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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{6} : **C11D 17/00**	**A1**	**(11) International Publication Number:** **WO 96/10625** **(43) International Publication Date:** 11 April 1996 (11.04.96)

(21) International Application Number: PCT/EP95/03859

(22) International Filing Date: 28 September 1995 (28.09.95)

(30) Priority Data:
94307166.2 30 September 1994 (30.09.94) EP
(34) Countries for which the regional or international application was filed: AT et al.

(71) Applicant *(for all designated States except AU BB CA GB IE LK MN MW NZ SD)*: UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant *(for AU BB CA GB IE LK MN MW NZ SD only)*: UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4 4BQ (GB).

(72) Inventors: VAN DE BERGH, Carlo, Johannes; 25 Heronpark Way, Spital, Merseyside LN63 9GN (GB). BIJL, Dirk, Johannes; Schaatsbaan 25, NL-2992 CN Barendrecht (NL). DUNCAN, Diane; 72 Parkhill Road, Prenton Wirral, Merseyside L42 9JD (GB). FALK, Nancy, Ann; Apartment 2, 732 Sixth Street, Lyndhurst, NJ 07071 (US). DE GROOT, Jeffey; 12 Dovepoint Road, Meols, Wirral, Merseyside L47 6AR (GB). VAN DE LINDEN, Erik; Santhorst 73, NL-2352 KC Leiderdorp (NL). MACHIN, David; 32 Brabcote Road, Oxton, Brikenhead L43 6TJ (GB). TOET, Wilhelmina, Karin; Mozartlaan 22, NL-3161 RL Rhoon (NL). WALSH, Michael, Francis; 60 Garth Drive, Chester, Cheshire CH2 2AG (GB).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: DETERGENT COMPOSITION

(57) Abstract

The present invention relates to aqueous liquid detergent compositions that comprise a stucture of lamellar droplets of surfactant material, wherein said composition comprises relatively high levels of nonionic surfactant material. The invention further relates to a process of preparing aqueous liquid detergent compositions that comprise lamellar droplets of surfactant material.

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DETERGENT COMPOSITION

Technical Field

The present invention relates to aqueous liquid detergent compositions that comprise a structure of surfactant material and to a process of preparing aqueous liquid detergent compositions that comprise lamellar droplets of 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 have been gaining in popularity since their market introduction 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.

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.

Structured liquids can either be internally structured, in which case the structure is formed by primary ingredients, preferably by surfactant material, or they can be externally structured in which case the structure is provided by a three dimensional matrix structure using secondary additives like preferably polymers and silicate material. Externally structured liquids may however provide a high viscosity, especially upon storage. This generally makes internally structured liquids preferred over externally structured.

Some of the different kinds of internally structured liquids 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 addition of further surfactant and/or electrolyte, various structures of surfactant material may form. An example thereof are lyotropic liquid crystalline phases. These phases may e.g. be present in the form of lamellar structures or in the form of hexagonal structure.

Although generally being defined as two or more bi-layers of surfactant material, for the purpose of this invention lamellar structures are defined as one or more bi-layers of surfactant material. However, preferably, lamellar structures according to the invention contain at least two bi-layers of surfactant material. These two bi-layers will form a stack. The lamellar structure may exist in various forms, e.g. lamellar planar structures and lamellar droplets of surfactant bi-layers (the bi-layers are concentrically stacked).

It is noted that various terms are used in the art for lamellar structures. Examples of such terms are anisotropic surfactant phase, as e.g. described in EP-A-572,723, and spherulites, as described in EP-A-0,151,884.

Liquids with lamellar droplets provide a 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 dispersed structuring phase in liquids with lamellar droplets of surfactant material consists of an onion-like configuration comprising concentric bilayers surfactant molecules between which water is trapped. Presence and identity of bi-layers of surfactant material 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 by electron microscopy. Concentric bi-layers of surfactant material can be easily detected when viewed under a transmission microscope, such as a thin film techniques. Additionally, they may be detected using a microscope under polarised light. When maltese or extinction crosses appear, they contain concentric bi-layers. Concentric bi-layers can further be detected by way of Freeze Fraction Electron Microscopy, a method well-known to the skilled man.

WO 91/00331 discloses aqueous structured liquid detergent compositions comprising lamellar droplets of surfactant material. The compositions comprise relatively high nonionic levels, e.g. 50-100% by weight of the total surfactant. These liquids have also been described in "Physical stability and microstrucure of concentrated dispersions of lamellar liquid-crystalline droplets containing nonionic surfactants in aqueous electrolyte solution", Schepers, Toet and Van de Pas, American Chemical Society, Vol. 9, No.4, 1993. Some of the exemplified liquids comprise lamellar droplets consisting of an isotropic core surrounded by concentrically stacked bi-layers, see in particular figure 4.

WO 91/09107 describes the use of high shear in the preparation of aqueous liquid detergent compositions comprising a deflocculating polymer.

WO 91/16409 discloses aqueous liquids with lamellar surfactant droplets and comprising primary alkyl sulphate material, fatty acid and nonionic surfactants.

EP-A-346,995 discloses aqueous liquid detergent compositions comprising lamellar droplets of surfactant material and a deflocculating polymer having hydrohylic backbone and a hydrophobic sidechain. The Examples disclose structured liquids which contain lamellar droplets of surfactant material.

EP-A-328,176 discloses structured liquid detergent compositions which comprises non-encapsulated liquid surfactant droplets (phase biii). Examples XI-XIV disclose liquids with lamellar droplets of surfactant material (phase ci or a so-called G-phase) and a phase called the "isotropic detergent" which is identified as phase biii. The nonionic surfactant level in Example XIV is 50% by weight of the total surfactant.

EP-A-328,177 discloses liquids with lamellar droplets and comprising Salting-Out Resistant surfactant material which is used as a stabiliser in the liquid. Alkylpolyglucoside is an example of such a SOR surfactant material.

Intermediate document EP-A-623,670 discloses liquid compositions comprising particular stabilisers. The described liquids may comprise high nonionic levels and comprise isotropic droplets of surfactant material dispersed in a continuous isotropic or anisotropic phase. The structure of droplets flocculates and requires the particular stabiliser in order to be pourable.

Document "Physics of Amphiliphiles: Micelles, Vesicles and Microemulsions" by De Giorgio and Corti, 185, North Holland, discloses nonionic-water liquids with a lamellar and an L2 phase, see pages 17-19.

GB-A-1,068,554 discloses aqueous emulsions comprising surfactant, potassium salts and stabiliser material.

EP-A-354,010 discloses aqueous liquids comprising a sperulitic phase and nonionic surfactants.

EP-A-430,330 discloses aqueous liquids with an anisotropic (or neat) phase which do not comprise a solid phase.

EP-A-572,723 discloses lamellar structured compositions comprising a polyhydroxy fatty acid amide and EP-A-328,177 discloses lamellar structured liquids comprising stabilising surfactants.

EP-A-86,614 discloses aqueous liquid detergent compositions comprising lamellar droplets of surfactant material that may contain nonionic surfactant material and solid particles. The exemplified liquids that contain nonionic surfactants however are diluted.

We have now found a physical form for liquid detergent compositions that not only allows preparation of physically stable liquids, but it also has high formulation flexibility and various ingredients may included without adversely effecting stability. A further advantage of the liquid form is the high enzyme stability.

Further, we have found that liquid detergent composition comprising lamellar droplets of surfactant material, wherein the surfactant material comprises high levels of nonionic surfactant, may show stability problems, high viscosities and/or a drift in the viscosity upon storage, in particular at higher temperatures.

We have further found that high nonionic liquids can be prepared physically stable, low viscous and/or having low viscosity drift upon storage, by including a stabilising agent. Thus, we have found that aqueous liquid detergent compositions with lamellar droplets comprising high levels of nonionic surfactant material can be stably formulated by including a stabilising agent in the liquid. These nonionic surfactant containing liquid compositions may either have an internal radial symmetry or may lack such a structure. The surfactant in these liquids may comprise up to 100% of nonionic surfactant, i.e. without any anionic surfactant (ratio 1:0), but may also comprise nonionic and anionic surfactants in the ratio as specified hereunder.

Further, we have found that the stability and/or deflocculation of liquid detergent composition comprising lamellar droplets of surfactant material, wherein the surfactant material comprises high levels of nonionic surfactant, may be improved by carefully adjusting the sodium to potassium ratio of the liquid. These nonionic surfactant containing liquid compositions may either have an internal radial symmetry or they may lack such a structure. The surfactant in these liquids may comprise up to 100% of nonionic surfactant, i.e. without any anionic surfactant (ratio 1:0) but may also comprise nonionic and anionic surfactants in the ratio as specified hereunder.

Further, we have found that the stability and/or deflocculation of liquid detergent composition comprising lamellar droplets of surfactant material, wherein the surfactant material comprises high levels of nonionic surfactant, may be improved by also including high levels of solid particles in the liquid.

Further, we have found that the physical stability and/or deflocculation, in particular at higher temperatures, of liquid detergent composition comprising lamellar droplets of surfactant material, wherein the surfactant material comprises high levels of nonionic surfactant, may be improved by carefully choosing the conditions of the preparation process.

Statement of the Invention

The invention provides an aqueous structured liquid detergent composition comprising lamellar droplets of surfactant material, said composition comprising a weight ratio of nonionic surfactant to anionic surfactants that is smaller than 95:5 and that is higher than 50:50, said composition comprising:

i) a nonionic sugar stabilising agent containing a sugar unit selected from apiose, arabinose, galactose, lyxose, mannose, gallose, altrose, idose, arabinose, ribose, talose, xylose, maltose, lactose, sucrose and sorbitan;

ii) at least 10%, preferably at least 15% by weight of solid particles;

iii) anionic surfactants selected from C12-C18 alkyl sulphate, sulphonate, mono unsaturated fatty acids and mixtures thereof, wherein the anionic sulphate or sulphonate comprises at least 3 c-atoms on both sides of the C-atom to which the sulphate or sulphonate group is attached;

iv) enzymes; or

v) mixtures thereof.

The invention further provides an aqueous structured liquid detergent composition comprising lamellar droplets of surfactant, wherein said surfactant comprises material present in concentric bi-layer form consisting of one or more bi-layers of surfactant material that have a joined thickness which is smaller than the radius of the droplet, wherein the composition comprises

i) a nonionic sugar stabilising agent containing a sugar unit selected from apiose, arabinose, galactose, lyxose, mannose, gallose, altrose, idose, arabinose, ribose, talose, xylose, maltose, lactose, sucrose and sorbitan;

ii) at least 10%, preferably at least 15% by weight of solid particles;

iii) anionic surfactants selected from C12-C18 alkyl sulphate, sulphonate, mono unsaturated fatty acids and mixtures thereof, wherein the anionic sulphate or sulphonate comprises at least 3 c-atoms on both sides of the C-atom to which the

sulphate or sulphonate group is attached;
iv) enzymes; or
v) mixtures thereof.

The invention further provides a process of preparing aqueous liquid detergent compositions with lamellar droplets that comprise surfactant material, said liquid comprising nonionic surfactants at a level of more than 50% by weight of the total surfactant material, said process comprising the mixing of water, electrolyte material and surfactant material to create a lamellar structure, characterised in that thereafter lamellar structure is subjected to a post-shear operation.

The invention further provides a process of preparing aqueous liquid detergent compositions with lamellar droplets that comprise surfactant material comprising nonionic surfactants at a level of more than 50% by weight of the total surfactant material, wherein a mixture of water, electrolyte material and surfactant material is prepared from which a lamellar structure is created, characterised in that the viscosity of the mixture is increased by:

a) adjusting the Na:K molar ratio to a ratio of from 10:1 to 1:10;
b) by adding polymer material;
c) by adding at least 5% by weight of solid particles; and
d) combinations thereof.

Description of the Invention

Structure that lacks internal radial symmetry

The liquid form of the present invention enables formulation of liquid detergent compositions comprising relatively high nonionic surfactant levels and relatively low anionic surfactant without giving in on physical stability, having a high formulation flexibility (i.e. various ingredients may included without adversely effecting stability) and further having a high enzyme stability.

The concentric bi-layer form of the surfactant in the droplets of the liquids according to the invention consists of one or more bi-layers of surfactant material that have a joined thickness that is smaller than the radius of the droplet. Preferably, the joined thickness is smaller than 99% of the radius, more preferably 50% of the radius, most preferably smaller than 25% of the radius, in particular smaller than 10% of the radius.

Preferably, the compositions according to the invention have one or more concentric bi-layers of surfactant material that form a shell which is present on the outside of the droplet. Preferably, the droplet further comprises surfactant material, preferably present in a non-concentric form inside this shell of concentric bi-layers of surfactant material. This surfactant material may e.g. be present in the form of planar structures, micelles, solution or liquid surfactant phase. Other materials, such as salt, water and enzymes may also be present inside the droplets. Preferably, the lamellar droplets of surfactant do not contain solid particles with a size larger than 1μm, more preferably with a size larger than 0.1μm, most preferably with a size larger than 0.01μm.

Compositions according to this aspect of the invention may contain nonionic surfactants at a level of 100% by weight of the total surfactants. Preferably, the ratio of nonionic to anionic surfactants is smaller than 95:5 and e.g. higher than 50:50. More preferably, the ratio is smaller than

90:10, most preferably smaller than 85:15. More preferably, the ratio is higher than 55:45, most preferably higher than 60:40. Ratios that are in particular preferred are higher than 65:35, e.g. ratios that are higher than 70:30. For the purpose of this invention, the nonionic to anionic surfactant weight ratios are based on the ionic form of the anionic surfactant.

Preferably, compositions according to this aspect of the invention contain a ratio of nonionic surfactant, having an SOR (salting-out resistance) of less than 6.4, to anionic surfactants that meet the nonionic to anionic ratios. SOR is as defined hereunder.

Preferably, compositions according to this aspect of the invention further comprise from 1.5 to 5% by weight of a decoupling polymer as defined hereunder. We have found that liquids with lamellar droplets that contain high levels of nonionic surfactant can be stabilised by using relatively high levels of decoupling polymer. Although not wishing to be bound by any theory, these polymers appear to stabilise the above mentioned, asymmetric structure. We have further found that solid particles may be suspended in such liquids and the formulation flexibility of these liquids is high.

Liquids containing lamellar droplets which lack an internal radial symmetry, may be detected by way of light or electron microscopy and preferably by way of transmission (e.g. film) or freeze fractioning. Preferably polarised light is used for light microscopy and in that case no bi-refringence can be seen in the core of the droplets and, depending on the thickness of the bilayers, bi-refringence can be seen on the outside of the droplets.

We have found that by carefully adjusting the Na+:K+ molar ratio, the stability of the relatively high nonionic liquids can be further improved. Preferably, the Na+:K+ molar ratio in the liquid is at most 10:1, more preferably at most 8:1, most preferably at most 5:1, in particular preferred is at most 3:1, e.g. at most 2:1. Preferably, the Na+:K+ molar ratio is at least 1:10, more preferably at least 1;8, most preferably at least 1:5. In particular preferred is the molar ratio of at least 1:3. A suitable molar ratio is at least 1:2.

Stabilising Agent

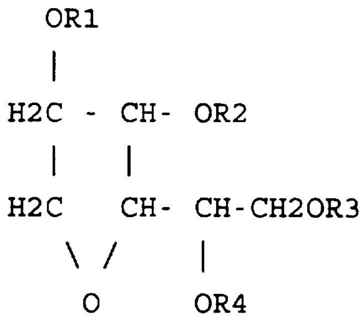
Preferably, the stabilising agent is a nonionic polyhydroxy stabilising agent which contains 1 or 2 sugar units, preferably 1 sugar unit and, preferably, the sugar unit is a pentose or hexose ring structure. The stabilising agent preferably contains free hydroxy groups.

Preferably, the sugar unit is selected from aldoses such as apiose, arabinose, galactose, lyxose, mannose, gallose, altrose, idose, arabinose, ribose, talose, xylose, maltose, lactose, sucrose and sorbitan.

Preferably, the sugar stabiliser comprises an alk(en)yl side-chain that is C6 or higher, preferably C8 or higher, more preferably C10 or higher; from 0 to 30 alkylene oxide groups, preferably ethylene oxide groups, may be present between the sugar ring and the alk(en)yl side chain; and the alk(en)yl side chain may be connected to the sugar ring or the EO groups by way of ether or ester bonds.

Preferred stabilising agents are ethers, esters and amides of an acid (or alcohol) with an alk(en)yl chain and a sugar unit. An example of such a compound has the formula R2-CO-NR1-Z, wherein R1 is H a C1-4 hydrocarbyl, 2-hydroxyethyl, 2-hydroxy propyl, or a mixture thereof, R2 is C5-C31 hydrocarbyl and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain, or an alkoxylated derivative thereof. These compounds have e.g. been described in EP-A-572,723.

A preferred stabilising agent is a sorbitan derivative, more preferably an ester of sorbitan and one or more fatty acids and/or an ether of sorbitan and one or more ethoxy groups and/or a mixture thereof. Most preferably, the sorbitan derivative have the following structure:



wherein:
- R1-4 is -(CH2CH2O)n-R'1-4

and wherein:
- n is 0 to 30, preferably to 20; and
- R'1-4 is H or C10-C20 fatty acid.

Suitable compounds are polysorbate 20 (Tween 20®, ex ICI; a monolaurate with EO=20 and HLB=16.7); Polysorbate 21 (Tween 21®, ex ICI; a trioleate with EO=4 and HLB=13.3); Sorbital laurate (Span 20® ex ICI; a monolaurate with an HLB=8.6); and Sorbitan trioleate (Span 85®, ex ICI; a trioleate with HLB of 1.8).

Preferably, the composition comprises at least 0.1%, more preferably at least 0.5%, most preferably at least 1.0% by weight of stabilising agent and preferably at most 20%, more preferably at most 15%, most preferably at most 10%, in particular at most 7.5% by weight of the composition, e.g. at most 5% by weight of the composition.

Preferably, compositions according to this aspect of the invention contain a ratio of nonionic surfactant (having an SOR of less than 6.4) to anionic surfactants that meet the nonionic to anionic ratios. SOR is as defined hereunder.

Solid Particles

A further embodiment of the invention relates to aqueous liquid detergent compositions with lamellar droplets that comprise high levels of nonionic surfactant material as well as at least 5% by weight of solid particles.

Preferably, the level of solid particles is at least 10% by weight, more preferably at least 15% by weight and most preferably at least 20% by weight. Preferably, the level of solid particles is at most 25% by weight, more preferably at most 35% by weight, most preferably at most 30% by weight of the composition.

Preferably, the solid particles are selected from zeolite, STP, silicate material and mixtures thereof, and more preferably zeolite material and/or silicate material, most preferably zeolite material.

Although not wishing to be bound by any theory, it is believed that solid particles not only add to the structuring of the liquids, but also positively influence the molar ratio of the ions in the liquid. Both effects result in liquids with lamellar droplets of surfactant material that are more stable. Moreover, we believe that the solid particles provide a further structuring in the liquid which enhances the physical stability.

Preferably, aqueous liquid detergent compositions according to this aspect of the invention contain relatively high levels of nonionic surfactant material can be made stable by incorporating solid particles and using highly concentrated liquids. Preferably, the liquids comprise water at a level of at most 50%, more preferably at most 40% by weight of the composition.

Anionic Surfactants

Preferably, compositions according to the invention comprise anionic surfactants selected from C12-C18 alkyl sulphate, C12-C18 alkyl sulphonate, mono unsaturated fatty acids and mixtures thereof. Preferably, anionic surfactants are selected from secondary C12-C18 alkyl sulphate, sulphonate and mixtures thereof, more preferably these anionic surfactants molecules comprise at least 3 C-atoms on both sides of the C-atom to which the sulphate or sulphonate group is attached. Without wishing to be bound, it is believed that the V-shape of these surfactants assist in creating the structure. Preferably, the ratio between nonionics and these anionic surfactants (selected from secondary C12-C18 alkyl sulphate and sulphonate and C12-C22 fatty acids) is from 50:50 to 95:5. More preferably, the ratio is smaller than 90:10, most preferably smaller than 85:15. Most preferably, the ratio is higher than 55:45, in particular higher than 60:40. Ratios that are more in particular preferred are higher than 65:35, e.g. ratios that are higher than 70:30. Preferably, the level of these anionics surfactants is at least 5%, more preferably at least 10%, most preferably at least 15% by weight of the composition. Preferably, the level of these anionics surfactants is at most 50%, more preferably at most 45%, most preferably at most 35%, e.g. at most 30% by weight of the composition. Other anionic surfactants may also be present.

Preparation Process

Surprisingly, we have found that applying post shear to the liquids of the invention leads to stability upon storage, even upon storage at higher temperatures. For the purpose of this invention, "post-shear" is defined also to include "extension", terminology well known to the skilled man.

Post shear may be applied by way of a extrusion plastometer, a shear valve, a colloid mill or combinations thereof. Shear rates are preferably at least 3,000/s, more preferably at least 5,000/s and preferably at most 30,000/s for an extrusion plastometer, the back pressure is preferably from 0.1 to 10 bar for a shear valve and the shear rate is preferably from 1,000/s to 100,000/s for a colloid mill.

Surprisingly, it has been found that the stability upon storage of relatively high nonionic liquids with lamellar droplets can be improved by creating a high viscosity environment during the formation of lamellar droplets of surfactant material. Without wishing to be bound by any theory, it is believed that if the liquid has a high viscosity, the resulting liquids with lamellar droplets will be more stable. It is further believed that the viscosity of the continuous phase of the liquid with lamellar droplets of surfactant material, which consists of a mixture of water and electrolyte material without the surfactant, might be an important factor in realising this stability improvement.

The viscosity of the continuous phase, i.e. water and electrolyte material without surfactant material, and consequently the stability of the resulting liquid with lamellar droplets of surfactant material can be increased by a method selected from:

a) adjusting the Na:K molar ratio to a ratio of from 10:1 to 1:10;
b) by adding polymer material;
c) by adding at least 5% by weight of solid particles; and
d) combinations thereof.

Preferably, the Na+:K+ molar ratio in the mixture of water, electrolyte and surfactant is adjusted to a ratio of at most 8:1, more preferably at most 5:1, most preferably at most 3:1, e.g. at most 2:1. Preferably, the Na+:K+ ratio is at least 1:8, more preferably at least 1:5 and most preferably at least 1:3. A suitable molar ratio is at least 1:2.

Preferably, polymer material is added to the mixture of water, electrolyte and surfactant at a level of from 0.1 to 5% by weight of the mixture.

Preferably, solid particles are added to the mixture of water, electrolyte material and surfactant material at a level of at least 10% by weight of solid material, more preferably at least 15% by weight, most preferably at least 20% by weight, in particular at least 25% by weight, e.g. at least 30% by weight. Preferably at most 50% by weight of the composition.

Preferably, the solid material is selected from zeolite, STP, silicate and mixtures thereof.

Surfactant Material

Compositions of the invention also comprise surfactant materials, preferably at a level of at least 10% by weight of the composition, more preferred at least 15% by weight, most preferred at least 20% by weight of the composition; and preferably at a level of at most 70% by weight, more preferably at most 60%, most preferably at most 50% by weight.

The surfactant material may comprise one or more surfactants selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and 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.

Nonionic Surfactants

Preferably, compositions according to the invention comprise high levels of nonionic surfactant with a low electrolyte tolerance. It has been found that it is advantageous to use these kind of nonionic surfactants to create the structure of the liquids of the present invention.

Composition of the invention preferably comprise nonionic surfactants having an SOR of less than 6.4, preferably less than 6.0. The test herein prescribed for electrolyte tolerance is termed the measurement of salting-out resistance (SOR). For this test, 200 ml is prepared of a 5% by weight aqueous solution of the surfactant in question. Trisodium nitrolotriacetate (NTA) is added at room termperature (ca 25°C) until phase separation occurs, as observed the onset of cloudiness. The amount of NTA added at this point, as expressed in gram equivalents added to 1 litre of the surfacatn solution (1 mol of NTA = 3 eq.) is the salting-out resistance of the surfactant. Where convenient, the abbreviation SOR will be used for salting-out resistance.

Preferably, the weight ratio of nonionic surfactant with a SOR of less than 6.4 to anionic surfactants is smaller than 95:5 and higher than 50:50. Preferably, the ratio is smaller than 90:10, more preferably smaller than 85:15. Preferably, the ratio is higher than 55:45, more preferably higher than 60:40, most preferably higher than 65:35, e.g. higher than 70:30.

Additionally, compositions of the present invention may preferably further comprise surfactant material (including nonionic surfactant material) with an SOR of 6.4 or higher. Although not wishing to be bound by any theory, it is believed that a higher level of surfactant with higher SOR may lead to liquids with droplets that show internal radial symmetry.

<u>Anionic Surfactants</u>

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.

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.

Other Surfactant Material

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-70,074. 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.

Salting-Out Electrolyte

Compositions according to the invention may optionally also contain electrolyte in an amount sufficient to bring about structuring of the detergent active material. Preferably, the compositions contain from 0% (preferably 1%) to 60%, especially from 5% (preferably 10%) to 45% of a salting-out electrolyte. Salting-out electrolyte has the meaning ascribed in specification EP-A-79,646, that is all electrolytes having a lyotropic number of less than 9.5, preferably less than 9.0. Preferred salting-out electrolytes are selected from alkali metal and ammonium salts of phosphates (including pyro, ortho and poly phosphates), silicates, borates, carbonates, sulphates, citrates nitriloacetate and succinates.

Builders

It is preferred that compositions according to the present invention include detergency builder material, some or all of which may be electrolyte.

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. Sometimes it is however 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 ethylenediamine-tetraacetic 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-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.

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

Decoupling Polymer

Preferably, composition according to the present invention further comprises from 1.5 to 5% by weight of a decoupling polymer selected from deflocculating polymer having a hydrophilic backbone and one or more hydrophobic side-chains, or being a block copolymer having alternating hydrophobic and hydrophilic groups, or having nonionic monomers and ionic monomers.

Several types of deflocculating polymers have been described in the art. EP-A-346,995 describes deflocculating polymers having a hydrophilic backbone and one or more hydrophobic side-chains, WO 91/06622 describes deflocculating polymers being a block copolymer consisting of alternating hydrophobic and hydrophilic groups, WO 91/06623 describes deflocculating polymers consisting of nonionic monomers and ionic monomers and GB 2 237 813 describes deflocculating polymers consisting of a hydrophobic backbone and one or more hydrophilic side-chains.

Preferably, the deflocculating polymer is present at a level of from 1.5 to 5 % by weight of the composition.

Water

Preferably, 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.

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 (at a level of 0.5-5% by weight) 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 Properties

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 nad higher than 100mPas, especially preferred between 100 and 750 mPas at 21 s-1.

Liquid compositions according to the invention are physically stable and have a relatively low viscosity, In the context of the present invention, physical stability is defined in terms of the maximum separation compatible with most manufacturing and retail requirements. 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.

Preferably, liquid compositions of the invention have a pH of between 6 and 14, more preferred from 6.5 to 13, especially preferred from 7 to 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

Apart from the above mentioned processes of preparation, a preferred method for the preparation of liquid detergent compositions involves the dispersing of the electrolyte ingredient (if present) 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- if any-, the detergent active material (possibly as a premix) under stirring and thereafter cooling the mixture and adding any temperature sensitive minor ingredients such as enzymes perfumes etc. The deflocculating polymer may for example be added after the electrolyte ingredient or as the final ingredient. Preferably, the deflocculating polymers are added prior to the formation of the lamellar structure.

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 now be illustrated by way of the following non-limiting Examples.

EXAMPLES

Example 1

The following compositions were prepared by mixing the ingredients in the order listed.

FORMULATION (in wt%)		1	2
Water		16.43	18.43
KOH Sol(49%)		13.27	13.27
Citric acid (anhydrous)		7.0	7.0
Glycerol		4.17	4.17
Borax		2.92	2.92
Zeolite		18.0	18.0
Polymer	1)	1.5	1.5
LAS acid*		6.25	6.25
Dobanol 23 E3*	2)	13.33	13.33
Dobanol 23 E6.5*	3)	13.33	13.33
Span 20*	4)	2.0	-
Minors		1.8	1.8
Phase separation (after 2 months at 45°C; in mm)		0	5
Na+:K+ ratio		1:1	1:1

* These ingredients were added as a premix

1) Polymer A11 of EP 346,995

2) C12 to C13 nonionic ethoxylated with on average 3 EO groups, ex Shell

3) C12 to C13 nonionic ethoxylated with on average 6.5 EO groups, ex Shell

4) Sorbitan laurate, ex ICI

The composition with the stabiliser showed no phase separation whereas the composition without had a 5mm phase separation upon storage.

Example 2

The following formulations were prepared by mixing the ingredients in the order listed.

FORMULATION (in % by weight)		3	4
Water			
Citric acid		7	7
Zeolite		18	18
Polymer	1)	1.5	1.5
Span 85	5)	-	2
Actives	6)	33	33
Separation (in mm) (after 4 weeks at 45°C)		0	0
Initial Viscosity (cp at 25°C at 21/s)		1460	2500
Viscosity Drift (cp after 4 weeks)		540	250

5) Sorbitan trioleate, ex ICI

6) Premix as in Example 1 with a NI/LAS ratio was 80:20

This experiment shows that product formulations with stabiliser show reduced viscosity drifts.

Example 3

The following formulations were prepared by mixing the ingredients in the order listed.

FORMULATION (in %wt)	5	6	7	8
Water	to 100			
Citric Acid	7	7	7	7
Zeolite	18	18	18	18
Polymer 1)	1.5	1.5	2	2
Stabiliser*	2 7)	2 8)	4 7)	4 8)
Active level* 9)	31	31	31	31

Separation (in mm)	0	0	0	0
Initial Viscosity (in cp at 25°C at 21/s)	1420	1430	1770	1730
Viscosity Drift (in cp at 25°C after 4 weeks at 21/s)	280	240	250	270

* These ingredients were added as a premix

7) Span 85 which is Sorbitan trioleate (HLB 1.8), ex ICI

8) Span 20 which is Sorbitan monolaurate (HLB 8.6), ex ICI

9) Premix according to Example 1 with a NI/LAS weight ratio was 80:20.

All formulations comprising the stabiliser show good stability, low viscosity and a low viscosity drift.

Example 4

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

FORMULATION (in %wt)	9	10
Water	balance	balance
Citric Acid	11	13
Zeolite	13.3	13.3
DCP	1.5	1.5
Stabiliser*	-	2.0 10)
Active level 11)*	33	33
Separation (after 4 weeks in mm)	4	1
Viscosity drift (in cp at 25°C at 21/s) (after 4 weeks @ ambient)	380	180

* These ingredients were added as a premix

10) Tween 20, Sorbitan Monolaurate, ex ICI

11) Premix as in Example 1; NI/LAS weight ratio was 80:20.

Although not completely comparable, the formulations with the stabiliser has lower separation and lower viscosity drift upon storage.

Example 5

This Example illustrates the benefit of post shear and the use of various stabilisers in stabilisation of high nonionic formulations. The compositions were prepared by adding the ingredients in the order listed at a temperature of 50-55°C.

FORMULATION	11	12	13	14
Water	to 100	to 100	to 100	to 100
KOH (49%)	16.71	16.71	16.71	16.71
Citric acid	9.14	9.14	9.14	9.14
Glycerol	4.17	4.17	4.17	4.17
Borax	2.92	2.92	2.92	2.92
Sodium bicarbonate	3.5	3.5	3.5	3.5
Zeolite 4A(as 100%)	13.33	13.33	13.33	13.33
Polymer A-11 (33%)	5.05	5.05	5.05	5.05
LAS acid*	6.25	6.25	6.25	6.25
Synperonic A3*	13.33	13.33	13.33	13.33
Synperonic A7*	13.33	13.33	13.33	13.33
Stabiliser*	None	2% Sp 85 7)	2% Tw 20 10)	2%Tw 21 12)
COOL to 30°C				
Perfume	0.4	0.4	0.4	0.4
pH	9.1	9.1	9.3	9.3
Na+:K+ ratio	1:1.2	1:1.2	1:1.2	1:1.2

* These ingredients were added as a premix

12) Tween 21 is sorbitan monolaurate with 4 EO groups.

Unsheared

Initial viscosity (mPas)	1250	1890	1940	1450
Viscosity (4W at 20°C)	1420	1880	2060	1470
Viscosity (4W at 50°C)	1700	2350	2300	1830
Mean sepn. during 4 W 20°C	2.2%	1.2%	1.0%	2.0%
Mean sepn. during 4W 50°C	3.6%	3.0%	2.8%	3.4%

Post sheared#

Initial viscosity (mPas)	1330	2030	2100	1490
Viscosity (4W at 20°C)	1550	1690	2010	1260
Mean sepn. during 4 W 20°C	zero	zero	zero	zero
Mean sepn. during 4W 50°C	zero	zero	zero	zero

Extrusion plastometer used to deliver a shear of 10,000 sec^{-1}

Example 6

This provides an example of high nonionic formulations and illustrates the benefits of the presence of solid particles and the use of post shear. The compositions were prepared by adding the ingredients in the order listed at a temperature of 50-55°C. Apart from the zeolite levels, formulations 15 and 16 are equivalent, the ingredients of composition 16 are present in the same ratio as in composition 15.

Formulation	15	16	17

Water	to 100	to 100	to 100
KOH (49%)	21.43	16.92	16.92
Citric acid	10.97	9.14	9.14
Glycerol	5.0	4.17	4.17
Borax	3.5	2.92	2.92
Sodium bicarbonate	4.0	3.33	3.33
Zeolite 4A (as 100%)	-	13.33	13.33
Polymer A-11 (33%)	6.06	5.05	2.53
Oleic acid	7.5	6.25	6.25
Synperonic A3	16.0	13.33	13.33
Synperonic A7	16.0	13.33	13.33
Silicone antifoam	0.2	0.17	0.17
pH	10.8	10.6	10.4
Na+:K+ ratio	1:2.89	1:1.15	1:1.15
Unsheared			
Initial viscosity (mPas)	495	1185	980
Viscosity (4W at 20°C)	605	1310	1110
Viscosity (4W at 50°C)	480	1490	1290
Mean sepn. - 4W 20°C	1.2%	zero	1.0%
Mean sepn. - 4W 50°C	10.0%	0.8%	1.2%
Post sheared[#]			
Initial viscosity (mPas)	510	1490	890
Viscosity (4W at 20°C)	640	1360	1200
Mean sepn. - 4W 20°C	zero	zero	zero
Mean sepn. - 4W 50°C	zero	zero	zero

[#] Extrusion plastometer used to deliver a shear of 10,000 sec^{-1}

Example 7

This illustrates the benefits of using higher solid levels in a high nonionic formulation.

The compositions were prepared by adding the ingredients in the order listed at a temperature of 50-55°C.

Formulation	18	19
Water	to 100	to 100
KOH (49%)	13.27	13.27
Citric acid	7.0	7.0
Glycerol	4.17	4.17
Borax	2.92	2.92
Zeolite 4A (as 100%)	15.5	18.0
Polymer A-11 (33%)	5.05	5.05
LAS acid*	6.25	6.25
Synperonic A3*	13.33	13.33
Synperonic A7*	13.33	13.33
Span 20*	2.0	2.0
COOL to 30°C		
Perfume	0.4	0.4
pH	7.9	7.9
Na+:K+ ratio	1:1.15	1:1

* These ingredients were added in the form of a premix

Unsheared		
Initial viscosity (mPas)	990	1790
Viscosity (4W at 20°C)	1180	1930
Viscosity (4W at 50°C)	1660	2180
Mean sepn. during 4W 20°C	0.8%	zero
Mean sepn. during 4W 50°C	1.8%	zero

The composition was sheared with an extrusion plastometer at a shear rate of 10,000 sec^{-1}.

Example 8

The following example demonstrates that post-shear can also be effective using a device which would be practical to use in factories - namely a shear valve. This was a diaphragm valve - the diaphragm is screwed down until a suitably narrow constriction to flow is achieved.

The compositions were prepared by adding the ingredients in the order listed at a temperature of 50-55°C.

Formulation	20
Water	to 100
KOH (49%)	16.71
Citric acid	9.14
Glycerol	4.17
Borax	2.92
Sodium bicarbonate	3.5
Zeolite 4A (as 100%)	13.33
Polymer A11 (33%)	5.05
LAS acid*	6.25
Synperonic A3*	13.33
Synperonic A7*	13.33
Span 20*	2.0
Cool to 30°C	
Perfume	0.4
pH	9.1

* These ingredients were added in the form of a premix

The formulation was either stored at 20°C, or submitted to post-shear by using a shear valve. Results were:-

FORMULATION	21	22	23
Shear device	None	Shear valve	Shear valve
Back pressure	-	2 bar	7 bar
Initial viscosity	1550	1580	1510
4 week viscosity	1720	1600	1540
4 week separation	1%	zero	zero

This example shows that post-shear with a shear-valve improves the viscosity and stability characteristics of liquid detergent compositions.

Example 9

The following liquid was prepared by adding the ingredients in the order listed while keeping the temperature as close to 50°C as possible. The actives were added as premix. The formulation was cooled to 30°C before addition of perfume.

FORMULATION	24
Water	6.53
KOH (49%)	16.71
Citric acid	9.14
Glycerol	4.17
Borax	2.92
Sodium bicarbonate	3.5
Zeolite 4A (80%)	16.67
Polymer # (33%)	5.05
Linear alkyl benzene sulphonic acid*	6.25
Synperonic A3*	13.33
Synperonic A7*	13.33
Span 20 (sorbitan monolaurate)*	2.0
Perfume	0.4

polymer A-11 as described in EP 346 995.

* These ingredients were added in the form of a premix

Samples of the liquid were passed through an extrusion plastometer. The results were:

	Post shear rate (1000/sec)						
	0	2	5	10	19	29	36
4 weeks sepn (20 degC)	Yes	Yes	No	No	No	No	No
4 weeks sepn (50 degC)	Yes	Yes	Yes	No	Yes	Yes	Yes
4 weeks mean visc (21/s)	1700	1660	1870	1610	1130	1160	1150

This example not only shows that applying post-shear to high nonionic liquids is beneficial as it reduces separation at 20°C. For this formulation there appears to be an optimum post shear rate around 10,000 reciprocal seconds as physical stability is achieved with little change in viscosity. Generally, the optimum degree of post shear will be formulation dependent and can be established by experiment for any given formulation.

Example 10

Formulation 24 of Example 9 was prepared. Samples of the liquid were passed through an diaphragm shear valve. The results were:-

	Shear valve		
	Unsheared	Low shear(2 bar)	High shear(7 bar)
Batch 1			
Sepn (20C)	Yes	No	No
Mean visc	1690	1620	1610
Batch 2			
Sepn (20C)	Yes	No	No
Mean visc	1540	1430	1360

It can be seen that application of post shear, this time via use of a shear valve, has conferred physical stability with relatively little change in viscosity.

Example 11

The following formulation was prepared:

<u>FORMULATION</u> <u>(% by weight)</u>	<u>25</u>
K-LAS	8.1
Synperonic A7	15.5
Synperonic A3	15.5
Glycerol	4.9
Borax 10aq	3.4
K-citrate 4aq	12.4
Polymer	1.0
Water	39.2
Na+:K+ ratio	1:4.49

Formulation 25 contains lamellar droplets that lack internal symmetry and contain non-concentric surfactant material.

<u>Example 12</u>

The following formulation was prepared:

<u>FORMULATION</u> <u>(% by weight)</u>	<u>26</u>
Priolene 6902	6.09
Synperonic A7	12.98
Synperonic A3	12.98
Glycerol	4.06
Borax 10aq	2.84
KOH (50%)	16.15
Na-carbonate	3.25
Citric Acid 1aq.	9.74
Zeolite	16.23
Polymer	0.8
Water & minors	ad 100
pH	9.84
Na+:K+ ratio	2:1

Formulation 26 contains lamellar droplets that lack internal symmetry and contain non-concentric surfactant material.

Example 13

The following formulation was prepared by premixing the sulfate and nonionic and adding this premix to a solution of citrate, borate, glycerol and the polymer. Thereafter, the mixture stirred with an overhead stirrer for 30 minutes at room temperature.

Ingredients	weight %
Sodium secondary alcohol sulfate 1)	20
Nonionic 2)	20
Sodium citrate dihydrate	10
Sodium tetraborate decahydrate	3.5
Glycerol	5
Polymer 3)	1
Water	to 100%
Viscosity 4)	200 mPas

1) Average total alkyl chain length 15.2, total of 2 and 3 isomer content 22%)
2) C12-13 ethoxylated with 6.5 EO on average
3) Polymer of A11 of EP-A-0,346,995
4) Measured with a Haake constant-stress theometer at 21s^{-1}

The formulation was studied under polarized light microscopy and no Maltese crosses were identified. The liquid contains droplets with a size in the range of 2-20 μm; these lack radial symmetry; the joined thickness of the bi-layers in the droplets is smaller than the radius of the droplet (less than 25%, i.e. less than about 10%, of the radius); the droplets consist only of a few lamellar bi-layers, as found using a transmission electron microscope. The composition shows high flexibility in incorporation of ingredients.

Example 14

Substituting the secondary sulphate of the formulation of Example 13 with a secondary sulphate having 62% of the 2 and 3 isomers (ratio of nonionic to secondary alkyl sulphate comprising at least 3 C-atoms on both sides of the C-atom to which the sulphate group is attached is from 72:28) resulted in a liquid with droplets that comprise lamellar bi-layers and a core comprising a non-concentric lamellar phase; the joined thickness of the bi-layers is between 50 and 99% of the radius.

Example 15

Increasing the level of the secondary sulphate of the above formulation (22% 2,3 isomers) of Example 13 to 27% and lowering the nonionic level to 13% (ratio of nonionic to secondary alkyl sulphate comprising at least 3 C-atoms on both sides of the C-atom to which the sulphate group is attached is from 35:65) resulted in a liquid with droplets that have full bilayer radial symmetry.

Example 16

The following liquid was prepared:

Fatty acid		6
Nonionic 1	1)	13
Nonionic 2	2)	13
Glycerol		4
Borax 10aq		3
KOH (50%)		16
Na2CO3		3
Citric acid		10
Zeolite 4A		16
Polymer	3)	2

Antifoam & Enzymes	1
Water	ad 100 4)

1) Nonionic 1 is Synperonic A7, ex ICI
2) Nonionic 2 is Synperonic A3, ex ICI
3) Polymer A11 of EP 346995
4) pH: about 9.8

The liquid did not show phase separation during 5 weeks at 37°C. The droplets in the liquid showed no radial symmetry. At increasing polymer concentrations, the droplets become smaller. The enzyme half live is high (protease larger than 10 weeks and lipase 5 weeks at 37°C). Stability is further increased if post shear is applied, if higher polymre levels are used and if zeolite level is increased.

Example 17

The following liquid was prepared. Post shear was applied.

Oleic acid		7.5
Nonionic 1	1)	16
Nonionic 2	2)	16
Glycerol		5
Borax 10aq		3.5
KOH (50%)		to pH of 9
Na2CO3		4
Polymer	3)	1.5
Citric acid		7.1
Enzymes		1
Water (& minors)		ad 100

1) Nonionic 1 is Synperonic A7, ex ICI
2) Nonionic 2 is Synperonic A3, ex ICI
3) Polymer A11 of EP 346995

The liquid contains droplets that lack radial symmetry.

Example 18

The following liquids were made by dissolving the alkali in water, adding the glycerol, the Na-citrate, the borax, the polymer and the active premix, whereafter the mixture was stirred:

Ingredients	Composition 1 % by weight
Na-LAS	7.9
Nonionic 1 1)	15.8
Nonionic 2 2)	15.8
Glycerol	4.9
Borax 10aq	3.5
Na-citrate . 2aq	9.9
Polymer 3)	1.0
Water	ad 100

1) Synperonic A7
2) Synperonic A3
3) Polymer A11 of EP 346,995

Composition 2 was made by adding on top of composition 1 20% by weight of zeolite 4A material, ex Wissalith P (added during preparation before the active premix).

Composition 3 was made by adding 2% of polymer to the composition 1 instead of 1% by weight.

Composition 4 was made by adding 2% of polymer to the composition 2 instead of 1% by weight.

Composition 5 was made by adding 0% of polymer to the composition 1 instead of 1% by weight.

The following results were obtained:

	Composition				
	1	2	3	4	5
1 week:					
% Phase Separation	27	0	9	0	0
Viscosity	90	344	155	573	8480
1 month:					
% Phase Separation	34	1	22	1	0
Viscosity	105	333	142	686	2372

It can be concluded that stability increases and/or viscosity improves with addition of solid particles and/or by adding more polymer.

Liquid compositions 1-4 contain droplets that have a structure lacking internal symmetry.

Composition 4 does not show no phase separation after 1 week. The composition was centrifuged and the zeolite was removed, whereafter the resulting liquid was remixed. The remixed composition (which is equal to composition 3) showed phase separation after a week storage similar to composition 3. It can be concluded that presence of solid particles increases stability.

Example 19

A following base liquid was prepared:

Ingredients	% by weight
Nonionic 1)	13
Nonionic 2)	13
LAS acid	6
Zeolite	13
Polymer 3)	1.5
Enzyme & stabilisers	7
Water & electrolyte	ad 100

1) Synperonic A3
2) Synperonic A7
3) Polymer A11 of EP 346,995

Span 20 was add at various levels and the following stabilities were obtained:

Level (% by weight)	0	2	4	6.5
Separation after 4 weeks; 37°C	4.5	3.5	4.25	3.25

This illustrates the possitive effects of Spans on the viscosity of high nonionic liquid. Viscosity drift was also improved.

<u>Example 20</u>

Enzyme stability was measured in the liquid of Example 19 and found to be very good: 92% for lipase and 74% for protease after 4 weeks at 37°C.

<u>Example 21</u>

Various levels of solid particles were added to the liquid of Example 19 and the following results were obtained:

Zeolite level (% by weight)	13	15.5	18	20
Separation (4 weeks ambient)	4	2	0	0

This shows that solid particles can stabilise high nonionic liquids. The same composition without solid particles showed high separation after 4 weeks at ambient.

<u>Example 22</u>

The liquids of Examples 1 and 2I and 2K of EP-A-623670 were prepared.

Example 1 resulted in a liquid which, when studied under the electron microscope, was found to contain surfactant droplets in an isotropic continuous phase. The surfactant droplets did not show birefringent under the electron microscope. Study of the droplets with freeze-fraction electron microscopy revealed that the surfactant droplets had a lamellar coating on the outside and stacks of surfactant in the core. The level of solid particles was estimated to be about 5% by weight of the composition.

The liquids of Examples 2I and 2K were prepared and they were studied under the electron microscope and found to be complete spherulites.

Claims

1. Aqueous structured liquid detergent composition comprising lamellar droplets of surfactant material, said composition comprising a weight ratio of nonionic surfactant to anionic surfactants that is smaller than 95:5 and that is higher than 50:50, said composition comprising:

- i) a nonionic sugar stabilising agent containing a sugar unit selected from apiose, arabinose, galactose, lyxose, mannose, gallose, altrose, idose, arabinose, ribose, talose, xylose, maltose, lactose, sucrose and sorbitan;
- ii) at least 10%, preferably at least 15% by weight of solid particles;
- iii) anionic surfactants selected from C12-C18 alkyl sulphate, sulphonate, mono unsaturated fatty acids and mixtures thereof, wherein the anionic sulphate or sulphonate comprises at least 3 c-atoms on both sides of the C-atom to which the sulphate or sulphonate group is attached;
- iv) enzymes; or
- v) mixtures thereof.

2. Aqueous structured liquid detergent composition comprising lamellar droplets of surfactant, wherein said surfactant comprises material present in concentric bi-layer form consisting of one or more bi-layers of surfactant material that have a joined thickness which is smaller than the radius of the droplet, wherein the composition comprises:

- i) a nonionic sugar stabilising agent containing a sugar unit selected from apiose, arabinose, galactose, lyxose, mannose, gallose, altrose, idose, arabinose, ribose, talose, xylose, maltose, lactose, sucrose and sorbitan;

ii) at least 10%, preferably at least 15% by weight of solid particles;

iii) anionic surfactants selected from C12-C18 alkyl sulphate, sulphonate, mono unsaturated fatty acids and mixtures thereof, wherein the anionic sulphate or sulphonate comprises at least 3 c-atoms on both sides of the C-atom to which the sulphate or sulphonate group is attached; or

iv) enzymes; or

v) mixtures thereof.

3. Composition according to claims 1-2, characterised in that the composition further comprises from 1.5 to 5% by weight of a decoupling polymer.

4. Composition according to claims 1-3, characterised in that the Na+:K+ ratio is from 10:1 to 1:10.

5. Composition according to claims 1-3, characterised in that the composition further comprises enzyme material.

6. Process of preparing aqueous liquid detergent compositions with lamellar droplets that comprise surfactant material, said liquid comprising nonionic surfactants at a level of more than 50% by weight of the total surfactant material, said process comprising the mixing of water, electrolyte material and surfactant material to create a lamellar structure, characterised in that thereafter lamellar structure is subjected to a post-shear operation.

7. Process of preparing aqueous liquid detergent compositions with lamellar droplets that comprise

surfactant material comprising nonionic surfactants at a level of more than 50% by weight of the total surfactant material, wherein a mixture of water, electrolyte material and surfactant material is prepared from which a lamellar structure is created, characterised in that the viscosity of the mixture is increased by:

a) adjusting the Na:K molar ratio to a ratio of from 10:1 to 1:10;
b) by adding polymer material;
c) by adding at least 5% by weight of solid particles; and
d) combinations thereof.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 95/03859

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	EP,A,0 359 308 (UNILEVER NV ET AL.) 21 March 1990 see the whole document ---	1
Y	WO,A,91 00331 (UNILEVER PLC ET AL.) 10 January 1991 cited in the application see claims ---	1
Y	EP,A,0 178 006 (UNILEVER NV ET AL.) 16 April 1986 see column 4, line 1 - line 8 see claims ---	1
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search 24 January 1996	Date of mailing of the international search report 19.02.1996
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Authorized officer Pelli Wablat, B

Interr   ıal Application No
PCT/EP 95/03859

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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