A detergent composition having shading dyes and lipase

The invention relates to detergent compositions having shading dyes and lipase. It has been determined that combination of lipase with specific shading dyes provides lower redeposition of soil. This is manifested as higher reflectance and lower yellowing, especially over multiple washes on knitted cotton, knitted polyester and polyester fabrics.

Disclosed is a detergent composition comprising:
(i) a surfactant;
(ii) a hydrophobic dye;
(iii) a direct dye;
(iv) an acid dye; and,
(v) lipase.
Description

Field of Invention

[0001] The present invention relates to detergent compositions having shading dyes and lipase.

Background and Related Art

[0002] Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of the common general knowledge in the field.

[0003] White clothes are very popular. They may be made from a variety of fabrics such as 100% cotton, polyester-cotton blends (poly cotton), 100% polyester or nylon. It is known that fabrics, especially white fabrics, tend to develop a yellowish tinge over a period. This may happen due to incomplete removal of soil, deposition of oily skin residues, and oxidation of sebum. Yellowing of white fabrics is not an instant or short term phenomenon. White fabrics have to be washed and worn several times to perceive the yellowish tinge.

[0004] This problem may be solved to some extent by use of fluorescers. They absorb ultra violet light and emit visible light causing yellowed garments to look brighter. The problem may also be solved by using shading dyes. These dyes add a blue tint to fabrics, thereby masking the yellowish tinge and making the fabrics look whiter and brighter. Shading dyes help maintain and re-invigorate whiteness. Fluorescers and shading dyes are known to deposit on fabrics. Some shading dyes deposit only on some specific types of fabrics. This may depend on chemical interactions between fabrics and dyes. For example, hydrophobic shading dyes deposit on hydrophobic fabrics. Direct and acid dyes, which are blue and violet, show particular utility on cotton. Solvent and disperse dyes give benefits on polyester, nylon and elastane fabrics. It has been noticed that accumulation of soil or sebum on fabrics prevents, or at least reduces the deposition of shading dyes. This may be due to incomplete removal of soil or sebum during washing.

[0005] Detergent compositions having a combination of shading dyes are known.

[0006] Such combinations are generally used so that the compositions include dyes that may deposit on variety of fabrics.

[0007] EP1921132 A2 (Unilever, 2008) discloses a laundry treatment composition having a surfactant and a combination of dyes which together have a visual effect on the human eye as a single dye having a peak absorption wavelength on cotton of from 540 nm to 650 nm. One of the dyes is a photostable dye which is substantive to cotton.

[0008] WO 2010/145887 A1 (Unilever, 2010) discloses laundry treatment composition having an anionic dye-polymer which provides for improved shading of fabrics and facilitating soil removal. The application teaches a composition having surfactant and a dye-polymer obtained by polymerisation of a dye monomer and an alkene co-monomer. This application is silent about the effect of a combination of shading dye and lipase on lowering the redeposition of soil.

[0009] Enzymes, particularly lipase, have been used in detergent compositions for enhanced cleaning. It is known that lipase aids grease removal. Lipase catalyses hydrolysis of triglycerides which form a major component of many commonly encountered fatty soils such as sebum, animal fats (e.g. lard, ghee, butter) and vegetable oils (e.g. olive oil, sunflower oil, peanut oil).

[0010] Detergent compositions having lipase and shading dyes have also been disclosed.

[0011] US2007191250 A1 (P&G) discloses detergent compositions which include certain lipase variants and shading dyes selected from dyes and dye-clay conjugates. This application discloses that the action of lipase results in malodour because of hydrolysis of triglycerides functionalized with short chain fatty acyl units. Such triglycerides release malodorous volatile fatty acids after lipolysis. This problem has been solved in the past by using a combination of a shading dye with certain lipase variants, which is believed to increase the level of grease removal leading to better accessibility of the shading dye to the fabric surface and hence, improved deposition.

[0012] We have determined that combination of lipase with specific shading dyes provides lower redeposition of soil. This is manifested as higher reflectance and lower yellowing, especially over multiple washes on knitted cotton, knitted polyester and polyester fabrics.

Summary of the Invention

[0013] According to a first aspect the invention provides a detergent composition which includes a surfactant, a hydrophobic dye, a direct dye; an acid dye and lipase.

[0014] According to a second aspect the invention provides a method of laundering fabrics which includes a step of treating the fabrics with a composition according to the first aspect.

[0015] According to a third aspect the invention provides a method of treating fabrics, the method comprising the steps of:
(i) treating fabrics with an aqueous solution which includes:

(a) 0.3 g/l to 10 g/l surfactant;
(b) 0.1 ppb to 500 ppm hydrophobic dye;
(c) 0.1 ppb to 500 ppm direct dye;
(d) 0.1 ppb to 500 ppm acid dye; and,
(e) 0.3 ppb to 10 ppm lipase;

(ii) rinsing the fabrics; and,

(iii) drying the fabrics.

[0016] According to a fourth aspect the invention provides use of a composition of the first aspect to reduce redeposition of soil on fabrics.

[0017] The term "comprising" is meant not to be limiting to any subsequently stated elements but rather to encompass non-specified elements of major or minor functional importance. In other words the listed steps, elements or options need not be exhaustive. Whenever the words "including" or "having" are used, these terms are meant to be equivalent to "comprising" as defined above.

[0018] Except in the operating and comparative examples, or where otherwise explicitly indicated, all numbers in this description indicating amounts of material ought to be understood as modified by the word "about".

[0019] It should be noted that in specifying any range of concentration or amount, any particular upper concentration can be associated with any particular lower concentration or amount.

[0020] The terms weight percent, percent by weight, % by weight, wt%, and the like are synonyms that refer to the concentration of a substance as the weight of that substance divided by the weight of the composition and multiplied by 100.

[0021] The recitation of numerical ranges by endpoints includes all numbers subsumed within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5).

[0022] As used in this specification and the appended claims, the singular forms "a", "an", and "the" include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to a composition containing "a compound" includes a mixture of two or more compounds. As used in this specification and the appended claims, the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

[0023] For complete understanding of features and advantages of the invention, reference should be made to the following detailed description.

Detailed Description of the Invention

[0024] As used herein, the term "detergent composition" includes granular or powder compositions, liquids, tablets, bars and gels.

Surfactants

[0025] The detergent compositions include 2 wt% to 70 wt % surfactant, most preferably 10 to 30 wt%. Preferred compositions include anionic or non-ionic surfactants. More preferred compositions include a mixture of the two.


[0027] Suitable anionic surfactants which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphaating higher C5 to C15 alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C8 to C20 benzene sulphonates, particularly sodium linear secondary alkyl C10 to C15 benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The preferred anionic detergent compounds are sodium C6 to C15 alkyl benzene sulphonates and sodium C12 to C15 alkyl sulphates. Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides.

[0028] Suitable nonionic surfactants which may be used include, in particular, the reaction products of compounds
having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols
with alkylene oxides, especially ethylene oxide (EO) either alone or with propylene oxide. Specific nonionic detergent
compounds are C₆ to C₂₂ alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene
oxide per molecule, and the condensation products of aliphatic C₆ to C₁₈ primary or secondary linear or branched
alcohols with ethylene oxide, generally 5 to 40 EO.

**Preferred surfactant systems are mixtures of anionic with nonionic surfactants, in particular the groups and
examples of anionic and nonionic surfactants pointed out in EP-A-346 995 (Unilever). Especially preferred is surfactant
system that is a mixture of an alkali metal salt of a C₆ to C₂₂ primary alcohol sulphates together with a C₁₂ to C₁₈ primary
alcohol 3 to 7 EO ethoxylate.**

**Preferred compositions may include 4 wt% to 25 wt% nonionic surfactants.**

**Shading dyes**

**As used herein the term “shading dye” means dyes which when formulated in detergent compositions can
deposit onto fabrics when the fabrics are contacted with wash liquor having the detergent compositions thus altering the
tint of the fabric through absorption of visible light. Shading dyes are also known as hueing agents.**

**Shading of white fabrics may be done with any colour depending on consumer preference. Blue and Violet are
particularly preferred shades and consequently preferred dyes or mixtures of dyes are ones that give a blue or violet
shade on white fabrics. Therefore preferred shading dyes are blue or violet. Such dyes give a blue or violet colour to
white fabrics. The hue angle is 240° to 345°, more preferably 260° to 320° and most preferably 270° to 300°.**

**Shading dyes may be classified into several classes and in several ways. One way is to classify the dyes
depends on their structures. Examples include Azo dyes and Anthraquinone dyes. Another way is to classify them
according to their mode of application. Examples include direct dyes and acid dyes, disperse, vat, and solvent dyes.
According to another method of classification, dyes are called Hydrophobic or Hydrophilic depending on their affinity for
fabrics. Yet another way of classifying shading dyes depends on whether the dyes deposit onto fabrics after a single-
wash to show their effect, or whether they deposit after multiple washes. Dyes that deposit in a single-wash are called
one-wash dyes. Examples include Acid Violet 50 (AV50).**

**The others are called build-up dyes. Some examples include Direct Violet 9 (DV9) and Solvent Violet 13 (SV13).**

**Detergent compositions according to the invention include three dyes:**

1. **Hydrophobic dye**

2. **Disperse dye**

3. **It is preferred that the disperse dye is an Anthraquinone dye. Preferred Anthraquinone dyes may be represented
   by the following structure:**
wherein R1, R4, R5, and R8 are independently selected from the groups consisting of -H, -OH, -NH₂, NHCOCH₃ and -NO₂, such that a maximum of only one -NO₂ group and a maximum of two -H are present as R1, R4, R5, and R8 substituents; and R2, R3, R6, and R7 is selected from -H, F, Br, Cl or -NO₂, and -Oaryl.

[0042] Preferred disperse dyes include Disperse Violet 27 (DV27) Disperse Violet 26 (DV26), Disperse Violet 28 (DV28), Disperse Violet 63 (DV63) and Disperse Violet 77 (DV77). Disperse Violet 28 (DV28) is the most preferred disperse dye.

[0043] Another preferred anthraquinone dye is Solvent Violet 13 (SV13). It is a synthetic anthraquinone dye with bright bluish violet hue. It is insoluble in water and soluble in acetone, toluene, and benzene. Its chemical formula is C₂₁H₁₅NO₃, and its structure is 1-hydroxy-4-(p-tolylamino)-anthraquinone, or 1-hydroxy-4-[(4-methylphenyl)amino]-9,10-anthracenedione or 1-hydroxy-4-(4-methylanilino) anthraquinone.

[0044] Mono-azo dyes are also preferred hydrophobic dyes. They may be represented by the following structure:

\[
\text{D-N=N-N-N-R}^3 \text{-R}^4
\]

where R3 and R4 are optionally substituted C₂ to C₁₂ alkyl chains having optionally therein ether (-O-) or ester links, the chain being optionally substituted with -Cl, -Br, -CN, -NO₂, and -SO₂CH₃; and, D denotes an aromatic or heteroaromatic group.

[0045] The aromatic rings may be further substituted preferably by -Cl, -Br, -CN, -NO₂, -SO₂CH₃ and -NHCOR; and R is selected from -CH₃, -C₂H₅, and -CH₂Cl.

[0046] Structures of most preferred mono-azo dyes are:

where X and Y are selected from -Cl, -Br, -CN, -NO₂, -SO₂CH₃ and -NHCOR and R is selected from -CH₃, -C₂H₅, and -CH₂Cl groups. Preferably X is NHCOCH₃ or NHCOCH₂Cl.

[0047] Particularly preferred hydrophobic dyes are SV13 and DV28; and DV28 is the most preferred hydrophobic dye. DV28 may be sourced from DyStar.

[0048] Preferred compositions include 0.0001 wt% to 0.008 wt%, preferably 0.0003 wt% to 0.006 wt% hydrophobic dye. When the hydrophobic dye is DV28, the preferred range is 0.001 wt% to 0.006 wt%. When the hydrophobic dye is SV13, the preferred range is 0.0003 wt% to 0.0025 wt%. It is preferred that DV28 is included in the form of an adjunct. The adjunct may preferably be made of inorganic carriers like soda ash, Sodium sulphate or zeolite. The adjunct may also include a dispersant e.g. lignin sulphonate.
2. Direct dye

[0049] Preferred direct dyes are bis-azo direct violet dyes of the formula:

\[
\begin{array}{c}
\text{Y} - \text{N} - \text{NH} - \text{N} - \text{A} - \text{NH} - \text{Z} \\
\text{OCH}_3 \\
\text{CH}_3 \\
\text{O}_2\text{S}
\end{array}
\]

where Z is H or phenyl, the A ring is preferably substituted by a methyl and methoxy group at the positions indicated by arrows, the A ring may also be a naphthyl ring, the Y group is a phenyl or naphthyl ring, which is substituted by sulphate group and may be mono or disubstituted by methyl groups.

[0050] Non-limiting examples of these dyes are Direct Violet 5, 7, 9, 11, 26, 31, 35, 41 and 51 and DV99. Further non-limiting examples of these dyes are also Direct Blue 34, 70, 71, 72, 75, 78, 82, and 120. The most preferred direct dye is Direct Violet 9 (DV9). DV99 is also preferred. Such dyes have been described in WO2005/003274 A1 (Unilever). DV9 may be sourced from BASF.

[0051] Other preferred direct dyes may be tris-azo direct blue dyes of the formula:

\[
\begin{array}{c}
\text{X} - \text{N} - \text{N} - \text{A} - \text{NH} - \text{B} - \text{N} - \text{C}
\end{array}
\]

where at least two of the A, B and C napthyl rings are substituted by a sulphonate group, the C ring may be substituted at the 5 position by an NH$_2$ or NHPPh group, X is a phenyl or naphthyl ring substituted with upto 2 sulphonate groups and may be substituted at 2 position with a OH group and may also be substituted with an NH$_2$ or NHPPh group.

[0052] As such dyes are substantive, only a small amount is required to provide enhanced whiteness effect hence preferred compositions include 0.00001 wt% to 0.004 wt%, preferably 0.0001 wt% to 0.004 wt% direct dye. When the direct dye is DV9, the preferred range is 0.00001 wt% to 0.004 wt%. It is preferred that DV9 is included in the form of an adjunct. The adjunct may preferably be made of inorganic carriers like soda ash, Sodium sulphate or zeolite. The adjunct may also include a surfactant or dispersant e.g. nonionic surfactants.

[0053] In another embodiment the direct dye may be covalently linked to a photobleach, for example as described in WO2006/024612 A1 (Ciba SC Holding AG).

3. Acid dye

[0054] The detergent compositions also include an acid dye.

[0055] Cotton substantive acid dyes give benefits to fabrics which contain cotton. Preferred dyes and mixes of dyes are blue or violet. Preferred acid dyes are azine dyes. Their core structure as follows:
wherein Rₐ, Rₕ, Rₖ and Rₜ are selected from: H, an branched or linear C₁ to C₇ alkyl chain, benzyl a phenyl, and a naphthyl; the dye is substituted with at least one -SO₃⁻ or -COO⁻ group; the B ring does not carry a negatively charged group or salt thereof; and the A ring may further substituted to form a naphthyl;
the dye is optionally substituted by groups selected from: amine, methyl, ethyl, hydroxyl, methoxy, ethoxy, phenoxy, Cl, Br, I, F, and NO₂.

With respect to the azine dye of described core structure, it is preferred that the A ring is further substituted to form a naphthyl. The dye is preferably substituted by two -SO₃⁻ groups and there is no other charged substituent. One skilled in the art will appreciate that the metal cation that is exemplified as Sodium may be easily varied and such is within the scope of the invention, for example, such as alkali earth metals and alkaline earth metals and these are preferred, in particular Potassium and Calcium.

One skilled in the art will appreciate that apart from the requirement that the azine dye is substituted with at least one SO₃⁻ or COO⁻ group and that the B ring does not carry a negatively charged group or salt thereof the latitude to vary substituents is large without affecting the efficacy of the dye to deposit on cotton as required. The groups Rₐ, Rₕ, Rₖ and Rₜ as specified above may carry other substituents.

Preferred azine dye has the following structure:

\[
\begin{align*}
R₁, R₂, R₃ \text{ and } R₄ \text{ is selected from the group consisting of: H, Me, Et, n-Pr and i-Pr; and the dye is optionally substituted by a methoxy group.}
\end{align*}
\]

A further preferred dye is of the following structure:

\[
\begin{align*}
R₁, R₂, R₃ \text{ and } R₄ \text{ as specified above may carry other substituents.}
\end{align*}
\]

Preferred azine dyes are: Acid Blue 98, Acid Violet 50, and Acid Blue 59, more preferably Acid Violet 50 (CAS No. 6837-46-3; C.I. 50325) and Acid Blue 98. Most preferably the azine dye is Acid Violet 50 (AV50). This dye may be sourced from Clariant.

Preferred compositions include 0.00001 wt% to 0.1 wt%, preferably 0.0001 wt% to 0.01 wt%, and most preferably 0.0005 wt% to 0.005 wt% azine dye. When the dye is AV50, the preferred range is 0.0001 wt% to 0.005 wt%. It is preferred that AV50 dye is included in the form of an adjunct. The adjunct may preferably be made of inorganic carriers like soda ash, Sodium sulphate or zeolite. The adjunct may also include a surfactant or dispersant and a binder.

Other preferred non-azine acid dyes are Acid Violet 17, Acid Black 1, Acid Red 51, Acid Red 17 and Acid Blue 29.

The dyes may be incorporated in a variety of ways. For example dyes which are not sensitive to heat may be included in the slurry which is to be spray dried.

Another way of incorporating dyes into particulate detergent products is to add them to adjunct granules which are post-dosed to a base powder. In this case there may be concentration of dye in the granules which could present the risk of spotting and dye damage on the fabrics. This can be avoided if the concentration of dye in the granules is less than 0.1 wt%. The dyes may be incorporated in the form of granules, which are made of carriers such as light soda ash, bentonite,
Lipase

[0065] The detergent compositions according to the invention include lipase. Lipase (also known as esterase) is an enzyme which catalyses hydrolysis of ester bonds of edible fats and oils, i.e. triglycerides, into free fatty acids, mono- and diglycerides and glycerol. It is believed that the primary function of lipase is to reduce build-up of sebum. The use of lipase is of special interest for low temperature washes as then oils and fats are in the solid state and therefore more difficult to remove. It is also believed that the action of lipase is not manifested during the main-wash, but in between washes. It is believed that first the lipase gets adsorbed on top of soil during main-wash, but its action is inhibited by surfactants. During the rinse stage, lipase remains adsorbed and degrades the soil matrix. Lipase is also suitable for detergent compositions that contain higher amount of anionic surfactants, typically 20 to 40 wt%. Lipase is also believed to remove difficult stains like tomato oil, pasta sauce, pesto, motor oil, colourless oils like olive oil and corn oil. It is believed that lipase continues its action during the drying stage forming fatty acids, diglycerides and monoglycerides. When clothes are soiled again, some lipase is already present on the cloth. Thereafter, during the next wash, newly deposited soil, and to a lesser extent the residual soil matrix, are entrained. It is also believed that absorption of lipase increases with ionic strength of the detergent composition.

[0066] Preferred lipase enzymes include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from Humicola, more preferably ones which include a polypeptide having an amino acid sequence which has at least 90 % sequence identity with the wild-type lipase derived from Humicola lanuginose, most preferably strain DSM 4109.

[0067] Examples of useful lipases include lipases from Humicola (synonym Thermomyces), e.g. from H. lanuginosa (T. lanuginosus) as described in EP258068 and EP305216 or from H. insolens as described in WO96/13580, a Pseudomonas lipase, e.g. from P. alcaligenes or P. pseudoalcaligenes (EP218272), P. cepacia (EP331376), P. stutzeri (GB 1,372,034), P. fluorescens, Pseudomonas sp. strain SD 705 (WO95/06720 and WO96/27002), P. wisconsinensis (WO96/12012), a Bacillus lipase, e.g. from B. subtilis (Dartois et al. (1993), Biochirica et Biophysica Acta, 1131, 253-360), B. stearothermophilus (JP64/744992) or B. pumilus (WO 91/16422).


[0069] Preferred lipase enzymes are available under the trademarks LIPOCLEAN®, LIPOLASE®, LIPOLASE® Ultra and LIPEX®, LIPEX® is particularly preferred, and LIPEX® 100 TB is further particularly preferred. The activity of commercial lipase is commonly expressed as Lipase Units or LU. Different lipase preparations may have different activities. For fungal lipases these may range from 2,000 to 2,000,000 LU per gram. The activity may also be represented as FIP units/g or FCC III LU/g. One of these new Lipase Units is equivalent to ten of the old LU, or 1,000 FIP units/g = 10,000 LU/g.

[0070] Preferred compositions include lipase having 5 to 20000 LU/g.

[0071] In order to prevent accidents and to alleviate safety concerns, commercial lipases are always coated with an inert material. Therefore, commercial lipases that are used for detergent powders, bars and tablets are in granular form containing very low amount of active lipase and balance of adjunct materials.

[0072] The granulates contain lipase concentrate, inorganic salt, binders and coating materials. They are free-flowing so that there is no lumping, and the granulates dissolve faster.

[0073] On the other hand, lipases fit for liquid detergents are available in liquid form. An example is LIPEX® 100 L.

[0074] Preferred compositions have 0.0001 wt% to 0.1 wt% lipase. Further preferred compositions have 0.0009 wt% to 0.00186 wt% lipase.

[0075] In addition to surfactant, shading dyes and lipase, the detergent compositions may also include other known ingredients. These ingredients include:

Hydrotrope

[0076] The term "hydrotrope" generally means a compound with the ability to increase solubility, preferably aqueous solubility of certain slightly soluble organic compounds. Examples include sodium xylene sulfonate.

Solvents

[0077] In the case of liquid or gel compositions, the compositions may include a solvent such as water or an organic solvent such as isopropyl alcohol or glycol ethers.
Metal chelation agents

[0078] The compositions may include a metal chelating agent such as carbonates, bicarbonates, and sesquicarbonates. The metal chelating agent can be a bleach stabiliser (i.e. heavy metal sequestrant). Suitable metal chelation agents include ethylenediaminetetraacetate (EDTA), diethylenetriamine pentaacetate (DTPA), ethylenediamine disuccinate (EDDS), and the polynaphosphates such as the DEQUEST®, ethylenediamine tetramethylene phosphonate (EDTMP) and diethylenetriamine pentamethylene phosphate (DETPMP).

Builders or complexing agents

[0079] Builders may be selected from calcium sequestrant materials, precipitating materials, calcium ion-exchange materials and mixtures thereof.

[0080] Examples of calcium sequestrant builders include alkali metal polyphosphates, such as sodium tripolyphosphate and organic sequestrants, such as ethylene diamine tetra-acetic acid. Examples of precipitating builders include sodium orthophosphate and sodium carbonate. Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP 0384070.

Low cost formulations preferably include carbonate (including bicarbonate and sesquicarbonate) and/or citrates as builders.

[0081] Where a builder is present, the compositions may suitably contain less than 20 wt %, preferably less than 10 wt% by weight, and most preferably less than 10 wt% builders.

Other shading dyes

[0082] In addition to a hydrophobic dye, a direct dye and an acid dye; preferred compositions may also include other dyes. Such dyes may be selected from:

Basic dyes

[0083] Basic dyes are organic dyes which carry a net positive charge. They deposit onto cotton. They are of particular utility for used in compositions that contain predominantly cationic surfactants. Dyes may be selected from the basic violet and basic blue dyes listed in the Colour Index International. Preferred examples include triarylmethane basic dyes, methane basic dye, anthraquinone basic dyes, Basic Blue 16, Basic Blue 71, Basic Blue 159, Basic Blue 19, Basic Blue 35, Basic Violet 38, Basic Violet 48, Basic Violet 3, Basic Violet 75, Basic Violet 95, Basic Violet 122, Basic Violet 124, Basic Violet 141. Thiazolium dyes may also be used. Examples include Basic Blue 41, 54, 65, 66, 67, 162 and 164.

Reactive dyes

[0084] Reactive dyes are dyes which contain an organic group capable of reacting with cellulose and linking the dye to cellulose with a covalent bond. They deposit onto cotton. Preferably the reactive group is hydrolysed or reactive group of the dyes have been reacted with an organic species such as a polymer, so as to link the dye to this species. Dyes may be selected from the reactive violet and reactive blue dyes listed in the Colour Index International.

[0085] Preferred examples include Reactive Blue 19, Reactive Blue 163, Reactive Blue 182 and Reactive Blue 96.

Dye conjugates

[0086] Dye conjugates are formed by binding direct, acid or basic dyes to polymers or particles via physical forces.

[0087] Depending on the choice of polymer or particle, they may deposit on cotton or synthetics. These have been described in WO2006/055787 A1 (P&G).

Photo-bleach

[0088] Preferred compositions may include a photo-bleach, preferably phthalocyanines at 0.00001 wt% to 1 wt%.

Other enzymes

[0089] In addition to lipase, one or more other enzymes may also be present in preferred compositions. Such enzymes
include proteases, alpha-amylases, cellulases, peroxidases/oxidases, pectate lyases, and mannanases.

[0090] Suitable proteases include those of animal, vegetable or microbial origin. Microbial origin is preferred. Chemically modified or protein engineered mutants are included. The protease may be a serine protease or a metallo protease, preferably an alkaline microbial protease or a trypsin-like protease. Preferred commercially available protease enzymes include ALCALASE®, SAVINASE®, PRIMASE®, DURALASE®, DYRAZYM®, ESPERASE®, EVERLASE®, POLARZYM®, KANNASE®, MAXATASE®, MAXACAL®, MAXAPEM®, PROPERASE®, PURAFACT® and PURAFECT® OxP.

[0091] Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from Bacillus, e.g. a special strain of B. lichenformis. Commercially available amylases are DURAMYL®, TERMAMYL®, TERMAMYL® Ultra, NATALASE®, STAINZYME®, FUNGAMYL® BAN®, RAPIDASE® and PURASTAR®.

[0092] Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants may also be used. Suitable cellulases include cellulases from the genera Bacillus, Pseudomonas, Humicola, Fusarium, Thielavia, Acremonium, e.g. the fungal cellulases produced from Humicola insolens, Thielavia terrestris, Myceliophthora thermophila, and Fusarium oxysporum. Commercially available cellulases include CELLUZYME®, CAREZYME®, ENDOLASE®, RENOZYME®, CLAZINASE® and PURADAX® HA. Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants may also be used. Examples of useful peroxidases include peroxidases from Coprinus, e.g. from C. cinereus, and variants thereof as those described in WO 93/24618, WO 95/10602, and WO 98/15257. Commercially available peroxidases include GUARDZYME® and NOVOZYM® 51004.

Enzyme stabilizer

[0093] Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyl such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708. Where alkyl groups are sufficiently long to form branched or cyclic chains, the alkyl groups encompass branched, cyclic and linear alkyl chains. The alkyl groups are preferably linear or branched, most preferably linear.

Perfume

[0094] Preferred compositions may also include perfumes. The perfumes could be of natural origin or synthetic. They include single compounds and mixtures. Specific examples of such components may be found in Perfume and Flavor Chemicals by S. Arctander 1969, Montclair, N.J. (USA).

[0095] By perfume in this context is not only meant a fully formulated product fragrance, but also selected components of that fragrance, particularly those which are prone to loss, such as the so-called top notes. The perfume may be used in the form of neat oil or an encapsulated form.

Fluorescent agents

[0096] In order to further improve whiteness, preferred compositions may include a fluorescent agent (also called optical brightener). Fluorescent agents are well known and many such fluorescent agents are available commercially.

[0097] Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the Sodium salts. Total amount of the fluorescent agent or agents which may be used in preferred compositions is generally from 0.005 wt% to 2 wt%, more preferably 0.01 wt% to 0.1 wt%. Preferred classes of fluorescent include di-styryl biphenyl compounds, e.g. TINOPAL® CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. TINOPAL® DMS pure Xtra and BLANKOPHOR® HRH, and Pyrazoline compounds, e.g. BLANKOPHOR® SN. Preferred fluorocoulers are: sodium 2 (4-styryl-3-sulfophenyl) -2H-naphthol [ 1, 2-d] trazole, disodium 4,4'- bis ([ 4-anilino-6- (N methyl-N-2 hydroxyethyl) amino 1,3,5- triazin-2-yl] amino ) stilbene-2-2' disulfonate, disodium 4, 4'-bis ([4-anilino-6-morpholino-1,3,5-triazin-2-yl]) amino) stilbene-2-2' disulfonate, and disodium 4, 4' -bis (2- sulfostyryl) biphenyl.

Polymers

[0098] The compositions may include one or more polymers. Examples are carboxymethylcellulose, poly (vinylpyrrolidone), poly(ethylene glycol), poly(vinyl alcohol), poly(vinylpyridine- N-oxide), poly(vinylimidazole), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

[0099] Modern detergent compositions typically employ polymers as dye-transfer inhibitors. These prevent migration
of dyes, especially during long soak times. Any suitable dye-transfer inhibitor may be used in preferred compositions.

Generally, such dye-transfer inhibitors include polyvinyl pyrrolidone polymers, polyanine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof.

Nitrogen-containing, dye binding, DTI polymers are preferred. Of these polymers and copolymers of cyclic amines such as vinyl pyrrolidone, and/or vinyl imidazole are preferred. Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (as a class, referred to as "PVPVI") are also preferred. These copolymers can be either linear or branched. Suitable PVPVI polymers include SOKALAN® HP56, available commercially from BASF. The invention will now be explained in greater details with non-limiting examples of preferred compositions.

EXAMPLES:

Example 1: Effect of preferred and control compositions on redeposition of soil

A control NTR (Non-Tower Route) base detergent composition was made. Another control composition (C-1) was made. This contained three shading dyes; DV9, DV28 and AV50, but did not contain lipase. The shading dyes were post-dosed. Two more control compositions (C-2 and C-3) were made. These contained lipase at varying levels, but no shading dye. A preferred composition was made by further post-doing lipase into control composition C-1. The formulations have been described in table-1.

Table-1

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NDOM* means: Non Detergent Organic Matter
** 0.1 g LIPEX®. 100 TB contains about 0.00186 g lipase
***0.05 g LIPEX®. 100 TB contains about 0.00093 g lipase
DV9®, this was 0.5 g soda ash adjunct containing 0.00375 g DV9 dye
DV28®, this was 0.5 g soda ash adjunct containing 0.006 g DV28 dye
AV50®- this was 1.5 g Sodium sulphate adjunct containing 0.0045 g AV50 dye

Soil redeposition and fabric yellowing study- hand wash protocol (1, 3 and 5 washes)

This experiment was conducted on three types of commercial cloth test monitors; knitted cotton, knitted polyester, and poly cotton. Before the cloth test monitors were washed, their colour, expressed as CIE L*a*b* values, and
their reflectance value, measured in R460 values, were determined by GRETAG MACBETH® Coloreye UV spectrophotometer (UV-excluded mode). CIE L*a*b* (CIELAB) is the most complete colour space specified by the International Commission on Illumination (Commission Internationale d’Eclairage). It describes all the colours visible to the human eye and was created to serve as a device independent model to be used as a reference. These values were recorded as b* (unwashed) and R460 (unwashed).

[0103] Four grams of the detergent powder were dissolved in 1 litre 24 °F.H. (French Hardness) water to get a solution. To this solution, standard commercially available soil strips were added. Three types of soil strips were added; STANLEY® clay strips supplied by Warwick Equest, Stanley, County Durham, UK, (at 0.2 g/l), multi-mix soil strips having a mixture of olive oil, lipstick, cooking oil, tea solution, jam, curry, grass stain, chocolate and clay (at 4 g/l) and a Soil Ballast Fabric SBL2004® strip sold by WFK Testgewebe GmbH (at 6 g/l). The detergent solution containing soil strips was stirred for one minute with a glass rod to release the soils in solution. Thereafter, 10 pieces of each cloth test monitor (size of each piece - 10 cm X 10 cm) were added at liquor to cloth ratio of 10:1. To the solution, ballast of cotton: polyester (50:50) was added to maintain the liquor to cloth ratio. The cloth test monitors were allowed to soak in the detergent solution containing the soils for 30 minutes. The solution was manually stirred for one minute, after every 10 minutes.

[0104] Thereafter all the cloth test monitors were rinsed twice with 24 °F.H. water. For some test monitors, this process was carried out only once and the rinsed cloth test monitors were dried in shade. Thereafter, the b* and R460 values were determined again as described earlier. These values were noted as b*(washed) and R460(washed). For some cloth test monitors, this procedure was repeated two more times (i.e. total 3 washes) after which the test monitors were rinsed and dried. For some cloth test monitors, the procedure was repeated four more times (i.e. total 5 washes) before the monitors were rinsed and dried. Thereafter, the b* and R460 values were determined again as described earlier. These values were noted as b*(washed) and R460(washed).

[0105] Soil redeposition was measured as the difference between the R460 values at the end of 1 wash, 3 washes and 5 washes.

The difference (ΔR460) was calculated as follows:

\[ \Delta R_{460} = R_{460}(\text{unwashed}) - R_{460}(\text{washed}) \]

[0106] Higher values of ΔR460 indicate higher difference in whiteness of the unwashed cloth and the washed cloth. Therefore, higher difference indicates that the clothes were lesser white after wash. In other words, it indicates higher levels of soil redeposition. Therefore, compositions that provided lower values of ΔR460 were preferred.

[0107] Fabrics on which the suspended dirt deposits during wash normally appear dull, grey or yellow. Positive values of b* indicates yellowness, which occurs due to higher soil redeposition; whereas negative values indicate blue hue. Higher values of b* indicate yellowing. The difference between b* values of washed and unwashed cloth (indicated as Δb*) is calculated as follows:

\[ \Delta b^* = b^*(\text{washed}) - b^*(\text{unwashed}) \]

Higher Δb* values indicated higher yellowing, i.e. higher levels of soil redeposition. Therefore, compositions that provided lower values of Δb* were preferred.

[0108] In summary, preferred compositions are the ones that provide lower values of ΔR460 and lower values of Δb* on all fabrics.

Table-2

<table>
<thead>
<tr>
<th>Number of washes</th>
<th>knitted cotton/ Δb*</th>
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The data indicates that amongst all the compositions, preferred composition Ex-1 shows lower yellowing (manifested as lower $\Delta b^*$ values), and lesser drop in reflectance (manifested as lower values of $\Delta R_{460}$) on all types of fabrics. The effect was more pronounced after 3 and 5 washes, especially on knitted cotton and knitted polyester fabrics.

Example 2: Machine wash studies with composition having lipase with two shading dyes and three shading dyes

The compositions of the various formulations tested in the machine wash study are included in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>Ingredients</th>
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<th>Ex-2</th>
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<th>Ex-4</th>
<th>Ex-5</th>
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<tr>
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<tr>
<td>Perfume</td>
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<tr>
<td>Soda speckles</td>
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<td>NDOM* and other minors to</td>
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</tbody>
</table>

NDOM* means: Non Detergent Organic Matter

** 0.1 g LIPEX® 100 TB contains about 0.00186 g lipase

AV50@ - this was 1.5 g Sodium sulphate adjunct containing 0.0045 g AV50 dye

DV9@, this was 0.5 g soda ash adjunct containing 0.00375 g DV9 dye

DV28@, this was 0.5 g soda ash adjunct containing 0.003 g DV28 dye

This experiment was conducted on three types of commercial cloth test monitors; knitted cotton, nylon elastane and woven cotton. Before the cloth test monitors were washed, their colour, expressed as CIE $L^*a^*b^*$ values were determined as described earlier. These values were recorded as $b^*$ (unwashed).

Detergent powder at a dosage level of 1.5 grams/litre was added to dispenser of a washing machine. Three
types of soils strips used in Example-1 were added to the machine. The cloth test monitors were soaked in 24 °F.H. (French Hardness) water at ambient temperature for 20 minutes. The washing cycle was set at 20 minutes. The cloth to liquor ratio in the washing machine was 1:20. Thereafter all the cloth test monitors were rinsed twice with 24 °F.H. water. For some test monitors, this process was carried out once and the rinsed cloth test monitors were dried in shade. Thereafter, the b* values were determined again as described earlier. These values were noted as b*(washed). For some cloth test monitors, this procedure was repeated two more times (i.e. total 3 washes) after which the test monitors were rinsed and dried. For some cloth test monitors, the procedure was repeated four more times (i.e. total 5 washes) before the monitors were rinsed and dried. Thereafter, the b* values were determined again as described earlier. These values were noted as b*(washed).

The difference between b* values was determined as described earlier. The data is presented in table 4.

The data indicates that that amongst all the compositions, preferred composition Ex-5 having three shading dye and lipase shows lower yellowing (manifested as lower Δb* values). The effect was more pronounced after 3 and 5 washes, especially on knitted cotton and woven cotton fabrics.

It will be appreciated that the illustrated examples provide a detergent composition having a combination of lipase with specific shading dyes provides lower redeposition of soil on fabrics, which is manifested as higher reflectance and lower yellowing, especially over multiple washes on knitted cotton, knitted polyester and polyester fabrics.

It should be understood that the specific forms of the invention herein illustrated and described are intended to be representative only as certain changes may be made therein without departing from the clear teachings of the disclosure.

Although the invention has been described with reference to specific embodiments, it will be appreciated by those skilled in the art that the invention may be embodied in many other forms.

**Claims**

1. A detergent composition comprising:
   - (i) a surfactant;
   - (ii) a hydrophobic dye;
   - (iii) a direct dye;
   - (iv) an acid dye; and,
   - (v) lipase.

2. A detergent composition as claimed in claim 1 comprising 0.0001 wt % to 0.008 wt% hydrophobic dye.

3. A detergent composition as claimed in claim 1 or 2 wherein said hydrophobic dye is a disperse dye.

4. A detergent composition as claimed in claim 1 or 2 wherein said disperse dye is an anthraquinone dye.

5. A detergent composition as claimed in any one of the preceding claims comprising 0.00001 wt% to 0.004 wt% direct dye.

6. A detergent composition as claimed in any one of the preceding claims wherein said direct dye is a bis-azo dye.
7. A detergent composition as claimed in any one of the preceding claims wherein said acid dye is an azine dye.

8. A detergent composition as claimed in any one of the preceding claims comprising 0.00001 wt% to 0.1 wt% azine dye.

9. A detergent composition as claimed in any one of the preceding claims comprising 0.0001 wt% to 0.1 wt% lipase.

10. A method of laundering fabrics which comprises the step of treating the fabrics with a composition according to claim 1.

11. A method of treating fabrics comprising the steps of:

   (i) treating fabrics with an aqueous solution comprising:

   (a) 0.3 g/l to 10 g/l surfactant;
   (b) 0.1 ppb to 500 ppm hydrophobic dye;
   (c) 0.1 ppb to 500 ppm direct dye;
   (d) 0.1 ppb to 500 ppm acid dye; and,
   (e) 0.3 ppb to 10 ppm lipase; and,

   (ii) rinsing said fabrics; and,
   (iii) drying the fabrics

12. Use of a composition according to claim 1 to reduce redeposition of soil on fabrics.
**DOCUMENTS CONSIDERED TO BE RELEVANT**

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The present search report has been drawn up for all claims.

**TECHNICAL FIELDS SEARCHED (IPC)**

C11D
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For more details about this annex: see Official Journal of the European Patent Office, No. 12/82
REFERENCES CITED IN THE DESCRIPTION

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