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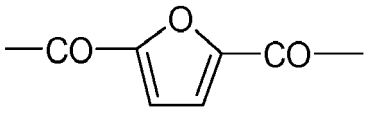
(54) DETERGENT COMPOSITIONS CONTAINING RENEWABLY SOURCED SOIL RELEASE POLYESTERS

(57) A laundry detergent composition comprising
a) one or more polyesters comprising two or more structural units (a1), one or more structural units (a2) and either one or two terminal structural groups (a3)



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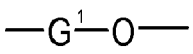

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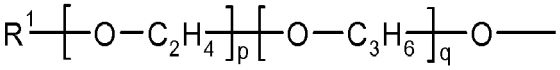

(a3)

wherein
G^1
is one or more (OC_nH_{2n}) with n being a number of from 2 to 10, preferably from 2 to 6 and more preferably (OC_2H_4), (OC_3H_6), (OC4H8) or (OC_6H_{12}),
R^1
is a $C_{1\text{-}30}$ alkyl, preferably $C_{1\text{-}4}$ alkyl and more preferably methyl,
p
is, based on a molar average, a number of from 1 to 200, preferably from 2 to 150 and more preferably from 3 to 120,
q
is, based on a molar average, a number of from 0 to 40, preferably from 0 to 30, more preferably from 0 to 20, and most preferably from 0 to 10, where the (OC_3H_6)- and (OC_2H_4)-groups of the terminal group (a3) may be arranged blockwise, alternatingly, periodically and/or statistically, preferably blockwise and/or statistically, either of the groups (OC_3H_6)- and (OC_2H_4)- can be linked to R^1- and -O, adjacent structural units (a1) are connected by the structural unit (a2), in the case that only one terminal group (a3) is present in the polymer, the other terminal group is selected from the group consisting of OH, OCH_3, and G^1OH and both terminal groups may be only linked to a structural unit (a1)
and

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b) one or more surfactants.

Description

[0001] The invention relates to laundry detergent compositions comprising polyesters based on renewably sourced raw materials. The compositions display good soil release performance compared to compositions containing no soil release polymer.

[0002] Polyester containing fabrics can be surface modified to increase the hydrophilicity of the fabric, which can improve soil removal. Such surface modification can be achieved through direct treatment of the fabric, as outlined for example in GB 1,088,984, or more preferably through deposition of a surface modifying polymer in a washing process, as disclosed for example in US 3,962,152. The renewable soil release finish imparted through washing ensures the continuous protection of the fiber from oily stains.

[0003] The polymers used in these processes typically consist of a polyester midblock with either one or two endblocks of polyethylene glycol, as further outlined in US 3,959,230 and US 3,893,929.

[0004] The use of nonionic soil release agents in liquid laundry detergents is well known in the art. GB 1,466,639, US 4,132,680, US 4,702,857, EP 0 199 403, US 4,711,730, US 4,713,194 and US 4,759,876 disclose aqueous detergent compositions containing soil release polymers.

[0005] Typically the polyesters described in the prior art comprise glycol terephthalate or glycol terephthalate / polyglycol terephthalate co-polymers. This is governed by the fact that most polyesters used in fiber making comprise ethylene terephthalate units. This structural similarity between polyester substrate and soil release polyester is often considered to be a prerequisite for a functioning soil release polymer.

[0006] However, many of the polyesters described in the prior art are difficult to formulate in some laundry detergent formulations due to being too hydrophobic. Moreover, they are based on raw materials sourced from non-renewable feedstocks such as crude oil. There is also a growing consumer perception that "phthalate"-based ingredients may pose a general health risk; polyethylene terephthalate - polyoxyethylene terephthalate polymers would fall into this group. In the interests of the environment and of consumer perception, there is therefore a drive for renewably sourced soil release polymers exhibiting improved cleaning on polyethylene terephthalate and polyethylene terephthalate containing materials, which are nevertheless themselves not based on terephthalates or at least contain reduced amounts of terephthalate units. In the extreme case of complete terephthalate replacement, this would allow the marketing of phthalate-free detergents displaying superior cleaning in the second and subsequent washes. Therefore, alternative structural moieties must be sought, which can be both renewably sourced and result in polymers with sufficient soil release properties.

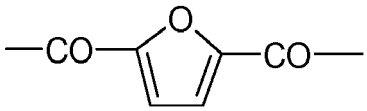
[0007] Besides being based on raw materials sourced from non-renewable feedstocks, polyesters described in the prior art are prepared in high energy demanding processes via direct esterification or transesterification. Due to the limited solubility of terephthalic acid in typical reaction mixtures, elevated temperatures and pressures are required for a direct esterification process. In the case of transesterification, distillates of low boiling alcohols are obtained which need to be disposed of. In the interest of the environment, there is a drive for soil release polymers, which can be prepared by more benign production processes.

[0008] Therefore, the problem to be solved by the present invention was to provide laundry detergent compositions containing polyesters which are based on renewably sourced raw materials and which display good soil release performance and which, due to their more hydrophilic structure, are easy to formulate in liquid laundry detergents.

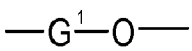
[0009] Surprisingly, it has been found that this problem can be solved by incorporation of one or more polyesters based on 2,5-furandicarboxylic acid into laundry detergent compositions comprising one or more surfactants.

[0010] Therefore, the invention provides laundry detergent compositions comprising:

a) one or more polyesters comprising two or more structural units (a1), one or more structural units (a2) and either one or two terminal groups (a3)



(a1)



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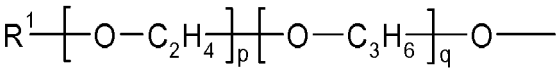


(a3)

wherein

G^1 is one or more of (OC_nH_{2n}) with n being a number of from 2 to 10, preferably from 2 to 6 and more preferably (OC_2H_4), (OC_3H_6), (OC_4H_8) or (OC_6H_{12}),

R^1 is C_{1-30} alkyl, preferably C_{1-4} alkyl and more preferably methyl,

p is, based on a molar average, a number of from 1 to 200, preferably from 2 to 150 and more preferably from 3 to 120,

q is, based on a molar average, a number of from 0 to 40, preferably from 0 to 30, more preferably from 0 to 20, and most preferably from 0 to 10, where

the (OC_3H_6)- and (OC_2H_4)-groups of the terminal group (a3) may be arranged blockwise, alternatingly, periodically and/or statistically, preferably blockwise and/or statistically,

either of the groups (OC_3H_6)- and (OC_2H_4)- can be linked to R^1- and -O, adjacent structural units (a1) are connected by the structural unit (a2), in the case that only one terminal group (a3) is present in the polymer, the other terminal group is selected from the group consisting of OH, OCH_3, and G^1OH, and

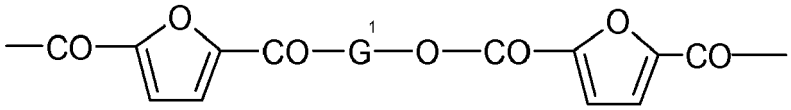
both terminal groups may only be linked to structural unit (a1),

and

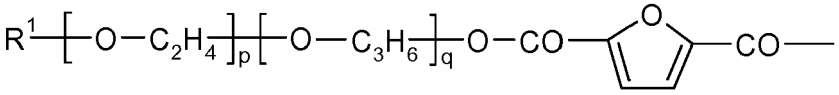
b) one or more surfactants.

[0011] One advantage of the laundry detergent composition of the invention is the high content of renewably based carbon of the polyester a), in cases where the amount of structural units (a1) and (a2) in the polymer is high.

[0012] In the one or more polyesters a) structural units (a1) are linked via structural unit (a2), which results in the following structural entity:



[0013] The terminal group (a3) may not be linked to structural unit (a2) but may be linked to structural unit (a1), which results in the following structural entity:



[0014] In the case that one polyester molecule comprises two or more of structural units (a2), the definition of the group G^1 may vary between these structural units (a2). Furthermore, in the case that one polyester molecule comprises two of the terminal groups (a3) the definition of R^1 may vary in these terminal groups.

[0015] In the case that both p and q of the terminal group (a3) adopt non-zero values, the (OC_3H_6)- and (OC_2H_4)-groups may be arranged blockwise, alternatingly, periodically and/or statistically, preferably blockwise and/or statistically. This means that in one instance the groups (OC_3H_6)- and (OC_2H_4)- may be arranged, for example, in a purely statistically or blockwise form but may also be arranged in a form which could be considered as both statistical and blockwise, e.g. small blocks of (OC_3H_6)- and (OC_2H_4)- arranged in a statistical manner, or in a form where adjacent instances of statistical and blockwise arrangements of the groups (OC_3H_6)- and (OC_2H_4)- exist.

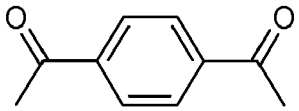
[0016] Both of (OC_3H_6)- and (OC_2H_4)- may be bonded to R^1- and -O. This means for example, that both R^1- and -O may be connected to a (OC_3H_6)- group, they may both be connected to a (OC_2H_4)- group or they may be connected to different groups selected from (OC_2H_4)- and (OC_3H_6)-.

[0017] In the one or more polyesters a) of the invention, the sum of p and q of the terminal group (a3), based on a molar average, is preferably a number of from 1 to 200, more preferably a number of from 5 to 150 and even more preferably a number of from 10 to 75.

[0018] In the one or more polyesters a), R^1 is preferably methyl.

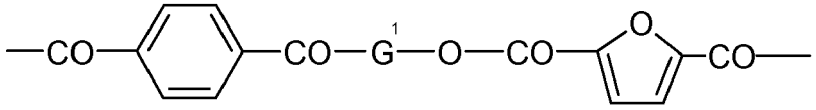
[0019] In the one or more polyesters a), G^1 is preferably (OC_2H_4) or (OC_3H_6).

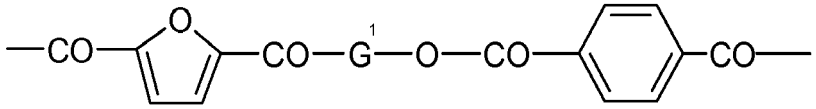
[0020] In one preferred embodiment of the invention, the one or more polyesters a) additionally comprise one or more of the structural unit (a4), which may be linked to structural units (a1) or other structural units (a4) via the structural unit (a2), or directly linked to a terminal group:

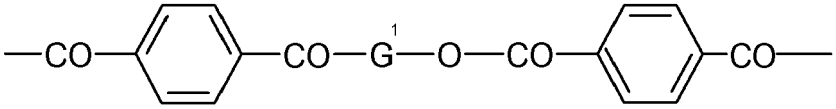


(a4)

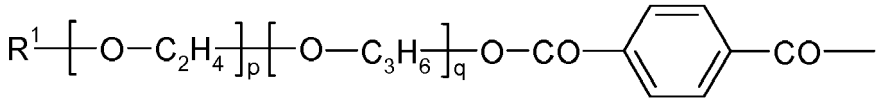
[0021] In the case that the one or more polyesters a) comprise the structural units (a4), these units may be linked to each other or to structural units (a1) via the structural unit (a2), which may result in the following structural entities:







[0022] In addition, the terminal group (a3) may also be linked to the structural unit (a4), which results in the following structural entity:



[0023] The average molecular weight (M_w) of the one or more polyesters a) is preferably in the range of from 2000 to 20000 g/mol.

[0024] The average molecular weight (M_w) of the one or more polyesters a) may be determined by GPC analysis, preferably as detailed in the following: 10 μl of sample is injected onto a PSS Suprema column of dimensions 300 x 8 mm with porosity 30 Å and particle size 10 μm. The detection is monitored at 235 nm on a multiple wavelength detector. The employed eluent is 1.25 g/l of disodium hydrogen phosphate in a 45 / 55 % (v/v) water / acetonitrile mixture. Separations are conducted at a flow-rate of 0.8 ml/min. Quantification is performed by externally calibrating standard samples of different molecular weight polyethylene glycols.

[0025] In the one or more polyesters a), the average number of repeating structural unit (a1) is preferably from 2 to 60, more preferably from 2 to 50, even more preferably from 3 to 40 and most preferably from 4 to 30, and within this preferred embodiment may be 4, 5, 6, 7, 8, 9, 10, 11, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29 or 30.

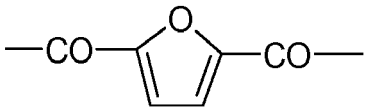
[0026] In the one or more polyesters a), the total amount of the terminal group (a3), based on the total weight of the polyester, is preferably at least 40 wt.-%, more preferably at least 50 wt.-%, even more preferably at least 60 wt.-% and most preferably at least 70 wt.-%.

[0027] In the one or more polyesters a), the total amount of structural units (a1) and (a2) and of the terminal group (a3), based on the total weight of the polyester, is preferably at least 50 wt.-%, more preferably at least 60 wt.-%, even more preferably at least 70 wt.-%, and most preferably at least 80 wt.-%.

[0028] In one preferred embodiment of the invention, the amount of structural unit (a4) in the one or more polyesters a), based on the total weight of the polyester, is preferably at least 0.1 wt.-%, more preferably from 0.1 wt.-% to 50 wt.-%, and even more preferably from 0.5 wt.-% to 40 wt.-%.

[0029] In another preferred embodiment of the invention, the structural units are exclusively selected from the group consisting of repeating structural units (a1) and (a2).

[0030] In one particularly preferred embodiment of the invention, the one or more polyesters a), described in the following and further referred to as "Polyester A", comprise structural units exclusively selected from the group consisting of structural units (a1) and (a2) and the terminal group (a3), where two or more of structural units (a1), one or more of structural units (a2) and either one or two of the terminal groups (a3) must be present



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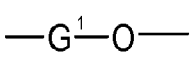

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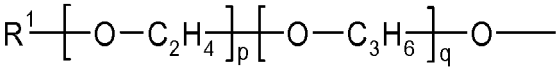


(a3)

wherein

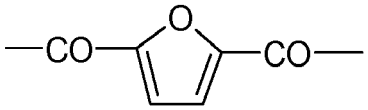
G^1 is (OC_3H_6)
R^1 is CH_3,
p is based on a molar average, a number of from 10 to 50,
q is 0.

[0031] In Polyester A, adjacent structural units (a1) are connected by structural unit (a2). Furthermore, in the case that only one terminal group (a3) is present in the polymer, the other terminal group is selected from the group consisting of OH, OCH_3, and G^1OH. Both terminal groups may only be linked to the structural unit (a1).

[0032] In Polyester A, the average number of structural units (a1) is preferably from 2 to 30, more preferably from 3 to 20, and even more preferably from 4 to 15.

[0033] The average molecular weight (Mw) of Polyester A is preferably from 2000 to 20000 g/mol.

[0034] In another particularly preferred embodiment of the invention, the one or more polyesters a), described in the following and further referred to as "Polyester B", comprise structural units exclusively selected from the group consisting of structural units (a1) and (a2) and the terminal group (a3), where two or more of the repeating structural units (a1), one or more of the repeating structural units (a2) and either one or two of the terminal groups (a3) must be present



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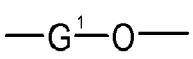

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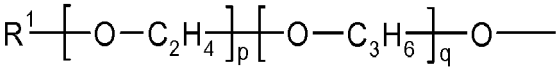


(a3)

wherein

G^1 is (OC_3H_6);
R^1 is CH_3;
p is, based on a molar average, a number of from 10 to 50 and
q is, based on a molar average, a number of from 2 to 5.

[0035] In Polyester B, adjacent structural units (a1) are connected by the structural unit (a2). Furthermore, in the case that only one terminal group (a3) is present in the polymer, the other terminal group is selected from the group consisting of OH, OCH_3, and G^1OH. Both terminal groups may only be linked to the structural unit (a1). Furthermore, the (OC_3H_6)- and (OC_2H_4)-groups of the terminal group (a3) are arranged blockwise.

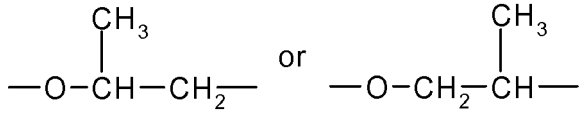
[0036] In Polyester B, the average number of structural units (a1) is preferably from 2 to 30, more preferably from 3 to 20, and even more preferably from 4 to 15.

[0037] The average molecular weight (Mw) of Polyester B is preferably from 2000 to 20000 g/mol.

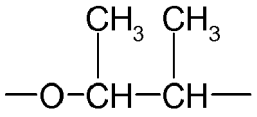
The groups $-OC_2H_4$ in the structural units "R^1-$(OC_2H_4)_p$-$(OC_3H_6)_q$-O-" and in the structural units G^1 are of the formula

-O-CH_2-CH_2-.

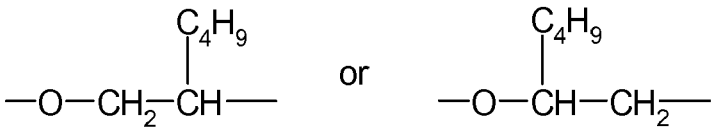
[0038] The groups -OC_3H_6 in the structural units "R^1-$(OC_2H_4)_p$-$(OC_3H_6)_q$-O-" and in the structural units G^1 are of the formula -O-$CH(CH_3)$-CH_2- or -O-CH_2-$CH(CH_3)$-, i.e. of the formula



[0039] The groups (OC_4H_8) in the structural units G^1 are preferably of the formula -O-$CH(CH_3)$-$CH(CH_3)$-, i.e. of the formula



[0040] The groups (OC_6H_{12}) in the structural units G^1 are preferably of the formula -O-CH_2-$CH(n\text{-}C_4H_9)$- or -O-$CH(n\text{-}C_4H_9)$-CH_2-, i.e. of the formula



[0041] The invention further provides a laundry detergent composition comprising one or more polyesters

a) obtainable through a polymerization reaction of the following monomers:

I) 2,5-furandicarboxylic acid or its ester,
II) one or more alkylene glycols of the formula $HOC_nH_{2n}OH$, with n being a number of from 2 to 10, preferably from 2 to 6 and more preferably HOC_2H_4OH, HOC_3H_6OH, HOC_4H_8OH or $HOC_6H_{12}OH$,
III) one or more alkyl capped polyalkylene glycols of the formula

$$R^1\text{-}(OC_2H_4)_p\text{-}(OC_3H_6)q\text{-}OH$$

wherein

R^1 is a $C_{1\text{-}30}$ alkyl, preferably a $C_{1\text{-}4}$ alkyl and more preferably methyl, the (OC_3H_6)- and (OC_2H_4)-groups may be arranged blockwise, alternating, periodically and/or statistically, preferably blockwise and/or statistically, and wherein the connections of the groups (OC_3H_6)- and (OC_2H_4)- can be linked to R^1- and -OH,

p is based on a molar average, a number of from 1 to 200, preferably from 2 to 150 and more preferably from 3 to 120,

q is based on a molar average, a number of from 0 to 40, preferably from 0 to 30, more preferably from 0 to 20, and most preferably from 0 to 10,

IV) optionally one or more further monomers, that are different from the monomers I) to III), preferably selected from the group consisting of aromatic dicarboxylic acids, their derivatives and the salts thereof, more preferably terephthalic acid, phthalic acid, isophthalic acid, 3-sulfophthalic acid, 4-sulfophthalic acid, 5-sulfoisophthalic acid and their salts, and even more preferably terephthalic acid and its ester and

b) one or more surfactants.

[0042] The polyesters of component a) obtainable through a polymerization reaction of the monomers I), II), III) and optionally IV) are referred to in the following as "Polyester C".

[0043] The sum of p and q in monomer III), based on a molar average, is preferably a number of from 1 to 200, more preferably a number of from 5 to 150 and even more preferably a number of from 10 to 75.

[0044] R^1 in the definition of monomer III) is preferably methyl.

[0045] Monomer II) is preferably HOC_2H_4OH or HOC_3H_6OH.

[0046] The one or more optional monomers IV) are preferably selected from the group consisting of aromatic dicarboxylic acids, their derivatives and the salts thereof, more preferably terephthalic acid, phthalic acid, isophthalic acid, 3-sulfophthalic acid, 4-sulfophthalic acid, 5-sulfoisophthalic acid and their salts, and even more preferably terephthalic acid and its ester.

[0047] The average molecular weight (M_w) of Polyester C is preferably from 2000 to 20000 g/mol.

[0048] The average number of repeating structural units of Polyester C resulting from monomer I) in the polymerization is preferably from 2 to 60, more preferably from 2 to 50, even more preferably from 3 to 40 and most preferably from 4 to 30.

[0049] The amount of Polyester C resulting from monomer III) in the polymerization, based on the total weight of the polyester, is preferably at least 40 wt.-%, more preferably at least 50 wt.-%, even more preferably at least 60 wt.-% and most preferably at least 70 wt.-%.

[0050] The amount of structural units of Polyester C resulting from monomers I) and II) in the polymerization plus the amount of terminal groups resulting from monomer III), based on the total weight of the polyester, is preferably at least 50 wt.-%, more preferably at least 60 wt.-%, even more preferably at least 70 wt.-%, and most preferably at least 80 wt.-%.

[0051] The amount of Polymer C resulting from optional monomer IV) in the polymerization, based on the total weight of the polyester, is preferably at least 0.1 wt.-%, more preferably from 0.1 wt.-% to 50 wt.-%, and even more preferably from 0.5 wt.-% to 40 wt.-%.

[0052] Preferably, Polyester C is obtainable through polymerizing exclusively monomers I), II) and III).

[0053] In another preferred embodiment of the laundry detergent composition, the polyesters of component a), described in the following and further referred to as "Polyester A^1", are obtainable through a polymerisation reaction of the following monomers:

I) 2,5-furandicarboxylic acid or its ester,
II) HOC_3H_6OH,
III) one or more alkyl capped polyalkylene glycols of the formula

$$R^1\text{-}(OC_2H_4)_p\text{-}(OC_3H_6)_q\text{-}OH$$

wherein

R^1 is CH_3,
p is based on a molar average, a number of from 10 to 50 and
q is 0.

[0054] In Polyester A^1, the average number of structural units resulting from monomer I) is preferably from 2 to 30, more preferably from 3 to 20, and even more preferably from 4 to 15.

[0055] The average molecular weight (Mw) of Polyester A^1 is preferably from 2000 to 20000 g/mol.

[0056] In another preferred embodiment of the laundry detergent composition, the polyesters of component a), described in the following and further referred to as "Polyester B^1", are obtainable through a polymerisation reaction of the following monomers:

I) 2,5-furandicarboxylic acid or its ester,
II) HOC_3H_6OH and
III) one or more alkyl capped polyalkylene glycols of the formula

$$R^1\text{-}(OC_2H_4)_p\text{-}(OC_3H_6)_q\text{-}OH$$

wherein

R^1 is CH_3,

p is based on a molar average, a number of from 10 to 50 and

q is based on a molar average, a number of from 2 to 5.

[0057] In Polyester B^1, the average number of repeating structural units resulting from monomer I) is preferably from 2 to 30, more preferably from 3 to 20, and even more preferably from 4 to 15.

[0058] The average molecular weight (Mw) of Polyester B^1 is preferably from 2000 to 20000 g/mol.

[0059] The one or more polyesters of component a) are present in the laundry detergent compositions of the invention in an amount of preferably at least 0.1 wt.-%, more preferably from 0.1 wt.-% to 10 wt.-%, even more preferably from 0.2 wt.-% to 5 wt.-% and most preferably from 0.25 wt.-% to 3 wt.-%, in each case based on the total weight of the laundry detergent composition.

[0060] For the preparation of the polyesters of component a), typically a two stage process is used of either direct esterification of diacids and diols or transesterification of diesters and diols, followed by a polycondensation reaction under reduced pressure. A suitable process for the preparation of the polyesters of component a) comprises heating suitable starting compounds for structural units (a1), (a2), optionally (a4) and terminal group (a3) with the addition of a catalyst, to temperatures of 160 to 220°C, expediently beginning 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.

[0061] Typical transesterification and condensation catalysts known in the art can be used for the preparation of the copolymers, such as antimony, germanium and titanium based catalysts. Preferably, tetraisopropyl orthotitanate (IPT) and sodium acetate (NaOAc) are used as the catalyst system in the synthesis of the polymers contained in the inventive laundry detergent compositions.

[0062] The polyesters of component a) may advantageously be prepared by a process which comprises heating 2,5-furandicarboxylic acid or its ester, one or more alkylene glycols, and R^1-$(OC_2H_4)_p$-$(OC_3H_6)_q$-OH, wherein R^1, p and q are as described herein, 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.

[0063] In a preferred embodiment of the invention the process is characterized in that

a) furan-2,5-dicarboxylic acid dimethyl ester, one or more alkylene glycols, and R^1-$(OC_2H_4)_p$-$(OC_3H_6)_q$-OH, wherein R^1, p and q are as described herein, 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 the pressure is then 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 180°C to 240°C and a pressure of from 0.1 to 10 mbar and preferably of from 0.5 to 5 mbar to form the polyester.

[0064] In a further preferred embodiment of the invention the process is characterized in that

a) furan-2,5-dicarboxylic acid, one or more alkylene glycols, and R^1-$(OC_2H_4)_p$-$(OC_3H_6)_q$-OH, wherein R^1, p and q are as described herein, 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 water and the pressure is then 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 esterification, and

b) in a second step the reaction is continued at a temperature of from 180°C to 240°C at a pressure of from 0.1 to 10 mbar and preferably of from 0.5 to 5 mbar to form the polyester.

[0065] Non-ionic soil release polyesters based on glycol terephthalate or glycol terephthalate / polyglycol terephthalate co-polymers can be prepared by a two stage process of either direct esterification of diacids and diols or transesterification of diesters and diols, followed by a polycondensation reaction under reduced pressure. Due to the limited solubility of terephthalic acid in the reaction mixture elevated temperatures and pressures are required for synthesis via the direct esterification process. In the case of furan-2,5-dicarboxylic acid, the transesterification can be performed efficiently at ambient pressure and moderate temperatures giving a significant energy cost advantage. Furthermore, the condensation product water in the direct esterification process has an improved ecological footprint compared to methanol typically obtained in a transesterification process.

Surfactants

[0066] The laundry detergent compositions of the invention comprise one or more surfactants, component b).

[0067] Surfactants assist in removing soil from textile materials and also assist in maintaining removed soil in solution or suspension in the wash liquor.

[0068] Preferably, the one or more surfactants of component b) of the laundry detergent compositions are selected from the group consisting of anionic, nonionic, cationic and zwitterionic surfactants, and more preferably from the group consisting of anionic, nonionic and zwitterionic surfactants.

Anionic Surfactants

[0069] Preferred anionic surfactants are alkyl sulfonates and alkyl ether sulfates.

[0070] Preferred alkyl sulfonates are alkylbenzene sulfonates, particularly linear alkylbenzene sulfonates (LAS) having an alkyl chain length of C_8-C_{15}. Possible counter ions for concentrated alkaline liquids are ammonium ions, e.g. those generated by the neutralization of alkylbenzene sulfonic acid with one or more ethanolamines, for example monoethanolamine (MEA) and triethanolamine (TEA), or alternatively, alkali metals, e.g. those arising from the neutralization of alkylbenzene sulfonic acid with alkali hydroxides. The linear alkyl benzene sulfonate surfactants may be LAS with an alkyl chain length of preferably from 8 to 15 and more preferably from 12 to 14. The neutralization of the acid may be performed before addition to the laundry detergent compostitions or in the formulation process through excess addition of neutralizing agent.

[0071] Preferred alkyl ether sulfates (AES) are alkyl polyethoxylate sulfate anionic surfactants of the formula

$$R^2O(C_2H_4O)_ySO_3^-M^+$$

wherein

R^2 is a saturated or unsaturated alkyl chain having preferably from 10 to 22 carbon atoms, and more preferably from 12 to 16 carbon atoms,

M^+ is a cation which makes the compound water-soluble, preferably an ammonium cation, a substituted ammonium cation, an alkali metal cation, or other material chosen from the list of buffers,

y averages preferably from 1 to 15, more preferably from 1 to 3 and even more preferably is 3.

Nonionic Surfactants

[0072] Nonionic surfactants include primary and secondary alcohol ethoxylates, especially C_8-C_{20} aliphatic alcohol ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} 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.

[0073] When included therein, the laundry detergent composition contains preferably from 0.2 wt.-% to 40 wt.-% and more preferably 1 wt.-% to 20 wt.-% of a nonionic 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").

[0074] Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 35 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol.

Zwitterionic Surfactants

[0075] The laundry detergent composition may comprise up to 10 wt.-% of a zwitterionic surfactant, e.g. amine oxide or betaine.

Typical amine oxides used are of the formula

$$R^3N(O)(CH_2R^4)_2$$

wherein

R^3 is a long chain moiety and each CH_2R^4 are short chain moieties,
R^4 is preferably selected from the group consisting of H, CH_3 and $-CH_2OH$.

[0076] In general R^3 is a primary or branched hydrocarbyl moiety with a chain length of from 8 to 18, which can be saturated or unsaturated. Preferably, R^3 is a primary alkyl moiety.

[0077] Preferred amine oxides have compositions wherein R^3 is a C_8-C_{18} alkyl and R^4 is H. These amine oxides are illustrated by C_{12-14} alkyldimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide.

[0078] A preferred amine oxide material is Lauryl dimethylamine oxide, also known as dodecyldimethylamine oxide or DDAO. Such an amine oxide material is commercially available from The Global Amines Company Pte. Ltd. under the trade name Genaminox® LA.

[0079] Betaines may be alkyldimethyl betaines or alkylamido betaines, wherein the alkyl groups have C_{12-18} chains.

[0080] In one preferred embodiment of the invention, the one or more surfactants of component b) of the laundry detergent compositions are selected from the group consisting of anionic and nonionic surfactants.

[0081] In another preferred embodiment of the invention, the one or more surfactants of component b) of the laundry detergent compositions are selected from the group consisting of linear alkyl benzene sulfonates, alkyl ether sulfates, nonionic surfactants, amine oxides and betaines, and preferably the one or more surfactants of component b) of the laundry detergent compositions are selected from the group consisting of linear alkyl benzene sulfonates, alkyl ether sulfates and nonionic surfactants.

Additional Surfactants

[0082] Other surfactants than the preferred LAS, AES, and nonionic surfactants may be added to the mixture of detersive surfactants.

[0083] Although less preferred, some alkyl sulfate surfactant may be used, especially the non-ethoxylated C_{12-15} primary and secondary alkyl sulfates. Soap may also be used. Levels of soap are preferably lower than 10 wt.-%.

[0084] Preferably, the one or more surfactants of component b) of the inventive laundry detergent compositions, are present in an amount of at least 5 wt.-%, more preferably from 5 wt.-% to 65 wt.-%, even more preferably from 6 to 60 wt.-% and extraordinarily preferably from 7 wt.-% to 55 wt.-%, in each case based on the total weight of the laundry detergent composition.

Further Optional Ingredients

[0085] In addition to the essential ingredients as claimed, the laundry detergent compositions may comprise one or more optional ingredients, e.g. they may comprise conventional ingredients commonly used in detergent compositions, especially laundry detergent compositions. Examples of optional ingredients include, but are not limited to builders, bleaching agents, bleach active compounds, bleach activators, bleach catalysts, photobleaches, dye transfer inhibitors, colour 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, hydrotropes, 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.

Polyalkoxylated polyethyleneimine

[0086] For detergency boosting, it is advantageous to use a second polymer alongside the soil release polymers in the laundry detergent compositions of the present invention. This second polymer is preferably a polyalkoxylated polyethyleneimine (EPEI). Polyethylene imines are materials composed of ethylene imine units $-CH_2CH_2NH-$ 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 bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, and the like. Specific methods for preparing these polyamine backbones are disclosed in US 2,182,306, US 3,033,746, US 2,208,095, US 2,806,839, and US 2,553,696.

Other Polymers

[0087] In addition to the polyester soil release polymer and the optional EPEI, the laundry detergent compositions

may comprise other polymeric materials, for example: dye transfer inhibition polymers, anti redeposition polymers and cotton soil release polymers, especially those based on modified cellulosic materials. Especially, when EPEI is not present, the laundry detergent composition may further comprise a polymer of polyethylene glycol and vinyl acetate, for example the lightly grafted copolymers described in WO 2007/138054. Such amphiphilic graft polymers based on water soluble polyalkylene oxides as graft base and side chains formed by polymerisation of a vinyl ester component have the ability to enable reduction of surfactant levels whilst maintaining high levels of oily soil removal.

Hydrotropes

[0088] In the context of this invention a hydrotrope is a solvent that is neither water nor conventional surfactant that aids the solubilisation of the surfactants and other components, especially polymer and sequestrant, in the liquid to render it isotropic. Among suitable hydrotropes there may be mentioned as preferred: monopropylene glycol (MPG), glycerol, sodium cumene sulfonate, ethanol, other glycols, e.g. dipropylene glycol, diethers and urea. MPG and glycerol are preferred hydrotropes.

Enzymes

[0089] It is preferable that at least one or more enzymes selected from protease, mannanase, pectate lyase, cutinase, esterase, lipase, amylase, and cellulase may be present in the laundry detergent compositions. Less preferred additional enzymes may be selected from peroxidase and oxidase. The enzymes are preferably present with corresponding enzyme stabilizers. The total enzyme content is preferably from 0 wt.-% to 5 wt.-%, more preferably from 0.5 wt.-% to 5 wt.-% and even more preferably from 1 wt.-% to 4 wt.-%.

Sequestrants

[0090] Sequestrants are preferably included. Preferred sequestrants include organic phosphonates, alkanehydroxy phosphonates and carboxylates available under the DEQUEST trade mark from Thermphos. The preferred sequestrant level is less than 10 wt.-% and preferably less than 5 wt.-% of the laundry detergent composition. A particularly preferred sequestrant is HEDP (1- Hydroxyethylidene -1 , 1 ,-diphosphonic acid), for example sold as Dequest 2010. Also suitable but less preferred as it gives inferior cleaning results is Dequest® 2066 (diethylenetriamine penta(methylene phosphonic acid) or Heptasodium DTPMP).

Buffers

[0091] In addition to agents optionally included for the generation of anionic surfactants, e.g. from LAS or fatty acids, the presence of buffer is preferred for pH control. Possible buffers are one or more ethanolamines, e.g. monoethanolamine (MEA) or triethanolamine (TEA). They are preferably used in the laundry detergent composition at levels of from 1 to 15 wt.-%. Other suitable amino alcohol buffer materials may be selected from the group consisting of compounds having a molecular weight above 61 g/mol, which includes MEA. Suitable materials also include, in addition to the already mentioned materials: monoisopropanolamine, diisopropanolamine, triisopropanolamine, monoamino hexanol, 2-[(2-methoxyethyl) methylamino]-ethanol, propanolamine, N-methylethanolamine, diethanolamine, monobutanolamine, isobutanolamine, monopentanolamine, 1-amino-3-(2-methoxyethoxy)-2-propanol, 2-methyl-4- (methylamino)-2-butanol and mixtures thereof.

[0092] Potential alternatives to amino ethanol buffers are alkali hydroxides such as sodium hydroxide or potassium hydroxide.

[0093] It may be advantageous to include fluorescer and/or bleach catalyst in the laundry detergent compositions as further high efficiency performance additives. Perfume and colorants will also desirably be included. The laundry detergent compositions may additionally contain viscosity modifiers, foam boosting agents, preservatives (e.g. bactericides), pH buffering agents, polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents and ironing aids. The laundry detergent compositions may further comprise pearlisers and/or opacifiers or other visual cues and shading dye.

Packaging and dosing

[0094] The laundry detergent compositions may be packaged as unit doses in a polymeric film soluble in the wash water. Alternatively the laundry detergent compositions may be supplied in multidose plastics packs with a top or bottom closure. A dosing measure may be supplied with the pack either as a part of the cap or as an integrated system.

[0095] Further preferred embodiments of the invention may arise from the combination of above described preferred

embodiments.

[0096] The invention will now be further described with reference to the following nonlimiting examples.

EXAMPLES

[0097] 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.-%).

Polymer Preparation

General procedure for the preparation of the polyesters of the Examples

[0098] The polyester synthesis may be carried out by the reaction of 2,5-furandicarboxylic acid or its ester, alkylene glycols, alkyl capped polyalkylene glycols and optionally dimethyl terephthalate (DMT) using sodium acetate (NaOAc) and tetraisopropyl orthotitanate (IPT) as the catalyst system. The synthesis is a two-step procedure. The first step is a (trans)esterification and the second step is a polycondensation.

(Trans)esterification

[0099] The reactants were weighed into a reaction vessel at room temperature under a nitrogen atmosphere. The mixture was heated to an internal temperature of 65 °C for melting and homogenization, followed by the addition of 200 μl tetraisopropyl orthotitanate.

[0100] Within 2 hours, the temperature of the reaction mixture was continuously increased to 210°C under a weak nitrogen flow and held at this temperature for 2 hours. During the transesterification, methanol was released from the reaction and was distilled out of the system, whereas in the case of an esterification water is released from the reaction and distilled out of the system. After 2 h at 210°C, nitrogen was switched off and the pressure reduced to 400 mbar over 3 h.

Polycondensation

[0101] The mixture was heated up to 230°C. At 230°C the pressure was reduced to 1 mbar over 160 min. Once the polycondensation reaction had started, the glycol or mixture of glycols was distilled out of the system. The mixture was stirred for 4 h at 230°C and a pressure of 1 mbar. After the end of this time period, the inner pressure of the reaction vessel was set back to 1 bar using N_2 and the polymer melt was subsequently removed from the reactor and allowed to solidify.

[0102] Key to reactants used in the examples 1 to 14

mPEG750	is mono hydroxy-functional polyethylene glycol monomethyl ether, average molecular weight 0,75 KDa (Polyglykol M 750, Clariant).
mPEG2000	is mono hydroxy-functional polyethylene glycol monomethyl ether, average molecular weight 2 KDa (Polyglykol M 2000, Clariant).
mPEG5000	is mono hydroxy-functional polyethylene glycol monomethyl ether, average molecular weight 5 KDa (Polyglykol M 5000, Clariant).
EG	is ethylene glycol
PG	is propylene glycol
FDCME	is furan-2,5-dicarboxylic acid dimethyl ester
FDCA	is furan-2,5-dicarboxylic acid
FDBE	is furan-2,5-dicarboxylic acid dibutyl ester
DMT	is dimethyl terephthalate
IPT	is tetraisopropyl orthotitanate

NaOAc is sodium acetate

Table I - Polymer examples 1 to 6

Component	1	2	3	4	5	6
FDCME	184.15	69.06	36.83	18.42	36.83	36.83
FDCA						
FDBE						
DMT				19.42		
EG			12.41			
PG	121.74	45.65	15.22	30.44	30.44	30.44
mPEG750						100
mPEG2000	500	250	100	100		
mPEG5000					100	
IPT	0.2	0.2	0.1	0.1	0.1	0.1
NaOAc	0.5	0.5	0.25	0.3	0.3	0.3

Table II - Polymer examples 7 to 13

Component	7	8	9	10	11	12	13*
FDCME			11.05	14.73	92.08	108.82	92.08
FDCA		4.59					
FDBE	40.23						
DMT							
EG							
PG	18.26	3.65	7.3	9.13	60.87	71.94	60.87
mPEG750							
mPEG2000	100	20	12	10	200	181.82	250
mPEG5000							
IPT	0.08	0.016	0.016	0.016	0.2	0.2	0.2
NaOAc	0.2	0.04	0.04	0.04	0.5	0.5	0.5
*In this example the polycondensation temperature was 210 °C.							

[0103] Liquid laundry detergent compositions containing exemplary polyesters A series of exemplary liquid laundry detergent compositions, both excluding and including soil release polymer, were prepared according to Table III.

[0104] Key to ingredients used in the compositions of Table A

LAS is C_{12-14} linear alkylbenzene sulfonate, sodium salt
SLES 2EO is sodium lauryl ether sulfate with 2 moles EO (Genapol® LRO, Clariant).
NI 7EO is C_{12-15} alcohol ethoxylate 7EO nonionic (Genapol® LA070, Clariant)
Fatty Acid is a C_{12-18} stripped palm kernel fatty acid
SRP is a polyester prepared according to examples from Tables I and II

Table III - Liquid laundry detergent compositions for performance testing

Ingredient	wt.-% a.m.	
	1	2
LAS	5.20	5.20
SLES 2EO	6.50	6.50
NI 7EO	5.20	5.20
Fatty Acid	2.80	2.80
Glycerol	2.40	2.40
Ethanol	1.20	1.20
Sodium citrate	1.70	1.70
Sodium tetraborate decahydrate	2.00	2.00
SRP	0.00	1.00
Demin water and NaOH to adjust pH	ad 100	ad 100
pH Value	8.4	8.4
Appearance at room temperature	clear	clear

Soil Release Test

[0105] The inventive liquid laundry detergent compositions containing the polyesters of component a) and prepared according to the compositions listed in Table III, were tested for their soil release performance according to the "Dirty-Motor Oil" Test (DMO-Test) using a Lini Apparatus. The conditions for the test are listed in Table B.

Table IV - Washing conditions - Soil Release Test

Equipment	Linitest Plus (SDL Atlas)
Water hardness	14°dH
Washing temperature	40°C
Washing time	30 min
Detergent concentration	4.3 g/l
Soiled Fabric : Liquor Ratio	1 : 40

[0106] As test fabric, white polyester and polycotton standard swatches (WFK 30A and WFK 20A, from WFK Testgewebe GmbH) were used. The fabrics were prewashed three times with the stored liquid laundry detergent compositions. The swatches were then rinsed, dried and soiled with 25 μl of dirty motor oil. After 1 hour the soiled fabrics were washed again with the same stored liquid laundry detergent compositions used in the pre-washing step. After rinsing and drying the washed swatches, a measurement of the remission of the stained fabric at 457 nm was made using a spectrophotometer (Datacolor 650).

[0107] The soil release performance is shown as an improvement in soil removal of the swatches washed with one of the formulations 2 from Table III compared with formulation 1 of Table III:

$$\Delta R = R_{form\,2} - R_{form\,1}$$

[0108] The washing results obtained for the liquid laundry detergent compositions comprising the inventive soil release polymers are shown in Table V, expressed as ΔR along with the 95% confidence intervals.

Table V - Washing results

Example No.	Biosourced wt.-% excl. (a3)	Polyester		Polycotton	
		ΔR	95% CI	ΔR	95% CI
1	100	4.1	1.3	11.2	0.5
2	100	3.4	0.85	11.5	1.2
3	100	1.1	0.50	8.3	0.8
4	70	7.9	0.7	17.9	0.7
5	100	0.9	0.5	9.0	0.3
6	100	1.6	0.6	5.3	1.2
7	100	2.9	0.5	9.3	0.6
8	100	2.4	0.5	11.5	0.3
9	100	3.6	0.8	8.7	1.1
10	100	1.8	0.3	5.8	0.7
11	100	4.5	0.5	9.2	0.6
12	100	2.7	0.5	10.9	0.6
13	100	3.1	0.8	8.8	0.9

Biosourced material content calculation

[0109] The weight content of bio-sourced material shown in Table V is related to the hydrophobic block of the polymer and calculated according to the theoretical composition comprising the structural units (a1), (a2) and optionally (a4). The excess of used glycol and MeOH of the transesterification are therefore not taken into account in the calculation. The used EG, PG (a2) and furan (a1) components are assumed to be 100% bio sourced.

[0110] The biosourced material content, biosourced wt.-%, is then calculated as:

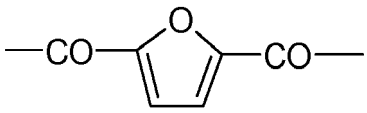
$$\text{Biosourced wt.-\%} = 100 - \text{(a4) wt.-\%}$$

[0111] Where (a4) wt.-% is the weight percentage of structural units (a4) in the resulting polymer.

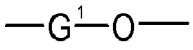
Claims

1. A laundry detergent composition comprising

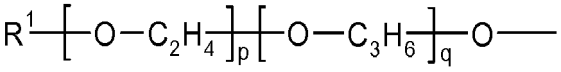
a) one or more polyesters comprising two or more structural units (a1), one or more structural units (a2) and either one or two terminal structural groups (a3)



(a1)



(a2)



(a3)

wherein

G^1 is one or more (OC_nH_{2n}) with n being a number of from 2 to 10, preferably from 2 to 6 and more preferably (OC_2H_4), (OC_3H_6), (OC_4H_8) or (OC_6H_{12}),
R^1 is a C_{1-30} alkyl, preferably C_{1-4} alkyl and more preferably methyl,
p is, based on a molar average, a number of from 1 to 200, preferably from 2 to 150 and more preferably from 3 to 120,
q is, based on a molar average, a number of from 0 to 40, preferably from 0 to 30, more preferably from 0 to 20, and most preferably from 0 to 10, where the (OC_3H_6)- and (OC_2H_4)-groups of the terminal group (a3) may be arranged blockwise, alternatingly, periodically and/or statistically, preferably blockwise and/or statistically, either of the groups (OC_3H_6)- and (OC_2H_4)- can be linked to R^1- and -O, adjacent structural units (a1) are connected by the structural unit (a2), in the case that only one terminal group (a3) is present in the polymer, the other terminal group is selected from the group consisting of OH, OCH_3, and G^1OH and both terminal groups may be only linked to a structural unit (a1)

and

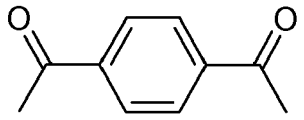
b) one or more surfactants.

2. The laundry detergent composition according to claim 1, **characterized in that** in the one or more polyesters of component a) the sum of p and q, based on a molar average, is a number of from 1 to 200, preferably a number of from 5 to 150 and more preferably a number of from 10 to 75.

3. The laundry detergent composition according to claim 1 or 2, **characterized in that** in the one or more polyesters of component a) R^1 is methyl.

4. The laundry detergent composition according to one or more of claims 1 to 3, **characterized in that** in the one or more polyesters of component a) G^1 is (OC_2H_4) or (OC_3H_6).

5. The laundry detergent composition according to one or more of claims 1 to 4, **characterized in that** the one or more polyesters of component a) additionally comprise one or more structural units (a4), which may be indirectly linked to structural units (a1) or other structural units (a4) via the structural units (a2), or directly linked to a terminal group:



(a4)

6. The laundry detergent composition according to one or more of claims 1 to 5, **characterized in that** the average molecular weight (M_w) of the one or more polyesters of component a) is from 2000 to 20000 g/mol.

7. The laundry detergent composition according to one or more of claims 1 to 6, **characterized in that** the average number of structural units (a1) in the one or more polyesters of component a) is from 2 to 60, preferably from 2 to 50, more preferably from 3 to 40 and even more preferably from 4 to 30.

8. The laundry detergent composition according to one or more of claims 1 to 7, **characterized in that** the total amount of the terminal group (a3) in the one or more polyesters of component a), based on the total weight of the polyester, is at least 40 wt.-%, preferably at least 50 wt.-%, more preferably at least 60 wt.-% and even more preferably at least 70 wt.-%.

9. The laundry detergent composition according to one or more of claims 1 to 8, **characterized in that** the total amount of structural units (a1) and (a2) and of terminal group (a3) in the one or more polyesters of component a), based on the total weight of the polyester, is at least 50 wt.-%, preferably at least 60 wt.-%, more preferably at least 70 wt.-%, and even more preferably at least 80 wt.-%.

10. The laundry detergent composition according to one or more of claims 5 to 9, **characterized in that** the amount of structural units (a4) in the one or more polyesters of component a), based on the total weight of the polyester, is at least 0.1 wt.-%, preferably from 0.1 wt.-% to 50 wt.-%, and more preferably from 0.5 wt.-% to 40 wt.-%.

11. The laundry detergent composition according to one or more of claims 1 to 4 and 6 to 9, **characterized in that** the structural units in the one or more polyesters of component a) are exclusively selected from the group consisting of

structural units (a1) and (a2).

12. The laundry detergent composition according to one or more of claims 1 to 11, **characterized in that** the one or more polyesters of component a) are present in an amount of at least 0.1 wt.-%, preferably from 0.1 wt.-% to 10 wt.-%, more preferably from 0.2 wt.-% to 5 wt.-% and even more preferably from 0.25 wt.-% to 3 wt.-%, in each case based on the total weight of the laundry detergent composition.

13. The laundry detergent composition according to one or more of claims 1 to 12, **characterized in that** the one or more surfactants of component b) are selected from the group consisting of anionic, nonionic, cationic and zwitterionic surfactants.

14. The laundry detergent composition according to claim 13, **characterized in that** the one or more surfactants of component b) are selected from the group consisting of linear alkyl benzene sulfonates, alkyl ether sulfates, nonionic surfactants, amine oxides and betaines, and preferably selected from the group consisting of linear alkyl benzene sulfonates, alkyl ether sulfates and nonionic surfactants.

15. The laundry detergent compositions according to one or more of claims 1 to 14, **characterized in that** the one or more surfactants of component b) are present in an amount of at least 3 wt.-%, preferably from 3 wt.-% to 65 wt.-%, more preferably from 4 to 60 wt.-% and even more preferably from 5 wt.-% to 55 wt.-%, in each case based on the total weight of the laundry detergent composition.

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EUROPEAN SEARCH REPORT

Application Number
EP 17 20 4076

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	JP 2015 105373 A (KAO CORP) 8 June 2015 (2015-06-08) * claims 1-2; examples 1-7; table 1 * * paragraphs [0034] - [0038] *	1-15	INV. C11D3/00 C11D3/37
A	EP 3 235 848 A1 (STICHTING WAGENINGEN RES [NL]) 25 October 2017 (2017-10-25) * claim 1; example 2; table 1; compound Polyester A * * paragraphs [0043] - [0045] *	1-15	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	23 May 2018	Agra-Gutierrez, C

CATEGORY OF CITED DOCUMENTS

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