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(54) **Detergent composition comprising soil-release polymers of improved storage stability**

(57) The present invention relates to a detergent composition, in particular a liquid laundry detergent composition, comprising at least one lipase, at least one soil-release polymer comprising ester moieties and at least one compound which stabilizes said at least one soil-release polymer in the presence of said lipase, to a method for stabilizing such a soil-release polymer in detergent composition comprising a lipase and to the use of certain compounds for stabilizing soil-release polymers comprising ester moieties in detergent compositions further comprising at least one lipase.

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Description

[0001] The present invention relates to a detergent composition, in particular a liquid laundry detergent composition, comprising at least one lipase, at least one soil-release polymer comprising ester moieties and at least one compound which stabilizes said at least one soil-release polymer in the presence of said lipase, to a method for stabilizing such a soil-release polymer in a detergent composition comprising a lipase and to the use of certain compounds for stabilizing soil-release polymers comprising ester moieties in detergent compositions further comprising at least one lipase.

[0002] The removal of greasy and oily soil from a substrate, particularly from textile fibres, still is a challenging task, in particular at temperatures equal to or below 60 °C. To improve removal of such soils in automatic laundering at temperatures equal to or below 60 °C, nowadays lipase enzymes commonly are incorporated into detergent formulations.

[0003] However, even in the presence of a lipase the removal of oily soil from synthetic fibres, in particular polyester fibres, still is difficult due to the hydrophobic character of the polyester fabrics to which oily material preferentially "adheres". Polyester fabrics are mostly copolymers of ethyleneglycol and terephthalic acid. To improve soil removal from polyester fabrics, so called soil-release polymers have been developed which at least in part have a structure similar to that of the synthetic fibres and therefore preferentially adhere to said fibres. These soil-release polymers comprise at least one hydrophobic part and at least one hydrophilic part. Upon contact with the (hydrophobic) fibre during washing, the hydrophobic part of the polymer aligns itself along the fibre surface, while the hydrophilic part of the polymer orients itself away from the fibre surface. The hydrophilic film formed on the fibre surface significantly reduces the affinity of hydrophobic soil to the fibre in comparison to an untreated fibre and thus facilitates removal of greasy and oily soil from the textile. In addition, soil-release polymers usually further show an anti-redeposition effect for dirt present in the washing liquor by dispensing it therein. Liquid detergents comprising such soil release polymers are available for example from Henkel KGaA (Düsseldorf, Germany).

[0004] In order to combine the positive effects of both, lipase and soil-release polymers, furthermore detergent compositions are available, comprising both, a lipase as well as a soil-release polymer.

[0005] While a positive effect of both compounds on the removal of greasy and oily soils from textiles comprising synthetic fibres (i.e. textiles consisting of synthetic fibres as well as textiles consisting of a mixture of synthetic fibres and fibres obtained from natural sources, such as for example cotton) clearly can be demonstrated, it turns out that in particular in liquid detergent compositions comprising soil-release polymers having ester moieties, said soil-release polymers are not stable in the presence of a lipase. In consequence, their oil removing capacity significantly drops upon storage. A change in the molecular weight of said polymers in detergent compositions upon storage can be monitored using for example gel permeation chromatography.

[0006] Accordingly, the object of the present invention was to provide a method for stabilizing soil-release polymers comprising ester moieties in the presence of a lipase in a detergent composition during storage, preferably in a liquid detergent composition. A further object of the present invention was to provide a detergent composition, comprising at least one lipase as well as at least one soil-release polymer with an improved storage stability of the soil-release polymer in the composition with respect to an unstabilized detergent composition of incidentally the same composition.

[0007] It has surprisingly been found that compounds selected from the group consisting of boric acid or water soluble-borates capable of forming boric acid; boronic acids or water-soluble salts thereof; formic acid or water-soluble salts thereof; ions of calcium, magnesium or zinc or mixtures thereof, are able to stabilize an ester groups comprising soil-release polymer in the presence of a lipase in a liquid detergent composition during storage of the composition. The stabilizing capacity can be demonstrated by the oil-removing capacity of the composition as well as the reduced decrease in molecular weight of the soil release polymer during storage of the composition. Without wishing to be bound by theory it is believed that the afore-mentioned substances act as an inhibitor of the lipase in the detergent composition. However, surprisingly the afore-mentioned compounds do not negatively affect the performance of the detergent composition with respect to the removal of oily and greasy soil during use and thus do not seem to inhibit lipase activity during the washing process.

[0008] Thus, the present invention provides a detergent composition comprising at least one lipase, at least one ester moieties comprising soil-release polymer in an amount of at least 0.25 wt.-%, based on the whole composition, and at least one compound which stabilizes said at least one soil-release polymer in the presence of said lipase during storage of the composition and is selected from the group consisting of boric acid or water-soluble borates capable of forming boric acid in an amount of from 1.0 to 5.5 wt.-%, based on the whole composition and calculated on the basis of boric acid; boronic acids or water-soluble salts thereof in an amount of from 0.001 to 1 wt.-%, based on the whole composition; formic acid or water-soluble salts thereof in an amount of from 0.005 to 0.5 wt.-%, based on the whole composition; lactic acid in an amount of from 1 to 10 wt.-%, based on the whole composition; water-soluble salts of calcium, magnesium or zinc in an amount of from 0.01 to 100 mmol, preferably of from 0.1 to 10 mmol per liter of the composition, or mixtures thereof.

[0009] The composition of the present invention preferably may represent a liquid laundry detergent composition, including pourable gel formulations. Preferably the composition of the present invention may have a viscosity of up to

about 10.000 mPa·s, as measured on a Brookfield RVT at 20 rpm at 25 °C with a # 5 spindle after 24 hours. Preferably the composition of the present invention is a composition for use in household washing machines. Preferably the composition of the present invention may comprise of from 20 to 90 wt.-%, more preferably of from 30 to 80 wt.-%, even more preferably of from 40 to 75 wt.-% and most preferably of from 50 to 70 wt.-% of at least one liquid carrier, including the particulary preferred ranges of 52 to 68 wt.-% and 55 to 65 wt.-%, based on the whole composition.

[0010] Said liquid carrier preferably is a solvent or a mixture of solvents selected from the group consisting of water, alcohols or mixtures thereof. In particular suitable are monohydric primary and secondary C_1-C_4 alcohols, exemplified by methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol and tert-butanol. Further preferred are C_2-C_6 polyols comprising 2 to 6 hydroxy groups, exemplified by 1,3-propaneglycol, ethylene glycol, glycerine and 1,2-propaneglycol. Polyalkylene glycols, for example polyethylene glycol, may be used as well.

[0011] Preferably, mixtures of the afore-mentioned solvents may be employed. Preferably a mixture of water and at least one alcohol may be employed as a liquid carrier, wherein the ratio of the amount of water to the amount of alcohol (s) present in the composition preferably may be in the range of from 1:1 to 20:1, more preferably of from 2:1 to 10:1, even more preferably of from 3:1 to 7:1. The alcoholic part of the liquid carrier preferably represents a mixture of at least two different alcohols, preferably of at least one monohydric C_1-C_4 alcohol and a C_2-C_6 diol. Most preferably the liquid carrier may represent a mixture of ethanol and 1,2-propyleneglycol. Preferably, the amount of the C_2-C_6 diole to the monohydric C_1-C_4 alcohol (based on their respective weight in the composition, wt.-%/wt.-%) is in the range of from 0.5:1 to 20:1, more preferably of from 1:1 to 10:1, even more preferably of from 1.5:1 to 5:1.

[0012] The at least one lipase present in the detergent composition according to the present invention may be of any suitable origin, such as for example vegetable, animal, bacterial, fungal and yeast origin. With respect to optimum stability and pH activity, bacterial and fungal lipases are preferred, which may be modified chemically or by protein-engineering.

[0013] Preferably, the lipase present in the detergent composition according to the present invention is a triacylglycerol lipase suitable to be incorporated into detergent compositions, in particular into liquid laundry detergent compositions. Such lipases are commercially available, for example under the trademark name of Lipex 100L, Lipolase 100L or Lipozyme TL 100L, all from Novozymes A/S (Bagsvaerd, Denmark), without being limited to these.

[0014] Preferably, the detergent composition of the present invention comprises a lipase which has an activity of at least 10 KLU/g in its commercially available formulation (usually comprising about 1 to 5 wt.-% enzyme in the formulation), more preferably of at least 25 KLU/g, even more preferably at least 50 KLU/g and most preferably of 100 KLU/g (kilo lipase units per gram of the commercially available enzyme formulation), as determined on a tributyrine substrate at 30 °C and a pH of 7.0 according to the method available from Novozymes A/S upon request.

[0015] In the composition of the present invention the at least one lipase preferably may be present in an amount which provides about at least 10, preferably at least 50, more preferably at least 150, even more preferably at least 200, even more preferably at least 250 and most preferably at least 300 LU (lipase units) per gram of the detergent composition of the present invention. One lipase unit is defined as the amount of enzyme which, under standard conditions measured as described above, liberates 1 mmol titratable butyric acid per minute from tributyrine.

[0016] Expressed in wt.-%, the lipase preferably may be present in the composition of the present invention in an amount of from 0.001 to about 0.05 wt.-%, more preferably of from 0.002 to 0.02 wt.-%, based on the lipase protein content in the whole composition (and not the amount of a commercially available lipase formulation added to the composition).

[0017] The at least one soil-release polymer present in the composition of the present invention preferably comprises terephthalate ester moieties and more preferably represents a copolymer comprising terephthalate ester moieties. Even more preferably it may represent a copolyester comprising terephthaloyl, alkylene glycol and polyalkylene glycol units. The copolymer further may comprise monomeric units substituted with anionic groups, such as for example sulfonated isophthaloyl units. Even more preferably the soil-release polymer of the present invention may represent a copolymer comprising polyethylene terephtalate and polyoxyethylene terephtalate blocks. Particularly preferably the soil release polymer may represent a copolymer having random blocks of polyethylene terephtalate (PET) and polyethylene oxide terephtalate (PEOT). Suitable polymers are commercially available under the trademark names of Marloquest L235M or Marloquest HSCB (Sasol, Johannesburg, South Africa), Texcare SRN 170 (Clariant, Muttenz, Switzerland) and Repelotex Crystal (Rhodia, La Defense, France).

[0018] Preferably the soil-release polymer used in the composition of the present invention is liquid at room temperature (23 +/- 2 °C). In the composition of the present invention the amount of soil-release polymer(s) may be at least 0,25 wt.-%, preferably at least 0.3 wt.-%, more preferably at least 0.35 wt.-%, even more preferably at least 0.4 wt.-% and most preferably at least 0.5 wt.-%, based on the whole composition. Preferably the composition does not comprise more than 5 wt.-%, more preferably not more than 4 wt.-%, even more preferably not more than 3 wt.-% and most preferably not more than 2 wt.-% of said soil release polymer(s). Said amounts are to be understood with respect to the amount of "pure" soil-release polymer in the composition of the present invention and not with respect to a commercially available solution of said polymer, which is added to the composition and includes solvents, such as for example water.

[0019] In the composition of the present invention the ratio of the amount of soil release polymer to the amount of

lipase present in the composition (wt.-%/wt.-%) preferably may be in the range of from 10:1 to 200:1, more preferably of from 20:1 to 150:1, even more preferably of from 40:1 to 120:1 and most preferably of from 60:1 to 100:1, including the particularly preferred ranges of from 70:1 to 90:1 and of from 75:1 to 85:1. Herein, both the amount of soil-release polymer as well as the amount of lipase are calculated based on the amount of the respective "pure" compound in the compostion and not on the basis of a commercially available formulation added to the composition, thus omitting any solvents, stabilizers, etc. which may be present in the commercially available formulations of the soil-release polymer and/or the lipase.

[0020] In terms of the present invention, a compound which stabilizes the soil-release polymer in the presence of a lipase during storage of the detergent composition is any compound, which, when added to the detergent composition in the amount given below, reduces the extent for rate of degradation of the soil-release polymer in comparison to a detergent composition of otherwise the same composition but not comprising said compound. Stabilization of the soil release polymer in the detergent composition can be monitored by gel permeation chromatography which further is described in the examples.

[0021] Some of the compounds which may be used for stabilizing the soil-release polymer in the presence of the lipase during storage of the composition of the present invention have been previously described as ingredients in detergent composition comprising enzymes for they are known to inhibit protease activity and thus stabilize enzymes in the presence of a protease. However, the fact that these compounds may also serve as a stabilizer for soil-release polymers in the presence of a lipase, while not inhibiting lipase activity in a subsequent washing process is quite surprising and has not been described previously.

[0022] In terms of the present invention a water-soluble borate capable of forming boric acid in the composition includes boric oxide, borax and further alkali metal borates, such as for example sodium ortho-, meta- and pyroborate as well as sodium pentaborate. The amount of these water-soluble borates is calculated on the basis of boric acid which may be derived from said compounds. For example from 1 mol borax ($Na_2[B_4O_5(OH)_4]\cdot 8H_2O$), having a molecular weight of 381.44 g/mol, four moles of boric acid $(BOH)_3$, having a molecular weight of 61,84 g/mol may be obtained. Thus 381.44 g of borax correspond to 247.36 g of boric acid in terms of the present invention.

[0023] The amount of boric acid or water-soluble borates in the composition preferably is above 1 wt.-%, preferably above 1.5 wt.-%, more preferably of 2 wt.-% and may be in the range of from 2.5 to 5.0 wt.-% and more preferably of 3.0 to 5.0 wt.-%, based on the whole composition.

[0024] In addition to or instead of boric acid, boronic acids may be used for stabilizing the soil-release polymer in the composition of the present invention in an amount of 0.001 to 1 wt.-%, preferably of 0.01 to 0.7 wt.-% and even more preferably of 0.02 to 0.5 wt.-%, based on the whole composition.

[0025] Alkyl as well as aryl boronic acids or water-soluble salts thereof may be used in terms of the present invention, however, aryl boronic acids or water-soluble salts thereof are preferred. Particular preferably said aryl boronic acid may be selected from the group consisting of 2-formylphenylboronic acid, 3-formylphenylboronic acid, 4-formylphenylboronic acid, 2-acetaminophenylboronic acid, 3-acetaminophenylboronic acid, 4-acetamoniphenylboronic acid, 4-carboxyphenylboronic acid, naphtalene-1-boronic acid, naphtalene-2-boronic acid and 6-hydroxynaphtalene-2-boronic acid, wherein 4-formylphenylboronic acid is particularly preferred. The amount of the boronic acid or water-soluble salts thereof in the composition of the present invention preferably may be in the range of from 0.001 to 1 wt.-%, more preferably in the range of from 0.01 to 0.7 wt.-% and most preferably in the range from 0.02 to 0.5 wt.-%.

[0026] Formic acid or a water-soluble salt thereof in an amount of from 0.005 to 0.5 wt.-%, based on the whole composition, may be used for stabilizing the soil-release polymer in the presence of the lipase as well. Particularly preferred is sodium formate. The preferred amount of formic acid or a water-soluble salt thereof is in the range of from 0.01 to 0.05 wt.-%.

[0027] Furthermore, water-soluble salts of calcium, magnesium or zinc which upon dissolution in the detergent composition of the present invention provide a concentration of calcium, magnesium and/or zinc ions in the range of from 0.01 to 100 mmol, preferably of 0.1 to 10 mmol per liter of the composition may be used. Suitable salts are for example calcium chloride, calcium hydroxide, calcium sulfate, calcium acetate and the like, as well as the corresponding magnesium or zinc salts, without being limited to these.

[0028] All of the above mentioned compounds may be used as a single compound or may be used as a combination of at least two or at least three of the compounds in the composition, whereas the use of at least one borate or boronic acid is particularly preferred.

[0029] In the composition of the present invention the ratio of the amount of the compound which stabilizes the soil release polymer to the amount of lipase present in the composition (wt.-%/wt.-%) preferably may be in the range of (i) from 100:1 to 1000:1, more preferably of from 150:1 to 750:1 and most preferably of from 200:1 to 600:1, if said compound represents boric acid or a water-soluble borate capable of forming boric acid, calculated on the basis of boric acid, or (ii) in the range of from 1:1 to 50:1, more preferably of from 1.2:1 to 20:1 and most preferably of from 2:1 to 10:1, if said compound represents a boronic acid, a water-soluble salt thereof, formic acid or a water-soluble salt thereof. Herein, the amount of lipase is calculated based on the amount of the respective "pure" enzyme in the composition and not on

the basis of a commercial available formulation added to the composition of the present invention, thus omitting any solvents, stabilizers, etc. which may be present in the commercially available enzyme formulations.

[0030] The pH of the composition of the present invention preferably may be in the range of from 7.0 to 13, more preferably of from 7.0 to 12, even more preferably of from 7.0 to 11 and most preferably of from 7.0 to 9.5. For adjusting the pH of the composition acids, bases as well as pH buffers may be used, which is well known to a person skilled in the art.

[0031] The composition of the present invention preferably further comprises at least one surfactant. Said surfactant may be selected from the group consisting of anionic, cationic, non-ionic as well as amphoteric surfactants, and preferably may be selected from the group consisting of anionic or non-ionic surfactants or mixtures thereof. More preferably, the composition of the present invention comprises a mixture of anionic and non-ionic surfactants. If surfactants are present in the composition of the present invention, their amount preferably may be in the range of from 10 to 50 wt.-%, more preferably of from 15 to 45 wt.-%, even more preferably of from 20 to 40 wt.-%, and most preferably of from 25 to 35 wt.-%, based on the whole composition. Preferably the composition comprises at least 2 anionic surfactants and at least 1 non-ionic surfactant, wherein the ratio of the combined amount of anionic surfactants to the amount of non-ionic surfactants preferably is greater than 1:1 and more preferably is in the range of from 1.1:1 to 5:1.

[0032] Surfactants suitable to be used in detergents, in particular in combination with enzymes are well known in the state of the art and include for example alkylbenzenesulfonic acids or salts thereof and alkylsulfonic acids or salts thereof. Suitable anionic alkylbenzene sulfonic or alkylsulfonic surfactants include in particular C_5-C_{20}, preferably C_{10}-C_{16}, even more preferably C_{11}-C_{13} alkylbenzenesulfonates, in particular linear alkylbenzene sulfonates (LAS), alkylestersulfonates, primary or secondary alkenesulfonates, sulfonated polycarboxylic acids and any mixtures thereof. Alkylethersulfates may be used as well.

[0033] As non-ionic surfactants preferably non-ionic ethoxylated, ethoxylated and propoxylated or propoxylated linear or branched monohydric aliphatic alcohols of natural or synthetic origin may be used. The preferred degree of ethoxylation and/or propoxylation may be in the range of from 3 to 9 EO and/or PO units per molecule. Preferred examples may include ethoxylated C_{12}-C_{l5} oxoalcohols with 3 to 9 EO units and linear ethoxylated C_{12}-C_{14} alcohols with 3 to 9 EO units.

[0034] In addition to the lipase the composition of the present invention preferably may comprise at least one further enzyme, which preferably may be selected from the group consisting of proteases, amylases, mannanases, cellulales, peroxidases, pectinases, further esterases or a mixture thereof.

[0035] These enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferably, the enzymes may be of bacterial of fungal origin and may be modified chemically or by protein engineering. Enzymes suitable to be incorporated into detergent compositions are known in the state of the art and are commercially available for example under the trademark names of Liquianase Novozyme A/S, Denmark), Alkalase or Savinase (Novozymes A/S, Denmark) for proteases, Termamyl (Novozymes A/S, Denmark) or Stainzyme Novozyme A/S, Denmark) for amylase or Mannaway Novozyme A/S, Denmark) for mannanase, without being limited to these. Sutiable enzymes are available from further manufacturers as well, such as for example Genencore. Numerous other enzymes suitable to be incorporated into detergent compositions, in particular into liquid laundry detergent compositions, may be found in the literature.

[0036] Preferably the composition of the present invention may comprise at least two further enzymes in addition to the lipase, more preferably at least three further enzymes, and even more preferably, at least four further enzymes, which preferably may be selected from the group comprising proteases, amylases, mannanases, cellulases and peroxidases, pectinases or further esterases, in particular from proteases, alpha-amylases, cellulases and mannanases. Preferably, the composition of the present invention may comprise at least one of each a proteases, alpha-amylases, cellulases and mannanases.

[0037] The composition further may comprise one or more compounds selected from the group consisting of of alkalis, bleaching agents, bleach activators, bleach catalysts, builders, colorants, chelating agents, dyes, dye transfer inhibitors, foam-inhibitors, hydrotropes, optical brighteners, perfumes, pigments, pH buffers, preservatives or soaps.

[0038] Alkalis suitable to be included in the composition of the present invention include alkaline or alkaline earths, i.e. earth metal hydroxide such as, for example, sodium hydroxide, alkaline or alkaline metal carbonates, mono-, di- or triethanolamine or water-soluble silicates.

[0039] Bleaching agents which may be included in the composition of the present invention include inorganic peroxygen bleaching compounds, such as, for example, perborates, percarbonates, sodium peroxide, persulfates, without being limited to these, as well as organic bleaching agents such as, for example, meta-chloroperbenzoic acid, 4-nonylamino-4-oxyperoxybutanoic acid, decanoyloxybenzoic acid, salts thereof or mixtures thereof, without being limited to these.

[0040] The afore-mentioned bleaching agents may preferably be combined with a bleach activator, leading to the *in situ* production of the peroxide acid derived from the bleach activator. Suitable bleach activators, for example, include nonanyloxybenzenesulfonate (NOPS) and tetraacetylethylenediamine (TAED). Bleach catalysts suitable to be included in the composition of the present invention include for example manganese oxalates, manganese complexes of 1,4,7-trimethyl-1,4,7-triazacyclononan or manganese proteinates.

[0041] To improve the color of the composition and/or the optical appearance of the fabrics to be treated with the

composition of the present invention, said composition further may comprise colorants, dyes and/or pigments.

[0042] For controlling the pH of the composition or the washing liquor derived thereof, as well as its mineral hardness, inorganic as well as organic builders may be incorporated into the composition. In addition, these builders may assist in the removal of particulate soil. If present in the composition according to the present invention, the builder or the mixture of builders preferably will be present in an amount of from 0,1 to 25 wt.-%, based on the whole composition. Suitable inorganic detergent builders include alkaline, ammonium or alkanolammonium salts of polyphosphates, including tripolyphosphates, pyrophosphates and polymeric meta-phosphates, phosphonates, silicates, carbonates, sulfates and aluminosilicates. Preferably, the composition of the present invention comprises less than 5 wt.-% of a polyphosphate builder, based on the whole composition.

[0043] In addition to or instead of an inorganic builder the composition of the present invention may as well comprise an organic detergent builder, including polycarboxylate builders in the form of their acid or a salt, including alkali metal salts such as potassium, sodium and lithium salts. Further organic detergent builders suitable to be used in the composition of the present invention include complexing agents such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), succinic acid, polyacrylic acid, polymaleic acid, citric acid, methyl glycin diacetic acid (MGDA), iminodisuccinic acid (IDS), glutamic acid-N,N-diacetic acid (GLDA) or water-soluble salts thereof. In particular if citric acid is used as a builder, fatty acids, in particular C_{12}-C_{18} fatty acids, may be incorporated into the composition of the present invention to provide additional builder activity.

[0044] In addition to the chelating agents already mentioned as builders, the detergent composition may optionally comprise one or more iron and/or manganese chelating agents, including aminocarboxylates, aminophosphonates, such as for example the phosphonates commercially available under the trademark name DEQUEST.

[0045] Furthermore, the composition may comprise a foam inhibitor. Typical foam inhibitors to be used in liquid laundry detergent compositions are well known to a person skilled in the art and include paraffines, fatty acids and salts thereof, fatty acid esters as well as polyorganosiloxane oils, mixtures of silicone and silacated silica, and the like, without being limited to these.

[0046] The present invention furthermore provides a method of stabilizing a soil-release polymer in a detergent composition which further comprises lipase, by combining said soil-release polymer and said lipase with a compound for stabilizing a soil-release polymer comprising ester moieties selected from the group consisting of boric acid or water-soluble borates capable of forming boric acid; boronic acids or water-soluble salts thereof; formic acid or water-soluble salts thereof; water-soluble salts of calcium, magnesium or zincor mixtures thereof.

[0047] In terms of the present invention, the term "combining" includes any order of addition of the three mentioned substances, i.e. all three compounds may be simultaneously added to the composition, one compound may be added before adding the two other compounds, two compounds may be simultaneously added before the last of these three compounds is added, etc.

[0048] Preferably, the method of stabilizing soil-release polymers according to the present invention is a method of stabilizing one of the soil-release polymers described above in a liquid laundry detergent composition, preferably a liquid laundry detergent composition as described above.

[0049] The method of the present invention further relates to the use of a compound selected from the group consisting of boric acid or water-soluble borates capable of forming boric acid: boronic acids or water-soluble salts thereof; formic acid or water-soluble salts thereof; water-soluble salts of calcium, magnesium or zinc or mixtures thereof for stabilizing a soil-release polymer comprising ester moieties in the presence of a lipase.

[0050] Said compound preferably is used for stabilizing compositions, wherein both said soil-release polymer as well as said lipase are present in a detergent composition, preferably a detergent composition according to the present invention as already described above.

List of figures

[0051]

Figure 1 shows the oil removing capacity of a commercially available product, which comprises a soil-release polymer, on a polyester test fabric after storing the product for 4, 12 and 19 weeks (test were carried out in the 5th, 13th and 20th week, respectively) (example 1).

Figure 2 shows the oil removing capacity of a commercially available product, which comprises a soil-release polymer, on a test fabric composed of a mixture of polyester and cotton after storing the product for 4, 12 and 19 weeks (test were carried out in the 5th, 13th and 20th week, respectively) (example 1).

Figure 3 shows the oil removing capacity of compositions 1 to 6 of example 2 on a polyester test fabric.

Figure 4 shows the oil removing capacity of compositions 1 to 6 of example 2 on test fabric composed of a mixture of polyester and cotton.

Figure 5 shows the change in oil removing capacity of compositions 1 to 5 of example 2 on a test fabric composed of a mixture of polyester and cotton.

Figure 6 shows the change in retention time of the soil-release polymer in detergent composition with increasing storage time as measured by GPC analysis (example 2).

Figure 7 shows the change in retention time of the soil-release polymer in detergent compositions comprising varying amounts of a stabilizer before and after a storage time of four weeks as measured by GPC analysis (example 3).

Examples

Dirty-Motor-Oil-Test

[0052] The Dirty-Motor-Oil-Test (DMO test) serves to evaluate the removal of synthetic oil from a hydrophobic fabric, which had previously been washed with a detergent comprising a soil release polymer. It serves to monitor the stability and thus the performance of the soil-release polymer after different storage times of the detergent composition. At first, test fabrics are prewashed in the presence of a soil-release polymer, so that the soil-release polymer may be adsorbed on the fabric and thus may form a protective film on said fabric surface. Then a defined amount of oil is applied to the fabric and dried thereon. The protecting film formed by said polymer should prevent the oil from adhering directly to the fibre, thus facilitating the removal of oil from a pre-treated fabric during the following main wash. Using photometric measurements, differences in the extent of soil removal and thus the performance of the soil-release polymers may be quantified.

[0053] Washing tests were carried out in a Linitest which has eight little "beakers" and simulates eight European drum type washing machines. The washing temperature was set to 40 °C, and the heating rate was set to 2 °C per minute. The time for one washing cycle was set to 30 minutes, for both a prewash and the main wash cycle. Rotations were set to 40 rotations per minute. 250 mL of washing liquor were used per beaker and washing cycle. As a soil 50 mL of used synthetic motor oil were applied to each piece of fabric.

[0054] As test fabrics, fabric pieces having a of a size of 11 cm x 18 cm, made of polyester the Wfk 30 A from Wfk (Krefeld, Germany) or polyester/cotton (Wfk 20 A from Wfk) were used. Each single test was carried out using four fabrics.

1. Prewashing

[0055] In each of the eight beakers of the Linitests four of the afore-mentioned test fabrics were placed. To adopt the amount of detergent to that typically used in a usual household washing machine (75 mL detergent per 16 L water), in the Linitest a solution of 4.7 mL of the respective detergent composition in 1 L of water was used, which previously had been stirred for about 5 to 10 minutes to obtain a homogenous solution. After adding 250 mL of said washing liquor in each beaker, the beakers were closed and a 30 minute washing cycle as described above was started. After each cycle the fabrics were rinsed using about 1 to 2 L of cold water. Said prewashing and rinsing cycle was carried out three times per fabric.

2. Contamination with soil

[0056] After the afore-mentioned prewashing cycles, the swatches were placed on a 1 cm high ring with a diameter of 5 cm and 50 μL of the used synthetic motor oil were pipetted in the middle of the swatches. The soiled swatches were left to dry on the rings for about 18 hours, before their reflectance was measured at 420 nm using a Minolta spectrophotometer CM 3.600 D (Minolta).

3. Main wash

[0057] For the main wash, the prewashed and soiled swatches were washed once for 30 minutes in the Linitest using a washing liquor concentration as described above. The swatches were then dried and evaluated at 420 nm using the Minolta spectrophotometer as described above.

[0058] The oil removal (OR), i.e. the cleaning capacity of the detergent with respect to the removal of the oily soil, was calculated according to the following formula:

$$OR\ (oil\ removal)\ in\ \% = \frac{R3-R2}{R1-R2} \times 100$$

wherein R1 is the reflectance value obtained using the Minolta spectrophotometer as described above of the swatch after the prewash, R2 is the reflectance value obtained after contamination with oil and R3 is the reflectance value obtained after the main wash. The higher the OR value obtained, the better is the washing result.

3. Gel permeation chromatography (GPC)

[0059] The change in the molecular mass distribution of the soil-release polymer in the detergent after storage was measured by gel permeation chromatography, wherein substances are separated based on their hydrodynamic volume.
[0060] Upon ester hydrolysis of the soil-release polymer due to lipase digestion and/or alkaline hydrolysis, the molecular weight distribution of the soil-release polymer is shifted towards a lower molecular weight, which can be seen by an increasing retention time in the GP-chromatogram.
[0061] GPC was carried out using a Bedman System Gold apparatus (GME) with a SDV 5 M linear S column (polymer standard device) using 1,4-dioxane (Merck) at a flow of 1 ml/min, following the absorbance at 244 nM.

Example 1: Decrease in oil removal in a commercially available liquid detergent

[0062] A commercially available liquid detergent comprising a soil-release polymer was stored at room temperature for several weeks. A decrease in oil-removal performance can be observed in said commercially available product upon storage, as shown below.
[0063] At first, test fabrics were prewashed using this commercially available product and soiled as described above.
[0064] The test fabrics were then washed in a main wash cycle as described above with the commercially available product which already had been stored for 8 weeks and which was stored for 5 additional weeks, respectively, as the test was carried out. As can be seen from figures 1 and 2, the oil removing capacity of the product decreases with an increasing storage time for both, fabrics consisting of polyester and fabrics consisting of a mixture of polyester and cotton, wherein the effect is more pronounced for pure polyester fabrics (figure 1).

Example 2: Influence of lipase on the stability of soil-release polymers

[0065] A typical liquid detergent composition of the following composition was used in all further experiments (table 1):

Table 1

Compound	**Amount [wt.-%]**
Nonionic Surfactant (ethoxylated C_{10}-C_{18} alcohol with 7 EO units)	12
Anionic surfactants (dodecylbenzene sulfonic acid + sodium laureth sulfate)	17
Propylene glycol	7.5
Citric acid	3
Fatty acid	3
Ethanol	3
Sodium hydroxide	3.5
Sodium diethylenetriamine pentamethylene phosphonate	1
Minors (optical brightener, foam inhibitor, perfume, various enzymes inclung a protease, an amylase and a mannanase))	>1%
water	up to 100

[0066] To said liquid detergent composition (pH about 8) neither comprising a lipase nor a soil release polymer, a lipase and/or a soil-release polymer comprising polyethylene terephtalate and polyoxyethylene terephtalate units were added before the water was added up to 100 wt.-%. The added amounts of the commercially available lipase formulation Lipex 100 L (Novozymes) having an activity of 100 KLU/g and a protein content of 2,2 wt.% in said formulation and of

the soil-release polymer formulation Marloquest L 235 M (Sasol), comprising 70 wt.% of the soil-release polymer, are shown in table 2.

Table 2

Composition No.	Lipex 100 L	Marloquest L235M)
1	0,3%	-
2	-	0,76%
3	0,1%	0,76%
4	0,3%	0,76%
5	0,5%	0,76%
6	0,3%	1,0%

[0067] Compositions 1 to 6 were stored at room temperature for a total of 19 weeks. Evaluation of the oil-removing capacity according to the DMO-Test and the molecular weight distribution of the soil-release polymer using GPC as described above were carried out before storage and after 4, 8, 12 and 19 weeks of storage, respectively.

[0068] Figures 3 and 4 show the oil removing capacity of compositons 1 to 6 according to table 1 on polyester and polyester/cotton fabrics, respectively before storage. It can be seen that the oil removing capacity can be increased significantly by the addition of a soil-release polymer. At least on polyester, an additional slight increase of oil removing capacity can be observed when additionally lipase is added to the formulation. On the other hand increasing the amount of soil-release polymer in the presence of 0.3 wt.% of the commercially available lipase formulation does not further increase the oil removing capacity at the starting point.

[0069] Figure 5 summarizes the results from the DMO-Tests obtained on a fabric consisting of a mixture of polyester and cotton using the formulations stored for 0 (starting point), 4, 12 and 19 weeks, respectively. It can be seen that in the absence of a soil-release polymer, the oil-removing capacity nearly stays the same for the whole storage time. Adding a soil-release polymer clearly increases the oil-removing capacity, both, in the presence and the absence of a lipase. With an increasing lipase content in the formulation, the oil-removing capacity decreases with storage time. A slight decrease in the oil-removing capacity can even be observed in the composition comprising the soil-release polymer, but no lipase. Said decrease may be due to alkaline ester hydrolysis, as the formulation has an alkaline pH.

[0070] With increasing storage time a degradation of the polymer can be observed which is more pronounced in the presence of increasing amounts of lipase, as can be seen by the shift in retention time from GPC analysis towards longer retention times which is shown in figure 6.

Example 3: Stabilization of a soil-release polymer in liquid detergent compositions

[0071] To the composition of table 1 different amounts of boric acids and lactic acid as well as the commercially available lipase formulation Lipex 100 L and the soil-release polymer formulation Marloquest L 235 M were added, as shown in table 3, before water was added ad 100 wt.-%.

Table 3

Composition no.	Lipex 100L	MarloquestL235M	Other ingredients
1	0.3%	-	1.5% boric acid
2	0.3%	0.76%	-
3	0.3%	0.76%	1.5% boric acid
4	0.3%	0.76%	3.0% boric acid
5	0.3%	0.76%	4.5% lactic acid
6	-	0.76%	1.5% boric acid

[0072] Degradation of the soil-release polymer in these formulations was evaluated by analyzing the shift in GPC retention time after storing these products for 4 weeks at room temperature.

[0073] The results are presented in figure 7. It can be seen that degradation of the polymer is reduced by adding lactic

or boric acid to the formulation, wherein better results are obtained using boric acid. Increasing the amount of boric acid increases the polymer stability during storage. The formulation comprising the soil-release polymer and the lipase, but no boric or lactid acid (product 2 in table 3) showed an oil-removal of 21,3 % on the fabric consisting of polyester and 39,7 % on a fabric consisting of a mixture of polyester and cotton, while in the presence of 1.5 wt.% of boric acid (product 3 in table 3) the oil-removal was found to be 24 % for polyester and 43,4 % on polyester/cotton. In the presence of 3 wt. % boric acid (product 4 in table 3) the oil-removal was found to be 24,9 % on polyester and 43,5 % on polyester/cotton.

Claims

1. A detergent composition, comprising at least one lipase, at least one soil-release polymer, comprising ester moieties, in an amount of at least 0.25 wt.-%, based on the whole composition, and at least one compound which stabilizes said at least one soil-release polymer in the presence of said lipase during storage of the composition and is selected from the group consisting of boric acid or water-soluble borates capable of forming boric acid in an amount of from more than 1 wt.-% to 5.5 wt.-%, based on the whole composition and calculated on the basis of boric acid, boronic acids or water-soluble salts thereof in an amount of from 0.001 to 1 wt.-%, based on the whole composition, formic acid or water-soluble salts thereof in an amount of from 0.005 to 0.5 wt.-%, based on the whole composition, lactic acid in an amount of from 1 to 10 wt.%, based on the whole composition; water-soluble salts of calcium, magnesium or zinc in an amount of from 0.01 to 100 mmol per liter of the composition or mixtures thereof.

2. The composition according to claim 1, wherein the composition is a liquid laundry detergent composition, preferably for use in household washing machines, which preferably comprises of from 20 to 90 wt.-%, more preferably of from 30 to 80 wt.-% and even more preferably of from 50 to 70 wt.-% of a liquid carrier, selected from the group consisting of water, alcohols or mixtures thereof.

3. The composition according to claim 1 or 2, wherein the at least one lipase is a triacylglycerol lipase and preferably is present in the composition in an amount of from 0.001 to about 0.05 wt-%, more preferably of from 0.002 to 0.02 wt.%, based on the whole composition.

4. The composition according to any of claims 1 to 3, wherein the at least one soil-release polymer comprises terephthalate ester moieties and preferably represents a copolymer, more preferably a copolyester comprising terephthaloyl, alkylene glycol and polyalkylenglykol units and even more preferably a copolymer comprising polyethylene terephthalate and polyoxyethylene terephthalate units.

5. The composition according to any of claims 1 to 4, wherein the amount of the soil release polymer(s) in the composition is at least 0.3 wt.-%, preferably at least 0.35 wt.-%, more preferably at least 0.4 wt.-% and most preferably at least 0.5 wt.-%, based on the whole composition.

6. The composition according to any of claims 1 to 5, wherein the ratio of the amount of soil release polymer to the amount of lipase present in the composition (wt.-%/wt.-%) is in the range of from 10:1 to 200:1, preferably of from 20:1 to 150:1, more preferably of from 40:1 to 120:1 and even more preferably of from 60:1 to 100:1.

7. The composition according to any of claims 1 to 6, wherein the ratio of the amount of the compound which stabilizes the soil release polymer to the amount of lipase present in the composition (wt.-%/wt.-%) is in the range of (i) from 100:1 to 1000:1, preferably of from 150:1 to 750:1 and most preferably of from 200:1 to 600:1, if said compound represents boric acid or a water-soluble borate capable of forming boric acid, calculated on the basis of boric acid, or (ii) in the range of from 1:1 to 50:1, preferably of from 1.2:1 to 20:1 and most preferably of from 2:1 to 10:1, if said compound represents a boronic acid, a water-soluble salt thereof, formic acid or a water-soluble salt thereof.

8. The composition according to any of claims 1 to 9, wherein the pH of the composition is in the range of from 7.0 to 13, preferably of from 7.0 to 12, more preferably of from 7.0 to 11 and most preferably of from 7.0 to 9.5.

9. The composition according to any of claims 1 to 10, further comprising at least one surfactant, preferably selected from the group consisting of anionic and nonionic surfactants or a mixture thereof, more preferably a mixture of anionic and non-ionic surfactants, in an amount of from 10 to 50 wt-%, based on the whole composition.

10. The composition according to any of claims 1 to 11, further comprising at least one further enzyme, preferably selected from the group consisting of proteases, amylases, mannanases, cellulases, peroxidases, pectinases, further

esterases or a mixture thereof.

11. The composition according to any of claims 1 to 12, further comprising one or more compounds selected from the group consisting of alkalis, bleaching agents, bleach activators, bleach catalysts, builders, colorants, chelating agents, dyes, dye transfer inhibitors, foam-inhibitors, hydrotropes, optical brighteners, perfumes, pigments, pH buffers, preservatives or soaps.

12. A method for stabilizing a soil-release polymer comprising ester moieties in a detergent composition which further comprises a lipase by combining said soil-release polymer and said lipase with a compound for stabilizing said soil-release polymer selected from the group consisting of boric acid or water-soluble borates capable of forming boric acid, boronic acids or water-soluble salts thereof, formic acid or water-soluble salts thereof, water-soluble salts of calcium, magnesium or zinc or mixtures thereof.

13. The method of claim 12, wherein the detergent composition is a liquid detergent composition, preferably a detergent composition according to any of claims 1 to 11.

14. Use of a compound selected from the group consisting of boric acid or water-soluble borates capable of forming boric acid, boronic acids or water-soluble salts thereof, formic acid or water-soluble salts thereof, water-soluble salts of calcium, magnesium or zincor mixtures thereof for stabilizing a soil-release polymer comprising ester moieties in the presence of a lipase.

15. The use according to claim 14, wherein both, said soil-release polymer as well as said lipase are present in a detergent composition, preferably a detergent composition according to any of claims 1 to 11.

Figure 1

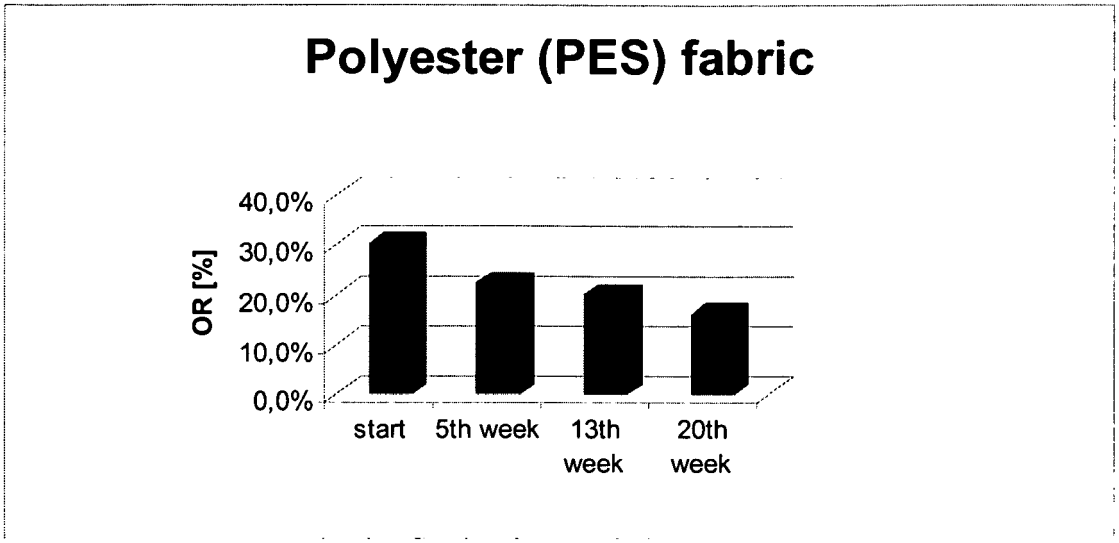


Figure 2

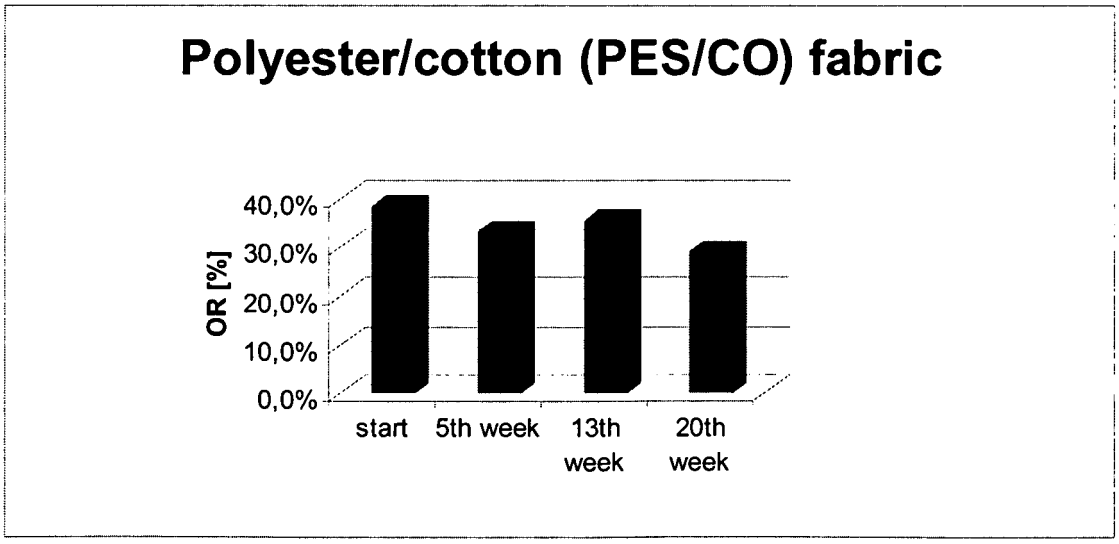


Figure 3

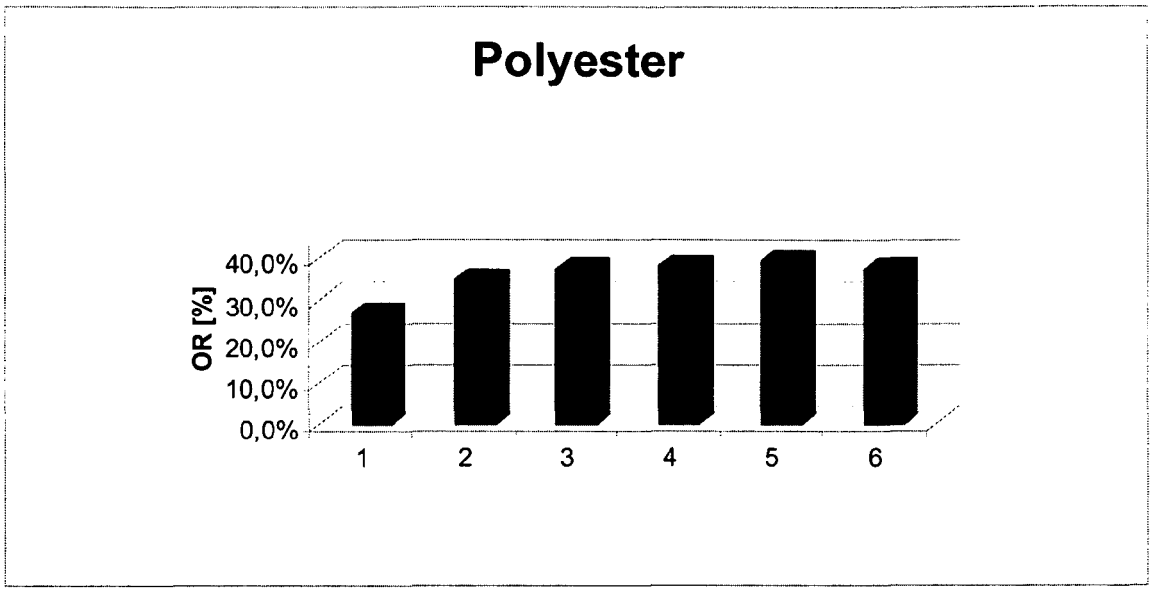


Figure 4

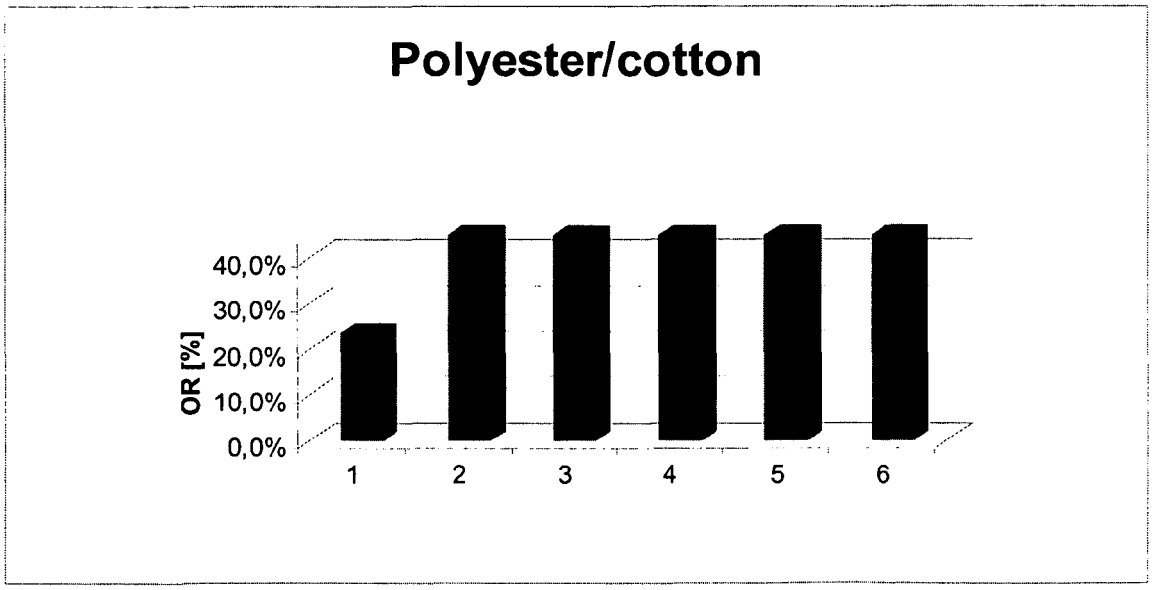


Figure 5

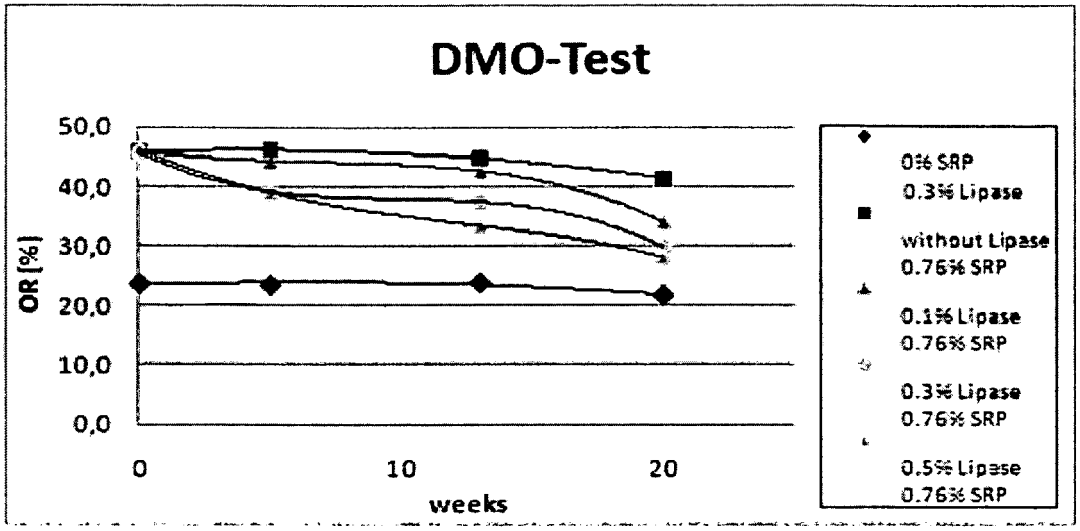


Figure 6

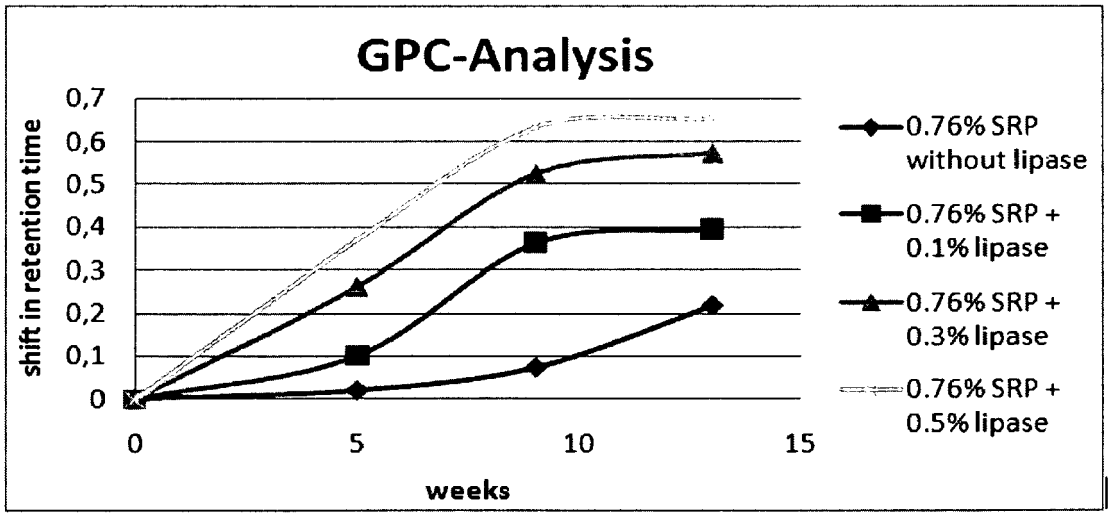
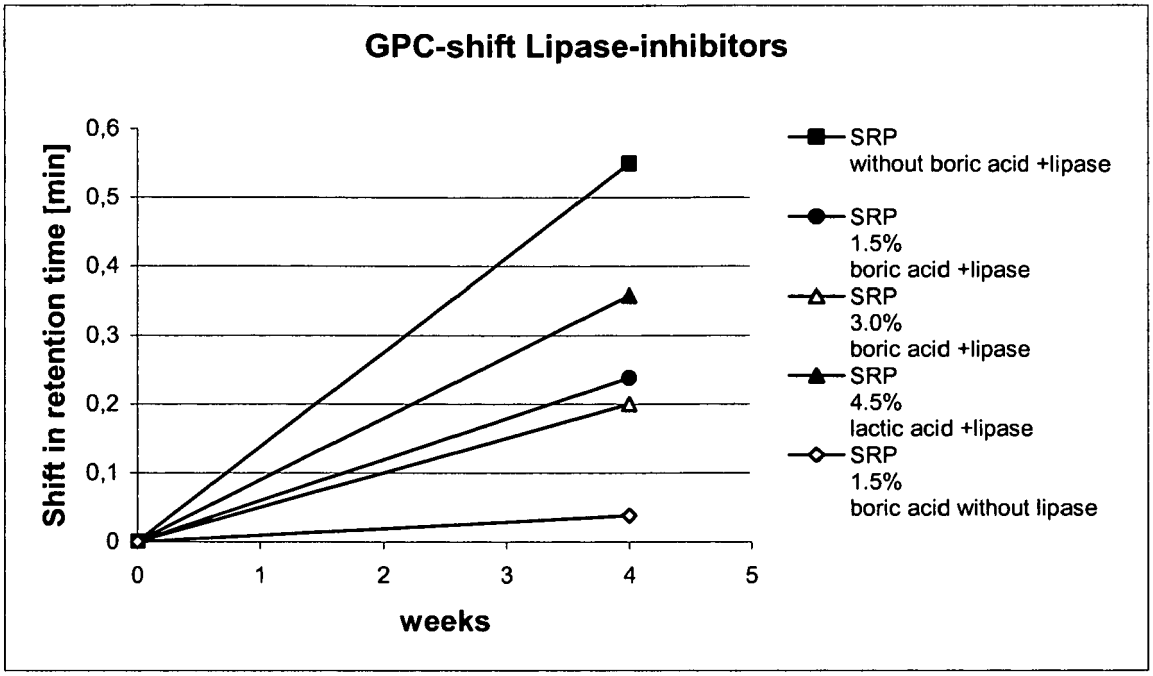


Figure 7


GPC-shift Lipase-inhibitors
Shift in retention time [min]
0,6
0,5
0,4
0,3
0,2
0,1
0
0
1
2
3
4
5
weeks
SRP without boric acid +lipase
SRP 1.5% boric acid +lipase
SRP 3.0% boric acid +lipase
SRP 4.5% lactic acid +lipase
SRP 1.5% boric acid without lipase

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EUROPEAN SEARCH REPORT

Application Number
EP 11 00 4982

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C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	24 October 2011	Culmann, J

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