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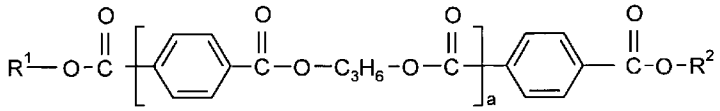
(54) Title: POLYESTERS



(I)

(57) Abstract: Polyesters according to the following formula (I) are described formula (I) wherein R^1 and R^2 independently of one another are $X-(OC_2H_4)_n-(OC_3H_6)_m$ wherein X is C_{1-4} alkyl, the $-(OC_2H_4)$ groups and the -(OC3H6) groups are arranged blockwise and the block consisting of the $-(OC_3H_6)$ groups is bound to a COO group or are $HO-(C_3H_6)$, n is based on a molar average a number of from 12 to 120, m is based on a molar average a number of from 1 to 10, and a is based on a molar average a number of from 4 to 9. The inventive polyesters have an advantageous stability in alkaline environment, possess a beneficial solubility and advantageously are clearly soluble in alkaline compositions such as alkaline heavy duty washing liquids and also possess advantageous soil release properties.

Polyesters

The invention relates to new polyesters and a process for their preparation. The polyesters are e.g. useful as soil release agents in laundry detergent and fabric care products.

The term "soil release agent" is applied to materials that modify the fabric surface minimizing the subsequent soiling and making the cleaning of the fabric easier on further washing cycles.

Laundry detergent compositions containing polyesters have been widely disclosed in the art.

DE 10 2007 013 217 A1 and WO 2007/079850 A1 disclose anionic polyesters that may be used as soil release components in washing and cleaning compositions.

DE 10 2007 005 532 A1 describes aqueous formulations of soil release oligo- and polyesters with a low viscosity. The aqueous formulations may e.g. be used in washing and cleaning compositions.

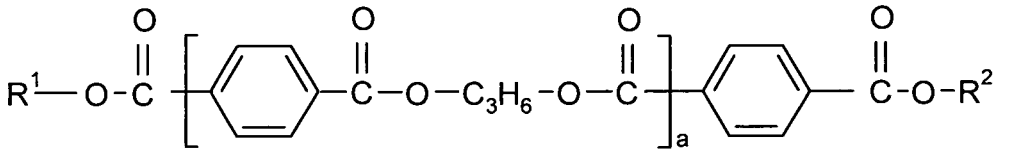
EP 0 964 015 A1 discloses soil release oligoesters that may be used as soil release polymers in detergents and that are prepared using polyols comprising 3 to 6 hydroxyl groups.

EP 1 661 933 A1 is directed to at room temperature flowable, amphiphilic and nonionic oligoesters prepared by reacting dicarboxylic acid compounds, polyol compounds and water-soluble alkylene oxide adducts and their use as additive in washing and cleaning compositions.

However, many of the polyesters described in the prior art are in need of improved stability in an alkaline environment. Especially in alkaline heavy duty washing liquids polyesters often show turbidity upon incorporation and by alkaline hydrolysis thereby also losing soil release power.

Therefore, it was the object of the present invention to provide new polyesters which have an advantageous stability in alkaline environment, possess a beneficial solubility and advantageously are clearly soluble in alkaline compositions such as alkaline heavy duty washing liquids and also possess advantageous soil release properties.

Surprisingly this object is solved by polyesters according to the following formula (I)



(I)

wherein

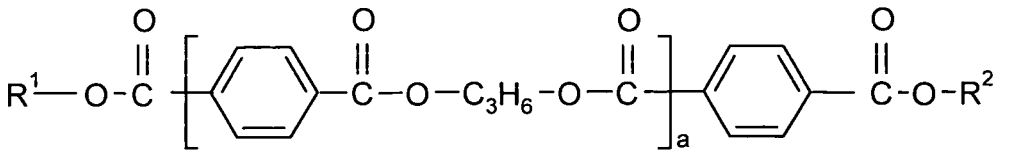
R^1 and R^2 independently of one another are $X-(OC_2H_4)_n-(OC_3H_6)_m$ wherein X is C_{1-4} alkyl and preferably methyl, the $-(OC_2H_4)$ groups and the $-(OC_3H_6)$ groups are arranged blockwise and the block consisting of the $-(OC_3H_6)$ groups is bound to a COO group or are $HO-(C_3H_6)$, and preferably are independently of one another $X-(OC_2H_4)_n-(OC_3H_6)_m$,

n is based on a molar average a number of from 12 to 120 and preferably of from 40 to 50,

m is based on a molar average a number of from 1 to 10 and preferably of from 1 to 7, and

a is based on a molar average a number of from 4 to 9.

Therefore, a subject matter of the present invention are polyesters according to the following formula (I)



(I)

wherein

R^1 and R^2 independently of one another are $X-(OC_2H_4)_n-(OC_3H_6)_m$ wherein X is C_{1-4} alkyl and preferably methyl, the $-(OC_2H_4)$ groups and the $-(OC_3H_6)$ groups are arranged blockwise and the block consisting of the $-(OC_3H_6)$ groups is bound to a COO group or are $HO-(C_3H_6)$, and preferably are independently of one another $X-(OC_2H_4)_n-(OC_3H_6)_m$,

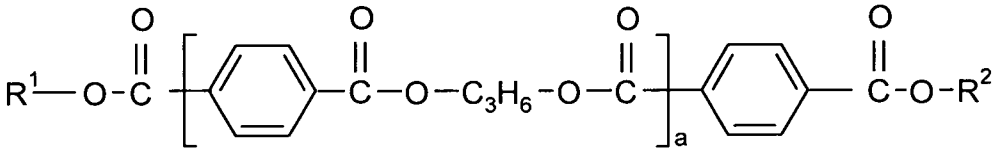
n is based on a molar average a number of from 12 to 120 and preferably of from 40 to 50,

m is based on a molar average a number of from 1 to 10 and preferably of from 1 to 7, and

a is based on a molar average a number of from 4 to 9.

In the inventive polyesters group "X" is C_{1-4} alkyl and preferably is methyl.

In a preferred embodiment of the invention the inventive polyesters are according to the following formula (I)



(I)

wherein

R^1 and R^2 independently of one another are $H_3C-(OC_2H_4)_n-(OC_3H_6)_m$ wherein the $-(OC_2H_4)$ groups and the $-(OC_3H_6)$ groups are arranged blockwise and the block consisting of the $-(OC_3H_6)$ groups is bound to a COO group or are $HO-(C_3H_6)$, and preferably are independently of one another $H_3C-(OC_2H_4)_n-(OC_3H_6)_m$,

n is based on a molar average a number of from 40 to 50,

m is based on a molar average a number of from 1 to 7, and

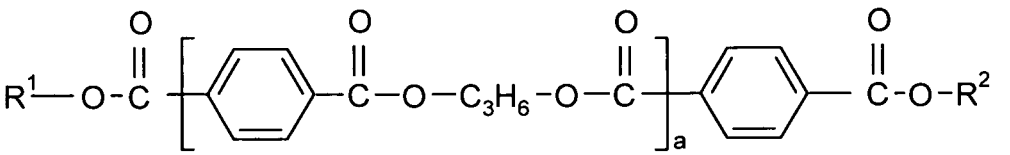
a is based on a molar average a number of from 4 to 9.

In the inventive polyesters variable “a” based on a molar average preferably is a number of from 5 to 8 and more preferably is a number of from 6 to 7.

In the inventive polyesters variable "m" based on a molar average preferably is a number of from 2 to 5.

In the inventive polyesters variable "n" based on a molar average preferably is a number of from 43 to 47, more preferably is a number of from 44 to 46 and even more preferably is 45.

In one particularly preferred embodiment of the invention the inventive polyesters are according to the following formula (I)



(I)

wherein

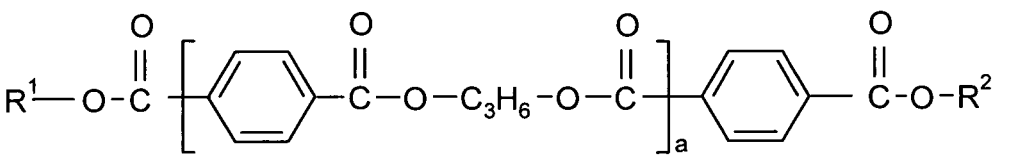
R^1 and R^2 independently of one another are $H_3C-(OC_2H_4)_n-(OC_3H_6)_m$ wherein the $-(OC_2H_4)$ groups and the $-(OC_3H_6)$ groups are arranged blockwise and the block consisting of the $-(OC_3H_6)$ groups is bound to a COO group,

n is based on a molar average a number of from 44 to 46,

m is based on a molar average 2, and

a is based on a molar average a number of from 5 to 8.

Among these polyesters the polyesters according to formula (I)



(I)

wherein

R^1 and R^2 independently of one another are $H_3C-(OC_2H_4)_n-(OC_3H_6)_m$ wherein the $-(OC_2H_4)$ groups and the $-(OC_3H_6)$ groups are arranged blockwise

and the block consisting of the -(OC_3H_6) groups is bound to a COO group,

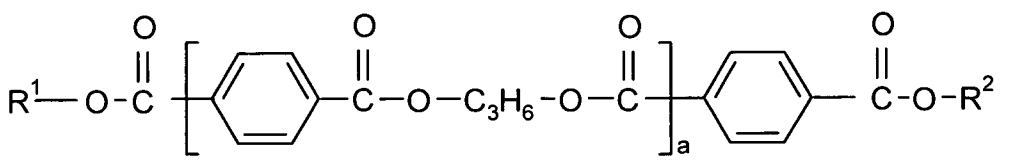
n is based on a molar average 45,

m is based on a molar average 2, and

a is based on a molar average a number of from 6 to 7

are especially preferred.

In another particularly preferred embodiment of the invention the inventive polyesters are according to the following formula (I)



(I)

wherein

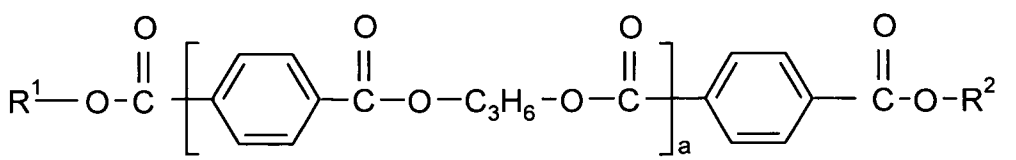
R^1 and R^2 independently of one another are H_3C-(OC_2H_4)$_n$-(OC_3H_6)$_m$ wherein the -(OC_2H_4) groups and the -(OC_3H_6) groups are arranged blockwise and the block consisting of the -(OC_3H_6) groups is bound to a COO group,

n is based on a molar average a number of from 44 to 46,

m is based on a molar average 5, and

a is based on a molar average a number of from 5 to 8.

Among these polyesters the polyesters according to formula (I)



(I)

wherein

R^1 and R^2 independently of one another are H_3C-(OC_2H_4)$_n$-(OC_3H_6)$_m$ wherein the -(OC_2H_4) groups and the -(OC_3H_6) groups are arranged blockwise and the block consisting of the -(OC_3H_6) groups is bound to a COO group,

n is based on a molar average 45,

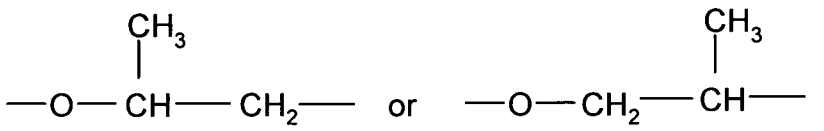
m is based on a molar average 5, and

a is based on a molar average a number of from 6 to 7

are especially preferred.

The groups -O-C_2H_4- in the structural units "X-$(OC_2H_4)_n$-$(OC_3H_6)_m$" or "H_3C-$(OC_2H_4)_n$-$(OC_3H_6)_m$" are of the formula -O-CH_2-CH_2-.

The groups -O-C_3H_6- in the structural units indexed with "a", in the structural units "X-$(OC_2H_4)_n$-$(OC_3H_6)_m$" or "H_3C-$(OC_2H_4)_n$-$(OC_3H_6)_m$" and in the structural units HO-(C_3H_6) are of the formula -O-$CH(CH_3)$-CH_2- or -O-CH_2-$CH(CH_3)$-, i.e. are of the formula



The inventive polyesters may be used in substance, i.e. as such, but may also be provided as aqueous solutions. The aqueous solutions are e.g. beneficial with respect to their handling and e.g. the metering of the inventive polyester is very easy. Preferably, the aqueous solutions comprise the inventive polyesters in an amount of from 25 to 70 weight-% based on the total mass of the aqueous solution.

Therefore, a further subject matter of the invention is an aqueous solution comprising an inventive polyester in an amount of from 25 to 70 weight-% based on the total mass of the aqueous solution. These aqueous solutions may even consist of the inventive polyester and water.

The inventive polyesters may advantageously be used in washing or laundry detergent compositions. Besides the inventive polyesters these washing or laundry detergent compositions may comprise one or more optional ingredients, e.g. they may comprise conventional ingredients commonly used in laundry detergent

compositions. Examples of optional ingredients include, but are not limited to builders, surfactants, bleaching agents, bleach active compounds, bleach activators, bleach catalysts, photobleaches, dye transfer inhibitors, color protection agents, anti-redeposition agents, dispersing agents, fabric softening and antistatic agents, fluorescent whitening agents, enzymes, enzyme stabilizing agents, foam regulators, defoamers, malodour reducers, preservatives, disinfecting agents, hydrotopes, fibre lubricants, anti-shrinkage agents, buffers, fragrances, processing aids, colorants, dyes, pigments, anti-corrosion agents, fillers, stabilizers and other conventional ingredients for washing or laundry detergent compositions.

The inventive polyesters have an advantageous stability in alkaline environment, possess a beneficial solubility and advantageously are clearly soluble in alkaline compositions such as heavy duty washing liquids and also possess advantageous soil release properties. In washing or laundry detergent compositions they result in a beneficial washing performance, in particular also after storage. Furthermore, the inventive polyesters possess advantageous foam suppressing properties. This is not only advantageous when the washing or laundry detergent compositions comprising the inventive polyesters are applied but also advantageously reduces foaming during handling of the inventive polyesters.

The inventive polyesters may advantageously be prepared by a process which comprises heating dimethyl terephthalate (DMT), 1,2-propylene glycol (PG), and $X-(OC_2H_4)_n-(OC_3H_6)_m-OH$, wherein X is C_{1-4} alkyl and preferably methyl, the $-(OC_2H_4)$ groups and the $-(OC_3H_6)$ groups are arranged blockwise and the block consisting of the $-(OC_3H_6)$ groups is bound to the hydroxyl group -OH and n and m are as defined for the inventive polyesters, with the addition of a catalyst, to temperatures of from 160 to 220 °C, firstly at atmospheric pressure, and then continuing the reaction under reduced pressure at temperatures of from 160 to 240 °C.

Therefore, a further subject matter of the invention is a process for the preparation of the inventive polyesters which comprises heating dimethyl terephthalate (DMT), 1,2-propylene glycol (PG), and $X-(OC_2H_4)_n-(OC_3H_6)_m-OH$, wherein X is C_{1-4} alkyl

and preferably methyl, the -(OC_2H_4) groups and the -(OC_3H_6) groups are arranged blockwise and the block consisting of the -(OC_3H_6) groups is bound to the hydroxyl group -OH and n and m are as defined for the inventive polyesters, with the addition of a catalyst, to temperatures of from 160 to 220°C, firstly at atmospheric pressure, and then continuing the reaction under reduced pressure at temperatures of from 160 to 240 °C.

Reduced pressure preferably means a pressure of from 0.1 to 900 mbar and more preferably a pressure of from 0.5 to 500 mbar.

In a preferred embodiment of the invention the inventive process is characterized in that

a) dimethyl therephthalate, 1,2-propylene glycol, X-$(OC_2H_4)_n$-$(OC_3H_6)_m$-OH, wherein X is C_{1-4} alkyl and preferably methyl, and a catalyst are added to a reaction vessel, heated under inert gas, preferably nitrogen, to a temperature of from 160 °C to 220 °C to remove methanol and then pressure is reduced to below atmospheric pressure, preferably to a pressure of from 200 to 900 mbar and more preferably to a pressure of from 400 to 600 mbar for completion of the transesterification, and

b) in a second step the reaction is continued at a temperature of from 210 °C to 240 °C and at a pressure of from 0.1 to 10 mbar and preferably of from 0.5 to 5 mbar to form the polyester.

Sodium acetate (NaOAc) and tetraisopropyl orthotitanate (IPT) is preferably used as the catalyst system in the inventive process.

The examples below are intended to illustrate the invention in detail without, however, limiting it thereto. Unless explicitly stated otherwise, all percentages given are percentages by weight (% by wt. or wt.-%).

General procedure for the preparation of the polyesters of the Examples

The polyester synthesis is carried out by the reaction of dimethyl terephthalate (DMT), 1,2-propylene glycol (PG), and methyl polyalkyleneglycol using sodium acetate (NaOAc) and tetraisopropyl orthotitanate (IPT) as the catalyst system. The synthesis is a two-step procedure. The first step is a transesterification and the second step is a polycondensation.

Transesterification

Dimethyl terephthalate (DMT), 1,2-propylene glycol (PG), methyl polyalkyleneglycol, sodium acetate (anhydrous) (NaOAc) and tetraisopropyl orthotitanate (IPT) are weighed into a reaction vessel at room temperature.

For the melting process and homogenization, the mixture is heated up to 170 °C for 1 h and then up to 210 °C for a further 1 h sparged by a nitrogen stream. During the transesterification methanol is released from the reaction and is distilled out of the system (distillation temperature < 55 °C). After 2 h at 210 °C nitrogen is switched off and the pressure is reduced to 400 mbar over 3 h.

Polycondenzation

The mixture is heated up to 230 °C. At 230 °C the pressure is reduced to 1 mbar over 160 min. Once the polycondenzation reaction has started, 1,2-propylene glycol is distilled out of the system. The mixture is stirred for 4 h at 230 °C and a pressure of 1 mbar. The reaction mixture is cooled down to 140 - 150 °C. Vacuum is released with nitrogen and the molten polymer is transferred into a glass bottle.

Example I:

Amount [g]	Amount [mol]	Raw Material [Abbreviation]
101.95	0.53	DMT
84.0	1.104	PG
343.5	0.15	H_3C-$(OC_2H_4)_{45}$-$(OC_3H_6)_5$-OH
0.5	0.0061	NaOAc
0.2	0.0007	IPT

An inventive polyester according to formula (I) is obtained wherein

R^1 and R^2 are H_3C-$(OC_2H_4)_n$-$(OC_3H_6)_m$ wherein the -(OC_2H_4) groups and the -(OC_3H_6) groups are arranged blockwise and the block consisting of the -(OC_3H_6) groups is bound to a COO group,

n is based on a molar average 45,

m is based on a molar average 5, and

a is based on a molar average a number of from 6 to 7.

Example II:

Amount [g]	Amount [mol]	Raw Material [Abbreviation]
101.95	0.53	DMT
84.0	1.104	PG
317.4	0.15	H_3C-$(OC_2H_4)_{45}$-$(OC_3H_6)_2$-OH
0.5	0.0061	NaOAc
0.2	0.0007	IPT

An inventive polyester according to formula (I) is obtained wherein

R^1 and R^2 are H_3C-$(OC_2H_4)_n$-$(OC_3H_6)_m$ wherein the -(OC_2H_4) groups and the -(OC_3H_6) groups are arranged blockwise and the block consisting of the -(OC_3H_6) groups is bound to a COO group,

n is based on a molar average 45,

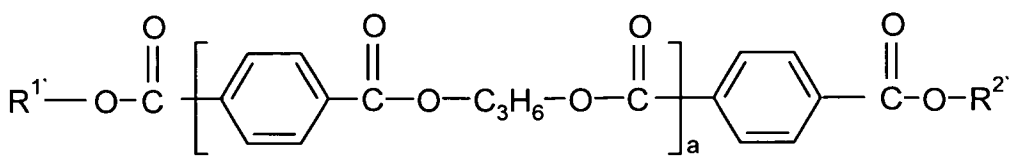
m is based on a molar average 2, and

a is based on a molar average a number of from 6 to 7.

Example III: Comparative Example

Amount [g]	Amount [mol]	Raw Material [Abbreviation]
44.7	0.23	DMT
38	0.50	PG
301.1	0.14	H_3C-$(OC_2H_4)_{45}$-$(OC_3H_6)_2$-OH
0.5	0.0061	NaOAc
0.2	0.0007	IPT

A comparative polyester of formula (I′) is obtained



(I′)

wherein

$R^{1'}$ and $R^{2'}$ are H_3C-$(OC_2H_4)_{n'}$-$(OC_3H_6)_{m'}$ wherein the -(OC_2H_4) groups and the -(OC_3H_6) groups are arranged blockwise and the block consisting of the -(OC_3H_6) groups is bound to a COO group,

n` based on a molar average is 45,

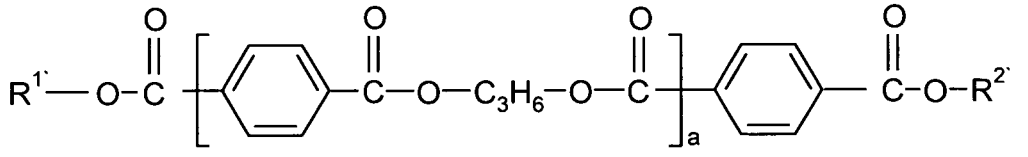
m` based on a molar average is 2, and

a is based on a molar average a number of from 2 to 3.

Example IV: Comparative Example

Amount [g]	Amount [mol]	Raw Material [Abbreviation]
101.95	0.53	DMT
84.0	1.1	PG
206.0	0.1	H_3C-$(OC_2H_4)_{45}$-$(OC_3H_6)_2$-OH
0.5	0.0061	NaOAc
0.2	0.0007	IPT

A comparative polyester of formula (I´) is obtained



(I´)

wherein

$R^{1`}$ and $R^{2`}$ are H_3C-$(OC_2H_4)_{n`}$-$(OC_3H_6)_{m`}$ wherein the -(OC_2H_4) groups and the -(OC_3H_6) groups are arranged blockwise and the block consisting of the -(OC_3H_6) groups is bound to a COO group,

n` based on a molar average is 45,

m` based on a molar average is 2, and

a based on a molar average is a number of approximately 10.

Stability test in detergent formulation

1 wt.-% (based on the total weight of the detergent formulation) of the polyesters of Examples I to IV and of the commercially available soil release polymer "TexCare SRN100" was used in a detergent formulation (the composition of the detergent formulations is given in Table A below) and the pH value was set with caustic to pH 8.2. The turbidity of the 5 formulations was determined. The prepared formulations were stored at 60 °C for 8 days. Afterwards, the hydrolysis of the polyesters was determined and compared to the hydrolysis of the commercially available soil release polymer "TexCare SRN100" by GPC analysis. The results are given in Table B below.

TexCare SRN100 is a polyester comprising -OOC-(1,4-phenylene)-COO- structural units and -O-CH_2CH_2-O- structural units.

Table A Detergent formulation

Ingredient	wt.-%
MPG	15.00
TEA	4.18
NI 7EO	7.28
LAS acid	4.85
SLES 3EO	2.42
Empigen® BB	0.86
Prifac 5908	0.86
EPEI	3.14
Perfume	1.39

Polyester (selected from the polyesters of Examples I to IV and TexCare SRN100)	1.00
Demineralized water and NaOH to adjust to pH 8.2	ad 100

Key to ingredients used:

MPG	is mono propylene glycol.
TEA	is triethanolamine.
NI 7EO	is C_{12-15} alcohol ethoxylate 7EO nonionic Neodol® 25-7 (ex Shell Chemicals).
LAS acid	is C_{12-14} linear alkylbenzene sulphonic acid.
SLES 3EO	is sodium lauryl ether sulphate with 3 moles EO.
Empigen® BB	is Cocobetaine ex Huntsman.
Prifac® 5908	is saturated lauric fatty acid ex Croda.
EPEI	is Sokalan HP20 - ethoxylated polyethylene imine cleaning polymer: PEI(600) 20EO ex BASF.
Perfume	is free oil perfume.
TexCare SRN100	is soil release polymer ex Clariant.

Table B Turbidity of formulation comprising polyester and stability of polyester therein

Polyester	Turbidity	Degree of Hydrolysis
TexCare SRN100	clearly soluble	100 %
Example I (inventive)	clearly soluble	45 %
Example II (inventive)	clearly soluble	48 %
Example III (comparative)	clearly soluble	72 %
Example IV (comparative)	turbid	42 %

%-values for polyesters of Examples I to IV in comparison / relation to TexCare SRN100.

Soil Release Test:

The polyesters of Examples I and II were tested for their soil release performance according to the "Dirty-Motor Oil" Test (DMO-Test).

The polyesters of Examples I and II were used in concentrations of 1 wt.-% (based on the total weight of the detergent formulation used) and the formulations were stored according to the stability test. The formulations were those described above for the stability test. As test fabric a white polyester standard fabric (30A) was used. The prewashed fabrics (the fabrics were prewashed with the stored detergent formulations comprising the polyesters of Examples I and II) were soiled with dirty motor oil. After 1h the soiled fabrics were washed again with the stored detergent formulations comprising the polyesters of Examples I and II. The washing conditions for the "prewash" and for the washing procedure after soiling with dirty motor oil were as given in Table C.

Table C Washing conditions

Washing machine	Linitest
Hardness of water	15 °H
Washing temperature	40 °C
Washing time	30 min
Detergent concentration	6 g/L

The washing results obtained for the stored formulations comprising the polyesters of Examples I and II are shown in Table D. Table D also shows the washing result obtained for a detergent formulation comprising 1 wt.-% of TexCare SRN100. The composition of this detergent formulation comprising TexCare SRN100 was as described above for the stability test. In case of TexCare SRN100 the conditions for the "prewash" and for the washing procedure after soiling were similar to the

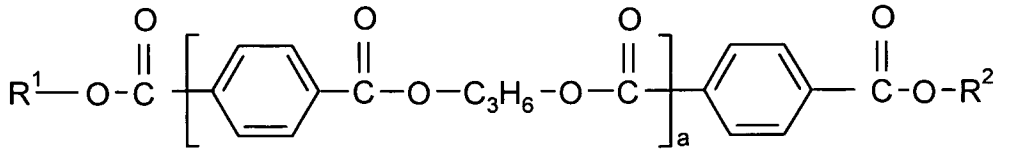
conditions used for the detergent formulations comprising the polyesters of Examples I and II but with the exception that in case of TexCare SRN100 the "prewash" and the washing procedure after the soiling of the fabrics with dirty motor oil was done using "fresh" detergent formulation (no alkaline storage).

Table D Test results (washing performance)

Polyester	results for "fresh" formulation or after storage	Washing Performance
TexCare SRN100	fresh	100 %
Example I	after storage	96 %
Example II	after storage	107 %

Patent Claims:

1. Polyester according to the following formula (I)



(I)

wherein

R^1 and R^2 independently of one another are $X\text{-}(OC_2H_4)_n\text{-}(OC_3H_6)_m$ wherein X is $C_{1\text{-}4}$ alkyl and preferably methyl, the $\text{-}(OC_2H_4)$ groups and the $\text{-}(OC_3H_6)$ groups are arranged blockwise and the block consisting of the $\text{-}(OC_3H_6)$ groups is bound to a COO group or are $HO\text{-}(C_3H_6)$, and preferably are independently of one another $X\text{-}(OC_2H_4)_n\text{-}(OC_3H_6)_m$,

n is based on a molar average a number of from 12 to 120 and preferably of from 40 to 50,

m is based on a molar average a number of from 1 to 10 and preferably of from 1 to 7, and

a is based on a molar average a number of from 4 to 9.

2. Polyester according to claim 1, characterized in that

R^1 and R^2 independently of one another are $H_3C\text{-}(OC_2H_4)_n\text{-}(OC_3H_6)_m$ wherein the $\text{-}(OC_2H_4)$ groups and the $\text{-}(OC_3H_6)$ groups are arranged blockwise and the block consisting of the $\text{-}(OC_3H_6)$ groups is bound to a COO group or are $HO\text{-}(C_3H_6)$, and preferably are independently of one another $H_3C\text{-}(OC_2H_4)_n\text{-}(OC_3H_6)_m$,

n is based on a molar average a number of from 40 to 50,

m is based on a molar average a number of from 1 to 7, and

a is based on a molar average a number of from 4 to 9.

3. Polyester according to claim 1 or 2, characterized in that a based on a molar average is a number of from 5 to 8.

4. Polyester according to claim 3, characterized in that a based on a molar average is a number of from 6 to 7.

5. Polyester according to one or more of claims 1 to 4, characterized in that m based on a molar average is a number of from 2 to 5.

6. Polyester according to one or more of claims 1 to 5, characterized in that n based on a molar average is a number of from 43 to 47.

7. Polyester according to claim 6, characterized in that n based on a molar average is a number of from 44 to 46.

8. Polyester according to claim 7, characterized in that n based on a molar average is 45.

9. Polyester according to one or more of claims 1 to 3 and 5 to 7, characterized in that

R^1 and R^2 independently of one another are $H_3C-(OC_2H_4)_n-(OC_3H_6)_m$ wherein the $-(OC_2H_4)$ groups and the $-(OC_3H_6)$ groups are arranged blockwise and the block consisting of the $-(OC_3H_6)$ groups is bound to a COO group,

n is based on a molar average a number of from 44 to 46,

m is based on a molar average 2, and

a is based on a molar average a number of from 5 to 8.

10. Polyester according to claim 9, characterized in that n based on a molar average is 45, and a based on a molar average is a number of from 6 to 7.

11. Polyester according to one or more of claims 1 to 3 and 5 to 7, characterized in that

R^1 and R^2 independently of one another are $H_3C-(OC_2H_4)_n-(OC_3H_6)_m$ wherein the $-(OC_2H_4)$ groups and the $-(OC_3H_6)$ groups are arranged blockwise

and the block consisting of the -(OC_3H_6) groups is bound to a COO group,

n is based on a molar average a number of from 44 to 46,

m is based on a molar average 5, and

a is based on a molar average a number of from 5 to 8.

12. Polyester according to claim 11, characterized in that n based on a molar average is 45, and a based on a molar average is a number of from 6 to 7.

13. Process for the preparation of a polyester according to one or more of claims 1 to 12, characterized in that it comprises heating dimethyl terephthalate, 1,2-propylene glycol, and X-$(OC_2H_4)_n$-$(OC_3H_6)_m$-OH, wherein X is C_{1-4} alkyl and preferably methyl, the -(OC_2H_4) groups and the -(OC_3H_6) groups are arranged blockwise and the block consisting of the -(OC_3H_6) groups is bound to the hydroxyl group -OH and n and m are as defined in claim 1, with the addition of a catalyst, to temperatures of from 160 to 220 °C, firstly at atmospheric pressure, and then continuing the reaction under reduced pressure at temperatures of from 160 to 240 °C.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/002194

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G63/183 C08G63/672 C11D3/37
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 practicable, 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 1 661 933 A1 (SASOL GERMANY GMBH [DE]) 31 May 2006 (2006-05-31) cited in the application	1-8,13
A	page 4, line 10, paragraph 0048 - page 4, line 20, paragraph 0050; example 1	9-12

X	WO 01/58980 A1 (DU PONT [US]) 16 August 2001 (2001-08-16) page 1, line 8 - page 2, line 2; examples 1-27; table I	1-4

A	EP 0 185 427 A2 (PROCTER & GAMBLE [US]) 25 June 1986 (1986-06-25) page 10, line 31 - page 23, line 9; claim 1; examples Polymer 1, Embodiments III and IV	1-13

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[X] Further documents are listed in the continuation of Box C.

[X] 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 application or patent 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	Date of mailing of the international search report
16 September 2013	20/09/2013

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

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/000158 A1 (RHODIA CHINA CO LTD [CN]; LIU ZHAOQING [CN]; LIN DAOBING [CN]; LI QIAO) 6 January 2011 (2011-01-06) examples 29-31; table 2	1-13
A	WO 2009/138177 A1 (CLARIANT INT LTD [CH]; MORSCHHAEUSER ROMAN [DE]; LANG FRANK-PETER [DE]) 19 November 2009 (2009-11-19) example Polyester 2; table 1	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/002194

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1661933 A1	31-05-2006	DE 102004056785 A1	01-06-2006
		EP 1661933 A1	31-05-2006
WO 0158980 A1	16-08-2001	AR 025381 A1	27-11-2002
		AT 252124 T	15-11-2003
		BR 0017104 A	14-01-2003
		CA 2396465 A1	16-08-2001
		CN 1434835 A	06-08-2003
		DE 60006005 D1	20-11-2003
		DE 60006005 T2	05-08-2004
		EP 1261658 A1	04-12-2002
		ES 2207540 T3	01-06-2004
		JP 4819278 B2	24-11-2011
		JP 2004502793 A	29-01-2004
		MX PA02007737 A	23-10-2002
		TW 520381 B	11-02-2003
		US 6353062 B1	05-03-2002
		WO 0158980 A1	16-08-2001
EP 0185427 A2	25-06-1986	AU 580122 B2	05-01-1989
		AU 5153685 A	26-06-1986
		CA 1315286 C	30-03-1993
		DE 3585505 D1	09-04-1992
		DK 599785 A	22-06-1986
		EP 0185427 A2	25-06-1986
		FI 855117 A	22-06-1986
		GB 2168989 A	02-07-1986
		GR 853077 A1	17-04-1986
		HK 50394 A	27-05-1994
		IE 58784 B1	17-11-1993
		JP 2588507 B2	05-03-1997
		JP 2596409 B2	02-04-1997
		JP H07166192 A	27-06-1995
		JP S61209299 A	17-09-1986
WO 2011000158 A1	06-01-2011	CN 102482405 A	30-05-2012
		EP 2448992 A1	09-05-2012
		US 2012059185 A1	08-03-2012
		WO 2011000158 A1	06-01-2011
WO 2009138177 A1	19-11-2009	DE 102008023803 A1	26-11-2009
		EP 2276824 A1	26-01-2011
		JP 2011521025 A	21-07-2011
		US 2011098418 A1	28-04-2011
		WO 2009138177 A1	19-11-2009