrotropierenden Materials, das nicht Glycerin ist, als Stabilisator für flüssige Detergent-Zusammensetzungen, enthaltend eine Dispersion von lamellaren Tröpfchen der detergentaktiven Materialien in einer wässerigen kontinuierlichen Phase und einen Aussalz-Elektrolyt.

5. Verwendung gemäß Anspruch 4, worin das hydrotropierende Material ausgewählt ist aus der Gruppe:

(i) Alkalimetallarylsulfonate, ausgewählt aus Natriumxylolsulfonat, Natriumtoluolsulfonat, Natriumcumolsulfonat, Natriumtetralinsulfonat, Natriumnaphthalinsulfonat, und die kurzkettigen Alkyl-Derivate derselben,
(ii) einwertige und zweiwertige Alkohole und Derivate derselben, ausgewählt aus niederen Alkoholen, wie Ethanol, Isopropanol, Propylenglykol und Ethylenglykol, Monoethanolamin, Triethanolamin und 1,2 -Propylenglykoldibutylether, und höhere Alkohole mit 3 bis 10 Kohlenstoffatomen, worin die Kohlenstoffkettenlänge zumindest 4 Kohlenstoffatome kürzer ist als die durchschnittliche Kettenlänge der Hydrocarbylkette der in der Zusammensetzung verwendeten Surfactantmaterialien,
(iii) Kohlenwasserstoffmaterialien, ausgewählt aus $C_{8\ 12}$-Paraffinen, worin die Kohlenwasserstoffkette der Kohlenwasserstoffkette zumindest 2 Kohlenstoffatome kürzer ist als die durchschnittliche Kettenlänge der Hydrocarbylkette der in der Zusammensetzung verwendeten Surfactants, und
(iv) organische Lösungsmittelmaterialien, ausgewählt aus Limonen, Linalool, Benzylalkohol, Diglyme, Dibutylphthalat und Terpen,

und Mischungen derselben.

Revendications

1. Composition détergente liquide physiquement stable, qui comprend :
une dispersion de gouttelettes lamellaires de matières détergentes actives dans une phase aqueuse continue possédant des propriétés de suspension de solides, ladite composition comprenant un électrolyte de relargage et de 0,05 à 20 % en poids d'une matière hydrotrope autre que le glycérol et la triéthanolamine, le rapport pondéral de l'électrolyte de relargage à l'hydrotrope étant compris entre 20:1 et 1:1, ladite composition ayant un pH de 7,5 à 12,5.

2. Composition détergente liquide selon la revendication 1, qui comprend de 1 à 35 % d'un électrolyte de relargage et au moins 1,0 % en poids d'une matière hydrotrope.

3. Composition selon les revendications 1 et 2 dans laquelle la matière hydrotrope est choisie parmi :

(i) les arylsulfonates de métaux alcalins choisis parmi le xylènesulfonate de sodium, le toluènesulfonate de sodium, le cumènesulfonate de sodium, le tetralinesulfonate de sodium, le naphtalènesulfonate de sodium et leurs dérivés à chaîne alkylique courte ;

(ii) des mono- et di-alcools et leurs dérivés choisis parmi les alcools inférieurs tels que l'éthanol, l'isopropanol, le propylène-glycol et l'éthylène-glycol, la monoéthanolamine et l'éther dibutylique de 1,2-propylène-glycol ainsi que les alcools supérieurs contenant de 3 à 10 atomes de carbone, la longeur de la chaîne de carbone étant plus courte d'au moins 4 atomes de carbone que la longueur moyenne de la chaîne hydrocarbyle dans les matières tensioactives utilisées dans la composition ;

(iii) les matières hydrocarbonées choisies parmi les paraffines en C_{8-12}, la chaîne hydrocarbonée étant plus courte d'au moins 2 atomes de carbone que la longueur moyenne de la chaîne hydrocarbyle des tensioactifs utilisés dans la composition ; et

(iv) les Solvants organiques choisis parmi le limonène, le linalool, l'alcool benzylique, le diglyme, le phtalate de dibutyle et le terpène ; et leurs mélanges.

4. Utilisation de 0,05 à 20% en poids par rapport à la composition totale d'une matière hydrotrope autre que le glycérol à titre de stabilisant pour les compositions détergentes liquides, comprenant une dispersion de gouttelettes lamellaires de détergents actifs au sein d'une phase continue et un électrolyte de relargage.

5. Utilisation selon la revendication 4, dans laquelle la matière hydrotrope est choisie parmi :

(i) les arylsulfonates de métaux alcalins choisis parmi le xylènesulfonate de sodium, le toluènesulfonate de sodium, le cumènesulfonate de sodium, le tetralinesulfonate de sodium, le naphtalènesulfonate de sodium et leurs dérivés à chaîne alkylique courte ;

(ii) des mono- et di-alcools et leurs dérivés choisis parmi les alcools inférieurs tels que l'éthanol, l'isopropanol, le propylène-glycol et l'éthylène-glycol, la monoéthanolamine et l'éther dibutylique de 1,2-propylène-glycol ainsi que les alcools supérieurs contenant de 3 à 10 atomes de carbone, la longeur de la chaîne de carbone étant plus courte d'au moins 4 atomes de carbone que la longgueur moyenne de la chaîne hydrocarbyle dans les matières tensioactives utilisées dans la compositions ;

(iii) les matières hydrocarbonées choisies parmi les paraffines en C_{8-12}, la chaîne hydrocarbonée étant plus courte d'au moins 2 atomes de carbone que la longueur moyenne de la chaîne hydrocarbyle des tensioactifs utilisés dans la composition ; et

(iv) les solvants organiques choisis parmi le limonène, le linalool, l'alcool benzylique, le diglyme, le phtalate de dibutyle et le terpène ; et leurs mélanges.