



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP90/01667 <b>(22) International Filing Date:</b> 4 October 1990 (04.10.90)  <b>(30) Priority data:</b> 89202580.0                      12 October 1989 (12.10.89)      EP <i>(34) Countries for which the regional or international application was filed:</i> 8927728.9                      7 December 1989 (07.12.89)      GB  <b>(71) Applicant (for GB only):</b> UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).  <b>(71) Applicant (for all designated States except GB US):</b> UNILEVER N.V. [NL/NL]; P.O. Box 137, NL-3000 DK Rotterdam (NL).		<b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> VAN DE PAS, Johannes, Cornelis [NL/NL]; Philips Willemstraat 6, NL-3136 CV Vlaardingen (NL). SCHEPERS, Frederik, Jan [NL/NL]; Albertine Agneslaan 234, NL-3136 NE Vlaardingen (NL). VERHEUL, Rudolf, Cornelis, Stefanus [NL/NL]; Albrecht Thaelaan 49, NL-3571 EG Utrecht (NL).  <b>(74) Agent:</b> JOPPE, Hermina, L., P.; Unilever N.V., Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL).  <b>(81) Designated States:</b> AU, CA, CH (European patent), DE (European patent), ES (European patent), FI, FR (European patent), GB (European patent), IT (European patent), NL (European patent), SE (European patent), US.  <b>Published</b> <i>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.</i>
<b>(54) Title:</b> LIQUID DETERGENTS  <b>(57) Abstract</b>  A liquid detergent composition comprising a dispersion of lamellar droplets of detergent active materials in an aqueous continuous phase, said composition comprising a deflocculating polymer and said composition having a pH of more than 12.5		

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LIQUID DETERGENTS

The present invention is concerned with aqueous liquid detergent compositions which contain sufficient

5 detergent-active material and, optionally, sufficiently dissolved electrolyte to result in a structure of lamellar droplets dispersed in a continuous aqueous phase.

10 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.

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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

20 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  
25 US 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  
30 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.

35 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  
5 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  
10 is around 0.6 (say from 0.5 to 0.7), 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 1 Pas at a shear rate of  $21\text{s}^{-1}$ ). This volume fraction also endows useful  
15 solid-suspending properties.

A problem in the formulating of liquid detergent compositions is to prevent the occurrence of flocculation. When flocculation occurs between the  
20 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.

25

It is an object of the invention to minimise flocculation of liquid detergent compositions of the lamellar droplet type. It is a second object of the present invention to formulate stable liquid detergent  
30 compositions which are of relative high pH and relative low viscosity.

It has been suggested in GB 1,506,427 to formulate liquid detergent compositions containing five essential  
35 ingredients in specific relative amounts. The compositions described contain from 3-12 % by weight of

a potassium alkylbenzenesulphonate, 2-8 % by weight of a potassium soap of a C<sub>8-22</sub> fatty acids or polymers thereof and 0.5 to 5 % by weight of a nonionic detergent active material, wherein the relative ratios of the active ingredients are within narrowly defined ranges. Compositions according to this patent comprise from 1-25 % of an alkali metal tripolyphosphate and from 0.1-2 % of a specific copolymer of maleic anhydride with vinylmethylether, ethylene or styrene, partially esterified with the nonionic detergent active material. GB 1,589,971 relates to similar compositions wherein part of the alkali metal tripolyphosphate is replaced by tetrapotassium pyrophosphate. The pH of the exemplified compositions is 12.5, which would generally be too low for certain purposes such as for example the industrial cleaning of fabrics, the viscosity of the products is 550 mPas or more at 30 s<sup>-1</sup>.

Surprisingly, it has now been found that stable liquid detergent compositions of the lamellar droplet type and of high pH and acceptable viscosity, can be formulated, provided that they comprise a deflocculating polymer. Suitable deflocculating polymers are for example polymers comprising a hydrophilic backbone and one or more hydrophobic sidechains.

Accordingly the present invention relates to a liquid detergent composition comprising a dispersion of lamellar droplets of detergent active materials in an aqueous continuous phase, said composition comprising a deflocculating polymer (possibly comprising a hydrophilic backbone and one or more hydrophobic sidechains), said composition having a pH of more than 12.5.

Preferably compositions of the invention are stable. In the context of the present invention, stability for

these systems can be defined in terms of the maximum separation compatible with most manufacturing and retail requirements. That is, the 'stable' compositions will yield no more than 10 %, preferably no more than 5 %, most preferred no more than 2% by volume phase

- 5 separation as evidenced by appearance of 2 or more separate phases when stored at 25°C for 21 days from the time of preparation.

- 10 Preferably, compositions of the invention have a pH of more than 12.5, more preferred more than 13.0, especially preferred more than 13.5. These high pH values render the products of the invention especially suitable for the preparation of liquid detergent
- 15 compositions intended for use in the industrial cleaning of fabrics.

Compositions of the invention preferably have a viscosity of less than 2,500 especially less than

- 20 1,000 mPas at 21 s<sup>-1</sup>, more preferred less than 750 mPas, most preferred less than 500 mPas, especially preferred between 100 and 400 mPas at 21 s<sup>-1</sup>.

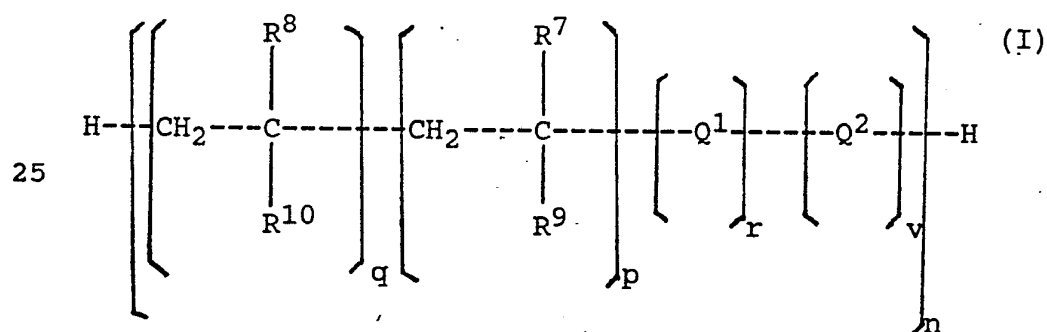
Suitable deflocculating polymers for use in compositions of the present invention are for instance described in our copending European patent application 89201530.6 (EP 346 995). Generally the hydrophilic backbone of the

- 25 polymer is predominantly linear ( the main chain of the backbone constitutes at least 50 %, preferably more than 75 %, most preferred more than 90% by weight of the backbone), suitable monomer constituents of the hydrophilic backbone are for example unsaturated C<sub>1-6</sub> acids, ethers, alcohols, aldehydes, ketones or esters, sugar units, alkoxy units, maleic anhydride and
- 30 saturated polyalcohols such as glycerol. Examples of suitable monomer units are acrylic acid, methacrylic

acid, maleic acid, vinyl acetic acid, glucosides, ethylene oxide and glycerol. The hydrophilic backbone made from the backbone constituents in the absence of hydrophilic side-groups is relatively water-soluble at ambient temperature and a pH of between 10.0 and 15.0. Preferably the solubility is more than 1g/l, more preferred more than 5 g/l most preferred more than 10 g/l. Most preferably the hydrophilic backbone remains soluble in these concentrations in the presence of up to 40 % by weight of electrolytes (e.g. sodium citrate).

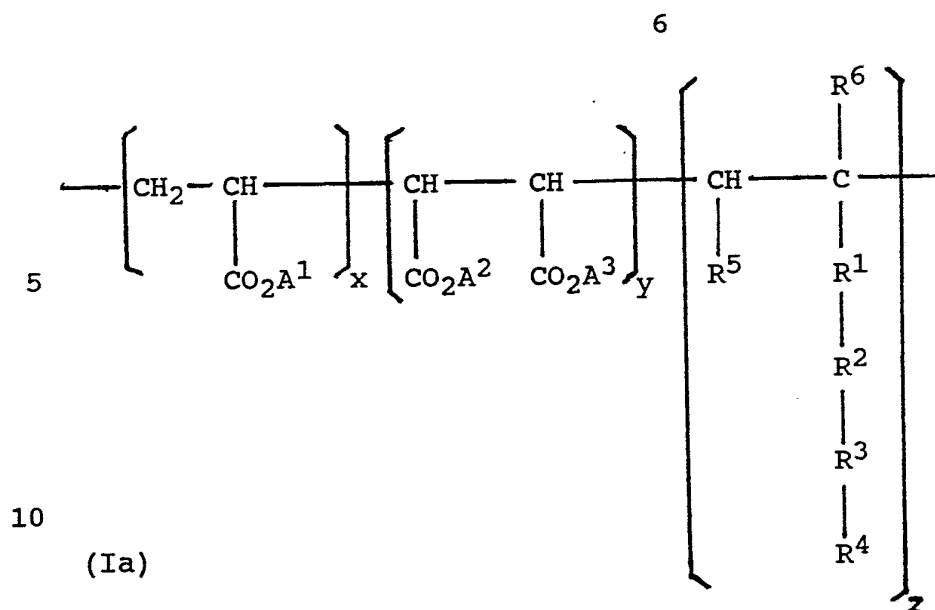
Preferably the hydrophobic sidegroups are composed of relatively hydrophobic alkoxy groups for example butylene oxide and/or propylene oxide and/or alkyl or alkenyl chains having from 5 to 24 carbon atoms. The hydrophobic groups may be connected to the hydrophilic backbone via relatively hydrophilic bonds for example a poly ethoxy linkage.

Preferred polymers are of the formula:



wherein:

$\text{Q}^2$  is a molecular entity of formula (Ia):



wherein:

R<sup>1</sup> represents -CO-O-, -O-, -O-CO-, -CH<sub>2</sub>-, -CO-NH- or is absent; especially it has been found that a -CO-O linkage is more stable at high pH values than a -O-CO-link.

$R^2$  represents from 1 to 50 independently selected alkyleneoxy groups preferably ethylene oxide or propylene oxide groups, or is absent, provided that when  $R^3$  is absent and  $R^4$  represents hydrogen or contains no more than 4 carbon atoms, then  $R^2$  must contain an alkyleneoxy group preferably more than 5 alkyleneoxy groups with at least 3 carbon atoms;

R<sup>3</sup> represents a phenylene linkage, or is absent;

R<sup>4</sup> represents hydrogen or a C<sub>1-24</sub> alkyl or a C<sub>2-24</sub> alkenyl group, with the provisos that

a) when  $R^1$  represents  $-O-CO-$ ,  $R^2$  and  $R^3$  must be absent and  $R^4$  must contain at least 5 carbon atoms;

b) when  $R^2$  is absent,  $R^4$  is not hydrogen and when



also  $R^3$  is absent, then  $R^4$  must contain at least 5 carbon atoms;

$R^5$  represents hydrogen or a group of formula  $-\text{COOA}^4$ ;

5

$R^6$  represents hydrogen or  $\text{C}_{1-4}$  alkyl; and

$A^1$ ,  $A^2$ ,  $A^3$  and  $A^4$  are independently selected from hydrogen, alkali metals, alkaline earth metals, ammonium and amine bases and  $\text{C}_{1-4}$ , or  $(\text{C}_2\text{H}_4\text{O})_t\text{H}$  wherein  $t$  is from 1-50, and wherein the monomer units may be in random order.

$Q^1$  is a multifunctional monomer, allowing the branching of the polymer, wherein the monomers of the polymer may be connected to  $Q^1$  in any direction, in any order, therewith possibly resulting in a branched polymer. Preferably  $Q^1$  is trimethyl propane triacrylate (TMPTA), methylene bisacrylamide or divinyl glycol.

20

$n$  is at least 1,  $z$  and  $v$  are 1; and  $(x + y + p + q + r) : z$  is from 4 : 1 to 1,000 : 1, preferably from 6 : 1 to 250 : 1; in which the monomer units may be in random order; and preferably either  $p$  and  $q$  are zero, or  $r$  is zero;

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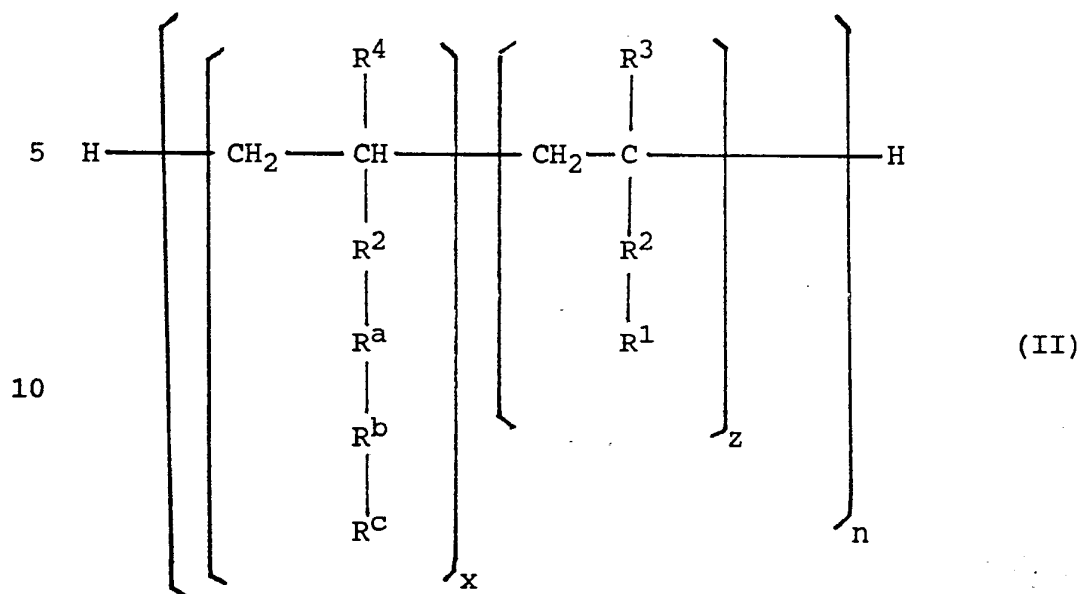
$R^7$  and  $R^8$  represent  $-\text{CH}_3$  or  $-\text{H}$ ;

$R^9$  and  $R^{10}$  represent substituent groups such as amino, amine, amide, sulphonate, sulphate, phosphonate, phosphate, hydroxy, carboxyl and oxide groups, preferably they are selected from  $-\text{SO}_3\text{Na}$ ,  $-\text{CO}-\text{O}-\text{C}_2\text{H}_4-\text{OSO}_3\text{Na}$ ,  $-\text{CO}-\text{O}-\text{NH}-\text{C}(\text{CH}_3)_2-\text{SO}_3\text{Na}$ ,  $-\text{CO}-\text{NH}_2$ ,  $-\text{O}-\text{CO}-\text{CH}_3$ ,  $-\text{OH}$ ;

35 Preferably polymers for use in compositions of the invention are substantially free of hydrolysable groups

such as carbonyl groups for increased polymer stability at high pH values. Particularly preferred polymers for use in compositions of the invention comprise hydrophilic backbones constituted by acid groups such as acrylic acid and at least one hydrophobic side chain which is constituted of from 5 to 75 relatively water-insoluble alkoxy groups such as propoxy units optionally linked to the hydrophylic backbone via a poly-alkoxy linkage constituted of from 1-10 relatively watersoluble alkoxy groups such as ethoxy units. Other preferred polymers are copolymers of acid groups such as acrylic acid and alpha olefins comprising at least 5 carbon atoms. Polymers as in formula IA, wherein  $R^1$  is  $-CO-O-$  are more preferred than polymers wherein  $R^1$  is  $-O-CO-$ , because of the better stability at high pH's of the former.

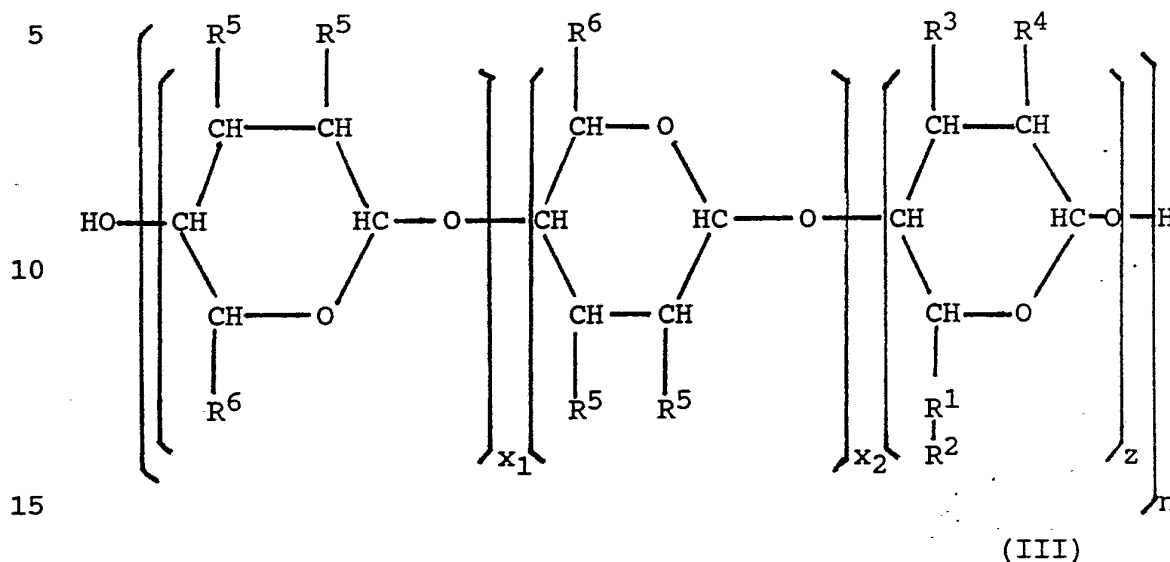
Other preferred polymers for use in compositions of the invention are described in our copending British patent applications 8924479.2, 8924478.4 and 8924477.6. Of the polymers described in those patent applications, especially the use of polymers in accordance with GB patent application 8924478.4 is preferred. These polymers are constituted of nonionic monomers and ionic monomers, wherein the ionic monomer is from 0.1 to 50 % by weight of the polymer. Especially preferred polymers of this type are of the formula:



wherein: x, z and n are as above;

- R<sup>3</sup> and R<sup>4</sup> represent hydrogen or C<sub>1-4</sub> alkyl;
  - R<sup>2</sup> represents -CO-O-, -O-, -O-CO-,  
-CH<sub>2</sub>-, -CO-NH-, or is absent;
  - R<sup>1</sup> represents -C<sub>3</sub>H<sub>6</sub>-N<sup>+</sup>-(CH<sub>3</sub>)<sub>3</sub>(Cl<sup>-</sup>),  
-C<sub>2</sub>H<sub>4</sub>-OSO<sub>3</sub><sup>-</sup>(Na<sup>+</sup>), -SO<sub>3</sub><sup>-</sup>(Na<sup>+</sup>),  
-C<sub>2</sub>H<sub>4</sub> N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub> Cl<sup>-</sup>, -C<sub>2</sub>H<sub>4</sub> N<sup>+</sup>(C<sub>2</sub>H<sub>6</sub>)<sub>2</sub> Cl<sup>-</sup>,  
-CH<sub>2</sub> N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub> Cl<sup>-</sup>, -CH<sub>2</sub> N<sup>+</sup>(C<sub>2</sub>H<sub>6</sub>)<sub>2</sub> Cl<sup>-</sup> or  
benzyl-SO<sub>3</sub><sup>-</sup>(Na<sup>+</sup>);
  - R<sup>a</sup> is CH<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub> or is absent;
  - R<sup>b</sup> represents from 1 to 50 independently  
selected alkylene oxide groups, preferably  
ethylene oxide groups or is absent;
  - R<sup>c</sup> represents -OH or -H;
- and wherein if R<sup>2</sup>, R<sup>a</sup> and R<sup>b</sup> are absent, then R<sup>c</sup>  
is preferably not -H.

Other preferred polymers have the formula:



Wherein:

- 20 -  $x = x_1 + x_2$   
 -  $x, z$  and  $n$  are as defined above  
 -  $R^1$  represents  $-\text{CH}_2\text{O}-$  or  $-\text{O}-$ ;  
 -  $R^2$  represents  $-\text{CH}_2\text{COO}^-\text{Na}^+$  or  $-\text{C}_3\text{H}_6\text{ON}^+(\text{CH}_3)_3\text{Cl}^-$   
 -  $R^3$  and  $R^4$  represent  $-\text{OH}$ ,  $\text{CH}_2\text{OH}$ ,  $-\text{O}(\text{C}_3\text{H}_6\text{O})_p\text{-H}$ ,  
 25  $-\text{CH}_2-\text{O}(\text{C}_3\text{H}_6\text{O})_p\text{-H}$  or  $-\text{OCH}_2\text{COO}^-\text{Na}^+$  or  
 $-\text{O}-\text{C}_3\text{H}_6\text{ON}^+(\text{CH}_3)_3\text{Cl}^-$   
 -  $R^5$  represents  $-\text{OH}$ ,  $-\text{NH}-\text{CO}-\text{CH}_3$  or  $-\text{O}(\text{C}_3\text{H}_6\text{O})_p\text{-H}$   
 -  $R^6$  represents  $-\text{OH}$ ,  $-\text{CH}_2\text{OH}$ ,  $-\text{CH}_2-\text{OCH}_3$ ,  $-\text{O}(\text{C}_3\text{H}_6\text{O})_p\text{-H}$  or  
 $-\text{CH}_2-\text{O}-(\text{C}_3\text{H}_6\text{O})_p\text{-H}$   
 30 -  $p$  is from 1 - 10.

Preferably polymers for use in compositions have a molecular weight (as determined as in our co-pending European patent application 346 995) of between 500 and  
 35 100,000, more preferred from 1,000 to 20,000, especially preferred from 1,500 to 10,000. Polymers for

use in compositions of the invention may for example be prepared by using conventional aqueous polymerisation procedures, suitable methods are for example described in the above mentioned co-pending european patent  
5 application.

Generally the deflocculating polymer will be used at from 0.01 to 5 % by weight of the composition, more preferably from 0.1 to 3.0, especially preferred from  
10 0.25 to 2.0 %.

Compositions of the invention also comprise detergent active materials, preferably at a level of from 1 to 70% by weight of the composition, more preferred a level of  
15 5 to 40 % by weight, most preferred from 10 to 35 % by weight.

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

In the widest definition the detergent-active material  
25 in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided mutually compatible) mixtures thereof. For example, they may be chosen from any of the classes, sub-classes and  
30 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  
35 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<sub>6</sub>-C<sub>18</sub>) 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 328 177, especially the use of alkyl poly glycoside surfactants such as for example disclosed in EP 70 074. Also alkyl mono glucosides may be used.

Preferably the level of nonionic surfactants is more than 1 % by weight of the composition, preferably from 2.0 to 20.0% by weight of the composition, more preferred from 5.0 to 19 %, especially preferred from 10.0 to 18.0 %.

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 detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C<sub>8</sub>-C<sub>18</sub>) alcohols produced, for example, from tallow or coconut oil, sodium and potassium alkyl (C<sub>9</sub>-C<sub>20</sub>) benzene sulphonates, particularly sodium linear secondary alkyl (C<sub>10</sub>-C<sub>15</sub>) 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<sub>8</sub>-C<sub>18</sub>) 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<sub>8</sub>-C<sub>20</sub>) with sodium bisulphite and those derived from reacting paraffins with SO<sub>2</sub> and Cl<sub>2</sub> and then hydrolyzing 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<sub>10</sub>-C<sub>20</sub> alpha-olefins, with SO<sub>3</sub> and then neutralizing and hydrolyzing the reaction product. The preferred anionic detergent compounds are sodium (C<sub>11</sub>-C<sub>15</sub>) alkyl benzene sulphonates, sodium (C<sub>16</sub>-C<sub>18</sub>) alkyl sulphates and primary (C<sub>10</sub>-C<sub>24</sub>) alkyl sodium or potassium sulphate.

Generally the level of the above mentioned anionic surfactant materials is from 1-15 % by weight of the composition. Preferably, however, low levels of these anionic materials are used, for example less than 5 %,

more preferred less than 3 % by weight of the composition, especially preferred less than 2.5 %. Preferably the weight ratio of the above mentioned synthetic anionic surfactant materials to the nonionic surfactant materials is less than 1:2, more preferred less than 1:3, especially preferred from 1:4 to 1:10.

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. Preferably the level of soap in compositions of the invention is from 5-35 % by weight of the composition, more preferred from 10-25 %.

The compositions optionally also contain electrolyte in an amount sufficient to bring about lamellar structuring of the detergent-active material. Preferably the compositions contain from 1% to 60%, especially from 10 to 45% of a salting-out electrolyte. Salting-out electrolyte has the meaning ascribed to in specification EP-A-79 646, that is those electrolytes which have a lyotropic number of less than 9.5. Optionally, some salting-in electrolyte (as defined in the latter specification) may also be included.

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



Examples of phosphorus-containing inorganic  
detergency builders include the water-soluble salts,  
especially alkali metalpyrophosphates, orthophosphates,  
polyphosphates and phosphonates. Specific examples of  
5 inorganic phosphate builders include sodium and  
potassium tripolyphosphates, phosphates and  
hexametaphosphates. Phosphonate sequestrant builders may  
also be used. For many reasons, including environmental  
reasons it is however preferred to minimise the amount  
10 of phosphate builders. Especially the amount of alkali  
metal phosphate builders, such as sodium  
tripolyphosphate is preferably less than 0.5 % by weight  
of the composition, more preferred less than 0.1 %,  
especially preferred compositions of the invention are  
15 substantially free of phosphate builder materials.

Examples of non-phosphorus-containing inorganic  
detergency builders, when present, include water-soluble  
alkali metal carbonates, bicarbonates, silicates and  
20 crystalline and amorphous aluminosilicates. Specific  
examples include sodium carbonate (with or without  
calcite seeds), potassium carbonate, sodium and  
potassium bicarbonates, silicates and zeolites. For high  
pH compositions according to the invention the use of  
25 silicate builders is preferred, these materials are  
especially advantageous because of their buffering  
capacities at pH values above 12.5.

In the context of inorganic builders, we prefer to  
30 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  
35 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.

- 5 Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids, CMOS, tartrate mono succinate,  
10 tartrate di succinate 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  
15 301.882. 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  
20 would occur if substantially all were dissolved. Typical amounts are from 0.5 to 4.5% by weight.

- It is further possible to include in the compositions of the present invention, alternatively, or in addition to  
25 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  
30 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  
35 1000. Use of such polymers is generally described in our EP 301,883. Typical levels are from 0.5 to 4.5% by

weight.

Especially preferred compositions of the present invention are of low viscosity (less than 500 mPas at 21 s-1) and are substantially free of suspended solid materials such as undissolved builder materials. Preferably the level of less soluble builder materials such as sodium tripolyphosphate is less than 1 %, more preferred less than 0.5 %, more preferred less than 1 %, most preferred the builder material for use in compositions of the invention are completely water-soluble.

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. Especially preferred is the use of from 5-20 % by weight of the composition of a silicate builder material, preferably a metasilicate builder material.

Preferably compositions of the invention comprise from 5 to 99 % by weight of water, more preferred from 10- 50 %, most preferred from 15 to 40 %.

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), anti-redeposition agents, germicides and colourants.

- 5 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  
10 sensitive ingredients -if any- in water of elevated temperature, followed by the addition of the builder material, the deflocculating polymer and the detergent active material under light stirring and finally cooling the mixture and adding any temperature sensitive minor  
15 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  
20 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  
25 following Examples.

EXAMPLE I

The following compositions were made by adding the KOH plus the silicate ingredients to water of ambient temperature under stirring followed by the addition of the deflocculating polymer. The detergent active materials are premixed and subsequently added to the aqueous mixture. Finally the remaining ingredients are added. The pH of the compositions is around 14.0.

10

Ingredient	A	B	C	D	E	F	G
ABS (Marlon AS3)	-	2.3	2	4	-	-	-
15 Soap (Prifac 9470)	16	18.7	--	--	--	--	--
Soap (Priolene 6902)	--	--	16	16	16	16	15
Nonionic (Plurafac LF403)	14	14	7.2	10	9	9	9
Nonionic (Marlipal 13/60)-	-	-	4.8	--	6	6	6
20 Neutral waterglass (100%)	10	10	10	10	10	10	10
KOH (100%)	13.7	14.5	14	10	13	13	13
Polymer 1)	1	1	1	1	1	1	--
Water	<-----balance ----->						

25 1) polymer A-11 as described in EP 346 995

Composition A had a viscosity of 280 mPas at 21 s<sup>-1</sup>, composition B of 490 mPas at 21s<sup>-1</sup>, compositions C-F had viscosities of about 300 mPas. Composition G

30 (comparison) was unstable (more than 10 % phase separation upon storage for three weeks), no viscosity was measured of this composition. Compositions A-F were stable lamellar dispersions of active materials in the aqueous base. The lamellar phase volume of these

35 compositions was from 0.5 to 0.67.

Example II

The following compositions were prepared as in example I

<u>Ingredient(%wt)</u>	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
Plurafac LF403	27	12	12	12
LAS (Marlon AS3)	6	5	5	12
oleate	6	19	19	12
sodium citrate	10	10	7.5	10
KOH	5.1	6.4	8.8	7.5
Neutral waterglass(34 %)	7.5	7.5	15	7.5
polymer <sup>1)</sup>	1.5	1.5	1.5	1.5
water	<-----balance----->			
viscosity (mPas at 21 s <sup>-1</sup> )	444	264	348	288

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

The pH of the compositions was 14 or more.

The performance of the compositions was tested by washing at 60 °C at a dosage of 5 g/l in the presence of standard stained clothes AS 9. The following scores were obtained:

<u>Composition</u>	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
cleaning score	53	63	64	59

Example III

The following compositions were made as in the previous examples:

<u>Ingredient (% wt)</u>	<u>I</u>	<u>II</u>
Surfactants <sup>1)</sup>	40	40
sodium citrate	7.5	7.5
KOH	9	9
Neutral water glass	5	5
polymer <sup>2)</sup>	1.0	--
polymer <sup>3)</sup>	--	1.5
water	<--balance-->	

1) mixture of Synperonic A7, Marlon AS3 and Oleate in a weight ratio of 2.5 : 1 : 2.

2) a copolymer of acrylic acid and alpha (C<sub>12</sub>) olefinic monomers in a mole ratio of 20 : 1 and a molecular weight of 4800.

3) polymer A-11 as described in EP 346 995

Composition I had a viscosity of 1,680 mPas at 21 s<sup>-1</sup>, composition II had a viscosity of 648 mPas at 21 s<sup>-1</sup>.

Both compositions had a viscosity of 14 or more.

Example IV

The following compositions were made as in the previous examples

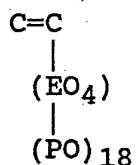
Ingredient (% wt)	A	B	C	D	E
Nonionic <sup>1)</sup>	10	12	12	11.7	-
Nonionic <sup>2)</sup>	-	-	-	-	12
Marlon AS3	4	5	2	-	2
Priolene 6903	-	-	16	-	-
Priolene 6902	16	19	-	9.2	-
Priolene 6900	-	-	-	-	16
Prifac 7904	-	-	-	6.4	-
KOH	9.8	9.8	13	13.5	13.4
Neutral waterglass	10.2	10.2	9.9	10	10.2
Tinopal CBSX	0.2	0.2	-	-	-
Polymer <sup>3)</sup>	1	1	2.8	1.8	-
Polymer <sup>4)</sup>	-	-	-	-	1
Water	<-----balance----->				

1) plurafac LF 403

2) marlipal 013/60

3) polymer A-11 of EP 346995

4) copolymer of acrylic acid and a monomer of the formula



in a molar ratio 25:1, having a molecular weight of 3100.

The compositions had a pH of 14 or more, all formulations were physically stable for more than 1 month upon storage at 37°C.



EXAMPLE V

The following formulations were made by adding the ingredients in the listed order:

<u>INGREDIENT (% wt)</u>	<u>A</u>	<u>B</u>
water	8.5	8.5
sodium citrate 2aq	8.6	8.6
Neutral water glass (34 %)	22.5	22.5
KOH (50 %)	22.0	22.0
Polymer 1) (29 %)	3.4	--
Polymer 2) (25 %)	--	3.4
Marlipal 013/60	16.0	16.0
Priolene 6902	12.7	12.7
Marlon AS3	6.3	6.3

1) a copolymer of acrylic acid and alpha (C<sub>12</sub>) olefinic monomers in a mole ratio of 33 : 1 and a molecular weight of 8700.

2) a copolymer of acrylic acid and alpha (C<sub>12</sub>) olefinic monomers in a mole ratio of 50 : 1 and a molecular weight of 7100.

Both compositions had a pH of more than 14. The viscosity of composition A was 504 mPas at 21 s<sup>-1</sup>, the viscosity of composition B was 384 mPas at 21 s<sup>-1</sup>.

CLAIMS

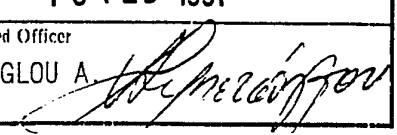
1. A liquid detergent composition comprising a dispersion of lamellar droplets of detergent active materials in an aqueous continuous phase, said composition comprising a deflocculating polymer and said composition having a pH of more than 12.5.
2. Composition according to claim 1, wherein the deflocculating polymer is of the formula I, II or III as described hereabove.
3. Composition according to claim 1 wherein the deflocculating polymer comprises a hydrophilic backbone and one or more hydrophobic side-chains.
4. Composition according to claim 1 yielding no more than 10% 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.
5. Composition according to claim 1 having a pH of more than 13.0.
6. Composition according to claim 1 having a viscosity of less than 500 mPas at 21s<sup>-1</sup>.
7. Composition according to claim 1 comprising from 0.01 to 5.0% by weight of deflocculating polymers.

8. Composition according to claim 1 comprising from 5-40% by weight of detergent active materials.
9. Composition according to claim 8 comprising from 5.0 - 19.0% of nonionic surfactants.
10. Composition according to claim 1 comprising from 5-20% of a silicate builder material, said composition being substantially free of phosphate builder materials.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 90/01667

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C11D17/00 ; C11D3/37		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C11D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	EP,A,0301883 (UNILEVER) 01 February 1989 see page 2, line 20 - page 4, line 21; claims 1, 7; table II (cited in the application) ---	1, 8-10
A	EP,A,0151884 (ALBRIGHT & WILSON LTD) 21 August 1985 see page 26, paragraph 3 - page 35, paragraph 3; claim 2; examples 78 (cited in the application) ---	1, 8-10
A	FR,A,2309629 (UNILEVER) 26 November 1976 see page 1, line 1 - page 4, line 34; claims 1, 4; example 1 (cited in the application) ---	1, 3, 7-9
A	US,A,3235505 (M.E. TUVELL) 15 February 1966 see column 1, lines 8 - 61; claims 1, 6-8, 10 ---	1
-/--		
<p><sup>10</sup> Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"T" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
04 FEBRUARY 1991	18 FEB 1991	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	SERBETSOGLOU A. 	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category <sup>a</sup>	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A,P	EP,A,0346995 (UNILEVER) 20 December 1989 see page 14, lines 43 - 46; claims 1-5, 10, 23; table 1t (cited in the application) ---	1-4, 6-10

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9001667

SA 40903

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office FDP file on  
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04/02/91

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