

(19)



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(11)

**EP 0 802 971 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:  
**11.08.1999 Bulletin 1999/32**

(51) Int Cl.<sup>6</sup>: **C11D 17/00, C11D 3/37, C11D 3/00**

(21) Application number: **96900948.9**

(86) International application number:  
**PCT/EP96/00123**

(22) Date of filing: **04.01.1996**

(87) International publication number:  
**WO 96/21720 (18.07.1996 Gazette 1996/33)**

(54) **DETERGENT COMPOSITION**

WASCHMITTEL

COMPOSITION DE DETERGENT

(84) Designated Contracting States:  
**DE ES FR GB IT**

(30) Priority: **12.01.1995 EP 95300175**

(43) Date of publication of application:  
**29.10.1997 Bulletin 1997/44**

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**FR-A- 2 276 378**                      **GB-A- 2 137 652**  
**US-A- 3 959 230**                      **US-A- 3 962 152**

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**Description**TECHNICAL FIELD

5 **[0001]** The present invention relates to detergent compositions comprising soil-release polymers.

BACKGROUND & PRIOR ART

**[0002]** Use of soil-release polymers is well documented in the patent literature.

10 **[0003]** EP-A-272,033 (P&G) discloses soil-release polymers comprising oxypropyleneoxy moieties. US-A-3,962,152 (P&G) describes soil-release polymers containing polyethyleneglycol units having low molecular weight, wherein the molar ratio of terephthalate to polyethyleneglycol of 1.33 to 1.54 and wherein the molecular weight is in the range of 25,000 to 55,000. It is indicated that these polymers may be incorporated in solid detergent compositions. EP-A-201,124 (P&G) discloses soil-release polymers that contain two polyethyleneglycol units between which 3 to 5 ethylene-terephthalate units are positioned and the Examples further describe that the polymer mix is fractioned in ethanol to remove an ethanol-insoluble fraction, which method is also used in EP-A-199,403. EP-A-253,567 (P&G) discloses compositions comprising quaternary ammonium surfactant and soil-release polymers comprising a molar ratio of terephthalate to polyethyleneglycol of from 3:1 to 1.67:1. WO-A-95/18207 discloses liquids with high levels of nonionic surfactant and soil-release polymers. These polymers are present in these isotropic liquids in a dissolved state.

20 **[0004]** Soil-release polymers that are commercially available include Permalose® (ex ICI), Repel-O-Tex® (ex Rhone Poulenc), Sokalan 9798X® (ex BASF) and Zelcon® 6126 (ex Dupont).

**[0005]** It has been found that problems may occur in delivering polymers to the wash liquor in an effective way. Soil-release polymers, in particular commercially available soil release polymers, generally have only low solubility and dissolve and disperse slowly in the wash liquor, which may lead to the polymers being less effective in the wash. This is in particular true for soil-release polymers in granule form. US-A-4,569,772 (Colgate) and US-A-4,571,303 (Colgate) describes that co-granules of soil-release polymer and polyacrylate may be used in detergent compositions.

25 **[0006]** It has further been found that soil-release polymers tend to become less active upon storage, e.g the polymer itself, or the polymer in a liquid or solid detergent composition. US-A-4,569,772 (Colgate) and US-A-4,571,303 (Colgate) describe that hydrolysis may occur under the influence of alkaline material.

30 **[0007]** It has further been found that the activity of soil-release polymer tends to decrease after incorporation in the detergent composition and storage as compared to addition of the polymer directly to the wash load, i.e. "over the top".

**[0008]** It has further been found difficult to prepare physically and chemically stable detergent compositions that comprise soil-release polymers. Liquid detergent compositions may become inhomogeneous, e.g. ingredients may separate and/or solid particles may sediment. Further, the number of interactions between the ingredients of liquid detergent compositions generally makes it difficult to prepare compositions which are chemically stable, especially upon storage. Even though its components have a more or less fixed position, soil-release polymer may also be chemically unstable in the solid detergent compositions, e.g. as a consequence of contact with moisture. EP-A-199,403 (P&G) and EP-A-576,777 (P&G) describe isotropic liquid detergent compositions that comprise particular soil-release polymers. These polymers may however hydrolyse upon storage, resulting in low soil-release effectivity. Further, stabilising ingredients are required to stably incorporate the soil-release polymer in the isotropic liquid.

40 **[0009]** Surprisingly, we have found a way to overcome one or more of the above identified problems.

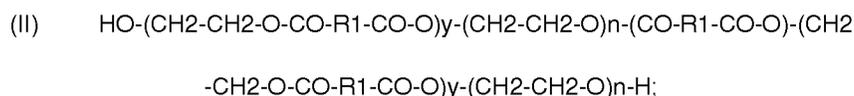
DEFINITION OF THE INVENTION

45 **[0010]** The present invention is directed to a liquid detergent composition comprising surfactant material, electrolyte material and soil-release polymer, characterised in that the composition has a structure and comprises precipitated soil-release polymer.

**[0011]** The present invention is further directed to a process for preparing a structured liquid detergent composition comprising surfactant material, electrolyte material and a soil-release polymer by blending the ingredients characterised in that the polymer is added to the detergent compositions at a temperature below the melting point of the polymer and a temperature about the cloud point of the polymer in the liquid.

50 **[0012]** The present compositions comprise a soil-release polymer composition, which may comprise one or more polymers of the following general formulae I or II:

55 (I)  $\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{R}_1-\text{CO}-\text{O})_x-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{H}$ ;



wherein R1 is a phenyl, y is (independently) 0, 1 or 2, x is 1, 2 or 3 and wherein n is from 10 to 100.

**[0013]** Preferably, the polymer of formula (I) is present in the polymer composition at a level of from 20 to 100% by weight of the polyester material. Preferably, the polymer of formula (II) is present in the polymer composition at a level of from 20 to 100% by weight of the polyester composition. It is preferred to have at most 60% by weight of the total of polyester material of polymers I and/or II present in the polymer composition, more preferably 80%, most preferably substantially 100%, as it is preferred that the polymer composition is water-soluble.

**[0014]** Other soil-release polymers which are copolymers of ethylene glycol, polyoxyethylene glycol and terephthalic acid are described in GB-A-2 137 652.

**[0015]** The present invention is further directed to a method of washing with a composition according to claim 1, wherein the wash liquor has a pH of at least 6 and at most 10.

## DETAILED DESCRIPTION OF THE INVENTION

### Liquid Compositions

**[0016]** EP-A-576,777(P&G) describes the use of PVP to keep the soil-release polymer in solution. EP-A-401, 123 (Colgate) discloses soil-release polymer containing iso-terephthalate units that may be included in liquid detergent compositions. A further complication for preparing detergent compositions comprising soil-release polymer is that the polymers may hydrolyse under influence of alkaline material.

**[0017]** We have however found a way to overcome the physical and chemical stability problems. We have unexpectedly found that the soil-release polymer can be physically and chemically stably incorporated in liquid detergent composition comprising surfactant material, electrolyte material, wherein the composition has a structure.

**[0018]** Even though the polymer is (partially) precipitated, we have found that it remains effective as soil-release even after storage.

**[0019]** This is even more surprising as the prior art generally teaches away from including salt in detergent compositions comprising soil-release polymer. GB-A-2,172,608 (Colgate) and DE-A-34 11 941 (Colgate) describe that ionizable salts are to be excluded from its composition to overcome destabilisation of the liquid.

**[0020]** Without wishing to be bound by any theory, it is believed that the electrolyte precipitates or salts out the polymer. The resulting polymer particles or droplets are thought not to be subject to hydrolysis during storage. Furthermore, it appears that, contrary to what was believed in the art, the precipitated soil-release polymer remains effective during the wash, even after incorporation in the liquid.

**[0021]** Soil-release polymers can also be precipitated or salted-out in other ways, e.g. by raising the temperature (preferably in the absence of water-insoluble polymers) or by evaporating the reaction mixture after preparation of the polymer (preferably in the absence of water-insoluble polymer particles). For the purpose of the invention, precipitated, salted out and emulsions of soil-release polymer are all considered as precipitated soil-release polymer.

**[0022]** The effectiveness of the precipitated soil-release polymer is even more surprising as we have found that water-insoluble polymer components that may be present in polymer compositions may adversely influence the soil-release performance of the polymer composition. This problem applies in particular to polymer compositions that are incorporated in detergent compositions. Without wishing to be bound by any theory, it has been found that water-insoluble polymer components are not effective as soil-release agent, e.g. due to their low solubility in the wash liquor. It is however believed that, e.g. as a consequence of temperature changes, the water-insoluble polymer components, or more in particular the polyoxyethylene groups, may melt and become pasty or liquid, e.g. during polymer preparation or during detergent preparation. In such a state, the water-insoluble polymer components may blend with active soil-release polymer material. If the temperature subsequently drops below the melting temperature of the water-insoluble polymer components, then the active soil-release polymer material may be trapped inside the water-insoluble polymer component. This may lead to an overall decrease in soil-release activity. We have found that, at least partially, avoiding the presence of high levels of water-insoluble polymer components in the soil-release polyester composition results in effective soil-release in the wash, even after storage at various temperatures.

**[0023]** Preferably, the weight average particle size of soil-release polymer particles in the liquid is from 1 to 500µm.

**[0024]** Preferably, at least 80% of the polyester is present as precipitated particles in the detergent composition, more preferably at least 90% by weight of the polyester is present as precipitated particles in the detergent composition, most preferably substantially 100% of the polyester.

**[0025]** Preferably, the liquid detergent composition according to this aspect of the invention comprises a polymer

mixture that comprises one or more polymers of the formulae I and II as defined below.

**[0026]** Preferably, the total level of electrolyte is from 1 to 60% by weight of the composition, more preferably from 5 to 45% by weight, most preferably from 10 to 30% by weight.

**[0027]** Preferably, compositions according to the invention comprise salting-out electrolyte having a lyotropic value of less than 9.5 and preferably less than 9.0. Salting-out electrolyte has the meaning ascribed in specification EP-A-0,079 646. Preferred salting-out electrolytes are selected from alkali metal and ammonium salts of phosphates (including pyro, ortho and poly phosphates), silicates, borates, carbonates, sulphates, citrates, NTA and succinates. Preferably, the liquid compositions contain at least 1% by weight of a salting-out electrolyte, more preferably at least 2%, most preferably at least 5% by weight and preferably at most 20% by weight, more preferably at most 15% by weight of a salting-out electrolyte. Optionally, some salting-in electrolyte (as defined in the latter specification) may also be included.

**[0028]** As hydrotrope material may break up the structure of the liquids and may lead to dissolvign of the soil-release polymer in the liquid composition, it is preferred only to use levels of hydrotrope material of lower than 10%, more preferably lower than 5%, most preferably lower than 3%.

**[0029]** We have found that the invention is in particular useful for liquids with contain material with alkaline surfaces. Such surfaces tend to deactivate soil-release polymers, whereas we have surprisingly found that the deactivation is far lower in liquids according to the present invention. Therefore, preferably the liquids comprise alkaline material selected from zeolite, carbonate, silicate and clay material.

#### Polymer material

**[0030]** We have found that the soil release polymers of the invention do not only show good soil-release activity, but we have also found that they may be used in preparing detergent compositions comprising the specific polymer composition wherein the compositions are stable upon storage and remain effective in soil-release in the wash after storage.

**[0031]** Preferably, the polymer mixture that is incorporated into detergent compositions comprises low levels of water-insoluble polymer material, preferably less than 40% by weight of the polyester of water-insoluble polyester material when the mixture is dissolved at 1% in water at a temperature of 25°C. More preferably, less than 30% by weight is water-insoluble, most preferably less than 20%, in particular less than 10%, e.g. substantially 0% by weight of the polyester. It is noted that the structured liquids of the invention are in particular useful as they also allow suspending of the insoluble fraction of the polymer, which could not be achieved by liquids of the prior art.

**[0032]** Polymer compositions with low levels of water-insoluble polymers can be prepared by various ways including centrifuging and altering the processing route, e.g. by using lower levels of terephthalate and/or using higher molecular weight PEG.

**[0033]** We have further found that high soil-release activity results from selecting polymer compositions with a number average molar ratio between terephthalate and polyethyleneglycol of lower than 3:1 and higher than 1.4:1, more preferably lower than 2.5:1 and higher than 1.54:1.

**[0034]** We have found that it is preferred to use polyethyleneglycol units in the polymer composition of the invention that contain 10 to 100 units of ethyleneglycol. Preferably, they have a molecular weight of higher than about 1500, more preferably higher than about 2000, most preferably higher than about 2200, in particular higher than about 2500 and preferably at most about 5000, more preferably at most about 4000, most preferably at most about 3000.

**[0035]** It will be understood that terephthalate, ethyleneglycol and polyethyleneglycol units as described in the this specification and as used in the polymer structure of the invention, are terephthalate, ethyleneoxyde and polyethyleneoxide moieties in the polymer.

**[0036]** Preferably, the number average molecular weight of the polymers in said polymer composition is between 500 and 10,000, preferably more than 1,000, more preferably more than 2,000, most preferably more than 3,000. But preferably less than 9,000, more preferably less than 8,000. Molecular weight can be determined by various methods, e.g. NMR-spectroscopy, Matrix Assisted Laser Desorption Ionisation - time of flight- Mass Spectrometry (MALDI-tof-MS) or Gel Permeation Chromatography (GPC).

**[0037]** The terephthalate unit that is used for the preparation of polymer compositions of the invention may be selected from ortho, meta and preferably para phenyl-dicarboxylates.

#### Detergent Compositions

**[0038]** We have found that detergent compositions comprising the polymer composition according to the above aspect of the invention show excellent soil-release activity. We have further found that water-insoluble polymer components in the polymer composition may adversely influence the soil-release performance of detergent compositions comprising the polymer composition.

**[0039]** Preferably, the soil-release polymer is present in the detergent composition at a level of at least 0.01%, more

preferably at least 0.1, most preferably at least 0.25 and preferably at most 10%, more preferably at most 5%, most preferably at most 3% by weight of the composition.

#### Structured liquids

5 [0040] Two general and separate classes of liquids compositions exist, i.e. isotropic liquids in which all ingredients are dissolved and structured liquids. Structured liquids can either be internally structured, whereby the structure is formed by primary ingredients (e.g. surfactant material) and/or by providing a three dimensional matrix structure using secondary additives (e.g. polymers, clay and/or silicate material).

10 [0041] Various kinds of liquids, that are internally structured with surfactant material, are described in the reference H.A. Barnes, "Detergents", Ch.2. in K. Walters (Ed), "Rheometry: Industrial Applications", J. Wiley & Sons, Letchworth 1980. In general, the degree of ordering of such systems increases with increasing surfactant and/or electrolyte concentrations. Examples of structured liquids are given in US-A-4,244,840, EP-A-160 342, EP-A-38 101 and EP-A-140 452.

15 [0042] At very low concentrations of surfactant and/or electrolyte, the surfactant can exist as a molecular solution, or as a solution of spherical micelles, both of these solutions being isotropic, i.e. they are not structured. With the addition of further surfactant and/or electrolyte structures of surfactant material may form.

[0043] Various forms of such structures exists, e.g. bi-layers. They are referred to by various terms such as rod-like micelles, anisotropic surfactant phase, planar lamellar structures, lamellar droplets and liquid crystalline phases. Often different workers have used different terminology to refer to the structures which are really the same. For instance, in European patent specification EP-A-0,151,884, lamellar droplets are called spherulites.

20 [0044] A preferred form of lamellar structures are lamellar droplets of surfactant material in which the dispersed structuring phase is generally believed to consist of an onion-like configuration comprising concentric bilayers surfactant molecules, between which water is trapped, the aqueous phase. Liquids with a lamellar droplets structure are preferred as systems in which such droplets are close-packed provide a very desirable combination of physical stability and solid-suspending properties with useful flow properties, i.e. low viscosity with stability. Such liquids have for example been described in A. Jurgens, Microstructure and Viscosity of Liquid Detergent, Tenside Surfactants Detergent 26 (1989) 222 and J.C. van de Pas, Liquid Detergents, Tenside Surfactants Detergents 28 (1991) 158. The presence and identity of a surfactant structuring system in a liquid may be determined by means known to those skilled in the art for example, optical techniques, various rheometrical measurements, X-ray or neutron diffraction, and sometimes, electron microscopy.

30 [0045] The most preferred structured liquids are liquid detergent compositions comprising lamellar droplets of surfactant material.

#### Process of preparation of liquid detergent composition

[0046] Surprisingly, we have found that soil-release polymers can be stably incorporated in liquid detergent compositions, whilst remaining its soil-releasing activity, by adding the polymer at a temperature below the melting point of the polymer and above the cloud point of the polymer in the liquid.

40 [0047] We have found that the melting point of the polyoxyethylene parts in the soil-release polymer illustrates the melting point of the polymer well. Preferably, the melting point of at least 80% by weight (preferably 90% by weight) of the polyoxyethylene of the polymer is at least 30°C, more preferably at least 40°C, most preferably at least 50°C and preferably at most 110°C.

[0048] The cloud point is well-known to the skilled man. The cloud behaviour of the polymers can be studied by monitoring the transmission at 460 nm of a 1% by weight clear aqueous solutions at various electrolyte levels, as a function of temperature using a UV-spectro-photometer. At the cloud temperature, the clear solution becomes turbid. The cloud temperature is determined as the peak in the first derivative of the transmission versus temperature plot.

[0049] Preferably, the cloud point of the polymer in the liquid is at most 25°C, more preferably at most 22°C, most preferably at most 20°C, in particular at most 17°C. The cloud point will preferably be higher than 0°C.

50 [0050] A preferred method for preparing liquid detergents involves dispersing of the electrolyte ingredient together with the minor ingredients except for the temperature and pH sensitive ingredients, such as enzymes, perfumes, etc -if any- in water of elevated temperature, followed by the addition of the builder material -if any-, the surfactant material (possibly as a premix) under stirring and thereafter cooling the mixture and adding any pH and temperature sensitive minor ingredients, such as soil-release polymer of the present invention. The deflocculating polymer may for example be added after the electrolyte ingredient or as the final ingredient. The soil-release polymer is preferably added as a solution or dispersion.

55

Surfactant material

**[0051]** Solid and Liquid compositions of the invention also comprise surfactant materials, preferably at a level of at least 1% by weight of the composition, more preferred at least 5% by weight, most preferred at least 10% by weight of the composition; and preferably at a level of at most 70% by weight, more preferably at most 40%, most preferably at most 35% by weight.

**[0052]** In the widest definition the surfactant material in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided mutually compatible) mixtures thereof.

**[0053]** Suitable nonionic surfactants include for example aliphatic alcohols, acids, amides or alkyl phenols with alkyl oxides, especially ethylene 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 ethylene-di-amine. Preferably the level of nonionic surfactant materials is from 1 to 50 % by weight of the composition, more preferred from 2 to 30%.

**[0054]** Compositions of the present invention may contain synthetic anionic surfactant ingredients. 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. Examples of suitable synthetic anionic surfactant compounds are sodium and potassium C<sub>8</sub>-C<sub>18</sub> alkyl sulphates, sodium and potassium alkyl (C<sub>9</sub>-C<sub>20</sub>) benzene sulphonates and ether variants thereof. Generally the level of the above mentioned non-soap anionic surfactant materials is from 1 to 40 % by weight of the composition, more preferred from 2 to 25%.

**[0055]** It is also possible, and sometimes preferred, to include an alkali metal soap of a C<sub>12</sub>-C<sub>18</sub> carboxylic acid. Preferably the level of soap is from 1 to 35% by weight of the composition, more preferred from 5 to 25%.

Electrolyte material

**[0056]** Compositions according to the invention may comprise electrolyte material, some or all of which may be builder material. It is noted that for the purpose of the invention, the term electrolytes includes builder material.

**[0057]** In any event, it is preferred that compositions according to the present invention include detergency builder material, some or all of which may be electrolyte. In this context it should be noted that some surfactant materials such as for example soaps, also have builder properties.

**[0058]** Examples of phosphorous containing inorganic detergency builders 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. Examples of organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates.

**[0059]** Preferably, the level of non-soap builder material is from 5 to 40% by weight of the composition, more preferred from 5 to 25% by weight of the composition.

Deflocculating Polymers

**[0060]** Liquid detergent compositions preferably comprise a deflocculating polymer, e.g. as described in WO-A-91/06622, WO-A-91/06623, GB-A-2,237,813, WO-A-91/09109, PCT Application No. WO 94/03575 and/or EP-A-0,346,995. In general, the deflocculating polymer will be used at levels of from 0.01 to 5% by weight of the composition, more preferably from 0.1 to 3.0% especially preferred from 0.25 to 2.0%.

Optional Ingredients

**[0061]** Apart from the ingredients already mentioned, a number of optional ingredients may also be present, for example lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid, inorganic salts such as sodium sulphate, and usually, present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases, amylases and lipases (including Lipolase (Trade Mark) ex Novo), enzyme stabilisers, anti-redeposition agents, germicides and colorants.

Product Forms

[0062] Detergent compositions according to the present invention are liquid. Preferably, the compositions of the present invention are concentrated.

[0063] Liquid compositions of the invention preferably have a viscosity of less than 2,500 mPas at 21 s<sup>-1</sup>, more preferred less than 1,500 mPas, most preferred less than 1,000 mPas and preferably higher than 100, more preferably higher than 500 mPas at 21 s<sup>-1</sup>. Liquid compositions according to the invention are physically stable, i.e. they will yield no more than 10 %, preferably no more than 5 %, most preferred no more than 2% by volume phase separation as evidenced by appearance of 2 or more separate phases when stored at 25°C for 21 days from the time of preparation.

[0064] Preferably, the pH, as provided to the wash liquor, preferably by a liquid, is at least 6, more preferably at least 7.5, most preferably at least 8. Preferably the pH is at most 10, more preferably at most 9.

[0065] The invention will be illustrated by way of the following non-limiting Examples.

EXAMPLES**General methods**

[0066] Polymers were dispersed in water at 1% by weight. Insoluble fractions were separated from the soluble fractions using ultracentrifugation and subsequent freeze drying. To obtain information about the monomer distribution, molecular weight and monomer ratio, chemical composition of the polymer fractions were studied using <sup>1</sup>H and <sup>13</sup>C NMR-spectroscopy, Matrix Assisted Laser Desorption Ionisation - time of flight- Mass Spectrometry (MALDI-tof-MS), UV-spectroscopy, IR-spectroscopy and Gel Permeation Chromatography (GPC). The Malditof has been described in M. Karas, U. Bahr, U. Giesmann, Mass Spectrometry Review 10 (1991) 335 and can be used in combination with NMR to determine the type of polymers.

**Washing performance method**

[0067] Polyester swatches were prewashed several times under standard European conditions with the liquid to be tested. The prewashed polyester swatches were contaminated with a heptane stock solutions containing oleic-acid, mono-oleate, squalane, squalene, wax-ester, di-olein and tri-olein. The contaminated swatches were washed under model conditions with a non-enzyme liquid optionally containing soil-release polymer. The swatches were dried and extracted with THF after addition of an internal standard. The THF extracts were added to a GC-Vial and the THF was evaporated using a Reactie-Vap evaporating unit under a Nitrogen flow. The -OH groups were shielded, whereafter the vials were filled up with hexane and capped. The samples were analyzed by GC-FID. Reflectance was determined before the test ( $K_{s_{before}}$ ), of unsoiled polyester ( $K_{s_0}$ ) and after the test ( $K_{s_{after}}$ ). For each piece of polyester, the percentage stain removal was calculated, using: %Detergency =  $[K_{s_{after}} - K_{s_{before}}] / [K_{s_0} - K_{s_{before}}]$  Experiments were performed with, at least, three swatches and percentage stain removal was calculated by taking the average.

Example 1

[0068] The thermal behaviour of the polymers was studied using Differential Scanning Calorimetry and Light Microscopy. Clear melting temperatures peaks were found, reflecting the melting of the polyoxyethylene chains. Table 1 shows the peak value of the melting peak for various polymers. The composition of the polymers is given. All polymers are soluble in water (at 1% by weight).

Table 1

Polymer	ET <sup>a</sup>	POE <sup>b</sup>	PEG Mw <sup>c</sup>	Peak <sup>d</sup>
A	23	77	1500	36°C
B	14	86	*3000	47°C
A is the soluble fraction of Permalose, ex ICI				
B is Repel-O-Text, ex Rhone Poulenc				

<sup>a</sup> Weight percentage of ethyleneterephthalate.

<sup>b</sup> Weight percentage of polyoxyethylene.

<sup>c</sup> Molecular weight of PEG, used in the synthesis.

<sup>d</sup> Peak value of the melting peak.

\* thought to be 3000

[0069] All polymers are liquid above the melting temperature. Clearly, the melting temperature of the polyoxyethylene chains increases with increasing molecular weight of the polyoxyethylene moieties.

### Example 2

[0070] The cloud behaviour of the polymers was studied by following the transmission at 460 nm of a 1% (by weight) clear aqueous solutions as function of temperature using a UV-spectro-photometer. At the cloud temperature, the clear aqueous solution becomes turbid. The cloud temperature is determined as the peak in the first derivative of the transmission versus temperature plot. Typical cloud temperatures are given in Table 2. Also cloud temperatures in the presence of NaCl and sodium citrate are listed.

Table 2

Polymer	Electrolyte <sup>a</sup>	ET <sup>b</sup>	POE <sup>c</sup>	T(cloud)
A	-	23	77 (1500)	53°C
A	NaCl, 3%	23	77 (1500)	31°C
A	NaCl, 6%	23	77 (1500)	25°C
A	NaCit, 1%	23	77 (1500)	35°C
A	NaCit, 2%	23	77 (1500)	230C
B	-	14	86 (3000)	>80°C
B	NaCl, 3%	14	86 (3000)	60°C
B	NaCl, 6%	14	86 (3000)	50°C
B	NaCit, 1%	14	86 (3000)	60°C
B	NaCit, 2%	14	86 (3000)	52°C

<sup>a</sup> Electrolyte type, and concentration by weight (NaCit = sodium citrate).

<sup>b</sup> Weight percentage ethyleneterephthalate in the polymer.

<sup>c</sup> Weight percentage polyoxyethylene in the polymer and (molecular weight).

[0071] Clearly, the cloud temperature decreases dramatically when electrolytes are present. Stronger salting-out electrolytes, such as sodium citrate are more effective in bringing about a decrease of cloud temperature. The cloud temperature increases with increasing molecular weight of the polyoxyethylene moieties as well as with decreasing weight percentage of ethyleneterephthalate.

### Example 3

[0072] The soil release capacities of polymer A according to the present invention were tested according to the above washing performance method and the same method was used for determining the dirty motor oil removal. The following results were obtained. Polymer A, which is completely soluble in water, comprises 23% ethylene-terephthalate groups and 77% polyoxyethylene groups. The polymer is dispersed at a level of 0.5% by weight in a liquid detergent composition, as given in Table 3. The polymer was added under the melting point and stored above its clouding point, i.e. the polymer was precipitated. The liquid showed good stability.

Table 3:

Component	Wt. %
Polymer A	0.5% or 0%
Linear Alkyl benzene sulfonates	16.5
Alkylpolyethoxylates	9
Fatty acid	4.5
Citric acid	8.2
Borax	1.5

EP 0 802 971 B1

Table 3: (continued)

Component	Wt. %
Glycerol	2.0
Zeolite	15
Protease enzyme	.4
Amylase enzyme	.5
Water and minors	to balance 100

[0073] Three prewash were performed (at 40°C, 12°FH) with and without soil release polymer. After soiling, main wash was performed without soil release polymer. Results are collected in Table 4.

Table 4

Conditions	Stain	% Detergency <sup>a</sup>	% Removal <sup>b</sup>
- SRP	dirty motor oil	15	
+ SRP	dirty motor oil	70	
- SRP	triolein		25
+ SRP	triolein		78

<sup>a</sup> Percentage detergency, as determined by reflectance.

<sup>b</sup> Percentage removal, as determined by extraction method.

[0074] Polymer A\*, i.e. composition of polymer A with also present the water-insoluble fraction, was also dispersed in the above liquid formulation, at a percentage of 0.5%. This formulation showed acceptable storage stability and gave less good %detergency (due to the lower level of active soil-release polymer as compared with polymer A).

[0075] Polymer B that is not according to the present invention gave a % removal of only 40%.

Example 4

[0076] The following composition was prepared by adding the ingredients in the order listed. The formulation was cooled after addition of the active premix to a temperature of about 30°C at which point the minors were added.

Ingredients	by weight %
Water	to 100
Fluorescer	0.1
KOH	9.8
Citric acid	8.2
Glycerol	2
Borax	1.5
Zeolite	15
Stabilising Polymer A11 1)	1
Active Premix 2)	30
Minors	1.4

1) Polymer A11 of EP-A-346995

2) Active Premix consists of LAS acid, ethoxylated nonionic and fatty acid.

[0077] Soil-Release Polymer (Permalose TM, ex ICI) at a level of 0.5% by weight of the composition was added at various stages to the above formulation. In an embodiment of the invention, (Composition 1) the SRP polymer was added at the end of the preparation process at room temperature. In a comparative example (composition A), the SRP polymer was added to the water at the beginning of the process. In another comparative example (composition B), the SRP polymer was added before the addition of the active premix. In another comparative example (composition C), the SRP polymer was added after addition of the premix, but before cooling. The following results were obtained:

Washing results	
Composition 1	1
Composition A	3
Composition B	3
Composition C	*
scores: 1 - good performance 2 - middle performance 3 - low performance * Comparative example Composition C was not taken to completion as preparation resulted in major processing problems. Degraded or phase changed polymer with chewing-gum-like consistency occurs and polymer becomes attached to the paddles and baffles in the vessel.	

**[0078]** Only composition 1 showed both good formulation viscosity and good washing results.

Example 5

**[0079]** Four polymers were prepared and characterised by MALDI-tof-MS and analysed in detail by NMR, identifying details of the distribution between chemical structures.

Polymer 1: Polymer, comprising 81% Polyethylene Oxide (MW 2000), 3.5 % Ethylene Oxide and 15.5% Terephthalate groups; average Molecular Weight (NMR) 3900.

Polymer 2: Polymer, comprising 88% Polyethylene Oxide (MW 3000), 2.3 % Ethylene Oxide and 9.7% Terephthalate groups; average Molecular Weight (NMR) 4700.

Polymer 3: Polymer, comprising 77% Polyethylene Oxide (MW 1500), 4.4 % Ethylene Oxide and 18.6% Terephthalate groups; average Molecular Weight (NMR) 3100.

Polymer 4: Polymer, comprising 92% Polyethylene Oxide (MW 4000), 1.4 % Ethylene Oxide and 6.6% Terephthalate groups; average Molecular Weight (NMR) 5700.

**[0080]** The melting points of the polymers were measured by Differential Scanning Calorimetry as peak value:

Polymer 1: 41.1°C

Polymer 2: 49.6°C

Polymer 3: 37.1°C

Polymer 4: 55.6°C

**[0081]** These polymers meet the (preferred) melting temperatures of the invention.

**[0082]** The T<sub>c</sub> (cloud points) of the water-soluble fraction were determined by UV turbidity measurements at 500 nm of a 1% solution in water.

Polymer 1. 64.7°C

Polymer 2. 75.2°C

Polymer 3. 57°C

Polymer 4. > 85°C

**[0083]** These cloud points are higher than the preferred cloud points according to the invention. Addition of salt however leads to a decrease in cloud point which is illustrated with Polymer 3 at various Citrate and NaCl concentrations:

Citrate %	T <sub>cloud</sub> point in °C
0	57
0.5	40
1.0	34
1.5	29
2.0	22

EP 0 802 971 B1

NaCl %	Tcloud point in °C
0	57
1	40
2	35
3	32
4	28
5	<25

[0084] The % water-insoluble components of the polymer mixtures were:

Polymer 1	29% insol
Polymer 2	20% insol
Polymer 3	35% insol
Polymer 4	22% insol

[0085] These polymers meet the (preferred) levels of water-insoluble components in the polymer mixture.

Example 6

[0086] Polymers 1, 2, 3 and 4 of example 5 were added to the liquid of Table 3 at a level of 0.5% and a temperature of between 25-30°C. Liquids were also prepared with polymer X (a polymer with an insoluble fraction of 65%) and without a soil-release polymer. The liquids were tested according to the washing performance method identified above. Removal of each individual component was determined quantitatively. Shown is the removal (in %) of the triglyceride component:

Composition with:	% removal of triglyceride component
Polymer 1	50.2
Polymer 2	38.5
Polymer 3	50.4
Polymer 4	42.2
Polymer X #	30.0
No polymer	26.0
#: Polymer X has 65% of insoluble material.	

[0087] Removal characteristics of the other components of the model stain show similar behaviour.

Example 7

[0088] The following liquids were prepared:

LAS ACID	7.6
NONIONIC 7EO	2.4
STPP	21
CAUSTIC	0.7
BORAX/GLYCEROL	7
MINORS	0.6
WATER	to 100

LAS ACID	7
NONIONIC	4.8
ZEOLITE	20

(continued)

CITRIC ACID	2.5
Carboxylate polymer	present
CAUSTIC	1.4
BORAX/GLYCEROL	7
MINORS	2.6
WATER	to 100

[0089] Soil release polymer 3 of Example 4 was added to both liquids at a temperature of lower than 30°C and precipitated. The resulting liquids were stable and showed improved washing performance.

### Claims

1. Liquid detergent composition comprising surfactant material, electrolyte material and soil-release polymer, characterised in that the composition has a structure and comprises precipitated soil-release polymer.
2. Composition according to claim 1, wherein the electrolyte has lyotropic value of less than 9.5.
3. Composition according to claims 1-2, wherein the average particle size of soil-release polymer particles is from 1 to 500 µm.
4. Composition according to claims 1-3, wherein at least 60% by weight of the polymer dissolves in a 1% solution in water.
5. Process for preparing a structured liquid detergent composition comprising surfactant material, electrolyte material and a soil-release polymer by blending the ingredients characterised in that the polymer is added to the detergent compositions at a temperature below the melting point of the polymer and a temperature above the cloud point of the polymer in the liquid.
6. Process according to claim 5, wherein the melting point is at least 30°C and the cloud point is at most 25°C.
7. Method of washing with a composition according to claim 1, wherein the wash liquor has a pH of at least 6 and at most 10.

### Patentansprüche

1. Flüssige Waschmittel-Zusammensetzung, enthaltend Tensid-Material, Elektrolyt-Material und schmutzfreisetzendes Polymeres, dadurch gekennzeichnet, daß die Zusammensetzung eine Struktur hat und ausgefälltes schmutzfreisetzendes Polymeres enthält.
2. Zusammensetzung gemäß Anspruch 1, worin der Elektrolyt einen lyotropen Wert von weniger als 9,5 hat.
3. Zusammensetzung gemäß den Ansprüchen 1-2, worin die durchschnittliche Teilchengröße der schmutzfreisetzenden Polymer-Teilchen im Bereich von 1 bis 500 µm liegt.
4. Zusammensetzung gemäß den Ansprüchen 1-3, worin zumindest 60 Gewichtsprozent des Polymeren sich in einer 1%-Lösung in Wasser auflöst.
5. Verfahren zur Herstellung einer strukturierten flüssigen Waschmittel-Zusammensetzung, enthaltend Tensid-Material, Elektrolyt-Material und ein schmutzfreisetzendes Polymeres durch Mischen der Bestandteile, dadurch gekennzeichnet, daß das Polymere zu der Waschmittel-Zusammensetzung bei einer Temperatur unterhalb des Schmelzpunkts des Polymeren und einer Temperatur oberhalb des Trübungspunkts des Polymeren in der Flüssigkeit zugesetzt wird.

6. Verfahren gemäß Anspruch 5, worin der Schmelzpunkt zumindest 30°C und der Trübungspunkt höchstens 25°C ist.

5 7. Verfahren des Waschens mit einer Zusammensetzung gemäß Anspruch 1, worin die Waschflüssigkeit einen pH-Wert von zumindest 6 und höchstens 10 hat.

### Revendications

10 1. Composition détergente liquide comprenant un tensioactif, un électrolyte et un polymère de libération des salissures, caractérisée en ce que la composition a une structure et comprend un polymère de libération des salissures précipité.

15 2. Composition selon la revendication 1, dans laquelle l'électrolyte a une valeur lyotrope de moins de 9,5.

3. Composition selon les revendications 1-2, dans laquelle la granulométrie moyenne des particules de polymère de libération des salissures va de 1 à 500 µm.

20 4. Composition selon les revendications 1-3, dans laquelle au moins 60 % en poids du polymère se dissolvent dans une solution à 1 % dans l'eau.

25 5. Procédé de préparation d'une composition détergente liquide structurée comprenant un tensioactif, un électrolyte et un polymère de libération des salissures en mélangeant les ingrédients, caractérisé en ce qu'on ajoute le polymère aux compositions détergentes à une température en dessous du point de fusion du polymère et à une température au-dessus du point de turbidité du polymère dans le liquide.

6. Procédé selon la revendication 5, dans lequel le point de fusion est d'au moins 30°C et le point de turbidité est d'au plus 25°C.

30 7. Procédé de lavage avec une composition selon la revendication 1, dans laquelle la liqueur de lavage a un pH d'au moins 6 et au plus 10.

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