(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 692 842 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
05.02.2014 Bulletin 2014/06

(21) Application number: **12178620.6**

(22) Date of filing: **31.07.2012**

(51) Int Cl.:
C11D 1/02 $^{(2006.01)}$
C11D 1/83 $^{(2006.01)}$
C11D 1/94 $^{(2006.01)}$
C11D 3/30 $^{(2006.01)}$
C11D 3/37 $^{(2006.01)}$

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(71) Applicants:
- **Unilever PLC**
  London, Greater London EC4Y 0DY (GB)
  Designated Contracting States:
  CY GB IE MT
- **UNILEVER NV**
  3013 AL Rotterdam (NL)
  Designated Contracting States:
  AL AT BE BG CH CZ DE DK EE ES FI FR GR HR HU IS IT LI LT LU LV MC MK NL NO PL PT RO RS SE SI SK SM TR

(72) Inventor: **The designation of the inventor has not yet been filed**

(74) Representative: **Bristow, Stephen Robert**
Unilever PLC
Unilever Patent Group
Colworth House
Sharnbrook
Bedford, MK44 1LQ (GB)

(54) Concentrated liquid detergent compositions

(57) A concentrated alkaline liquid detergent composition comprising:
a) 5 to 60 wt% surfactant comprising anionic surfactant and optionally nonionic surfactant and optionally amphoteric surfactant and optionally soap of which at least 35% of the total surfactant is anionic non-soap surfactant,
b) at least 1 wt% triethanolamine (TEA),
c) at least 30 wt% water
d) at least 0.5 wt% soil release polymer

characterised in that:

(i) the soil release polymer has the formula (I), and

$$X\text{-}[(OCH_2CH_2)_q\text{-}]\text{-block-}[(OCH_2CH(CH_3))_p]\text{-}[(OC(O)\text{-}G^1\text{-}C(O)O\text{-}G^2)_n]\text{-}OC(O)\text{-}G^1\text{-}C(O)O\text{-}[((CH_3)CHCH_2O)_p\text{-}]\text{-block-}[(CH_2CH_2O)_q]\text{-}X \quad (I)$$

wherein the G^1 moieties are all 1,4-phenylene moieties; the G^2 moieties are all C_{1-4} alkyl substituted ethylene moieties, each X is C_{1-4} alkyl, preferably methyl or n-butyl; each q is from 12 to 120; each p is from 1 to 10, preferably 2 to 5; and n is from 2 to 10.

EP 2 692 842 A1

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] This invention relates to concentrated aqueous alkaline liquid detergent compositions with low intrinsic foaming and in particular to liquids comprising soil release polymer (SRP) substantive to polyester fabrics. In this specification, unless indicated to the contrary, no distinction is made between polymer and oligomer. Both are termed polymers.

BACKGROUND

[0002] It has been proposed to use polyester based SRPs in detergent compositions, especially in laundry detergent compositions to promote improved soil removal from polyester fabrics. Such polymers may have a polyester midblock with one or two end blocks of capped polyethylene glycol attached to the midblock via ester linkages.

[0003] US 4759876 (Colgate) proposes an aqueous liquid concentrate comprising such a SRP. The preferred liquids have around 80 wt% of the surfactant system as nonionic which gives these compositions low in wash foaming and furthermore is expected to provide the concentrated compositions with low intrinsic foaming. The compositions are formulated to be acidic and triethanolamine free to protect the SRP.

[0004] The SRP used is a copolymer of polyethylene terephthalate and polyoxyethylene terephthalate of molecular weight 22 000 wherein the polyoxyethylene is of molecular weight 3 400, the molar ratio of polyethylene terephthalate to polyoxyethylene terephthalate units is about 3:1 and the proportion of ethylene oxide to phthalic moiety in the polymer is about 22:1.

[0005] WO2009/153184 (Unilever) proposes to dose a main wash surfactant at low levels so that the in wash surfactant level is lower than normal. What would be the consequential unsatisfactory wash performance, resulting from the low in-wash surfactant levels, is boosted by inclusion of unusually high levels of specific polymers and enzymes in the liquid. A key polymer, preferably included at high levels in the composition, is SRP substantive to polyester. The one used in the examples of WO2009/153184, is of polyester chemistry (terephthalic acid/propandiol condensation polymer with methoxy PEG 750 end cap). It is sold under the trade name TexCare® SRN170 by Clariant. The examples of this document suggest using a higher ratio of non-soap anionic surfactant to nonionic than is found in the examples of US 4759876.

[0006] Concentrated detergent liquids following the principles set out in WO2009/153184 may suffer from high levels of intrinsic foaming. By intrinsic foaming is meant that the concentrated composition itself forms a foam layer when subjected to aeration. This is a problem for handling of the compositions in the factory, particularly the bottle filling operation. It is, however, a considerable problem when the consumer will dose the composition using a volume measure, as is frequently the case for detergent compositions used for laundry. If the composition foams as it is dispensed through a nozzle or some similar dispensing device the mass dose will be too low for the measured volume dose and the consumer will not obtain the expected performance from her product. Compositions with increased levels of solvent hungry ingredients, in particular sequestrants, may exhibit even higher intrinsic foaming. High levels of perfume, the incorporation of ethoxylated polyethyleneimine and the use of amino based counter ions also tend to make intrinsic foaming more significant.

[0007] Use of an additional antifoam system is possible. The introduction of silicone antifoam could be considered, but it cannot be stably incorporated into the low viscosity compositions that suffer most from intrinsic foaming. Furthermore, if an external structuring system was to be used to suspend the silicone it would add cost and use up valuable formulation space. Thus a more efficient solution is desired.

[0008] EP 1 661 933 (Sasol) describes amphiphilic non-ionic oligoesters that have soil release properties after storage in alkaline detergent liquid. In the exemplary formulae a PO block of up to 10, but preferably 2 to 4 may be added between the midblock esters and the PEG endblock. The tested material has 4 such PO repeat units added. The mid block is essentially 1,4 - phenylene and 1,2 propylidene. Neither TEA nor alkoxylated polyethyleneimine is used with these polymers. The examples show that the soil release performance of this polymer after storage is superior to a polymer not having a PO block.

SUMMARY OF THE INVENTION

[0009] According to the present invention there is provided a concentrated alkaline liquid detergent composition comprising:

a) 5 to 60 wt% surfactant comprising anionic surfactant and optionally nonionic surfactant and optionally amphoteric surfactant and optionally soap of which at least 35% of the total surfactant is anionic non-soap surfactant,
b) at least 1 wt% triethanolamine (TEA),

c) at least 30 wt% water
d) at least 0.5 wt% soil release polymer
characterised in that:

(i) the soil release polymer has the formula (I), and X-[(OCH$_2$CH$_2$)$_q$-]-block-[(OCH$_2$CH(CH$_3$))$_p$]-[(OC(O)-G^1-C(O)O-G^2)$_n$]-OC(O)-G^1-C()O- [((CH$_3$)CHCH$_2$O)$_p$-]-block-[(CH$_2$CH$_2$O)q]-X (I)

wherein the G^1 moieties are all 1,4-phenylene moieties; the G^2 moieties are all C$_{1-4}$ alkyl substituted ethylene moieties, each X is C$_{1-4}$ alkyl, preferably methyl or n-butyl; each q is from 12 to 120; each p is from 1 to 10, preferably 2 to 5; and n is from 2 to 10.

[0010] The compositions are especially useful as laundry detergent compositions.

[0011] Because the non-soap anionic surfactant is believed to be the main source of the intrinsic foaming the ratio of non-soap anionic surfactant to soil release polymer should preferably be at most 25:1, more preferably 15:1 and most preferably at most 9:1.

[0012] The polyesters soil release polymers of formula (I) have surprisingly been found to confer significant intrinsic antifoaming benefits to the concentrated detergent liquids.

[0013] Preferably the composition further includes at least 2 wt% nonionic alkoxylated polyethyleneimine with at least 3 moles of alkoxylation per nitrogen.

[0014] The block polyesters of formula (I) are linear block polyesters. n preferably ranges from 3 to 9, especially for polymers made from dimethyl terephthalate, and 1,2-propylene glycol.

[0015] The most preferred linear block polyesters are those where n is from 6 to 8.

[0016] Most preferably, in the formula (I), p is 2 and q is from 18 to 60.

[0017] In one embodiment at least 10% of the groups G^2 are dimethylene substituted. This optional modification helps to keeps the esters in the midblock intact as fabric substantivity and thus soil release properties are otherwise lost and the improved resistance to hydrolysis is of no practical significance. This midblock modification appears to make no difference to the anti foam properties of the polymer.

[0018] The end blocks - [((CH$_3$)CHCH$_2$O)$_p$-]-block-[(CH$_2$CH$_2$O)$_q$]-X may both be present, alternatively only one of the two possible end blocks needs to be present, throughout this specification and claims references to end blocks include the situation where one or other end block is missing unless the context requires otherwise. Preferably the polymer has two end blocks. If one of the end blocks is missing then capping group X will similarly be missing from that end.

[0019] The alkaline liquid detergent compositions may comprise the polymer (d) in amounts of up to 15 wt%, preferably from 1 to 10 wt%, most preferably from 1.5 to 7 wt%. Preferably the alkaline concentrated detergent liquid composition is isotropic. The composition may comprise at least 5 wt% non-soap anionic surfactant. Suitably the liquid may comprise linear alkyl benzene sulphonate (LAS), Alkyl ether sulphate (AES), Nonionic and optionally an amine oxide or betaine, the LAS being formed from LAS acid, neutralized at least in part, with TEA. Amines may also be used as the counter ion for the AES. It is preferred for stability reasons to keep the total level of alkali metal ions less than 1 wt% of the composition.

[0020] To maximise the benefit of the other cleaning technologies that are essentially or optionally included in the liquid, especially anionic surfactant, the liquid is alkaline. It is preferred that the maximum concentrated composition pH is 8.4, more preferably at most 8.2.

DETAILED DESCRIPTION OF THE INVENTION

[0021] The invention is a combination of a selected group of polyester soil release polymers with surprising antifoaming properties and a liquid detergent base that has high intrinsic foaming.

[0022] All percentages are weight percent except where indicated otherwise or where the context makes it obvious that something else is intended.

The polyester soil release polymer (with antifoam properties)

[0023] The invention requires the selection of a soil release polymer with a polyester mid block and its incorporation into an alkaline concentrated detergent liquid, comprising surfactant and triethanolamine.

[0024] The SRPs with suitable antifoam effect have the formula (I):

X-[(OCH$_2$CH$_2$)$_q$-]-block-[(OCH$_2$CH(CH$_3$))$_p$]-[(OC(O)-G^1-C(O)O-G^2)n]-OC(O)-G^1-C(O)O-[((CH$_3$)CHCH$_2$O)$_p$-]-block-[(CH$_2$CH$_2$O)$_q$]-X (I)

X-[(OCH$_2$CH$_2$)$_q$-]-block-[(OCH$_2$CH(CH$_3$))$_p$]- and - [((CH$_3$)CHCH$_2$O)$_p$-]-block-[(CH$_2$CH$_2$O)$_q$]-X are generally connected at the ends of the polymer backbone or mid block. The mid block is responsible for making the polymer fabric substantive, particularly towards polyester fabrics. The endcaps of large blocks of EO groups are highly hydrophilic and can be considered to swing away from the fabric to provide the surface modification that promotes soil release. Thus it is an essential feature of the polymers of the present invention to have capped EO end block(s).

[0025] The polymer will be nonionic. Ionic polymers are generally not phase stable in concentrated alkaline detergent liquids.

Mid block or backbone

[0026] The mid block]-[(OC(O)-G^1-C(O)O-G^2)$_n$]-OC(O)-G^1-C(O)O- is responsible for making the polymer fabric substantive, particularly towards polyester fabrics. It has little effect on the antifoam properties of the polymer.

[0027] The esters in the midblock may in practice be formed either way around.

[0028] The G^1 moieties comprise 1,4-phenylene moieties.

[0029] The G^2 moieties are substituted ethylene moieties having C_{1-4} alkyl substituents. A preferred mono substituted ethylene moiety is 1,2 propylene which is derived from the condensation of 1,2 propane diol.

[0030] For the G^2 moieties, most preferred substituted ethylene moieties are the monomethyl substituted G^2 formed from 1,2-propylene diol , and the dimethyl substituted G^2 formed from 2,3 butylene diol. The use of 1,2 di methyl substituted ethylene shows superior protection of adjacent ester bonds due to that fact that it is always going to be the case that there is a methyl group on the carbon atom adjacent to the ester. The contrasts with the situation for the monomethyl material formed from 1,2 propane diol. In that case the methyl group may arrange itself adjacent to the ester or it may alternatively arrange itself to be on the carbon of the ethylene that is more remote from the ester.

[0031] 2,3 butylene is a meso stereo isomeric compound. It is thought that once reacted into the polymer chain the different forms behave in similar ways as far as the hindering of hydrolysis is concerned. The optically active RR or SS diastereoisomers are preferred over the RS (meso) diastereoisomer. Thus, the preferred form of the 2,3 butylene glycol used is the RR or SS optically active forms either isolated, or as a racemic mixture. In practice a mixture of the meso and racemic forms has been found to give satisfactory results.

[0032] A preferred diol to form the desired group G^2 may be selected from the group of diols of formula (II):

syn n+1,n+2 alkylene diol (II)

n being an integer from 1 to c-3, where c is the number of carbons in the alkylene chain.

[0033] The most preferred diols are syn 2,3 butane diol and 1,2 propane diol.

[0034] G^2 may comprise up to 20 mol% moieties derived from 2,3 butane diol derivatives, i.e. an ethylene moiety with a methyl group substituted on each carbon in the backbone.

[0035] It has been found that the value of n needs to be at least 2 in order for the antifoam polymers used in the invention to have sufficient polyester substantivity. The maximum value for n can range up to 26. By comparison, polyesters used in fibre making typically have a much higher molecular weight with n from 50 to 250. Typically, n ranges from 2 to 16, preferably 4 to 9 most preferably 6 to 8. Generally, the larger the n value, the less soluble is the polymer. Because it is an average, n is not necessarily a whole number for the polymer in bulk.

End block

[0036] The following examples suggest that it is the propoxylation of the end blocks that gives the antifoam benefit. The degree of propoxylation should be from 1 to 10 propylene oxide units on average per end block. It is in a block. 2 to 5 PO is preferred due to having the right balance of antifoam properties. The antifoam benefit does not seem to increase linearly with the amount of propoxylation.

[0037] The polymers have an EO block that has more alkoxy units than the PO block, preferably the EO block has at least 1.5 times the number of moles or units (q) as the PO block (p), more preferably at least 5 times as many, even 10 times as many, or more. q is at least 6, and is preferably at least 10. The value for q usually ranges from 18 to 80. Typically, the value for q is in the range of from 30 to 70, preferably 40 to 70.

[0038] The terminal end cap X on the EO blocks is preferably as small as possible. X is preferably methyl, ethyl, or n-butyl and most preferably methyl or n-butyl.

[0039] As the value for q increases, the value for n in the midblock should be increased so that the polymer will deposit well on the fabric during laundering.

[0040] Since p and q are made by anionic polymerisation routes this results in blocks with discrete block lengths in contrast to the midblock made by polycondensation routes.

Molecular weight

[0041] Preferred polymers for use in liquid detergent compositions have molecular weights Mw within the range of from 1000 to 20 000, preferably from 1500 to 10 000. Preferably the molecular weight is greater than 4 000. The polydispersity of the polymers is preferred to be less than 3.

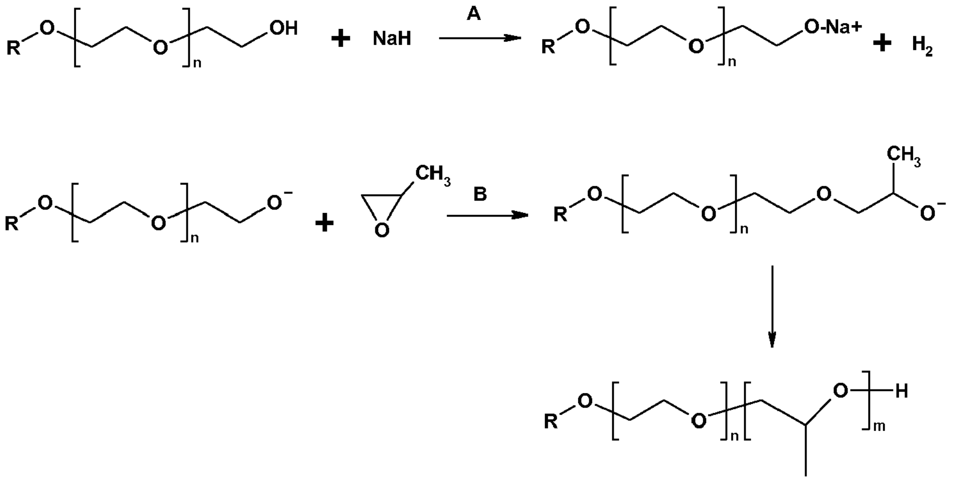
Preparation of the polymer

[0042] The soil release polymers of the present invention can be prepared by methods known to the person skilled in the art. US 4,702, 857 and US 4,711,730 describe a method of synthesis that may be adapted to produce the block polyesters of the present invention. In one process the end blocks are made in a separate process and then added to the mid block. A suitable process to manufacture the block copolymers used for the end blocks is described below.

End block manufacture

[0043] The PO/EO end blocks may be preformed by anionic polymerisation of propylene oxide using a preformed mono-functional PEG as the initiator. Such a process is, for example, described in M. I. Malik, B. Trathnigg, C.O. Kappe, Macromol. Chem. Phys., 2007, 208, 2510-2524.

[0044] The reaction scheme is set forth below:



Reaction A: Sodium hydride reacts with PEG to yield activated chain ends.

Reaction B: The addition of PO proceeds at the ends of the PEG chains to form a block of PO.

[0045] An alternative process forms the mid block and reacts it with PO and mPEG.

Mid block manufacture

[0046] The mid block may be formed by condensation of methyl esters of terephthalic acid with the appropriate aliphatic diol, preferably using an excess of one of them as set forth in more detail in the following examples. If the dicarboxylic acid is used in alkyl ester form, the reaction is suitably carried out in the presence of a base catalyst, at an elevated temperature, for example, 120 to 180°C, and, if desired, under reduced pressure. The lower alcohol, normally methanol, generated during the reaction is distilled off.

[0047] Suitable catalysts include alkyl and alkaline earth metals, for example, lithium, sodium, calcium and magnesium, as well as transition and Group IIB metals, for example, antimony, manganese, cobalt and zinc. The catalysts are usually used as oxides, carbonates or acetates. A preferred catalyst comprises antimony trioxide and calcium acetate.

[0048] The esters and oligomers produced in the condensation (ester interchange) reaction may then be polymerised to the desired molecular weight, by raising the temperature further, typically to 180 to 250 °C.

[0049] The degree of polymerisation may be monitored by gel permeation chromatography, NMR, and end-group titrations.

The detergent liquids

[0050] Following the approach proposed in WO2009/153184 the preferred liquids have high amounts of soil release polymer, EPEI, enzymes, and sequestrant relative to the total detersive surfactants level. By careful selection of these performance ingredients to be ones that perform better when in wash surfactant levels are lower, the overall detergency of the wash liquor can be adjusted to match that of a wash liquor delivered from a conventional liquid which has broadly similar levels of performance additives and higher levels of surfactants in the wash liquor. The issues with such an approach to concentration are twofold. First the additives that exhibit this high performance property in combination must be found and then they must be stably incorporated into the concentrated liquid which has surfactants in the normal range or slightly lower than normal for a concentrated liquid but performance additives included at much higher levels than normal in the concentrated liquid. Because of the degree of difficulty in putting the full formulation together with so many constraints the selection of a multifunctional soil release polymer so that it not only provides effective soil release performance but also solves the intrinsic foaming problem is highly advantageous and unexpected for the person skilled in formulating liquid detergents.

[0051] The amount of surfactant makes up at least 5 wt% of the total liquid composition, preferably it makes up from 12 to 60 wt%. The compositions according to the invention most preferably have total active detersive surfactant levels of at least 15 wt%.

[0052] The compositions may be concentrated laundry detergent compositions designed to be added to a 10 litre wash in small doses that require them to be diluted in at least 500 times their own volume of water to form a main wash liquor comprising at most 0.5 g/l surfactant. They may also be concentrated compositions designed for hand wash or top loading automatic washing machines. In hand wash less water may be used and in top loading automatic washing machines a higher amount of water would normally be used.

[0053] The dose of detergent liquid is adjusted accordingly to give similar wash liquor concentrations.

Surfactants

[0054] Surfactants assist in removing soil from the textile materials and also assist in maintaining removed soil in solution or suspension in the wash liquor. Anionic or blends of anionic and nonionic surfactants are a preferred feature of the present invention. The amount of anionic surfactant is preferably at least 5 wt%.

[0055] To obtain the full benefit of the invention it is preferred that the ratio of nonionic surfactant to total surfactant is at most 3:2. Compositions with higher levels of nonionic do not suffer from intrinsic foaming to such an extent.

Anionic

[0056] Preferred alkyl sulphonates are alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}. The preferred counter ion for concentrated alkaline liquids is one or more ethanolamines, for example monoethanolamine (MEA) and triethanolamine (TEA). This introduces TEA into the composition.

[0057] The linear alkyl benzene sulphonate surfactants may be Detal LAS with an alkyl chain length of from 8 to 15, more preferably 12 to 14.

[0058] It is further desirable that the composition comprises an alkyl polyethoxylate sulphate anionic surfactant of the formula (II):

$$RO(C_2H_4O)_xSO_3^-M^+ \qquad (II)$$

where R is an alkyl chain having from 10 to 22 carbon atoms, saturated or unsaturated, M is a cation which makes the compound water-soluble, especially an ammonium or substituted ammonium cation, or less preferably an alkali metal, and x averages from 1 to 15.

[0059] Preferably R is an alkyl chain having from 12 to 16 carbon atoms, x averages from 1 to 3, preferably x is 3; M may be an ethanolamine, or other material chosen from the list of buffers, to avoid ion exchange of sodium with the counter ion of the LAS. However, since some sodium can be tolerated the counter ion can be sodium if low levels of this surfactant are used. The anionic surfactant sodium lauryl ether sulphate (SLES) may be used provided total alkali metal salts in the composition remain low. An average of 3 moles of ethylene oxide per mole is preferred.

Nonionic

[0060] Nonionic surfactants include primary and secondary alcohol ethoxylates, especially C_8-C_{20} aliphatic alcohol ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{l5} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkyl polyglycosides, glycerol monoethers and polyhydroxy amides (glucamide). Mixtures of nonionic surfactant may be used. When included therein the composition contains from 0.2 wt% to 40 wt%, preferably 1 wt% to 20 wt%, more preferably 5 to 15 wt% of a non-ionic surfactant, such as alcohol ethoxylate, nonylphenol ethoxylate, alkylpolyglycoside, alkyldimethylamineoxide, ethoxylated fatty acid monoethanolamide, fatty acid monoethanolamide, polyhydroxy alkyl fatty acid amide, or N-acyl N-alkyl derivatives of glucosamine ("glucamides").

[0061] Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 35 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol.

Amine Oxide

[0062] The composition may comprise up to 10 wt% of an amine oxide of the formula (III):

$$R^1\ N(O)(CH_2\ R^2)_2 \qquad \text{(III)}$$

[0063] In which R^1 is a long chain moiety each CH_2R^2 are short chain moieties. R^2 is preferably selected from hydrogen, methyl and $-CH_2OH$. In general R^1 is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated, preferably, R^1 is a primary alkyl moiety. R^1 is a hydrocarbyl moiety having chain length of from about 8 to about 18. Preferred amine oxides have R^1 is C_8-C_{18} alkyl, and R^2 is H. These amine oxides are illustrated by $C_{12\text{-}14}$ alkyldimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide.

[0064] A preferred amine oxide material is Lauryl dimethylamine oxide, also known as dodecyldimethylamine oxide or DDAO. Such an amine oxide material is commercially available from Huntsman under the trade name Empigen® OB.

[0065] Amine oxides suitable for use herein are also available from Akzo Chemie and Ethyl Corp. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers.

[0066] Whereas in certain of the preferred embodiments R^2 is H, it is possible to have R^2 slightly larger than H. Specifically, R^2 may be CH_2OH, such as: hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbis(2- hydroxyethyl)amine oxide.

[0067] Preferred amine oxides have the formula:

$$O^- - N^+(Me)_2R^1 \qquad \text{(IV)}$$

where R^1 is $C_{12\text{-}16}$ alkyl, preferably $C_{12\text{-}14}$ alkyl; Me is a methyl group.

Zwitterionic

[0068] Nonionic-free systems with up to 95 %wt LAS can be used provided that some zwitterionic surfactant, such as carbobetaine, is present. A preferred zwitterionic material is a betaine available from Huntsman under the name Empigen® BB. Betaine improves particulate soil detergency in the compositions of the invention.

Additional surfactants

[0069] Other surfactants than the preferred LAS, AES, and nonionic may be added to the mixture of detersive surfactants. However, cationic surfactants are preferably substantially absent.

[0070] Although less preferred, some alkyl sulphate surfactant (PAS) may be used, especially the non-ethoxylated $C_{12\text{-}15}$ primary and secondary alkyl sulphates.

[0071] Soap may be used. Levels of soap are preferably lower than 5 wt%; more preferably lower than 3 wt% most preferably lower than 1 wt%.

EPEI

[0072] For detergency boosting it is advantageous to use a second polymer with the soil release polymers of the present invention this is a polyalkoxylated polyethyleneimine.

[0073] Polyethylene imines are materials composed of ethylene imine units -CH2CH2NH- and, where branched, the hydrogen on the nitrogen is replaced by another chain of ethylene imine units. These polyethyleneimines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulphite, sulphuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, and the like. Specific methods for preparing these polyamine backbones are disclosed in U.S. Pat. No. 2,182,306, Ulrich et al., issued Dec. 5, 1939; U.S. Pat. No. 3,033,746, Mayle et al., issued May 8, 1962; U.S. Pat. No. 2,208,095, Esselmann et al., issued Jul. 16, 1940; U.S. Pat. No. 2,806,839, Crowther, issued Sep. 17, 1957; and U.S. Pat. No. 2,553,696, Wilson, issued May 21, 1951.

[0074] Preferably, the EPEI comprises a polyethyleneimine backbone of about 300 to about 10000 weight average molecular weight; and the polyalkoxylation comprises polyethoxylation. The polymer is nonionic and has no permanent quaternisation of the polyamine nitrogens; although they may be protonated depending on the pH. A preferred nonionic EPEI may be represented as PEI(X)YEO where X represents the molecular weight of the unmodified PEI and Y represents the average moles of ethoxylation per nitrogen atom in the polyethyleneimine backbone. The ethoxylation may range from 3 to 40 ethoxy moieties per polyalkoxyl chain, preferably it is in the range of 16 to 26, most preferably 18 to 22. A minority of the ethoxy units may be replaced by propoxy units.

[0075] When present the alkoxylated polyethyleneimine polymer is present in the composition at a level of between 0.01 and 25 wt%, and preferably at a level of at least 2 wt% and/or less than 9.5 wt%, most preferably from 3 to 9 wt% and with a ratio of non-soap surfactant to EPEI of from 2:1 to 7:1, preferably from 3:1 to 6:1, or even to 5:1.

Other polymers

[0076] In addition to the polyester soil release polymer with antifoam properties and the optional EPEI the composition may comprise other polymeric materials, for example: dye transfer inhibition polymers, anti redeposition polymers and cotton soil release polymers, especially those based on modified cellulosic materials. Especially when EPEI is not present the composition may further comprise a polymer of polyethylene glycol and vinyl acetate, for example the lightly grafted copolymers described in WO2007/138054. Such amphiphilic graft polymers based on water soluble polyalkylene oxides as graft base and side chains formed by polymerisation of a vinyl ester component have the ability to enable reduction of surfactant levels whilst maintaining high levels of oily soil removal.

Hydrotrope

[0077] In the context of this invention a hydrotrope is a solvent that is neither water nor conventional surfactant that aids the solubilisation of the surfactants and other components, especially polymer and sequestrant, in the liquid to render it isotropic. Among suitable hydrotropes there may be mentioned as preferred: MPG (monopropylene glycol), glycerol, sodium cumene sulphonate, ethanol, other glycols, e.g. di propylene glycol, diethers and urea. MPG and glycerol are preferred hydrotropes.

Enzymes

[0078] It is preferable that at least one or more enzymes selected from protease, mannanase, pectate lyase, cutinase, esterase, lipase, amylase, and cellulase may be present in the compositions. Less preferred additional enzymes may be selected from peroxidase and oxidase. The enzymes are preferably present with corresponding enzyme stabilizers. The total enzyme content is preferably at least 2 wt%, even as high as at least 4 wt%.

Sequestrants

[0079] There is not room to include high levels of builders in the concentrated compositions. Thus, sequestrants are preferably included. Such materials tend to have low solubility in the concentrated liquids so the multifunctionality of the antifoam soil release polymer assists in stably incorporating these materials into the compositions.

[0080] Preferred sequestrants include organic phosphonates, alkanehydroxy phosphonates and carboxylates available under the DEQUEST trade mark from Thermphos.

[0081] The preferred sequestrant level is less than 10 wt% and preferably less than 5 wt% of the composition. A particularly preferred sequestrant is HEDP (1-Hydroxyethylidene -1,1,-diphosphonic acid), for example sold as Dequest 2010. Also suitable but less preferred as it gives inferior cleaning results is Dequest® 2066 (Diethylenetriamine penta (methylene phosphonic acid or Heptasodium DTPMP).

Buffers

[0082] In addition to the 1% TEA the presence of buffer is preferred for pH control; preferred buffers are MEA, and TEA. They are preferably used in the composition at levels of from 5 to 15 wt%, including the 1% TEA. Other suitable buffer materials may be selected from the group consisting of amino alcohol compounds having a molecular weight above 61 g/mol, which includes MEA. Suitable materials also include, in addition to the already mentioned materials: monoisopropanolamine, diisopropanolamine, triisopropanolamine, monoamino hexanol, 2-[(2-methoxyethyl) methylamino]-ethanol, propanolamine, N-methylethanolamine, diethanolamine, monobutanolamine, isobutanolamine, monopentanolamine, 1-amino-3-(2-methoxyethoxy)- 2-propanol, 2-methyl-4-(methylamino)-2-butanol and mixtures thereof.

Further Optional Ingredients:

[0083] It may be advantageous to include fluorescer and /or bleach catalyst in the compositions as further high efficiency performance additives. Their inclusion is also made easier by the soap reduction made possible by inclusion of the propoxylated polyester soil release polymers. Perfume and colorants will desirably be included in the compositions. The compositions may contain viscosity modifiers, foam boosting agents, preservatives (e.g. bactericides), pH buffering agents, polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, antistatic agents and ironing aids. The compositions may further comprise, pearlisers and/or opacifiers or other visual cues and shading dye.

Packaging and dosing

[0084] The liquids may be packaged as unit doses in polymeric film soluble in the wash water. Alternatively the liquids may be supplied in multidose plastics packs with a top or bottom closure. A dosing measure may be supplied with the pack either as a part of the cap or as an integrated system.

[0085] The invention will now be further described with reference to the following non-limiting examples.

EXAMPLES

Key to ingredients used:

[0086]

MPG	is mono propylene glycol.
TEA	is triethanolamine.
MEA	is Monoethanolamine.
NI 7EO	is C12-15 alcohol ethoxylate 7EO nonionic Neodol® 25-7 (ex Shell Chemicals).
LAS acid	is C12-14 linear alkylbenzene sulphonic acid.
Prifac® 5908	is saturated lauric fatty acid ex Croda.
SLES 3EO	is sodium lauryl ether sulphate with 3 moles EO.
EPEI	is Sokalan HP20 - ethoxylated polyethylene imine cleaning polymer: PEI(600) 20EO ex BASF.
Perfume	is free oil perfume.
Dequest® 2010	is HEDP (1-Hydroxyethylidene-1,1,-diphosphonic acid).
Empigen® OB	is Amine oxide ex Huntsman.
TexCare SRN-170	is soil release polymer ex Clariant.
SRP 1	is an antifoam soil release polymer with propoxylation and having: G^2 = 80 mol% monomethyl ethylene 20 mol% 1,2 dimethyl ethylene, p=3 q=45, X=Methyl, n=6-7.
SRP 2	is an antifoam soil release polymer with propoxylation and having G^2 100 mol% monomethyl ethylene, p=5 q=45, X=Methyl, n=6-7.
SRP 3	is an antifoam soil release polymer with propoxylation and having G^2 100 mol% monomethyl ethylene, p=2 q=45, X=Methyl, n=6-7.
Preservative	is Proxel GLX antimicrobial preservative, a 20% solution of 1,2 benzisothiazolin-3-one in dipropylene glycol and water ex Arch Biocides.
Colorant	is a mixture of equal part patent blue and acid yellow

Example 1 - concentrated liquid compositions with SRP

[0087] A series of compositions designed to be dosed at 35 ml per wash was formulated with no SRP, with prior art SRPs and with propoxylated SRPs. The compositions used are given in Table 1. They were subjected to a foam evaluation using the following protocol:

[0088] A 30 ml sample of the concentrated detergent composition was added to a 100 ml measuring cylinder. The cylinder was sealed and shaken 20 times to generate foam. The cylinder was left to stand for 1 minute and the foam height measured. The protocol was repeated up to 6 times for each sample and the average taken. The results are given in Table 2.

[0089] It can be seen from Table 2 that TexCare® SRN240, a polymer of similar molecular weight and construction to that of the propoxylated SRPs (but without any propoxylation), causes the composition to foam and is very similar to that of the base alone and TexCare® SRN170. All three propoxylated SRPs cause a significant reduction in foaming.

Table 1 - Liquid detergent compositions

		Compositions Wt % as 100%					
Ingredient	**%AD**	**1**	**2**	**3**	**4**	**5**	**6**
Demin water and MEA to adjust pH	100	balance	balance	balance	balance	balance	balance
MPG	100	20.00	20.00	20.00	20.00	20.00	20.00
TEA	100	2.00	2.00	2.00	2.00	2.00	2.00
NI 7EO	100	7.28	7.28	7.28	7.28	7.28	7.28
LAS Acid	97.1	4.85	4.85	4.85	4.85	4.85	4.85
Prifac 5908	100	0.69	0.69	0.69	0.69	0.69	0.69
SLES 3EO	70	2.42	2.42	2.42	2.42	2.42	2.42
Empigen OB	30	0.86	0.86	0.86	0.86	0.86	0.86
EPEI	80	3.14	3.14	3.14	3.14	3.14	3.14
Dequest 2010	60	1.50	1.50	1.50	1.50	1.50	1.50
TexCare SRN-170	70	0.00	2.14	0.00	0.00	0.00	0.00
SRP 1	100	0.00	0.00	2.14	0.00	0.00	0.00
SRP 2	100	0.00	0.00	0.00	2.14	0.00	0.00
SRP 3	100	0.00	0.00	0.00	0.00	2.14	0.00
TexCare SRN-240	40	0.00	0.00	0.00	0.00	0.00	2.14
Preservative	20	0.01	0.01	0.01	0.01	0.01	0.01
Colorant & Fluorescer	0.1	0.06078	0.06078	0.06078	0.06078	0.06078	0.06078
Perfume	100	1.43	1.43	1.43	1.43	1.43	1.43
Total	100	100.00	100.00	100.00	100.00	100.00	100.00
Viscosity @25°C and 23 s-1 (Pas)		0.0633	0.0527	0.0660	0.0659	0.0656	-

Table 2

	Foam volume (ml)							
Composition	**Rep 1**	**Rep 2**	**Rep 3**	**Rep 4**	**Rep 5**	**Rep 6**	**Ave**	**StDev**
1	30	42	35	-	-	-	35.67	6.03
2	22	30	25	34	26	27	27.33	4.17
3	1	1	1	-	-	-	1	0
4	3	3	3	-	-	-	3	0
5	2	2	2	2	2	2	2	0
6	-	-	-	35	25	33	31	5.29

Claims

1. A concentrated alkaline liquid detergent composition comprising:

a) 5 to 60 wt% surfactant comprising anionic surfactant and optionally nonionic surfactant and optionally am-

photeric surfactant and optionally soap of which at least 35% of the total surfactant is anionic non-soap surfactant,
b) at least 1 wt% triethanolamine (TEA),
c) at least 30 wt% water
d) at least 0.5 wt% soil release polymer
characterised in that:

(i) the soil release polymer has the formula (I), and $X\text{-}[(OCH_2CH_2)_q\text{-}]\text{-block-}[(OCH_2CH(CH_3))_p]\text{-}[(OC(O)\text{-}G^1\text{-}C(O)O\text{-}G^2)_n]\text{-}OC(O)\text{-}G^1\text{-}C(O)O\text{-}[((CH_3)CHCH_2O)_p\text{-}]\text{-block-}[(CH_2CH_2O)_q]\text{-}X$ (I)

wherein the G^1 moieties are all 1,4-phenylene moieties; the G^2 moieties are all C_{1-4} alkyl substituted ethylene moieties, each X is C_{1-4} alkyl, preferably methyl or n-butyl; each q is from 12 to 120; each p is from 1 to 10, preferably 2 to 5; and n is from 2 to 10.

2. A composition according to claim 1 in which the ratio of non-soap anionic surfactant to soil release polymer is at most 9:1.

3. A composition according to any preceding claim wherein each G^2 has one or two C_{1-4} alkyl substituents with at most one on each carbon.

4. A composition according to any preceding claim wherein the C_1-4 alky moieties are methyl moieties.

5. A composition according to any preceding claim comprising at least 2 wt% alkoxylated polyethylene imine.

6. A composition according to any preceding claim comprising at least 5 wt% anionic surfactant.

7. A composition according to any preceding claim comprising Alkyl ether sulphate anionic surfactant.

8. A composition according to any preceding claim comprising LAS, the LAS being neutralised from LAS acid, at least in part, with TEA.

9. A composition according to any preceding claim comprising at least 2 wt% of the soil release polymer (c).

10. A composition according to any preceding claim comprising at least three enzymes.

11. A composition according to any preceding claim comprising at least 1 wt% sequestrant.

12. A composition according to any preceding claim comprising at least 0.5 wt% amine oxide.

13. A composition according to any preceding claim comprising up to 25 wt% hydrotrope.

14. A composition according to any preceding claim comprising at most 1 wt% alkali metal ions.

15. A composition according to any preceding claim with a viscosity measured at 23 s^{-1} at 25 °C of less than 0.1 Pa.s.

16. A composition according to any preceding claim comprising less than 5 wt%, soap, preferably less than 3 wt%, most preferably less than 1 wt%.

Europäisches
Patentamt
European
Patent Office
Office européen
des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 12 17 8620

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
E	WO 2012/104159 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN]; CARSWELL) 9 August 2012 (2012-08-09) * tables 9,10 *	1-16	INV. C11D1/02 C11D1/83 C11D1/94 C11D3/30 C11D3/37
A	EP 0 523 956 A2 (UNILEVER PLC [GB]; UNILEVER NV [NL]) 20 January 1993 (1993-01-20) * examples 7-9 *	1-16	
A	GB 1 466 639 A (PROCTER & GAMBLE) 9 March 1977 (1977-03-09) * example I *	1-16	
A,D	EP 1 661 933 A1 (SASOL GERMANY GMBH [DE]) 31 May 2006 (2006-05-31) * paragraph [0024] *	1-16	
			TECHNICAL FIELDS SEARCHED (IPC)
			C11D

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	21 November 2012	Richards, Michael

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 12 17 8620

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

21-11-2012

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2012104159 A1	09-08-2012	NONE	
EP 0523956 A2	20-01-1993	AU 663322 B2	05-10-1995
		AU 2037092 A	21-01-1993
		BR 9202740 A	23-03-1993
		CA 2073791 A1	18-01-1993
		DE 69208549 D1	04-04-1996
		DE 69208549 T2	01-08-1996
		EP 0523956 A2	20-01-1993
		ES 2085570 T3	01-06-1996
		US 5330672 A	19-07-1994
		ZA 9205368 A	17-01-1994
GB 1466639 A	09-03-1977	BE 830614 A1	29-12-1975
		CA 1049367 A1	27-02-1979
		DE 2527793 A1	15-01-1976
		FR 2276378 A1	23-01-1976
		GB 1466639 A	09-03-1977
		IT 1039388 B	10-12-1979
		NL 7507505 A	30-12-1975
EP 1661933 A1	31-05-2006	DE 102004056785 A1	01-06-2006
		EP 1661933 A1	31-05-2006

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 4759876 A **[0003] [0005]**
- WO 2009153184 A **[0005] [0006] [0050]**
- EP 1661933 A **[0008]**
- US 4702857 A **[0042]**
- US 4711730 A **[0042]**
- US 2182306 A, Ulrich **[0073]**
- US 3033746 A, Mayle **[0073]**
- US 2208095 A, Esselmann **[0073]**
- US 2806839 A, Crowther **[0073]**
- US 2553696 A, Wilson **[0073]**
- WO 2007138054 A **[0076]**

Non-patent literature cited in the description

- **M. I. MALIK ; B. TRATHNIGG ; C.O. KAPPE.** *Macromol. Chem. Phys.,* 2007, vol. 208, 2510-2524 **[0043]**