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ABSTRACT

This application relates to laundry care compositions comprising carboxylate fabric shading dyes and methods of treating a textile comprising such laundry care compositions.
LAUNDRY CARE COMPOSITIONS CONTAINING DYES

FIELD OF INVENTION

This invention relates to laundry care compositions comprising fabric shading dyes and methods of treatment of fabrics using such compositions.

BACKGROUND OF THE INVENTION

As textile substrates age, their color tends to fade or yellow due to exposure to light, air, soil, and natural degradation of the fibers that comprise the substrates. To counteract this unwanted effect, laundry detergent manufacturers incorporate shading dyes into their products. The purpose of shading dyes is typically to counteract the fading and yellowing of the textile substrates by providing a blue-violet hue to the laundered fabrics, reducing the visual impact of the yellowing. There are many disclosures of shading dyes in detergents. However, formulating detergent compositions with shading dyes is challenging: not only do the compositions need to provide good product appearance, they also need to deposit the shading dyes evenly onto fabrics during the treatment step and provide consistent hue throughout the product life-cycle.

SUMMARY OF THE INVENTION

This invention relates to a laundry care composition comprising from 0.00001 wt % to 0.5 wt % carboxylate dye having the structure of Formula I:

\[
\text{D}+\text{L}-\text{CO}_2\text{M}
\]

wherein D is a dye moiety selected from benzodifuranes, methines, triphenylmethanes, naphthalimides, pyrazoles, napthoquinones, anthraquinones and mono- and di-azo dyes and mixtures thereof; azo dyes being particularly preferred, wherein the compound D+H, preferably has a maximum extinction coefficient greater than about 1000 liter/mol/cm at the \(\lambda_{\text{max}}\) in the wavelength range from 400 nm to 750 nm in methanol solution, preferably a maximum extinction coefficient from about 20,000 to about 100,000 liter/mol/cm at the \(\lambda_{\text{max}}\) in the wavelength range of about 540 nm to about 630 nm, and most preferably a maximum extinction coefficient from about 20,000 to about 65,000 liter/mol/cm at the \(\lambda_{\text{max}}\) in the wavelength range of about 560 nm to about 610 nm; and L is an organic linking group preferably having a molecular weight from 14 to 1000 Daltons or 14 to 600 or 28 to 300, preferably consisting essentially only of C, H and optionally additionally O and/or N, and in the sequence of bonds starting from the carbonyl carbon of the \(\text{C(O)}\text{OM}\) group and ending at the dye moiety, any \(-\text{C}_r(\text{O})-\text{O}_s\) groups are incorporated such that the oxygen atom \(\text{O}_s\) is encountered prior to the carbonyl carbon \(\text{C}_r,\) preferably L is a \(\text{C}_1-\text{C}_2\) alkyne chain having optionally therein ether (\(-\text{O}-\)) and/or ester and/or amide links, the chain being optionally substituted for example with \(-\text{OH}, -\text{CN}, -\text{NO}_2, -\text{SO}_2\text{CH}_3, -\text{Cl}, -\text{Br}\); and M is any suitable counterion, typically hydrogen, sodium or potassium ion.

In one aspect of the invention L may comprise formula 2:

\[
\text{Dye}+\text{L}-\text{CO}_2\text{M}
\]

The present invention also comprises a method of treating a textile, the method comprising the steps of (i) treating the textile with an aqueous solution comprising a laundry care additive and from 1 ppm to 500 ppm of a carboxylate dye; and (ii) rinsing and drying the textile, the carboxylate dye comprising a dye having a structure of Formula I above.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

As used herein, the term “alkoxy” is intended to include C1-C8 alkoxy and alkoxy derivatives of polyols having repeating units such as butylene oxide, glycidol oxide, ethylene oxide or propylene oxide.

As used herein, unless otherwise specified, the terms “alkyl” and “alkyl capped” are intended to include C1-C18 alkyl groups, and in one aspect, C1-C6 alkyl groups.

As used herein, unless otherwise specified, the term “aryl” is intended to include C3-C12 aryl groups.

As used herein, unless otherwise specified, the term “aryllalkyl” is intended to include C1-C18 alkyl groups and, in one aspect, C1-C6 alkyl groups.

The terms “ethylene oxide,” “propylene oxide” and “butylene oxide” may be shown herein by their typical designation of “EO,” “PO” and “BO,” respectively.

As used herein, the term “laundry care composition” includes, unless otherwise indicated, granular, powder, liquid, gel, paste, unit dose, bar form and/or flake type washing agents and/or fabric treatment compositions, including but not limited to products for laundering fabrics, fabric softening compositions, fabric enhancing compositions, fabric refreshing compositions, and other products for the care and maintenance of fabrics, and combinations thereof. Such compositions may be pre-treatment compositions for use prior to a washing step or may be rinse added compositions, as well as cleaning auxiliaries, such as bleach additives and/or “stain-stick” or pre-treat compositions or substrate-laden products such as dryer added sheets.

As used herein, the term “detergent composition” is a sub-set of laundry care compositions and includes cleaning compositions including but not limited to products for laundering fabrics. Such compositions may be pre-treatment composition for use prior to a washing step or may be rinse added compositions, as well as cleaning auxiliaries, such as bleach additives and “stain-stick” or pre-treat types.

As used herein, “cellulosic substrates” are intended to include any substrate which comprises at least a majority by weight of cellulose. Cellulose may be found in wood, cotton, linen, jute, and hemp. Cellulosic substrates may be in the form of powders, fibers, pulp and articles formed from powders, fibers and pulp. Cellulosic fibers, include, without limitation, cotton, rayon (regenerated cellulose), acetate (cellulose acetate), triacetate (cellulose triacetate), and mixtures...
thereof. Articles formed from cellulosic fibers include textile articles such as fabrics. Articles formed from pulp include paper.

As herein used, the term "maximum extinction coefficient" is intended to describe the molar extinction coefficient at the wavelength of maximum absorption (also referred to herein as the maximum wavelength), in the range of 400 nanometers to 750 nanometers.

As herein used, "average molecular weight" of the thiophene azo carboxylate dyes is reported as an average molecular weight, as determined by its molecular weight distribution; as a consequence of their manufacturing process, the thiophene azo carboxylate dyes disclosed herein may contain a distribution of repeating units in their polymeric moiety.

The test methods disclosed in the Test Methods Section of the present application should be used to determine the respective values of the parameters of Applicants' inventions.

As herein used, articles such as "a" and "an" when used in a claim, are understood to mean one or more of what is claimed or described.

As herein used, the terms "includes" and "including" are meant to be non-limiting.

As herein used, the term "solid" includes granular, powder, bar and tablet product forms.

As herein used, the term "fluid" includes liquid, gel, paste and gas product forms.

Unless otherwise noted, all component or composition levels are in reference to the active portion of that component or composition, and are exclusive of impurities, for example, residual solvents or by-products, which may be present in commercially available sources of such components or compositions.

All percentages and ratios are calculated by weight unless otherwise indicated. All percentages and ratios are calculated based on the total composition unless otherwise indicated.

**Dye**

Suitable dyes are selected from the group comprising carboxylate dyes having the structure of Formula 1:

$$D-\text{CO}_2\text{M}$$

wherein D is a dye moiety selected from benzodifuranes, methines, triphenylmethanes, naphthalimides, pyrazoles, naphthquinones, anthraquinones and mono- and di-azo dyes and mixtures thereof, azo dyes being particularly preferred, wherein the compound D-H, preferably has a maximum extinction coefficient greater than about 1000 liter/mole/cm at the λmax in the wavelength range from 400 nm to 750 nm in methanol solution, preferably a maximum extinction coefficient from about 20,000 to about 100,000 liter/mole/cm at the λmax in the wavelength range of about 540 nm to about 630 nm, and most preferably a maximum extinction coefficient from about 20,000 to about 65,000 liter/mole/cm at the λmax in the wavelength range of about 540 nm to about 610 nm; and L is an organic linking group preferably having a molecular weight from 14 to 1000 Daltons or 14 to 600 or 28 to 300, preferably consisting essentially only of C, H and optionally additionally O and/or N, and in the sequence of bonds starting from the carbonyl carbon of the C(O)(OM) group and ending at the dye moiety, any —(C₆H₄)(O)— groups are incorporated such that the oxygen atom O₃ is encountered prior to the carbonyl carbon C₆, preferably L is a C₁₂₋₂₀ alkyne chain having optionally therein ether (—O—) and/or ester and/or amide links, the chain being optionally substituted for example with —OH, —CN, —NO₂, —SO₂CH₃, —Cl, —Br, and M is any suitable counterion, typically hydrogen, sodium or potassium ion.

In one aspect of the invention L may comprise formula 2:

$$\text{Dye-L'}-\overset{\text{O}}{\text{C}}\text{=S}-\overset{\text{L'}}{\text{C}}\text{=S-L'-CO}_2\text{M}$$

As examples of L, there may be mentioned ethylene, trimethylene, tetramethylene, hexamethylene, isopropylene, decamethylene, hexadecamethylene and —(CH₂CH₂O)n—CH₂—, where n is from 1 to 9.

In a preferred embodiment, the carboxylate dye comprises the structure of Formula 3:

$$R^1$$

$$\text{N=N}$$

$$\text{R}^2$$

$$\text{Z}$$

$$\text{N}$$

$$\text{L'-CO}_2\text{M}$$

wherein R is a C₁₋₂₀ or C₂₋₁₂ alkyne chain having optionally therein ether (—O—) and/or ester and/or amide links, the chain being optionally substituted for example with —OH, —CN, —NO₂, —SO₂CH₃, —Cl, —Br; R¹ and R² are independently selected and may be hydrogen but are preferably each independently selected from electron-withdrawing groups such as —CN, —NO₂, —SO₂CH₃, —Cl, —Br; Z is an electron-withdrawing group preferably selected from cyano, sulphamoyl, N,N-diethylsulphamoyl, N-ethylsulphamoyl, trifluormethyl, ethylsulphonyl, nitro, N-methylsulphamoyl, chloro, bromo, most preferably Z is nitro; Y is hydrogen, lower (C₁₋₄) alky, halogen —NHCOR, preferably H, CH₃ —Cl; X is hydrogen, lower (C₁₋₄) alkoxy, and halogen, preferably H, methoxy, ethoxy and —Cl.

As examples of lower (C₁₋₄) alkyld and/or alkoxy (C₁₋₄) radicals there may be mentioned methyl, ethyl, n-propyl, and n-butyl, ethoxy and methoxy. As examples of the optionally substituted lower (C₁₋₄) alkyld radicals represented by R there may be mentioned hydroxy lower alkyl such as β-hydroxyethyl, cyano lower alkyl such as β-cyanoethyl, lower alkoxy lower alkyl such as β-(methoxy- or ethoxy)-ethyl and γ-methoxypropyl, aryl lower alkyl such as benzyl and β-phenyl-ethyl, lower alkoxy carbonyl lower alkyl such as β-methoxycarbonyl ethyl, and acyloxylower alkyls such as β-acetoxyethyl.
The dye may comprise a dye of Formula 4 in which the Z, R, X, Y and L groups are as defined above:

![Formula 4](image)

In some aspects, dyes having carboxylic acid groups with a pKa value below 4, or below 3, or even below 2, may be preferred as carboxylic acid groups are well known to have potentially deleterious interactions with multivalent metal ions such as, for example, Cu$^{2+}$, Mg$^{2+}$, and Fe$^{3+}$ among others, which may be present in the wash or on fabrics. Without wishing to be bound by theory, it is believed that dyes with carboxylic acid groups having lower pKa values have decreased interaction with such metal ions, leading to improved consistency in performance across the wide range of wash conditions used by consumers.

In a preferred embodiment, the carboxylate dye comprises the structure of Formula 5:

![Formula 5](image)

wherein D is an aromatic or heteroaromatic group, preferably a heteroaromatic group, even more preferably a thiophene group; R$_1$ is C$_1$-C$_4$ alkyl preferably methyl; R$_2$ and R$_3$ are independently selected from the group consisting of alkyl, alkenyl, alkynyl, and polyalkyleneoxy moieties, preferably alkyl and polyalkyleneoxy moieties, even more preferably at least one R$_2$ and R$_3$ are polyalkyleneoxy moieties, most preferably polyoxymethylene moieties, provided that at least one of R$_2$ and R$_3$ comprises a carboxylic acid group, preferably one with a pKa value below about 4, or even below about 3 or even below about 2.

In one aspect of the invention, the composition is in the form of a single or multi-compartment unit dose laundry care composition.

**DYE SYNTHESIS EXAMPLES**

**Synthesis Example 1**

![Dyes](image)

C. I. Disperse Violet 55 is converted to Dye 1 using the hydrolysis procedure disclosed in EP 2085434 A1, Example 11, followed by formation of the sodium salt via treatment with NaH in THF (or treatment with Na$_2$CO$_3$ in water). The product is isolated as the sodium salt.

**Synthesis Example 2**

![Dyes](image)

C. I. Disperse Blue 148 is converted to Dye 2 using the hydrolysis procedure disclosed in EP 2085434 A1, Example 6. The product is isolated as the sodium salt.

**Synthesis Example 3**

![Dyes](image)
[0036] C. I. Disperse Blue 85 is converted to Dye 3 using the sequential alkylation and hydrolysis procedures disclosed in EP 2085434 A1, Examples 5 and 6, respectively. The product is isolated as the sodium salt.

Synthesis Example 4

[0037]

C.I. Disperse blue 106

[0038] C. I. Disperse Blue 106 is converted to Dye 4 using the sequential alkylation and hydrolysis procedures disclosed in EP 2085434 A1, Examples 5 and 6, respectively. The product is isolated as the sodium salt.

Dye 4

[0039]

C.I. Disperse Violet 12

[0040] C. I. Disperse Blue 12 is converted to Dye 5 using the sequential alkylation and hydrolysis procedures disclosed in EP 2085434 A1, Examples 5 and 6, respectively. The product is isolated as the sodium salt.

Synthesis Example 6

[0041]

C.I. Disperse Violet 13

[0042] C. I. Disperse Blue 13 is converted to Dye 6 using the sequential alkylation and hydrolysis procedures disclosed in EP 2085434 A1, Examples 5 and 6, respectively. The product is isolated as the sodium salt.

Dye 6

[0043]

C.I. Disperse Violet 24
C. I. Disperse Blue 24 is converted to Dye 7 using the sequential alkylation and hydrolysis procedures disclosed in EP 2085434 A1, Examples 5 and 6, respectively. The product is isolated as the sodium salt.

Synthesis Example 8

Dye 8' is prepared according to the procedure disclosed in U.S. Pat. No. 3,793,305, Example 4, except that N-(2-cyanoethyl)-N-hexyl-m-toluidine is used in place of N-(2-cyanoethyl)-N-ethyl-m-toluidine. Dye 8' is converted to Dye 8 according to the procedure described in Example 1 above.

Synthesis Example 9

Dye 9 is prepared according to the sequence described in Example 8, except that N-(2-cyanoethyl)-N-decyl-m-toluidine is used in place of N-(2-cyanoethyl)-N-ethyl-m-toluidine.

Synthesis Example 10

Dye 10' is prepared according to the procedure disclosed in the Journal of the Society of Dyers and Colourists, 1984, 100(10), 316-19, except that ethyl 3-[(N-hexyl-N-phenyl)amino]propionate is used in place of N-Ethyl-N-2-(methoxy carbonyl)ethylamine. Dye 10 is prepared from dye 10' using the hydrolysis procedure disclosed in EP 2085434 A1, Example 6. The product is isolated as the sodium salt.
Synthesis Example 11

[0051]

Dye 11 is prepared according to Example 1 of GB 1,428,395 using 3-[(N-hexyl-N-phenyl)amino]propionic acid in place of N-ethyl-N-(carboxyethyl)-m-toluidine.

Synthesis Example 12

[0053]

Dye 12 is prepared according to Example 2 of GB 1,428,395 using 3-[(N-hexyl-N-phenyl)amino]propionic acid in place of N-ethyl-N-(carboxyethyl)-m-toluidine.

Synthesis Example 13

[0054]

Dye 13’

[0055]
Dye 13' is prepared according to the procedures described inWO 2011/17719 A2 using 15-(3-methylphenyl)-6,9,12-tetraoxa-15-azatetradecan-1-ol, which is prepared according to the procedure disclosed inWO 2011/17719 A2 for the preparation of 15-(3-methylphenyl)-6,9,12-tetraoxa-15-azatetradecan-1-ol, except that N-ethyl-m-toluidine is replaced by N-octyl-m-toluidine. Dye 13' is converted to Dye 13 using the sequential alkylation and hydrolysis procedures disclosed in EP 2085434 A1, Examples 5 and 6, respectively. The product is isolated as the sodium salt.

The dye may be incorporated into the composition in the form of a mixture of reaction products formed by the organic synthesis route used: such a reaction mixture will typically comprise a mixture of the dyes of formula I and II, in addition, reaction products of side reactions and/or suitable examples of unreacted starting materials. Although it may be preferred to remove impurities other than the dyes as defined in formula I, it may not be necessary, so the mixture of reaction products may be used directly in a composition according to the invention.

Typically the dye or mixture of dyes of formula I will be present in the composition in an amount from 0.00001 to 5 wt% of the composition, more usually an amount from 0.0001 to 1 wt% or 0.5 wt% of the composition.

Where the dye is first formed into a pre-mix, for example a particle or concentrated liquid for incorporation into the composition, the dye may be present at a level of from 0.001 or even 0.01 or greater, up to an amount of 2 wt%, or 10 wt% based on the weight of the pre-mix.

The compositions of the present invention typically comprises in addition to the dye, one or more laundry care adjunct materials.

Suitable adjunctions may be, for example to assist or enhance cleaning performance, for treatment of the substrate for example, for example by softening or freshening, or to modify the aesthetics of the composition as is the case with perfume agents, colorants, non-fabric-shading dyes or the like. Suitable adjunction materials include, but are not limited to, surfactants, builders, chelating agents, dye transfer inhibiting agents, dispersants, enzymes, and enzyme stabilizers, catalytic materials, bleach activators, hydrogen peroxide, sources of hydrogen peroxide, peroxides, peracids, polymeric dispersing agents, clay soil removal/anti-redeposition agents, brighteners, suds suppressors, dyes, hueing dyes, perfumes, perfume delivery systems, structure elasticizing agents, fabric softeners, carriers, hydrotropes, processing aids, solvents, additional dyes and/or pigments, some of which are discussed in more detail below. In addition to the disclosure below, suitable examples of other adjunctions and levels of use are found in U.S. Pat. Nos. 5,576,282, 6,306,812 B1 and 6,326,348 B1 that are incorporated by reference.

Additional Fabric Hueing Agents.

Although it is not preferred to incorporate additional fabric shading dyes, in addition to the thiopeheneazo dye, the composition may comprise one or more additional fabric hueing agents. Fabric shading can be accomplished through application of any suitable ingredient as known in the art. Preferred fabric shading agents include fabric shading dyes, pigments and mixtures thereof.

The additional fabric shading dye (sometimes referred to as hueing, bluing or whitening agents) typically provides a blue or violet shade to fabric. The additional fabric shading dye can be used either alone or in combination to create a specific shade of hueing and/or to shade different fiber types. This may be provided for example by mixing a red and green-blue dye to yield a blue or violet shade. The additional fabric shading dye may be selected from any chemical class of dye as known in the art, including but not limited to acidine, anthraquinone (including polycyclic quinones), azure, azo (e.g., monoazo, disazo, trisazo, tetrakisazo, polyazo), benzodifuranone, benzodifuranone, carotenoid, coumarin, cyanine, diazohemicyanine, diphenylmethane, formazan, hemicyanine, indigoids, methane, naphthalimides, naphtoquinone, nitro, nitrone, phthalocyanine, pyrazolone, stilbene, styryl, triarylmethane, triphenylmethane, xanthenes and mixtures thereof.

Suitable additional fabric shading dyes include small molecule dyes, polymeric dyes and dye-clay conjugates. Preferred additional fabric shading dyes are selected from small molecule dyes and polymeric dyes.

Small Molecule Dyes

Suitable small molecule dyes may be selected from the group consisting of dyes falling into the Colour Index (C.I., Society of Dyers and Colourists, Bradford, UK) classifications of Acid, Direct, Basic, Reactive, Solvent or Disperse dyes. Preferably such dyes can be classified as Blue, Violet, Red, Green or Black, and provide the desired shade either alone or in combination with other dyes or in combination with other agent ingredients. Reduction small amounts of hydrolyzed dye as source, and in detergent formulations or in the wash may undergo additional hydrolysis. Such hydrolyzed dyes and mixtures may also serve as suitable small molecule dyes.


[0068] In another aspect suitable small molecule dyes include dyes with CAS No.'s 52583-54-7, 42783-06-2, 2107589-10-1, 30466-25-8, 122063-39-2, 167940-11-6, 52259-04-0, 105076-77-5, 84425-43-4, and 87606-56-2, and non-azo dyes Disperse Blue 250, 354, 364, Solvent Violet 8, Solvent blue 43, 57, Lumogen F Blue 650, and Lumogen F Violet 570.

[0069] In another aspect suitable small molecule dyes include azo dyes, preferably mono-azo dyes, covalently bound to phthalocyanine moieties, preferably Al- and Siphthalocyanine moieties, via an organic linking moiety.

[0070] Polymeric Dyes

[0071] Suitable polymeric dyes include dyes selected from the group consisting of polymers containing covalently bound (sometimes referred to as conjugated) chromogens, (also known as dye-polymer conjugates), for example polymers with chromogen monomers co-polymerized into the backbone of the polymer and mixtures thereof.

[0072] Polymeric dyes include: (a) Reactive dyes bound to water soluble polyester polymers via at least one and preferably two free OH groups on the water soluble polyester polymer. The water soluble polyester polymers can be comprised of comonomers of a phenyl dicarboxylate, an oxaliclyleneoxy and a polyoxyalkyleneoxy; (b) Reactive dyes bound to polyamides which are polyalkylamines that are generally linear or branched. The amines in the polymer may be primary, secondary and/or tertiary. Polyethylenimine in one aspect is preferred. In another aspect, the polyamides are ethoxylated; (c) Dye polymers having dye moieties carrying negatively charged groups obtained by copolymerization of an alkene bound to a dye-containing anionic group and one or more further alkene comonomers not bound to a dye moiety; (d) Dye polymers having dye moieties carrying positively charged groups obtained by copolymerization of an alkene bound to a dye containing an anionic group and one or more further alkene comonomers not bound to a dye moiety; (e) Polymericazo polyoxyalkylene dyes containing carboxylate groups; in some aspects those having carboxylic acid groups with a pKa value below 4 or below or even below 2, may be preferred as carboxylic acid groups are well known to have potentially deleterious interactions with multivalent metal ions such as, for example, Ca++, Mg++, Fe++ among others, which may be present in the wash or on fabrics, and those acids with lower pKa values are believed to have less ability to interact with such metal ions, leading to improved consistency in performance across widely varying wash conditions; and (f) dye polymer conjugates comprising at least one reactive dye and a polymer moiety selected from the group consisting of a hydroxyl moiety, a primary amine moiety, a secondary amine moiety, a thiol moiety and combinations thereof; said polymers preferably selected from the group consisting of polysaccharides, proteins, polyalkyleneimines, polymides, polyols, and silicones. In one aspect, carboxymethyl cellulose (CMC) may be covalently bound to one or more reactive blue, reactive violet or reactive red dye such as CMC conjugated with C.I. Reactive Blue 19, sold by Megazyme, Wicklow, Ireland under the product name AZO-CM-CELIULOSE, product code S-ACMC,

[0073] Other suitable polymeric dyes include polymeric dyes selected from the group consisting of alkoxyalted triphenyl methane polymeric colourants, alkylated carbocycly and alkylated heterocyclic azo colourants, including alkoxyalted thiophene polymeric colourants, and mixtures thereof. Preferred polymeric dyes comprise the optionally substituted alkoxyalted dyes, such as alkylated triphenylmethane polymeric colourants, alkylated carbocyclic and alkylated heterocyclic azo colourants including alkoxyalted thiophene polymeric colourants, and mixtures thereof, such as the fabric-substantive colourants sold under the name of Liquitint® (Milliken, Spartanburg, S.C., USA).

[0074] Suitable polymeric bluing agents are illustrated below. As with all such alkoxyalted compounds, the organic synthesis may produce a mixture of molecules having different degrees of alkoxylation During a typical ethoxylation process, for example, the randomness of the ethylene oxide addition results in a mixture of oligomers with different degrees of ethoxylation. As a consequence of its ethylene oxide number distribution, which often follows a Poisson law, a commercial material contains substances with somewhat different properties. For example, in one aspect the product resulting from an ethoxylation is not a single compound containing five (CH2CH2O) units as the general structure (Formula A, with x+y=5) may suggest. Instead, the product is a mixture of several homologs whose total of ethylene oxide units varies from about 2 to about 10. Industrially relevant processes will typically result in such mixtures, which may normally be used directly to provide the fabric shading dye, or less commonly may undergo a purification step.

[0075] Preferably, the fabric shading dye may have the structure:

\[
\begin{align*}
\text{H}_3C & \quad \text{N} & \quad \text{S} & \quad \text{O} & \quad \text{CH}_2\text{CH}_2\text{O}_x\text{H} \\
\text{H}_3C & \quad \text{N} & \quad \text{S} & \quad \text{O} & \quad \text{CH}_2\text{CH}_2\text{O}_y\text{H}
\end{align*}
\]

wherein the index values x and y are independently selected from 1 to 10. In some aspects, the average degree of ethoxylation, x+y, sometimes also referred to as the average number of ethoxylation groups, is from about 3 to about 12, preferably from about 4 to about 8. In some embodiments the average degree of ethoxylation, x+y, can be from about 5 to about 6. The range of ethoxylation present in the mixture varies depending on the average number of ethoxylation incorporated. Typical distributions for ethoxylation of toluidine with
either 5 or 8 ethoxylates are shown in Table II on page 42 in the Journal of Chromatography A 1989, volume 462, pp. 39-47. The whitening agents are synthesized according to the procedures disclosed in U.S. Pat. No. 4,912,203 to Kluger et al.; a primary aromatic amine is reacted with an appropriate amount of ethylene oxide, according to procedures well known in the art. The polyethyleneoxy substituted m-toluidine useful in the preparation of the colorant can be prepared by a number of well known methods. It is preferred, however, that the polyethyleneoxy groups be introduced into the m-toluidine molecule by reaction of the m-toluidine with ethylene oxide. Generally the reaction proceeds in two steps, the first being the formation of the corresponding N,N-dihydroxyethyl substituted m-toluidine. In some aspects, no catalyst is utilized in this first step (for example as disclosed at Column 4, lines 16-25 of U.S. Pat. No. 3,927,044 to Foster et al.). The dihydroxyethyl substituted m-toluidine is then reacted with additional ethylene oxide in the presence of a catalyst such as sodium (described in Preparation II of U.S. Pat. No. 3,157,633 to Kuhn), or it may be reacted with additional ethylene oxide in the presence of sodium or potassium hydroxide (described in Example 5 of U.S. Pat. No. 5,071,440 to Haines et al.). The amount of ethylene oxide added to the reaction mixture determines the number of ethyleneoxy groups which ultimately attach to the nitrogen atom. In some aspects, it may be advantageous to dissolve the whitening agent in a solvent which may be protic or aprotic. Typically for ease of handling and formulation such whitening agents may be dissolved in polar protic solvents such as, for example, a low molecular weight polyethylene glycol such as PEG200. In some aspects, an excess of a polyethyleneoxy substituted coupler, such as a m-toluidine coupler, may be employed in the formation of the whitening agent and remain as a component in the final colorant mixture. In certain aspects, the presence of excess coupler or diluting solvent may confer advantageous properties to a mixture in which it is incorporated such as the raw material, a pre-mix, a finished product or even the wash solution prepared from the finished product.

[0076] The fabric shading dye may preferably have the following structure:

![Chemical structure]  

[0077] In one aspect, a fabric shading mixture comprises a fabric shading agent having the structure:

![Chemical structure]
Wherein:

[0079] \( R_1 \) is \( C_1-C_6 \) alkyl preferably methyl;

[0080] R2 and R3 are independently selected from the group consisting of alkyl, alkenyl, and polyalkyleneoxy moieties, preferably alkyl and polyalkyleneoxy moieties, even more preferably at least one and R3 are polyalkyleneoxy moieties, most preferably polyoxymethylene moieties, provided that at least one of R2 and R3 comprises a carboxylic acid group, preferably one with a pKa value below about 4, or even below about 3 or even below about 2;

[0081] D is an aromatic or heteroaromatic group, preferably a heteroaromatic group, even more preferably a thiophene group.

The ordinarily skilled artisan understands that even substantially pure starting materials used in industrial preparations may contain minor or trace components that could be carried forward along with the intended starting materials to form other minor or trace components not necessarily captured in the list above, which is intended to be illustrative and not exhaustive. For example, when utilizing 3-methyl aniline as a starting material, there could be minor components present such as aniline or 2-methyl aniline. Each of these could participate in the coupling reaction with the D-NH₂ group and form a unique mixture of materials present at very low levels. A similar possibility exists for the aromatic or heteroaromatic amine employed. For example, using 5-amino-3-methyl-2,4-thiophenedicarboxonitrile as a starting material, low levels of other aminothiophenes may be present that can be carried forward in a similar manner resulting in additional minor components. Such low level contaminants in a starting material may include, for example, aminothiophenes D'-NH₂ of the following structure:

wherein \( R_4 \) and \( R_5 \) are independently selected from —CN, —C(O)NH₂, and —CO₂H, and \( R_5 \) is selected from H and \( C_4-C_6 \) alkyl, provided that when both \( R_4 \) and \( R_5 \) are —CN, \( R_5 \) is other than methyl. As will be appreciated by one skilled in the art, such low level D'-NH₂ may be carried forward along with the intended starting D-NH₂ to form other minor or trace components such as those illustrated in the list above, provided the minor aminothiophene radical D' is substituted for D in the structures shown above. Said another way, each aminothiophene present at the beginning of the synthetic process has the ability to be carried forward to a mixture of products, including D'-NH₂ present as minor components in the starting D-NH₂.

[0082] As will be appreciated by those skilled in the art the above noted unreacted starting materials and additional components to said bluing agent will typically be present at levels that are unlikely to significantly impact said bluing agent’s performance, as perceived by the average consumer. As will further be appreciated, when present at levels that may impact said bluing agent’s performance, or the overall performance of a detergent formulation containing said mixture, as perceived by the average consumer, such additional components may be removed or retained as desired.

[0083] Non-limiting examples of suitable fabric shading dyes are:

Dye Formula 1

Dye Formula 2
-continued

Dye Formula 3

Dye Formula 4

Dye Formula 5

Dye Formula 6

Dye Formula 7
[0084] Dye-Clay Conjugates

[0085] Suitable dye clay conjugates include dye clay conjugates selected from the group comprising at least one cationic/basic dye and a smectite clay; a preferred clay may be selected from the group consisting of Montmorillonite clay, Hectorite clay, Saponite clay and mixtures thereof. In another aspect, suitable dye clay conjugates include dye clay conjugates selected from the group consisting of a clay and one cationic/basic dye selected from the group consisting of CI. Basic Yellow 1 through 108, CI. Basic Orange 1 through 69, CI. Basic Red 1 through 118, CI. Basic Violet 1 through 51, CI. Basic Blue 1 through 164, CI. Basic Green 1 through 14, CI. Basic Brown 1 through 23, CI. Basic Black 1 through 11. In still another aspect, suitable dye clay conjugates include dye clay conjugates selected from the group consisting of Montmorillonite Basic Blue B7 CI. 42595 conjugate, Montmorillonite Basic Blue B9 CI. 52015 conjugate, Montmorillonite Basic Violet V3 CI. 42555 conjugate, Montmorillonite Basic Green G1 CI. 42040 conjugate, Montmorillonite Basic Red R1 CI. 45160 conjugate, Montmorillonite CI. Basic Black 2 conjugate, Hectorite Basic Blue B7 CI. 42595 conjugate, Hectorite Basic Blue B9 CI. 52015 conjugate, Hectorite Basic Violet V3 CI. 42555 conjugate, Hectorite Basic Green G1 CI. 42040 conjugate, Hectorite Basic Red R1 CI. 45160 conjugate, Hectorite CI. Basic Black 2 conjugate, Saponite Basic Blue B7 CI. 42595 conjugate, Saponite Basic Blue B9 CI. 52015 conjugate, Saponite Basic Violet V3 CI. 42555 conjugate, Saponite Basic Green G1 CI. 42040 conjugate, Saponite Basic Red R1 CI. 45160 conjugate, Saponite CI. Basic Black 2 conjugate and mixtures thereof.

Pigments

[0086] Suitable pigments include pigments selected from the group consisting of flavanthrone, indanthrone, chlorinated indanthrone containing from 1 to 4 chlorine atoms, pynanthrone, dichloropyranthrone, monobromodichloropyranthrone, dibromodichloropyranthrone, tetrabromopyranthrone, perylene-3,4,9,10-tetracarboxylic acid diimide, wherein the imide groups may be unsubstituted or substituted by CI-C3-alkyl or a phenyl or heterocyclic radical, and wherein the phenyl and heterocyclic radicals may additionally carry substituents anthracyrindinecarboxylic acid amides, violanthrone, isoviolanthrone, dioxazine pigments, copper phthalocyanine which may contain up to 2 chlorine atoms per molecule, polychloro-copper phthalocyanine or polychloro-copper phthalocyanine containing up to 14 bromine atoms per molecule and mixtures thereof. Other suitable pigments are described in WO2008/090091. In another aspect, suitable pigments include pigments selected from the group consisting of Ultramarine Blue (C.I. Pigment Blue 29), Ultramarine Violet (C.I. Pigment Violet 15), Monastral Blue and mixtures thereof. Particularly preferred are Pigment Blues 15 to 20, especially Pigment Blue 15 and/or 16. Other suitable pigments include those selected from the group consisting of Ultramarine Blue (C.I. Pigment Blue 29), Ultramarine Violet (C.I. Pigment Violet 15), Monastral Blue and mixtures thereof.

[0087] The amount of additional fabric shading dye present in the finishing composition of the invention is typically from 0.0001 to 0.005 wt % based on the total cleaning composition, preferably from 0.0001 to 0.005 wt %. Based on the wash liquor, the concentration of additional fabric shading dye is typically from 1 ppm to 5 ppm, preferably from 10 ppm to 500 ppm. Of course this will depend on the equivalent weight of the additional fabric shading agent. These values are generally acceptable when the equivalent weight (EW) of the
additional fabric shading agent, the molecular weight (MW) divided by the number of dye chromophores in the shading agent, is between 200 and 2000. Where the equivalent weight of the shading agent is >2000, these ranges should be multiplied by the equivalent weight of the additional shading agent divided by 2000. Thus if a shading agent has a MW of 1,000 with a single dye chromophore, its EW is the same as its MW. If the MW is 5,000 and the shading agent has two chromophores, its EW would be 2,500 and the ranges indicated above should be multiplied by (2,500/2,000), so that for example the amount of such an additional fabric shading dye present in the cleaning composition of the invention is typically from 0.00125 to 0.0625 wt% based on the total cleaning composition. Such corrections to levels may be required depending on the number of chromophores attached to a polymer of high MW, for example.

[0088] The additional fabric shading dye and/or pigment may be incorporated into the detergent composition as part of a reaction mixture which is the result of the organic synthesis for the dye, pigment or brightener molecule, with optional purification step(s). Such reaction mixtures generally comprise the desired dyeing molecule itself and in addition may comprise un-reacted starting materials and/or by-products of the organic synthesis route.

[0089] Encapsulates.

[0090] The composition may comprise an encapsulate. In one aspect, an encapsulate comprising a core, a shell having an inner and outer surface, said shell encapsulating said core. The core may comprise any laundry care adjunct, though typically the core may comprise material selected from the group consisting of perfumes; brighteners; dyes; insect repellants; silicones; waxes; flavors; vitamins; fabric softening agents; skin care agents in one aspect, paraffins; enzymes; anti-bacterial agents; bleaches; sensates; and mixtures thereof; and said shell may comprise a material selected from the group consisting of polyethylene; polyamides; polynylalcohols, optionally containing other co-monomers; polystyrenes; polyisoprenes; polycarbonates; polyesters; polyacrylates; aminoplasts, in one aspect said aminoplast may comprise a polyurea, polyurethane, and/or polyurea-thane, in one aspect said polyurea may comprise polyoxyethyleneur and/or melamine formaldehyde; polylefins; polysaccharides, in one aspect said polysaccharide may comprise cellulose and/or chitosan; gelatin; shells; epoxy resins; vinyl polymers; water insoluble inorganics; silicone; and mixtures thereof. Preferred encapsulates comprise perfume. Preferred encapsulates comprise a shell which may comprise melamine formaldehyde and/or cross linked melamine formaldehyde. Preferred encapsulates comprise a core material and a shell, said shell at least partially surrounding said core material, is disclosed. At least 75%, 85% or even 90% of said encapsulates may have a fracture strength of from 0.2 MPa to 10 MPa, and a benefit agent leakage of from 0% to 20%, or even less than 10% or 5% based on total initial encapsulated benefit agent. Preferred are those in which at least 75%, 85% or even 90% of said encapsulates may have (i) a particle size of from 1 microns to 80 microns, 5 microns to 60 microns, from 10 microns to 50 microns, or even from 15 microns to 40 microns, and/or (ii) at least 75%, 85% or even 90% of said encapsulates may have a particle wall thickness of from 30 nm to 250 nm, from 80 nm to 180 nm, or even from 100 nm to 160 nm. Formaldehyde scavengers may be employed with the encapsulates, for example, in a capsule slurry and/or added to a composition before, during or after the encapsulates are added to such composition. Suitable capsules that can be made by following the teaching of US 2008/0305982 A1; and/or US 2009/0247449 A1. Alternatively, suitable capsules can be purchased from Appleton Papers Inc. of Appleton, Wis. USA.

[0091] In a preferred aspect the composition may comprise a deposition aid, preferably in addition to encapsulates. Preferred deposition aids are selected from the group consisting of cationic and nonionic polymers. Suitable polymers include cationic starches, cationic hydroxyethylcellulose, polyvinylformaldehyde, locust bean gum, mannan, xylloglucan, tamarind gum, polyethyleneetherphthalate and polymers containing dimethyldimethoxyl methacrylate, optionally with one or more monomers selected from the group comprising acrylic acid and acrylamide.

[0092] Perfume.

[0093] Preferred compositions of the invention comprise perfume. Typically the composition comprises a perfume that comprises one or more perfume raw materials, selected from the group as described in WO08/87497. However, any perfume useful in a laundry care composition may be used. A preferred method of incorporating perfume into the compositions of the invention is via an encapsulated perfume particle comprising either a water-soluble hydroxyl compound or melamine-formaldehyde or modified polyvinyl alcohol. In one aspect the encapsulate comprises (a) an at least partially water-soluble solid matrix comprising one or more water-soluble hydroxyl compounds, preferably starch; and (b) a perfume oil encapsulated by the solid matrix. In a further aspect the perfume may be pre-complexed with a polyanine, preferably a polyethyleneimine so as to form a Schiff base.

[0094] Polymers.

[0095] The composition may comprise one or more polymers. Examples are optionally modified carboxymethylcellulose, poly(vinyl-pyrollidone), poly (ethylene glycol), poly (vinyl alcohol), poly(vinylpyridine-N-oxide), poly(vinylimidazole), polyacrylates such as polycrylates, maleic/acidic acid copolymers and lauryl methacrylate/ acrylic acid co-polymers.

[0096] The composition may comprise one or more amphiphilic cleaning polymers such as the compound having the following general structure: bis ((C2H4O)n(C4H8O)m) (CH3) - N+ - C2H3 - N+ - (CH3)4 - bis ((C2H4O)n(C4H8O)m), wherein n = from 20 to 30, and m from 3 to 8, or sulfonated or sulphonated variants thereof. In one aspect, this polymer is sulfonated or sulphonated to provide a zwitterionic soil suspension polymer.

[0097] The composition preferably comprises amphiphilic alkoxylated grease cleaning polymers which have balanced hydrophilic and hydrophobic properties such that they remove grease particles from fabrics and surfaces. Preferred amphiphilic alkoxylated grease cleaning polymers comprise a core structure and a plurality of alkylate groups attached to that core structure. These may comprise alkoxyated polyalkylenamines, preferably having an inner polyethylene oxide block and an outer polypropylene oxide block. Typically these may be incorporated into the compositions of the invention in amounts of from 0.005 to 10 wt %, generally from 0.5 to 8 wt %.

[0098] Alkoxylated polycarboxylates such as those prepared from polycrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/07281 and PCT 90/01815. Chemically, these materials comprise polycarboxylates having one ethoxy
side-chain per every 7-8 acrylicate units. The side-chains are of the formula \(-\text{(CH}_3\text{CH}_2\text{O})_m \text{(CH}_3\text{)}_n\text{CH}_2\) wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the poly-acrylate “backbone” to provide a “comb” polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated poly-carboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

[0099] Mixtures of cosurfactants and other adjunct ingredients, are particularly suited to be used with an amphiphilic graft co-polymer. Preferred amphiphilic graft co-polymer(s) comprise (i) polyethylene glycol backbone; and (ii) and at least one pendant moiety selected from polyvinyl acetate, polyvinyl alcohol and mixtures thereof. A preferred amphiphilic graft co-polymer is Sokalan HP22, supplied from BASF. Suitable polymers include random graft copolymers, preferably a polyvinyl acetate grafted polyethylene oxide copolymer having a polyethylene oxide backbone and multiple polyvinyl acetate side chains. The molecular weight of the polyethylene oxide backbone is preferably about 6000 and the weight ratio of the polyethylene oxide to polyvinyl acetate is about 40 to 60 and no more than 1 grafting point per 50 ethylene oxide units. Typically these are incorporated into the compositions of the invention in amounts from 0.005 to 10 wt%, more usually from 0.05 to 8 wt%. Preferably the composition comprises one or more carboxylate polymer, such as a maleate/acrylate random copolymer or polyacrylate homopolymer. In one aspect, the carboxylate polymer is a polyacrylate homopolymer having a molecular weight of from 4,000 Da to 9,000 Da, or from 6,000 Da to 9,000 Da. Typically these are incorporated into the compositions of the invention in amounts from 0.005 to 10 wt%, or from 0.05 to 8 wt%.

[0100] Preferably the composition comprises one or more soil release polymers. Examples include soil release polymers having a structure as defined by one of the following Formulæ (VI), (VII) or (VIII):

\[ (\text{OCOR}_1^\prime-\text{CHR}_1^\prime)\text{O}-\text{OC}-\text{Ar}^\prime-\text{CO}-\text{OR}_2= (\text{VI}) \]
\[ (\text{OCOR}_2^\prime-\text{CHR}_2^\prime)\text{O}-\text{OC}-\text{Ar}^\prime-\text{CO}^\prime= (\text{VII}) \]
\[ (\text{OCOR}_3^\prime-\text{CHR}_3^\prime)\text{O}-\text{OR}_2= (\text{VIII}) \]

wherein:

[0101] a, b and c are from 1 to 200;
[0102] d, e and f are from 1 to 50;
[0103] Ar is a 1,4-substituted phenylene;
[0104] s is 1,3-substituted phenylene substituted in position 5 with SO₂Me;
[0105] Me is Li, K, Mg/2, Ca/2, Al/3, ammonium, mono-, di-, or tri-, or tetraalkylammonium wherein the alkyl groups are \(\text{C}_3-\text{C}_{16}\) alkyl or \(\text{C}_9-\text{C}_{10}\) hydroxylalkyl, or mixtures thereof;
[0106] \(\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5\) and \(\text{R}^6\) are independently selected from H or \(\text{C}_1-\text{C}_{18}\) n- or iso-alkyl; and
[0107] \(\text{R}^7\) is a linear or branched \(\text{C}_1-\text{C}_{18}\) alkyl, or a linear or branched \(\text{C}_2-\text{C}_{30}\) alkenyl, or a cycloalkyl group with 5 to 9 carbon atoms, or a \(\text{C}_2-\text{C}_{30}\) aryl group, or a \(\text{C}_2-\text{C}_{30}\) aralkyl group.

[0108] Suitable soil release polymers are polyester soil release polymers including Repel-o-tex polymers, including Repel-o-tex SF, SF-2 and SRP6 supplied by Rhodia. Other suitable soil release polymers include Texcure polymers, including Texcure SRA100, SRA300, SRN100, SRN170, SRN240, SRN300 and SRN325 supplied by Clariant. Other suitable soil release polymers are Marloquest polymers, such as Marloquest SL supplied by Sasol.

[0110] Preferably the composition comprises one or more cellulose polymer, including those selected from alkyl cellulose, alkyl alkoxyalkyl cellulose, carboxyalkyl cellulose, alkyl carboxyalkyl cellulose. Preferred cellulose polymers are selected from the group comprising carboxymethyl cellulose, methyl cellulose, methyl hydroxyethyl cellulose, and mixtures thereof. In one aspect, the carboxymethyl cellulose has a degree of carboxymethyl substitution from 0.5 to 0.9 and a molecular weight from 100,000 Da to 300,000 Da.

[0111] Enzymes.

[0112] Preferably the composition comprises one or more enzymes. Preferred enzymes provide cleaning performance and/or fabric care benefits. Examples of suitable enzymes include, but are not limited to, hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, mannanases, pectate lyases, keratinases, reductases, oxidases, phosphorylases, lipoxynases, liganinas, pullulanases, tannases, pentosanases, malolases, \(\beta\)-glucanases, arabinoxidases, hyaluronidase, chondroitinase, laccase, and amylases, or mixtures thereof. A typical combination is an enzyme cocktail that may comprise, for example, a protease and lipase in conjunction with amylase. When present in the composition, the aforementioned additional enzymes may be present at levels from about 0.00001% to about 2%, from about 0.0001% to about 1% or even from about 0.001% to about 0.5% enzyme protein by weight of the composition.

[0113] Proteases.

[0114] Preferably the composition comprises one or more proteases. Suitable proteases include metalloproteases and serine proteases, including neutral or alcaline microbial serine proteases, such as subtilisins (EC 3.4.21.62). Suitable proteases include those of animal, vegetal or microbial origin. In one aspect, such suitable protease may be of microbial origin. The suitable proteases include chemically or genetically modified mutants of the aforementioned suitable proteases. In one aspect, the suitable protease may be a serine protease, such as an alkaline microbial protease or/and a trypsin-type protease. Examples of suitable neutral or alkaline proteases include:

[0115] (a) subtilisins (EC 3.4.21.62), including those derived from Bacillus, such as Bacillus lenta, B. halophilus, B. subtilis, B. amylogalactocleaves, Bacillus pumilus and Bacillus gibsonii described in U.S. Pat. No. 6,312,936 B1, U.S. Pat. No. 5,679,630, U.S. Pat. No. 4,760,025, U.S. Pat. No. 7,262,042 and WO09/021867.

[0116] (b) trypsin-type or chymotrypsin-type proteases, such as trypsin (e.g., of porcine or bovine origin), including the Fusarium protease described in WO 89/06270 and the chymotryptic protease derived from Cellumonas described in WO 05/052161 and WO 05/052146.

[0117] (c) metalloproteases, including those derived from Bacillus amylogalactocleaves described in WO 07/044993 A2.

[0118] Protase enzymes include those derived from Bacillus gibsonii or Bacillus Lentus.

[0119] Suitable commercially available protease enzymes include those sold under the trade names Alcalase®, Savi-nase®, Prinase®, Durazyme®, Polarylzyme®, Kannase®, Liqueunanase®, Liqueunan Ultra®, Savinase Ultra®, Ovozyme®, Neutrase®, EVERlast® and Eserponge® by Novozymes A/S (Denmark), those sold under the tradenames
Maxataze®, Maxacap®, Maxapem®, Properaize®, Purafect®, Purafect Prime®, Purafect Ox®, FN3R®, FN4R®, Excellase® and Purafect OXP® by Genencor International, Inc., those sold under the trademarks Opticlean® and Optimize® by Solvay Enzymes, those available from Henkel/Kemira, namely BLAP (sequence shown in Fig. 29 of U.S. Pat. No. 5,522,604 with the following mutations S99D+S101R+S303A+V304I+159S; hereinafter referred to as BLAP), BLAP R (BLAP with S37+V41+V199M+V205I+L217D), BLAP X (BLAP with S37+V41+V205I) and BLAP F49 (BLAP with S37+V41+A194P+V199M+V205I+L217D)—all from Henkel/Kemira; and KAP (Bacillus alkalinophilus subsilin) with mutations A230V+S526G+S259N) from Kao.

[0120] Amylases.

[0121] Preferably the composition may comprise an amylase. Suitable alpha-amylases include those of bacterial or fungal origin. Chemically or genetically modified mutants (variations) are included. A preferred alkaline alpha-amylase is derived from a strain of Bacillus, such as Bacillus licheniformis, Bacillus amyloliquifaciens, Bacillus stearamphophilius, Bacillus subtilis, or other Bacillus spp., such as Bacillus sp. NCIB 12289, NCIB 12512, NCIB 12513, DSM 3575 (U.S. Pat. No. 7,153,818) DSM 12368, DSMZ no. 12649, KSM AP1378 (WO 97/00324), KSM K36 or KSM K38 (EP 1,022,334). Preferred amylases include:

[0122] (a) the variants described in WO 94/02597, WO 94/18314, WO96/23874 and WO 97/43424, especially the variants with substitutions in one or more of the following positions versus the enzyme listed as SEQ ID No. 2 in WO 96/23874: 15, 23, 105, 106, 124, 128, 133, 154, 156, 181, 188, 190, 197, 202, 208, 209, 243, 264, 304, 305, 301, 408, and 444.

[0123] (b) the variants described in U.S. Pat. No. 5,856,164 and WO99/23211, WO 96/23873, WO00/06060 and WO 00/06243, especially the variants with one or more substitutions in the following positions versus the AAL60 enzyme listed as SEQ ID No. 12 in WO 00/06243:


[0125] (c) variants exhibiting at least 90% identity with SEQ ID No. 4 in WO00/06243, the wild-type enzyme from Bacillus sp722, especially variants with deletions in the 183 and 184 positions and variants described in WO 00/06060, which is incorporated herein by reference.

[0126] (d) variants exhibiting at least 95% identity with the wild-type enzyme from Bacillus sp.707 (SEQ ID NO:7 in U.S. Pat. No. 6,093,562), especially those comprising one or more of the following mutations M202, M208, S255, R172, and/or M261. Preferably said amylase comprises one or more of M202L, M202V, M202S, M202T, M202I, M202Q, M202W, S255N and/or R172Q. Particularly preferred to be comprised are the M202I or M202T mutants.

[0127] (e) variants described in WO 09/14930, particularly those exhibiting at least 90% identity with SEQ ID NO: 1 or SEQ ID NO:2 in WO 09/14930, the wild-type enzyme from Geobacillus Stearamphophilius or a truncated version thereof.

[0128] Suitable commercially available alpha-amylases include DURAMYL®, LIQUEZYM®, TERMAMYL®, TERMAMYL ULTRA®, NATALASE®, SUPRAMYL®, STAINZYM®, STAINZYM PLUS®, FUNGAMYL® and BAN® (Novozymes A/S, Bagsvaerd, Denmark), KEMZYM® AT 9000 Biozym Biotech Trading GmbH Wehlstrasse 27b A-1200 Wien Austria, RAPIDASE®, PURASTAR®, ENZYSIZE®, OPTIMIZE HT PLUS®, POWERASE® and PURASTAR OXAM® (Genencor International Inc., Palo Alto, Calif.) and KAM® (Kao, 14-10 Nihonbashishi Kayabacho, 1-chome, Chuo-ku Tokyo 103-8210, Japan). In one aspect, suitable amylases include NATALASE®, STAINZYM® and STAINZYM PLUS® and mixtures thereof.

[0129] Lipases.

[0130] Preferably the composition comprises one or more lipases, including “first cycle lipases” such as those described in U.S. Pat. No. 6,939,702 B1 and US PA 2009/0217464. Preferred lipases are first-wash lipases. In one embodiment of the invention the composition comprises a first wash lipase. First wash lipases includes a lipase which is a polypeptide having an amino acid sequence which: (a) has at least 90% identity with the wild-type lipase derived from Humicola lanuginosa strain DSM 4106; (b) compared to said wild-type lipase, comprises a substitution of an electrically neutral or negatively charged amino acid at the surface of the three-dimensional structure within 15A of E1 or Q249 with a positively charged amino acid; and (c) comprises a peptide addition at the C-terminal; and/or (d) comprises a peptide addition at the N-terminal and/or (e) meets the following limitations: (i) comprises a negative amino acid in position E210 of said wild-type lipase; (ii) comprises a negatively charged amino acid in the region corresponding to positions 90-101 of said wild-type lipase; and (iii) comprises a neutral or negative amino acid at a position corresponding to N94 or said wild-type lipase and/or has a negative or neutral net electric charge in the region corresponding to positions 90-101 of said wild-type lipase. Preferred variants of the wild-type lipase from Thermomyces lanuginosus comprising one or more of the T231R and N233R mutations. The wild-type sequence is the 269 amino acids (amino acids 23-291) of the Swissprot accession number Swiss-Prot O59952 (derived from Thermomyces lanuginosus (Humicola lanuginosa)). Preferred lipases would include those sold under the tradenames Lipex® and Lipex® and Lipolase® and Whitezyme® (Novozymes A/S, Bagsvaerd, Denmark).

[0131] Endoglucanases. Other preferred enzymes include microbial-derived endoglucanases exhibiting endo-beta-1,4-glucanase activity (E.C. 3.2.1.4), including a bacterial polypeptide endogenous to a member of the genus Bacillus which has a sequence of at least 90%, 94%, 97% and even 99% identity to the amino acid sequence SEQ ID NO:2 in U.S. Pat. No. 7,141,403S and mixtures thereof. Suitable endoglucanases are sold under the tradenames Celluclast® and Whitezyme® (Novozymes A/S, Bagsvaerd, Denmark).

[0132] Pectate Lyases.

[0133] Other preferred enzymes include pectate lyases sold under the tradenames Peectar®e, Peectar®, Xpect® and mannases sold under the tradenames Mannaway® (all from Novozymes A/S, Bagsvaerd, Denmark), and Purabrite® (Genencor International Inc., Palo Alto, Calif.).

[0134] Bleaching Agents.

[0135] It may be preferred for the composition to comprise one or more bleaching agents. Suitable bleaching agents other than bleaching catalysts include photobleaches, bleaching activators, hydrogen peroxide, sources of hydrogen peroxide, pre-formed peroxides and mixtures thereof. In general, when a bleaching agent is used, the compositions of the present
invention may comprise from about 0.1% to about 50% or even from about 0.1% to about 25% bleaching agent or mixtures of bleaching agents by weight of the subject composition. Examples of suitable bleaching agents include:

(1) photobleaches for example sulfonated zinc phthalocyanine sulfonated aluminium phthalocyanines, xanthene dyes and mixtures thereof;

(2) pre-formed peracids: Suitable preformed peracids include, but are not limited to compounds selected from the group consisting of pre-formed peroxycarboxylic acids or salts thereof typically a percarboxylic acids and salts, percarboxylic acids and salts, perimide acids and salts, peroxycarboxylsulfonic acids and salts, for example, Oxone® and mixtures thereof. Suitable examples include peroxycarboxylic acids or salts thereof, or peroxysulfonic acids or salts thereof. Typical peroxycarboxylic acid salts suitable for use herein have a chemical structure corresponding to the following chemical formula:

\[
\begin{align*}
\text{R}^{14} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\text{O} & \quad \text{Y}
\end{align*}
\]

wherein: \( \text{R}^{14} \) is selected from alkyl, aralkyl, cycloalkyl, aryl or heterocyclic groups; the \( \text{R}^{14} \) group can be linear or branched, substituted or unsubstituted; having, when the peracid is hydrophobic, from 6 to 14 carbon atoms, or from 8 to 12 carbon atoms and, when the peracid is hydrophilic, less than 6 carbon atoms or even less than 4 carbon atoms; \( \text{Y} \) is any suitable counter-ion that achieves electric charge neutrality; preferably \( \text{Y} \) is selected from hydrogen, sodium or potassium. Preferably, \( \text{R}^{14} \) is a linear or branched, substituted or unsubstituted \( \text{C}_{6-14} \) alkyl. Preferably, the peroxycarboxylic acid or salt thereof is selected from peroxylhexanoic acid, peroxycaprylic acid, peroxycrotonic acid, peroxynonanoic acid, peroxycarboxylic acid, any salt thereof, or any combination thereof. Particularly preferred peroxycarboxylic acids are phthalimido-peroxylhexanoic acids, in particular \( \text{C}_{6-14} \) alkyl phthalimido-peroxylhexanoic acid (PAP). Preferably, the peroxycarboxylic acid or salt thereof has a melting point in the range of from 30°C to 60°C.

[0136] The pre-formed peroxycarboxylic acid or salt thereof can also be a peroxysulfonic acid or salt thereof, typically having a chemical structure corresponding to the following chemical formula:

\[
\begin{align*}
\text{R}^{15} & \quad \text{O} \\
\text{O} & \quad \text{Z}
\end{align*}
\]

wherein: \( \text{R}^{15} \) is selected from alkyl, aralkyl, cycloalkyl, aryl or heterocyclic groups; the \( \text{R}^{15} \) group can be linear or branched, substituted or unsubstituted, and \( \text{Z} \) is any suitable counter-ion that achieves electric charge neutrality, preferably \( \text{Z} \) is selected from hydrogen, sodium or potassium. Preferably \( \text{R}^{15} \) is a linear or branched, substituted or unsubstituted \( \text{C}_{6-14} \) alkyl. Preferably such bleach components may be present in the compositions of the invention in an amount from 0.01 to 50%, most preferably from 0.1% to 20%.

(3) sources of hydrogen peroxide, for example, inorganic perhydrate salts, including alkali metal salts such as sodium salts of perborate (usually mono- or tetra-hydrate), percarbonate, persulphate, perphosphate, persilicate salts and mixtures thereof. In one aspect of the invention the inorganic perhydrate salts are selected from the group consisting of sodium salts of perborate, percarbonate and mixtures thereof. When employed, inorganic perhydrate salts are typically present in amounts of from 0.6% to 40 wt%, or 1 to 30 wt% of the overall fabric and home care product and are typically incorporated into such fabric and home care products as a crystalline solid that may be coated. Suitable coatings include, inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as water-soluble or dispersible polymers, waxes, oils or fatty soaps; and

(4) bleach activators having \( \text{R}^1-(\text{C}-(\text{O})-\text{L}) \) wherein \( \text{R} \) is an alkyl group, optionally branched, having, when the bleach activator is hydrophobic, from 6 to 14 carbon atoms, or from 8 to 12 carbon atoms and, when the bleach activator is hydrophilic, less than 6 carbon atoms or even less than 4 carbon atoms; and \( \text{L} \) is leaving group. Examples of suitable leaving groups are benzoic acid and derivatives thereof—especially benzene sulphonate. Suitable bleach activators include dodecanoyl oxybenzene sulphonate, decanoyl oxybenzene sulphonate, decanoyl oxybenzoic acid or salts thereof, 3,5,5-trimethyl hexanoyloxybenzene sulphonate, tetraacetyl ethylene diamine (TAED) and nonanoyloxybenzene sulphonate (NOBS). Suitable bleach activators are also disclosed in WO 98/17767. While any suitable bleach activator may be employed, in one aspect of the invention the subject composition may comprise NOBS, TAED or mixtures thereof.

(5) Bleach Catalysts. The compositions of the present invention may also include one or more bleach catalysts capable of accepting an oxygen atom from a peroxycarboxylic acid and/or salt thereof, and transferring the oxygen atom to an oxidizable substrate. Suitable bleach catalysts include, but are not limited to: inimium cations and polynions; inimium zwitterions; modified amines; modified amine oxides; N-sulphonyl imines; N-sulphonyl imines; N-acyl imines; thiadiazole dioxides; perfluororimines; cyclic sugar ketones and alpha amino-ketones and mixtures thereof. Suitable alpha amino ketones are for example as described in WO 2012/000846 A1, WO 2008/015443 A1, and WO 2008/014965 A1. Suitable mixtures are as described in USPA 2007/0173430 A1.

[0138] Without wishing to be bound by theory, the inventors believe that controlling the electrophilicity and hydrophobicity in this above described manner enables the bleach ingredient to be delivered substantially only to areas of the fabric that are more hydrophobic, and that contain electron rich soils, including visible chromophores, that are susceptible to bleaching by highly electrophilic oxidants.

[0139] In one aspect, the bleach catalyst has a structure corresponding to general formula below:

\[
\begin{align*}
\text{N} & \quad \text{OSO}^\theta \\
\text{O} & \quad \text{R}^\theta
\end{align*}
\]

wherein \( \text{R}^{13} \) is selected from the group consisting of 2-ethylhexyl, 2-propylheptyl, 2-butylcloctyl, 2-pentylmononyl,
2-hexadecyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, iso-nonyl, iso-decyl, iso-tridecyl and iso-pentadecyl;
(6) The composition may preferably comprise catalytic metal complexes. One preferred type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium, tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequester having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methyleneephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. No. 4,430,243.

[0141] If desired, the compositions herein can be catalyzed by means of a manganese compound. Such compounds and levels of use are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. No. 5,576,282. Cobalt bleach catalysts useful herein are known, and are described, for example, in U.S. Pat. No. 5,597,936; U.S. Pat. No. 5,595,367. Such cobalt catalysts are readily prepared by known procedures, such as taught for example in U.S. Pat. No. 5,597,936, and U.S. Pat. No. 5,595,967.

[0142] Compositions herein may also suitably include a transition metal complex of ligands such as bispidones (WO 05/042532 A1) and/or macropolymeric rigid ligands—abbreviated as “MRL’s.” As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per hundred million of the active MRL species in the aqueous washing medium, and will typically provide from about 0.005 ppm to about 25 ppm, from about 0.05 ppm to about 10 ppm, or even from about 0.1 ppm to about 5 ppm, of the MRL in the wash liquor.

[0143] Suitable transition-metal in the transition-metal bleach catalyst include, for example, manganese, iron and chromium. Suitable MRLs include 5,12-diethyl-1,5,8,12-tetraazabicyclo[6.6.2]heptadecane.

[0144] Suitable transition metal MRLs are readily prepared by known procedures, such as taught for example in WO 00/32601, and U.S. Pat. No. 6,225,464.

[0145] When present, the source of hydrogen peroxide/peracid and/or bleach activator is generally present in the composition in an amount of from about 0.1 to about 60 wt%, from about 0.5 to about 40 wt% or even from about 0.6 to about 10 wt% based on the fabric and home care product. One or more hydrophobic peracids or precursors thereof may be used in combination with one or more hydrophilic peracid or precursor thereof.

[0145] Typically hydrogen peroxide source and bleach activator will be incorporated together. The amounts of hydrogen peroxide source and peracid or bleach activator may be selected such that the molar ratio of available oxygen (from the peroxide source) to peracid is from 1:1 to 35:1, or even 2:1 to 10:1.

[0146] Surfactant.

[0147] Preferably the composition comprises a surfactant or surfactant system. The surfactant can be selected from nonionic, anionic, cationic, amphoteric, amphotolytic, amphiphilic, zwitterionic, semi-polar nonionicsurfactants and mixtures thereof. Preferred compositions comprise a mixture of surfactants/surfactant system. Preferred surfactant systems comprise one or more anionic surfactants, most preferably in combination with a co-surfactant, most preferably a nonionic and/or amphoteric and/or zwitterionic surfactant.

[0148] Prefered surfactant systems comprise both anionic and nonionic surfactant, preferably in weight ratios from 90:1 to 1:90. In some instances a weight ratio of anionic to nonionic surfactant of at least 1:1 is preferred. However a ratio below 10:1 may be preferred. When present, the total surfactant level is preferably from 0.1% to 60%, from 1% to 50% or even from 5% to 40% by weight of the subject composition.

[0149] Preferably the composition comprises an anionic detergent surfactant, preferably sulphate and/or sulphonate surfactants. Preferred examples include alkyl benzene sulphonates, alkyl sulphates and alkyl alkoxylated sulphates. Preferred sulphonates are C₆₋₁₈ alkyl benzene sulphonate. Suitable alkyl benzene sulphonate (LAS) may be obtained, by sulphonating commercially available linear alkyl benzene (LAB); suitable LAB includes low 2-phenyl LAB, such as those supplied by Sasol under the tradename Isochem® or those supplied by Petresa under the tradename Petrelab®, other suitable LAB include high 2-phenyl LAB, such as those supplied by Sasol under the tradename Hyblene®. A suitable anionic detergent surfactant is alkyl benzene sulphonate that is obtained by DETAL catalyzed process, although other synthesis routes, such as HF, may also be suitable. In one aspect a magnesium salt of LAS is used.

[0150] Prefered sulphate detergent surfactants include alkyl sulphate, typically C₆₋₁₈ alkyl sulphate, or predominately C₁₂ alkyl sulphate. A further preferred alkyl sulphate is alkyl alkoxylated sulphate, preferably a C₆₋₁₈, alkyl alkoxylated sulphate. Preferably the alkoxylating group is an ethoxylating group. Typically the alkyl alkoxylated sulphate has an average degree of alkylation of from 0.5 to 30 or 20, or from 0.5 to 10. Particularly preferred are C₆₋₁₈ alkyl ethoxylated sulphate having an average degree of ethoxylation of from 0.5 to 10, from 0.5 to 7, from 0.5 to 5 or even from 0.5 to 3.

[0151] The alkyl sulphate, alkyl alkoxylated sulphate and alkyl benzene sulphonates may be linear or branched, substituted or un-substituted. When the surfactant is branched, preferably the surfactant will comprise a mid-chain branched sulphate or sulphonate surfactant. Preferably the branching groups comprise C₄₋₁₄ alkyl groups, typically methyl and/or ethyl groups.

[0152] Preferably the composition comprises a nonionic detergent surfactant. Suitable non-ionic surfactants are selected from the group consisting of: C₆₋₁₈ alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C₆₋₁₈ alkyl phenol alkoxylates wherein the alkoxylate units may be ethyleneoxy units, propyleneoxy units or a mixture thereof; C₆₋₁₈ C₁₄-₁₈ alcohol and C₆₋₁₈ C₁₂ alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic® from BASF; C₁₄-₁₈ mid-chain branched alcohols; C₁₄-₁₂ C₂₂ mid-chain branched alkyl alkoxylates, typically having an average degree of alkylation of from 1 to 30; alkylpolyoxycarboxides; polyhydroxy fatty acid amides; ether capped poly(oxy-alkylated) alcohol surfactants; and mixtures thereof.

[0153] Suitable non-ionic detergent surfactants include alkyl polyglycoside and/or an alkyl alkoxylated alcohol.
50, most preferably from 1 to 30, from 1 to 20, or from 1 to 10. In one aspect, the alkyl alkoxylated alcohol may be a C₆₋₁₈ alkyl ethoxylated alcohol having an average degree of ethoxylation of from 1 to 10, from 1 to 7, more from 1 to 5 or from 3 to 7, or even below 3 or 2. The alkyl alkoxylated alcohol can be linear or branched, and substituted or unsubstituted.

[0154] Suitable nonionic surfactants include those with the tradename Lutensol® from BASF.

[0155] Suitable cationic detergents surfactants include alkyl pyridinium compounds, alkyl quaternary ammonium compounds, alkyl tertiary phosphonium compounds, and mixtures thereof.

[0156] Suitable cationic detergents surfactants are quaternary ammonium compounds having the general formula:

(R₁)(R₂)(R₃)(R₄)N⁺X⁻

[0157] wherein, R₁ is a linear or branched, substituted or unsubstituted C₆₋₁₈ alkyl or alkylalkenoyl moiety, R₂ and R₃ are independently selected from methyl or ethyl moieties, R₄ is a hydroxyl, hydroxymethyl or a hydroxyethyl moiety, X is an anion which provides charge neutrality, suitable anions include: halides, for example chloride; sulphate; and sulphonate. Suitable cationic detergents surfactants are mono-C₆₋₁₈ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides. Highly suitable cationic detergents surfactants are mono-C₆₋₁₈ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-C₆₋₁₈ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride. Mono-C₆₋₁₈ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride.

[0158] Suitable amphoteric/zwitterionic surfactants include amine oxides and betaines.

[0159] Amine-neutralized anionic surfactants-Anionic surfactants of the present invention and adjunct anionic surfactants, may exist in an acid form, and said acid form may be neutralized to form a surfactant salt which is desirable for use in the present detergent compositions. Typical agents for neutralization include the metal counterion base such as hydroxides, e.g. NaOH or KOH. Further preferred agents for neutralizing anionic surfactants of the present invention and adjunct anionic surfactants or surfactants in their acid forms include ammonia, amines, or amionolamines. Alkanolamines are preferred. Suitable non-limiting examples including monoethanolamine, diethanolamine, triethanolamine, and other linear or branched alkanolamines known in the art; for example, highly preferred alkanolamines include 2-amino-1-propanol, 1-aminopropanol, monoethanolpropanolamine, or 1-amino-3-propanol. Amine neutralization may be done to a full or partial extent, e.g. part of the anionic surfactant mix may be neutralized with sodium or potassium and part of the anionic surfactant mix may be neutralized with amines or alkanolamines.

[0160] Builders.

[0161] Preferably the composition comprises one or more builders or a builder system. When a builder is used, the composition of the invention will typically comprise at least 1%, from 2% to 60% builder. It may be preferred that the composition comprises less than 50% of phosphate salt and/or zeolite, for example from 1 to 10 or 5 wt % The composition may even be substantially free of strong builder; substantially free of strong builder means “no deliberately added” zeolite and/or phosphate. Typical zeolite builders include zeolite A, zeolite P and zeolite MAP. A typical phosphate builder is sodium tri-polyphosphate.

[0162] Chelating Agent.

[0163] Preferably the composition comprises chelating agents and/or crystal growth inhibitor. Suitable molecules include copper, iron and/or manganese chelating agents and mixtures thereof. Suitable molecules include amino carboxylates, aminophosphonates, succinates, salts thereof, and mixtures thereof. Non-limiting examples of suitable chelants for use herein include ethylenediaminetetraacetates, N-(hydroxymethyl)ethylenediaminetetraacetates, nitrilotriacetates, ethylene-diamine tetraacetates, triethylenetetraminehexacetates, diethylenetriamine-pentacettes, ethylenediamine, ethylenediaminotetraacetates (MDA), diethylenetriaminepentacettes, ethylenediaminetetraacetates (EDTA), ethylenediaminetetraacetates (EDTS), diethylenetriaminepentaacetates (DTPA), salts thereof, and mixtures thereof. Other non-limiting examples of chelants of use in the present invention are found in U.S. Pat. Nos. 7,445,644, 7,585,376 and 2009/0176684A1. Other suitable chelating agents for use herein are the commercial DEQUEST series, and chelants from Monsanto, DuPont, and Nalco, Inc.

[0164] Dye Transfer Inhibitor (DTI).

[0165] The composition may comprise one or more dye transfer inhibiting agents. In one embodiment of the invention the inventors have surprisingly found that compositions comprising polymeric dye transfer inhibiting agents in addition to the specified dye give improved performance. This is surprising because these polymers prevent dye deposition. Suitable dye transfer inhibitors include, but are not limited to, polyvinylpyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof. Suitable examples include PV-PK15, PV-PK30, ChromaBond S-400, ChromaBond S-403E and Chromabond S-100 from Ashland Aqualon and Sokalan HP165, Sokalan HP50, Sokalan HP53, Sokalan HP59, Sokalan® HP 56K, Sokalan® HP 66 from BASF. Other suitable DTIs are as described in WO2012/004134. When present in a subject composition, the dye transfer inhibiting agents may be present at levels from about 0.0001% to about 10%, from about 0.01% to about 5% or even from about 0.1% to about 3% by weight of the composition.

[0166] Fluorescent Brightener.

[0167] Preferably the composition comprises one or more fluorescent brighteners. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not limited to, derivatives of stilbene, pyrazine, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and cyclic and straight-chain naphthalene derivatives. Particularly preferred brighteners are selected from: sodium 2(4-aryl-3-sulphophenyl)-211-naphthol, 1,4-difluoro-4-bis-[4-anilino-6-(N-methyl-N-2 hydroxyethyl) amino] stilbene-2,2'-disulphonate, sodium 4,4'-bis-[4-anilino-6-(N-6-methoxo-1,3,5-triazin-2-yl)aminol bisthene-2,2'-disulphonate, and disodium 4,4'-bis-(2-sulfoanilido) biphenyl. Other examples of such brighteners are disclosed in the US patent application WO2012/004134. When used, the dye transfer inhibiting agents may be added to the composition at levels from about 0.0001% to about 10%, from about 0.01% to about 5% or even from about 0.1% to about 3% by weight of the composition.
nonlimiting examples of optical brighteners which are useful in the present compositions are those identified in U.S. Pat. No. 4,790,856 and U.S. Pat. No. 3,646,015.

A preferred brightener has the structure below:

\[
\begin{align*}
&\text{H}_2\text{N}-\text{N} &
&\text{SO}_3\text{Na} \\
&\text{N} &
&\text{SO}_3\text{Na} \\
&\text{N} &
&\text{N} \\
&\text{SO}_3\text{Na} &
&\text{NH}_2
\end{align*}
\]

Suitable fluorescent brightener levels include lower levels of from about 0.01, from about 0.05, from about 0.1 or even from about 0.2 wt % to upper levels of 0.5 or even 0.75 wt %.

In one aspect the brightener may be loaded onto a clay to form a particle.

Preferred brighteners are totally or predominantly (typically at least 50 wt %, at least 75 wt %, at least 90 wt %, at least 99 wt %) in alpha-crystalline form. A highly preferred brightener comprises C.I. fluorescent brightener 260, preferably having the following structure:

\[
\begin{align*}
&\text{NH}_2 &
&\text{SO}_3\text{Na} \\
&\text{N} &
&\text{SO}_3\text{Na} \\
&\text{N} &
&\text{N} \\
&\text{SO}_3\text{Na} &
&\text{NH}_2
\end{align*}
\]

This can be particularly useful as it dissolves well in cold water, for example below 30 or 25 or even 20°C.

Preferably brighteners are incorporated in the composition in micronized particulate form, most preferably having a weight average primary particle size of from 3 to 30 micrometers, from 3 micrometers to 20 micrometers, or from 3 to 10 micrometers.

The composition may comprise C.I. fluorescent brightener 260 in beta-crystalline form, and the weight ratio of: (i) C.I. fluorescent brightener 260 in alpha-crystalline form, to (ii) C.I. fluorescent brightener 260 in beta-crystalline form may be at least 0.1, or at least 0.6.

BE608047 relates to a process for making C.I. fluorescent brightener 260 in alpha-crystalline form.

Silicate Salts.

The composition may preferably also contain silicate salts, such as sodium or potassium silicate. The composition may comprise from 0 wt % to less than 10 wt % silicate salt, to 9 wt %, or to 8 wt %, or to 7 wt %, or to 6 wt %, or to 5 wt %, or to 4 wt %, or to 3 wt %, or even to 2 wt %, and preferably from above 0 wt %, or from 0.5 wt %, or even from 1 wt % silicate salt. A suitable silicate salt is sodium silicate.

Dispersants.

The composition may preferably also contain dispersants. Suitable water-soluble organic materials include the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Enzyme Stabilisers.

The composition may preferably comprise enzyme stabilizers. Any conventional enzyme stabilizer may be used, for example by the presence of water-soluble sources of calcium and/or magnesium ions in the finished fabric and home care products that provide such ions to the enzymes. In case of aqueous compositions comprising protease, a reversible protease inhibitor, such as a boron compound including borate, or preferably 4-formyl phenylboronic acid, phenylboronic acid and derivatives thereof, or compounds such as calcium formate, sodium formate and 1,2-propane diol can be added to further improve stability.

Solvant System.

The solvent system in the present compositions can be a solvent system containing water alone or mixtures of organic solvents either without or preferably with water. Preferred organic solvents include 1,2-propanediol, ethanol, glycerol, dipropylene glycol, methyl propane diol and mixtures thereof. Other lower alcohols, C1-C4 alkanolamines such as monoethanolamine and triethanolamine, can also be used. Solvent systems can be absent, for example from anhydrous solid embodiments of the invention, but more typically are present at levels in the range of from about 0.1% to about 98%, preferably at least about 1% to about 50%, more usually from about 5% to about 25%.

In some embodiments of the invention, the composition is in the form of a structured liquid. Such structured liquids can either be internally structured, whereby the structure is formed by primary ingredients (e.g. surfactant material) and/or externally structured by providing a three-dimensional matrix structure using secondary ingredients (e.g. polymers, clay and/or silicate material), for use e.g. as thickeners. The composition may comprise a structurant, preferably from 0.01 wt % to 5 wt %, from 0.1 wt % to 2.0 wt % structurant. Examples of suitable structurants are given in US2006/0205631A1, US2005/0203213A1, U.S. Pat. No. 7,294,611, U.S. Pat. No. 6,855,680. The structurant is typically selected from the group consisting of diglycerides and triglycerides, ethylene glycol distearate, microcrystalline cellulose, cellulose-based materials, microfiber cellulose, hydrophobically modified alkali-swelling emulsions such as Polygel W30 (3VSigma), biopolymers, xanthan gum, geelan...
gum, hydrogenated castor oil, derivatives of hydrogenated castor oil such as non-ethoxylated derivatives thereof and mixtures thereof, in particular, those selected from the group of hydrogenated castor oil, derivatives of hydrogenated castor oil, microfibrillar cellulose, hydroxyfunctional crystalline materials, long chain fatty alcohols, long chain fatty acids, clays and mixtures thereof. A preferred structurant is described in U.S. Pat. No. 6,855,680 which defines suitable hydroxyfunctional crystalline materials in detail. Preferred is hydrogenated castor oil. Non-limiting examples of useful structurants include. Such structurants have a thread-like structuring system having a range of aspect ratios. Other suitable structurants and the processes for making them are described in WO2010/034736.

[0185] The composition of the present invention may comprise a high melting point fatty compound. The high melting point fatty compound useful herein has a melting point of 25°C or higher, and is selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, and mixtures thereof. Such compounds of low melting point are not intended to be included in this section. Non-limiting examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992. When present, the high melting point fatty compound is preferably included in the composition at a level of from 0.1% to 40%, preferably from 1% to 30%, more preferably from 1.5% to 16% by weight of the composition, from 1.5% to 8% in view of providing improved conditioning benefits such as slippery feel during the application to wet hair, softness and moisturized feel on dry hair.

[0186] Cationic Polymer.

[0187] The compositions of the present invention may contain a cationic polymer. Concentrations of the cationic polymer in the composition typically range from 0.05% to 3%, in another embodiment from 0.075% to 2.0%, and in yet another embodiment from 0.1% to 1.0%. Suitable cationic polymers will have cationic charge densities of at least 0.5 meq/gm, in another embodiment at least 0.9 meq/gm, in another embodiment at least 1.2 meq/gm, in yet another embodiment at least 1.5 meq/gm, but in one embodiment also less than 7 meq/gm, and in another embodiment less than 5 meq/gm, at the pH of intended use of the composition, which pH will generally range from pH 3 to pH 9, in one embodiment between pH 4 and pH 8. Herein, “cationic charge density” of a polymer refers to the ratio of the number of positive charges on the polymer to the molecular weight of the polymer. The average molecular weight of such suitable cationic polymers will generally be between 10,000 and 10 million, in one embodiment between 50,000 and 5 million, and in another embodiment between 100,000 and 3 million.

[0188] Suitable cationic polymers for use in the compositions of the present invention contain cationic nitrogen-containing moieties such as quaternary ammonium or cationic protonated amino moieties. Any anionic counterions can be used in association with the cationic polymers so long as the polymers remain soluble in water, in the composition, or in a concentrate when the composition is stored. The counterions are physically and chemically compatible with the essential components of the composition or do not otherwise unduly impair product performance, stability or aesthetics. Non-limiting examples of such counterions include halides (e.g., chloride, fluoride, bromide, iodide), sulfate and methyl sulfate.


[0190] Other suitable cationic polymers for use in the composition include polyvinylammonium polymers, quaternary nitrogen-containing cellulosic ethers, synthetic polymers, copolymers of ethylated cellulose, guar and starch. When used, the cationic polymers herein are either soluble in the composition or are soluble in a complex coacervate phase in the composition formed by the cationic polymer and the amionic, amphoteric and/or zwitterionic surfactant component described hereinbefore. Complex coacervates of the cationic polymer can also be formed with other charged materials in the composition.


[0192] Nonionic Polymer.

[0193] The composition of the present invention may include a nonionic polymer as a conditioning agent. Polyalkylene glycols having a molecular weight of more than 1000 are useful herein. Useful are those having the following general formula:

\[
\text{H}_2\text{C}_\text{O} + \text{R}_5^9 \text{OH}
\]

[0194] wherein \( R_{59} \) is selected from the group consisting of \( \text{H} \), methyl, and mixtures thereof. Conditioning agents, and in particular silicones, may be included in the composition. The conditioning agents useful in the compositions of the present invention typically comprise a water insoluble, water dispersible, non-volatile, liquid that forms emulsified, liquid particles. Suitable conditioning agents for use in the composition are those conditioning agents characterized generally as silicones (e.g., silicone oils, cationic silicones, silicone gums, high refractive silicons and silicone resins), organic conditioning oils (e.g., hydrocarbon oils, polyolefins, and fatty esters) or combinations thereof, or those conditioning agents which otherwise form liquid, dispersed particles in the aqueous surfactant matrix herein. Such conditioning agents should be physiologically and chemically compatible with the essential components of the composition, and should not otherwise unduly impair product stability, aesthetics or performance.

[0195] The concentration of the conditioning agent in the composition should be sufficient to provide the desired conditioning benefits. Such concentration can vary with the condition agent, the conditioning performance desired, the average size of the conditioning agent particles, the type and concentration of other components, and other like factors.

[0196] The concentration of the silicone conditioning agent typically ranges from 5% to 10%. Non-limiting examples of suitable silicone conditioning agents, and optional suspending agents for the silicone, are described in U.S. Reissue Pat. No. 34,584; U.S. Pat. Nos. 5,104,646; 5,106,609; 4,152,416; 2,826,551; 3,964,500; 4,364,837; 6,607,717; 6,482,569; 5,807,956; 5,981,681; 6,207,782; 7,465,439; 7,641,767; 7,217,777; US Patent Application
Nos. 2007/0268373A1; 2005/0048549A1; 2007/0041929A1; British Pat. No. 849,433; German Patent No. DE 10036553, which are all incorporated herein by reference; Chemistry and Technology of Silicones, New York: Aca-
ademic Press (1968); General Electric Silicone Rubber Pro-
duct Data Sheets, SE 30, SE 33, SE 54 and SE 76; Silicon
Compounds, Petrochem. Inc. (1984); and in Encyclo-
pedia of Polymer Science and Engineering, vol. 15, 2d ed., pp
[0198] The compositions of the present invention may also
comprise components which contain one or more of such
conditioning agents described by the Procter & Gamble Company in
U.S. Pat. Nos. 5,674,478, and 5,700,122. Also suitable for use in
these conditioning agents described by the Procter & Gamble Company in
U.S. Pat. Nos. 5,674,478, 5,705,200, 4,663,158, 4,197,865, 4,217,
914, 4,381,919, and 4,452,853.
[0199] Hygiene Agent.
[0200] The compositions of the present invention may also
comprise components which deliver hygiene and/or malodour
benefits such as one or more of zinc ricinoleate, thymol,
quaternary ammonium salts such as Bardsac®, polyethyle-
namines (such as Luposkol®) from BASF® and zinc complexes
thereof, silver and silver compounds, especially those
that deliver slow-release Ag+ or nano-silver dispersions.
[0201] Probiotics.
[0202] The composition may comprise probiotics, such as
those described in WO2009/043709.
[0203] Suds Boosters.
[0204] The composition may preferably comprise one or
more of such suds boosters if high sudsing is desired. Suitable
examples are the C10-C14 alkanolamides or C10-C14 alkyl sulphates, which
are preferably incorporated at 1%-10% levels. The C10-C14
monoethanolamine and diethanol amides illustrate a typical class of
such suds boosters. Use of such suds boosters with high
sudsing surfactants such as the amine oxides, betaines
and sulfonates noted above is usually advantageous. If desired,
surfactants such as, but not limited to, amphoteric, acid,
and calcium salts such as
MgCl2, MgSO4, CaCl2, CaSO4 and the like, can be added at
levels of, typically, 0.1%-2%, to provide additional suds and
to enhance greasy removal performance.
[0205] Suds Suppressor.
[0206] Compounds for reducing or suppressing the forma-
tion of suds may be incorporated into the compositions of
the present invention. Suds suppression can be of particular
importance in the so-called "high concentration cleaning pro-
cess" as described in U.S. Pat. Nos. 4,489,455 and 4,489,574,
and in front-loading style washing machines. A wide variety of
materials may be used as suds suppressors, and suds sup-
pressors are well known to those skilled in the art. See, for
example, Kirk Othmer Encyclopedia of Chemical Technol-
Sons, Inc. 1979). Examples of suds suppressors include
monoalkylcarboxylic fatty acid and soluble salts therein,
high molecular weight hydrocarbons such as paraffin,
fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of
monovolatile alcohols, aliphatic C18-C40 ketones (e.g.,
sterore), N-alkylated amino triazines, waxy hydrocarbons
preferably having a melting point below about 100 °C, sili-
cone suds suppressors, and secondary alcohols. Suds sup-
pressors are described in U.S. Pat. Nos. 2,954,347; 4,265,779;
4,265,779; 3,455,839; 3,933,672; 4,652,392; 4,978,471;
4,983,316; 5,288,431; 4,639,489; 4,749,740; and 4,798,679;
4,075,118; European Patent Application No. 8907851.9; EP
100,072; and DOS 2,124,526.
[0207] For any detergent composition to be used in auto-
matic laundry washing machines, suds should not form to the
extent that they overwork the washing machine. Suds sup-
pressors, when utilized, are preferably present in a "suds sup-
pressing amount" as meant that the formula of the composition can select an amount of this
suds controlling agent that will sufficiently control the suds
to result in a low-sudsing laundry detergent for use in automatic
laundry washing machines. The compositions herein will
generally comprise from 0% to 10% of suds suppressor.
When utilized as suds suppressors, monobasic fatty
acids, and salts thereof, will be present typically in amounts
up to 5%, by weight, of the detergent composition. Preferably,
from 0.5% to 5% of fatty monobasic or suds suppressor is utilized.
Silicone suds suppressors are typically utilized in
amounts up to 2.0%, by weight, of the detergent composition,
although higher amounts may be used. Monostearin phospho-
late suds suppressors are generally utilized in amounts
ranging from 0.1% to 2%, by weight, of the composition.
Hydrocarbon suds suppressors are typically utilized in
amounts ranging from 0.01% to 5.0%, although higher
levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.
[0208] Pearlescent Agents.
[0209] Pearlescent agents as described in WO2011/163457
may be incorporated into the compositions of the invention.
[0210] Perfume.
[0211] Preferably the composition comprises a perfume,
preferably in the range from 0.001 to 3 wt%, most preferably
from 0.1 to 1 wt %. Many suitable examples of perfumes are
provided in the CFTA (Cosmetic, Toiletry and Fragrance
CFTA Publications and OPID 1993 Chemicals Buyers
Co. It is usual for a plurality of perfume components to be
present in the compositions of the invention, for example four,
five, six, seven or more. In perfume mixtures preferably
15 to 25 wt % are top notes. Top notes are defined by Poucher
(\'Journal of the Society of Cosmetic Chemists 6(2):80
[1951]). Preferred top notes include rose oxide, citrus oils,
linalyl acetate, lavender, linalool, dihydroxymethyl and cis-
3-hexanol.
[0212] Packaging.
[0213] Any conventional packaging may be used and the
packaging may be fully or partially transparent so that he
consumer can see the colour of the product which may be
provided or contributed to by the colour of the dyes essential
to the invention. UV absorbing compounds may be included
in some or all of the packaging.
[0214] Process of Making Compositions
[0215] The compositions of the invention may be made in
any useful form, as described above. They may be made by
any process chosen by the formulation, non-limiting examples
of which are described in the examples and in U.S. Pat.
No. 4,990,280; U.S. 20030087791A1; U.S. 20030087790A1;
U.S. 20050003983A1; U.S. 20040465264A1; U.S. Pat.
No. 4,762,636; U.S. Pat. No. 6,291,412; U.S. 2005027891A1;
EP 1070115A2; U.S. Pat. No. 5,679,584; U.S. Pat. No. 5,691,
[0216] When in the form of a liquid, the laundry care compositions of the invention may be aqueous (typically above 2 wt % or even above 5 or 10 wt % total water, up to 90 or up to 80 wt % or 70 wt % total water) or non-aqueous (typically below 2 wt % total water content). Typically the compositions of the invention will be in the form of an aqueous solution or uniform dispersion or suspension of surfactant, shading dye, and certain optional other ingredients, some of which may normally be in solid form, that have been combined with the normally liquid components of the composition, such as the liquid alcohol ethoxylate nonionic, the aqueous liquid carrier, and any other normally liquid optional ingredients. Such a solution, dispersion or suspension will be acceptable phase stable. When in the form of a liquid, the laundry care compositions of the invention preferably have viscosity from 1 to 1500 centipoises (1-1500 mPa*s), more preferably from 100 to 1000 centipoises (100-1000 mPa*s), and most preferably from 200 to 500 centipoises (200-500 mPa*s) at 20-1 and 21°C. Viscosity can be determined by conventional methods. Viscosity may be measured using an AR 550 rheometer from TA instruments using a plate steel spindle at 40 mm diameter and a gap size of 500 μm. The shear viscosity at 20 s-l and low shear viscosity at 0.05-1 can be obtained from a logarithmic shear rate sweep from 0.1 to 25-1 in 3 minutes time at 21°C. The preferred rheology described therein may be achieved using internal existing structuring with detergent ingredients or by employing an external rheology modifier. More preferably the laundry care compositions, such as detergent liquid compositions have a high shear rate viscosity of from about 100 centipoise to 1500 centipoise, more preferably from 100 to 1000 cps. Unit Dose laundry care compositions, such as detergent liquid compositions have high shear rate viscosity of from 400 to 1000 cps. Laundry care compositions such as laundry softening compositions typically have high shear rate viscosity of from 10 to 1000, more preferably from 10 to 500 cps, most preferably from 10 to 500 cps. Hand dishwashing compositions have high shear rate viscosity of from 300 to 4000 cps, more preferably 300 to 1000 cps.

[0217] The liquid compositions, preferably liquid detergent compositions herein can be prepared by combining the components thereof in any convenient order and by mixing, e.g., agitating, the resulting component combination to form a phase stable liquid detergent composition. In a process for preparing such compositions, a liquid matrix is formed containing at least a major proportion, or even substantially all, of the liquid components, e.g., nonionic surfactant, the non-surface active liquid carriers and other optional liquid components, with the liquid components being thoroughly admixed by imparting shear agitation to this liquid combination. For example, rapid stirring with a mechanical stirrer may usefully be employed. While shear agitation is maintained, substantially all of any anionic surfactants and the solid form ingredients can be added. Agitation of the mixture is continued, and if necessary, can be increased at this point to form a solution or a uniform dispersion of insoluble solid phase particulates within the liquid phase. After some or all of the solid-form materials have been added to this agitated mixture, particles of any enzyme material to be included, e.g., enzyme prills, are incorporated. As a variation of the composition preparation procedure hereinafter described, one or more of the solid components may be added to the agitated mixture as a solution or slurry of particles premixed with a minor portion of one or more of the liquid components. After addition of all of the composition components, agitation of the mixture is continued for a period of time sufficient to form compositions having the requisite viscosity and phase stability characteristics. Frequently this will involve agitation for a period of from about 30 to 60 minutes.

[0218] In one aspect of forming the liquid compositions, the dye is first combined with one or more liquid components to form a dye premix, and this dye premix is added to a composition formulation containing a substantial portion, for example more than 50% by weight, more specifically, more than 70% by weight, and yet more specifically, more than 90% by weight, of the balance of components of the laundry detergent composition. For example as described above, the dye premix and the enzyme component are added at a final stage of component additions. In another aspect, the dye is encapsulated prior to addition to the detergent composition, the encapsulated dye is suspended in a structured liquid, and the suspension is added to a composition formulation containing a substantial portion of the balance of components of the laundry detergent composition.

[0219] Pouches.

[0220] In a preferred embodiment of the invention, the composition is provided in the form of a unitized dose, either tablet form or preferably in the form of a liquid/solid (optionally granules)/gel/paste held within a water-soluble film in what is known as a pouch or pod. The composition can be encapsulated in a single or multi-compartment pouch. Multi-compartment pouches are described in more detail in EP-A-2133410. When the composition is present in a multi-compartment pouch, the composition of the invention may be in one or two or more compartments, thus the dye may be present in one or more compartments, optionally all compartments. Non-shading dyes or pigments or other aesthetics may also be used in one or more compartments. In one embodiment the composition is present in a single compartment of a multi-compartment pouch.

[0221] Suitable film for forming the pouches is soluble or dispersible in water, and preferably has a water-solubility/dispersability of at least 50%, preferably at least 75% or even at least 95%, as measured by the method set out hereafter using a glass filter with a maximum pore size of 20 microns: 

[0222] 50 grams±0.1 gram of pouch material is added in a pre-weighed 400 ml beaker and 245 ml±1 ml of distilled water is added. This is stirred vigorously on a magnetic stirrer set at 600 rpm, for 30 minutes. Then, the mixture is filtered through a folded qualitative sintered-glass filter with a pore size as defined above (max. 20 micron). The water is dried off from the collected filtrate by any conventional method, and the weight of the remaining material is determined (which is the dissolved or dispersed fraction). Then, the percentage solubility or dispersability can be calculated. Preferred film materials are polymeric materials. The film material can be obtained, for example, by casting, blow-moulding, extrusion or blown extrusion of the polymeric material, as known in the art. Preferred polymers, copolymers or derivatives thereof suitable for use as pouch material are selected from polyvinyl alcohols, polyvinyl pyrrolidone, polyalkylene oxides, acrylicamide, acrylic acid, cellulose, cellulose ethers, cellulose esters, cellulose amides, polyvinyl acetates, polyalkoxylic acids and salts, polyanionic acids or peptides, polyanimes, polyacrylamide, copolymers of maleic/ acrylic acids, polysaccharides including starch and gelatine, natural gums.
such as xanthum and carragum. More preferred polymers are selected from polyacrylates and water-soluble acrylate copolymers, methylcellulose, carboxymethylcellulose sodium, dextrin, ethylcellulose, hydroxyethyl cellulose, hydroxypropyl methylcellulose, maltoextrin, poly-

methaerylates, and most preferably selected from polyvinyl alcohols, polyvinyl alcohol copolymers and hydroxypropyl methyl cellulose (HPMC), and combinations thereof. Prefer-
able, the level of polymer in the pouch material, for example a PVA polymer, is at least 60%. The polymer can have any weight average molecular weight, preferably from about 1000 to 1,000,000, more preferably from about 10,000 to 300,000 yet more preferably from about 20,000 to 150,000. Nonaqueous polymers can also be used as the pouch material. This can be beneficial to control the mechanical and/or dis-
solution properties of the compartments or pouch, depending on the application thereof and the required needs. Suitable mixtures include for example mixtures wherein one polymer has a higher water-solubility than another polymer, and/or one polymer has a higher mechanical strength than another polymer. Also suitable are mixtures of polymers having dif-
f erent weight average molecular weights, for example a mixture of PVA or a copolymer thereof of a weight average molecular weight of about 10,000-40,000, preferably around 20,000, and of PVA or copolymer thereof, with a weight average molecular weight of about 100,000 to 300,000, preferably around 150,000. Also suitable herein are polymer blend compositions, for example comprising hydrolytically degradable and water-soluble polymer blends such as poly-

lactide and polyvinyl alcohol, obtained by mixing poly lactide and polyvinyl alcohol, typically comprising about 1-35% by weight poly lactide and about 65% to 99% by weight poly-
viny1 alcohol. Preferred for use herein are polymers which are from about 60% to about 98% hydrolysed, preferably about 80% to about 90% hydrolysed, to improve the dissolution characteristics of the material.

[0223] Naturally, different film material and/or films of different thickness may be employed in making the compart-
ments of the present invention. A benefit in selecting different films is that the resulting compartments may exhibit different solubility or release characteristics.

[0224] Most preferred film materials are PVA films known under the MonoSol trade reference M8630, M8900, M8779 (as described in the Applicants co-pending applications ref 44528 and 11599) and those described in U.S. Pat. No. 6,166, 117 and U.S. Pat. No. 6,787,512 and PVA films of corre-
sponding solubility and deformaibility characteristics.

[0225] The film material herein can also comprise one or more additive ingredients. For example, it can be beneficial to add plasticisers, for example glycerol, ethylene glycol, dieth-
ylene glycol, propylene glycol, sorbitol and mixtures thereof. Other additives include functional detergent additives to be delivered to the wash water, for example organic polymeric dispersants, etc.

[0226] Process for Making the Water-Soluble Pouch

The compositions of the invention in pouch form may be made using any suitable equipment and method. However the multi-compartment pouches are preferably made using the horizontal form filling process. The film is preferably wet-
ing, more preferably heated to increase the malleability thereof. Even more preferably, the method also involves the use of a vacuum to draw the film into a suitable mould. The vacuum drawing the film into the mould can be applied for 0.2 to 5 seconds, preferably 0.3 to 3 or even more preferably 0.5 to 1.5 seconds, once the film is on the horizontal portion of the surface. This vacuum may preferably be such that it provides an under-pressure of between ~100 mbar to ~1000 mbar, or even from ~200 mbar to ~600 mbar.

[0227] The moulds, in which the pouches are made, can have any shape, length, width and depth, depending on the required dimensions of the pouches. The moulds can also vary in size and shape from one to another, in this respect. For example, it may be preferred that the volume of the final pouches is between 5 and 300 ml, or even 10 and 150 ml or even 20 and 100 ml and that the mould sizes are adjusted accordingly.

[0228] Heat can be applied to the film, in the process commonly known as thermoforming, by any means. For example the film may be heated directly by passing it under a heating element or through hot air, prior to feeding it onto the surface or once on the surface. Alternatively it may be heated indi-
rectly, for example by heating the surface or applying a hot item onto the film. Most preferably the film is heated using an infra red light. The film is preferably heated to a temperature of 50 to 120° C., or even 60 to 90° C. Alternatively, the film can be wetted by any means, for example directly by spraying a wetting agent (including water, solutions of the film material or plasticizers for the film material) onto the film, prior to feeding it onto the surface or once on the surface, or indirectly by wetting the surface or by applying a wet item onto the film.

[0229] In the case of pouches comprising powders it is advantageous to pin prick the film for a number of reasons: (a) to reduce the possibility of film defects during the pouch formation, for example film defects giving rise to capture of the film can be generated if the stretching of the film is too fast; (b) to permit the release of any gases derived from the product enclosed in the pouch, as for example oxygen forma-
tion in the case of powders containing bleach; and/or (c) to allow the continuous release of perfume. Moreover, when heat and/or wetting is used, pin pricking can be used before, during or after the use of the vacuum, preferably during or before application of the vacuum. Preferred is thus that each mould comprises one or more holes which are connected to a system which can provide a vacuum through these holes, onto the film above the holes, as described herein in more detail.

[0230] Once a film has been heated/wetted, it is drawn into an appropriate mould, preferably using a vacuum. The filling of the moulded film can be done by any known method for filling (moving) items. The most preferred method will depend on the product form and speed of filling required. Preferably the moulded film is filled by in-line filling tech-
niques. The filled, open pouches are then closed, using a second film, by any suitable method. Preferably, this is also done while in horizontal position and in continuous, constant motion. Preferably the closing is done by continuously feed-
ing a second material or film, preferably water-soluble film, over and onto the web of open pouches and then preferably sealing the first film and second film together, typically in the area between the moulds and thus between the pouches.

[0231] Preferred methods of sealing include heat sealing, solvent welding, and solvent or wet sealing. It is preferred that only the area which is to form the seal, is treated with heat or solvent. The heat or solvent can be applied by any method, preferably on the closing material, preferably only on the areas which are to form the seal. If solvent or wet sealing or welding is used, it may be preferred that heat is also applied. Preferred wet or solvent sealing/welding methods include applying selectively solvent onto the area between the
moulds, or on the closing material, by for example, spraying or printing this onto these areas, and then applying pressure onto these areas, to form the seal. Sealing rolls and belts as described above (optionally also providing heat) can be used, for example.

[0232] The formed pouches can then be cut by a cutting device. Cutting can be done using any known method. It may be preferred that the cutting is also done in continuous manner, and preferably with constant speed and preferably while in horizontal position. The cutting device can, for example, be a sharp item or a hot item, whereby in the latter case, the hot item "burns" through the film/sealing area.

[0233] The different compartments of a multi-compartment pouch may be made together in a side-by-side style and consecutive pouches are not cut. Alternatively, the compartments can be made separately. According to this process and preferred arrangement, the pouches are made according to the process comprising the steps of:

[0234] a) forming an first compartment (as described above);
[0235] b) forming a recess within some or all of the closed compartment formed in step (a), to generate a second moulded compartment superposed above the first compartment;
[0236] c) filling and closing the second compartments by means of a third film;
[0237] d) sealing said first, second and third films; and
[0238] e) cutting the films to produce a multi-compartment pouch.

[0239] Said recess formed in step b is preferably achieved by applying a vacuum to the compartment prepared in step a).

[0240] Alternatively the second, and optionally third, compartment(s) can be made in a separate step and then combined with the first compartment as described in our co-pending application EP 0810142.5 which is incorporated herein by reference. A particularly preferred process comprises the steps of:

[0241] a) forming a first compartment, optionally using heat and/or vacuum, using a first film on a first forming machine;
[0242] b) filling said first compartment with a first composition;
[0243] c) on a second forming machine, deforming a second film, optionally using heat and vacuum, to make a second and optionally third moulded compartment;
[0244] d) filling the second and optionally third compartments;
[0245] e) sealing the second and optionally third compartment using a third film;
[0246] f) placing the sealed second and optionally third compartments onto the first compartment;
[0247] g) sealing the first, second and optionally third compartments; and
[0248] h) cutting the films to produce a multi-compartment pouch.

[0249] The first and second forming machines are selected based on their suitability to perform the above process. The first forming machine is preferably a horizontal forming machine. The second forming machine is preferably a rotary drum forming machine, preferably located above the first forming machine.

[0250] It will be understood moreover that by the use of appropriate feed stations, it is possible to manufacture multi-compartment pouches incorporating a number of different or distinctive compositions and/or different or distinctive liquid, gel or paste compositions.

[0251] Solid Form.

[0252] As noted previously, the laundry care compositions may be in a solid form. Suitable solid forms include tablets and particulate forms, for example, granular particles, flakes or sheets. Various techniques for forming detergent compositions in such solid forms are well known in the art and may be used herein. In one aspect, for example when the composition is in the form of a granular particle, the dye is provided in particulate form, optionally including additional but not all components of the laundry detergent composition. The dye particulate is combined with one or more additional particulates containing a balance of components of the laundry detergent composition. Further, the dye, optionally including additional but not all components of the laundry detergent composition, may be provided in an encapsulated form, and the shading dye encapsulate is combined with particulates containing a substantial balance of components of the laundry detergent composition. Suitable pre-mix particles for incorporation of dyes/benefit agents into laundry care compositions of the invention are described for example in WO2010/084039, WO2007/039042, WO2010/022775, WO2009/132870, WO2009/087033, WO2007/063577, WO2007/039042, WO2007/096052, WO2011/020991, WO2006/025598, WO2003/018740 and WO2003/018738.

[0253] Method of Use. The compositions of this invention, prepared as hereinbefore described, can be used to form aqueous washing/treatment solutions for use in the laundering/treatment of fabrics. Generally, an effective amount of such compositions is added to water, for example, in a conventional fabric automatic washing machine, to form such aqueous laundering solutions. The aqueous washing solution so formed is then contacted, typically under agitation, with the fabrics to be laundered/treated therewith. An effective amount of the liquid detergent compositions herein added to water to form aqueous laundering solutions can comprise amounts sufficient to form from about 500 to 7,000 ppm of composition in aqueous washing solution, or from about 1,000 to 3,000 ppm of the detergent compositions herein will be provided in aqueous washing solution.

[0254] Typically, the wash liquor is formed by contacting the laundry care composition with wash water in such an amount so that the concentration of the laundry care composition in the wash liquor is from above 0 g/l to 5 g/l, or from 1 g/l and to 4.5 g/l, or to 4.0 g/l, or to 3.5 g/l, or to 3.0 g/l, or to 2.5 g/l, or even to 2.0 g/l, or even to 1.5 g/l. The method of laundering fabric or textile may be carried out in a top-loading or front-loading automatic washing machine, or can be used in a hand-wash laundry application. In these applications, the wash liquor formed and concentration of laundry detergent composition in the wash liquor is that of the main wash cycle. Any input of water during any optional rinsing step(s) is not included when determining the volume of the wash liquor.

[0255] The wash liquor may comprise 40 litres or less of water, or 30 litres or less, or 20 litres or less, or 10 litres or less, or 8 litres or less, or even 6 litres or less of water. The wash liquor may comprise from above 0 to 15 litres, or from 2 litres, and to 12 litres, or even to 8 litres of water. Typically from 0.01 kg to 2 kg of fabric per litre of wash liquor is dosed into said wash liquor. Typically from 0.01 kg, or from 0.05 kg, or from 0.07 kg, or from 0.10 kg, or from 0.15 kg, or from 0.20 kg, or from 0.25 kg fabric per litre of wash liquor is dosed into
said wash liquor. Optionally, 50 g or less, or 45 g or less, or 40 g or less, or 35 g or less, or 30 g or less, or 25 g or less, or 20 g or less, or even 15 g or less, or even 10 g or less of the composition is contacted to water to form the wash liquor. Such compositions are typically employed at concentrations of from about 500 ppm to about 15,000 ppm in solution. When the wash solvent is water, the water temperature typically ranges from about 5°C to about 90°C. And, when the situs comprises a fabric, the water to fabric ratio is typically from about 1:1 to about 30:1. Typically the wash liquor comprising the laundry care composition of the invention has a pH of from 3 to 11.5.

In one aspect, such method comprises the steps of optionally washing and/or rinsing said surface or fabric, contacting said surface or fabric with any composition disclosed in this specification then optionally washing and/or rinsing said surface or fabric is disclosed, with optional drying step.

Drying of such surfaces or fabrics may be accomplished by any one of the common means employed either in domestic or industrial settings. The fabric may comprise any fabric capable of being laundered in normal consumer or institutional use conditions, and the invention is particularly suitable for synthetic textiles such as polyester and nylon and especially for treatment of mixed fabrics and/or fibres comprising synthetic and cellulosic fabrics and/or fibres. As examples of synthetic fabrics are polyester, nylon, these may be present in mixtures with cellulosic fibres, for example, polyacrylonitrile. The solution typically has a pH of from 7 to 11, more usually 8 to 10.5. The compositions are typically employed at concentrations from 500 ppm to 5,000 ppm in solution. The water temperatures typically range from about 5°C to about 90°C. The water to fabric ratio is typically from about 1:1 to about 30:1.

EXAMPLES

In the following examples, the dye of formula 1 can be any dye of formula 1 or mixtures thereof, in particular any of dyes 1 to 13 shown in the Dye Synthesis Examples above, or mixtures thereof.

Examples 1-6

Granular laundry detergent compositions for hand washing or washing machines, typically top-loading washing machines.

<table>
<thead>
<tr>
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<td>1,68 Silicate (SiO₂:Na₂O at ratio 1:6:1)</td>
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<td>MgSO₄</td>
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<td>Sodium Percarbonate</td>
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<td>Monohydrate MSDS</td>
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<td>Sulphonated zinc phthalocyanine</td>
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<td>Direct Violet Dye (DV9 or DV99 or DV66)</td>
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<td>Sulfate/Moisture</td>
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### Examples 7-13

Granular laundry detergent compositions typically for front-loading automatic washing machines.

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<td>(wt %)</td>
<td>(wt %)</td>
<td>(wt %)</td>
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<td>6.5</td>
<td>7.5</td>
<td>7.5</td>
<td>2.0</td>
</tr>
<tr>
<td>AES &amp;</td>
<td>0</td>
<td>4.8</td>
<td>1.0</td>
<td>5.2</td>
<td>4</td>
<td>4</td>
<td>2.5</td>
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<td>C12-14 Alkyl sulfate</td>
<td>1</td>
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<td>1</td>
<td>0</td>
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<td>C16-18 Dimethyl hydroxethylammonium chloride</td>
<td>0.75</td>
<td>0.94</td>
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<td>Crystalline layered silicate (b-Na2S2O5)</td>
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<td>0.5</td>
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<td>Citric Acid</td>
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<td>4</td>
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<td>3</td>
<td>2.5</td>
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<td>Silicate 2R (SiO2:Na2O at ratio 2:1)</td>
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<td>Soil release agent</td>
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<td>0.72</td>
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<td>Acrylic Acid/Maleic Acid</td>
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<td>Carboxymethylcellulose</td>
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<td>0.15</td>
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<tr>
<td>Protease - Purafect® (84 mg active/g)</td>
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<td>0.3</td>
<td>0.15</td>
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</tr>
<tr>
<td>Amylase - Stainzyme Plus® (20 mg active/g)</td>
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<td>0.15</td>
<td>0.2</td>
<td>0.3</td>
<td>0.15</td>
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<tr>
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<td>0</td>
<td>0</td>
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<tr>
<td>Amylase - Natalase® (8.85 mg active/g)</td>
<td>0.1</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Cellulase - Cellulase TM (15.6 mg active/g)</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
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<tr>
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<tr>
<td>TAED</td>
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<td>4</td>
<td>3.6</td>
<td>4</td>
<td>2.2</td>
<td>1.4</td>
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<tr>
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<td>13.2</td>
<td>16</td>
<td>14</td>
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<td>0.2</td>
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<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
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<td>MgSO4</td>
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<td>0.42</td>
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<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
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<tr>
<td>Soap</td>
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<td>0.15</td>
<td>0.05</td>
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<td>0.45</td>
<td>0.45</td>
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<td>Sulphonated zinc p-hydroxybenzene (active)</td>
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<td>0.0012</td>
<td>0.0007</td>
<td>0</td>
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<td>0.01</td>
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<td>0</td>
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<td>0.0001</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sulfate/Water &amp; Miscellaneous</td>
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<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
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</table>

A indicates test missing or illegible when filled.

### Examples 14-20

#### Heavy Duty Liquid Laundry Detergent Compositions

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<th>19</th>
<th>20</th>
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<td></td>
<td>(wt %)</td>
<td>(wt %)</td>
<td>(wt %)</td>
<td>(wt %)</td>
<td>(wt %)</td>
<td>(wt %)</td>
<td>(wt %)</td>
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<tr>
<td>AES C12-18 alkyl ethoxy (1.8) sulfate</td>
<td>11</td>
<td>10</td>
<td>4</td>
<td>6.32</td>
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<td>0</td>
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<td>AES &amp;</td>
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<td>0</td>
<td>2.4</td>
<td>0</td>
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<td>0</td>
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<td>Linear alkyl benzene</td>
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<td>8</td>
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<td>sulfonate/sulfonic acid</td>
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<td>0</td>
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<td>3.8</td>
<td>1.7</td>
<td>1.9</td>
<td>1.7</td>
<td>2.5</td>
<td>2.3</td>
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<td>Sodium hydroxide</td>
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<td>1.49</td>
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<td>0.7</td>
<td>0</td>
<td>0</td>
<td>To pH 8.2</td>
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<td>Monoethanolamine</td>
<td>5.5</td>
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<td>4.1</td>
<td>0.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>14 (wt %)</td>
<td>15 (wt %)</td>
<td>16 (wt %)</td>
<td>17 (wt %)</td>
<td>18 (wt %)</td>
<td>19 (wt %)</td>
<td>20 (wt %)</td>
</tr>
<tr>
<td>---</td>
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<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>AE9</td>
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<td>0.3</td>
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<td>0</td>
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<td>20.0</td>
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<td>0</td>
<td>2.4</td>
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<td>6</td>
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<tr>
<td>Chelsant (HEDP)</td>
<td>0.15</td>
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<td>0.07</td>
<td>0.5</td>
<td>0.11</td>
<td>0.8</td>
</tr>
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<td>Citric Acid</td>
<td>2.5</td>
<td>3.96</td>
<td>1.88</td>
<td>1.98</td>
<td>0.9</td>
<td>2.5</td>
<td>0.6</td>
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<tr>
<td>C_{12-14} dimethyl Amine Oxide</td>
<td>0.3</td>
<td>0.73</td>
<td>0.23</td>
<td>0.37</td>
<td>0</td>
<td>0</td>
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<tr>
<td>C_{12-14} Fatty Acid</td>
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<td>1.9</td>
<td>0.6</td>
<td>0</td>
<td>0.99</td>
<td>1.2</td>
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<td>4-formyl-phenylboronic acid</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0.05</td>
<td>0.02</td>
<td>0.01</td>
</tr>
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<td>Borex</td>
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<td>1.07</td>
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<td>Ethanol</td>
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<td>0.89</td>
<td>0</td>
<td>3</td>
<td>7</td>
</tr>
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</table>

A compound having the following general structure:

\[
\text{ba}(\text{C}_{n}\text{H}_{2n}\text{O})(\text{C}_{2n}\text{H}_{4n}\text{O})\text{in}(\text{CH}_{2})_{x}-N^{+}\text{-.}
\]

\[
\text{ba}(\text{C}_{3n}\text{H}_{6n}\text{O})(\text{C}_{2n}\text{H}_{4n}\text{O})\text{in}(\text{CH}_{2})_{x}-N^{+}\text{-.}
\]

wherein \( n = \) from 20 to 30, and \( x = \) from 3 to 8, or substituted or sulphonated variants thereof.

Ethoxylated \((\text{EO})_{x}\) tetraethylene pentamine

Ethoxylated Polyethyleneimine \(^2\)

Ethoxylated Polyethylene-diamine

1,2-Propanediol

Fluorescent Brightener

Hydrogenated castor oil derivative structurant

Perfume

Core Shell Melamine-formaldehyde

capsulate of perfume

Protease \((40.0\text{ mg active/g})\)

Mannanase: Mannaway \((25 \text{ mg active/g})\)

Amylase: Stainzyme \(\oplus (15 \text{ mg active/g})\)

Amylase: Natalie \(\oplus (29 \text{ mg active/g})\)

Xyloglucanase (Whitezyme \(\oplus, 20 \text{ mg active/g})\)

Lipex \(\oplus (18 \text{ mg active/g})\)

Dye of formula 1

Water, dyes & minors

Balance

*Based on total cleaning and/or treatment composition weight, a total of no more than 12% water

Examples 21 to 25

Unit Dose Compositions

[0263] This Example provides various formulations for unit dose laundry detergents. Such unit dose formulations can comprise one or multiple compartments.

[0264] The following unit dose laundry detergent formulations of the present invention are provided below.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>21</th>
<th>22</th>
<th>23</th>
<th>24</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylbenzene sulfonic acid C 11-13, 23.3% 2-phenyl isomer</td>
<td>14.5</td>
<td>14.5</td>
<td>14.5</td>
<td>14.5</td>
<td>14.5</td>
</tr>
<tr>
<td>C_{12-14} alkyl ethoxy 3 sulfate</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>C_{12-14} alkyl 7-ethoxylate</td>
<td>13.0</td>
<td>13.0</td>
<td>13.0</td>
<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Fatty Acid</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
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<tr>
<td>Enzymes (as % raw material net active)</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
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<tr>
<td>Ethoxylated Polyethyleneimine (^3)</td>
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<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Dye of formula 1</td>
<td>0.005</td>
<td>0.006</td>
<td>0.003</td>
<td>0.001</td>
<td>0.1</td>
</tr>
<tr>
<td>Hydroxyethane phosphonic acid</td>
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<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Brightener</td>
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<td>0.3</td>
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</tr>
<tr>
<td>P-diol</td>
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</tr>
</tbody>
</table>
Example 26

Multiple Compartment Unit Dose Compositions

[0265] Multiple compartment unit dose laundry detergent formulations of the present invention are provided below. In these examples the unit dose has three compartments, but similar compositions can be made with two, four or five compartments. The film used to encapsulate the compartments is polyvinyl alcohol.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>21</th>
<th>22</th>
<th>23</th>
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<th>25</th>
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<td>TIPA</td>
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<td></td>
</tr>
<tr>
<td>TEA</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cetene sulfonate</td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>cyclohexyl dimethanol</td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
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<tr>
<td>Structurat</td>
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<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
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<tr>
<td>perfume</td>
<td>1.9</td>
<td>1.9</td>
<td>1.9</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>buffers (monothanolamine)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvents (1,2 propanediol, ethanol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ingredients %</th>
<th>26</th>
<th>27</th>
<th>28</th>
<th>29</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxydrol</td>
<td>5.3</td>
<td>5.0</td>
<td>5.0</td>
<td>4.2</td>
</tr>
<tr>
<td>1,2-propanediol</td>
<td>10.0</td>
<td>15.3</td>
<td>17.5</td>
<td>16.4</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>0.5</td>
<td>0.7</td>
<td>0.6</td>
<td>0.9</td>
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<tr>
<td>Nonionic Surfact C24H47</td>
<td>20.1</td>
<td>14.3</td>
<td>13.0</td>
<td>18.6</td>
</tr>
<tr>
<td>Fluorescent Brightener 1-2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.02</td>
<td>0.3</td>
</tr>
<tr>
<td>Enzymes: Protease, amylase, mannanase, lipase, cellulase</td>
<td>1.5</td>
<td>1.5</td>
<td>3.0</td>
<td>0.4</td>
</tr>
<tr>
<td>and/or petrol yase</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C12-15 Fatty acid</td>
<td>16.4</td>
<td>6.0</td>
<td>11.0</td>
<td>13.0</td>
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<td>Na2CO3</td>
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<td>0.1</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Fluorescent Brightener 1-2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Enzymes: Protease, amylase, mannanase, lipase, cellulase</td>
<td>0.1</td>
<td>0.3</td>
<td>0.01</td>
<td>0.05</td>
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<tr>
<td>Polyethyleneimine ether sulphonate</td>
<td>To 100%</td>
<td>To 100%</td>
<td>To 100%</td>
<td>To 100%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of each compartment</td>
</tr>
<tr>
<td>Active material in Wt. %</td>
</tr>
<tr>
<td>perfume</td>
</tr>
<tr>
<td>Dye of formula 1</td>
</tr>
<tr>
<td>TiO2</td>
</tr>
</tbody>
</table>
-continued

| Sodium Sulfite | 0.4 | 0.4 | 0.4 | 0.3 | 0.3 | 0.3 |
| Acucel S05 | — | — | — | 2 | — | — |
| Rohm&Haas Hydrogenated castor oil | 0.14 | 0.14 | 0.14 | 0.14 | 0.14 | 0.14 |
| Base Composition | Add to | Add to | Add to | Add to | Add to | Add to |
| 26, 27, 28 or 29 | 100% | 100% | 100% | 100% | 100% | 100% |

| Composition |
| --- | --- | --- |
| A | B | C |
| 32 | | |
| 33 | | |

<table>
<thead>
<tr>
<th>Volume of each compartment</th>
<th>40 ml</th>
<th>5 ml</th>
<th>5 ml</th>
<th>40 ml</th>
<th>5 ml</th>
<th>5 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active material in Wt. %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfume</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Dye of formula 1</td>
<td>0</td>
<td>0</td>
<td>&lt;0.05</td>
<td>&lt;0.01</td>
<td>0</td>
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<td>TiO2</td>
<td>0.1</td>
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<td>—</td>
<td>0.1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Sodium Sulfite</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Acucel S05</td>
<td>1.2</td>
<td>—</td>
<td>—</td>
<td>2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Rohm&amp;Haas Hydrogenated castor oil</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>Base Composition</td>
<td>Add to</td>
<td>Add to</td>
<td>Add to</td>
<td>Add to</td>
<td>Add to</td>
<td>Add to</td>
</tr>
<tr>
<td>26, 27, 28, 29</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

### Example 34

**Bleach & Laundry Additive Detergent Formulations [9266]**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES®</td>
<td>11.3</td>
<td>6.0</td>
<td>15.4</td>
<td>16.0</td>
<td>12.0</td>
<td>10.0</td>
</tr>
<tr>
<td>LAS®</td>
<td>25.6</td>
<td>12.0</td>
<td>4.6</td>
<td>—</td>
<td>—</td>
<td>26.1</td>
</tr>
<tr>
<td>MEA-HEAS®</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3.5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>DTPA: Diethylene triamine pentaacetic acid</td>
<td>0.51</td>
<td>—</td>
<td>1.5</td>
<td>—</td>
<td>—</td>
<td>2.6</td>
</tr>
<tr>
<td>4,5-Dihydroxy-1,3-benzenebisulfonic acid</td>
<td>1.82</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.4</td>
</tr>
<tr>
<td>Dodecyl sodium sulfate</td>
<td>1.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>15</td>
</tr>
<tr>
<td>Copolymer of dimethyldinitrilo, 1,2- propylene glycol, methyl capped PEG</td>
<td>2.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Polymethyleneimine ethoxylated, PE600 E20</td>
<td>1.8</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Acrylic acid/maleic acid copolymer</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Acucel 880 (Hydrophobically Modified Non-Ionic Polyol)</td>
<td>2.0</td>
<td>1.8</td>
<td>2.9</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Protease (55 mg/g active)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Amylase (30 mg/g active)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Perfume</td>
<td>0.2</td>
<td>0.03</td>
<td>0.17</td>
<td>—</td>
<td>—</td>
<td>0.15</td>
</tr>
<tr>
<td>Brightener</td>
<td>0.21</td>
<td>0.005</td>
<td>0.006</td>
<td>0.002</td>
<td>0.007</td>
<td>0.008</td>
</tr>
<tr>
<td>Dye of formula 1</td>
<td>0.01</td>
<td>0.005</td>
<td>0.006</td>
<td>0.002</td>
<td>0.007</td>
<td>0.008</td>
</tr>
<tr>
<td>water, other optional agents/components*</td>
<td>100% to 100%</td>
<td>100% to 100%</td>
<td>100% to 100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

*Other optional agents/components include such suppressors, structuring agents such as those based on Hydrogenated Castor Oil (preferably Hydrogenated Castor Oil, Anionic PEO, solvents and/or Mica pearlescent aesthetic enhancers.*
Raw Materials and Notes for Composition Examples

[0267] LAS is linear alkylbenzenesulfonate having an average aliphatic carbon chain length C<sub>12</sub>–C<sub>14</sub> supplied by Stepan, Northfield, Ill., USA or Huntsman Corp. (HLAS is acid form). C<sub>12</sub>–C<sub>14</sub> Dimethylhydroxyethyl ammonium chloride, supplied by Clariant GmbH, Germany AES S is C<sub>12</sub>–C<sub>15</sub> alkyl ethoxy sulfate supplied by Stepan, Northfield, Ill., USA, AES 7 is C<sub>12</sub>–C<sub>15</sub> alcohol ethoxylate, with an average degree of ethoxylation of 7, supplied by Huntsman, Salt Lake City, Utah, USA AES is C<sub>10</sub>–C<sub>18</sub> alkyl ethoxy sulfate supplied by Shell Chemicals, AES 9 is C<sub>12</sub>–C<sub>13</sub> alcohol ethoxylate, with an average degree of ethoxylation of 9, supplied by Huntsman, Salt Lake City, Utah, USA HSAS or HC1617HSAS is a mid-branched primary alkyl sulfate with average carbon chain length of about 16–17 Sodium tripolyphosphate is supplied by Rhodia, Paris, France Zeolite A is supplied by Industrial Zeolite (UK) Ltd, Grays, Essex, UK 1.6R Silicate is supplied by Koma, Nestenica, Czech Republic Sodium Carbonate is supplied by Solvay, Houston, Tex., USA Polycarlylate MW 4500 is supplied by BASF, Ludwigshafen, Germany Carboxymethyl cellulose is Finnfix® V supplied by CP Kelco, Arnhem, Netherlands Suitable chelants are, for example, diethyleneetriamine pentaaetic acid (DTPA) supplied by Dow Chemical, Midland, Mich., USA or Hydroxyethane di phosphonate (HEDP) supplied by Solvita, St. Louis, Mo., USA Bagsvaerd, Denmark Savinase®, Natulase®, Staizyme®, Lipex®, Celluclast™, Mannaway® and Whitezyme® are all products of Novozymes, Bagsvaerd, Denmark. Proteases may be supplied by Genencor International, Palo Alto, Calif., USA, e.g. Purafect Prime® or by Novozymes, Bagsvaerd, Denmark (e.g. Liquanase®, Corosan®). Fluorescent Brightener 1 is Tinopal® AMS, Fluorescent Brightener 2 is Tinopal® CBS-X, Sulphonated zinc phthalocyanine and Direct Violet 9 is Pergalo® Violet BN-Z all supplied by Ciba Specialty Chemicals, Basel, Switzerland Sodium percarbonate supplied by Solvay, Houston, Tex., USA Sodium perborate is supplied by Degussa, Hanau, Germany NOBS is sodium nonanoyloxybenzenesulfonate, supplied by Future Fuels, Batesville, USA TAED is tetraacetylthylenediamine, supplied under the Peracetic® brand name by Clariant GmbH, Sulzbach, Germany S-ACMC is carboxymethylcellulose conjugated with C1. Reactive Blue 19, sold by Megaizyme, Wicklow, Ireland under the product name AZO-CM-CELLULOSE, product code S-ACMC. Soil release agent is Repel-o-Tex® PF, supplied by Rhodia, Paris, France Acrylic Acid/Maleic Acid Copolymer is molecular weight 70,000 and acrylate/maleate ratio 70:30, supplied by BASF, Ludwigshafen, Germany Na salt of Ethylene diamine-N,N'-disuccinic acid, (SS) isomer (EDDS) is supplied by Octel, Ellesmere Port, UK Hydroxyethane di phosphate (HEDP) is supplied by Dow Chemical, Midland, Mich., USA Suds suppressor agglomerate is supplied by Dow Corning, Midland, Mich., USA HSAS is mid-branched alkyl sulfate as disclosed in U.S. Pat. No. 6,020,303 and U.S. Pat. No. 6,060,443 C<sub>12</sub>–C<sub>14</sub> dimethyl Amine Oxide is supplied by Procter & Gamble Chemicals, Cincinnati, USA Random graft copolymer is a polyvinyl acetate grafted polyethylene oxide copolymer having a polyethylene oxide backbone and multiple polyvinyl acetate side chains. The molecular weight of the polyethylene oxide backbone is about 6000 and the weight ratio of the polyethylene oxide to polyvinyl acetate is about 40:60 and no more than 1 grafting point per 50 ethylene oxide units. Ethoxylated polyethyleneimine is polyethylenimine (MW~6000) with 20 ethyox groups per NH.

Cationic cellulose polymer is LK400, LR4000 and/or JR30M from Amerechol Corporation, Edgewater N.J. Note: all enzyme levels are expressed as % enzyme raw material

[0268] The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 mm” is intended to mean “about 40 mm”.

[0269] Every document cited herein, including any cross referenced or related patent or application, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

[0270] While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

What is claimed is:

1. A laundry care composition comprising from 0.00001 wt % to 0.5 wt % carboxylate dye having the structure of Formula I:

   D-L-CO-M

   Formula I

wherein D is a dye moiety selected from benzodifuranones, methines, triphenylmethanes, naphthalimides, pyrazoles, naphthoquinones, anthraquinones and mono- and di-azo dyes and mixtures thereof, L is an organic linking group, and in the sequence of bonds starting from the carbonyl carbon of the C(=O)OM group and ending at the dye moiety, any —(C<sub>3</subɦ(0)—O—) — groups are incorporated such that the oxygen atom O<sub>3</sub> is encountered prior to the carbonyl carbon C<sub>3</sub> and M is any suitable counterion.

2. A laundry care composition according to claim 1 wherein the dye is an anthraquinone or azo dye.

3. A laundry care composition according to claim 1 wherein the dye is an azo dye.
4. A laundry care composition according to claim 1 wherein the compound D-H, preferably has a maximum extinction coefficient greater than about 1000 liter/mol/cm at the \( \lambda_{\text{max}} \), in the wavelength range from 400 nm to 750 nm in methanol solution.

5. A laundry care composition according to claim 1 wherein the compound D-H has a maximum extinction coefficient from about 20,000 to about 100,000 liter/mol/cm at the \( \lambda_{\text{max}} \) in the wavelength range of about 500 nm to about 610 nm.

6. A laundry care composition according to claim 1 wherein group L has a molecular weight from 14 to 1000 Daltons.

7. A laundry care composition according to claim 1 wherein group L consists essentially only of C, H and optionally additionally O and/or N.

8. A laundry care composition according to claim 1 wherein group L is a C_{1-20} alkylenec having optionally therein ether (—O—) and/or ester and/or amide links, the chain being optionally substituted with —OH, —CN, —NO_2, —SO_2CH_3, —Cl, —Br.

9. A laundry care composition according to claim 1 comprising a laundry care adjunct.

10. A laundry care composition according to claim 1 comprising a laundry care adjunct wherein the laundry care adjunct comprises a first wash lipase.

11. A laundry care composition according to claim 1 wherein the laundry care adjunct comprises a fluorescent agent selected from: sodium 2-(4-styryl-3-sulfolyl)-2H-naphth[1,2-d]triadiazole, 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-morpholin-1,3,5-triazin-2-yl)amino]stilbene-2,2’ disulfonate, and disodium 4,4’-bis (2-sulfoethyl) biphenyl in an amount of from 0.005 to 2 wt % of the laundry care composition.

12. A laundry care composition according to claim 1 wherein the laundry care adjunct comprises a dye transfer inhibitor selected from the group consisting of:
   (a) polyvinylpyrrolidone polymers; or
   (b) polyamine N-oxide polymers; or
   (c) copolymers of N-vinylpyrrolidone and N-vinylimidazole; or
   (d) polyvinylloxazolidones; or
   (e) polyvinylimidazoles; or
   (f) mixtures thereof.

13. A laundry care composition according to claim 1 said laundry care composition being a unit dose pouch.

14. A laundry care composition according to claim 1 said laundry care composition being a multi-compartment unit dose product.

15. A laundry care composition according to claim 1 comprising, based on total laundry care composition weight, a total of no more than 15% water and from 10% to 70% of a water-miscible organic solvent having a molecular weight of greater than 70 Daltons.

16. A laundry care composition according to claim 1 comprising, based on total laundry care composition weight, a perfume microcapsule comprising a core and a shell that encapsulates said core, said perfume microcapsule having a D\([4.31]\) average particle of from about 0.01 microns to about 200 microns.

17. A method of treating a textile, the method comprising the steps of: (i) treating the textile with an aqueous solution comprising a laundry care adjunct and from 1 ppb to 500 ppm of a carboxylate dye; and (ii) rinsing and drying the textile, the dye comprising a dye having a structure of Formula I:

\[
D-L-CO_2M \quad \text{Formula I}
\]

wherein D is a dye moiety selected from benzodifuranes, methines, triphenylethanes, naphthalimides, pyrazoles, naphthoquinones, anthraquinones and mono- and di-azo dyes and mixtures thereof; and L is an organic linking group having a molecular weight from 14 to 1000 Daltons, and in the sequence of bonds starting from the carbonyl carbon of the C(O)OM group and ending at the dye moiety, any —(C\(_\text{6-20}\) (O)—O)— groups are incorporated such that the oxygen atom O\(_\text{6-20}\) is encountered prior to the carbonyl carbon C\(_\text{6-20}\); and M is any suitable counterion.

18. A method according to claim 17 wherein the L group is a C\(_\text{1-20}\) alkylenec having optionally therein ether (—O—) and/or ester and/or amide links, the chain being optionally substituted for example with —OH, —CN, —NO_2, —SO_2CH_3, —Cl, —Br.

19. A method according to claim 17 wherein the aqueous solution comprises from 0.05 to 3 g/l of a surfactant.