Abstract:
The present invention provides for the use of natural shading agents.
NATURAL SHADING AGENTS

FIELD OF INVENTION

The present invention concerns laundry shading dye compositions.

BACKGROUND OF THE INVENTION

In domestic washing, maintenance and enhancing of fabric whiteness may be achieved using synthetic organic fluorescers and synthetic organic shading dyes.


WO2001/28973 (Procter & Gamble) discloses a specific azulene compounds covalently linked to a phenolic antioxidant for use in cleaning composition to scavenge radicals.

The blue color of the mushroom *Lactarius indigo* is due to the azulene derivative (7-isopropenyl-4-methylazulen-1-yl)methyl stearate.

Azulenes are the general names for the blue to violet aromatic hydrocarbons derived from bicyclo[5.3.0]decapentaene. Azulenes occur in various liverworts, for example *Calypogeia azurea* contains 1,4-dimethylazulene and methyl-4-methylazulene-1-carboxylate.
Azulenes are discussed in Rompp Encyclopedia of Natural Products (Georg Thieme Verlag 2000).

There is a consumer desire for products which contain natural ingredients for maintaining and enhancing fabric whiteness.

SUMMARY OF INVENTION

We have found that naturally occurring blue-violet azulene compounds may be included in laundry detergents and deposit to fabrics enhancing the whiteness of fabric.

In one 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 solution of the naturally occurring blue or violet azulene dye, the aqueous solution comprising from 1 ppb to 1 ppm of the naturally occurring blue or violet azulene dye; and, from 0.2 g/L to 3 g/L of a surfactant; (ii) optionally rinsing the textile; and, (iii) drying the textile.

In another aspect the present invention provides a laundry detergent formulation comprising:

(i) from 0.0001 to 0.01 wt% of a naturally occurring blue or violet azulene dye;
(ii) an enzyme from 0.0001 wt% to 0.1 wt% protein; and,
(iii) from 2 to 70 wt% of a surfactant.

The azulenes used in the present invention are naturally occurring but the synthesised equivalent may be used.
DETAILED DESCRIPTION OF THE INVENTION

Naturally occurring azulenes include 1,4-dimethylazulene, methyl-4-methylazulene-1-carboxylate, linderazulene, and 5 ehuazulene, chamazulene and Guaiazulene. By naturally occurring is meant that the azulenes are found naturally in naturally occurring life, for example plants, animals, fungi, mushrooms, and marine life.

Natural azulenes are secondary metabolites of living organisms.

The azulene is preferable Guaiazulene (1,4-dimethyl-7-isopropylazulene).

The 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

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 C_6 to C_22 alkyl phenyl-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 C_8 to C_18 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 C_9 to C_22 alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C_9 to C_20 benzene sulphonates, particularly sodium linear secondary alkyl C_10 to C_15 benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The
preferred anionic detergent compounds are sodium C_{11} to C_{15} alkyl benzene sulphonates and sodium C_{12} to C_{18} 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 C_{15} to C_{18} primary alcohol sulphate together with a C_{12} to C_{18} primary alcohol 3 to 7 EO ethoxylate.

The nonionic detergent is preferably present in amounts greater than 10%, e.g. 25 to 90 wt % of the surfactant system. Anionic surfactants can be present for example in amounts in the range from about 5% to about 40 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 C\textsubscript{12} to C\textsubscript{22} alkyl chain.

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

\[ R_2 \]
\[ R_1 - N^+ - R_3 X^- \]
\[ R_4 \]

in which R\textsubscript{1} is a C\textsubscript{12} to C\textsubscript{22} alkyl or alkenyl chain; R\textsubscript{2}, R\textsubscript{3} and R\textsubscript{4} are independently selected from C\textsubscript{i} to C\textsubscript{4} alkyl chains and X\textsuperscript{-} 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 R\textsubscript{1} and R\textsubscript{2} are independently selected from C\textsubscript{12} to C\textsubscript{22} alkyl or alkenyl chain; R\textsubscript{3} and R\textsubscript{4} are independently selected from C\textsubscript{i} to C\textsubscript{4} alkyl chains and X\textsuperscript{-} 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
esquicarbonate) are preferred builders.

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%. 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\textsubscript{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 alumino-silicate (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 fluorescers 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-sulfo-phenyl)-2H-napthol [1,2-d] triazole, disodium 4,4'-bis{[(4-anilino-6-N-methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfo-styryl)biphenyl.

It is preferred that the aqueous solution used in the method has a fluorescer present. When a fluorescer is present in the aqueous 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 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 FN3™ (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.

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.
Experimental

Knitted white polyester (microfiber), knitted nylon-elastane (80:20) and white woven non-mercerised cotton fabrics were used together in 4g/L of a detergent which contained 15% Linear Alkyl benzene sulfonate (LAS) surfactant, 30% Na$_2$CO$_3$, 40% NaCl, remainder minors included calcite and fluorescer and moisture. Washes were conducted in demineralised water at room temperature with a liquor to cloth ratio of 30:1, for 30 minutes. This was then repeated three more times to accomplish 4 washes in total. Following the washes the cloths were rinsed twice in water, dried, the reflectance spectrum of the nylon-elastane was measured on a reflectometer and the colour expressed as CIE L$^*$ a$^*$ b$^*$ values (UV-excluded).

The experiment was repeated with the addition of 200ppb Guaiazulene to the wash solution. The Guaiazulene was added from a solution in ethanol. The deposition of Guaiazulene to the fabrics was expressed as the $A_b$ value such that $A_b = b$ (control) - $b$ (Guaiazulene) +ve values indicate a blueing/whitening of the fabric, due to Guaiazulene deposition.
The results are given in the table below:

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Claims:

1. A domestic method of treating a textile, the method comprising the steps of: (i) treating a textile with an aqueous solution of the naturally occurring blue or violet azulene dye, the aqueous solution comprising from 1 ppb to 1 ppm of the naturally occurring blue or violet azulene dye; and, from 0.2 g/L to 3 g/L of a surfactant; (ii) optionally rinsing the textile; and, (iii) drying the textile.

2. A domestic method of treating a textile according to claim 1, wherein the azulene dye is selected from: 1,4-dimethyl azulene; methyl-4-methylazulene-1-carboxylate; linderazulene; ehuazulene; chamazulene; and, guaiazulene.

3. A domestic method of treating a textile according to claim 1, wherein the azulene dye is 1,4-dimethyl-7-isopropylazulene:

![Chemical Structure](image-url)
4. A domestic method of treating a textile according to any one of the preceding claims, wherein the aqueous solution comprises 0.1 to 50 ppm of fluorescer.

5. A laundry detergent formulation comprising:
   (i) from 0.0001 to 0.01 wt% of a naturally occurring blue or violet azulene dye;
   (ii) an enzyme from 0.0001 wt% to 0.1 wt% protein; and,
   (iii) from 2 to 70 wt% of a surfactant.

6. A laundry detergent formulation according to claim 5, wherein the azulene dye is selected from: 1,4-dimethyl azulene; methyl-4-methylazulene-1-carboxylate; linderazulene; ehuazulene; chamazulene; and, guaiazulene.

7. A laundry detergent formulation according to claim 5, wherein the azulene dye is 1,4-dimethyl-7-isopropylazulene:
8. A laundry detergent composition according to any one of claims 5 to 7, wherein the laundry detergent formulation comprises a fluorescer selected from the group consisting of: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol [1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-\(N\) methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate, and disodium 4,4'-bis (2-sulfostyryl) biphenyl.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C11D3/40

**ADD.**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"R" document member of the same patent family

**Date of the actual completion of the international search**

4 February 2011

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

11/02/2011

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Form PCT/ISA/210 (second sheet) (April 2005)
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