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(54) **Bleaching compositions based on mixtures of cationic and nonionic surfactants**

Bleichmittelzusammensetzung auf der Basis von kationischer und nichtionischer Tensidmischungen

Compositions de blanchiment à base de mélanges d'agents tensio-actifs cationiques et non-ioniques

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(73) Proprietor: **THE PROCTER & GAMBLE COMPANY**  
**Cincinnati, Ohio 45202 (US)**

(72) Inventors:  
• **Polotti, Gianmarco (NMN)**  
**I-20099 Sesto San Giovanni, Milan (IT)**

- **Scialla, Stefano (NMN)**  
**I-00128 Rome (IT)**
- **Scoccianti, Raffaele (NMN)**  
**I-00153 Rome (IT)**

(74) Representative: **Engisch, Gautier et al**  
**Procter & Gamble**  
**European Technical Center N.V.**  
**Temselaan 100**  
**1853 Strombeek-Bever (BE)**

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**EP-A- 0 000 226**                      **EP-A- 0 004 121**  
**EP-A- 0 012 483**                      **GB-A- 2 179 364**

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**Description**Technical Field

5 **[0001]** The present invention relates to bleaching compositions. The compositions of the present invention are particularly useful for laundry bleaching.

Background

10 **[0002]** Compositions for the bleaching of laundry have been extensively described in the art. Bleaching compositions can be classified into peroxide bleaching compositions and hypochlorite bleaching compositions. Peroxide bleaching compositions have the advantage over hypochlorite bleaching compositions that they are generally considered as being somewhat safer to fabrics, specifically to colored fabrics. Peroxide compositions however have the inconveniency that they are often chemically unstable, which makes it difficult to formulate peroxide bleaching compositions which are sufficiently stable to be commercialized. A possible solution to this problem consists in formulating compositions with a high level of peroxide, to extend the "effective" period of the composition. A possible drawback of this solution is that compositions may reach the user which still comprise a high amount of peroxide, whereby possible skin itching may occur if the user's skin comes in contact with the peroxide composition. This itching phenomenon is quite moderate and fully reversible, but is does constitute potential discomfort for the user.

20 **[0003]** EP 0 000 226 relates to a laundry additive product comprising a substrate in combination with a peroxy compound precursor and surfactant system. The surfactant system comprises a nonionic surfactant having HLB 8-17 and a cationic surfactant.

**[0004]** EP 0 004 121 relates to a low phosphate laundry detergent comprising nonionic surfactant having HLB 5-14 and a quaternary ammonium surfactant having 2 chains which contain from 16 to 22 carbon atoms.

25 **[0005]** GB 2179364 relates to a fabric treating composition comprising insoluble builder salt particles and small amounts of urea additive or a higher alkyl quaternary ammonium surface active agent in a non-aqueous nonionic liquid surfactant composition.

**[0006]** It is thus an object of the present invention to formulate a composition comprising a peroxygen bleach in lower amounts, i.e. in amounts where substantially no itching occurs, and which yet remain effective in bleaching fabrics.

30 **[0007]** It has now been found that this object could be met by formulating an aqueous composition comprising, in addition to lower amounts of peroxygen bleach, a water-soluble cationic surfactant in combination with a hydrophilic nonionic surfactant.

Summary of the invention

35 **[0008]** The aqueous bleaching compositions of the present invention comprises a cationic surfactant according to the formula  $R_1R_2R_3R_4N^+X^-$ , where  $R_1$  is C8-C16 alkyl wherein each of  $R_2, R_3, R_4$  is independently C1-C4 alkyl or hydroxy alkyl, benzyl, or  $(C_2H_4O)_xH$  where  $x$  is from 2 to 5, not more than one of  $R_2, R_3, R_4$  being benzyl, and  $X$  is an anion, said composition further comprising a hydrophilic nonionic surfactant having an HLB above 13 and characterised in that the composition comprises hydrogen peroxide.

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Detailed description of the invention

45 **[0009]** The compositions according to the present invention are peroxide bleaching compositions. Thus the compositions herein comprise hydrogen peroxide. As discussed hereinbefore, a problem which may occur with compositions comprising hydrogen peroxide above a certain level, is that the skin of the user which comes in contact with the composition may itch. This itching phenomenon is harmless and quickly fully reversible, but it may nevertheless cause discomfort to the user. The compositions herein thus comprise hydrogen peroxide in amounts not causing any skin itching.

50 **[0010]** Hydrogen peroxide is present at from 1% to 10% by weight of the total composition preferably from 2% to 4%. Indeed, we have found that, when used in higher amounts, skin itching phenomenon start to appear.

**[0011]** Because the level of hydrogen peroxide, is reduced, there would result a poorer bleaching performance, compared to compositions with higher amounts of peroxygen bleach which in turn might cause skin itching. We have found that the bleaching performance at higher temperatures, e.g. as from 50°C could be maintained, even with lower amounts of peroxygen bleach, by formulating a specific surfactant system comprising a narrowly-defined cationic surfactant as well as a narrowly-defined hydrophilic nonionic surfactant.

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**[0012]** Accordingly, the compositions herein comprise a cationic surfactant according to the formula  $R_1R_2R_3R_4N^+X^-$ , where  $R_1$  is C8-C16 alkyl wherein each of  $R_2, R_3, R_4$  is independently C1-C4 alkyl or hydroxy alkyl, benzyl, or  $(C_2H_4O)$

xH where x is from 2 to 5, not more than one of R<sub>2</sub>,R<sub>3</sub>,R<sub>4</sub> being benzyl, and X is an anion. It is of course possible to use herein mixtures of different cationic surfactants according to the formula hereinabove.

**[0013]** Preferred alkyl chain length for R<sub>1</sub> is C<sub>12-15</sub>, particularly where the alkyl group is a mixture of chain length derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohol synthesis. Preferred groups for R<sub>2</sub>,R<sub>3</sub> and R<sub>4</sub> are methyl and hydroxyethyl groups and suitable anion X include halide, methosulfate, acetate and phosphate ions.

**[0014]** Examples of suitable cationic surfactant for use herein are:

coconut trimethyl ammonium chloride, preferred for use herein, or bromide as Cequartyl® from Rhone Poulenc and Empigen® 5141 from Albright & Wilson,  
 coconut methyl dihydroxyethyl ammonium chloride or bromide,  
 decyl triethyl ammonium chloride,  
 decyl dimethyl hydroxyethyl ammonium chloride or bromide,  
 C<sub>12-15</sub> dimethyl hydroxyethyl ammonium chloride or bromide,  
 coconut dimethyl hydroxyethyl ammonium chloride or bromide,  
 myristyl trimethyl ammonium methyl sulfate,  
 lauryl dimethyl benzyl ammonium chloride or bromide as Bacforbl® 80 from Sidobre, Sinove® and Bardac® 205 M from Lonza.  
 lauryl dimethyl (ethenoxy)<sub>4</sub> ammonium chloride or bromide.

**[0015]** The compositions herein comprise from 0.1% to 20% by weight of the total composition of said cationic surfactants, or mixtures thereof, preferably from 1% to 5%.

**[0016]** As a further essential ingredient, the compositions herein comprise a hydrophilic nonionic surfactant. We have found that the suitable nonionic surfactants for use herein are those having an HLB above 13. It is of course possible to use mixtures of said nonionic surfactants. A wide variety of nonionic surfactants are commercially available. Typically, nonionic surfactants are alkoxyated fatty alcohols. And the HLB of a given nonionic surfactant depends on the chain length of the fatty alcohol, the nature of the alkoxyating group as well as the degree of alkoxylation. Surfactant catalogs are available which list nonionic surfactants with their corresponding HLBs. Suitable for use herein are those which have an HLB of above 13. Such nonionic surfactants are commercially available for instance under the trade name Dobanol®, 91-8, 91-9, 91-10 and 91-12, all from Shell.

**[0017]** The compositions herein should comprise from 0.1% to 20% by weight of the total composition, preferably from 2% to 10% of said hydrophilic nonionic surfactant or mixtures thereof. In a preferred embodiment of the present invention, said cationic surfactant and said hydrophilic nonionic surfactant should be present in a weight ratio of cationic to nonionic of about 1:3.

The compositions herein can be advantageously formulated as emulsions comprising two nonionic surfactants with different HLBs. Indeed, by formulating in an aqueous medium at least two different nonionic surfactants having different HLBs, a stable emulsion can be obtained. This emulsion can then be used to formulate, in a single composition, different ingredients which are otherwise poorly compatible, e.g. a bleach activator with hydrogen peroxide. In this embodiment of the invention the compositions herein comprise at least one hydrophilic nonionic surfactant, which can be the nonionic surfactant described herein before, and a more hydrophobic nonionic surfactant. Suitable hydrophobic surfactants to form the hydrophobic phase of the emulsion typically have an HLB of less than about 9. The compositions of this embodiment can be made by mixing together all the hydrophilic ingredients, i.e. water, said hydrophilic nonionic surfactant, said cationic surfactant and all other hydrophilic ingredients such as dyes, optical brighteners. Separately, all hydrophobic ingredients are mixed, i.e. said hydrophobic nonionic surfactant together with other, optional, hydrophobic ingredients which are to be formulated in the composition, such as perfumes, solvents, enzymes, bleach activators and polymers. Then, both mixtures are mixed together. If the composition comprises a bleach activator, i.e. a peracid precursor, it is preferable to choose a hydrophobic bleach activator which can be formulated in said hydrophobic mixture, and thus remains separated from the hydrophilic peroxygen bleach. This adds to the chemical stability of the compositions, thus its performance as more oxygen remains available throughout time. A suitable hydrophobic bleach activator for use herein includes acetyl triethyl citrate, as described in WO 93/12067, as well as compounds according to the formula R-O-O-R' where R and R' are independently alkyl, alkenyl, alkanoyl, aryl, aroyl, alkylaryl or alkylaroyl radicals.

**[0018]** We have observed that the pH of the compositions herein plays a role in the chemical stability of the composition. Accordingly, the compositions herein are preferably formulated at a pH of from 1 to 7, preferably 3 to 5. A variety of suitable means can be used for adjusting the pH of the compositions, including organic or inorganic acids, alkanolamines and the like. It may be desirable to use alkanolamines herein, as we have found that alkanolamines have an effect on the viscosity of the product, and thus can be used as viscosity regulators, if necessary.

**[0019]** The compositions herein may comprise a variety of optional ingredients. A preferred optional feature of the

compositions herein is the presence of radical scavengers, which are beneficial to the stability of the compositions herein. Suitable radical scavengers for use herein include the well known substituted mono and di hydroxy benzenes and their analogs, alkyl and aryl carboxylates, and mixtures thereof. Preferred radical scavengers for use herein include butyl hydroxy toluene, mono-tert-butyl hydroquinone, benzoic acid, toluic acid, t-butyl catechol, benzylamine, 1,1,3-tris (2-methyl-4-hydroxy-5-t-butylphenyl) butane, commercially available under the trade name Topanol CA ® ex ICI, as well as n-propyl-gallate. Radical scavengers, when used, are typically present herein in amounts ranging from 0.01% to 2% by weight of the total composition, preferably 0.01% to 0.2%.

**[0020]** The compositions herein may further comprise other optionals, including anionic and cationic surfactants, to be formulated in the hydrophilic phase herein, builders and chelants, as well as aesthetics, including dyes and perfumes and the like.

**[0021]** The compositions according to the present invention are useful as laundry bleaches, including for the pre-treatment of stains on laundry items prior washing. Indeed, pretreatment of fabrics before washing allows a close contact of the product with the stains, and the bleaching mechanism described herein occurs at a later stage, when the pretreated fabrics are contacted with warm water. The compositions herein can also be formulated as detergent compositions per se, or as detergency additives, to be used in addition to a detergent. Compositions herein can further be used as dishwashing compositions, or as hard surface cleaners, provided that contact with warm water occurs at some point in time in the washing process.

**[0022]** The present invention further encompasses a process of bleaching fabrics, dishes or hard surfaces wherein said fabrics, dishes or hard surfaces are contacted with a bleaching liquor comprising a composition according to any of the preceding claims in an aqueous medium at a temperature of from 30°C to 90°C, and said bleaching liquor is subsequently rinsed off of said fabrics, dishes or hard surfaces. In one embodiment of this process, the composition described herein is first applied to fabrics, as a so-called pretreater, preferably to the stained portions of said fabrics, and said pretreated fabrics are subsequently contacted with an aqueous medium at a temperature of from 30°C to 70°C, for a period of time sufficient to bleach said fabrics. In this embodiment, said bleaching liquor is formed at the time the fabrics are introduced in said aqueous medium. Subsequently, said bleaching liquor is rinsed off of said fabrics.

**[0023]** The present invention is further illustrated by the following examples and data.

Examples - Experimental Part

**[0024]** The following formulations according to the present invention are made by mixing the listed ingredients in the listed proportions (in weight %).

Composition 1	
Dobanol ® 91-8	3%
Coconut trimethyl ammonium chloride	1%
H2O2	4%
Sodium Coconut Alkyl Sulfate	10%
Dobanol ® 23-3	5%
Water and minors	to balance
pH	4
Composition 2	
Dobanol ® 91-8	3%
Coconut trimethyl ammonium chloride	1%
H2O2	4%
Sodium Coconut Alkyl Sulfate	4%
Dobanol ® 23-3	10%
Water and minors	to balance
pH	4
Composition 3	
Dobanol ® 91-10	3%
Coconut trimethyl ammonium chloride	1%
H2O2	4%
Sodium Coconut Alkyl Sulfate	2%

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(continued)

Composition 3	
Dobanol ® 23-3	7%
Water and minors	to balance
pH	4
Composition 4	
Dobanol 91-8	3%
Bardac ® 205M	1%
H2O2	4%
Sodium Coconut Alkyl Sulfate	2%
Dobanol ® 23-3	5%
Water and minors	to balance
pH	4

**[0025]** The present invention concerns the incorporation of a specific cationic/nonionic surfactant system in a liquid peroxygen bleaching composition which allows to reduce the amount of peroxygen bleach without losing performance. The technical data below illustrate the present invention. The tests are made with the following conditions. The tests are performed on cotton fabrics, with 6 replicates per test. The fabrics are stained as indicated hereinabove, and 0.2g of prototype is applied to the stains, prior to washing. Then the fabrics are washed in a Launder-O-meter, with 5 g of Dash Ultra Powder in 500 ml water. There is no waiting period between application of the prototype on the stains, and the subsequent washing.

**[0026]** Prototype A is a composition as composition 1 hereinabove, but without Dobanol® 91-8 and without cationic surfactant. Prototype B is the same as Prototype A, but with 7% level instead of 4% Hydrogen peroxide. The results are listed in the table below.

Stains	Prototype 1 vs. Prototype B 40° C	Comp. 1 vs. Prototype B 40° C	Prototype A vs. Prototype B 60° C	Comp. 1 vs. Prototype B 60° C
Grass	-0.8 s	-0.2	-1.0 s	-0.3
Cocoa	+0.1	+0.3	-0.9	0.0
Tea	-0.4	-0.4	-0.7	-0.2
Wine	-0.8	-0.3	-0.7 s	0.0
Vegetal Oil	-1.0 s	+0.1	-1.0 s	0.0
Blood	-3.2 s	-1.7 s	-4.0 s	-0.8 s

The results are expressed as panel score units as evaluated by expert judges. Comparing Prototype A vs Prototype B shows that a decrease in H2O2 leads to a loss of performance. Comparing Composition 1 vs Composition B shows that Composition 1 is as good as prototype B, even though it has about half less H2O2.

**[0027]** Another test is performed as in the previous experiment. In this test, composition 2 exemplified hereinbefore is compared to a reference composition. The reference is an activated bleaching composition comprising hydrogen peroxide and acetyl triethyl citrate. More specifically, the formulation comprises 6% H2O2, 3.5% acetyl triethyl citrate, 6% Lutensol ® TO3, 8% Dobanol ® 45-7, 1.5% Sodium Alkyl Sulfate, 0.3% Citric Acid, 0.2%, water to balance, pH=4).

Prototype 2 vs. reference

**[0028]**

	40° C	60° C
Grass	+ 0.2	0.0
Cocoa	+0.0	+0.2
Tea	-0.6	-0.2
Wine	-0.1	0.0
Vegetal Oil	-0.5	-0.5

(continued)

	40° C	60° C
Mineral Oil	+0.3	+0.3
Make Up	+0.92s	+0.9s
Tomato	+0.92s	+0.4
Sebum	-0.67	+0.5
Blood	-1.0s	-4.0 s

**[0029]** This comparison shows that a composition according to the present invention performs better than an activated bleaching composition comprising a higher amount of hydrogen peroxide.

## Claims

1. An aqueous bleaching composition comprising from 1% to 10% by weight of the total composition of hydrogen peroxide a cationic surfactant according to the formula  $R^1R^2R^3R^4N^+X^-$ , or mixtures thereof, where  $R^1$  is C8-C16 alkyl wherein each of  $R^2, R^3, R^4$  is independently C1-C4 alkyl or hydroxy alkyl, benzyl, or  $(C_2H_4O)_xH$  where  $x$  is from 2 to 5, not more than one of  $R^2, R^3, R^4$  being benzyl, and  $X$  is an anion, said composition further comprising a hydrophilic nonionic surfactant having an HLB above 13, or mixtures thereof.
2. A composition according to claim 1 which comprises hydrogen peroxide, in amounts of from 2% to 4% by weight of the total composition.
3. A composition according to the preceding claims which comprises from 0.1 % to 20% by weight of the total composition of said cationic surfactants, or mixtures thereof, preferably from 1 % to 5%.
4. A composition according to the preceding claims wherein said cationic surfactant is coconut trimethyl ammonium chloride.
5. A composition according to the preceding claims which comprises from 0.1% to 20% by weight of the total composition of said nonionic surfactant, or mixtures thereof, preferably from 2% to 10%.
6. A composition according to the preceding claims where said cationic surfactant and said hydrophilic nonionic surfactant are present in a weight ratio of said cationic surfactant to said hydrophilic nonionic surfactant of about 1:3.
7. A composition according to any of the preceding claims which is formulated as an emulsion comprising at least two nonionic surfactants having different HLBs.
8. A composition according to any of the preceding claims which further comprises a bleach activator.
9. The use of a composition according to any of the preceding claims in a process of bleaching fabrics, disks or hard surfaces.
10. A process of bleaching fabrics, wherein said fabrics are pretreated by applying thereon, preferably on the stained portions of said fabrics, a composition according to claims 1 to 8, and said pretreated fabrics are subsequently contacted with an aqueous medium at a temperature of from 30°C to 70°C, thereby forming a bleaching liquor, for a period of time sufficient to bleach said fabrics, and said bleaching liquor is subsequently rinsed off of said fabrics.

## Patentansprüche

1. Wäßrige Bleichzusammensetzung, umfassend 1 Gew.-% bis 10 Gew.-% der Gesamtzusammensetzung an Wasserstoffperoxid, ein kationisches Tensid gemäß der Formel  $R^1R^2R^3R^4N^+X^-$ , oder Mischungen davon, worin  $R^1$  C<sub>8</sub>-C<sub>16</sub>-Alkyl ist und worin  $R^2, R^3, R^4$  jeweils unabhängig voneinander C<sub>1</sub>-C<sub>4</sub>-Alkyl oder -Hydroxyalkyl, Benzyl oder  $(C_2H_4O)_xH$  darstellen, worin  $x$  von 2 bis 5 reicht, wobei nicht mehr als einer von  $R^2, R^3, R^4$  Benzyl ist, und  $X$  ein Anion darstellt, wobei die Zusammensetzung weiterhin ein hydrophiles nichtionisches Tensid mit einem HLB ober-

halb 13 umfaßt, oder Mischungen davon.

2. Zusammensetzung nach Anspruch 1, welche Wasserstoffperoxid in Anteilen von 2 Gew.-% bis 4 Gew.-% der Gesamtzusammensetzung umfaßt.
3. Zusammensetzung nach den vorangehenden Ansprüchen, welche 0,1 Gew.-% bis 20 Gew.-% der Gesamtzusammensetzung an den kationischen Tensiden, oder Mischungen davon, umfaßt, bevorzugt 1 Gew.-% bis 5 Gew.-%.
4. Zusammensetzung nach den vorangehenden Ansprüchen, worin das kationische Tensid Kokosnußtrimethylammoniumchlorid ist.
5. Zusammensetzung nach den vorangehenden Ansprüchen, welche 0,1 Gew.-% bis 20 Gew.-% der Gesamtzusammensetzung an dem nichtionischen Tensid, oder Mischungen davon, umfaßt, bevorzugt von 2 Gew.-% bis 10 Gew.-%.
6. Zusammensetzung nach den vorangehenden Ansprüchen, worin das kationische Tensid und das hydrophile nichtionische Tensid in einem Gewichtsverhältnis von kationischem Tensid zu hydrophilem nichtionischem Tensid von ungefähr 1:3 vorliegen.
7. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, welche als Emulsion, mindestens zwei nichtionische Tenside mit unterschiedlichen HLBs umfassend, formuliert ist.
8. Zusammensetzung nach mindestens einem der vorangehenden Ansprüche, welche weiterhin einen Bleichaktivator umfaßt.
9. Verwendung einer Zusammensetzung nach mindestens einem der vorangehenden Ansprüche in einem Verfahren zum Bleichen von Textilien, Geschirr oder harten Oberflächen.
10. Verfahren zum Bleichen von Textilien, worin die Textilien durch Anwendung einer Zusammensetzung nach den Ansprüchen 1 bis 8 darauf, bevorzugt auf die beschmutzten Teile der Textilien, vorbehandelt werden, und die vorbehandelten Textilien anschließend mit einem wäßrigem Medium bei einer Temperatur von 30°C bis 70°C in Kontakt gebracht werden, wobei eine Bleichlauge gebildet wird, für eine Zeitdauer ausreichend zum Bleichen der Textilien, und worin die Bleichlauge anschließend von den Textilien abgespült wird.

## Revendications

1. Composition de blanchiment aqueuse comprenant 1 % à 10 %, en poids de la composition totale de peroxyde d'hydrogène, un agent tensioactif cationique de formule  $R^1R^2R^3R^4N^+X^-$ , ou un de leurs mélanges, où  $R^1$  est un groupe alkyle en  $C_8-C_{16}$ , où chacun des groupes  $R^2$ ,  $R^3$  et  $R^4$  est indépendamment un groupe alkyle ou hydroxyalkyle en  $C_1-C_4$ , benzyle ou  $(C_2H_4O)_xH$ , où x a une valeur de 2 à 5, pas plus d'un des groupes  $R^2$ ,  $R^3$  et  $R^4$  étant un groupe benzyle, et X est un anion, ladite composition comprenant par ailleurs un agent tensioactif non ionique hydrophile ayant un HLB supérieur à 13, ou un de ses mélanges.
2. Composition selon la revendication 1, qui comprend du peroxyde d'hydrogène en quantités de 2 % à 4 % en poids de la composition totale.
3. Composition selon les revendications précédentes, qui comprend 0,1 % à 20 %, en poids de la composition totale, desdits agents tensioactifs cationiques ou de leurs mélanges, de préférence 1 % à 5 %.
4. Composition selon les revendications précédentes, dans laquelle ledit agent tensioactif cationique est le chlorure de coprahtriméthylammonium.
5. Composition selon les revendications précédentes, qui comprend 0,1 % à 20 %, en poids de la composition totale, dudit agent tensioactif non ionique ou d'un de ses mélanges, de préférence 2 % à 10 %.
6. Composition selon les revendications précédentes, dans laquelle ledit agent tensioactif cationique et ledit agent

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tensioactif non ionique hydrophile sont présents dans un rapport pondéral dudit agent tensioactif cationique audit agent tensioactif non ionique hydrophile d'environ 1:3.

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7. Composition selon l'une quelconque des revendications précédentes, qui est formulée en émulsion comprenant au moins deux agents tensioactifs non ioniques ayant différents HLB.
8. Composition selon l'une quelconque des revendications précédentes, qui comprend par ailleurs un activateur de blanchiment.
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9. Utilisation d'une composition selon l'une quelconque des revendications précédentes dans un procédé de blanchiment de tissus, de plats ou de surfaces dures.
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10. Procédé de blanchiment de tissus, dans lequel lesdits tissus sont prétraités en leur appliquant, de préférence sur les parties tachées desdits tissus, une composition selon les revendications 1 à 8, et lesdits tissus prétraités sont ensuite mis en contact avec un milieu aqueux à une température de 30 à 70°C, formant ainsi une liqueur de blanchiment, pendant une période de temps suffisante pour blanchir lesdits tissus, et ladite liqueur de blanchiment est ensuite éliminée desdits tissus par rinçage.

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