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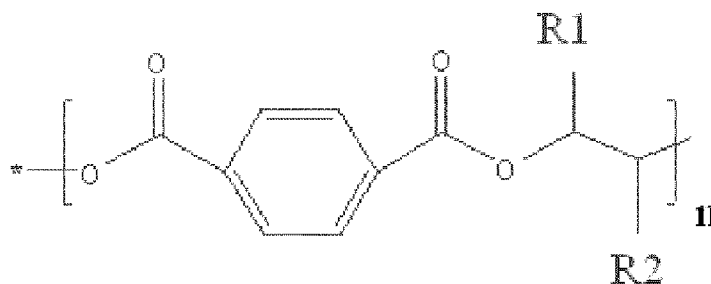
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(54) Title: ALKALINE LIQUID DETERGENT COMPOSITIONS



(57) **Abstract**: An aqueous alkaline isotropic concentrated detergent liquid composition with an undiluted pH of at least 7.8 and at most 9 comprising: a) 10 to 60 wt% non-soap surfactant, b) 0 to 20 wt% hydrotrope, c) 0 to 4 wt% soap, d) 0 to 10 wt% nonionic EPEI, e) at least 1 wt% triethanolamine, characterised in that dissolved in the alkaline isotropic liquid there is: f) at least 1 wt%, preferably at least 1.5 wt% of a polyester substantive nonionic soil release polymer of the type E-M-L-E, where the midblock M is connected to a generally hydrophilic end block E and blocks E each comprise capped oligomers of polyethylene glycol remote from the midblock, with at least 10 EO repeat units, the end blocks being free from ester bonds, either directly or via linking moiety L which comprises the motif: B-Ar-B where B is selected from urethane, amide and ester moieties and Ar is, 4 phenylene, and midblock M comprises the motif: wherein R1 and R2 may be the same or different selected from C1-C4 alkyl, C1-C4 alkoxy and Hydrogen, provided that R1 and R2 may not both be hydrogen, n is at least 2, preferably more than 5, the ester bonds may be 2 formed the other way around (not shown), if they are so reversed then all of them will be so reversed, G3107 (C) CPL -78- wherein the composition comprising the polymer provides soil release less than a ΔE of 5 with DMO on woven polyester after storage of the polymer in the detergent composition at 60°C for 8 days at a pH >7.5.



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ALKALINE LIQUID DETERGENT COMPOSITIONS

TECHNICAL FIELD

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This invention relates to alkaline liquid detergent compositions comprising soil release polymer (SRP) substantive to polyester fabrics, the soil release polymers assist with cleaning of oily soils from fabrics comprising polyester during a laundry wash process.

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BACKGROUND

There is spanning many years and in many documents disclosure of polymeric or oligomeric soil release agents designed to assist with the removal of soils from fabrics comprising polyester fibres. In this specification, unless indicated to the contrary, no distinction is made between polymer and oligomer. Both are termed polymers.

Many SRPs intended to promote improved soil removal from polyester fabrics are themselves polyesters. We have found that these prior art polyesters are unsuitable for use in alkaline laundry liquids. The patent specifications, or other documents, disclosing the SRPs may be unclear in that regard as examples are possibly given of use of the polymer in such a liquid. The fact is that the resistance of most prior art polyester SRPs to hydrolytic attack is insufficient to allow them to be incorporated into alkaline liquid detergent compositions with sufficient stability that their performance is not compromised due to hydrolytic breakdown on storage of the composition. This hydrolysis is made even worse when triethanolamine (TEA) is used in the composition. TEA is commonly used as a neutralising agent and buffer in detergent liquids and has now been found to catalyse the decomposition of

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many polyester SRPs, especially if they comprise ethylene oxide or unsubstituted ethylene next to an ester bond. Most soil release polymers designed to be substantive to polyester do comprise such ethylene oxide or ethylene moieties, or both. Many such polymers have these moieties (or a polyethylene glycol group) in the polymer mid block. Such moieties in the polymer mid block, especially those adjacent to ester moieties, have now been found to be a major factor in SRP decomposition via hydrolysis.

Many proposals have been made for SRPs to have a permanent charge, including balanced positive and negative charges on different moieties in the SRP. We have now found that such charged polymers are unsuitable for use in liquid compositions that comprise other charged species, especially anionic surfactants.

There have been proposals for polyester SRPs of the type E-M-E. M is the fabric substantive mid block and each E is a generally hydrophilic end block, preferably comprising a block of ethylene oxide repeat units such as mPEG (methyl endcapped polyethylene glycol) that acts to modify the normally hydrophobic polyester fabric surface once the fabric substantive mid block has caused the SRP to deposit on the surface. It is this type of E-M-E SRP that we wish to stabilise in alkaline detergent liquid compositions, especially compositions comprising anionic surfactant and TEA.

WO2009/153184 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. One of the key polymers that is preferably included at high levels in the composition is a SRP substantive to polyester. The one used in the examples of WO2009/153184, and also one of the three preferred on page 39, is of polyester chemistry (terephthalic

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acid/propandiol condensation polymer with methoxy PEG 750 end cap). It is sold under the trade name Texcare® SRN170 by Clariant. It is now thought that this material is substantially linear.

- 5 We have found that the storage stability of the SRP included in the examples of WO2009/153184 is not sufficient for a commercial product that may be subjected to high temperatures and needs to give performance that is not compromised by storage for long periods of time. Thus it is desirable to replace this SRP with a modified SRP that is sufficiently resistant to hydrolysis
- 10 in alkaline detergent compositions, especially those comprising anionic surfactant and most preferably further comprising TEA, and yet retains the excellent soil release performance, that is the case for Texcare®SRN 170 when freshly formulated into such an alkaline liquid composition.
- 15 In practice, despite the vast array of options that present themselves from the literature it seems that not many SRPs are soluble in alkaline detergent liquids. If solubility is not achieved the liquid turns hazy and the product performance may be compromised, especially if the lack of solubility leads to uneven distribution of the SRP through the composition. Solubility of an SRP
- 20 in a composition is defined as its ability to remain isotropic within the composition and not produce the unwanted hazing effect. Thus solubility may simply be determined for any given SRP in a given composition.

EP 1 661 933 (Sasol) describe amphiphilic non-ionic oligoesters that have soil

25 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 adjacent to the mid block. The tested material has 4 PO. The mid block is essentially 1,4 – phenylene and 1,2 propylidene. TEA is not used with these

30 polymers.

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We have now found several modified SRPs that have the required alkaline stability, formulation compatibility and polyester soil release performance. These SRPs and other SRPs that can be conceived by the skilled worker without the need for further inventive effort once the information concerning the SRPs we have produced is known, when formulated into alkaline liquid detergents, provide a novel group of stable compositions that may be linked together and generalised to form a single inventive concept that is broader than the compositions comprising the individual SRPs. The resulting invention therefore encompasses further groups of polymers that the skilled person, aware of the teaching in this patent specification, would expect to have the same or similar properties in the alkaline liquids of the type claimed.

SUMMARY OF THE INVENTION

According to the present invention there is provided an aqueous alkaline isotropic concentrated detergent liquid composition with an undiluted pH of at least 7.8 and at most 9 comprising:

- a) 10 to 60 wt% non-soap surfactant,
- b) 0 to 20 wt% hydrotrope,
- c) 0 to 4 wt% soap,
- d) 0 to 10 wt% nonionic EPEI,
- e) at least 1 wt% triethanolamine (TEA),

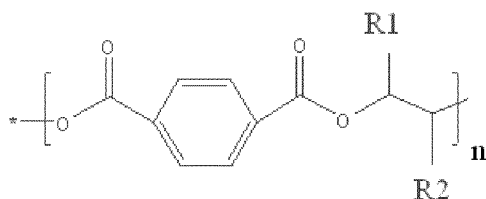
characterised in that dissolved in the alkaline isotropic liquid there is:

- f) at least 1 wt%, preferably at least 1.5 wt% of a polyester substantive nonionic soil release polymer of the type E-M-L-E, where the midblock M is connected to a generally hydrophilic end block E and blocks E each comprise capped oligomers of polyethylene glycol remote from the midblock, with at least 10 EO repeat units, the end blocks being free from ester bonds, either directly or via linking moiety L which comprises the motif:

B-Ar-B where B is selected from urethane, amide and ester moieties and Ar is 1,4 phenylene,

- 5 -

and midblock M comprises the motif:



- 5 wherein R1 and R2 may be the same or different selected from C1-C4 alkyl, C1-C4 alkoxy and Hydrogen, provided that R1 and R2 may not both be hydrogen, n is at least 2, preferably more than 5, the ester bonds may be formed the other way around (not shown), if they are so reversed then all of them will be so reversed,

10

wherein the composition comprising the polymer provides soil release less than a ΔE of 5 with DMO on woven polyester after storage of the polymer in the detergent composition at 60°C for 8 days at a pH >7.5.

- 15 The end blocks E 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 E. If one of the end blocks is missing then capping group
- 20 X will similarly be missing from that end.

- Preferably each E comprises C1-C4 capped chains of polyethylene glycol remote from the midblock, with at least 10 EO repeat units, the end blocks being free from ester bonds, because the substituted ethylene moiety in the
- 25 mid block motif cannot link directly to an end block E the mid block is connected to that end block E (when it is present) via a linking moiety L, wherein the polymer has a molecular weight Mw of at least 4000 and is provided with sufficient hindering of its ester bonds to provide soil release

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greater than a ΔE of 5 with DMO on woven polyester after storage of the polymer at 37°C for 8 weeks, or at 60°C for 8 days, at a pH >7.5 in a composition in the presence of 1% or more TEA. When the end block that would be attached to linking moiety L is absent the linking moiety may also be absent. The polymer must then take the form E-M.

By a soil release value ΔE of 5 or less we intend to cover removal of the DMO from an initial stain reflectance of 42 down to at most 5. In fact the likely removal is more than that.

Preferably each E in polymer (f) comprises alkyl capped oligomers of polyethylene glycol, and the polymer has a molecular weight M_w of at least 4000. More preferably each E comprises C1-C4 capped oligomers of polyethylene glycol.

Linking moiety L may itself be of the form ester-Ar-ester, (B is an ester) but some protection of the end block attached via that linking group L may be afforded by replacing one or both ester moieties B with more hydrolysis resistant urethane or amide moieties. It is important to keep 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.

The alkaline liquid detergent compositions may comprise the polymer (f) in amounts of from 1 to 15 wt%, preferably from 1 to 10 wt%, most preferably from 1.5 to 7 wt%.

Preferably the alkaline isotropic concentrated detergent liquid composition comprises at least 5 wt% anionic surfactant. Suitably the liquid may comprise LAS, SLES, Nonionic and optionally betaine, the LAS being neutralised from LAS acid, at least in part, with TEA,

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To maximise the benefit of the other cleaning technologies that are essentially or optionally included in the liquid, especially anionic surfactant, the liquid has an undiluted pH of at least 7.8. The alkaline detergent liquid has an undiluted pH of at most 9, preferably at most 8.4, even at most 8.2.

5

Desirably R1 and R2 in the mid block motif are selected from H and Me.

Prior art unstable polymers comprise mPEG as E and use esters throughout M and L. The more stable of this type of polymer disclosed in the prior art, for example Texcare 240 use ethylene substituted by one Me and one H in the midblock M and the Linking group L. This single methyl side group of the otherwise linear motive does not provide sufficient hindering of the adjacent esters. A number of strategies can be used to increase the degree of hindering of the ester bonds and thereby to improve the polymer's resistance to alkaline hydrolysis.

15

A first strategy is to insert a polypropylene oxide block as part of the endblock E situated between the ester bonds at the end of the mid block M and the polyethylene oxide hydrophilic block forming the part of endblock E furthest from the midblock M. Such PO insertions have been mentioned in the prior art but their significance for improved alkaline stability has not been recognised.

20

A second strategy is to introduce into the midblock M ethylene that is substituted by 2 methyl groups. That is both R1 and R2 are methyl. Not all of the substituted ethylene groups should be replaced in this way. A convenient way to achieve this is to use a mixture of a minor part of 2,3 butandiol with a major part of the conventionally used 1,2 propandiol to form the mid block M.

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In a third strategy the endblock E may comprise at least 40, preferably at least 45 EO groups and the ratio of the number of EO groups in each of the end blocks E to the number of repeat units in the midblock n is from 4 to 8.

- 5 Each of these strategies may be employed on its own, or even more preferred combinations of 2 or even all three of the strategies may be used.

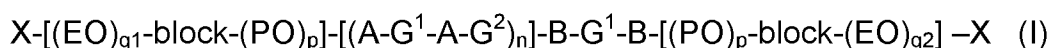
Compositions in WO09153184 had high levels of soap for antifoam effect when the compositions are used in front loading automatic washing machines.

- 10 We have now found that this may require too much hydrotrope to stabilise the composition. Thus it is preferred for the amount of fatty acid added to the composition (soap precursor before neutralisation) to be kept to a maximum of 1.5 wt% to facilitate the hydrotrope levels claimed, especially at the lower levels of hydrotrope. Keeping the soap level low means that the compositions
15 may be formulated with low levels of hydrotrope (less than 15 wt%, even less than 12 wt%. This low hydrotrope level means that only certain SRPs and especially the ones according to the invention can be incorporated in isotropic form (dissolve in the composition). Many known polymers, especially those using groups other than esters as B and those having very high molecular
20 weight mid blocks M will cause undesirable hazing of the composition.

- We have found that formulation flexibility is best with the SRPs having end esters in the midblock motif and B protected by blocks of PO, slightly less preferred are SRPs with large EO groups and large mid blocks and least
25 preferred, but still acceptable are the SRPs made using 2,3 butandiol as a diol to form the mid block M.

Suitable polyester soil release polymers (f) are preferably selected from those having the general formula (I):

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where EO is ethylene oxide ($\text{CH}_2\text{CH}_2\text{O}$);

where PO is at least 80 wt% propylene oxide ($\text{CH}_2\text{CH}(\text{CH}_3)\text{O}$), and preferably 100% PO units;

5

where p is a number from 0 to 60, and when p is not zero is preferably from 2 to 50, more preferably from 5 to 45, even more preferably from 6 to 40, yet more preferably from 7 to 40 and most preferably from 8 to 40, even from 11 to 35;

10

where q1 and q2 is a number from 6 to 120, preferably 18 to 80, most preferably 40 to 70, provided that q2 is greater than p and preferably q2 is at least 1.5 times as large as p;

15

where X is a capping moiety, preferably selected from C_{1-4} alkyl, branched and unbranched;

where n is a number from 2 to 26; preferably 5 to 15;

20

A and B are selected from ester, amide and urethane moieties;

when the moieties A and B adjacent to the PO blocks are esters then it is preferred that p is not zero,

25

alternatively, it is preferred that the ratio of $(q1+q2):n$ is from 4 to 10 and that q2 is from 40 to 120;

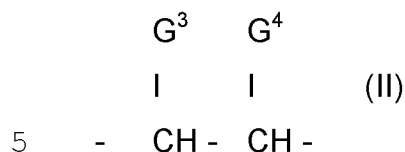
G^1 comprises 1,4 phenylene;

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G^2 is ethylene, which may be substituted;

- 10 -

It is preferred that moieties G^2 are all ethylene of formula (II)



wherein G^3 and G^4 are selected from Hydrogen, C_{1-4} alkyl and C_{1-4} alkoxy, provided that at least one of G^3 and G^4 is not hydrogen and that at least 10% of the groups G^2 have neither G^3 nor G^4 as hydrogen. Preferably when G^3 and G^4 are not hydrogen then they are methyl moieties. Preferably the non H substituents, more preferably the methyl moieties, are arranged in syn configuration on the ethylene backbone $-CH-CH-$ of moieties G^2 .

In formula (I) the groups correspond to the general formula E-M-L-E as follows:

E is $X-[(EO)_{q1}\text{-block-}(PO)_p]-$ and $-[(PO)_p\text{-block-}(EO)_{q2}]-X$

M is $-[(A-G^1-A-G^2)_n]-$; and

L is $-[B-G^1-B]-$

Because it is an average, n is not necessarily a whole number for the polymer in bulk. The same holds true, to a lesser extent, for p, q_1 and q_2 . Since p and q_1 and q_2 are made by anionic polymerisation routes (resulting in polymer blocks with very discreet block lengths) as against the midblock made by polycondensation routes (resulting in polymer blocks with more polydisperse block lengths).

In formula (I) the moiety $[(A-G^1-A-G^2)_n]-B-G^1-B-$ forms the polymer mid block or backbone and is described in more detail below. For the advantages of the invention to be achieved, by hindering of the hydrolytic attack on ester bonds, the moieties A and B nearest to any PO blocks are esters. Without wishing to

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be bound by theory it is believed that the defined PO blocks adjacent to those end ester moieties hinder the hydrolysis of those ester moieties. The protection of those ester moieties has been found to provide a significant benefit in terms of overall polymer stability. This is thought to be due to the hydrolysis starting from the end of the midblock which immediately cleaves the functional EO end block from the mid block, fabric substantive, part of the polymer, if it occurs. This separation of the hydrophilic PEO end blocks (EO)_q from the fabric substantive (e.g. phenylene/alkylene containing) mid block reduces the soil release properties of the polymer.

As is taught in the prior art the moieties B may be different from the moieties A. For example moieties B may be selected from the more hydrolytically stable amide or urethane linking moieties. The same freedom does not apply to the moieties A. These must be essentially esters in order to retain the fabric substantivity of the mid block motif.

When p is zero it is preferred for q₂, and q₁, if present, to be at least 40. Furthermore we have determined that for such polymers it is desirable that they are provided with a large mid block where n is at least 5 and preferably at least 8 as this seems to confer advantages for sustained soil release after prolonged storage under alkaline conditions.

Preferably the moieties G¹ are 1,4 phenylene for maximum fabric substantivity of the mid block motif.

If the mid block is formed by the condensation of an ester of terephthalic acid with a diol a preferred diol to form the desired group G² may be selected from the group of diols of formula (III):

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

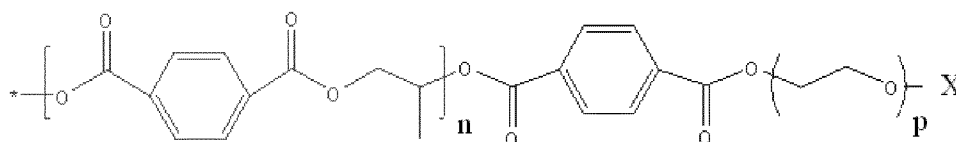
- 12 -

n being an integer from 1 to c-3, where c is the number of carbons in the alkylene chain. The most preferred diols are syn 2,3 butane diol and 1,2 propane diol.

- 5 when q1 is 0, or from 40 to 120, and q2 is from 40 to 120, n is preferably a number from 5 to 26 and the ratio of (q1+q2):n is from 4 to at most 10, preferably from 5 to 8;

Formula (IV) shows a suitable polymer where the mid block is formed entirely from oxypropylene moieties and terephthaloyl moieties (1,4-dicarboxy-phenylene and 1,2 propylene), linked via ester groups to one or more capped polyethylene glycol end blocks, one of which is depicted as having p units of ethylene oxide (q2). The polyester substantive motif in the mid block is repeated n times.

15



(IV)

DETAILED DESCRIPTION OF THE INVENTION

- 20 The invention is a combination of a selected group of polyester soil release polymers with high performance and stability and a liquid detergent base that holds the polymer stably in solution or dissolution and yet does not cause unwanted destruction of the polymer structure and performance via hydrolysis as we have found to be the case with prior art preferred polymers when
- 25 incorporated into such isotropic alkaline detergent liquids.

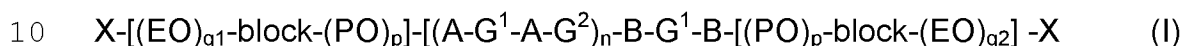
All percentages are weight percent except where indicated otherwise or where the context makes it obvious that something else is intended.

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The hydrolytically stable Soil release polymer (with hindered bonds)

The invention requires the selection of a stable high performance soil release polymer and its incorporation into an alkaline concentrated detergent liquid, comprising surfactant and triethanolamine that is known to catalyse the polymer hydrolysis.

A preferred family of suitable SRPs have the formula (I):

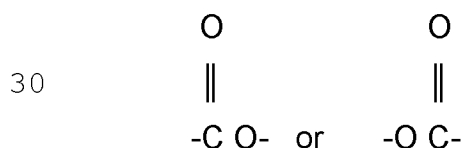


$X-[(EO)_{q1}\text{-block-}(PO)_p]-$ and $-[(PO)_p\text{-block-}(EO)_{q2}]-X$ are generally connected at the ends of the polymer backbone or mid block. The mid block is responsible for making the polymer fabric substantive, particularly towards polyester fabrics. The endcaps of large blocks of EO groups 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).

Mid block or backbone

The mid block $[(A-G^1-A-G^2)_r]-B-G^1-B$ (-M-L-) is responsible for making the polymer fabric substantive, particularly towards polyester fabrics.

The linking moieties A are essentially esters. It is preferred that moieties B in linking group L are also esters. In the polymer structure such an ester may be formed either way around and it may thus take the form of the moiety:



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The A moieties preferably consist entirely of such ester moieties.

The G¹ moieties comprise 1,4-phenylene moieties.

5 It is possible, as taught by the prior art, to partially substitute some of these 1, 4 phenylene moieties with other arylene or alkarylene moieties, for example 1,3-phenylene, 1,2-phenylene, 1,8-naphthylene, 1,4-naphthylene, 2,2'-biphenylene, 4,4'-biphenylene and mixtures thereof. However, such substitution is undesirable as it adversely affects the ability of the mid block to
10 deposit onto polyester fabric. A minor amount, less than 10 mol%, of such substitution is permissible, but not preferred.

The G² moieties are ethylene moieties, or more preferably substituted ethylene moieties having C₁₋₄ alkyl or alkoxy substituents. The G² moieties
15 may consist entirely of ethylene, or substituted ethylene moieties, or these moieties may be partially replaced with a minor part of other compatible moieties. A preferred substituted ethylene moiety is 1,2 propylene which is derived from the condensation of 1,2 propane diol. It is preferred to fully avoid the use of unsubstituted ethylene. It is also desirable to minimize partial
20 replacement with oxyalkylene moieties, for best soil release activity.

Thus G² may comprise from 80 to 100 mol% mono and di substituted ethylene moieties, and from 0 to 20 mol% other compatible moieties.

25 For the G² moieties, suitable substituted ethylene moieties are the monomethyl substituted G² formed from 1,2-propylene diol, and the dimethyl substituted G² formed from 2,3 butylene diol. Without wishing to be bound by theory it is thought that the 1,2 di methyl substituted ethylene shows superior protection of adjacent ester bonds due to that fact that it is always going to be
30 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

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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.

- 5 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 so 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
10 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.

As disclosed above, it is possible to have a minor part, for example up to 10 mol%, of the G^2 moieties other than the preferred substituted ethylene
15 moieties. The degree of partial replacement with these other moieties should be such that the fabric substantivity of the mid block is not too adversely affected.

Generally, the degree of partial replacement of G^1 or G^2 which can be
20 tolerated will depend upon the number of repeat units n in the mid block, i.e. longer mid blocks can have greater partial replacement. So for a polymer where n is at least 5 the degree of replacement of the preferred G^1 and G^2 in the fabric substantive motif may be as high as 20 mol%. However, it is desirable to minimize such partial replacement, for best soil release activity it
25 is preferably absent.

Preferably, G^2 comprises from 80 to 100 mol% substituted ethylene moieties and from 0 to 20 mol% other compatible moieties which give a carbon chain length of 2 in the backbone. Such moieties include 2,3 butane diol
30 derivatives, i.e. an ethylene moiety with a methyl group substituted on each carbon in the backbone.

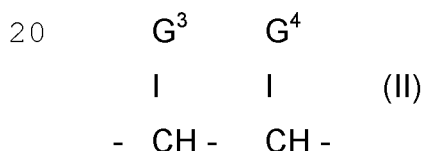
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The skilled person will appreciate that although linear polymer backbones are preferred some degree of branching can be introduced by using triols or 1,3,5 phenylene moieties and these too may be used as substituent G^1 and or G^2 groups provided that at least 80 mol% of those groups are the preferred moieties described above.

The polymer should preferably be nonionic as ionic polymers are generally not phase stable in concentrated alkaline detergent liquids.

It has been found that the value of n needs to be at least 2 in order for the stable 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. Generally, the larger the n value, the less soluble is the polymer.

Preferred G^2 moieties are essentially substituted ethylene moieties, selected from substituted ethylene of formula (II)



wherein G^3 and G^4 are selected from Hydrogen, C1-4 alkyl and C1-C4 alkoxy provided that at least one of G^3 and G^4 is not hydrogen and that at least 10 mol%, preferably at least 20 mol% of the groups G^2 have neither G^3 nor G^4 as hydrogen. Preferably when G^3 and G^4 are not hydrogen then they are methyl moieties. Preferably the non Hydrogen substituents, more preferably the methyl moieties, are arranged in syn configuration on the ethylene backbone.

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If the mid block is formed by the condensation of an ester of terephthalic acid with a diol the preferred diol to form the desired group is selected from the group of diols of formula (III):

5 syn $n+1, n+2$ alkylene diol (III)

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

10 The most preferred diols are syn 2, 3 butane diol and 1,2 propane diol.

Especially preferred are mixtures of up to 80 mol% 1,2 propylene with the condensation product of SS or RR 2,3 butylene; each X is C_{1-4} alkyl, preferably methyl or n -butyl; each q is from 12 to 80; each p is from 0 to 50; n is from 3 to 10;

In a preferred embodiment, the polymeric soil release agents according to the present invention have the formula (V):

20 $X-[(EO)_q(PO)_p]-[(OC(O)-G^1-C(O)O-G^2)_n]-OC(O)-G^1-C(O)O-[(PO)_p(EO)_q]-X$ (V)

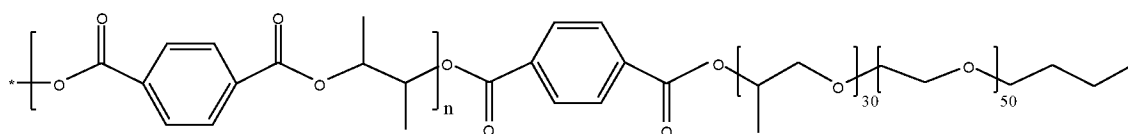
wherein :

- each of the G^1 moieties is a 1,4-phenylene moiety;
- the G^2 moieties are each selected from the group consisting of monomethyl ethylene and dimethyl ethylene, provided that the dimethyl ethylene has the two methyl groups on separate carbons and that this moiety forms at least 20 mol% of the moieties G^2
- each X is C_1-C_4 alkyl; each q is from 40 to 70; n is from 3 to 10.

Preferably, in the formula (V), G^2 moieties comprise a mixture of from 40 to 90 mol% monomethyl substituted ethylene moieties, and from 10 to 60 mol% 1,2 dimethyl ethylene moieties.

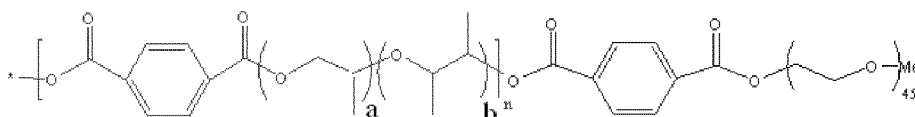
- 18 -

In most preferred embodiments of the present invention, the polymeric soil release agents have the formula (VI) or (VII):



5

(VI)



(VII)

- 10 Where in formula VII $a+b=1$ and "a" lies in the range 0 to 0.8 and in both formulae,
n has the value from 2 to 20.

End block

- 15 The soil release polymer may comprise statistical mixtures of material with two end blocks E and material with one or other option for a single end block E. In the case that the end block is on the mid block motif then the linking moiety L may be replaced by an alcohol termination on the polymer.
- 20 The end blocks $X-[EO]_q1$ and $[EO]_q2-X$ may be the conventional capped PEG groups of various molecular weight or alternatively, in the case where p is not zero, they may be blocked mPEG/PPG groups i.e. $X-[(EO)_q\text{-block-(PO)}_p]-$ and $-[(PO)_p\text{-block-(EO)}_q]-X$. The end blocks are preferably connected to the polymer mid block M or linking block L by ester moieties, A and B.

25

To obtain the combination of hydrolytic stability and soil release properties when stored in, and delivered from, an alkaline liquid optional end block PO

- 19 -

groups may be arranged in blocks adjacent the end ester moieties of the mid block M and the linking part L and the end block EO groups are similarly arranged in blocks more remote from the mid block. Pure, i.e. 100%, EO and PO blocks are preferred. Thus a preferred EO block is made using a capped
5 PEG such as methyl capped PEG, or mPEG. The molecular weight M_w of the mPEG may be in the range 700 to 3000 Da.

When present the PO block should comprise at least 80% by number PO units. We have determined that a stat block PO/EO block confers some
10 improvement of resistance to hydrolysis of the end ester moieties A and B. However, to avoid this hydrophobic block becoming unnecessarily large it is preferred that it comprises as much as possible of the ester bond hindering PO units. Preferably it consists of at least 90% and most preferably 100%, by number, PO units. The number, p , of units in the PO block is from 2 to 50,
15 more preferably from 5 to 45, even more preferably from 6 to 40, yet more preferably from 7 to 40 and most preferably from 8 to 40, even from 11 to 35;

Preferred polymers have an EO block that has more units than the PO block, when present, preferably the EO block has at least 1.5 times the number of
20 moles or units (q_2) as the PO block (p).

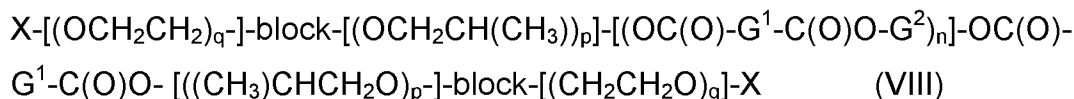
The terminal end cap X on the EO block is preferably as small as possible, for example C_1 - C_4 alkyl. X is preferably methyl, ethyl, or n-butyl and most preferably methyl or n-butyl.
25

When p is not zero, 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.

30 As the value for q increases, the value for n should be increased so that the polymer will deposit well on the fabric during laundering.

- 20 -

Preferred compounds of formula (I) are polymers having formula (VIII):



5

wherein the G^1 moieties are all 1,4-phenylene moieties; the G^2 moieties are all 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 2 to 50, preferably 6 to 40; and n is from 2 to 10.

10

The block polyesters of formula VIII are linear block polyesters. For these preferred linear block polyesters, n preferably ranges from 3 to 9, especially for those made from dimethyl terephthalate, and 1,2-propylene glycol. The most preferred of these linear block polyesters are those where n is from 3 to 5.

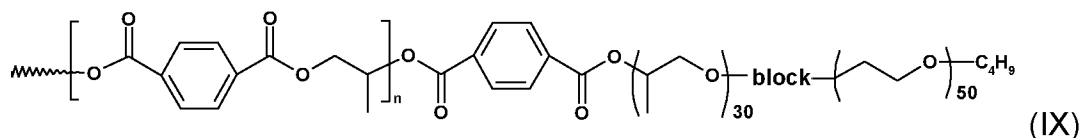
15

Most preferably, in the formula (VIII), in the polymer according to the present invention p is from 11 to 50 and q is from 18 to 60.

20

A particularly preferred embodiment of this type of soil release polymer of formula (I) has the formula (IX), where n is at most 15, preferably at most 12 and more preferably at most 9 and n is at least 2, preferably at least 3 and more preferably at least 4, for example n is from 2 to 15, preferably 3 to 12 more preferably 4 to 9.

25



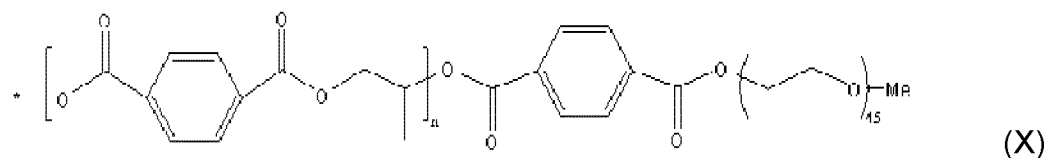
As the value for q increases, the value for n should be increased so that the compound will deposit better on the fabric during laundering.

- 21 -

q1 is either zero, or is at least 40, preferably about 45 and q2 is at least 40, preferably about 45. We have found that the ratio of the end block to mid block is important for the soil release and stability. The prior art polymer Texcare® SRN 240 appears to have almost the same end block (a methyl capped PEG of a molecular weight of approximately 2000), yet it proved to be unsuitable for use in alkaline liquid compositions, particularly those comprising triethanolamine (TEA).

As the value for q1+q2 increases, the value for n should be increased to keep the ratio within the defined limits and to ensure that the compound will deposit well on the fabric during laundering.

Preferred compounds of the present invention are polyesters having the formula (X):



where n is at least 7.

Molecular weight

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.

The polydispersity of the polymers is preferred to be less than 3.

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Preparation of the polymer

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
 5 4,711,730 describe a method of synthesis that may be adapted to produce the block polyesters of the present invention.

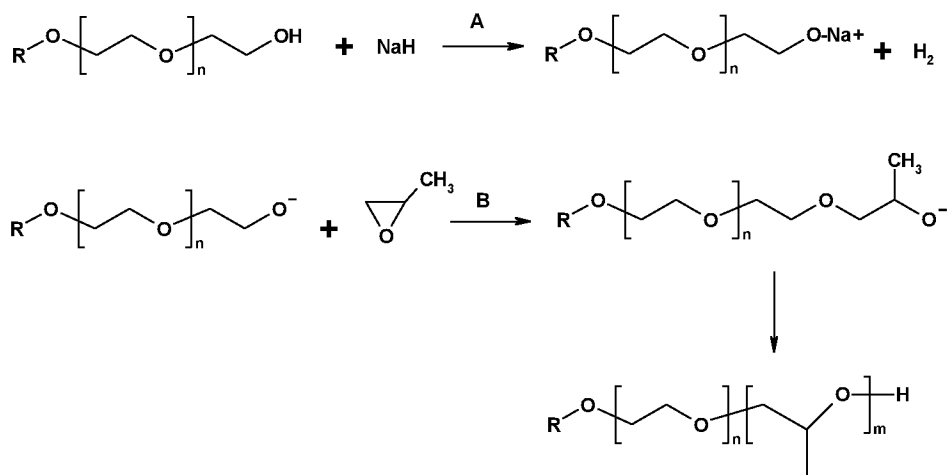
In a preferred process the end blocks are made in a separate process and then added to the mid block. A suitable process to manufacture the block
 10 copolymers used for the end blocks is described below.

End block manufacture

The mPEG for variants of the polymer without PO blocks in the end blocks
 15 (p=0) may be prepared by methods known to the person skilled in the art.

In a preferred process the optional PO/EO end blocks are 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,
 20 B. Trathnigg, C.O. Kappe, *Macromol. Chem. Phys.*, **2007**, 208, 2510-2524.

The reaction scheme is set forth below:



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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.

5

An alternative, but less controllable and therefore less preferred, process to construct the end blocks would be to take the mid block and react it with PO and mPEG.

10 Mid block manufacture

It is preferred to manufacture the mid block 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
15 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.

20 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.

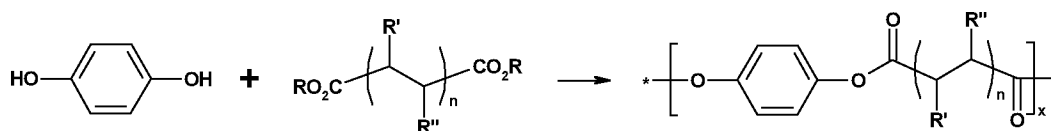
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The esters and oligomers produced in the condensation (ester interchange) reaction may then be polymerised to the desired molecular weight, by raising the temperature further, typically to 180 to 250 °C.

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

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However, it is also possible to obtain a very similar polyester recognition motif with the ester moieties reversed if the starting materials are aliphatic bicarboxylic acids and aromatic bisalcohol. For example, hydroquinone may be used as the aromatic alcohol and derivatives of succinic acid may be used as the carboxylic acid (in this case, R' and R'' = H).



10 The isotropic liquids

The amount of deterative surfactant makes up at least 10 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

15 deterative surfactant levels of at least 15 wt%.

The compositions may be concentrated 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

20 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. The dose of detergent liquid is adjusted accordingly to give similar wash liquor concentrations.

25

Surfactants

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

- 25 -

present invention. The amount of anionic surfactant is preferably at least 5 wt%.

Preferably, the anionic surfactant forms the majority of the non soap
5 surfactant (a).

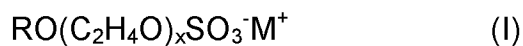
Anionic

Preferred alkyl sulphonates are alkylbenzene sulphonates, particularly linear
alkylbenzene sulphonates having an alkyl chain length of C₈-C₁₅. The counter
10 ion for anionic surfactants is generally an alkali metal, typically sodium,
although other counter-ions such as MEA, TEA or ammonium can be used.

Preferred linear alkyl benzene sulphonate surfactants are Detal LAS with an
alkyl chain length of from 8 to 15, more preferably 12 to 14.

15

It is further desirable that the composition comprises an alkyl polyethoxylate
sulphate anionic surfactant of the formula (I):



20

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 alkali metal, ammonium or substituted ammonium cation, and x
averages from 1 to 15.

25

Preferably R is an alkyl chain having from 12 to 16 carbon atoms, M is
Sodium and x averages from 1 to 3, preferably x is 3; This is the anionic
surfactant sodium lauryl ether sulphate (SLES). It is the sodium salt of lauryl
ether sulphonic acid in which the predominantly C₁₂ lauryl alkyl group has
30 been ethoxylated with an average of 3 moles of ethylene oxide per mole.

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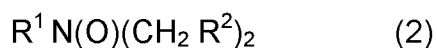
Nonionic

Nonionic surfactants include primary and secondary alcohol ethoxylates, especially C₈-C₂₀ aliphatic alcohol ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ 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").

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C₈-C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 35 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol.

Amine Oxide

The composition may comprise up to 10 wt% of an amine oxide of the formula (2):



In which R¹ is a long chain moiety each CH₂R² are short chain moieties. R² is preferably selected from hydrogen, methyl and -CH₂OH. In general R¹ is a primary or branched hydrocarbyl moiety which can be saturated or

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unsaturated, preferably, R¹ is a primary alkyl moiety. R¹ is a hydrocarbyl moiety having chain length of from about 8 to about 18.

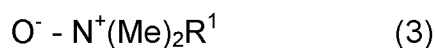
Preferred amine oxides have R¹ is C₈-C₁₈ alkyl, and R² is H. These amine
5 oxides are illustrated by C₁₂₋₁₄ alkyldimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide.

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

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.

15 Whereas in certain of the preferred embodiments R² is H, it is possible to have R² slightly larger than H. Specifically, R² may be CH₂OH, such as: hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbis(2-
20 hydroxyethyl)amine oxide.

Preferred amine oxides have the formula:



25 where R¹ is C₁₂₋₁₆ alkyl, preferably C₁₂₋₁₄ alkyl; Me is a methyl group.

Zwitterionic

Nonionic-free systems with up to 95 %wt LAS can be used provided that
30 some zwitterionic surfactant, such as sulphobetaine, is present. A preferred zwitterionic material is a betaine available from Huntsman under the name

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Empigen® BB. Betaines, improve particulate soil detergency in the compositions of the invention.

Additional surfactants

- 5 Other surfactants than the preferred LAS, SLES, nonionic and zwitterionic (betaine) may be added to the mixture of deterative surfactants. However cationic surfactants are preferably substantially absent.

Although less preferred, some alkyl sulphate surfactant (PAS) may be used,
10 especially the non-ethoxylated C₁₂₋₁₅ primary and secondary alkyl sulphates. A particularly preferred material, commercially available from Cognis, is Sulphopon 1214G.

Other Polymer

15

EPEI

A particularly preferred class of polymer for use in combination with the soil release polymers of the present invention is polyethylene imine, preferably modified polyethylene imine. Polyethylene imines are materials composed of
20 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,
25 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,
30 1951.

- 29 -

Preferably, the EPEI comprises a polyethyleneimine backbone of about 300 to about 10000 weight average molecular weight; wherein the modification of the polyethyleneimine backbone is intended to leave the polymer without quaternisation. Such nonionic EPEI may be represented as PEI(X)YEO

5 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 9 to 40 ethoxy moieties per modification, preferably it is in the range of 16 to 26, most preferably 18 to 22.

10

The polyethyleneimine polymer is present in the composition preferably at a level of between 0.01 and 25 wt%, but more 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 15 6:1, or even to 5:1.

Other polymer types

In addition to a soil release polymer there may be used dye transfer inhibition polymers, anti redeposition polymers and cotton soil release polymers, 20 especially those based on modified cellulosic materials.

Hydrotrope

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 25 other components in the aqueous 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.

30

- 30 -

Enzymes

It is preferable that at least one or more enzymes may be present in the compositions.

5 Lipase

Lipase is a particularly preferred enzyme. The composition preferably contains from about 5 to about 20000 LU/g of a lipase. Preferred lipase enzymes include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases
10 from *Humicola*, more preferably ones which comprise a polypeptide having an amino acid sequence which has at least 90% sequence identity with the wild-type lipase derived from *Humicola lanuginosa*, most preferably strain DSM 4109. The amount in the composition is higher than typically found in liquid detergents. This can be seen by the ratio of non-soap surfactant to lipase
15 enzyme, in particular. A particularly preferred lipase enzyme is available under the trademark Lipoclean™ from Novozymes.

As noted above, suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of
20 useful lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g. from *H. lanuginosa* (*T. lanuginosus*) as described in EP 258 068 and EP 305 216 or from *H. insolens* as described in WO 96/13580, a *Pseudomonas* lipase, e.g. from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 218 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens*,
25 *Pseudomonas* sp. strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* (WO 96/12012), a *Bacillus* lipase, e.g. from *B. subtilis* (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422). As noted above the preferred ones have a high degree of homology with the wild-type
30 lipase derived from *Humicola lanuginosa*.

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Other examples are lipase variants such as those described in WO 92/05249, WO 94/01541, EP 407 225, EP 260 105, WO 95/35381, WO 96/00292, WO 95/30744, WO 94/25578, WO 95/14783, WO 95/22615, WO 97/04079 and WO 97/07202.

5

Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, Lipex™ and Lipoclean™ (Novozymes A/S).

10 In addition to or as an alternative to lipase one or more other enzymes may be present. However lipase is particularly preferred.

Advantageously, the presence of relatively high levels of calcium in the poorly built or unbuilt compositions of the invention has a beneficial effect on the turnover of certain enzymes, particularly lipase enzymes and preferably lipases from *Humicola*.

20 The preferred lipases include first wash lipases which comprise a polypeptide having an amino acid sequence which has at least 90% sequence identity with the wild-type lipase derived from *Humicola lanuginosa* strain DSM 4109 and compared to said wild-type lipase, comprises a substitution of an electrically neutral or negatively charged amino acid within 15 A of E1 or Q249 with a positively charged amino acid; and may further comprise:

(I) a peptide addition at the C-terminal;

25

(II) a peptide addition at the N-terminal;

(III) meets the following limitations:

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- i. comprises a negatively charged amino acid in position E210 of said wild-type lipase;
- 5 ii. comprises a negatively charged amino acid in the region corresponding to positions 90-101 of said wild-type lipase; and
- iii. comprises a neutral or negatively charged amino acid at a position corresponding to N94 of said wild-type lipase; and/or
- 10 iv. has a negative charge or neutral charge in the region corresponding to positions 90-101 of said wild-type lipase; and
- v. mixture thereof.

These are available under the LipexTM brand from Novozymes. A similar
15 enzyme from Novozymes but believed to fall outside of the above definition is sold by Novozymes under the name LipocleanTM and this is also preferred.

Phospholipase:

The method of the invention may be carried out in the presence of
20 phospholipase classified as EC 3.1.1.4 and/or EC 3.1.1.32. As used herein, the term phospholipase is an enzyme which has activity towards phospholipids. Phospholipids, such as lecithin or phosphatidylcholine, consist of glycerol esterified with two fatty acids in an outer (sn-1) and the middle (sn-2) positions and esterified with phosphoric acid in the third position; the
25 phosphoric acid, in turn, may be esterified to an amino-alcohol. Phospholipases are enzymes which participate in the hydrolysis of phospholipids. Several types of phospholipase activity can be distinguished, including phospholipases A₁ and A₂ which hydrolyze one fatty acyl group (in the sn-1 and sn-2 position, respectively) to form lysophospholipid; and
30 lysophospholipase (or phospholipase B) which can hydrolyze the remaining fatty acyl group in lysophospholipid. Phospholipase C and phospholipase D

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(phosphodiesterases) release diacyl glycerol or phosphatidic acid respectively.

Protease:

5 Suitable proteases include those of animal, vegetable or microbial origin. Microbial origin is preferred. Chemically modified or protein engineered mutants are included. The protease may be a serine protease or a metallo protease, preferably an alkaline microbial protease or a trypsin-like protease. Preferred commercially available protease enzymes include Alcalase™,
10 Savinase™, Primase™, Duralase™, Dyrzym™, Esperase™, Everlase™, Polarzyme™, and Kannase™, (Novozymes A/S), Maxatase™, Maxacal™, Maxapem™, Properase™, Purafect™, Purafect OxP™, FN2™, and FN3™ (Genencor International Inc.).

15 Cutinase:

The method of the invention may be carried out in the presence of cutinase. classified in EC 3.1.1.74. The cutinase used according to the invention may be of any origin. Preferably cutinases are of microbial origin, in particular of bacterial, of fungal or of yeast origin.

20 Amylase:

Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from *Bacillus*, e.g. a
25 special strain of *B. licheniformis*, described in more detail in GB 1,296,839, or the *Bacillus* sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

30

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Cellulase:

Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera *Bacillus*, *Pseudomonas*, *Humicola*,

- 5 *Fusarium*, *Thielavia*, *Acremonium*, e.g. the fungal cellulases produced from *Humicola insolens*, *Thielavia terrestris*, *Myceliophthora thermophila*, and *Fusarium oxysporum* disclosed in US 4,435,307, US 5,648,263, US 5,691,178, US 5,776,757, WO 89/09259, WO 96/029397, and WO 98/012307. Commercially available cellulases include Celluzyme™,
- 10 Carezyme™, Endolase™, Renozyme™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao Corporation).

Peroxidases/oxidases:

- 15 Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful peroxidases include peroxidases from *Coprinus*, e.g. from *C. cinereus*, and variants thereof as those described in WO 93/24618, WO 95/10602, and WO 98/15257. Commercially available peroxidases include
- 20 Guardzyme™ and Novozym™ 51004 (Novozymes A/S).

Pectate Lyases:

Pectate lyases (also called polygalacturonate lyases): Examples of pectate lyases include pectate lyases that have been cloned from different bacterial

25 genera such as *Erwinia*, *Pseudomonas*, *Klebsiella* and *Xanthomonas*, as well as from *Bacillus subtilis* (Nasser et al. (1993) FEBS Letts. 335:319-326) and *Bacillus* sp. YA-14 (Kim et al. (1994) Biosci. Biotech. Biochem. 58:947-949). Purification of pectate lyases with maximum activity in the pH range of 8-10 produced by *Bacillus pumilus* (Dave and Vaughn (1971) J. Bacteriol. 108:166-

30 174), *B. polymyxa* (Nagel and Vaughn (1961) Arch. Biochem. Biophys. 93:344-352), *B. stearothermophilus* (Karbassi and Vaughn (1980) Can. J.

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Microbiol. 26:377-384), *Bacillus* sp. (Hasegawa and Nagel (1966) J. Food Sci. 31:838-845) and *Bacillus* sp. RK9 (Kelly and Fogarty (1978) Can. J. Microbiol. 24:1164-1172) have also been described. Any of the above, as well as divalent cation-independent and/or thermostable pectate lyases, may be used in practicing the invention. In preferred embodiments, the pectate lyase comprises the pectate lyase disclosed in Heffron et al., (1995) Mol. Plant-Microbe Interact. 8: 331-334 and Henrissat et al., (1995) Plant Physiol. 107: 963-976. Specifically contemplated pectate lyases are disclosed in WO 99/27083 and WO 99/27084. Other specifically contemplated pectate lyases (derived from *Bacillus licheniformis*) are disclosed in US patent no. 6,284,524 (which document is hereby incorporated by reference). Specifically contemplated pectate lyase variants are disclosed in WO 02/006442, especially the variants disclosed in the Examples in WO 02/006442 (which document is hereby incorporated by reference).

Examples of commercially available alkaline pectate lyases include BIOPREP™ and SCOURZYME™ L from Novozymes A/S, Denmark.

Mannanases:

Mannanase: Examples of mannanases (EC 3.2.1.78) include mannanases of bacterial and fungal origin. In a specific embodiment the mannanase is derived from a strain of the filamentous fungus genus *Aspergillus*, preferably *Aspergillus niger* or *Aspergillus aculeatus* (WO 94/25576). WO 93/24622 discloses a mannanase isolated from *Trichoderma reesei*. Mannanases have also been isolated from several bacteria, including *Bacillus* organisms. For example, Talbot et al., Appl. Environ. Microbiol., Vol.56, No. 11, pp. 3505-3510 (1990) describes a beta-mannanase derived from *Bacillus stearothermophilus*. Mendoza et al., World J. Microbiol. Biotech., Vol. 10, No. 5, pp. 551-555 (1994) describes a beta-mannanase derived from *Bacillus subtilis*. JP-A-03047076 discloses a beta-mannanase derived from *Bacillus* sp.

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JP-A-63056289 describes the production of an alkaline, thermostable beta-mannanase. JP-A-63036775 relates to the *Bacillus* microorganism FERM P-8856 which produces beta-mannanase and beta-mannosidase. JP-A-08051975 discloses alkaline beta-mannanases from alkalophilic *Bacillus* sp.

5 AM-001. A purified mannanase from *Bacillus amyloliquefaciens* is disclosed in WO 97/11164. WO 91/18974 describes a hemicellulase such as a glucanase, xylanase or mannanase active. Contemplated are the alkaline family 5 and 26 mannanases derived from *Bacillus agaradhaerens*, *Bacillus licheniformis*, *Bacillus halodurans*, *Bacillus clausii*, *Bacillus* sp., and *Humicola insolens*
10 disclosed in WO 99/64619. Especially contemplated are the *Bacillus* sp. mannanases concerned in the Examples in WO 99/64619.

Examples of commercially available mannanases include Mannaway™ available from Novozymes A/S Denmark.

15

The enzyme and any perfume/fragrance or pro-fragrance present may show some interaction and should be chosen such that this interaction is not negative. Some negative interactions may be avoided by encapsulation of one or other of enzyme and pro-fragrance and/or other segregation within the
20 product.

Enzyme Stabilizers:

Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol such as propylene glycol or glycerol, a sugar
25 or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

30

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Fluorescent Agents:

It may be advantageous to include fluorescer in the compositions. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in the composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.5 wt %.

Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN.

Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-naphthol[1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfoslyryl)biphenyl.

Bleach Catalyst:

Detergent compositions according to the invention may comprise a weight efficient bleach system. Such systems typically do not utilise the conventional percarbonate and bleach activator approach.

The present invention may be used in a formulation that is used to bleach via air, or an air bleach catalyst system. Suitable complexes and organic molecule (ligand) precursors for forming complexes are available to the skilled worker, for example, from: WO 98/39098; WO 98/39406, WO 97/48787, WO 00/29537; WO 00/52124, and WO00/60045, incorporated by reference. An example of a preferred catalyst is a transition metal complex of MeN4Py ligand (N,N-bis(pyridin-2-yl-methyl)-1-,1-bis(pyridin-2-yl)-1-aminoethane).

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Suitable bispidon catalyst materials and their action are described in WO02/48301.

Photobleaches may also be employed. In the context of the present invention a “photobleach” is any chemical species that forms a reactive bleaching species on exposure to sunlight, and preferably is not permanently consumed in the reaction. Preferred photo-bleaches include singlet oxygen photo-bleaches and radical photo-bleaches. Suitable singlet oxygen photo-bleaches may be selected from, water soluble phthalocyanine compounds, particularly metallated phthalocyanine compounds where the metal is Zn or Al-Z1 where Z1 is a halide, sulphate, nitrate, carboxylate, alkanolate or hydroxyl ion. Preferably the phthalocyanin has 1-4 SO₃X groups covalently bonded to it where X is an alkali metal or ammonium ion. Such compounds are described in WO2005/014769 (Ciba).

When present, the bleach catalyst is typically incorporated at a level of about 0.0001 to about 10wt%, preferably about 0.001 to about 5wt%.

Perfume

Given that the composition of the present invention is designed to be used at very low levels of product dosage, it is advantageous to ensure that perfume is employed efficiently.

A particularly preferred way of ensuring that perfume is employed efficiently is to use an encapsulated perfume. Use of a perfume that is encapsulated reduces the amount of perfume vapour that is produced by the composition before it is diluted. This is important when the perfume concentration is increased to allow the amount of perfume per wash to be kept at a reasonably high level.

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It is even more preferable that the perfume is not only encapsulated but also that the encapsulated perfume is provided with a deposition aid to increase the efficiency of perfume deposition and retention on fabrics. The deposition aid is preferably attached to the encapsulate by means of a covalent bond,
5 entanglement or strong adsorption, preferably by a covalent bond or entanglement.

Further Optional Ingredients:

The compositions of the invention may contain one or more other ingredients.
10 Such ingredients include 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, anti-static agents and ironing aids. The compositions may further comprise, colorants, pearlisers and/or
15 opacifiers, and shading dye.

Shading dyes

Shading dye can be used to improve the performance of the compositions used in the method of the present invention. The deposition of shading dye
20 onto fabric is improved when they are used in compositions of the invention and according to the process of the invention. Preferred dyes are violet or blue. It is believed that the deposition on fabrics of a low level of a dye of these shades, masks yellowing of fabrics. A further advantage of shading dyes is that they can be used to mask any yellow tint in the composition itself.

25

Suitable and preferred classes of dyes are discussed below.

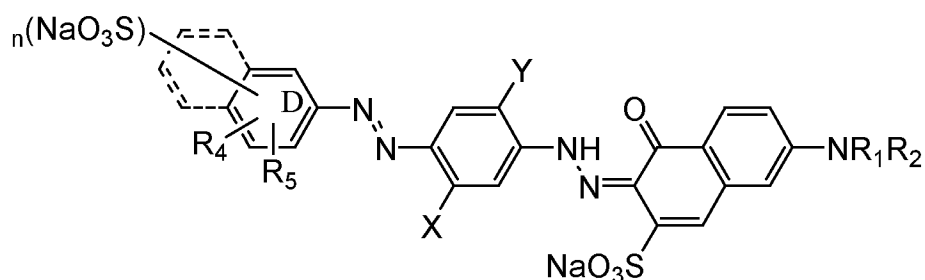
Direct Dyes:

Direct dyes (otherwise known as substantive dyes) are the class of water
30 soluble dyes which have an affinity for fibres and are taken up directly. Direct violet and direct blue dyes are preferred.

- 40 -

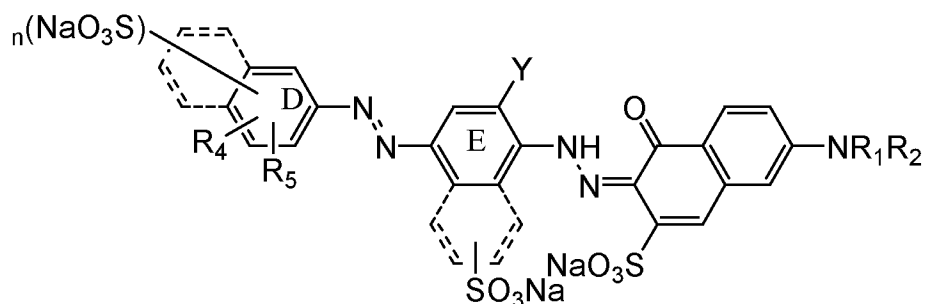
Preferably bis-azo or tris-azo dyes are used.

Most preferably, the direct dye is a direct violet of the following structures:



5

or



10

wherein:

ring D and E may be independently naphthyl or phenyl as shown;

R₁ is selected from: hydrogen and C₁-C₄-alkyl, preferably hydrogen;

15 R₂ is selected from: hydrogen, C₁-C₄-alkyl, substituted or unsubstituted phenyl and substituted or unsubstituted naphthyl, preferably phenyl;

R₃ and R₄ are independently selected from: hydrogen and C₁-C₄-alkyl, preferably hydrogen or methyl;

20 X and Y are independently selected from: hydrogen, C₁-C₄-alkyl and C₁-C₄-alkoxy; preferably the dye has X= methyl; and, Y = methoxy and n is 0, 1 or 2, preferably 1 or 2.

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Preferred dyes are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, and direct violet 99. Bis-azo copper containing dyes such as direct violet 66 may be used. The benzidine based dyes are less preferred.

- 5 Preferably the direct dye is present at 0.000001 to 1 wt% more preferably 0.00001 wt% to 0.0010 wt% of the composition.

In another embodiment the direct dye may be covalently linked to the photo-bleach, for example as described in WO2006/024612.

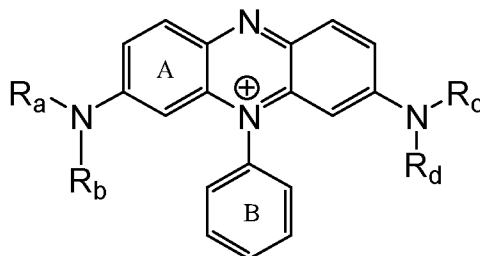
10

Acid dyes:

Cotton substantive acid dyes give benefits to cotton containing garments.

Preferred dyes and mixes of dyes are blue or violet. Preferred acid dyes are:

- 15 (i) azine dyes, wherein the dye is of the following core structure:



wherein R_a , R_b , R_c and R_d are selected from: H, a branched or linear C1 to C7-alkyl chain, benzyl a phenyl, and a naphthyl;

20

the dye is substituted with at least one SO_3^- or $-\text{COO}^-$ group;

the B ring does not carry a negatively charged group or salt thereof;

and the A ring may further substituted to form a naphthyl;

- 25 the dye is optionally substituted by groups selected from: amine, methyl, ethyl, hydroxyl, methoxy, ethoxy, phenoxy, Cl, Br, I, F, and NO_2 .

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Preferred azine dyes are: acid blue 98, acid violet 50, and acid blue 59, more preferably acid violet 50 and acid blue 98.

Other preferred non-azine acid dyes are acid violet 17, acid black 1 and acid
5 blue 29.

Preferably the acid dye is present at 0.0005 wt% to 0.01 wt% of the formulation.

10 *Hydrophobic dyes:*

The composition may comprise one or more hydrophobic dyes selected from benzodifuranes, methine, triphenylmethanes, naphthalimides, pyrazole, naphthoquinone, anthraquinone and mono-azo or di-azo dye chromophores.

Hydrophobic dyes are dyes which do not contain any charged water
15 solubilising group. Hydrophobic dyes may be selected from the groups of disperse and solvent dyes. Blue and violet anthraquinone and mono-azo dye are preferred.

Preferred dyes include solvent violet 13, disperse violet 27 disperse violet 26,
20 disperse violet 28, disperse violet 63 and disperse violet 77.

Preferably the hydrophobic dye is present at 0.0001 wt% to 0.005 wt% of the formulation.

25 *Basic dyes:*

Basic dyes are organic dyes which carry a net positive charge. They deposit onto cotton. They are of particular utility for used in composition that contain predominantly cationic surfactants. Dyes may be selected from the basic violet and basic blue dyes listed in the Colour Index International.

30 Preferred examples include triarylmethane basic dyes, methane basic dye, anthraquinone basic dyes, basic blue 16, basic blue 65, basic blue 66, basic

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blue 67, basic blue 71, basic blue 159, basic violet 19, basic violet 35, basic violet 38, basic violet 48; basic blue 3, basic blue 75, basic blue 95, basic blue 122, basic blue 124, basic blue 141.

5 *Reactive dyes:*

Reactive dyes are dyes which contain an organic group capable of reacting with cellulose and linking the dye to cellulose with a covalent bond. They deposit onto cotton.

10 Preferably the reactive group is hydrolysed or reactive group of the dyes has been reacted with an organic species such as a polymer, so as to link the dye to this species. Dyes may be selected from the reactive violet and reactive blue dyes listed in the Colour Index International.

15 Preferred examples include reactive blue 19, reactive blue 163, reactive blue 182 and reactive blue, reactive blue 96.

Dye conjugates:

Dye conjugates are formed by binding direct, acid or basic dyes to polymers or particles via physical forces. Dependent on the choice of polymer or particle they deposit on cotton or synthetics. A description is given in WO2006/055787.

Particularly preferred dyes are: direct violet 7, direct violet 9, direct violet 11, 25 direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, direct violet 99, acid blue 98, acid violet 50, acid blue 59, acid violet 17, acid black 1, acid blue 29, solvent violet 13, disperse violet 27, disperse violet 26, disperse violet 28, disperse violet 63, disperse violet 77 and mixtures thereof.

30

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Shading dye can be used in the absence of fluorescer, but it is especially preferred to use a shading dye in combination with a fluorescer, for example in order to reduce yellowing due to chemical changes in adsorbed fluorescer.

5 Builders and sequestrants

The detergent compositions may also optionally contain relatively low levels of organic detergent builder or sequestrant material. Examples include the alkali metal, citrates, succinates, malonates, carboxymethyl succinates, carboxylates, polycarboxylates and polyacetyl carboxylates. Specific
10 examples include sodium, potassium and lithium salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. Other examples are DEQUESTTM, organic phosphonate type sequestering agents sold by Thermphos and alkanehydroxy phosphonates.

15 Other suitable organic builders include the higher molecular weight polymers and copolymers known to have builder properties. For example, such materials include appropriate polyacrylic acid, polymaleic acid, and polyacrylic/polymaleic acid copolymers and their salts, such as those sold by BASF under the name SOKALANTM.

20 If utilized, the organic builder materials may comprise from about 0.5% to 20 wt%, preferably from 1 wt% to 10 wt%, of the composition. The preferred builder level is less than 10 wt% and preferably less than 5 wt% of the composition. A preferred sequestrant is HEDP (1-Hydroxyethylidene -1,1,-
25 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).

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Buffers

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.

5

External Structurants

The compositions may have their rheology modified by use of a material or materials that form a structuring network within the composition. Suitable structurants include hydrogenated castor oil, microfibrinous cellulose and natural based structurants such as citrus pulp fibre. Citrus pulp fibre is particularly preferred especially if lipase enzyme is included in the composition.

10

Visual Cues

The compositions may, and preferably do, comprise visual cues of solid material that is not dissolved in the composition. Preferably they are used in combination with an external structurant to ensure that they remain in suspension. Preferred visual cues are lamellar cues formed from polymer film and possibly comprising functional ingredients that may not be as stable if exposed to the alkaline liquid. Enzymes and bleach catalysts are examples of such ingredients. Also perfume, particularly microencapsulated perfume.

15

20

Packaging and dosing

The liquids may be packaged as unit doses in polymeric film adapted to be insoluble until added to the wash water. More preferred the liquids are supplied in multiuse 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.

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Method of use

Following the teaching in WO2009/153184 the liquids according to the invention are intended to be formulated to allow them to be dosed to a typical front loading automatic washing machine at a dosage level of 20ml. The low in wash surfactant level being compensated by the presence of enzymes, the stable soil release polymer and optional additional high efficacy cleaning ingredients, such as EPEI. However, the invention is also suitable for the more conventional dosage levels of about 35 ml. the obtain suitable liquids of this type all that is necessary is to add further water and possibly perfume to the 20ml type of liquid. The soil release polymers claimed are also stable in these more dilute compositions.

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

EXAMPLESSoil Release (DMO) evaluation:

DMO is dirty motor oil. Soil release polymer was dissolved or dispersed in concentrated alkaline liquid detergent bases to make the concentrated alkaline liquid detergent compositions given in Table 1.

MPG	is mono propylene glycol.
TEA	is triethanolamine.
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.
Empigen® BB	is an alkyl betaine ex Huntsman (Coco dimethyl carbobetaine).

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	EPEI	is Sokalan HP20 – ethoxylated polyethylene imine cleaning polymer: PEI(600) 20EO ex BASF.
	Perfume	is free oil perfume.
	SRP	is soil release polymer.
5	PCF	is Herbacel AQ plus citrus fibre, a powdered citrus peel fruit material ex Herba foods.
	SLES 1EO	is Sodium Lauryl Ether Sulphate with average of 1EO.
	Prifac® 5908	is saturated lauric fatty acid ex Croda.
	MEA	is Monoethanolamine.
10	NaOH	is 47% sodium hydroxide solution.
	Dequest® 2066	is Diethylenetriamine penta(methylene phosphonic acid (or Heptasodium DTPMP).
	Dequest® 2010	is HEDP (1-Hydroxyethylidene -1,1,-diphosphonic acid).
	Lipex®	is Lipex 100L ex Novozymes.
15	Carezyme®	is a cellulase ex Novozymes.
	Stainzyme 12L	is an amylase formulated for liquids ex Novozymes.
	Mannaway	is a mannanase ex Novozymes.

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Table 1 – Liquid detergent compositions

	Composition A (5x)	Composition B (3x)
Component	Ingredient (as 100% active) %	
Demin water (initial - more added when pH is adjusted)	27.85	45.91
MPG	20.00	20.00
TEA	2.00	1.14
NI 7EO	12.74	7.28
LAS acid	8.49	4.85
Prifac® 5908	1.50	0.86
SLES 3EO	4.24	2.42
Empigen® BB	1.50	0.86
EPEI	5.50	3.14
SRP	3.75	2.14
Perfume	2.43	1.39
pH adjustment hole*	10.00	10.00
TOTAL	100.00	100.00

* comprising NaOH to required pH, and demineralised water balance.

Essentially the 3x Composition B is a dilution of the 5x Composition A (i.e. the 5x ingredient percentage concentration x 20/35. A 5x composition is one designed to have a recommended dose per wash of 20ml; A 3x composition is one that has a recommended dose per wash of about 35ml. The exceptions to the scaling between Compositions A and B are the water level and the MPG hydrotrope level which was kept at 20% for both compositions.

10

The compositions, comprising the polymer, were stored to allow the polymer to be exposed to conditions where it may undergo hydrolysis, with consequent reduction of the soil release performance.

Thus whilst the theoretical level of polymer dosed to the wash is stated to be 50ppm the actual level used after storage would have been lower due to polymer degradation during storage.

5 Wash Method

All washes and pre-washes were carried out in a Tergotometer containing 1 litre of wash liquor at 25°C. Wash liquors were prepared using 26°FH water. The Tergotometer speed was set at 100 oscillations/minute for all pre-washes and washes.

10

1.3 g/l of Composition A or 2.3 g/l of Composition B was added to water to make a wash liquor.

15

Two 30 minute pre-washes of knitted polyester test pieces were carried out with polyester and cotton ballast such that the total fabric weight was 40g and the ratio of cotton : polyester was 1:1. After each pre-wash the fabric was rinsed twice (for 20 seconds) in 26°FH water and dried. Fresh ballast was used for each pre-wash (and subsequent wash). After the polyester test pieces had dried, following the second pre-wash, they were stained using one drop of dirty motor oil (DMO) added from a disposable glass pipette. The stains were quickly stretched by hand in order to assist wicking and ensure a uniform stain, and left overnight before washing. Three replicate stained polyester test pieces were included in each wash; three repeat washes were carried out.

20

25

ΔE of the dried residual stain was measured (relative to clean unstained substrate, i.e. knitted polyester) using a Hunterlab Ultrascan XE reflectance spectrophotometer equipped with a UV filter at 420nm. Specular reflectance was included.

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Polymer stability screening

To test for the resistance of a polymer to hydrolysis the sample was included in composition B and then stored at 60°C in sealed glass containers for up to 8 days. Periodically the sample was subjected to ¹H NMR. Time to failure is defined as significant loss of polymer peaks as determined by examination of ¹H-NMR aromatic signals in the region of 7.9 - 8.1 ppm, corresponding to the aromatic proton signals. We use the term 'significant' when the appearing (new, as they are the breakdown product) signals due to the small molecule aromatic signals are greater than the remaining (original polymer aromatic proton signals), which, we have defined as the failure point for a polymer.

The compositions contained an amount of polymer sufficient to deliver to the wash when freshly prepared 50 ppm polymer and were buffered with TEA to pH 8. We have shown – see example 1b and 1c – that the actual storage stability of a SRP is in line with that predicted by the accelerated test. The amount of polymer in 3 x (composition B) is 2.14% and in 5 x (composition A) is 3.75% wt.

Comparative Examples

To illustrate the problem we first tested some prior art and known through public use polymers. These included the polymer Texcare®SRN 170 as disclosed in WO2009/153184. The results are given in Table 2.

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Table 2

Polymer name	Supplier	active ingred (wt%)	Probable building blocks	Mn	Time to failure (hrs)
Texcare® SRN170	Clariant	70	PEG-(TA-PG)	1,702	24
Texcare® SRN240	Clariant	40	PEG-(TA-PG)	7,220	72
Texcare® SRN300	Clariant	100	PEG-(TA-PG)(TA-PEG)	11,512	24
Marloquest® L235M	Sasol	70	PEG-PG-(TA-PG)	2,815	24
Marloquest® HSCB	Sasol	70	PEG-(TA-EG)	3,311	24
Repelotex® Crystal	Rhodia	70	PEG-(TA-PG)	1,868	24

Of these, the only SRP with marginal acceptability is Texcare SRN®240.

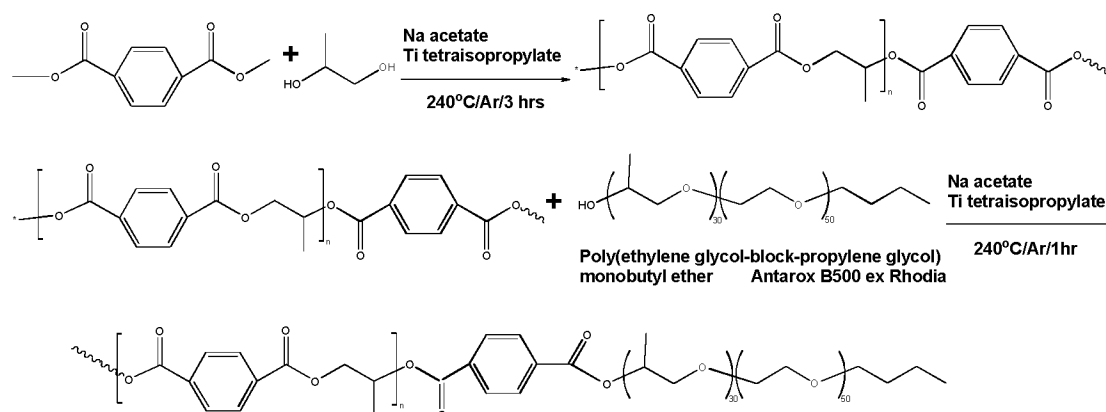
However, this polymer does not dissolve easily in alkaline detergent

- 5 compositions comprising up to 40% surfactant and EPEI so it is difficult to form an isotropic liquid using it as levels in excess of 1%.

The following are preparative methods and screening test results for six polymers suitable for use in the invention:

10

Example 1 - Synthesis of PO block EO end-capped terephthalate/propane diol polyester using 2-stage reaction process



- 15 Using a 3-necked 100 ml round bottom flask fitted with a digital thermometer, argon inlet and bubbler connected to an air condenser, dimethylterephthalate

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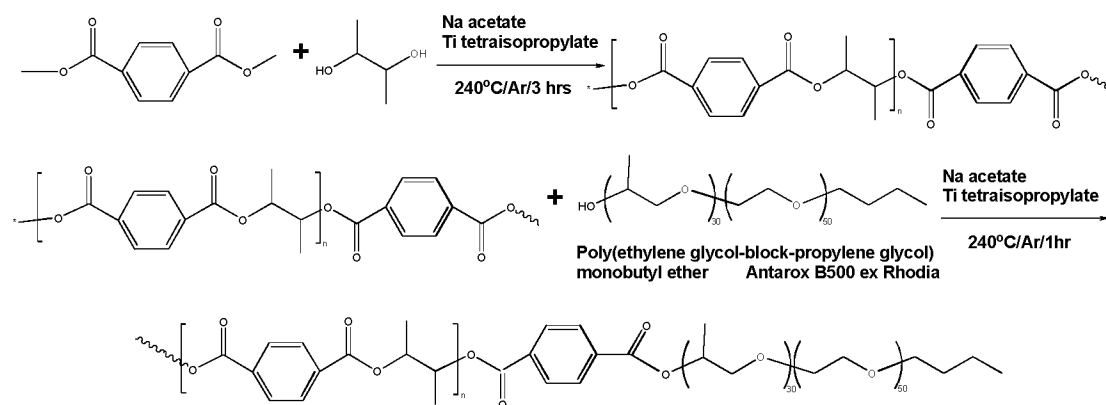
(3.88 g, 0.02 mol) and 1,2 propane diol (3.35 g, 0.04 mol) were weighed into the flask, which also contained a magnetic stirrer bar. Also added were the condensation catalyst titanium tetraisopropylate (0.004g, 1.4×10^{-5} mol) and sodium acetate (0.0074g, 9×10^{-5} mol). The contents of the flask were heated to 240°C to 260°C under a constant stream of argon and constant stirring. When the temperature of the molten mixture in the flask reached 160 °C, methanol was distilled off, indicating that polycondensation was occurring. Heating continued until the temperature of the mixture reached 240 °C, which was held for 3 hours. The contents of the flask was then allowed to cool to about 140 °C, at which point Antarox B500 (supplied by Rhodia) (6g, 0.003 mol) was added to the flask. Antarox B500 is a block copolymer with an n-butyl capped block of 50 ethylene oxide units polymerised with a block of 30 propylene oxide units. The propylene oxide end of the polymer is hydrophobic. The mixture was then reheated to 240 °C and held at this temperature for 1 hour. The product was purified by sublimation to remove any residual dimethylterephthalate. Final yield = 6.6g

$^1\text{H-NMR}$ (CDCl_3) – indicates $n = 7.7$

TD-SEC (THF) - av Mn = 1,616; av Mw = 2,904; av PD = 1.8

PD = polydispersity = M_w/M_n

Example 2 Synthesis of PO block EO end-capped terephthalate/2,3 butandiol polyester SRP using a 2-stage reaction process



5

The 2,3-butanediol used was a mixture of the racemic and meso forms from Aldrich: B84904, 2,3-Butanediol, 98%, CAS no. 513-89-5.

Using a 3-necked 100 ml round bottom flask fitted with a digital thermometer,
 10 argon inlet and bubbler connected to an air condenser, dimethylterephthalate (11.64g, 59.94 mmol) and 2,3 butandiol (10.80g, 119.89 mmol) were weighed into the flask, which also contained a magnetic stirrer bar. Also added were the condensation catalyst titanium tetraisopropylate (3 drops) and sodium acetate (2 small spatulas). The contents of the flask were heated under a
 15 constant stream of argon and constant stirring. When the temperature of the molten mixture in the flask reached 160°C, methanol was distilled off, indicating that polycondensation was occurring. Heating continued until the temperature of the mixture reached 240°C, which was held for 2.75 hours. The contents of the flask was then allowed to cool to about 140°C, at which
 20 point Antarox B500 (supplied by Rhodia) (11.99g, 5.99 mmol) was added to the flask and a further 3 drops of titanium tetraisopropylate. The mixture was reheated to 250°C and held at this temperature for 2.5 hours. The product was purified by sublimation to remove any residual dimethylterephthalate. Final yield = 18.9g.

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¹H-NMR (D₂O) – Accelerated data in concentrated Laundry liquid Composition B buffered with TEA to pH 8 and held at 60°C for 8 days (using ¹H-NMR as the polymer stability tracking tool) has shown the polymer of example 1 to be hydrolytically stable.

5

TD-SEC (THF) - av M_n = 4,800; av M_w = 14,150; av PD = 2.95

Example 3 - Synthesis of Poly(ethylene glycol) methyl ether 2000 end-capped terephthalate/2,3 butandiol polyester using a 2-stage reaction process

10

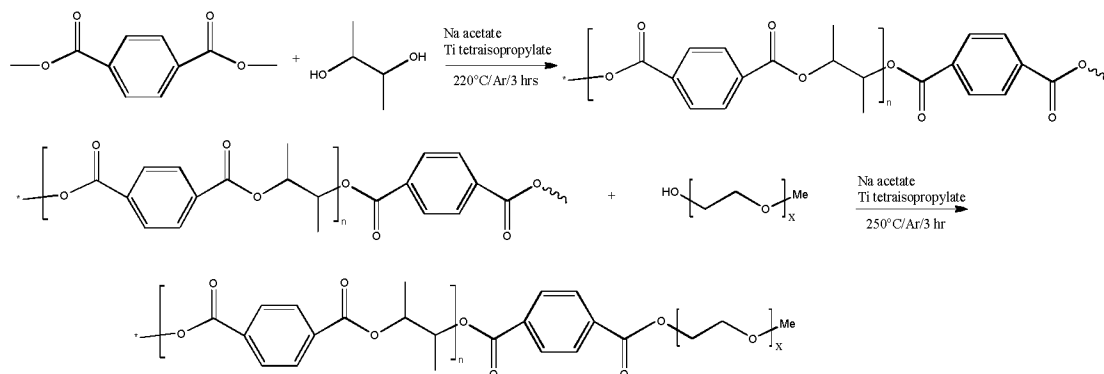
Using a 3-necked 100ml round bottom flask fitted with a digital thermometer, argon inlet and bubbler connected to an air condenser, dimethylterephthalate (11.64g, 59.94 mmol) and 2,3 butandiol (10.80g, 119.89 mmol) were weighed into the flask, which also contained a magnetic stirrer bar. Also added were the condensation catalyst titanium tetraisopropylate (3 drops) and sodium acetate (2 small spatulas). The contents of the flask were heated under a constant stream of Argon and constant stirring. When the temperature of the molten mixture in the flask reached 160°C, methanol was distilled off, indicating that polycondensation was occurring. Heating continued until the temperature of the mixture reached 220°C, which was held for 3 hours. The contents of the flask was then allowed to cool to about 140°C, at which point Poly(ethylene glycol) methyl ether 2000 (11.99g, 5.99 mmol) was added to the flask and a further 2 drops of titanium tetraisopropylate. The mixture was then heated to 250°C and held at this temperature for 3 hours. The product was purified by sublimation to remove any residual dimethylterephthalate. Final yield = 20.0g

15

20

25

- 55 -



Characterisation of polymer of Example 3:

- 5 TD-SEC (THF) - av M_n = 3,400; av M_w = 4,230; av PD = 1.23

The polymer of Example 3 was shown to be hydrolytically stable in concentrated Laundry liquid Composition B buffered with TEA to pH 8 at 60°C for 8 days (using $^1\text{H-NMR}$ (D_2O) as the polymer stability tracking tool).

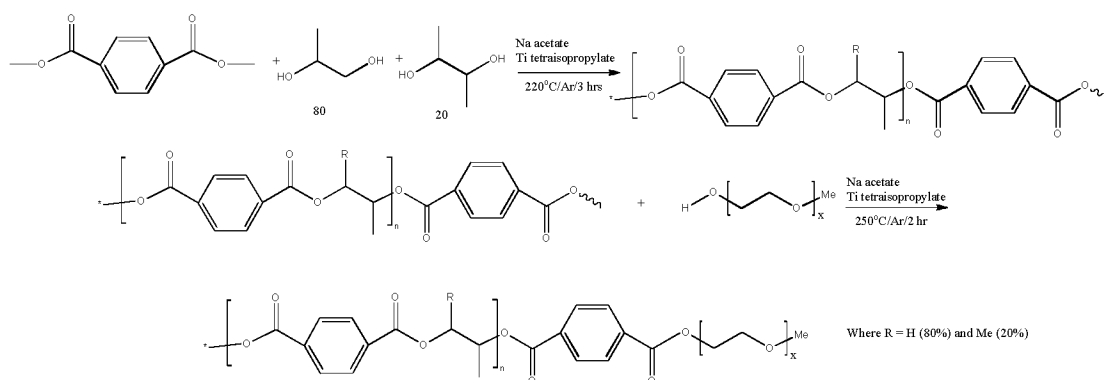
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Example 4 - Synthesis of Poly(ethylene glycol) methyl ether 2000 end-capped terephthalate/1,2 propandiol (80 mol.%) / 2,3-butandiol (20 mol.%) polyester using a 2-stage reaction process

- 15 Using a 3-necked 100ml round bottom flask fitted with a digital thermometer, argon inlet and bubbler connected to an air condenser, dimethylterephthalate (10.0g, 51.50 mmol) and 1,2 propandiol (6.27g, 82.40 mmol) and 2,3-butandiol (1.86g, 20.60 mmol) were weighed into the flask, which also contained a magnetic stirrer bar. Also added were the condensation catalyst
- 20 titanium tetraisopropylate (3 drops) and sodium acetate (1 small spatula). The contents of the flask were heated under a constant stream of argon and constant stirring. When the temperature of the molten mixture in the flask reached 160°C, methanol was distilled off, indicating that polycondensation was occurring. Heating continued until the temperature of the mixture reached
- 25 220°C, which was held for 3 hours. The contents of the flask was then allowed

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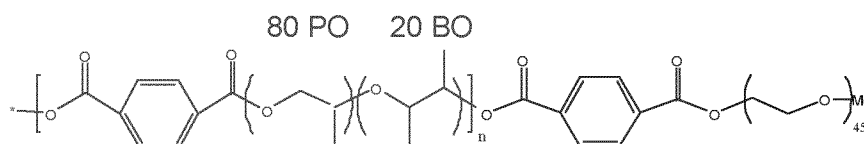
- to cool to about 140°C, at which point Poly(ethylene glycol) methyl ether 2000 (10.30g, 5.15 mmol) was added to the flask and a further 3 drops of titanium tetraisopropylate. The mixture was then heated to 250°C and held at this temperature for 2 hours. The product was purified by sublimation to remove any residual dimethylterephthalate. Final yield = 14.5g



Characterisation of polymer of Example 4:

- ¹H-NMR (d⁶-acetone) – Composition PO:BO = 85.9:14.1
Note that the theoretical ratio of 80:20 is found to be 86:14 by this NMR study.

TD-SEC (THF) - av M_n = 2,130; av M_w = 6,890; av PD = 3.24

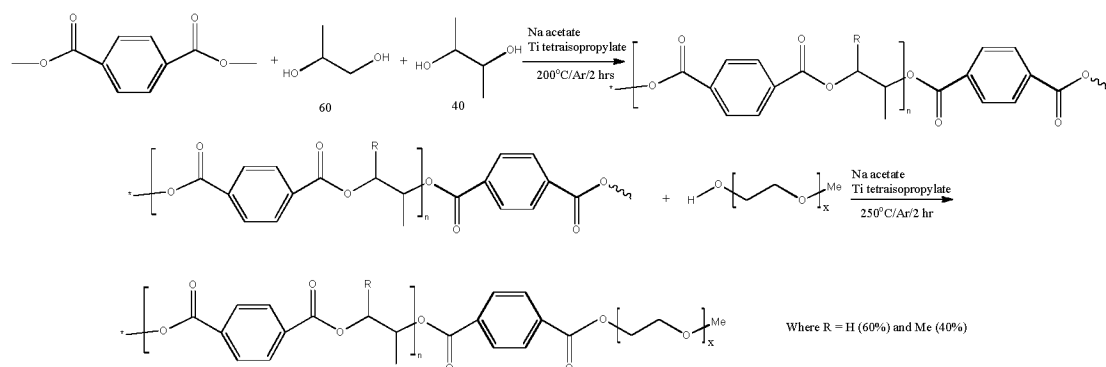


- The polymer of Example 4 was shown to be hydrolytically stable in concentrated Laundry liquid Composition B buffered with TEA to pH 8 at held at 60°C for 8 days (using ¹H-NMR as the polymer stability tracking tool).

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Example 5 - Synthesis of Poly(ethylene glycol) methyl ether 2000 end-capped terephthalate/1,2 propandiol (60 mol.%) / 2,3-butandiol (40 mol.%) polyester using a 2-stage reaction process

- 5 Using a 3-necked 100ml round bottom flask fitted with a digital thermometer, argon inlet and bubbler connected to an air condenser, dimethylterephthalate (10.0g, 51.50 mmol) and 1,2 propandiol (4.70g, 61.80 mmol) and 2,3-butandiol (3.71g, 41.20 mmol) were weighed into the flask, which also contained a magnetic stirrer bar. Also added were the condensation catalyst
- 10 titanium tetraisopropylate (3 drops) and sodium acetate (1 small spatula). The contents of the flask were heated under a constant stream of Argon and constant stirring. When the temperature of the molten mixture in the flask reached 160 °C, methanol was distilled off, indicating that polycondensation was occurring. Heating continued until the temperature of the mixture reached
- 15 200 °C, which was held for 2 hours. The contents of the flask was then allowed to cool to about 140 °C, at which point Poly(ethylene glycol) methyl ether 2000 (10.30g, 5.15 mmol) was added to the flask and a further 3 drops of titanium tetraisopropylate. The mixture was then heated to 250°C and held at this temperature for 2 hours. The product was purified by sublimation to
- 20 remove any residual dimethylterephthalate.
Final yield = 13.6g.



- 25 ¹H-NMR (D₂O) – The polymer of example 5 was shown to be hydrolytically stable in concentrated Laundry liquid Composition B buffered with TEA to pH

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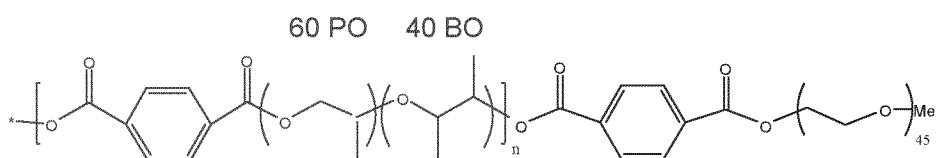
8 and held at 60°C for 8 days (using $^1\text{H-NMR}$ as the polymer stability tracking tool).

Characterisation:

- 5 $^1\text{H-NMR}$ (d^6 -acetone) – Composition PO:BO = 70.3:29.7

Note that the theoretical ratio of 60:40 is found to be 70:30 by this NMR study.

TD-SEC (THF) - av M_n = 2,910; av M_w = 10,530 av PD = 3.61



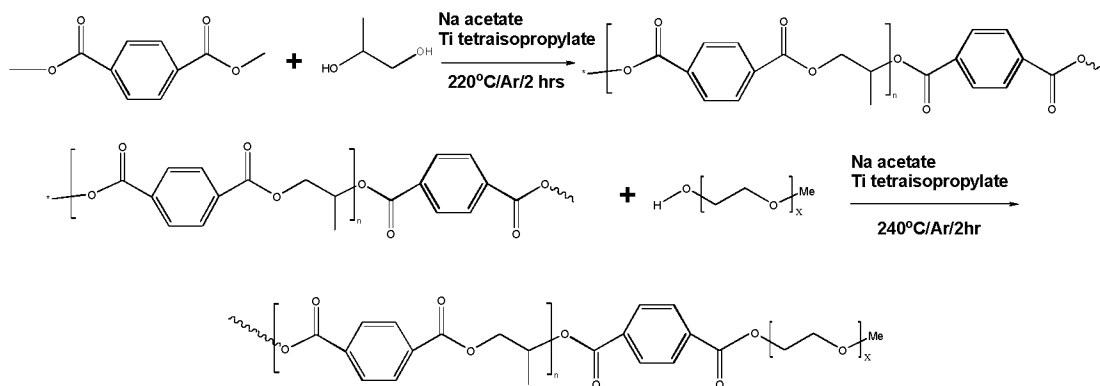
- 10 Example 6 – Synthesis of Poly(ethylene glycol) methyl ether 2000 end-capped terephthalate/1,2 propandiol polyester using a 2-stage reaction process

- Using a 3-necked 100ml round bottom flask fitted with a digital thermometer, argon inlet and bubbler connected to an air condenser, dimethylterephthalate
 15 (10.0g, 51.50 mmol) and 1,2 propandiol (7.84g, 103.00 mmol) were weighed into the flask, which also contained a magnetic stirrer bar. Also added was the condensation catalyst titanium tetraisopropylate (3 drops). The contents of the flask were heated under a constant stream of argon and constant stirring. When the temperature of the molten mixture in the flask reached 160°C,
 20 methanol was distilled off, indicating that polycondensation was occurring. Heating continued until the temperature of the mixture reached 220°C, which was held for 2 hours. A further amount of 1,2 propandiol (2.0g, 26.28 mmol) was added due to the loss by evaporation. The polymerisation was heated for a further 1 hour. The contents of the flask was then allowed to cool to about
 25 140°C, at which point Poly(ethylene glycol) methyl ether 2000 (10.30g, 5.15 mmol) was added to the flask and a further 3 drops of titanium

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tetraisopropylate and 1,2 propandiol (1.0g, 13.15 mmol. The mixture was then heated to 240°C and held at this temperature for 2 hours. The product was purified by sublimation to remove any residual dimethylterephthalate. Final yield = 13.3g

5



TD-SEC (THF) - av Mn = 2,700; av Mw = 7,650; av PD = 2.83

10

The polymer of example 6 was shown to be hydrolytically stable in concentrated Laundry liquid composition B buffered with TEA to pH 8 (using ¹H-NMR as the polymer stability tracking tool).

15 Example 1a

Freshly prepared polymer of Example 1 was included in detergent composition A such that the wash liquor concentration of soil release polymer was 100ppm. Comparative example C used half that level of Texcare® SRN170. The effectiveness of the SRP is indicated by a low ΔE in Table 3.

20

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Table 3

Example	ΔE
Example 1a using Polymer of example 1	0.62
Comparative example C	4.7

Thus it appears that the Example 1 polymer with polydispersity less than 3 has excellent soil release properties.

5

This polymer has been shown to be hydrolytically stable in concentrated Laundry liquid composition B buffered with TEA to pH 8 (using $^1\text{H-NMR}$ - D_2O - as the polymer stability tracking tool).

10 Examples 1b and 1c and comparative examples D and E

The polymer of Example 1 was tested for soil release properties after storage in (8 days at 60°C) and delivery from detergent compositions A (Example 1b) and B (Example 1c) over a range of pH. Control compositions using Texcare SRN®170 were made up as comparative examples D and E. Samples were
15 stored in closed screw-top glass jars in oven at either 60°C for 8 days, or 37°C for 8 weeks.

Polymer levels (based on level before storage) = 50 ppm

Data values given in Tables 4 and 5 are ΔE ($\Delta E = 0$ = complete DMO

20 removal; $\Delta E = 42$ for washed stain with no SRP in pre-wash formulation).

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Table 4 (60°C)

pH	Comparative Example D (Texcare SRN 170 in comp A)	Example 1b (Example 1 polymer in comp A)	Comparative Example E (Texcare SRN 170 in comp B)	Example 1c (Example 1 polymer in comp B)
6.5	6.7	2	6.8	2.3
7.5	22.4	2.1	18.2	2.4
8.5	35.1	16	36.1	15.4

Comparative example D was repeated using Texcare®SRN300 in place of
 5 Texcare® SRN170. The performance after storage under acidic conditions
 gave an excellent ΔE of 0.5. However, after storage at pH 8.5 this dropped to
 32.8. A ΔE value greater than 5 is unacceptable.

Table 5 (37°C)

10

pH	Comparative Example D (Texcare SRN 170 In A)	Example 1b (Example 1 polymer in comp A)	Comparative Example E (Texcare SRN 170 in comp B)	Example 1c (Example 1 polymer in comp B)
6.5	2.3	1.1	3.0	1.5
7.5	16.2	1.4	11.1	1.6
8.5	37.7	29.0	38.9	23.8

15

At alkaline pH the Texcare SRN170 polymer performance drops significantly.
 In contrast the polymer according to the invention maintains excellent
 performance under alkaline conditions, particularly at a pH below 8.5, even
 after storage under those alkaline conditions in the presence of TEA.

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Example 4a - Soil Release (DMO) evaluation:

The polymer of Example 4 was pre-dissolved/dispersed in Composition A (5x base). Two pre-washes were carried out prior to staining with DMO and subsequent washing for 30 mins in a tergotometer at 25°C. The experimental
5 polymer was included such that wash liquor conc. was 100ppm.

$$\Delta E = 3.15 \pm 0.65$$

The same composition with Texcare SRN170 @ 50 ppm:

$$\Delta E = 4.7 \text{ (zero means complete stain removal, no removal is 42).}$$

10

Examples 4a, 5a and Comparative Example F showing Soil release performance after accelerated aging

15 Polymers from examples 4 and 5 and a comparative polymer, Texcare ®SRN170, were stored in concentrated detergent liquid composition A containing 1% TEA in closed screw-top glass jars in an oven at 60°C for 8 days. Then they were tested for soil release performance in tergotometers using an in wash polymer concentration of 50 ppm. The ΔE results are given
20 in Table 6 below.

All polymers show excellent performance at pH 6.5; performance was also very good at pH 7.5 provided that the butandiol proportion was less than 40% of the total diol.

25

It was noted that after storage the compositions comprising the butane diol polymers showed better clarity of the liquid.

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Table 6

pH	E.g. 4a	E.g. 5a	E.g. F Texcare ®SRN170
6.5	4.7	5.7	6.7
7.5	6.3	19.2	22.4
8.5	34.9	35.0	35.1

For comparison, a washed stain without SRP in the prewash has a ΔE value of 42. Complete removal of the stain gives a ΔE of zero.

5

At alkaline pH the Texcare® SRN170 polymer performance drops significantly. In contrast the polymers according to the invention maintain good performance under alkaline conditions, particularly at a pH below 8.5, even after storage under those alkaline conditions in the presence of TEA.

10 The tested variation in the concentration of TEA does not appear to affect the result significantly.

Example 6a - Soil Release (DMO) evaluation:

15 The polymer of example 6 was included in composition A such that the wash liquor concentration of soil release polymer was 100ppm.

The DMO removal effectiveness of the SRP is indicated in Table 7 by a low ΔE . We have found that there is a good correlation between the 8 day at 60°C accelerated test and the 8 week at 37°C data for polymer stored in compositions A and B.

20

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Table 7

Composition and polymer	Storage	ΔE
Comp A with Texcare®SRN 240	Fresh	1.2
Comp A with Polymer Example 6	Fresh	1.5
Comp A with Texcare®SRN 240	after 8 wks @ 37 °C / TEA pH 8	35
Comp A with Polymer Example 6	8 days @ 60 °C / TEA pH 7.5	2.3
Texcare® SRN170 @ 50 ppm	Fresh	4.7

- From nmr spectra we have concluded that the Example 6 polymer using PEG 2K as the endcap looks to be very similar to Texcare® SRN 240 apart from
- 5 the ratio of the end block(s) to the polymer mid block. Evidence suggests that the Polymer of example 1 has a longer mid block. The nmr analysed difference in mid blocks between Texcare®SRN240 and the polymer of Example 1 is that the ratio of the end block units to the mid block repeat n for Texcare®SRN 240 is 15 to 22, whereas the ratio for the polymer of example 6
- 10 is about half this at 7 to 9. The value of n may be calculated assuming one or two end blocks per polymer chain. If there are two end blocks each with say 45 EO units then the size of the mid blocks and consequently the value of n is doubles compared to a polymer with only one end block of 45 EO units.
- 15 Texcare® SRN 240, does not appear to have any EO in the polymer mid block, but we do see higher intensity signals due to PEO end block(s), which, when, when ratioed with the methoxy end cap, come to about 42 repeat units, which appears to indicate that the manufacturer (Clariant) used a MeO-PEG 2K as the end cap.

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Texcare® SRN170 has been identified as mPEG750 end blocks and PO in mid block.

5 Texcare® SRN 300 contains EO and PO in the polymer mid block. Also see higher intensity signals for PEO, which could be from a long PEO incorporated in the mid block and/or from the end block.

10 Texcare® SRN 240 shows slightly better hydrolytic stability than Texcare® SRN 300 with TEA at pH 7 in Composition B, but both fail dramatically at pH 8. The same is true for Texcare® SRN170.

This contrasts with the improved stability at pH 8 using TEA that we have seen with the Example 6 polymer.

15 Example 6b

Example 6b is a composition, comprising polymer 6 in base composition A and comparative composition F is a composition comprising the Texcare SRN®170 polymer used in WO2009/153184 also in base composition A. These compositions were stored for 8 days in sealed glass containers in an oven at 60°C to allow the polymer to be exposed to accelerated conditions where it may undergo hydrolysis, with consequent reduction of the soil release performance. Then the potentially decomposed compositions were wash tested. The results are given in table 8. The method used was the same as for Example 6a except that the polymer concentration was reduced to 50ppm in the wash.

20

25

Whilst the theoretical level of polymer dosed to the wash is stated to be 50ppm the actual level used after storage would have been lower due to polymer degradation during storage.

30

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Table 8

pH	Example 6b (Polymer of Example 6 in Composition A)	Comparative example F (Texcare®SRN170 in Composition A)
6.5	4.1	6.7
7.5	2.3	22.4
8.5	34.9	35.1

Examples 7 to 17 are alkaline isotropic detergent liquid compositions comprising the stable soil release polymers described above.

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Table 9

Formulation	E.g. 7	E.g. 8	E.g. 9	E.g. 10	E.g. 11
Material	% as 100%	% as 100%	% as 100%	% as 100%	% as 100%
LAS Acid	4.85	8.49	8.49	7.26	6.97
SLES 3EO	2.42	4.24	4.24	3.59	3.44
NI 7EO	7.28	12.74	12.74	10.85	10.41
Prifac® 5908	0.85	1.50	1.50	2.56	2.46
Empigen® BB	0.86	1.50	1.50	1.50	1.50
EPEI	3.10	5.50	5.50	5.50	5.50
SRP ¹		3.75			
SRP ²	2.10				
SRP ³			3.75		
SRP ⁴				3.68	
SRP ⁵					3.68
NaOH	0.07	0.07	0.07		
TEA	2.00	3.50	3.50		
MPG	15.00	20.00	20.00	15.38	14.76
Glycerine				4.27	4.10
Dequest® 2010			2.62		2.00
Fluorescer		0.10	0.10		
Protease		1.75	1.75		
Stainzyme® 12L		0.700	0.700		
Carezyme® 1000L					
Lipex® or Lipoclean® 100L	2.00	3.00	3.00	3.00*	3.00*
Mannaway®		0.70	0.70		
PCF	0.25	0.25	0.25	0.21	0.20
Preservative	0.16	0.01	0.01		
Perfume	1.39	2.43	2.43		
Water and impurities	57.67	29.77	27.15	balance	balance
TOTAL	100	100	100	100	100

*A 3% hole was left in the base to accommodate lipase enzyme.

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In examples 7 to 17:

SRP¹ is the polymer of Example 1

SRP² is the polymer of Example 2

SRP³ is the polymer of Example 3

5 SRP⁴ is the polymer of Example 4

SRP⁵ is the polymer of Example 5

SRP⁶ is the polymer of Example 6

10

Table 10

Formulation	12	13	14	15	16	17
Material	% as 100%	% as 100%	% as 100%	% as 100%	% as 100%	% as 100%
LAS Acid	7.22	4.81	4.81	3.21	3.21	14.17
SLES 1EO	9.02	6.01	6.01	4.01	4.01	8.97
NI 7EO	1.81	1.20	1.20	0.80	0.80	
Empigen® BB	0.86	0.86	0.57	0.86	0.38	0.86
EPEI	3.10	3.10	2.07	3.10	1.38	3.10
SRP ¹	2.10	2.10				
SRP ²			1.40	2.10		
SRP ⁶					0.93	2.10
NaOH	0.93	0.62	0.62	0.27	0.27	1.40
TEA						4.00
Citric Acid Solution	1.25	1.25	1.25	1.25	1.25	1.00
MPG	4.91	3.27	3.27	2.18	2.18	5.00
Fluorescer	0.20	0.20	0.20	0.20	0.20	0.20
Savinase® Ultra 16L Ex	2.00	2.00	2.00	2.00	2.00	2.00
Colorant	0.003	0.003	0.00	0.00	0.003	0.003
Perfume	0.98	0.98	0.98	0.98	0.98	0.98
Water and minors	balance	balance	balance	balance	balance	balance
Total	100.00	100.00	100.00	100.00	100.00	

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Claims

1. An aqueous alkaline isotropic concentrated detergent liquid composition with an undiluted pH of at least 7.8 and at most 9 comprising:

- 5 a) 10 to 60 wt% non-soap surfactant,
- b) 0 to 20 wt% hydrotrope,
- c) 0 to 4 wt% soap,
- d) 0 to 10 wt% nonionic EPEI,
- e) at least 1 wt% triethanolamine,

10 characterised in that dissolved in the alkaline isotropic liquid there is:

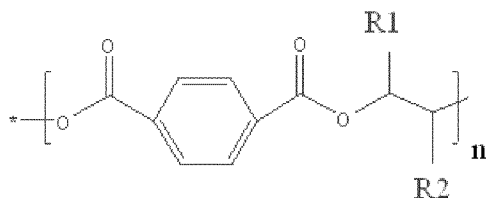
f) at least 1 wt%, preferably at least 1.5 wt% of a polyester substantive nonionic soil release polymer of the type E-M-L-E, where the midblock M is connected to a generally hydrophilic end block E and blocks E each comprise capped oligomers of polyethylene glycol remote from the midblock, with at

15 least 10 EO repeat units, the end blocks being free from ester bonds, either directly or via linking moiety L which comprises the motif:

B-Ar-B where B is selected from urethane, amide and ester moieties and Ar is 1,4 phenylene,

and midblock M comprises the motif:

20



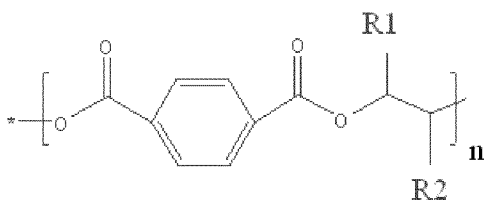
wherein R1 and R2 may be the same or different selected from C1-C4 alkyl, C1-C4 alkoxy and Hydrogen, provided that R1 and R2 may not both be

25 hydrogen, n is at least 2, preferably more than 5, the ester bonds may be formed the other way around (not shown), if they are so reversed then all of them will be so reversed,

- 70 -

wherein the composition comprising the polymer provides soil release less than a ΔE of 5 with DMO on woven polyester after storage of the polymer in the detergent composition at 60°C for 8 days at a pH >7.5.

- 5 2. A composition according to claim 1 in which the polymer (f) comprises a polyester substantive nonionic soil release polymer of the type E-M-L-E, where the midblock M comprises the motif:



10

Wherein R1 and R2 may be the same or different selected from C1-C4 alkyl and Hydrogen, provided that R1 and R2 may not both be hydrogen, n is at least 2, preferably more than 5, the ester bonds may be formed the other way around (not shown), if they are so reversed then all of them will be so

15

reversed,

and the one or two end blocks E each comprise alkyl capped oligomers of polyethylene glycol remote from the midblock, with at least 10 EO repeat units, the end blocks being free from ester bonds,

and L is a linking moiety B-Ar-B where B is an ester moiety and Ar is 1,4

20

phenylene,

wherein the polymer has a molecular weight Mw of at least 4000.

3. A composition according to claim 1 or claim 2 where R1 and R2 are selected from H and Me.

25

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

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5. A composition according to any preceding claim comprising SLES.

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

5

7. A composition according to any preceding claim wherein the liquid has an undiluted pH of at most 8.4, even at most 8.2.

8. A composition according to any preceding claim comprising at most 1.5 wt% soap surfactant.

10

9. A composition according to any preceding claim comprising at most 15 wt%, preferably at most 12 wt% hydrotrope.

10. A composition according to any preceding claim comprising at least 1 wt% of nonionic EPEI (d) and a total of at least 3 wt% of (d) and the hindered soil release polymer (f).

15

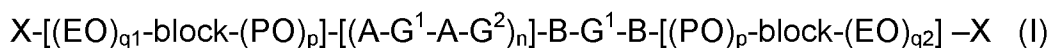
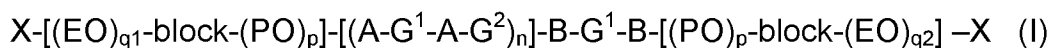
11. A composition according to any preceding claim comprising at least one enzyme.

20

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

13. A composition according to any preceding claim in which the polymer (f) has the general formula (I):

25



30

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where EO is ethylene oxide ($\text{CH}_2\text{CH}_2\text{O}$);

where PO is at least 80 wt% propylene oxide ($\text{CH}_2\text{CH}(\text{CH}_3)\text{O}$), and preferably 100% PO units;

5

where p is a number from 0 to 60, and when p is not zero is preferably from 2 to 50, more preferably from 5 to 45, even more preferably from 6 to 40, yet more preferably from 7 to 40 and most preferably from 8 to 40, even from 11 to 35;

10

where q1 and q2 is a number from 6 to 120, preferably 18 to 80, most preferably 40 to 70, provided that q2 is greater than p and preferably q2 is at least 1.5 times as large as p;

15

where X is a capping moiety, preferably selected from C_{1-4} alkyl, branched and unbranched;

where n is a number from 2 to 26; preferably 5 to 15;

20

A and B are selected from ester, amide and urethane moieties;

when the moieties A and B adjacent to the PO blocks are esters then it is preferred that p is not zero,

25

alternatively, it is preferred that the ratio of $(q1+q2):n$ is from 4 to 10 and that q2 is from 40 to 120;

G^1 comprises 1,4 phenylene;

30

G^2 is ethylene, which may be substituted;

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the polymer (f) being modified by at least one of modifications (i) to (iv):

(i) p is a number from 2 to 50, more preferably from 5 to 45, even more preferably from 6 to 40, yet more preferably from 7 to 40 and most preferably from 8 to 40, even from 11 to 35;

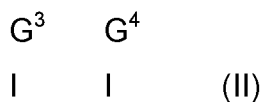
5

or

(ii) the ratio of $(q_1+q_2):n$ is from 4 to 10 and that q_2 is from 40 to 120;

or

10 (iii) moieties G^2 are all substituted ethylene of formula (II)



15

wherein G^3 and G^4 are selected from Hydrogen, C_{1-4} alkyl and C_{1-4} alkoxy, provided that at least one of G^3 and G^4 is not hydrogen and that at least 10% of the groups G^2 have neither G^3 nor G^4 as hydrogen. Preferably when G^3 and G^4 are not hydrogen then they are methyl moieties. Preferably the non H substituents, more preferably the methyl moieties, are arranged in syn configuration on the ethylene backbone $-CH-CH-$ of moieties G^2

20

or

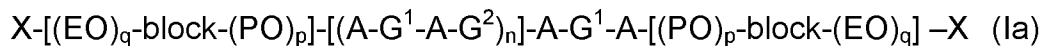
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(iv) combinations of two or three of modifications hindering strategies (i), (ii) and (iii).

14. A composition according to claim 13 in which polymer (f) is a soil release polymer with the formula (Ia):

30

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where EO is ethylene oxide (CH₂CH₂O);

5

where PO is propylene oxide (CH₂CH(CH₃)O);

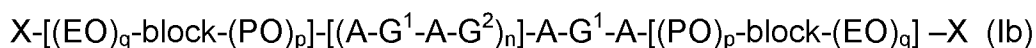
where p is a number from 2 to 50, more preferably from 5 to 45, even more preferably from 6 to 40, yet more preferably from 7 to 40 and most preferably from 8 to 40, even from 11 to 35;

10

where q is a number from 6 to 120, preferably 18 to 80, most preferably 40 to 70, provided that q is greater than p;

15. A composition according to claim 13 in which the polymer (f) has the

15 formula (Ib) :



where EO is ethylene oxide (CH₂CH₂O);

20

where PO is propylene oxide (CH₂CH(CH₃)O);

where n is a number from 2 to 26

25 where p is a number from 0 to 60, when present preferably from 2 to 50, more preferably from 5 to 45, even more preferably from 6 to 40, yet more preferably from 7 to 40 and most preferably from 8 to 40, even from 11 to 35;

where q is a number from 6 to 120, preferably 18 to 80, most preferably 40 to 70, provided that q is greater than p;

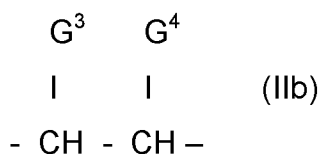
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- 75 -

where X is a capping moiety, preferably selected from C₁₋₄ alkyl, branched and unbranched;

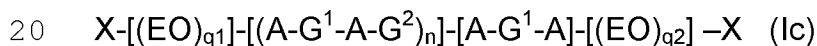
and the moieties G² are all substituted ethylene of formula (IIb)

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- 10 wherein G³ and G⁴ are selected from Hydrogen, C₁₋₄ alkyl and C₁₋₄ alkoxy, provided that at least one of G³ and G⁴ is not hydrogen and that at least 10% of the groups G² have neither G³ nor G⁴ as hydrogen. Preferably when G³ and G⁴ are not hydrogen then they are methyl moieties. Preferably the non H substituents, more preferably the methyl moieties, are arranged in syn
15 configuration on the ethylene backbone –CH-CH- of moieties G².

16. A composition according to claim 13 in which the polymer (f) has formula (Ic)



where the end blocks consist of q1 and q2 units of ethylene oxide (EO) or (CH₂CH₂O);

- 25 where q1 is 0, or from 40 to 120, and q2 is from 40 to 120;

where X is a capping moiety, preferably selected from C₁₋₄ alkyl, branched and unbranched;

- 30 where n is a number from 5 to 26;

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where the linking moieties A are esters;

characterised in that the ratio of $(q_1+q_2):n$ is from 4 to at most 10, preferably from 5 to 8.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/050945

A. CLASSIFICATION OF SUBJECT MATTER INV. C08G63/66 C11D3/00 C11D3/37 C11D17/00 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C08G C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 135 931 A1 (PROCTER & GAMBLE) 23 December 2009 (2009-12-23) examples -----	1-16
A	EP 0 185 427 A2 (PROCTER & GAMBLE) 25 June 1986 (1986-06-25) page 6, line 3 - line 19; claims; examples -----	1-16
A	US 5 256 168 A (MORRALL STEPHEN W ET AL) 26 October 1993 (1993-10-26) column 2, line 6 - line 55; claims -----	1-16
A	EP 0 518 401 A1 (PROCTER & GAMBLE) 16 December 1992 (1992-12-16) page 4, line 4 - line 21; claim 1 -----	1-16
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 16 April 2012	Date of mailing of the international search report 25/04/2012	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Hillebrecht, Dieter	

INTERNATIONAL SEARCH REPORT

Information on patent family members

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