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(54) Titre : COMPOSITION DETERGIVE  
 (54) Title: DETERGENT COMPOSITION

(57) **Abrégé/Abstract:**

The present invention relates to liquid detergent compositions comprising substantially linear, water soluble, highly salt-tolerant non-adsorbing, ionic polymers of MW 10,000 to 1,000,000 Daltons which, when added to structured heavy duty liquids, makes the liquid highly shear thinning without decreasing pour viscosity of the composition or increasing it to a point where it is too thick. The compositions are also stable.



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<p>(21) International Application Number: PCT/EP95/01711</p> <p>(22) International Filing Date: 4 May 1995 (04.05.95)</p> <p>(30) Priority Data:</p> <table border="0"> <tr> <td>08/242,224</td> <td>13 May 1994 (13.05.94)</td> <td>US</td> </tr> <tr> <td>08/402,675</td> <td>13 March 1995 (13.03.95)</td> <td>US</td> </tr> </table> <p>(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).</p> <p>(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).</p> <p>(72) Inventors: GARCIA, Rigoberto, Felipe; 117 Lakeside Drive, Nutley, NJ 07110 (US). VASUDEVAN, Tirucherai, Varahan; 17 Oakcrest Road, West Orange, NJ 07052 (US). POST, Albert, Joseph; 22 Dohrmann Avenue, Teaneck, NJ 07666 (US). HSU, Feng-Lung, Gordon; 99 Ivy Lane, Tenafly, NJ 07670 (US).</p>	08/242,224	13 May 1994 (13.05.94)	US	08/402,675	13 March 1995 (13.03.95)	US	<p>(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, 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).</p> <p><b>Published</b> <i>With international search report.</i></p> <p style="text-align: center; font-size: 2em; font-weight: bold;">2187520</p>
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<p>(57) Abstract</p> <p>The present invention relates to liquid detergent compositions comprising substantially linear, water soluble, highly salt-tolerant non-adsorbing, ionic polymers of MW 10,000 to 1,000,000 Daltons which, when added to structured heavy duty liquids, makes the liquid highly shear thinning without decreasing pour viscosity of the composition or increasing it to a point where it is too thick. The compositions are also stable.</p>							

DETERGENT COMPOSITION

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Field of the Invention

The present invention relates to aqueous liquid detergent  
5 compositions (heavy duty liquids or HDLs) which contain  
sufficient detergent active material and, optionally,  
sufficient dissolved electrolyte to result in a structure  
of lamellar droplets dispersed in a continuous aqueous  
phase. In particular, the invention is concerned with the  
10 formation of such compositions which are able to suspend  
relatively large solid particles without simultaneously  
causing an increase in the pour viscosity of the liquids.  
Such compositions are formed by adding water soluble,  
highly salt tolerant, substantially linear, ionic, non-  
15 adsorbing polymers to an HDL that enhance the shear  
thinning behavior of the HDLs.

Background & Prior Art

20 The use of water soluble polymers (e.g., polyacrylates) to  
modify the rheological properties of heavy duty liquids  
(HDLs) is known.

In each of US 5,006,273, US 5,108,644 and US 5,205,957, for  
25 example, viscosity reducing, water soluble polymers such as  
dextran, dextran sulfonate, polyacrylate, polymethacrylate,  
acrylatemaleate copolymer and polyethylene glycol and salts  
thereof are added to detergent compositions to lower the  
pour viscosity. In US 5,006,273, the polymer claimed is  
30 from a group consisting of dextran sulfonate (up to 200,000  
to 275,000 Daltons molecular weight), dextran (up to 20,000  
Daltons), polyacrylate (up to 5,000 Daltons), acrylate  
maleate copolymer (up to 70,000 Daltons) and polyethylene  
glycol (up to 10,000 Daltons). In US 5,205,957, the claimed  
35 molecular weight of the functional polymer is less than  
2000.

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The present invention differs from the cited references in a number of significant ways.

First and foremost, the polymers used in the present invention, which we refer to as structuring polymers, are viscosity enhancing polymers while similar polymers used in the cited art reduce viscosity.

Second, the molecular weight of the viscosity reducing polymer in the art is not critical and, in the case of polyacrylate, was 5,000 or 6000 Daltons. The molecular weight of the structuring polymer of the present invention, is preferably at least 10,000 Daltons. While not wishing to be bound by theory, it is believed the higher molecular weight increases shear thinning without decreasing the high shear viscosity which thereby renders the formulation more suitable for suspending large particles. Here, high shear viscosity means viscosity measured at or above a shear rate of  $21 \text{ sec}^{-1}$ . The viscosity measured at  $21 \text{ sec}^{-1}$  is, henceforth, denoted as the pour viscosity.

Third, while no ceiling level is given for level of surfactant in these references, no example is given with greater than 25% surfactant level. Levels could not be raised higher in the art because the lack of deflocculating polymer (such as the type discussed in U.S. Patent No. 5,147,576 to Montague et al.) would cause the lamellar droplets to flocculate. By contrast, the surfactant level in the compositions of the subject invention may be 30% by weight and have been used at levels as high as 45% and could go higher.

In short, in the references discussed above, lack of deflocculating polymer and the presence of viscosity reducing polymers are believed to have led to flocculation

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of the lamellar droplets, in particular at higher surfactant levels.

US 5,147,576 (Montague et al.) also teaches the use of water soluble polymer that improves stability of heavy duty liquids at the same pour viscosity or lower pour viscosity without affecting stability. Again, our application differs because the molecular weight of the structuring polymer is preferably different: the structuring polymer enhances pour viscosity and shear thinning behavior when the structuring polymer molecular weight exceeds a specified value. This is neither taught nor suggested in Montague et al. In addition, in the only formulation taught by Montague et al. where acrylates like those of the invention are used (see Table 1 at column 24), the formulation also includes sodium oleate as a major component. By contrast, applicants have unexpectedly found that the structuring polymer satisfying our specified molecular weight requirements enhances the pour viscosity of heavy duty liquids that do not contain sodium oleate as a major component. All unsaturated fatty acids such as sodium oleate above a modest level, approximately 2%, are excluded from our formulations primarily because they impart a disagreeable odor. Unsaturated fatty acids also act as a defoaming agent, which is undesirable in our case.

US 4,992,194 (Liberati et al.) also teaches the use of water soluble polymers of the type disclosed in Montague et al. for the same function, the decrease of pour viscosity of heavy duty liquids, but the specified liquids are characterized as pH jump formulations. A pH jump HDL, defined fully in Liberati et al., is one which contains components that will boost the pH of the wash liquor. Unexpectedly, we have found that the structuring polymer enhances the pour viscosity above a preferred surfactant concentration of approximately 30%, in contradiction to the

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teaching of Liberati et al. Furthermore, we have also unexpectedly found that the structuring polymer of a specified molecular weight range enhances the shear thinning behavior of the liquid.

5

In no art is it recognized that use of structuring polymers in compositions having a minimum surfactant level will enhance suspending power of that composition (as evidenced by the Sisko constant) without decreasing pour viscosity or  
10 raising it too high.

#### Summary of the Invention

The present invention relates to aqueous liquid detergent  
15 compositions having detergent surfactants and optionally salting-out electrolyte to result in a structure of lamellar droplets dispersed in an aqueous continuous phase. The composition further preferably contains at least 0.1% by weight deflocculating polymer as described below.

20

Unexpectedly, it has been found that when a substantially linear, water soluble, highly salt tolerant, non-adsorbing, ionic polymer having a molecular weight of at least 10,000 Daltons, which we refer to as the structuring polymer, is  
25 added to such compositions in an amount from about 0.1 to 20% by weight of the formulation, it is possible to enhance the suspending power of the composition without either decreasing the pour viscosity of the composition (i.e., viscosity measured at 21 sec<sup>-1</sup>) or increasing the pour  
30 viscosity above 5,000 mPas while still maintaining stability.

The present invention is directed to liquid detergent composition comprising lamellar droplets of surfactant  
35 material dispersed in an aqueous medium comprising a substantially linear, water-soluble, highly salt-tolerant,

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non-adsorbing, ionic, structuring polymer, wherein the composition has a Sisko index of 0.4 or less, as measured by the Sisko rheological model.

- 5 Preferred compositions are composition wherein said structuring polymer does not decrease the viscosity of the composition, as measured at 21 sec<sup>-1</sup>, relative to the viscosity prior to addition of said polymer.
- 10 Preferably, composition according to the invention further comprising solid particles with a particle size of more than 25 $\mu$ m to less than 5,000 $\mu$ m.

Preferably, the structuring polymer has a MW of 10,000 to 15 1,000,000 Daltons and is preferably selected from the group consisting of polyacrylates, acrylate maleate copolymer polystyrene sulfonate and dextran sulfate.

Preferably, the structuring polymer does not increase the 20 viscosity of compositions, as measured at 21 sec<sup>-1</sup> above 5,000 mPas.

Preferably compositions according to the invention result in no more than 5% bottom clear layer separation by volume 25 upon storage at 37°C for 30 days.

Preferably, composition according to the invention comprise surfactant material at a level of greater than 30% to about 80% by weight.

30

Preferably, composition according to the invention comprise from about 0.5 to 10% peroxygen bleach particles.

Preferred compositions according to the invention are 35 liquid detergent composition comprising:

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- (a) greater than 30% to about 80% by wt. of one or more surfactants predominantly present as lamellar drops dispersed in an aqueous medium containing at least 1% by wt. electrolyte, wherein said surfactant is selected from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants zwitterionic surfactants and mixtures thereof; and wherein unsubstituted fatty acids and salts thereof comprise no more than 2% of the total composition;
- 10 (b) 0.1 to 20% by wt. of a substantially linear, water soluble, highly salt tolerant, non-adsorbing, ionic polymer having a MW of 10,000 to 1,000,000 Daltons;
- wherein the composition has a Sisko index of 0.4 or less as measured by the Sisko rheological model;
- 15 wherein said structuring polymer does not decrease the viscosity of the composition, as measured at 21 sec<sup>-1</sup>, relative to the viscosity prior to addition of said polymer;
- wherein said polymer does not increase the viscosity, as measured at 21 sec<sup>-1</sup>, above 5000 mPas; and
- 20 wherein said composition results in no more than 5% bottom clear layer separation by volume upon storage at 37°C for 30 days.
- 25 More specifically, the invention is a liquid detergent composition preferably comprising:
- (a) greater than 30% by weight (i.e., 31% and greater), preferably greater than 30 to 80% by wt. of one or more surfactants predominantly present as lamellar drops dispersed in an aqueous medium containing 1% to 60%, preferably at least 7%, more preferably at least 15% electrolyte.
- 30 (b) 0.1% to 20% by weight, preferably 0.5% to 10%, more preferably 1.0% to 5.0% by weight deflocculating polymer;
- 35 and

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(c) 0.1 to 20% by weight of a substantially linear, water soluble, highly salt-tolerant, non-adsorbing, ionic polymer (also referred to as structuring polymer) having a molecular weight of at least 10,000 Daltons;

5 wherein said composition is highly shear thinning;

wherein said structuring polymer does not decrease the pour viscosity of the detergent liquid relative to pour viscosity prior to addition; and

wherein stability of said composition means no more than  
10 5% phase separation by volume upon storage at 37°C for 30 days.

### Definitions

15

#### Shear thinning

This is determined by the flow index  $n$  of the Sisko rheological model, given by H. Barnes, J. F. Hutton, K. Walters, An Introduction to Rheology, Elsevier, 1989 as  
20 follows:

$$\eta = \eta_{\infty} + k\gamma^{n-1}$$

wherein  $\eta$  and  $\eta_{\infty}$  are viscosity at a given shear rate and infinite shear viscosity, respectively,  $k$  and  $n$  are Sisko  
25 model constants and  $\gamma$  is the shear rate.

Using this equation,  $n$  should be less than about 0.4, preferably less than 0.35, more preferably less than 0.3;

30 A lower Sisko constant is a direct indication of increased suspending power of large particles.

#### Highly salt tolerant

The polymer is soluble in a solution containing 20% citrate  
35 or any other salt at a level to match the ionic strength of a 20% citrate solution;

**2187520**Substantially linear

The contribution to the molecular weight from the branched portion of the molecule is no more than 20%; and

5 Non-adsorbing

This refers to the lack of physical or chemical adsorption to the lamellar droplets.

10 Detailed description of the invention

The present invention relates to aqueous liquid detergent compositions which contain detergent surfactant (e.g. greater than 30% by wt.) and optionally dissolved electrolyte to result in a structure of lamellar droplets  
15 dispersed in an aqueous continuous phase.

The compositions of the invention are stable lamellar dispersions preferably comprising: greater than 30% surfactant (i.e., from 31% to 80%) by weight; greater than  
20 1% electrolyte; 0.1% to 20% by weight deflocculating polymer; and 0.1% to 20% by weight of a structuring polymer; wherein, said composition is highly shear thinning. Stable lamellar dispersions have no more than 5% phase separation by volume upon storage at 37°C for 30  
25 days. In addition these compositions may be substantially free of unsaturated fatty acids such as sodium oleate (i.e. no more than about 2%, preferably no more than 1%) and these may be absent.

30 Lamellar Dispersions

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  
35 Applications', J. Wiley & Sons, Letchworth 1980.

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Such lamellar dispersions are used to endow properties such as consumer-preferred flow behavior and/or turbid appearance. Many are also capable of suspending particulate solids such as detergency builders or abrasive particles.

5 Examples of such structured liquids without suspended solids are given in US 4,244,840, whilst examples where solid particles are suspended are disclosed in specifications EP-A-160,342; EP-A-38,101; and also in the

10 aforementioned 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 product may be detected by means known to those skilled in

15 the art, for example optical techniques, various rheometrical measurements, X-ray or neutron diffraction, and electron microscopy.

The droplets consists of an onion-like configuration of

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

25 In such liquids, there is a constant balance sought between stability of the liquid (generally, higher volume fraction of the dispersed lamellar phase, i.e., droplets, give better stability), the viscosity of the liquid (i.e., it

30 should be viscous enough to be stable but not so viscous as to be unpourable) and solid-suspending capacity (i.e., volume fraction high enough to provide stability but not so high as to cause unpourable viscosity).

35 A complicating factor in the relationship between stability and viscosity on the one hand and, on the other, the volume

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fraction of the lamellar droplets is the degree of flocculation of the droplets. When flocculation occurs between the lamellar droplets at a given volume fraction, the viscosity of the corresponding product will increase 5 owing to the formation of a network throughout the liquid. Flocculation may also lead to instability because deformation of the lamellar droplets, owing to flocculation, will make their packing more efficient. Consequently, more lamellar droplets will be required for 10 stabilization by the space-filling mechanism, which will again lead to a further increase of the viscosity.

The volume fraction of droplets is increased by increasing the surfactant concentration and flocculation between the 15 lamellar droplets occurs when a certain threshold value of the electrolyte concentration is crossed at a given level of surfactant (and fixed ratio between any different surfactant components). Thus, in practice, the effects referred to above mean that there is a limit to the amounts 20 of surfactant and electrolyte which can be incorporated whilst still having an acceptable product. In principle, higher surfactant levels are required for increased detergency (cleaning performance). Increased electrolyte levels can also be used for better detergency, or are 25 sometimes sought for secondary benefits such as building.

In US 5,147,576 (Montague et al.) it was found that addition of a deflocculating polymer allowed incorporation of more surfactant and/or electrolyte without compromising 30 stability or making the compositions unpourable. The deflocculating polymer is as defined in Montague et al. The level of deflocculating polymer in the present invention is 0.1% to 20% by weight, preferably 0.5% to 5% by weight, most preferably 1% to 3% by weight.

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The compositions of Montague et al., however, even with deflocculating polymer, may have poor solids suspending ability. This is evidenced by applicants visual observation of instability when particles in the size range of 500 to 5 750 microns, e.g. with a density that differed from the liquid density by 0.2 to 0.3 specific gravity units, were placed in such liquids.

In addition, in the only composition of Montague where a 10 polyacrylate-maleate like that of the invention is used, there is also found relatively large amounts of unsaturated fatty acids such as oleate. These not only impart a bad aroma, but also act as undesirable defoaming agents. Such 15 unsaturated acids are used in the present invention in amounts no greater than about 2% by wt., preferably no more than 1% by wt. and may be absent altogether.

#### pH-jump HDL

A sub-class of lamellar dispersions included in the liquid 20 detergent compositions, or HDLs, relevant to this invention are pH-jump HDLs. A pH-jump HDL is a liquid detergent composition containing a system of components designed to adjust the pH of the wash liquor. It is well known that organic peroxyacid bleaches are most stable at low pH (3- 25 6), whereas they are most effective as bleaches in moderately alkaline pH (7-9) solution. Peroxyacids such as described in EP-A-564,250, NAPAA, NAPSA, PAP and DPDA (see e.g. WO 95/06104) cannot be feasibly incorporated into a conventional 30 alkaline heavy duty liquid because of chemical instability. To achieve the required pH regimes, a pH jump system has been employed in this invention to keep the pH of the product low for peracid stability yet allow it to become moderately high in the wash for bleaching and detergency efficacy. One such system is borax 10H<sub>2</sub>O/ polyol. Borate 35

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ion and certain cis 1,2 polyols complex when concentrated to cause a reduction in pH. Upon dilution, the complex dissociates, liberating free borate to raise the pH. Examples of polyols which exhibit this complexing mechanism with borax include catechol, galactitol, fructose, sorbitol and pinacol. For economic reasons, sorbitol is the preferred polyol.

Sorbitol or equivalent component (i.e., 1,2 polyols noted above) is used in the pH jump formulation in an amount from about 1 to 25% by wt., preferably 3 to 15% by wt. of the composition.

Borate or boron compound is used in the pH jump composition in an amount from about 0.5 to 10.0% by weight of the composition, preferably 1 to 5% by weight.

Bleach component is used in the pH jump composition in an amount from about 0.5 to 10.0% by weight of the composition, preferably 1 to 5% by weight.

Structuring Polymer

The polymer of the liquids of the invention is a substantially linear, water soluble, highly salt tolerant, non-absorbing, ionic structuring polymer with a preferred molecular weight of at least 10,000 Daltons to 1 million Daltons, more preferably 12,000 Daltons to 500,000 Daltons.

By highly salt tolerant it is meant that the polymer is soluble in solution containing 20% citrate or any other salt at a level that matches the ionic strength of a 20% citrate solution. By substantially linear it is meant that the contribution to the molecular weight from the branched portion of the molecule is no more than 20%. By non-absorbing it is meant that there is no physical or chemical adsorption to the lamellar drops.

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Structuring polymers are preferably selected from the following anionic polymers: polyacrylic acids, copolymers of acrylic and maleic acids, polystyrene sulfonic acids, and the salts thereof, poly 2-hydroxy ethyl acrylate, 5 dextran sulfate, dextran sulfonate, poly 2-sulfato ethyl methacrylate, polyacryloamido methyl propane sulfonate, and the acid forms thereof. Particularly preferred are polyacrylic acids, copolymers of acrylic and maleic acids, polystyrene sulfonic acids and salts thereof, and dextran 10 sulfate.

Unexpectedly, applicants have discovered that the addition of substantially linear, water soluble, highly salt tolerant, non-adsorbing, ionic polymer (as defined above) 15 of preferred molecular weight at least 10,000 Daltons (i.e., referred to as structuring polymers) to the compositions described above allows much larger particles to be suspended than previously possible. Suspension properties are achieved by making the composition highly 20 shear thinning without decreasing the pour viscosity (i.e., it does not become thinner), without increasing the pour viscosity above 5000 mPas and naturally, without sacrificing stability.

25 Highly shear thinning can be quantified by the flow index of the Sisko rheological model, which is given by H. Barnes, J. F. Hutton, K. Walters, An Introduction to Rheology, Elsevier, 1989 as follows:

30 
$$\eta = \eta_{\infty} + k\dot{\gamma}^{n-1}$$

Using the equation, n should be less than about 0.40, preferably less than 0.35, more preferably less than 0.3. The Sisko constant is good indication of suspending power 35 of liquids.

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While not wishing to be bound by theory, these unexpected properties are believed to be caused because the solvated volume of the structuring polymer effectively adds to the dispersed phase volume, thereby increasing the volume fraction and increasing the viscosity, and it is also believed that the structuring polymer forms a network through the continuous phase in quiescent fluid, which is more easily disrupted at higher shear rates, thereby causing the fluid to be more shear thinning. By contrast, it is believed that lower molecular weight polymers compress the lamellar drops in the dispersed phase thereby reducing volume fraction and viscosity.

The level of structuring polymer in the present invention is preferably 0.1% to 20% by weight, more preferably 0.5% to 10% by weight, and most preferably from 1% to 3%. The average molecular weight of the structuring polymer is defined to be preferably greater than 10,000 Daltons and less than one million Daltons, more preferably greater than 12,000 Daltons and less than 500,000 Daltons.

#### Electrolytes

As used herein, the term electrolyte means any ionic water-soluble material. However, in lamellar dispersions, not all the electrolyte is necessarily dissolved but may be suspended as particles of solid because the total electrolyte concentration of the liquid is higher than the solubility limit of the electrolyte. Mixtures of electrolytes also may be used, with one or more of the electrolytes being in the dissolved aqueous phase and one or more being substantially only in the suspended solid phase. Two or more electrolytes may also be distributed approximately proportionally, between these two phases. In part, this may depend on processing, e.g the order of addition of components. On the other hand, the term 'salts' includes all organic and inorganic materials which may be

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included, other than surfactants and water, whether or not they are ionic, and this term encompasses the sub-set of the electrolytes (water-soluble materials).

- 5 The compositions may contain electrolyte in an amount sufficient to bring about structuring of the detergent surfactant material. Preferably, the compositions contain from 1% to 60%, more preferably from 7 to 45%, most preferably from 15% to 30% of a salting-out electrolyte.
- 10 Salting-out electrolyte has the meaning ascribed to in specification EP-A-79646. Salting-out electrolyte can be defined as having a lyotropic value of less than 9.5. Optionally, some salting-in electrolyte (as defined in the latter specification), i.e. having a lyotropic value of 9.5
- 15 or higher, may also be included, provided if of a kind and in an amount compatible with the other components and the compositions is still in accordance with the definition of the invention claimed herein.

20 Surfactants

- A very wide variation in surfactant types and levels is possible. The selection of surfactant types and their proportions, in order to obtain a stable liquid with the required structure will be fully within the capability of
- 25 those skilled in the art. However, it can be mentioned that an important sub-class of useful compositions is those where the detergent surfactant material comprises blends of different surfactant types, in particular nonionic and/or a non-alkoxylated anionic and/or an alkoxylated anionic
- 30 surfactants.

- The total detergent surfactant material in the present invention is present at levels of more than 10% by weight, preferably more than 20%, more preferably more than 30% and
- 35 preferably to about 80% by weight, more preferably up to 50% by weight of the total composition.

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

In the widest definition the detergent surfactant material in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic  
10 and amphoteric surfactants and mixtures thereof. For example, they may be chosen from any of the classes, subclasses 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  
15 (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, Munchen & Wien, 1981.

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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  
25 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  
30 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.

35 Other suitable nonionics which may be used include aldobionamides such as are taught in US Patent No. 5,389,279

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to Au et al. and polyhydroxyamides such as are taught in US Patent No. 5,312,954 to Letton et al.

5  
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  
10 alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher ( $C_8$ - $C_{18}$ ) alcohols produced, for example, from tallow or coconut oil, sodium and potassium alkyl ( $C_9$ -  
15  $C_{20}$ ) benzene sulphonates, particularly sodium linear secondary alkyl ( $C_{10}$ - $C_{15}$ ) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut  
20 oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulfuric 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  
25 isethionic acid and neutralized with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins ( $C_8$ - $C_{20}$ ) with sodium bisulphite and those derived from reacting paraffins with  $SO_2$  and  $Cl_2$  and  
30 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  $C_{10}$ - $C_{20}$  alpha-olefins, with  $SO_3$  and then neutralizing and hydrolyzing the reaction product. The  
35 preferred anionic detergent compounds are sodium ( $C_{11}$ - $C_{15}$ )

alkyl benzene sulphonates and sodium (C<sub>10</sub>-C<sub>18</sub>) alkyl sulphates.

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It is also possible to include an alkali metal soap of a long chain mono- or dicarboxylic acid for example one having 12 to 18 carbon atoms at low levels, for example less than 2% by weight of the composition. Higher levels of unsaturated fatty acid soaps, such as oleic acid and salts thereof, for example, would impart an undesirable odour and reduce the foam level of the composition.

#### Solid Particles

Preferably, liquids according to the invention comprise solid suspended particles. Preferably, these solid particles have a particle size of more than 25 $\mu$ m, more preferably more than 50 $\mu$ m, most preferably more than 100 $\mu$ m and in particular more than 200 $\mu$ m and preferably less than 5,000 $\mu$ m, more preferably less than 2,000 $\mu$ m, most preferably less than 1,000 $\mu$ m and in particular less than 800 $\mu$ m.

20

For the purpose of the present invention reference to particle size refers to the D(3,2) average particle diameter (unless stated differently), which is the average surface weighted, volume/weight mean diameter calculated or D(3,2) as described by M. Alderliesten, Anal. Proc. Vol. 21, May, 1984, 167-172. The particle size can for example be determined with a Malvern Mastersizer.

The solid suspended particles may be selected from solid surfactant, builder, bleach, abrasives and enzymes. For the purpose of this invention, capsules (e.g. comprising any of the above materials or perfume or fluorescer), are included within the scope of the definition of solid particles.

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Preferably, the solid particles are present at levels of from 0.1 to 40% by weight, preferably from 5 to 30% by weight of the composition.

#### 5 Other Ingredients

Preferably, the amount of water in the composition is from 5 to 69%, more preferred from 20 to 65%, most preferred from 25 to 50%. Especially preferred less than 45% by weight.

10

Some or all of the electrolyte (whether salting-in or salting-out), or any substantially water-insoluble salt which may be present, may have detergency builder properties. 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. The builder material is any capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the composition with other beneficial properties such as the generation of an alkaline pH, the suspension of soil removed from the fabric and the dispersion of the fabric softening clay material.

Examples of phosphorous-containing inorganic detergency builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Examples of non-phosphorus-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous aluminosilicates. In the context of inorganic builders, we prefer to include electrolytes which promote the solubility of other electrolytes, for example use of potassium salts to promote the solubility of sodium salts. Thereby, the amount of dissolved electrolyte can be increased

considerably (crystal dissolution) as described in UK patent specification GB 1,302,543.

Examples of organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates, carboxymethyl oxysuccinates, carboxymethyloxymalonates, ethylene diamine-N,N, disuccinic acid salts, polyepoxysuccinates, oxydiacetates, triethylene tetramine hexacetic acid salts, N-alkyl imino diacetates or dipropionates, alpha sulpho-fatty acid salts, dipicolinic acid salts, oxidized polysaccharides, polyhydroxy-sulphonates and mixtures thereof.

The deflocculating polymer is as defined in U.S. Patent No. 5,147,576 to Montague et al. This deflocculating polymer contains of hydrophilic backbone and at least one hydrophobic side chain (hydrophobicity and preferred monomers as defined in the patent). Other deflocculating polymers have been described in WO 91/06622 (deflocculating polymer comprising alternating hydrophobic/hydrophilic groups as defined in the publication), WO 91/06623 (deflocculating polymer comprising ionic and nonionic monomers as defined in the publication), GB-A-2,237,813 (deflocculating polymer comprising hydrophobic backbone and at least one hydrophilic sidechain), WO 91/09109 and/or WO 94/03575.

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

Although it is possible to incorporate minor amounts of hydrotropes such as lower alcohols (e.g., ethanol) or

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alkanolamines (e.g., triethanolamine), in order to ensure integrity of the lamellar dispersion we prefer that the compositions of the present invention are substantially free from hydrotropes. By hydrotrope is meant any water-  
5 soluble agent which tends to enhance the solubility of surfactants in aqueous solution.

Apart from the ingredients already mentioned, a number of other ingredients may also be present, for example lather  
10 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  
15 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  
20 (including Lipolase (Trade Mark) ex Novo), germicides and colorants.

The invention will now be illustrated by way of the following Examples. In all Examples, unless stated to the  
25 contrary, all percentages are by weight.

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EXAMPLES

The following materials were used.

Surfactants: Linear alkylbenzenesulfonic acid (LAS acid) and Neodol<sup>TM</sup>25-9 (alcohol ethoxylate; C<sub>12-15</sub>EO<sub>9</sub>) were of commercial grade and were supplied by Vista Chemicals and Shell Chemicals respectively.

Polymers: Low molecular weight (MW) polyacrylic acids, NSC 91B (MW 2800 Daltons), were supplied by National Starch and Chemicals. NSC #7706:2 (60,000 MW) was also supplied by National Starch. Sokalan<sup>TM</sup> PA50 (polyacrylic acid of MW = 12,500) was obtained from BASF Chemicals. Acumer<sup>TM</sup> 1530 (MW 190,000 Daltons) was obtained from Rohm and Haas.

Deflocculating polymer (Narlex DC1) was supplied by National Starch and Chemicals (the deflocculating polymer is an acrylic acid/lauryl methacrylic copolymer of M.W. of about 3800).

Dextran (MW 15-20K Daltons) and dextran sulfate (500,000 Daltons) was supplied by Polysciences Inc. Polystyrene sulfonate (MW 70K) was supplied by Aldrich. The acrylate maleate copolymers used were Sokalan CP-5 (MW 70K), Sokalan CP-7 (MW 50K), CP-9 (MW 12,000), CP13S (MW 20,000) and were supplied by BASF; and NSC 91D (MW 2,400) and NSC 91H (MW 8,000) were supplied by National Starch and Chemicals.

Inorganic Reagents: Sodium citrate dihydrate used was of analytical reagent grade and was purchased from Aldrich Chemicals. 50 weight percent sodium hydroxide of analytical reagent grade was supplied by Fisher Scientific Company.

Other Reagents: De-ionized water was used in all the formulations and for reagent dilution.

Example 1 (Comparative)

The following compositions were prepared by adding Sorbitol, Borax, NaOH solution and Na<sub>2</sub>SO<sub>4</sub>, in that order, to deionized water. This was followed by addition of the 5 deflocculating polymer (Narlex™ DC-1), and surfactant actives. This composition was continuously mixed and maintained at 55°C during the additions. To this composition, Sokalan PA 50 solution or an amount of deionized water equal in wt. to the Sokalan PA 50 solution 10 (i.e. to equilibrate the amount of surfactant) was added at room temperature.

## Base Formulation

	<u>Composition</u>	A #	B #
15	LAS - acid	15.1	15.1
	Neodol 25-9	6.9	6.9
	NaOH 50% solution	3.8	3.8
	Borax	5.0	5.0
	Sorbitol	20.0	20.0
20	Na <sub>2</sub> SO <sub>4</sub>	2.5	2.5
	Narlex DC1 (33% solution)	3.0	3.0
	Sokalan PA 50 (40% solution)	0.0	5.0
	Water, deionized	to 100.0	to 100.0
	Rheological properties		
25	Sisko Index	0.36	0.5
	Pour Viscosity (mPa.s @ 21 sec <sup>-1</sup> )	952	311

# = comparative example

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Comparative 1A and 1B above are compositions substantially similar to Example 1 of Liberati et al, US 4,992,194.

Addition of Sokalan PA 50 can be seen to decrease the pour viscosity of the formulation as taught by Liberati et al.

5 (see 1B). It is further noted that the Sisko index increases, i.e., the liquid becomes less shear thinning, which does not satisfy the objective of the present invention.

10

Example 2

The following composition was prepared by adding citrate and NaOH to water, followed by deflocculating polymer Narlex (DC-1) and detergent surfactants. The composition  
15 was continuously stirred and maintained at 55°C during the additions.

## Base Formulation:

<u>Composition.</u>	<u>Parts</u>
20 LAS - acid	31.0
Neodol 25-9	13.2
	Total surfactants 44.2
50% NaOH	7.9
25 Na-citrate 2.H <sub>2</sub> O (salt)	16.4
Deionized water	28.4
Narlex DC-1 (33% actives solution)*	3.1

30 Aqueous solutions of structuring polymer (polyacrylates of molecular weight 12.5K contained 40 weight percent active polymer while those of 60K and 190K contained 25 weight

percent active polymer) and additional deflocculating polymer (Narlex DC-1; contains 33% active polymer), if necessary, were added on top of the base formulation.

\* Defined as in Example 1

5 The following results were obtained.

	Added Polyacrylate		Narlex DC-1	Sisko Index	Pour Viscosity	% BLS <sup>(1)</sup>
	MW <sup>(2)</sup>	wt. %	wt. %		(mPa.s)	30 days @37°C
A#	none <sup>(3)</sup>	-	1.46	0.46	993	0
B#	2.8K	2.0	1.5	0.46	370	0
C	12.5K	2.0	1.46	0.15	1350	0
10 D	12.5K	2.0	1.95	0.14	1677	0
E	60K	0.5	1.5	0.21	1439	0
F	60K	0.5	1.98	0.17	1558	0
G	190K	0.5	1.0	0.26	534	0.017
H	190K	1.0	1.0	0.15	1357	0.016

15 # = comparative example

<sup>(1)</sup> %BLS = % of total volume that separates to form a bottom clear layer.

<sup>(2)</sup> MW corresponding to the polyacrylate tradenames are: 2.8K, NSC 91B; 12.5K, Sokalan PA 50; 60K, NSC #7706:2; 20 190K, Rohm and Haas Acumer 1530.

<sup>(3)</sup> Where no polyacrylate is added, an amount of water equal in weight to the polymer solution was added to equilibrate the surfactant levels.

25 Example 2 demonstrates the Sisko constant (illustrating the ability to stably suspend large particles); the viscosity

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and the stability of the structuring polymer molecular weight, and also, when taken with Comparative Example 1, illustrates the effect of the surfactant concentration in the formulation. Formulation of Example 2B, which includes  
5 a 2,800 molecular weight polyacrylate, does not make the liquid more shear thinning in comparison to the base liquid, 2A, as quantified by their equal Sisko indices. Formulations of Example 2C-H, with polyacrylates of molecular weight greater than 10,000, exhibit considerable  
10 shear thinning (Sisko index less than 0.3, indicating good suspending power of large particles) in comparison to the base. Comparative formulation 1B and formulations 2C and 2D all contain 12,500 molecular weight polyacrylate, Sokalan PA 50. Examples 2C and 2D show enhanced shear thinning  
15 behaviour compared to their base, Example 2A, while Comparative 1B actually shows reduced shear thinning compared to its base, Comparative 1A. The comparative and Example 2 are distinct in that the comparative has a surfactant level of about 22%, while the level is about 44%  
20 in Example 2.

Example 3

The following composition was prepared following the method of Example 2. Base Formulation:

	<u>Composition</u>	<u>Parts</u>
5	LAS-Acid	26.0
	Neodol 25-9	11.5
		Total surfactants 37.5
	50% NaOH	6.5
	Na-citrate 2H <sub>2</sub> O (salt)	16.3
10	Deionized water	33.2
	Narlex DC-1 (33% actives solution)	3.0

Aqueous solutions of structuring polymer (polyacrylates of  
 15 molecular weight 12.5K contained 40 weight percent active  
 polymer while those of 60K contained 25 weight percent  
 active polymer) and additional deflocculating polymer  
 (Narlex DC-1; contains 33% active polymer), if necessary,  
 were added on top of the base formulation. The following  
 20 results were obtained.

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Polyacrylate Added	MW (of polyacrylate)	Wt.% (of active)	DC-1 (wt.%)	Sisko Index	Pour Viscosity mPas 21s <sup>-1</sup>	% BLS (v/v) 30 days @ 37°C
None*#		-	1.5	0.48	315	0.4
	60K	0.5	1.5	0.20	577	1.4
5 None#		-	1.5	0.48	356	0.4
	60K	1.5	1.5	0.14	1,704	1.1
None#		-	1.5	0.49	309	0.4
	60K	2.0	1.5	0.09	2,282	0.0

# = comparative example

10 This example demonstrates that shear thinning increases (as shown by decreasing Sisko index indicating improved suspending power of large particles) with increasing polymer concentration.

\* Where no polyacrylate was added, an amount of water equal  
15 in weight to the amount of polyacrylate solution was added.

#### Example 4

The following composition was prepared. Structuring polymer  
20 containing 25 weight percent actives) was added prior to surfactants addition unlike in the previous two examples in which structuring polymer was added to the base formulation which contains surfactants.

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	<u>Composition</u>	<u>Parts</u>
	LAS-acid	21.0 - 31.5
	Neodol 25-9	9.0 - 13.5
		Total surfactants 30.0 - 45.0
5	50% NaOH	5.3 - 8.0
	Na-citrate 2H <sub>2</sub> O	14.2 - 18.4
	PAA 60K (25 wt% solution)*	0 - 8.0
10	Narlex DC-1 (33 wt% solution)	4.5
	De-ionized water	up to 100 parts

\* Polyacrylic acid (NSC #7706.2)

15 These ratios were maintained constant in various formulations:

LAS Acid / 50% NaOH = 3.9

LAS Acid/Neodol 25-9 = 2.33

20 Na-citrate. 2 H<sub>2</sub>O / (0.056 LAS Acid + 0.67 Narlex DC-1 +  
0.75 PAA 60K + 0.5 50% NaOH + DI water), all in parts =  
0.385

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The following results were obtained.

Surfactant level wt. %	PAA 60K wt. % (of active)	Sisko Index	Pour Viscosity mPas 21s <sup>-1</sup>	%BLS (v/v) 30 days @ 37°C
30.0	- #	Viscosity not	measured	0.0
30.0	1.0	Viscosity not	measured	28.0
37.5	- #	0.44	290	0.0
37.5	0.5	0.23	526	2.8
37.5	1.0	0.21	1,439	1.5
37.5	1.5	0.14	1,946	1.1
37.5	2.0	0.14	3,889	0.0
45.0	- #	0.48	787	0.0
45.0	1.0	0.05	4,719	0.0

15 # = comparative example

This example shows that at higher surfactant levels (more than 30% by weight) stable formulations can be obtained in the presence at structuring polymers. Further, this example shows that, irrespective of the point of addition of structuring polymer (i.e., whether added before or after surfactants addition), the desired shear thinning property can be achieved with this polymer. Furthermore, the low Sisko constant indicates good suspending power of large particles.

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Example 5

The following composition was prepared as follows.

Structuring polymer (aqueous solution of 70K molecular weight polystyrene sulfonate containing 25 weight percent actives) was added prior to surfactants addition unlike in examples 1 and 3 in which structuring polymer was added to the base formulation which contains surfactants.

<u>Composition</u>	<u>Parts</u>
10 LAS - Acid	24.5 - 31.5
Neodol 25-9	10.5 - 13.5
	Total surfactants 35.0 - 45.0
50% NaOH	6.0 - 8.0
Na-citrate 2.H <sub>2</sub> O	14.2 - 16.9
15 PSS 70K (25 wt% solution)*	0 - 8.0
Narlex DC-1 (33 wt% solution)	4.5
20 Deionized water	up to 100 parts

\* Polystyrene sulfonate

These ratios were maintained constant in various formulations:

25 BDA / 50% NaOH = 3.9

BDA/Neodol 25-9 = 2.33

Na-citrate. 2 H<sub>2</sub>O / (0.056 LAS Acid + 0.67 Narlex DC-1 + 0.75 PSS 70K + 0.5 50% NaOH + DI water), all in parts = 0.385

**2187520**

The following results were obtained.

	Surfactant level Parts	PSS 70K wt.% (of active)	Sisko Index	Pour Viscosity mPas 21s <sup>-1</sup>	%BLS (v/v) 30 days @ 37°C
5	35.0	- #	0.39	224	0.0
	35.0	1.0	0.23	264	1.3
	35.0	2.0	0.17	393	2.7
	40.0	- #	0.46	395	0.4
	40.0	1.0	0.21	517	0.5
10	40.0	2.0	0.13	735	1.2
	45.0	- #	0.48	638	0.3
	45.0	1.0	0.18	957	0.3
	45.0	2.0	0.16	2,003	0.0

# = comparative example

15

This example shows that different high molecular weight structuring polymers (e.g. PSS) will have the same effect of improving shear thinning (i.e. suspending power of large particles) without decreasing pour viscosity or raising it so high that the composition becomes unpourable.

20

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Example 6

The following composition was prepared as follows.

Structuring polymer (aqueous solution of 70K or 500K molecular weight polystyrenesulfonate containing 25 weight percent actives) was added prior to surfactants addition unlike in Examples 1 and 3 in which structuring polymer was added to the base formulation which contains surfactants.

<u>Composition</u>	<u>Parts</u>
LAS - Acid	24.5 - 31.5
10 Neodol 25-9	10.5 - 13.5
	Total surfactants 35.0 - 45.0
50% NaOH	6.0 - 8.0
Na-citrate 2.H <sub>2</sub> O	14.2 - 16.9
15 PSS 70K or 500K (25 wt% solution)	0 or 8.0
Narlex DC-1 (33 wt% solution)	4.5
Deionized water	up to 100 parts

20

These ratios were maintained constant in various formulations:

$$\text{BDA} / 50\% \text{ NaOH} = 3.9$$

$$\text{BDA}/\text{Neodol 25-9} = 2.33$$

25 Na-citrate. 2 H<sub>2</sub>O / (0.056 LAS Acid + 0.67 Narlex DC-1 + 0.75 PSS 70K + 0.5 50% NaOH + DI water), all in parts = 0.385

30 The following results were obtained.

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PSS concn. wt.%	Mol. wt. Daltons	Sisko Index "n"	Pour Viscosity mPas @ 21s <sup>-1</sup>	BLS % (V/V) 30 days @ 37°C
None#	-	0.44	319	0.0
5 1.5	70,000	0.26	397	1.8
2.0	500,000	0.22	1287	1.41

#= comparative example

This example shows that polystyrene sulfonate (PSS) of both  
 10 70,000 and 500,000 Daltons cause a steep decrease in Sisko  
 Index and improved suspending power of large particles,  
 without decreasing the pour viscosity or increasing it  
 above 5,000 mPas.

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Example 7

The following composition was prepared as follows:

Structuring polymer (aqueous solution of acrylate-maleate copolymer of different molecular weights) was added prior to surfactants addition as in Examples 4 and 5.

<u>Component</u>	<u>Parts</u>
LAS Acid	26.0
Neodol 25-9	11.5
10	Total surfactants 37.5
50% NaOH	6.5
Na-citrate 2.H <sub>2</sub> O	15.9-16.3
15 Acrylate-Maleate copolymers (25 wt.% solution)	0 or 8.0
Narlex DC-1 (33 wt% solution)	4.5
Deionized water	up to 100 parts

20

These ratios were maintained constant in various formulations:

$$\text{LAS Acid} / 50\% \text{ NaOH} = 3.9$$

$$\text{LAS Acid} / \text{Neodol 25-9} = 2.33$$

$$25 \text{ Na-citrate} \cdot 2\text{H}_2\text{O} / (0.056 \text{ LAS acid} + 0.67 \text{ Narlex DC 1} + 0.75 \text{ CP-5} + 0.5 \text{ 50\% NaOH}) = 0.385$$

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The following results were obtained.

Polymer	Mol. wt. Daltons	Sisko Index "n"	Pour Viscosity mPas @ 21s <sup>-1</sup>	BLS % (V/V) 30 days @ 37°C
None #	-	0.44	290	0.0
NSC 91D #	2,400	0.62	450	0.8
5 NSC 91H #	8,000	0.5	300	0.64
Sokalan CP 9	12,000	0.36	339	0.63
Sokalan 13S	20,000	0.23	1,283	0.0
Sokalan CP 7	50,000	0.20	1,095	1.12
Sokalan CP 5	70,000	0.19	905	0.6

10 #= comparative example

This example illustrates the molecular weight effect of acrylate-maleate copolymer in terms of inducing increased shear thinning behavior. Below 8,000 Daltons it can be seen that the polymers, if at all, reduces the shear thinning character as seen by an increase in Sisko Index as opposed to polymers above 12,000 Daltons which reduce the Sisko Index (and improve suspending power of large particles).

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Example 8

The following composition was prepared as follows. Structuring polymer (aqueous solution of 70,000 Daltons acrylate-maleate copolymer, Sokalan CP5) was added prior to 5 surfactants addition as in Examples 4 and 5.

<u>Component</u>	<u>Parts</u>
LAS Acid	26.0
Neodol 25-9	11.5
	Total surfactants 37.5
50% NaOH	6.5
Na-citrate 2H <sub>2</sub> O	15.9-16.3
Sokalan CP-5 (25 wt. solution)	0 - 8.0
15 Narlex DC-1 (33 wt% solution)	4.5
Deionized water	up to 100 parts

20

These ratios were maintained constant in various formulations.

LAS acid / 50% NaOH = 3.9;

25 LAS acid / Neodol 25-9 = 2.33

Na citrate 2H<sub>2</sub>O / (0.056 LAS acid + 0.67 Narlex DC-1 + 0.75 CP5 + 0.5 50% NaOH) = 0.385

The following results were obtained.

30

Sokalan CP-5 (wt.% of active)	Sisko Index	Pour Viscosity mPas 21s <sup>-1</sup>	%BLS (v/v) 30 days @ 37°C
0.0 #	0.44	290	0.0
5 0.5 #	0.41	426	0.4
1.5	0.18	657	1.3
2.0	0.19	905	0.6

#=comparative example

This example shows that increasing the polymer  
10 concentration results in reduction of Sisko Index (more  
shear thinning at higher polymer concentration; improved  
suspending power of large particles).

#### Example 9

15 The following composition was prepared as follows.  
Structuring polymer (aqueous solution of 500,000 Daltons  
Dextran Sulfate) was added prior to surfactants addition as  
in Examples 4 and 5.

<u>Composition</u>	<u>Parts</u>
20 LAS - Acid	26.0
Neodol 25-9	11.5
	Total surfactants 37.5
50% NaOH	6.5
Na-citrate 2.H <sub>2</sub> O	15.9 - 16.3
25 Dextran Sulfate (25 wt% solution)	0 - 8.0
Narlex DC-1 (33 wt% solution)	4.5
Deionized water	up to 100 parts

These ratios were maintained constant in various formulations:

$$\text{BDA} / 50\% \text{ NaOH} = 3.9$$

$$\text{BDA} / \text{Neodol 25-9} = 2.33$$

$$5 \text{ Na-citrate. } 2 \text{ H}_2\text{O} / (0.056 \text{ LAS Acid} + 0.67 \text{ Narlex DC-1} + 0.75 \text{ CP-5} + 0.5 \text{ 50\% NaOH}) = 0.385$$

The following results were obtained.

	% Active	Sisko Index	Pour Viscosity mPas $21\text{s}^{-1}$	%BLS (v/v) 30 days @ 37°C
10	0.0 #	0.44	-	0.0
	0.5	0.34	463	0.45
	1.0	0.22	668	1.18
	1.5	0.19	1,017	0.76
	2.0	0.17	1,478	0.73

15 # = comparative example

This Example again shows that increasing the polymer concentration results in reduction of Sisko Index indicating that the suspending powder of large particles improves.

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Example 10

A pH jump system differs from the previous examples by addition of borate and sorbitol, and a typical example of such a system is given by the following composition:

5

Base Composition

	<u>Composition A</u>	<u>Composition B</u>
<u>Component</u>	<u>wt.%</u>	<u>wt.%</u>
LAS - Acid	22.7	22.7
10 Neodol 25-9	10.4	10.4
Sorbitol 70%	4.3	21.0
Na-citrate 2H <sub>2</sub> O	10.0	6.0
NaOH 50% Solution	5.7	5.7
NaBorate 10H <sub>2</sub> O	1.0	5.0
15 Narlex DC-1 (33 wt% solution)	4.5	4.5
Water	to 100	to 100
Sokalan CP 5 (25 wt.% solution)	6.0	6.0
20 EDTA*	0.9	0.9
Tinopal CBS-X**	0.2	0.2

\* Ethylene diamine tetraacetic acid - Sequestrant

\*\* Tinopal CBS-X - Fluorescer

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The following results were obtained.

Composition	Sisko Index "n"	Pour Viscosity mPas $21s^{-1}$	%BLS (v/v) 30 days @ 37°C
A	0.18	657	1.1
B	0.30	649	1.2

5

This example shows that Sokalan CP5 renders the pH-jump formulation shear thinning in the range of Sorbitol of 3.0 to 14.7 wt.% and Borax of 1 to 5 wt.%.

10 Example 11

The following composition was prepared as follows. Structuring polymer (aqueous solution of PAA 60,000 Daltons) was post added to the pH jump formulation containing peracid bleach (TPCAP, N,N'-tetraphthaloyl-di  
15 (6-aminocaproic peracid)).

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	<u>Composition</u>	<u>Parts</u>
	LAS - Acid	22.7
	Neodol 25-9	10.4
		Total surfactants 33.1
5	50% NaOH	5.7
	Na-citrate 2H <sub>2</sub> O	8.2
	Borax	3.2
	Sorbitol (70% solution)	13.7
10	Narlex DC-1 (33 wt.% solution)	4.5
	Fluorescer	0.2
	EDTA	0.9
	Perfume	0.25
	DI H <sub>2</sub> O (deionized water)	16.9
15	TPCAP (30% wet cake)	11.4 (post-added)*
	PAA (35% solution)	2.0 (post-added)*

\* For formulation without PAA, 2.0 parts deionized water (DI) was added after TPCAP to make all formulations equal 20 on a detergent surfactant basis.

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The following results were obtained.

Formulation	Sisko Index	Pour Viscosity (mPas)	%BLS (v/v) 30 days @ 37°C
5 Base with no TPCAP & PAA #	0.50	528	0.0
Base with TPCAP & no PAA #	0.43	816	0.0
Base with TPCAP & PAA	0.29	1490	0.0

10 # = comparative example

This Example shows that the structuring polymer produces the desired shear thinning effect in pH jump formulations containing peracid bleach particles, enable suspension of large particles.

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AMENDED SHEET

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Example 12

The following composition was prepared as follows. Structuring polymer (aqueous solution of Sokalan CP-5) was post-added to the pH jump formulation containing peracid 5 bleach (TPCAP, N,N'-tetraphthaloyl-di(6-aminocaproic peracid)).

	<u>Composition</u>	<u>Parts</u>
	LAS Acid	22.7
	Neodol 25-9	10.4
10		Total surfactants 33.1
	50% NaOH	5.7
	Na-citrate 2H <sub>2</sub> O	8.2
	Borax	3.2
15	Sorbitol (70% solution)	13.7
	Narlex DC-1 (33 wt.% solution)	4.5
	Fluorescer	0.2
	EDTA	0.9
20	Perfume	0.25
	TPCAP (30% wt cake)	8.0 or 16.0
	Sokalan CP-5 (25% solution)	6.0
25	DI H <sub>2</sub> O	Balance to 100.0

\* For formulation without PAA, 2.0 parts de-ionized water (DI) was added after TPCAP addition to make all formulations equal on a detergent surfactant basis.

The following results were obtained.

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TPCAP level wt.%	Sisko Index "n"	Pour Viscosity mPas $21s^{-1}$	%BLS (v/v) 30 days @ 37°C
1.8	0.31	425	3.2
4.8	0.29	1,757	0.0

This example shows that the level of TPCAP does not have any significant impact on the Sisko Index and suspending power of large particles.

CLAIMS:

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1. Liquid detergent composition comprising lamellar droplets of surfactant material dispersed in an aqueous medium comprising a structuring polymer material, wherein the polymer is substantially linear, water-soluble, highly salt-tolerant, non-adsorbing and ionic, wherein the composition has a Sisko index of 0.4 or less, as measured by the Sisko rheological model, and wherein the composition contains greater than 30% by weight of said surfactant material, from 0.1 to 20% by weight of said structuring polymer, and at least 0.1% by weight of a deflocculating polymer.
2. Composition according to claim 1, wherein said structuring polymer does not decrease the viscosity of the composition, as measured at 21 sec<sup>-1</sup>, relative to the viscosity prior to addition of said polymer.
3. Composition according to claim 1 or 2, further comprising solid particles selected from solid surfactant, builder, bleach, abrasives and enzymes, and having a particle size of more than 25 $\mu$ m to less than 5,000 $\mu$ m.
4. Composition according to any one of claims 1-3, wherein the structuring polymer has a MW of 10,000 to 1,000,000 Daltons.
5. Composition according to any one of claims 1-4, wherein the structuring polymer is selected from the group consisting of polyacrylates, acrylate maleate copolymer polystyrene sulfonate and dextran sulfate.
6. Composition according to any one of claims 1-5, wherein said polymer does not increase the viscosity, as measured at 21 sec<sup>-1</sup> above 5,000 mPas.
7. Composition according to any one of claims 1-6, said composition resulting in no more than 5% bottom clear layer separation by volume upon storage at 37°C for 30 days.

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8. Composition according to any one of claims 1-7, wherein the surfactant material is selected from the group consisting of anionic, nonionic, cationic, amphoteric, zwitterionic surfactants and mixtures thereof; and wherein unsubstituted fatty acids and salts thereof comprise no more than 2% by weight of the total composition.
9. Composition according to any one of claims 1-8, wherein the composition comprises from 0.5 to 10% by weight peroxygen bleach particles.
10. Liquid detergent composition comprising:
  - (a) greater than 30% to 80% by wt. of one or more surfactants predominantly present as lamellar drops dispersed in an aqueous medium containing at least 1% by wt. electrolyte, wherein said surfactant is selected from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants and mixtures thereof; and wherein unsubstituted fatty acids and salts thereof comprise no more than 2% by wt. of the total composition;
  - (b) a structuring polymer
  - (c) at least 0.1% by weight of a deflocculating polymer, characterized in that the polymer is substantially linear, water soluble, highly salt-tolerant, non-adsorbing, ionic, is present at a level of from 0.1 to 20% by wt. and has a MW of 10,000 to 1,000,000 Daltons; wherein the composition has a Sisko index of 0.4 or less as measured by the Sisko rheological model; wherein said structuring polymer does not decrease the viscosity of the composition, as measured at 21 sec<sup>-1</sup>, relative to the viscosity prior to addition of said polymer; wherein said polymer does not increase the viscosity, as measured at 21 sec<sup>-1</sup>, above 5000 mPas; and wherein said composition results in no more than 5% bottom clear layer separation by volume upon storage at 37°C for 30 days.