The present invention provides a polymeric dye suitable for providing shading benefits to laundry textiles. The polymeric dye is a hydroxyalkyl cellulose selected from: hydroxypropyl cellulose; hydroxypropyl methylcellulose; hydroxybutyl cellulose; and, hydroxybutyl methylcellulose, wherein the hydroxyalkyl cellulose is covalently bound to reactive dye.
DYE POLYMER FOR LAUNDRY TREATMENT

FIELD OF INVENTION

The present invention relates to polymeric shading dye and their use in laundry applications

BACKGROUND OF THE INVENTION

WO2006/055787 (Procter & Gamble) discloses Laundry formulations containing a cellulose ether polymer covalently bound to a reactive dye for whitening fabric. Such polymers provide poor performance on polyester fabrics.

SUMMARY OF THE INVENTION

We have found that reactive dyes bound to hydroxypropyl cellulose; hydroxypropyl methylcellulose; hydroxybutyl cellulose; and, hydroxybutyl methylcellulose polymers deposit well to polyester and cotton fabrics.

In one aspect the present invention provides a laundry treatment composition comprising:

(i) from 2 to 70 wt% of a surfactant; and,
(ii) from 0.0001 to 20.0 wt%, preferably 0.1 to 2 wt%, of a blue or violet dye polymer, the blue or violet dye polymer is a hydroxyalkylcellulose selected from: hydroxypropyl cellulose; hydroxypropyl methylcellulose; hydroxybutyl cellulose; and, hydroxybutyl methylcellulose, wherein the hydroxyalkylcellulose is covalently bound to reactive dye.
In another aspect the present invention provides a domestic method of treating a textile, the method comprising the steps of:

(i) treating a textile with an aqueous wash liquor comprising the blue or violet dye polymer as defined in any one of claims 1 to 5, the aqueous solution comprising from 10 ppb to 5000 ppm, preferably 10ppm to 200ppm, of the blue or violet dye polymer; and, from 0.0 g/L to 3 g/L, preferably 0.3 to 3 g/L, of a surfactant; and,

(ii) optionally rinsing and drying the textile.

Preferably, the laundry treatment composition is granular.

DETAILED DESCRIPTION OF THE INVENTION

DYE POLYMER

The dye polymer is provided by reacting a hydroxyalkylcellulose with a reactive dye.

The reactive dye is preferably negatively charged.

The total loading of dyes on the hydroxyalkylcellulose is preferably in the range 0.001 wt % to 50 wt%, more preferably in the range 0.01 wt % to 10 wt %, most preferably in the range 0.1 wt % to 5 wt %.

The dye polymer is preferably blue or violet in colour. In this regard, a blue or violet colour is provided to the cloth to give a hue angle of 230 to 345, more preferably 260
to 330, most preferably 270 to 300. The cloth used is white bleached non-mercerised woven cotton sheeting.

Preferably, the weight average molar mass of the hydroxyalkylcellulose covalently bound to a reactive dye is from 2000 to 4000 000, more preferably from 20000 to 300000.

**REACTIVE DYES**

A reactive dye may be considered to be made up of a chromophore which is linked to a reactive group. Reactive dyes undergo addition or substitution reactions with -OH, -SH and -N¼ groups to form covalent bonds. The chromophore may be linked directly to the reactive group or via a bridging group. The chromophore serves to provide a colour and the reactive group covalently binds to a substrate.

Reactive dyes are described in Industrial Dyes (K. Hunger ed, Wiley VCH 2003). Many Reactive dyes are listed in the Colour Index (Society of Dyers and Colourists and American Association of Textile Chemists and Colorists).

Preferred reactive groups of the reactive dyes are dichlorotriazinyl, difluorochloropyrimidine, monofluorotrazinyl, dichloroquinoxaline, vinylsulf one, difluorotriazine, monochlorotriazinyl, bromoacrylicamide and trichloropyrimidine.

Most preferred reactive groups are monochlorotriazinyl; dichlorotriazinyl; and, vinylsulfonyl.
Chromophores of the reactive dye are preferably selected from azo, anthraquinone, phthalocyanine, formazan and triphenodioaxazine. More preferably the chromophore is selected from, azo, anthraquinone, and triphenodioaxazine, and most preferably, azo and anthraquinone.

Reactive dyes are preferably selected from reactive blue, reactive black, reactive red, reactive violet dyes. Preferably mixtures of reactive dyes are used to provide optimum shading effects. Preferred mixtures are selected from reactive black and reactive red; reactive blue and reactive red; reactive black and reactive violet; reactive blue and reactive violet. Preferably the number of blue or black dye moieties is in excess of the red or violet dye moieties. Most preferably a combination of a reactive blue and a reactive red dyes is used. When a combination of a reactive blue and a reactive red dye is used it is most preferred that the blue or violet dye polymer is covalently bound to a bis-azo reactive blue dye and a mono-azo reactive red dye and the molar ratio of the bis-azo reactive blue dye to the mono-azo reactive red dye bound to the blue or violet dye polymer is from 2:1 to 1:0.

Examples of reactive red dyes are: reactive red 21, reactive red 23, reactive red 180, reactive red 198, reactive red 239, reactive red 65, reactive red 66, reactive red 84, reactive red 116, reactive red 136, reactive red 141, reactive red 198, reactive red 218, reactive red 228, reactive red 238, reactive red 239, reactive red 245, reactive red 264, reactive red 267, reactive red 268, reactive red 269, reactive red 270, reactive red 271,
reactive red 272, reactive red 274, reactive red 275,
reactive red 277, reactive red 278, reactive red 280,
reactive red 281, and reactive red 282. The reactive red dye
is preferably a mono-azo dye.

Examples of reactive black azo dyes are reactive black 5,
reactive black 31, reactive black 47, reactive black 49.

Examples of reactive blue azo dyes are reactive blue 59,
reactive blue 171, reactive blue 238, reactive blue 260,
reactive blue 265, reactive blue 267, reactive blue 270,
reactive blue 271, reactive blue 275. Reactive blue azo dyes
are preferably bis-azo.

Examples of reactive blue triphenodioxazine dyes are
reactive blue 198, reactive blue 266, reactive blue 268,
reactive blue 269

Examples of reactive blue formazan dyes are reactive blue
220 and reactive blue 235.

Examples of preferred reactive blue phthalocyanine dyes are
reactive blue 7, reactive blue 11, reactive blue 14,
reactive blue 15, reactive blue 17, reactive blue 18,
reactive blue 21, reactive blue 23, reactive blue 25,
reactive blue 30, reactive blue 35, reactive blue 38,
reactive blue 41, reactive blue 71, reactive blue 72

Preferably, the reactive blue anthraquinone dye is of the
following form:
Preferably, the reactive group is selected from:
monochlorotriazinyl; dichlorotriazinyl; and, vinylsulfonyl.

Preferred reactive blue dyes are selected from: Reactive Blue 2; Reactive Blue 4; Reactive Blue 5; Reactive Blue 19; Reactive Blue 27; Reactive Blue 29; Reactive Blue 36; Reactive Blue 49; Reactive Blue 50; and, Reactive Blue 224.

Preferably the reactive blue azo dye, is a bis-azo dye of the form.

Where m=0, or 1.

Preferably, the reactive red azo dye is a reactive red mono-azo dye and preferred reactive red mono-azo dye is of the following form:
wherein the A ring may be phenyl or napthyl, n=0, 1 or 2 and the A ring may be further substituted by a reactive group. Preferably, the A ring is napthyl and is substituted by two sulphonate groups. Preferred reactive groups are monochlorotriazinyl; dichlorotriazinyl, vinylsulfonyl;

Preferred reactive red dyes are selected from: Reactive Red 1; Reactive Red 2; Reactive Red 3; Reactive Red 12; Reactive Red 17; Reactive Red 24; Reactive Red 29; Reactive Red 83; Reactive Red 88; Reactive Red 120; Reactive Red 125; Reactive Red 194; Reactive Red 189; Reactive Red 195; Reactive Red 198; Reactive Red 219; Reactive Red 220; Reactive Red 227; Reactive red 238; Reactive red 239; Reactive Red 241; Reactive Red 261; and, Reactive Red 253.

Most preferably the Hydroxypropyl cellulose is covalently linked to a mono-azo reactive red dye and an a bis-azo blue dye.
Hydroxyalkyl cellulose Polymer

The cellulose is selected from hydroxypropyl cellulose, hydroxypropyl methylcellulose, hydroxybutyl cellulose, and hydroxybutyl methylcellulose.

The degree of substitution of the hydroxylalkyl group is preferably greater than 0.1, more preferably greater than 0.2.

The degree of substitution of the methyl group, where present is preferably greater than 0.1, more preferably greater than 0.3.

Hydroxypropyl cellulose is most preferred.

Other Dyes

In a preferred embodiment of the invention, other shading colourants may be present. They are preferably selected from blue and violet pigment such as pigment violet 23, solvent and disperse dyes such as solvent violet 13, disperse violet 28, bis-azo direct dyes such as direct violet 9, 35, 51 and 99, and triphenodioxazine direct dyes such as direct violet 54.

Even more preferred is the presence of acid azine dyes as described in WO 2008/017570; the level of the acid azine dyes should be in the range from 0.0001 to 0.1 wt%.

Preferred acid azine dyes are acid violet 50, acid blue 59
and acid blue 98. Blue and Violet cationic phenazine dyes may also be present.

Photobleaches such as sulphonated Zn/Al phthalocyanins may be present.

**Surfactant**

The laundry composition comprises between 2 to 70 wt percent of a surfactant, most preferably 10 to 30 wt %. In general, the nonionic and anionic surfactants of the surfactant system may be chosen from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch" , H. Stache, 2nd Edn., Carl Hauser Verlag, 1981. Preferably the surfactants used are saturated.

Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are C₆ to C₂₂ alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C₅ to C₁₃ primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO.
Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals.

Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C₆ to C₈ alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C₉ to C₂₀ benzene sulphonates, particularly sodium linear secondary alkyl C₁₀ to C₁₅ benzene sulphonates; and sodium alkyl glycercyl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The preferred anionic detergent compounds are sodium C₁₁ to C₁₅ alkyl benzene sulphonates and sodium C₁₂ to C₁₅ alkyl sulphates. Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides.

Preferred surfactant systems are mixtures of anionic with nonionic detergent active materials, in particular the groups and examples of anionic and nonionic surfactants pointed out in EP-A-346 995 (Unilever). Especially preferred is surfactant system that is a mixture of an alkali metal salt of a C₁₆ to C₈ primary alcohol sulphate together with a C₁₂ to C₁₅ primary alcohol 3 to 7 EO ethoxylate.
The nonionic detergent is preferably present in amounts less than 50wt%, most preferably less than 20wt% of the surfactant system. Anionic surfactants can be present for example in amounts in the range from about 50% to 100 wt% of the surfactant system.

In another aspect which is also preferred the surfactant may be a cationic such that the formulation is a fabric conditioner.

**Cationic Compound**

When the present invention is used as a fabric conditioner it needs to contain a cationic compound.

Most preferred are quaternary ammonium compounds.

It is advantageous if the quaternary ammonium compound is a quaternary ammonium compound having at least one C₁₂ to C₂₂ alkyl chain.

It is preferred if the quaternary ammonium compound has the following formula:

\[ \text{R}^1 \text{N}^+ \text{R}^3 \text{X}^- \]

in which \( \text{R}^1 \) is a C₁₂ to C₂₂ alkyl or alkenyl chain; \( \text{R}^2 \), \( \text{R}^3 \) and \( \text{R}^4 \) are independently selected from C₁ to C₄ alkyl chains and \( \text{X}^- \) is a compatible anion. A preferred compound of this type
is the quaternary ammonium compound cetyl trimethyl
quaternary ammonium bromide.

A second class of materials for use with the present
invention are the quaternary ammonium of the above structure
in which R¹ and R² are independently selected from C₁₂ to C₂₂
alkyl or alkenyl chain; R³ and R⁴ are independently selected
from C₁ to C₄ alkyl chains and X⁻ is a compatible anion.

A detergent composition according to claim 1 in which the
ratio of (ii) cationic material to (iv) anionic surfactant
is at least 2:1.

Other suitable quaternary ammonium compounds are disclosed
in EP 0 239 910 (Proctor and Gamble).

It is preferred if the ratio of cationic to nonionic
surfactant is from 1:100 to 50:50, more preferably 1:50 to
20:50.

The cationic compound may be present from 1.5 wt % to 50 wt
% of the total weight of the composition. Preferably the
cationic compound may be present from 2 wt % to 25 wt %, a
more preferred composition range is from 5 wt % to 20 wt %.

The softening material is preferably present in an amount of
from 2 to 60% by weight of the total composition, more
preferably from 2 to 40%, most preferably from 3 to 30% by
weight.

The composition optionally comprises a silicone.
Builders or Complexing Agents

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate and organic sequestrants, such as ethylene diamine tetra-acetic acid.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0, 384, 070.

The composition may also contain 0-65 % of a builder or complexing agent such as ethylenediaminetetraacetic acid, diethylenetriamine-pentaacetic acid, alkyl- or alkenylsuccinic acid, nitrilotriacetic acid or the other builders mentioned below. Many builders are also bleach-stabilising agents by virtue of their ability to complex metal ions.

Zeolite and carbonate (carbonate (including bicarbonate and sesquicarbonate) are preferred builders.
Preferably the heterocyclic dyes are post-dosed into granular detergent formulation in the form of spray dried granules with a size of less than 200 microns, or in coloured cues with a size of greater than 0.4mm.

The composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate. This is typically present at a level of less than 15% w. Aluminosilicates are materials having the general formula:

\[ 0.8-1.5 \text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 0.8-6 \text{SiO}_2 \]

where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO\(_2\) units in the formula above. They can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. The ratio of surfactants to aluminosilicate (where present) is preferably greater than 5:2, more preferably greater than 3:1.

Alternatively, or additionally to the aluminosilicate builders, phosphate builders may be used. In this art the term phosphate' embraces diphosphate, triphosphate, and phosphonate species. Other forms of builder include silicates, such as soluble silicates, metasilicates, layered silicates (e.g. SKS-6 from Hoechst).
Preferably the laundry detergent formulation is a non-phosphate built laundry detergent formulation, i.e., contains less than 1 wt% of phosphate. Preferably the laundry detergent formulation is carbonate built.

**Fluorescent Agent**

The composition preferably comprises a fluorescent agent (optical brightener). Fluorescent agents are well known and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in the composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.1 wt %. Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN. Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol [1,2-d] triazole, disodium 4,4'-bis{[(4-anilino-6-α methyl-N=2 hydroxyethyl ) amino 1,3,5-triazin-2-yl ]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1, 3,5-triazin-2-yl) ]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfostyryl) biphenyl.

It is preferred that the wash solution used in the method has a fluorescer present. When a fluorescer is present in the wash solution used in the method it is preferably in the
range from 0.0001 g/l to 0.1 g/l, preferably 0.001 to 0.02 g/l.

Perfume

Preferably the composition comprises a perfume. The perfume is preferably in the range from 0.001 to 3 wt %, most preferably 0.1 to 1 wt %. Many suitable examples of perfumes are provided in the CTFA (Cosmetic, Toiletry and Fragrance Association) 1992 International Buyers Guide, published by CFTA Publications and OPD 1993 Chemicals Buyers Directory 80th Annual Edition, published by Schnell Publishing Co.

It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention it is envisaged that there will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume components.

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 [1955]). Preferred top-notes are selected from citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol.

Perfume and top note may be used to cue the whiteness benefit of the invention.
It is preferred that the laundry treatment composition does not contain a peroxygen bleach, e.g., sodium percarbonate, sodium perborate, and peracid.

**Polymers**

The composition may comprise one or more further polymers. Examples are carboxymethylcellulose, poly (ethylene glycol), poly (vinyl alcohol), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

Polymers present to prevent dye deposition, for example poly (vinylpyrrolidone), poly (vinylpyridine-N-oxide), and poly (vinylimidazole), are preferably absent from the formulation.

**Enzymes**

One or more enzymes are preferred present in a composition of the invention and when practicing a method of the invention.

Preferably the level of each enzyme is from 0.0001 wt% to 0.1 wt% protein.

Especially contemplated enzymes include proteases, alpha-amylases, cellulases, lipases, peroxidases/oxidases, pectate lyases, and mannanases, or mixtures thereof.
Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g. from *H. lanuginosa* (*T. lanuginosus*) as described in EP 258 068 and EP 305 216 or from *H. insolens* as described in WO 96/13580, a *Pseudomonas* lipase, e.g. from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 218 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens*, *Pseudomonas sp.* strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* (WO 96/12012), a *Bacillus* lipase, e.g. from *B. subtilis* (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422).


Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, Lipex™ (Novozymes A/S).

The method of the invention may be carried out in the presence of phospholipase classified as EC 3.1.1.4 and/or EC 3.1.1.32. As used herein, the term phospholipase is an enzyme which has activity towards phospholipids.

Phospholipids, such as lecithin or phosphatidylcholine, consist of glycerol esterified with two fatty acids in an
outer (sn-1) and the middle (sn-2) positions and esterified with phosphoric acid in the third position; the phosphoric acid, in turn, may be esterified to an amino-alcohol. Phospholipases are enzymes which participate in the hydrolysis of phospholipids. Several types of phospholipase activity can be distinguished, including phospholipases A1 and A2 which hydrolyze one fatty acyl group (in the sn-1 and sn-2 position, respectively) to form lysophospholipid; and lysophospholipase (or phospholipase B) which can hydrolyze the remaining fatty acyl group in lysophospholipid. Phospholipase C and phospholipase D (phosphodiesterases) release diacyl glycerol or phosphatidic acid respectively.

The enzyme and the shading dye may show some interaction and should be chosen such that this interaction is not negative. Some negative interactions may be avoided by encapsulation of one or other of enzyme or shading dye and/or other segregation within the product.

Suitable proteases include those of animal, vegetable or microbial origin. Microbial origin is preferred. Chemically modified or protein engineered mutants are included. The protease may be a serine protease or a metallo protease, preferably an alkaline microbial protease or a trypsin-like protease. Preferred commercially available protease enzymes include Alcalase™, Savinase™, Primase™, Duralase™, Dyrazym™, Esperase™, Everlase™, Polarzyme™, and Kannase™, (Novozymes A/S), Maxatase™, Maxacal™, Maxapem™, Properase™, Purafect™, Purafect OxP™, FN2™, and F3™ (Genencor International Inc.).
The method of the invention may be carried out in the presence of cutinase, classified in EC 3.1.1.74. The cutinase used according to the invention may be of any origin. Preferably cutinases are of microbial origin, in particular of bacterial, of fungal or of yeast origin.

Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from Bacillus, e.g. a special strain of B. licheniformis, described in more detail in GB 1,296,839, or the Bacillus sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.)

Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera Bacillus, Pseudomonas, Humicola, Fusarium, Thielavia, Acremonium, e.g. the fungal cellulases produced from Humicola insolens, Thielavia terrestris, Myceliophthora thermophila, and Fusarium oxysporum disclosed in US 4,435,307, US 5,648,263, US 5,691,178, US 5,776,757, WO 89/09259, WO 96/029397, and WO 98/012307. Commercially available cellulases include Celluzyme™, Carezyme™, Endolase™, Renozyme™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao Corporation).
Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful peroxidases include peroxidases from Coprinus, e.g. from C. cinereus, and variants thereof as those described in WO 93/24618, WO 95/10602, and WO 98/15257. Commercially available peroxidases include Guardzyme™ and Novozym™ 51004 (Novozymes A/S).


**Enzyme Stabilizers**

Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

Where alkyl groups are sufficiently long to form branched or cyclic chains, the alkyl groups encompass branched, cyclic and linear alkyl chains. The alkyl groups are preferably linear or branched, most preferably linear.
The indefinite article "a" or "an" and its corresponding
definite article "the" as used herein means at least one, or
one or more, unless specified otherwise.

5 Experimental

Example 1: Synthesis

1.0g cellulose (HPC or HEC) was dissolved in 300ml DI water
under magnetic stirring at room temperature; 70mg RB4/30mg
RR2 and 1.0g Na2C03 were added to the stirring aqueous
solution. The reaction was maintained at room temperature
for 48 hours. After the reaction was finished, the solution
was dialyzed with dialysis tube (MWCo = 7000) against flow
water for a week to remove the small molecule dye residues.
The final violet product was obtained by lyophilization of
the dialyzed solution.

Material:

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mw information</th>
<th>Provider</th>
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<tbody>
<tr>
<td>hydroxypropyl cellulose (HPC)</td>
<td>6-10cps (2% in water, 20 oC)</td>
<td>TCI</td>
</tr>
<tr>
<td>hydroxyethyl cellulose (HEC)</td>
<td>75-125mpa.s (2% in water, 20 oC)</td>
<td>Fluka</td>
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</table>

Example 2: Deposition

A laundry detergent formulation was created containing 33%
Linear alkyl benzene Sulfonate, 33% Na2SC6H4, 33% Na2CC6H3
And 1 wt% polymer. Three formulations were created with HPC
and HEC of example 1 as the polymer and also with the
polymer omitted as a control. The formulations was used at 3g/L to wash white polyester, white cotton and white nylon elastane at a L:C 30:1 in demineralised water for 30 minutes. The cloths were then removed, dried, and the reflectance spectrum measured using a reflectometer. The colour of the cloth was expressed as the CIE L*a*b* values. The extent of shading of the cloth was calculated as the Δb value such that

\[ \Delta b = b(\text{dye-polymer}) - b(\text{control}) \]

The results are shown in the table below

<table>
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<tr>
<th></th>
<th>cotton</th>
<th>polyester</th>
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<tr>
<td>HEC (comparative)</td>
<td>3.1</td>
<td>0.1</td>
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<tr>
<td>HPC</td>
<td>1.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The HPC dye-polymer has a greater deposition to polyester than the HEC, whilst also depositing on cotton.
We Claim:

1. A laundry treatment composition comprising:
   (i) from 2 to 70 wt% of a surfactant; and,
   (ii) from 0.0001 to 20.0 wt%, of a blue or violet dye polymer, the blue or violet dye polymer is a hydroxyalkylcellulose selected from: hydroxypropyl cellulose; hydroxypropyl methylcellulose; hydroxybutyl cellulose; and, hydroxybutyl methylcellulose, wherein the hydroxyalkylcellulose is covalently bound to reactive dye.

2. A laundry treatment composition according to claim 1, wherein the reactive dye is covalently bound to the hydroxyalkylcellulose group via a group selected from: dichlorotriazinyl; difluorochloropyrimidine; monofluorotrazinyl; dichloroquinaxaline; vinylsulfone; difluorotriazine; monochlorotriazinyl; bromoacrylamide; and, trichloropyrimidine.

3. A laundry treatment composition according to claim 1 or 2, wherein the chromophore of the reactive dye is selected from: azo; anthraquinone; phthalocyanine formazan; and, triphenodioxazine.

4. A laundry treatment composition according to claim 1 or 3, wherein the chromophore of the reactive dye is selected from: azo; anthraquinone; and, triphenodioxazine.

5. A laundry treatment composition according to any one of the preceding claims, wherein the blue or violet dye polymer is covalently bound to a bis-azo reactive blue dye and a
mono-azo reactive red dye and the molar ratio of the bis-azo reactive blue dye to the mono-azo reactive red dye bound to the blue or violet dye polymer is from 2:1 to 1:0.

6. A domestic method of treating a textile, the method comprising the steps of:
   (i) treating a textile with an aqueous wash liquor comprising the blue or violet dye polymer as defined in any one of claims 1 to 5, the aqueous solution comprising from 10 ppb to 5000 ppm, of the blue or violet dye polymer; and, from 0.0 g/L to 3 g/L of a surfactant; and,
   (ii) optionally rinsing and drying the textile.

7. A domestic method of treating a textile, according to claim 6, wherein the surfactant is present in the aqueous wash liquor in a concentration from 0.3 g/L to 3 g/L of the surfactant.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C11D3/40 C09B67/O0 C09B69/10

**B. FIELD SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C11D C09B

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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**Date of the actual completion of the international search**

27 April 2012

**Date of mailing of the international search report**

07/05/2012

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