



(19)

Europäisches  
Patentamt  
European  
Patent Office  
Office européen  
des brevets



(11)

EP 2 931 862 B1

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention  
of the grant of the patent:  
**29.04.2020 Bulletin 2020/18**

(51) Int Cl.:  
**C11D 3/20 (2006.01)** **C11D 3/40 (2006.01)**  
**C11D 17/04 (2006.01)**

(21) Application number: **13802950.9**

(86) International application number:  
**PCT/EP2013/075965**

(22) Date of filing: **09.12.2013**

(87) International publication number:  
**WO 2014/095459 (26.06.2014 Gazette 2014/26)**

**(54) METHOD TO PREVENT DISCOLORATION OF COLORED LIQUIDS**

VERFAHREN ZUR VERHINDERUNG DER VERFÄRBUNG VON GEFÄRBTEN FLÜSSIGKEITEN  
PROCÉDÉ POUR EMPÊCHER LA DÉCOLORATION DE LIQUIDES COLORÉS

(84) Designated Contracting States:  
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB  
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO  
PL PT RO RS SE SI SK SM TR**

(30) Priority: **17.12.2012 EP 12197548**

(43) Date of publication of application:  
**21.10.2015 Bulletin 2015/43**

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**WO-A1-00/36074 WO-A1-01/36542**  
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**Description**

[0001] The present application relates to a way for protecting dye-containing liquid compositions, such as textile or hard surface treatment compositions, from discoloration.

5 [0002] Liquid detergents have traditionally been sold in opaque bottles. However, use of clear (for the present purpose used synonymously with the terms transparent and translucent) bottles can be aesthetically appealing to consumers as they can see the color of the product, its consistency, and suspended particles if they are present.

10 [0003] However, the use of clear bottles can lead to destruction of colorant by UV light. By UV light is meant light having wavelength of about 250 to about 460 nanometers (nm). Specifically, UVA generally is in range 320-400 nm, UVB about 290 to 320 nm and UVC below 290 nm, down to about 250 nm.

[0004] It has been known in the art that UV absorbers or UV blockers can be added to the bottle material during manufacture of clear bottles to protect them from becoming brittle and to protect the ingredients inside the bottle. Another approach is the addition of UV absorbers or UV blockers to the formulation.

15 [0005] WO 2000/36074 A1 discloses a translucent or transparent aqueous heavy duty liquid in a clear bottle comprising colorant dye and fluorescent dye and/or UV absorber to protect said colorant dye.

[0006] Since all solutions add to the production costs of the product, there is a need for improving the color stability of liquid compositions, especially liquid detergent compositions, in a cost effective way.

[0007] Accordingly, it is an object of the present invention to provide a cheap way for stabilizing dye-containing liquid compositions, especially dye-containing liquid textile or hard surface treatment compositions.

20 [0008] This object is achieved by a method of reducing destruction of blue colorant dye in a liquid textile or hard surface treatment composition in a bottle that is permeable for UV light by adding ethanol to said composition, in an amount of at least 0.01 % by wt. of the liquid composition.

[0009] It has now surprisingly been found that the addition of ethanol effectively protects a colored liquid composition against destruction of the blue colorant dye. Since ethanol is a cheap chemical that is often and widely used, the color stability of dyed liquid compositions can be improved in a simple and cost effective way.

[0010] The liquid composition is a liquid textile or hard surface treatment composition. Liquid textile or hard surface treatment compositions are often intensively dyed and, in addition, are packaged in clear bottles.

[0011] The ethanol is added in amount of at least 0.01 % by wt. of the liquid composition. It has surprisingly been shown that already very little amounts of ethanol are sufficient to effectively reduce the destruction of a colorant dye in a liquid composition.

30 [0012] In another preferred embodiment the liquid composition comprises an anionic surfactant.

[0013] Anionic surfactants are important ingredients of many liquid compositions, especially of liquid textile or hard surface treatment compositions. It has been shown that anionic surfactants sometimes promote the destruction of colorant dyes. By adding ethanol to a colored liquid composition the colorant dye is stabilized against the UV light destruction even in the presence of anionic surfactants.

[0014] The colorant dye is a blue dye. It is even more preferred that the colorant dye is selected from the group consisting of Acid Blue 145, Acid Blue 9, Acid Blue 80, blue anthraquinone dyes, blue xanthene dyes and mixtures thereof. Ethanol is very effective in reducing the destruction of blue dyes being present in a liquid composition.

40 [0015] In a preferred embodiment the liquid composition is a transparent or translucent liquid composition since stabilization against discoloration/color change is especially necessary in this case.

[0016] The invention is described in greater detail below on the basis of examples, among other things.

[0017] The invention relates to method of reducing destruction of colorant dye in a liquid textile or hard surface treatment composition in a bottle that is permeable for UV light by adding ethanol to said composition.

45 [0018] Surprisingly, relatively small amounts of ethanol are sufficient to protect the colored liquid composition against destruction of the colorant dye. Accordingly, ethanol is added in amount of at least 0.01 % by wt. of the composition. In a preferred embodiment the ethanol is added in amount of at least 0.05 % by wt. of the composition and in an even more preferred embodiment ethanol is added in amount of at least 0.1 % by wt. of the composition. In general, there is no upper limit for the amount of ethanol added to the liquid composition. But it may be preferred that the ethanol is added in amount of up to 5 % by wt. of the composition, more preferably up to 1 % by wt. of the liquid composition and most preferred up to 0.5 % by wt. of the composition.

50 [0019] The invention is applicable to any type of blue colorant dye which may be destroyed by UV light. Non limiting examples of such include, but are not limited to the following: Acid Blue 145, Acid Blue 9, Acid Blue 80, anthraquinone dyes, and blue xanthene dyes. The colorant dyes may be present in an amount of from 0.0001% to 1% by wt. of the liquid composition and preferably in an amount of from 0.001 to 0.4% by wt. of the composition. The colorant dye is a blue colorant dye since these dyes showed to be most affected by UV light.

[0020] Preferably, the liquid composition is an aqueous liquid composition and contains water as main solvent. In a preferred embodiment the liquid composition is an aqueous liquid textile or hard surface treatment composition.

[0021] In addition to the ethanol and the blue colorant dye, a liquid composition may contain further ingredients that

further improve the applications-engineering or aesthetic properties of the liquid composition.

[0022] In the context of the present invention, a liquid textile or hard surface treatment composition by preference additionally contains one or more substances from the group of surfactants, builder, enzymes, non-aqueous solvents, perfume, thickeners, pH adjusting agents, fluorescing agents, hydrotopes, silicone oils, anti-redeposition agents, anti-gray agents, shrinkage preventers, wrinkle protection agents, dye transfer inhibitors, corrosion inhibitors, antistatic agents, bittering agents, ironing adjuvants, electrolytes, proofing and impregnation agents, swelling and anti-slip agents, softening compounds, biocidal compounds and UV absorbers.

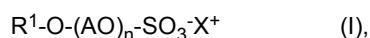
[0023] From the above mentioned further ingredients surfactants, enzymes, non-aqueous solvents, perfume, pH adjusting agents, fluorescing agents, silicone oils, soil-release polymers, anti-gray agents, dye transfer inhibitors, electrolytes and bittering agents are most preferred included into a liquid textile or hard surface treatment composition.

[0024] The compositions of the method of the invention may contain one or more surfactants selected from the group consisting of anionic, nonionic, cationic, ampholytic and zwitterionic surfactants and mixtures thereof. The preferred surfactants for use in the liquid textile or hard surface treatment composition are mixtures of anionic surfactants, mixtures of anionic surfactants and nonionic surfactants or mixtures of anionic and ampholytic surfactants although it is to be understood that any surfactant may be used alone or in combination with any other surfactant or surfactants. The surfactant should comprise at least 2.5 % by wt. of the composition.

[0025] It is preferred that the liquid textile or hard surface treatment composition comprises an anionic surfactant.

[0026] Anionic surfactants are important ingredients of liquid textile or hard surface treatment compositions because of their cleansing and emulsifying properties. Anionic surfactants are particularly good at keeping the dirt away from textile and hard surfaces, and removing oily soil residues from textile and hard surfaces.

[0027] For example, liquid textile or hard surface treatment compositions may contain a surfactant of the following general formula I:



wherein

R<sup>1</sup> is linear or branched, saturated or unsaturated, substituted or un-substituted hydrocarbon wherein the total number of carbon atoms is from 1 to 24;

AO is an ethylene oxide- (EO) or propylene oxide- (PO) group;

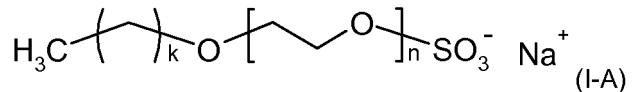
n is an integer from 1 to 50;

X is a monovalent metal cation, the n-th part of an n-valent metal cation, an ammonium cation or a substituted ammonium cation.

[0028] In formula (I) R<sup>1</sup> is a linear or branched, substituted or unsubstituted alkyl-, aryl- or alkylaryl group, preferably a linear, unsubstituted alkyl group, more preferably a fatty alcohol residue. Preferred residues R<sup>1</sup> are chosen from decyl-, undecyl-, dodecyl-, tridecyl-, tetradecyl, pentadecyl-, hexadecyl-, heptadecyl-, octadecyl-, nonadecyl-, eicosyl residues and their mixtures, wherein the residues with an even number of carbon atoms are preferred. Particularly preferred residues R<sup>1</sup> are derived from C<sub>12</sub>-C<sub>18</sub>-fatty alcohols, for example from coconut fatty alcohol, tallow fatty alcohol, lauryl-, myristyl-, cetyl- or stearyl alcohol or from C<sub>10</sub>-C<sub>20</sub>-oxo alcohols.

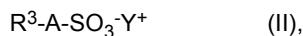
[0029] AO is an ethylene oxide (EO) or propylene oxide (PO) group, preferably an ethylene oxide group. The index n is an integral number from 1 to 50, preferably from 1 to 20 and most preferably from 2 to 10. Particularly preferred, n is 2, 3, 4, 5, 6, 7 or 8. X is a monovalent cation or the n-th part of an n-valent cation, preferred cations are alkali metal ions, especially Na<sup>+</sup> or K<sup>+</sup>, wherein Na<sup>+</sup> is particularly preferred. Further cations X<sup>+</sup> can be chosen from NH<sub>4</sub><sup>+</sup>, 1/2 Zn<sup>2+</sup>, 1/2 Mg<sup>2+</sup>, 1/2 Ca<sup>2+</sup>, 1/2 Mn<sup>2+</sup>, and their mixtures.

[0030] Particularly preferred surfactants of formula (I) are chosen from fatty alcohol ether sulphates of formula I-A



with k = 11 to 19, n = 2, 3, 4, 5, 6, 7 or 8. Most preferred representatives of this formula are Na-C<sub>12-14</sub> fatty alcohol ether sulphates with 2 EO (k = 11-13, n = 3 in formula I-A).

[0031] Other suitable anionic surfactants can be preferably chosen from fatty alcohol sulphates and/or alkyl benzene sulfonates. Accordingly, liquid textile or hard surface treatment compositions may contain a surfactant of the following general formula II:



wherein

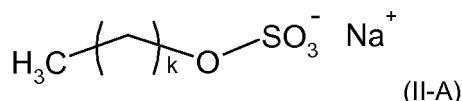
5 R<sup>3</sup> is linear or branched, saturated or unsaturated, substituted or un-substituted hydrocarbon wherein the total number of carbon atoms is from 1 to 24;  
 A is -O- or a chemical bond;  
 Y is a monovalent metal cation, the n-th part of an n-valent metal cation, an ammonium cation or a substituted ammonium cation.

**[0032]** In formula (II) R<sup>3</sup> is a linear or branched, substituted or unsubstituted alkyl-, aryl- or alkylaryl group, preferably a linear, unsubstituted alkyl group, more preferably a fatty alcohol residue. Preferred residues R<sup>1</sup> are chosen from decyl-, undecyl-, dodecyl-, tridecyl-, tetradecyl, pentadecyl-, hexadecyl-, heptadecyl-, octadecyl-, nonadecyl-, eicosyl residues and their mixtures, wherein the residues with an even number of carbon atoms are preferred. Particularly preferred residues R<sup>1</sup> are derived from C<sub>12</sub>-C<sub>18</sub>-fatty alcohols, for example from coconut fatty alcohol, tallow fatty alcohol, lauryl-, myristyl-, cetyl- or stearyl alcohol or from C<sub>10</sub>-C<sub>20</sub>-oxo alcohols.

**[0033]** A is -O- or a chemical bond. X is a monovalent cation or the n-th part of an n-valent cation, preferred cations are alkali metal ions, especially  $\text{Na}^+$  or  $\text{K}^+$ , wherein  $\text{Na}^+$  is particularly preferred. Further cations  $\text{X}^+$  can be chosen from  $\text{NH}_4^+$ ,  $\frac{1}{2}\text{Zn}^{2+}$ ,  $\frac{1}{2}\text{Mg}^{2+}$ ,  $\frac{1}{2}\text{Ca}^{2+}$ ,  $\frac{1}{2}\text{Mn}^{2+}$ , and their mixtures.

20 [0034] Depending on whether A is a bridging oxygen or a chemical bond, formula (II) describes sulphate surfactants or sulfonate surfactants.

**[0035]** Particularly preferred surfactants of formula (II) are chosen from fatty alcohol sulphates of formula (II-A)

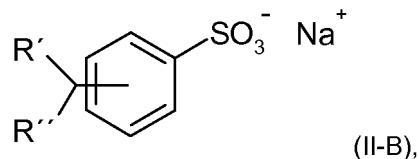


30 with  $k = 11$  to  $19$ . Most preferred representatives of this formula are Na-C<sub>12-14</sub> fatty alcohol sulphates ( $k = 11-13$  in formula II-A).

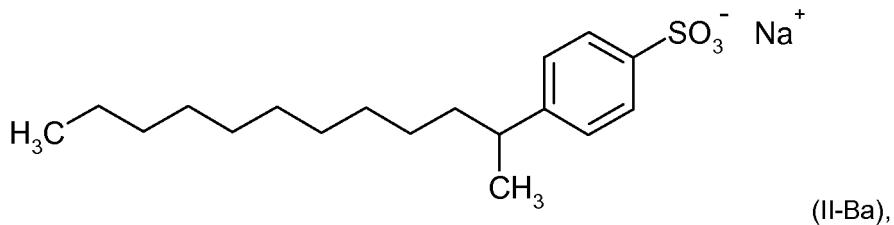
**[0036]** Even more preferred surfactants of formula (II) are sulfonate surfactants (A = chemical bond). Here, R<sup>3</sup> preferably is a linear or branched unsubstituted alkylaryl residue.

[0037] X is a monovalent cation or the n-th part of an n-valent cation, preferred cations are alkali metal ions, especially  $\text{Na}^+$  or  $\text{K}^+$ , wherein  $\text{Na}^+$  is particularly preferred. Further cations  $\text{X}^+$  can be chosen from  $\text{NH}_4^+$ ,  $\frac{1}{2}\text{Zn}^{2+}$ ,  $\frac{1}{2}\text{Mg}^{2+}$ ,  $\frac{1}{2}\text{Ca}^{2+}$ ,  $\frac{1}{2}\text{Mn}^{2+}$ , and their mixtures.

[0038] Such most preferred surfactants are chosen from linear or branched alkyl benzene sulfonates of formula C-2



45 in which R' and R" together have 9 to 19, preferably 11 to 15 and most preferably 11 to 13 C-atoms. A particularly preferred representative of this formula can be described by formula II-Ba:



**[0039]** It is preferred that the anionic surfactant is present at a level of from 1 % up to 20 % by weight of said composition and, preferably, at a level of from 2 % up to 15 % by weight of said composition.

**[0040]** The liquid textile or hard surface treatment composition may also contain a non-ionic surfactant as additional ingredient at a level up to 5 % by weight of the liquid textile or hard surface treatment composition.

**[0041]** The nonionic surfactant that can be used are by preference alkoxylated, advantageously ethoxylated, in particular primary alcohols having by preference 8 to 18 carbon atoms and an average of 1 to 12 mol ethylene oxide (EO) per mol of alcohol, in which the alcohol residue can be linear or preferably methyl-branched in the 2-position, or can contain mixed linear and methyl-branched residues, such as those that are usually present in oxo alcohol residues. Particularly preferred, however, are alcohol ethoxylates having linear residues made up of alcohols of natural origin having 12 to 18 carbon atoms, e.g. from coconut, palm, tallow, or oleyl alcohol, and an average of 2 to 8 EO per mol of alcohol. The preferred ethoxylated alcohols include, for example, C<sub>12-14</sub> alcohols with 3 EO, 4 EO, 5 EO, or 7 EO, C<sub>9-11</sub> alcohols with 7 EO, C<sub>13-15</sub> alcohols with 3 EO, 5 EO, 7 EO, or 8 EO, C<sub>12-18</sub> alcohols with 3 EO, 5 EO, or 7 EO, and mixtures thereof, such as mixtures of C<sub>12-14</sub> alcohol with 3 EO and C<sub>12-18</sub> alcohol with 7 EO. The degrees of ethoxylation indicated represent statistical averages, which can correspond to an integral or a fractional number for a specific product. Preferred alcohol ethoxylates exhibit a restricted distribution of homologs (narrow range ethoxylates, NRE). In addition to these non-ionic active detergent species, fatty alcohols with more than 12 EO can also be used. Examples of these are tallow fatty alcohol with 14 EO, 25 EO, 30 EO, or 40 EO. Nonionic active detergent species that contain EO and PO groups together in the molecule are also usable according to the present invention. Block copolymers having EO-PO block units or PO-EO block units, but also EO-PO-EO copolymers or PO-EO-PO copolymers, can be used in this context. Also usable, of course, are mixed alkoxylated nonionic active detergent species in which EO and PO units are distributed statistically rather than in block fashion. Such products are obtainable by the simultaneous action of ethylene oxide and propylene oxide on fatty alcohols. These non-ionic surfactants are obtainable, for example, under the commercial name Dehydol® (from Cognis).

**[0042]** Ampholytic surfactants can be broadly described as derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical may be a straight chain or a branched and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. A preferred ampholytic surfactant is cocamidopropyl betaine.

**[0043]** Preferably, the textile or hard surface treatment composition additionally contains a perfume composition in order to impart a pleasant scent to the laundry treated therewith and to the textile or hard surface treatment composition itself.

**[0044]** In a preferred embodiment, the liquid textile or hard surface treatment composition contains a perfume composition in a quantity of usually up to 3 wt.%, preferably 0.05 to 2 wt.%, particularly 0.1 to 1.5 wt.% and particularly preferably 0.2 to 1 wt.%, in each case based on the total liquid textile or hard surface treatment composition.

**[0045]** The perfume composition can contain individual fragrance compounds, for example the synthetic products of the type of the esters, ethers, aldehydes, ketones, alcohols and hydrocarbons. Preferably, however, mixtures of various fragrances are used which together produce an attractive scent. The perfume composition can also contain natural fragrance compounds as may be obtained from plant sources. The perfume composition of the textile or hard surface treatment composition can also contain at least one aromatherapy component such as an essential oil. In another preferred embodiment, the fabric washing liquid composition comprises an encapsulated perfume and a free perfume. The use of pro-fragrances in the perfume composition may be also advantageous.

**[0046]** The treatment compositions can be used to clean hard surfaces or textile fabrics. For the purposes of the present invention, hard surfaces for example comprise surfaces of stone or ceramic materials, rigid plastics materials, glass, porcelain or metal. Hard surfaces may be, for example, tableware, walls, tiles, work surfaces, painted surfaces, flooring or sanitary articles.

**[0047]** The textile or hard surface treatment composition is manufactured using usual and known methods and processes. For example, the constituents of the textile or hard surface treatment composition can be simply mixed in agitator vessels, the water, non-aqueous solvent, ethanol and surfactants usefully being prepared first. After cooling under stirring, if necessary at all, the further constituents are then added in portions.

**[0048]** Table 1 below shows the composition of three liquid hard surface treatment compositions E1 to E3. Quantities are indicated in wt% of active matter.

Table 1:

	E1	E2	E3
Alkyl benzene sulfonic acid, sodium salt	13	2	2
Cocamidopropyl betaine	1.5	--	--
Sodium lauryl ether sulfate (2 EO)	4	4	4
Perfume	0.2	0.4	0.33
Acid Blue 9	0.004	0.004	--

(continued)

	E1	E2	E3	
5	Acid Yellow 23	0.0014	--	--
	Blue anthraquinone dye	--	--	0.008
	NaCl	0.2	2.5	2.5
	Na <sub>2</sub> CO <sub>3</sub>	--	0.2	0.2
10	Bitrex®	0.001	--	--
	Ethanol	0.1	0.12	0.12
	Water	to make 100 wt.%		

15 [0049] When subjected to UV light (the lamp spectrum corresponded to natural sunlight) for 72 hours all three liquid hard surface treatment compositions E1 to E3 showed no or only little change in color. In contrast, identical liquid compositions but without ethanol showed after 72 hours exposure to UV light a substantial color fading and/or discoloration. All three liquid hard surface treatment compositions E1 to E3 were transparent.

20 [0050] For liquid hard surface treatment compositions E1 and a comparative composition that is identical to composition E1 except that it contains no ethanol the color change was quantitatively measured using the European Pharmacopoeia (EP) color scale. The measurements were carried out with a Hach Lange LICO 500 Colorimeter. The measured values before and after 72 hours UV light exposure are given in table 2.

Table 2: EP color values

Product	L*	a*	b*
<b>Initial</b>			
E1	57.7	-86.3	-2.9
E1 without ethanol	57.7	-86.3	-2.9
<b>After UV exposure</b>			
E1	60.2	-84.9	-3.6
E1 without ethanol	89.1	-5.3	0.3

25 [0051] The data in table 2 clearly show that the addition of ethanol has no impact on the EP color values and, thus, no impact on the color of a dyed liquid composition since both compositions exhibit exactly the same values for L\*, a\* and b\*.

30 [0052] The data also clearly show that the composition without ethanol undergoes a dramatic change in color and that little amounts of ethanol significantly reduce the destruction of colorant dye.

40 **Claims**

1. A method of reducing destruction of blue colorant dye in a liquid textile or hard surface treatment composition in a bottle that is permeable for UV light by adding ethanol to said composition, in an amount of at least 0.01 % by wt. of the liquid composition.
2. The method according to claim 1, **characterized in that** the composition is an aqueous liquid textile or hard surface treatment composition.
3. The method according to one of the preceding claims, **characterized in that** the liquid composition comprises an anionic surfactant.
4. The method according to one of the preceding claims, **characterized in that** the colorant dye is selected from the group consisting of Acid Blue 145, Acid Blue 9, Acid Blue 80, blue anthraquinone dyes, blue xanthene dyes and mixtures thereof.
5. The method according to one of the preceding claims, **characterized in that** the liquid composition is transparent or translucent.

**Patentansprüche**

- 5 1. Verfahren zum Reduzieren einer Zerstörung eines blaufärbenden Farbstoffs in einer flüssigen Zusammensetzung für eine Behandlung von Textil oder harten Oberflächen in einer für UV-Licht durchlässigen Flasche durch Zugeben von Ethanol zu der Zusammensetzung in einer Menge von mindestens 0,01 Gew.-% der flüssigen Zusammensetzung.
- 10 2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Zusammensetzung eine wässrige flüssige Zusammensetzung für die Behandlung von Textil oder harten Oberflächen ist.
- 15 3. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die flüssige Zusammensetzung ein anionisches Tensid umfasst.
4. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der färbende Farbstoff aus der Gruppe ausgewählt ist, die aus Patentblau 145, Patentblau 9, Patentblau 80, blauen Anthrachinonfarbstoffen, blauen Xanthenfarbstoffen und Mischungen davon besteht.
- 20 5. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die flüssige Zusammensetzung transparent oder transluzent ist.

**Revendications**

- 25 1. Procédé de réduction de la destruction d'un colorant bleu dans une composition de traitement textile liquide ou de surface dure dans une bouteille qui est perméable à la lumière ultraviolette en ajoutant de l'éthanol à ladite composition, en une quantité d'au moins 0,01 % en poids de la composition liquide.
- 30 2. Procédé selon la revendication 1, **caractérisé en ce que** la composition est une composition de traitement aqueuse liquide textile ou de surface dure.
3. Procédé selon l'une des revendications précédentes, **caractérisé en ce que** la composition liquide contient un tensioactif anionique.
- 35 4. Procédé selon l'une des revendications précédentes, **caractérisé en ce que** le colorant est choisi dans le groupe constitué par l'Acid Blue 145, l'Acid Blue 9, l'Acid Blue 80, les colorants anthraquinoniques bleus, les colorants xanthènes bleus et leurs mélanges.
5. Procédé selon l'une des revendications précédentes, **caractérisé en ce que** la composition liquide est transparente ou translucide.

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**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

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