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(54) Title: SOIL RELEASE POLYMERS

(57) Abstract: A linear soil release polymer with the formula (I): X-[$(EO)_q$-block-$(PO)_p$]-[(A-$R^1$-A-$R^2$)$_n$]-A-$R^1$-A-[$(PO)_p$-block-$(EO)_q$] -X (I) where the linking moieties A are esters, where the $R^1$ moieties are 1,4 - phenylene moities, where the $R^2$ moieties are substituted ethylene moieties having $C_{1-4}$ alkyl substituents and the $R^2$ moieties comprise substituted ethylene moieties derived from the condensation of 2,3 butane diol, where the EO blocks are 100% ethylene oxide ($CH_2CH_2O$), where the PO blocks are 100% propylene oxide ($CH_2CH(CH_3)O$), where p is a number from 2 to 50, preferably from 5 to 45, more preferably from 6 to 40, yet more preferably from 7 to 40 and most preferably from 8 to 40, even from 1 1 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 and preferably q is at least 1.5 times as large as p; where X is a suitable capping moiety, preferably selected from $C_{1-4}$ alkyl, branched and unbranched; where n is a number from 2 to 16.

# SOIL RELEASE POLYMERS

## TECHNICAL FIELD

This invention relates to improved soil release polymers which may be incorporated into alkaline liquid detergent compositions to assist with cleaning of oily soils from fabrics, particularly fabrics comprising polyester.

## BACKGROUND

US4411831 (Purex) relates to inclusion of soil release polymer (SRP) in a liquid detergent composition. It has as its object to provide a liquid detergent having soil-release properties and which is stable from separation and precipitation for extended periods of time. The stable aqueous detergent composition consists essentially of (by weight): 0.2 to 20.0% of an ethylene terephthalate/polyethylene oxide terephthalate copolymer; 5 to 40% of specific anionic detergent; Up to 40% of specific nonionic detergent; and a buffer sufficient to maintain the pH of the aqueous composition within the range of 5.0 to 9.0. The preferred soil-release polymers for these liquids are said to be: Zelcon 4780 (DuPont) and Milease T (ICI Americas). It is taught that when formulating the liquids one must protect against high pH or the development of a high pH upon storage. This is because the soil-release agents used will hydrolyze in the alkaline range. For these polymers the hydrolysis is said to become objectionable when the pH begins to exceed 8.5 and it can be a real problem above 9.0.

These types of polyester SRPs have, since then, been developed considerably to improve their performance, especially in powdered compositions. More recent

SRPs are, for example, described generally in EP991743 (Clariant) and EP2135931 (Procter & Gamble).

EP311342 (P&G) is concerned with end capped esters that are soil release agents which are product compatible with alkaline granular detergent compositions. The esters, which comprise asymmetrically substituted oxy-1,2-alkyleneoxy units and terephthaloyl units are sulphoaroyl end-capped. Polymers with charged end caps like these are generally unsuitable for liquid compositions.

One line of development for soil release polymers (or more accurately oligomers) has been to make them of low molecular weight. In this specification the term polymer is used for both polymers and oligomers irrespective of molecular weight. We have found that while such low molecular weight polymers have excellent performance in powder compositions the low molecular weight seems to have increased their susceptibility to loss of performance via alkaline hydrolysis when included in alkaline liquid detergents. Thus although the SRP exemplified in WO2009/153184 has excellent performance in a freshly made concentrated liquid detergent composition according to that invention, we have now determined that the resistance of the SRP to hydrolysis on storage in the detergent liquid at pH from 7.5 to 9.0 (and consequential loss of soil release performance) is insufficient for a robust commercial detergent liquid. As such an alkaline pH is useful for boosting the performance of the surfactants and other ingredients it is highly desirable to find a new polymer with better storage stability at alkaline pH. The inclusion of Triethanolamine (TEA) in the composition makes matters worse as it appears to catalyse the cleavage of ester bonds present in the SRP. Thus stability of the known SRP is insufficient even at neutral pH if TEA is incorporated as part of the buffer system of the detergent liquid.

The approach taken in WO2009/153184 is 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 high levels of specific polymers and enzymes in the liquid. One of the key polymers that are preferably included at high levels in the composition is a polyester SRP. The one used in the examples of WO2009/153184, and also one of the three preferred on page 39, is of polyester chemistry (terephthalic acid/propandiol copolymer with methoxy PEG 750 end cap). It is sold under the trade name Texcare® SRN 170 by Clariant. It is now thought that this material is substantially linear.

Despite attempts to reformulate the concentrated detergent liquids described in WO2009/153184, to eliminate TEA from the composition we have been unable to achieve that for a viable 20ml dose concentrated laundry detergent liquid. Thus, it is necessary to find a new SRP that is resistant to hydrolysis under moderately alkaline conditions, especially in the presence of TEA, and yet retains the excellent soil release properties of Texcare® SRN170.

WO 2006/133868 & WO 2006/133867 (Clariant) describe oligoesters of the type that would include Texcare® SRN170. The general formula is:

$$R^1\text{-}(O\text{-}R^2)_a\text{-}[OC(O)R^3C(O)(OR^4)_b]_c\text{-}O\text{-}C(O)R^5\text{-}C(O)O\text{-}(R^6\text{-}O)_d\text{-}R^7$$

While $R^2$ and $R^6$ may be alkylene, such as ethylene, propylene, butylene; ethylene is preferred and there is no disclosure of used of mixed alkylene oxides as end caps.

The use of 1,2, propane diol in the polymer backbone, as found in Texcare® SRN 170, is described in many publications, for example, in EP 629690 (P&G). It is also found in the earlier EP 185427 (P&G) where it is said to confer improved polymer solubility when used in place of ethylene glycol in the backbone. EP 185427 contains some general teaching about modification of the end groups away from the preferred capped EO repeat units. The examples are in line with

the general preference to use 100% EO repeat units, with a cap of a lower alkyl group.

The generic expression for the polymeric soil release agents of EP185427 is:

$$X\text{-}[(OCH_2CH_2)_n(OR^5)_m]\text{-}[(A\text{-}R^1\text{-}A\text{-}R^2)_u(A\text{-}R^3\text{-}A\text{-}R^2)_v]\text{-}A\text{-}R^4\text{-}A\text{-}[(R^5O)_m(CH_2CH_2O)_n]\ \text{-}X$$

In this formula, the moiety $[(A\text{-}R^1\text{-}A\text{-}R^2)_u(A\text{-}R^3\text{-}A\text{-}R^2)_v]\text{-}A\text{-}R^4\text{-}A\text{-}$ forms the backbone. Groups $X\text{-}[(OCH_2CH_2)_n(OR^5)_m]$ and $[(R^5O)_m\ (CH_2CH_2O)_n]\text{-}X$ are generally connected at the ends of the backbone.

In the backbone, the moieties A are preferably ester moieties. $R^1$ moieties are essentially 1,4-phenylene moieties. $R^2$ moieties are essentially ethylene moieties, or substituted ethylene moieties having $C_1$-$C_4$ alkyl or alkoxy substituents. Suitable ethylene or substituted ethylene moieties include ethylene, 1,2-propylene, 1,2-butylene, 1,2-hexylene, 3-methoxy-1,2-propylene and mixtures thereof. Preferably, the $R^2$ moieties are essentially ethylene moieties, 1,2-propylene moieties or mixtures thereof. Inclusion of a greater percentage of ethylene moieties tends to improve the soil release activity of the compounds. Inclusion of a greater percentage of 1,2-propylene moieties tends to improve the water solubility of the compounds. Preferred $R^3$ moieties are those which are substituted 1,3-phenylene moieties. The $R^4$ moieties are $R^1$ or $R^3$ moieties, or mixtures thereof.

The moieties $-(R^5O)-$ and $-(CH_2CH_2O)-$ of the end caps $[(R^5O)_m(CH_2CH_2O)_n]$ and $[(OCH_2CH_2)_n(OR^5)_m]$ can be mixed together or preferably form blocks of $-(R^5O)-$ and $-(CH_2CH_2O)-$ moieties. Preferably, the blocks of $-(R^5O)-$ moieties are located next to the backbone. When $R^5$ is the moiety $-R^2\text{-}A\text{-}R^6-$, m is 1; also, the moiety $-R^2\text{-}A\text{-}R^6-$ is preferably located next to the backbone of the compound.

For $R^5$, the preferred $C_3$-$C_4$ alkylene is $C_3H_6$ (propylene); when $R^5$ is $C_3$-$C_4$ alkylene, m is preferably from 0 to 5 and is most preferably 0. $R^6$ is preferably methylene or 1,4-phenylene.

The moiety -($CH_2CH_2O$)- preferably comprises at least 75% by weight of the moiety [$(R^5O)_m(CH_2CH_2O)_n$] and most preferably 100% by weight (m is 0). X can be H, $C_1$-$C_4$ alkyl or

wherein $R^7$ is $C_1$-$C_4$ alkyl. X is preferably methyl or ethyl, and most preferably methyl.

The value for each n is at least 6, but is preferably at least 10. The value for each n usually ranges from 12 to 113. Typically, the value for each n is in the range of from 12 to 43.

It is taught in EP185427, both in the general disclosure and from the examples that the preferred polymers do not have the group $R^5O$ present.

Similar disclosures are made in EP 199403 and EP 629690 and more recently it is repeated in EP 2 135 931.

EP 1 661 933 (Sasol) describe amphiphilic non-ionic oligoesters that have soil release properties after storage in alkaline detergent liquid.

In the exemplary formulae a PO block of up to 10, but preferably 2 to 4 may be adjacent to the mid block. The tested material has 4 PO. The mid block is essentially 1,4 – phenylene and 1,2 propylidene. No mention is made of forming a mid block using 2,3 butane diol or other diols that result in two alkyl substituents on an ethylene backbone.

Despite the large volume of prior art disclosures of soil release polymers based on polyester there remains a need for a polymer, or polymers that combine resistance to hydrolysis in alkaline liquids with good soil release performance on polyester fabrics.

## SUMMARY OF THE INVENTION

According to a first aspect of the present invention thereis provided a linear soil release polymer with the formula (I):

$$X\text{-}[(EO)_q\text{-block-}(PO)_p]\text{-}[(A\text{-}R^1\text{-}A\text{-}R^2)_n]\text{-}A\text{-}R^1\text{-}A\text{-}[(PO)_p\text{-block-}(EO)_q] - X \quad (I)$$

where the linking moieties A are esters,

where the $R^1$ moieties are 1,4 – phenylene moities ,

where the $R^2$ moieties are substituted ethylene moieties having $C_{1\text{-}4}$ alkyl substituents and the $R^2$ moieties comprise substituted ethylene moieties derived from the condensation of 2,3 butane diol,

where the EO blocks are 100% ethylene oxide ($CH_2CH_2O$),

where the PO blocks are 100% propylene oxide ($CH_2CH(CH_3)O$),

where p is a number from 2 to 50, preferably from 5 to 45, 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 and preferably q is at least 1.5 times as large as p;

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

where n is a number from 2 to 16.

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 and q. Since p and q are made by anionic polymerisation routes (resulting in polymer blocks with very discreet block lengths) as against the mid block made by polycondensation routes (resulting in polymer blocks with more polydisperse block lengths).

In formula (I) the moiety $[(A\text{-}R^1\text{-}A\text{-}R^2)_n]\text{-}A\text{-}R^1\text{-}A$- forms the polymer mid block or backbone and, apart from the choice of $R^2$, may be substantially identical to known polymer mid blocks for soil release polymers. These are 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 nearest to the PO blocks are esters. Without wishing to 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 mid block which immediately cleaves the functional EO end block from the mid block, fabric substantive, part of the polymer, if it occurs. This cleaving 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.

According to a second aspect of the invention there is provided an alkaline detergent liquid comprising at least 10 wt% non soap surfactant and at least 1 wt% of the soil release polymer according to the first aspect of the invention, preferably the liquid has an undiluted pH of at least 7.4, more preferably at least

7.8. To obtain the benefit of the improved hydrolytic stability it is preferable that the alkaline detergent liquid has an undiluted pH of at most 9, preferably at most 8.4, even at most 8.2. The liquid may comprise at least 1 wt% triethanolamine.

## DETAILED DESCRIPTION OF THE INVENTION

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

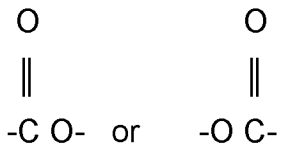
The invention provides a stable high performance soil release polymer suitable for incorporation in alkaline concentrated detergent liquids, even in the presence of triethanolamine, and having the formula (I):

$$X\text{-}[(EO)_q\text{-block-}(PO)_p]\text{-}[(A\text{-}R^1\text{-}A\text{-}R^2)_n\text{-}A\text{-}R^1\text{-}A\text{-}[(PO)_p\text{-block-}(EO)_q]\text{-}X \quad (I)$$

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

### Mid block or backbone

The linking moieties A are esters. In the polymer structure such an ester may be formed either way around and it may thus take the form of the moiety:



The $R^1$ moieties comprise 1,4-phenylene moieties.

The $R^2$ moieties are substituted ethylene moieties having $C_{1-4}$ alkyl substituents. A preferred substituted ethylene moiety is a mixture of 1,2 propylene which is derived from the condensation of 1,2 propane diol, and 2,3 butylene which is derived from the condensation of 2,3 butane diol.

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 compounds of the present invention to have sufficient polyester substantivity. The maximum value for n is generally determined by the process by which the compound is made, but can range up to 26, i.e. the soil release agents of the present invention are oligomers or low molecular weight polymers. 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.

End block

The polymer may have two end blocks, one on each end, or a single end block on one or the other end. The end block, when present, will link to a mid block ester moiety. The formulae given throughout the claims and description should be interpreted to include polymers having one or other variant of the single end block and polymers having two end blocks.

To obtain the combination of hydrolytic stability and soil release properties when stored in and delivered from an alkaline liquid the end block PO groups are arranged in blocks adjacent to the end ester moieties of the mid block 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 used. A preferred EO block is made using a capped PEG such as methyl capped PEG, or mPEG. The molecular weight Mw of the mPEG may be in the range 700 to 3000 Da.

The PO block consists of 100%, by number, PO units. The number, p, of units in the PO block is from 2 to 50, preferably from 5 to 45, 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, preferably the EO block has at least 1.5 times the number of moles or units (q) 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.

q is at least 6, but 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.

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.

Preferred compounds of the present invention are polymers having the formula (II):

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

wherein the $R^1$ moieties are all 1,4-phenylene moieties; the $R^2$ 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.

The block polyesters of formula II 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.
Most preferably, in the formula (II), in the polymer according to the present invention p is from 11 to 50 and q is from 18 to 60.

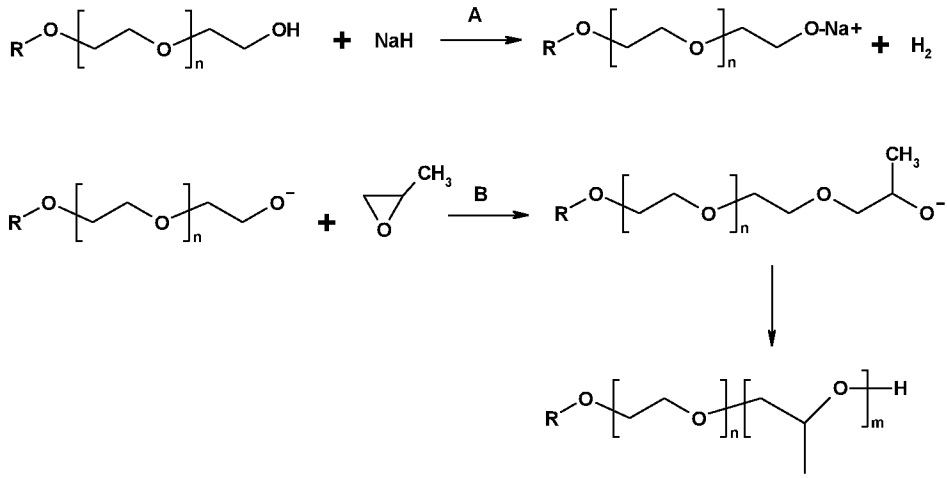
The soil release polymers of the present invention can be prepared by methods known to the person skilled in the art. US 4,702, 857 and US 4,711,730 describe a method of synthesis that may be adapted to produce the block polyesters of the present invention.

In 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 copolymers used for the end blocks is described below.

Manufacture of the end blocks

In a preferred process the 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, B. Trathnigg, C.O. Kappe, *Macromol. Chem. Phys.*, **2007**, 208, 2510-2524.

The reaction scheme is set forth below:




Reaction A: Sodium hydride reacts with PEG to yield activated chain ends.
Reaction B: The addition of PO proceeds at the ends of the PEG chains to form a block of PO.

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.

Mid block manufacture

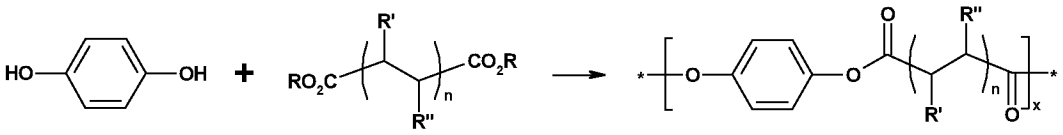
It is preferred to manufacture the mid block by condensation of methyl esters of terephthalic acid with the appropriate aliphatic diol, preferably using an excess of one of them as set forth in more detail in the following examples. If the dicarboxylic acid is used in alkyl ester form, the reaction is 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.

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.

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.

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

However, it is also possible to obtain a very similar polyester recognition motif with the ester moieties reversed if the starting materials are aliphatic biscarboxylic 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).



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.

The polymers of the present invention are suitable for incorporation into alkaline liquid detergent compositions. The polymers may be incorporated into detergent compositions in amounts of from 0.3 to 15 wt%, preferably from 1 to 10 wt%, most preferably from 1.5 to 7 wt%.

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

EXAMPLES

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

Soil 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 |
| Neodol 25-7 | is nonionic (ex Shell) a C12-15 alcohol with 7 moles EO |
| 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 |
| EPEI | is Sokalan ® HP20 – PEI(600) 20EO ex BASF |
| Perfume | is free oil perfume |

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 |
| Neodol 25-7 | 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 |
| Soil release polymer | 3.75 | 2.14 |
| Perfume | 2.43 | 1.39 |
| pH adjustment hole* | 10.00 | 10.00 |
| TOTAL | 100.00 | 100.00 |

* comprising NaOH (added from 47% solution) 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.

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, say, 50ppm the actual level used after storage would have been lower due to polymer degradation during storage.

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.

Product concentration of composition in table 1 added to the wash liquor was 1.3g/l for Composition A (5x).

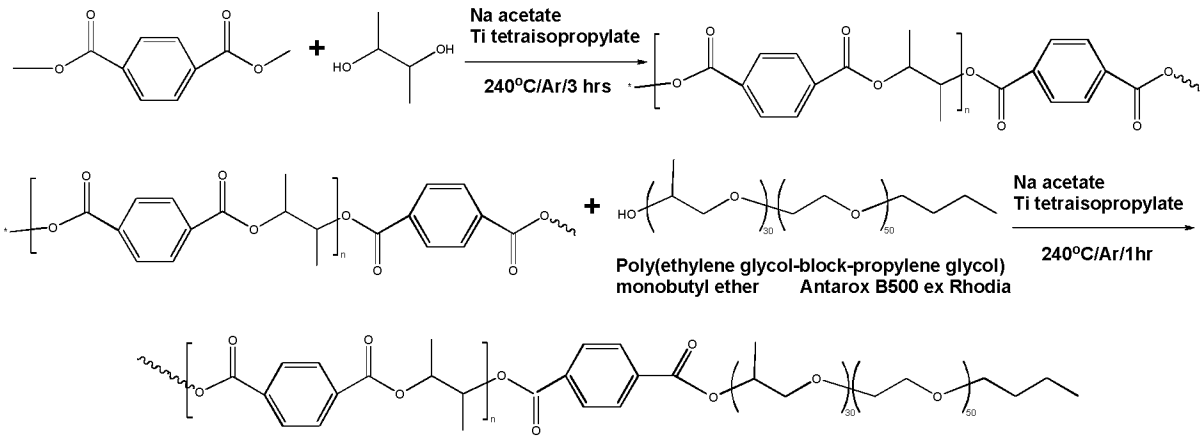
Two 30 minute pre-washes of knitted polyester test pieces were carried out with polyester and cotton ballast such that the total fabric weight was 40g and the ratio of cotton : polyester was 1:1. After each pre-wash the fabric was rinsed twice (for 20 seconds) in 26°FH water and dried. Fresh ballast 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.

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.

Examples 1 and 2 are two methods for synthesis of SRPs according to the invention. The two stage process of Example 1 is preferred due to the superior properties of the polymer produced.

Example 1 Synthesis of PO block EO end-capped terephthalate/2,3 butandiol polyester SRP using a 2-stage reaction process




Using a 3-necked 100 ml 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 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 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.

$^1$H-NMR ($D_2O$) – Accelerated data in concentrated Laundry liquid Composition B buffered with TEA to pH 8 and held at 60°C for 8 days (using $^1$H-NMR as the polymer stability tracking tool) has shown the polymer of example 1 to be hydrolytically stable.

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

Example 2 - Synthesis of PO block EO end-capped terephthalate/2,3 butandiol polyester using a 1-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 (11.64g, 59.94 mmol), 2,3 butandiol (10.80g, 119.89 mmol) and Antarox B500 (supplied by Rhodia) (11.99g, 5.99 mmol) were weighed into the flask, which also contained a magnetic stirrer bar. To the mixture was also added 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 240°C, which was held for 5 hours. The product was purified by sublimation to remove any residual dimethylterephthalate. Final yield = 19.7g. The product has the same structure as that produced for example 1, subject to the data below.

$^1$H-NMR ($D_2O$) – Accelerated data in concentrated Laundry liquid Composition B buffered with TEA to pH 8 and held at 60°C for 8 days (using $^1$H-NMR as the polymer stability tracking tool) has shown the polymer of example 2 to be hydrolytically stable.

TD-SEC (THF) - av $M_n$ = 3,700; av $M_w$ = 4,150; av PD = 1.12

Example 3 - Scale up of Example 1

To produce the polymer of example 3 we used the same synthetic procedure as for Example1 with the following:

DMT = 29.1g, 149.86 mmol

2,3-Butanol = 27.0g, 299.72 mmol

Antarox = 29.98g, 14.99 mmol

Sodium acetate = 2 small spatulas

Titanium isopropoxide (1st stage) = 3 drops

Titanium isopropoxide (2nd stage) = 3 drops

Yield = 54.2g

The polymer product of Example 3 was shown to have the structure shown for example 1. The polymer of example 3 was characterised:

TD-SEC (THF) - av $M_n$ = 2,700, av $M_w$ = 3,100; av PD = 1.14

The polymer was included in concentrated Laundry liquid Composition B buffered with TEA to pH 8.1 and held at 60°C for 8 days. Using $^1$H-NMR as the polymer stability tracking tool showed that this polymer was stable in alkaline detergent liquid.

Example 4

The polymer produced in Example 3 was used in Composition A buffered to pH 6.7 in a full scale wash test in a Miele front loading automatic washing machine dosed at 1.3 g/L product (50ppm polymer). Controls were the same composition without polymer (water balance) (Table 2) and the same composition using the prior art Texcare® SRN170 polymer (Table 3).

Table 2

| Prewash fatty stain data with base as the control | | | |
|---|---|---|---|
| **Stain** | **Delta R** | **LSD95p** | **LSD95n** |
| MakeUp2-CSS3-kPES | 0.06 | 0.63 | -0.63 |
| YellowCurry-CSS3-kPES | 0.25 | 0.57 | -0.57 |
| W30D-PS16 | 0.29 | 0.43 | -0.43 |
| W30C-PS16 | 0.77 | 1.42 | -1.42 |
| C09-PS16 | 0.97 | 1.18 | -1.18 |
| BlackShoePolish-CSS3-kPES | 0.98 | 3.05 | -3.05 |
| W10M-PS16 | 1.02 | 1.55 | -1.55 |
| W20D-PS16 | 1.57 | 2.30 | -2.30 |
| E101-PS16 | 2.15 | 3.29 | -3.29 |
| GreenCurry-CSS3-kPES | 3.39 | 0.59 | -0.59 |
| Lipstick-CSS3-kPES | 4.72 | 1.79 | -1.79 |
| MechanicalGrease-CSS3-kPES | 5.40 | 2.37 | -2.37 |
| TomatoSunflowerOil-CSS3-kPES | 7.55 | 1.69 | -1.69 |
| DendeOil-CSS3-kPES | 7.65 | 0.52 | -0.52 |
| CookingOilVioletDye-CSS3-kPES | 9.28 | 0.56 | -0.56 |
| RedCurry-CSS3-kPES | 11.92 | 1.27 | -1.27 |
| RaguSunflowerOil-CSS3-kPES | 13.43 | 2.12 | -2.12 |
| LardVioletDye-CSS3-kPES | 15.85 | 3.14 | -3.14 |
| DirtyMotorOil-CSS3-kPES | 17.58 | 1.23 | -1.23 |
| RedPepperOilWater-CSS3-kPES | 23.66 | 1.46 | -1.46 |

Table 3

| Prewash fatty stain data with Texcare®SRN170 as the control | | | |
|---|---|---|---|
| **Stain** | **Delta R** | **LSD95p** | **LSD95n** |
| BlackShoePolish-CSS3-kPES | -8.07 | 3.05 | -3.05 |
| Lipstick-CSS3-kPES | -6.83 | 1.79 | -1.79 |
| DirtyMotorOil-CSS3-kPES | -4.43 | 1.23 | -1.23 |
| GreenCurry-CSS3-kPES | -0.46 | 0.59 | -0.59 |
| W20D-PS16 | -0.39 | 2.30 | -2.30 |
| W30C-PS16 | -0.32 | 1.42 | -1.42 |
| RaguSunflowerOil-CSS3-kPES | -0.25 | 2.12 | -2.12 |
| CookingOilVioletDye-CSS3-kPES | -0.09 | 0.56 | -0.56 |
| TomatoSunflowerOil-CSS3-kPES | -0.08 | 1.69 | -1.69 |
| YellowCurry-CSS3-kPES | -0.05 | 0.57 | -0.57 |
| DendeOil-CSS3-kPES | -0.03 | 0.52 | -0.52 |
| RedPepperOilWater-CSS3-kPES | -0.01 | 1.46 | -1.46 |
| W10M-PS16 | 0.00 | 1.55 | -1.55 |
| MakeUp2-CSS3-kPES | 0.00 | 0.63 | -0.63 |
| E101-PS16 | 0.03 | 3.29 | -3.29 |
| W30D-PS16 | 0.04 | 0.43 | -0.43 |
| RedCurry-CSS3-kPES | 0.05 | 1.27 | -1.27 |
| LardVioletDye-CSS3-kPES | 0.17 | 3.14 | -3.14 |
| C09-PS16 | 0.38 | 1.18 | -1.18 |
| MechanicalGrease-CSS3-kPES | 0.43 | 2.37 | -2.37 |

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## Claims

1. A linear soil release polymer with the formula (I):

$$X\text{-}[(EO)_q\text{-block-}(PO)_p]\text{-}[(A\text{-}R^1\text{-}A\text{-}R^2)_n]\text{-}A\text{-}R^1\text{-}A\text{-}[(PO)_p\text{-block-}(EO)_q] - X \quad (I)$$

where the linking moieties A are esters,
where the $R^1$ moieties are 1,4 – phenylene moities ,
where the $R^2$ moieties are substituted ethylene moieties having $C_{1\text{-}4}$ alkyl substituents and the $R^2$ moieties comprise substituted ethylene moieties derived from the condensation of 2,3 butane diol,

where the EO blocks are 100% ethylene oxide ($CH_2CH_2O$),

where the PO blocks are 100% propylene oxide ($CH_2CH(CH_3)O$),

where p is a number from 2 to 50, preferably from 5 to 45, 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 and preferably q is at least 1.5 times as large as p;

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

where n is a number from 2 to 16.

2. A polymer according to claim 1 wherein the $R^2$ moieties consist entirely of substituted ethylene moieties, selected from 1,2 propylene which is derived from the condensation of 1,2 propane diol and 2,3 butylene which is derived from the condensation of 2,3 butane diol.

3. A polymer according to any preceding claim where n is a number from 3 to 16, preferably from 4 to 8.

4. A polymer according to any preceding claim in which the block EO is 100% EO, capped with a methyl group and formed from methyl capped PEG or mPEG with molecular weight Mw of the mPEG in the range 700 to 3000 Da.

5. A polymer according to any preceding claim wherein the EO block has more units than the PO block, preferably the EO block has at least 1.5 times the number of moles or units as the PO block.

6. A polymer according to any preceding claim with a molecular weight Mw from 1000 to 20 000, preferably from 1500 to 10 000.

7. A polymer according to any preceding claim with a polydispersity less than 3.

8. An alkaline detergent liquid comprising at least 10 wt% non soap surfactant and at least 1 wt% of the soil release polymer of any preceding claim, preferably the liquid has an undiluted pH of at least 7.4, more preferably at least 7.8.

9. An alkaline detergent liquid according to claim 8 comprising at least 10 wt% non soap surfactant and at least 1 wt% of the soil release polymer, wherein

the liquid has an undiluted pH of at most 9, preferably at most 8.4, even at most 8.2.

10. An alkaline detergent liquid according to claim 8 or claim 9 further comprising at least 1 wt% triethanolamine.

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/050941

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G63/66 C11D3/00
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. |
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| X | EP 0 220 156 A2 (PROCTER & GAMBLE [US])<br>29 April 1987 (1987-04-29)<br>claims 1,2,4<br>----- | 1-10 |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"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

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 29 March 2012 | 05/04/2012 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Niaounakis, Michael |

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