



- (51) International Patent Classification:  
*A61K 8/41* (2006.01) *A61Q 5/06* (2006.01)
- (21) International Application Number:  
PCT/JP2011/075238
- (22) International Filing Date:  
26 October 2011 (26.10.2011)
- (25) Filing Language: English
- (26) Publication Language: English
- (71) Applicant (for all designated States except US):  
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- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report (Art. 21(3))



**WO 2013/061477 A1**

(54) Title: HAIR COLORATION BY THERMAL TRANSFER TECHNOLOGY

(57) Abstract: The present invention relates to a method for dyeing keratin materials, in particular human keratin materials, in which at least one dry composition comprising at least one specific nitro dye is applied to the keratin materials, and the composition and/or the keratin materials is/are heated, causing the thermal transfer of the dye(s). The present invention is useful because the dyeing method according to the present invention using the thermal transfer technology can give coloration to keratin materials with an improved process providing dry, quick, and clean coloration, and can also be environmentally friendly.

## DESCRIPTION

## HAIR COLORATION BY THERMAL TRANSFER TECHNOLOGY

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## TECHNICAL FIELD

The present invention relates to a method for dyeing keratin materials, in particular human keratin materials, in which a dry composition comprising at least one specific nitro dye is used. It also relates to a laminated sheet comprising a film of said composition, and moreover, relates to a method for dyeing keratin materials, in particular human keratin materials, using said laminated sheet by thermal transfer technology.

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## BACKGROUND OF THE INVENTION

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Modifying the color of hair, in particular masking grey hair, has been known for a long time. Essentially, there are two types of technology which are used to dye human keratin fibers. The first method, known as "direct coloration" or "semipermanent dyeing", consists in changing or providing color by the application of a colored molecule which penetrates by diffusion into the hair and/or remains adsorbed on the hair surface. The second method, known as "oxidative coloration" or "permanent dyeing", consists in changing or providing color using, on the very inside of the fiber, an oxidative condensation of dye precursors which are weakly colored or colorless compounds. After this reaction, the dyes formed are insoluble and are trapped inside the hair. These two methods mentioned above make it possible to obtain numerous colors.

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On the other hand, these methods use products that are commonly prepared with liquid, gel, and/or cream formulations, which cause color transfer to scalp, clothes, and hairdressing accessories (combs, towels and so on) during and after the dyeing process. Moreover, the coloration time is generally long because of the relatively long leave-in time (typically approximately 30 minutes or more) and the shampoo after the dyeing process.

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## DISCLOSURE OF INVENTION

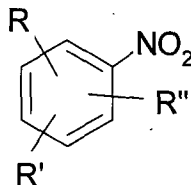
An objective of the present invention is to provide a new dyeing or coloring process for keratin materials, in particular human keratin materials, using the thermal transfer of specific nitro dyes, which makes it possible to rapidly and cleanly dye hair.

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The above objective can be achieved by a method for dyeing keratin materials, in particular human keratin materials, comprising the steps of:

- (i) applying at least one dry composition comprising at least one nitro dye to the keratin materials; and
- 5 (ii) heating the dry composition and/or the keratin materials to cause the vaporization or the sublimation of the nitro dye(s);

wherein said nitro dye(s) corresponds to the following formula (I):

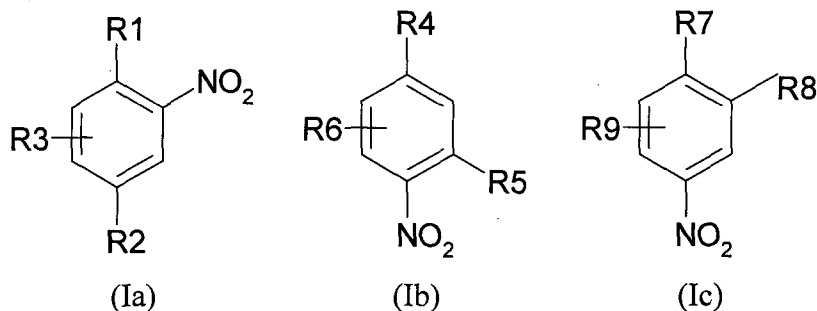


(I)

in which:

- **R** represents -NH<sub>2</sub>, -NHC<sub>2</sub>H<sub>4</sub>OH, -NHC<sub>3</sub>H<sub>6</sub>OH, -NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>, -OC<sub>2</sub>H<sub>4</sub>OH, -NHCH<sub>3</sub>,  
 10 or -OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH;
- **R'** represents -OH, -OCH<sub>3</sub>, -N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>, -NH<sub>2</sub>, -NHC<sub>2</sub>H<sub>4</sub>OH, -OC<sub>2</sub>H<sub>4</sub>OH,  
 -N(C<sub>2</sub>H<sub>4</sub>OH)(C<sub>2</sub>H<sub>5</sub>), -OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH, or -NHCH<sub>3</sub>; and
- **R''** represents a hydrogen atom, a halogen atom, or alkyl radical.

- 15 Preferably, the nitro dye for the present invention may correspond to the following formula (Ia), (Ib), or (Ic):



wherein:

- **R1** represents -NH<sub>2</sub>, -NHC<sub>2</sub>H<sub>4</sub>OH, -NHC<sub>3</sub>H<sub>6</sub>OH, or -NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>;
- **R2** represents -OH, -N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>, -NH<sub>2</sub>, -OC<sub>2</sub>H<sub>4</sub>OH, or -N(C<sub>2</sub>H<sub>4</sub>OH)(C<sub>2</sub>H<sub>5</sub>);
- 20 - **R3** represents a hydrogen atom or an alkyl radical;
- **R4** represents -OCH<sub>3</sub>, -OC<sub>2</sub>H<sub>4</sub>OH, -OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH, or -NHC<sub>2</sub>H<sub>4</sub>OH;
- **R5** represents -NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>, -NHCH<sub>3</sub>, or -NHC<sub>2</sub>H<sub>4</sub>OH;
- **R6** represents a hydrogen atom or a halogen atom;
- **R7** represents -OH or -NHC<sub>2</sub>H<sub>4</sub>OH;
- 25 - **R8** represents -NH<sub>2</sub> or -OCH<sub>3</sub>, and
- **R9** represents a hydrogen atom or a halogen atom.

The nitro dye used in the present invention may be selected from the group consisting of 4-amino-3-nitrophenol [610-81-1], 3-nitro-*para*-hydroxyethyl aminophenol [65235-31-6], 3-methylamino-4-nitrophenoxyethanol [59820-63-2], 2-nitro-5-glycerylmethylaniline [80062-31-3], HC Red No. 7 [24905-87-1], HC Violet No. 1 [82576-75-8], HC Red No. 3 [2871-01-4], HC Orange No. 2 [85765-48-6], HC Yellow No. 10 [109023-83-8], and mixtures thereof.

It is preferable that the heating temperature be between 100 and 600°C, preferably between 130 and 250°C, and more preferably between 140 and 220°C.

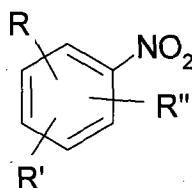
It is preferable that the heating time be between 0.01 and 30 seconds, preferably 0.1 and 10 seconds, and more preferably 0.1 to 5 seconds.

Moreover, it is preferable that the dry composition comprising said at least one specific nitro dye be in the form of a film.

The dry composition may comprise at least one binder material. Such binder material may be selected from the group consisting of film-forming polymers; celluloses; plastics such as polyester, polystyrene, ketone resin, epoxy resin, terpene phenol resin, polyamide, polysulfone, polyethersulfone, polyvinyl butyral, acrylonitrile, styrene resin and polyacrylate; and waxes such as carnauba wax and paraffin wax.

The present invention also relates to a laminated sheet comprising:

- (i) a film comprising the dry composition comprising:  
at least one nitro dye of formula (I):



(I)

in which:

- **R** represents -NH<sub>2</sub>, -NHC<sub>2</sub>H<sub>4</sub>OH, -NHC<sub>3</sub>H<sub>6</sub>OH, -NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>, -OC<sub>2</sub>H<sub>4</sub>OH, -NHCH<sub>3</sub>, or -OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH;
  - **R'** represents -OH, -OCH<sub>3</sub>, -N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>, -NH<sub>2</sub>, -NHC<sub>2</sub>H<sub>4</sub>OH, -OC<sub>2</sub>H<sub>4</sub>OH, -N(C<sub>2</sub>H<sub>4</sub>OH)(C<sub>2</sub>H<sub>5</sub>), -OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH, or -NHCH<sub>3</sub>; and
  - **R''** represents a hydrogen atom, a halogen atom, or an alkyl radical;
- and

- (ii) a support.

The support may comprise at least one material selected from the group consisting of an aluminum foil, a paper, and a synthetic material with a high glass transition temperature such as polyester, polycarbonate, polyamide, polyimide, and polyaramid.

5

The present invention also relates to a method for dyeing keratin materials, in particular human keratin materials, comprising the steps of:

- (i) applying the laminated sheet described above to the keratin materials; and
- (ii) heating said laminated sheet and/or the keratin materials.

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It is preferable that the heating temperature be between 100 and 600°C, preferably between 130 and 250°C, and more preferably between 140 and 220°C. It is preferable that the heating time be between 0.01 and 30 seconds, preferably between 0.1 and 10 seconds, and more preferably between 0.1 and 5 seconds.

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#### DETAILED DESCRIPTION OF THE INVENTION

The inventors performed diligent research and developed a thermal transfer technology which can give (1) dry, (2) quick, and (3) clean coloration (no stain to scalp, clothes, and hairdressing accessories such as combs, towels, and the like) to keratin materials, in particular human keratin materials, and also be (4) environmentally friendly.

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In particular, the present invention has the advantage of not requiring the use of a liquid dye product, which causes color transfer to scalp, clothes, and hairdressing accessories.

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Furthermore, the fact that a liquid dye product is not required and that a dry composition is used makes it possible to use dyes which are sparingly soluble or which are unstable in a liquid medium. This can contribute to further broadening the palette of colors possible. In addition, the color on the keratin materials obtained by the present invention can be resistant to washing, shampooing, rinsing, perspiration, sebum, light and the like.

30

Moreover, there is no need either for rinsing, or for shampooing and/or for drying the keratin materials treated, and thus, the process according to the present invention can be considered to be “environmentally friendly”.

35

Furthermore, since thermal transfer is rapid, the leave-in times are short.

Accordingly, the present invention can rapidly and cleanly dye the keratin materials compared to conventional coloring methods.

40

Finally, this method makes it possible to produce, in a simple manner, motifs on the materials treated, in particular on the hair.

- 5 In one embodiment of the present invention, a method for dyeing keratin materials using a dry composition is provided. The method comprises the steps of:
- (i) applying at least one dry composition comprising at least one nitro dye to the keratin materials; and
- (ii) heating said dry composition and/or the keratin materials to cause the
- 10 vaporization or sublimation of the nitro dye(s).

In the text which follows, when it is specified that the composition is “dry”, that means that the variation in the dry extract of such a composition, measured before and after a thermal treatment in an oven for one hour at 100°C, varies by 20% by weight or less,

15 preferably by 10% by weight or less.

It is preferable that the dry composition has a viscosity of more than 100 centipoises, preferably more than 1,000 centipoises. Typically, a “dry composition” is free or substantially free from water or lower (C<sub>1</sub>-C<sub>6</sub>) alcohols. For example, such a

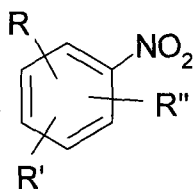
20 composition comprises less than 10% by weight, preferably less than 5% by weight, and more preferably less than 1% by weight of water or lower alcohols.

Human keratin materials used herein mean substances made from keratin, in particular keratin fibers, such as hair or eyelashes.

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The dry composition for the present invention comprises at least one specific nitro dye. A single type or two or more types of nitro dyes in combination may be used.

The nitro dye may be represented by the following formula (I):



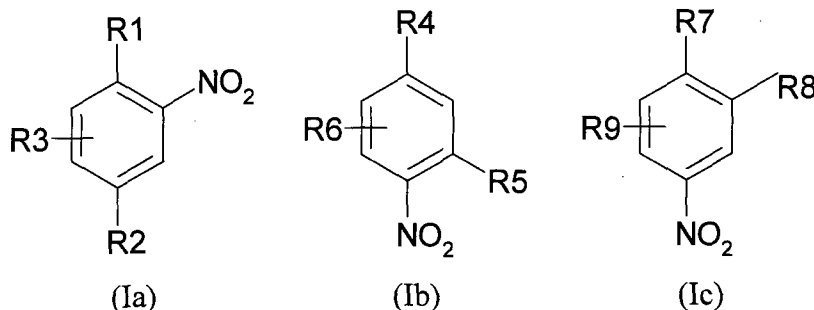
(I)

30 in which:

- R represents -NH<sub>2</sub>, -NHC<sub>2</sub>H<sub>4</sub>OH, -NHC<sub>3</sub>H<sub>6</sub>OH, -NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>, -OC<sub>2</sub>H<sub>4</sub>OH, -NHCH<sub>3</sub>, or -OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH;
- R' represents -OH, -OCH<sub>3</sub>, -N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>, -NH<sub>2</sub>, -NHC<sub>2</sub>H<sub>4</sub>OH, -OC<sub>2</sub>H<sub>4</sub>OH, -N(C<sub>2</sub>H<sub>4</sub>OH)(C<sub>2</sub>H<sub>5</sub>), -OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH, or -NHCH<sub>3</sub>; and

- **R**" represents a hydrogen atom, a halogen atom, or alkyl radical.

More specifically, the nitro dye may correspond to the following formula (Ia), (Ib), or (Ic):



5 wherein:

- **R1** represents -NH<sub>2</sub>, -NHC<sub>2</sub>H<sub>4</sub>OH, -NHC<sub>3</sub>H<sub>6</sub>OH, or -NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>;
- **R2** represents -OH, -N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>, -NH<sub>2</sub>, -OC<sub>2</sub>H<sub>4</sub>OH, or -N(C<sub>2</sub>H<sub>4</sub>OH)(C<sub>2</sub>H<sub>5</sub>);
- **R3** represents a hydrogen atom or an alkyl radical;
- **R4** represents -OCH<sub>3</sub>, -OC<sub>2</sub>H<sub>4</sub>OH, -OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH, or -NHC<sub>2</sub>H<sub>4</sub>OH;
- 10 - **R5** represents -NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>, -NHCH<sub>3</sub>, or -NHC<sub>2</sub>H<sub>4</sub>OH;
- **R6** represents a hydrogen atom or a halogen atom;
- **R7** represents -OH or -NHC<sub>2</sub>H<sub>4</sub>OH;
- **R8** represents -NH<sub>2</sub> or -OCH<sub>3</sub>, and
- **R9** represents a hydrogen atom or a halogen atom.

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The term "alkyl" as used herein refers to monovalent saturated aliphatic hydrocarbon groups, preferably having up to about 20 carbon atoms, preferably from 1 to 10 carbon atoms, and more preferably from 1 to 6 carbon atoms. The hydrocarbon chain may be either straight-chained or branched. This term is exemplified by groups such as  
 20 methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, tert-butyl, n-hexyl, n-octyl, tert-octyl and the like. Preferably, the alkyl radical is a methyl group.

The term "halogen" as used herein refers to an atom of chlorine, bromine, fluorine, or iodine. Preferably, the halogen atom is chlorine.

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More specifically, the nitro dye may be selected from the group consisting of  
 4-amino-3-nitrophenol, 3-nitro-*para*-hydroxyethyl aminophenol,  
 3-methylamino-4-nitrophenoxyethanol, 2-nitro-5-glycerylmethylaniline, HC Red No. 7  
 (4-N-hydroxyethyl-2-nitro-1,4-phenylenediamine), HC Violet No. 1  
 30 (2-(4-amino-2-methyl-5-nitrophenyl)aminoethanol), HC Red No. 3  
 (4-amino-2-nitro-N-(hydroxyethyl)aniline), HC Orange No. 2  
 (1-(2-aminoethyl)amino-4-(2-hydroxyethyl)-oxy-2-nitrobenzene), HC Yellow No. 10  
 (1,5-di(β-hydroxyethylamino)-2-nitro-4-chlorobenzene), and mixtures thereof.

The dry composition may comprise from 0.0001 to 100 % by weight, preferably 0.01 to 60% by weight, and more preferably 0.5 to 20% by weight of the nitro dye, relative to the total weight of the composition.

5

The dry composition may preferably be in the form of a film, because the handling of the composition is easy, and the nitro dye(s) in the dry composition can easily be transferred to keratin materials such as the hair.

10 When the dry composition is in the form of a film, the thickness of the film is not limited. For example, the thickness of the film may be between 0.01 mm and 2 mm, preferably between 0.02 mm and 2 mm, and more preferably between 0.05 mm and 1 mm.

15 The dry composition comprising at least one nitro dye mentioned above may further comprise at least one binder material.

As non-limiting illustrations of the binder material that may be used, alone or as a mixture, in the composition according to the invention, mention may be made of a  
20 film-forming polymer; celluloses; plastics such as polyester, polystyrene, ketone resin, epoxy resin, terpene phenol resin, polyamide, polysulfone, polyethersulfone, polyvinyl butyral, acrylonitrile, styrene resin and polyacrylate; and waxes such as carnauba wax and paraffin wax; and the like.

25 Regarding examples of the film-forming polymers, reference may be made in particular to the manual International Cosmetic Ingredient Directory and Handbook 2000 edition, Volume 2, pages 1744 to 1747 which relates to film-forming compounds.

Among the polymers capable of entering into the composition of the films comprising  
30 the nitro dye, there may be mentioned, for example, polymers derived from vinylpyrrolidone, polyvinyl alcohol, polyurethanes, polymers derived from caprolactam, vinyl lactam, vinyl acetate, polymers derived from acrylamide, polysaccharides capable of forming a film in the dry state such as cellulose derivatives, starches and derivatives, pullulan gum, gum arabic, pectins, alginates, carrageenans, galactomannans, agars,  
35 chitosans, chitins, polymers derived from hyaluronic acid, xanthan gum, karaya gum, proteins capable of forming a film in the dry state, such as gelatin, gluten, casein, zein, gliadin, hordein and their natural or synthetic derivatives, polymers derived from silicones, amphoteric or anionic polymers which are derived from monomers comprising at least one carboxylic, sulphonic or phosphoric functional group, acrylic  
40 copolymers of phosphorylcholine (lipidure), anion-cation complexes of the gum





dimethyl sulphate or with a dimethyl halide,

- the copolymers of acrylamide and methacryloyloxyethyltrimethylammonium chloride described, for example, in European Patent Application EP-A-080976,

- the copolymers of acrylamide and methacryloyloxyethyltrimethylammonium methosulphate,

- the vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers, quaternized or otherwise, such as the products sold under the name "GAFQUAT<sup>®</sup>" by the company ISP such as for example "GAFQUAT<sup>®</sup> 734" or "GAFQUAT<sup>®</sup> 755" or alternatively the products called "COPOLYMER<sup>®</sup> 845, 958 and 937". These polymers are described in detail in French Patents 2 077 143 and 2 393 573,

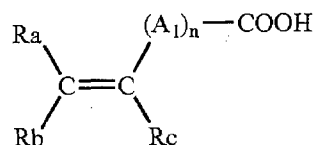
- the dimethylaminoethyl methacrylate/vinylcaprolactam/vinylpyrrolidone terpolymers such as the product sold under the name GAFFIX<sup>®</sup> VC 713 by the company ISP, and

- the quaternized vinylpyrrolidone/dimethylaminopropyl methacrylamide copolymer such as in particular the product sold under the name "GAFQUAT<sup>®</sup> HS 100" by the company ISP.

Among compounds of the family (4), there may be mentioned chitosan having a degree of deacetylation of 90% by weight, and pyrrolidone-chitosan carboxylate sold under the name KYTAMER<sup>®</sup> PC by the company AMERCHOL.

As regards the anionic film-forming polymers, they generally comprise at least one group derived from a carboxylic, sulphonic or phosphoric acid and have a number-average molecular mass of between about 500 and 5,000,000.

The carboxylic groups are more particularly provided by unsaturated mono- or dicarboxylic acid monomers such as those corresponding to the formula:



in which n is an integer from 0 to 10, A<sub>1</sub> denotes a methylene group, optionally linked to the carbon atom of the unsaturated group or to the neighboring methylene group, when n is greater than 1, through a heteroatom such as oxygen or sulphur, Ra denotes a hydrogen atom, or a phenyl or benzyl group, Rb denotes a hydrogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl group, in particular methyl, ethyl or carboxyl, Rc denotes a hydrogen atom or a lower alkyl group, a group -CH<sub>2</sub>-COOH, or a phenyl or benzyl group.

The preferred anionic film-forming polymers with carboxylic groups are:

A) The homo- or copolymers of acrylic or methacrylic acid or their salts and in particular the products sold under the names VERSICOL<sup>®</sup> E or K by the company

ALLIED COLLOID and ULTRAHOLD<sup>®</sup> by the company BASF, the copolymers of acrylic acid and of acrylamide, and the sodium salts of the polyhydroxycarboxylic acids.

5 **B)** The copolymers of acrylic or methacrylic acid with a monoethylene monomer such as ethylene, styrene, vinyl esters, acrylic or methacrylic acid esters, optionally grafted onto a polyalkylene glycol such as polyethylene glycol and optionally crosslinked. Such polymers are described in particular in French Patent 1 222 944 and German Patent Application 2 330 956. Copolymers of this type contain in their chain an acrylamide unit optionally N-alkylated and/or hydroxyalkylated as described especially in Luxembourg Patent Applications 75370 and 75371. There may also be mentioned  
10 the copolymers of acrylic acid and C<sub>1</sub>-C<sub>4</sub> alkyl methacrylate and the terpolymers of vinylpyrrolidone, acrylic acid and C<sub>1</sub>-C<sub>20</sub> alkyl, for example lauryl, methacrylate such as that sold by the company ISP under the name ACRYLIDONE<sup>®</sup> LM and the methacrylic acid/ethyl acrylate/tert-butyl acrylate terpolymers such as the product sold under the name LUVIMER<sup>®</sup> 100 P by the company BASF.

15 **C)** The copolymers derived from crotonic acid such as those containing in their chain vinyl propionate or acetate units and optionally other monomers such as methallyl or allyl esters, vinyl ether or vinyl ester of a linear or branched saturated carboxylic acid with a long hydrocarbon chain such as those containing at least 5 carbon atoms, it being possible for these polymers to be optionally grafted and crosslinked or alternatively  
20 another monomer which is a vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid. Such polymers are described, inter alia, in French Patents 1 222 944, 1 580 545, 2 265 782, 2 265 781, 1 564 110 and 2 439 798. A commercial product entering into this class is the resin 28-29-30 sold by the company NATIONAL STARCH.

25 **D)** The copolymers derived from C<sub>4</sub>-C<sub>8</sub> monounsaturated carboxylic acids or anhydrides chosen from:

- The copolymers comprising (i) one or more itaconic, fumaric or maleic acids or anhydrides and (ii) at least one monomer chosen from vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives, acrylic acid and its esters, the anhydride functions of  
30 these copolymers being optionally monoesterified or monoamidated. Such polymers are described in particular in U.S. Patent Nos. 2,047,398, 2,723,248, 2,102,113 and GB Patent 839805. Marketed products are especially those sold under the names GANTREZ<sup>®</sup> AN or ES by the company ISP.

- The copolymers comprising (i) one or more maleic, citraconic or itaconic anhydride  
35 units and (ii) one or more monomers chosen from allyl or methallyl esters optionally containing one or more acrylamide, methacrylamide or  $\alpha$ -olefin groups, acrylic or methacrylic esters, acrylic or methacrylic acid or vinylpyrrolidone in their chain, the anhydride functions of these copolymers being optionally monoesterified or monoamidated.

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These polymers are, for example, described in French Patents 2 350 384 and 2 357 241 by the applicant.

E) The polyacrylamides containing carboxylate groups.

- 5 The polymers comprising sulphonic groups are polymers containing vinylsulphonic, styrenesulphonic, naphthalenesulphonic or acrylamidoalkylsulphonic units.

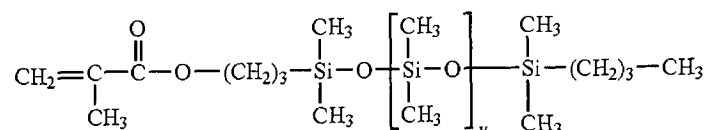
These polymers may be especially chosen from:

- 10 - The salts of polyvinylsulphonic acid having a molecular mass of between about 1,000 and 100,000 as well as the copolymers with an unsaturated comonomer such as acrylic or methacrylic acids and their esters as well as acrylamide or its derivatives, vinyl ethers and vinylpyrrolidone.
- The salts of polystyrenesulphonic acid such as the sodium salts sold for example under the name Flexan<sup>®</sup> 130 by NATIONAL STARCH. These compounds are described in  
15 Patent FR 2 198 719.
- The salts of polyacrylamidesulphonic acids, such as those mentioned in U.S. Patent No. 4,128,631 and more particularly polyacrylamidoethylpropanesulphonic acid.

20 According to the invention, it is also possible to use film-forming anionic polymers of the grafted silicone type comprising a polysiloxane portion and a portion consisting of a nonsilicone organic chain, one of the two portions constituting the principal chain of the polymer, the other being grafted onto the said principal chain. These polymers are for example described in patent applications EP-A-/412 704, EP-A-/ 412 707, EP-A-/640 105 and WO 95/00578, EP-A-/582 152 and WO 93/23009 and U.S. Patent Nos.  
25 4,693,935, 4,728,571 and 4,972,037.

Such polymers are, for example, the copolymers which can be obtained by free-radical polymerization starting with a mixture of monomers, consisting of:

- a) 50 to 90% by weight of tert-butyl acrylate;  
30 b) 0 to 40% by weight of acrylic acid;  
c) 5 to 40% by weight of silicone-containing macromer of formula:



with v being a number ranging from 5 to 700; the percentages by weight being calculated relative to the total weight of the monomers.

35

Further examples of grafted silicone polymers include in particular polydimethylsiloxanes (PDMS) onto which are grafted, via a chain link of

thiopropylene type, mixed polymer units of poly(meth)acrylic acid type or of poly(alkyl(meth)acrylate) type, and polydimethylsiloxanes (PDMS) onto which are grafted, via a chain link of thiopropylene type, polymer units of poly(isobutyl(meth)acrylate) type.

5

It is also possible use, as film-forming polymers, functionalized polyurethanes, containing silicone or not.

10 The polyurethanes particularly sought by the present invention are those described in the patents EP 0 751 162, EP 0 637 600, FR 2 743 297 and EP 0 648 485 and the patents EP 0 656 021 or WO 94/03510 and EP 0 619 111.

According to the invention, the anionic film-forming polymers are preferably chosen from the acrylic acid copolymers such as the acrylic acid/ethyl acrylate/  
15 N-tert-butylacrylamide terpolymers sold under the name ULTRAHOLD<sup>®</sup> STRONG by the company BASF, the copolymers derived from crotonic acid such as the vinyl acetate/vinyl tert-butylbenzoate/crotonic acid terpolymers and the crotonic acid/vinyl acetate/vinyl neododecanoate terpolymers sold in particular under the name Resine  
20 28-29-30 by the company NATIONAL STARCH, the polymers derived from itaconic, fumaric and maleic acids or anhydrides with vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives, acrylic acid and its esters such as the monoesterified maleic anhydride/methyl vinyl ether copolymers sold, for example, under the name  
GANTREZ<sup>®</sup> by the company ISP, the copolymers of methacrylic acid and of methyl methacrylate sold under the name EUDRAGIT<sup>®</sup> L by the company ROHM PHARMA,  
25 the copolymers of methacrylic acid and of ethyl acrylate sold under the name LUVIMER<sup>®</sup> MAEX or MAE by the company BASF and the vinyl acetate/crotonic acid copolymers and the vinyl acetate/crotonic acid copolymers grafted with polyethylene glycol sold under the name ARISTOFLEX<sup>®</sup> A by the company BASF and the polyurethane Luviset PUR<sup>®</sup> sold by the company BASF.

30

The anionic film-forming polymers which are most particularly preferred are those chosen from the monoesterified maleic anhydride/methyl vinyl ether copolymers sold under the name GANTREZ<sup>®</sup> ES 425 by the company ISP, the acrylic acid/ethyl acrylate/N-tert-butylacrylamide terpolymers sold under the name ULTRAHOLD<sup>®</sup>  
35 STRONG by the company BASF, the copolymers of methacrylic acid and of methyl methacrylate sold under the name EUDRAGIT<sup>®</sup> L by the company ROHM PHARMA, the vinyl acetate/vinyl tert-butylbenzoate/crotonic acid terpolymers and the crotonic acid/vinyl acetate/vinyl neododecanoate terpolymers sold under the name Resine  
28-29-30 by the company NATIONAL STARCH, the copolymers of methacrylic acid  
40 and ethyl acrylate sold under the name LUVIMER<sup>®</sup> MAEX or MAE by the company

BASF, the vinylpyrrolidone/acrylic acid/lauryl methacrylate terpolymers sold under the name ACRYLIDONE<sup>®</sup> LM by the company ISP and the polyurethane Luviset PUR<sup>®</sup> sold by the company BASF.

5 Among the amphoteric film-forming polymers which can be used, there may be mentioned those containing B and C units distributed randomly in the polymer chain where B denotes a unit which is derived from a monomer containing at least one basic nitrogen atom and C denotes a unit which is derived from an acidic monomer containing one or more carboxylic or sulphonic groups or alternatively B and C may  
10 denote groups which are derived from zwitterionic monomers of carboxybetaines or of sulphobetaines; B and C may also denote a cationic polymer chain containing primary, secondary, tertiary or quaternary amine groups, in which at least one of the amine groups carries a carboxylic or sulphonic group linked via a hydrocarbon group or alternatively B and C form part of a chain of a polymer with an  $\alpha$ -dicarboxylic ethylene  
15 unit in which one of the carboxylic groups has been caused to react with a polyamine containing one or more primary or secondary amine groups.

The amphoteric film-forming polymers corresponding to the definition given above which are more particularly preferred are chosen from the following polymers:

20

(1) The polymers resulting from the copolymerization of a monomer derived from a vinyl compound carrying a carboxylic group such as acrylic acid, methacrylic acid, maleic acid, alpha-chloroacrylic acid, and of a basic monomer derived from a substituted vinyl compound containing at least one basic atom (preferably an amino  
25 functional group) such as dialkylaminoalkyl methacrylate and acrylate, dialkylaminoalkyl methacrylamide and acrylamide. Such compounds are described in U.S. Patent No. 3 836 537. There may also be mentioned the sodium acrylate/acrylamidopropyltrimethylammonium chloride copolymer sold under the name POLYQUART KE 3033 by the company HENKEL.

30

The vinyl compound may also be a dialkyldiallylammonium salt such as diethyldiallyl ammonium chloride. The copolymers of acrylic acid and the latter monomer are offered under the names MERQUAT 280, MERQUAT 295 and MERQUAT PLUS 3330 by the company CALGON.

35

(2) The polymers containing units which are derived from:

a) at least one monomer chosen from acrylamides or methacrylamides substituted on the nitrogen atom by an alkyl group,

b) at least one acidic comonomer containing one or more reactive carboxylic groups,

40 and

c) at least one basic comonomer such as esters with primary, secondary, tertiary and quaternary amine substituents of acrylic and methacrylic acids and the product of quaternization of dimethylaminoethyl methacrylate with dimethyl or diethyl sulphate.

5 The N-substituted acrylamides or methacrylamides more particularly preferred are compounds whose alkyl groups contain from 2 to 12 carbon atoms, and more particularly N-ethylacrylamide, N-tert-butylacrylamide, N-tertoctylacrylamide, N-octylacrylamide, N-decylacrylamide, N-dodecylacrylamide as well as the corresponding methacrylamides.

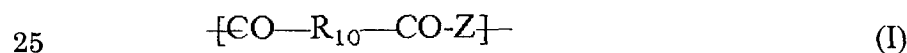
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The acidic comonomers are chosen more particularly from acrylic, methacrylic, crotonic, itaconic, maleic and fumaric acids as well as the alkyl monoesters having 1 to 4 carbon atoms of maleic or fumaric anhydrides or acids.

15 The basic comonomers preferred are methacrylates of aminoethyl, butylaminoethyl, N,N'-dimethylaminoethyl, N-tert-butylaminoethyl.

Particularly used are the copolymers whose CTFA name (4th ed., 1991) is octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer such as the products  
20 sold under the name AMPHOMER<sup>®</sup> or LOVOCRYL<sup>®</sup> 47 by the company NATIONAL STARCH.

(3) The partially or completely acylated and crosslinked polyaminoamides derived from polyaminoamides of general formula:



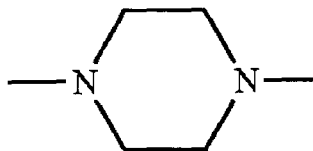
in which R<sub>10</sub> represents a divalent group derived from a saturated dicarboxylic acid, a mono- or dicarboxylic aliphatic acid with an ethylenic double bond, an ester of a lower alkanol having 1 to 6 carbon atoms of these acids or a group which is derived from the addition of any one of the said acids with a bis-primary or bis-secondary amine, and Z  
30 denotes a group which is derived from a bis-primary, mono- or bis-secondary polyalkylene-polyamine and preferably represents:

a) in a proportion of 60 to 100 mol %, the group



35 where x=2 and p=2 or 3, or alternatively x=3 and p=2, this group being derived from diethylenetriamine, triethylenetetraamine or dipropylenetriamine;

b) in a proportion of 0 to 40 mol %, the group (II) above, in which x=2 and p=1 and which is derived from ethylenediamine, or the group which is derived from piperazine:

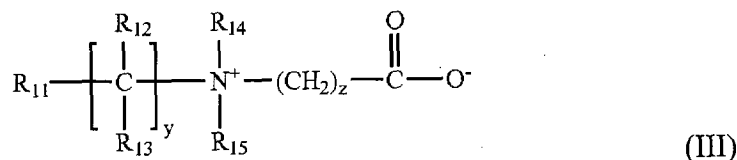


c) in a proportion of 0 to 20 mol %, the group  $\text{-NH-(CH}_2\text{)}_6\text{-NH-}$  which is derived from hexamethylenediamine, these polyamino amides being crosslinked by adding a bifunctional crosslinking agent chosen from the epihalohydrins, diepoxides, dianhydrides, bis-unsaturated derivatives, by means of 0.025 to 0.35 mol of crosslinking agent per amine group of the polyamino amide and acylated by the action of acrylic acid, chloroacetic acid or of an alkanesultone or of their salts.

The saturated carboxylic acids are preferably chosen from the acids having 6 to 10 carbon atoms such as adipic, 2,2,4-trimethyladipic and 2,4,4-trimethyladipic acids, terephthalic acid, and the acids with an ethylene double bond such as acrylic, methacrylic and itaconic acids.

The alkanesultones used in the acylation are preferably propane- or butanesultone, and the salts of the acylating agents are preferably the sodium or potassium salts.

(4) The polymers containing zwitterionic units of formula:



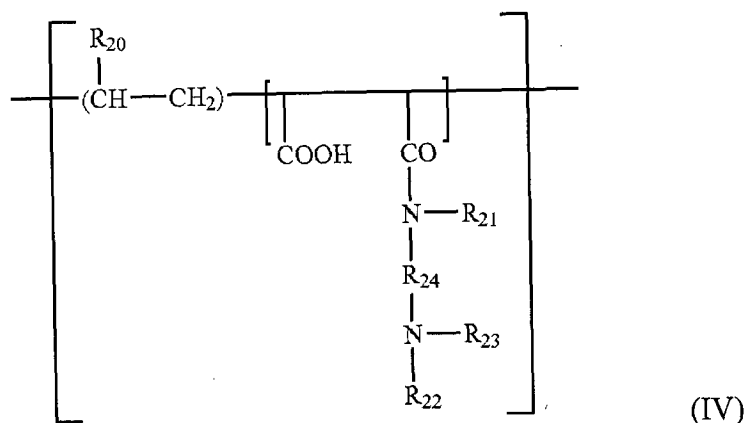
in which  $\text{R}_{11}$  denotes a polymerizable unsaturated group such as an acrylate, methacrylate, acrylamide or methacrylamide group,  $y$  and  $z$  represent an integer from 1 to 3,  $\text{R}_{12}$  and  $\text{R}_{13}$  represent a hydrogen atom or a methyl, ethyl or propyl group,  $\text{R}_{14}$  and  $\text{R}_{15}$  represent a hydrogen atom or an alkyl group such that the sum of the carbon atoms in  $\text{R}_{14}$  and  $\text{R}_{15}$  does not exceed 10.

The polymers comprising such units may also comprise units derived from nonzwitterionic monomers such as dimethyl- or diethylaminoethyl acrylate or methacrylate or alkyl acrylates or methacrylates, acrylamides or methacrylamides or vinyl acetate.

By way of example, there may be mentioned the copolymers of methyl methacrylate/ $\text{N,N}$ -dimethylcarboxyaminoethyl methacrylate.





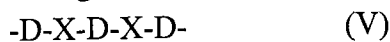


in which R<sub>20</sub> represents a hydrogen atom, a CH<sub>3</sub>O, CH<sub>3</sub>CH<sub>2</sub>O or phenyl group, R<sub>21</sub> denotes a hydrogen atom or a lower alkyl group such as methyl or ethyl, R<sub>22</sub> denotes a hydrogen atom or a C<sub>1</sub>-C<sub>6</sub> lower alkyl group such as methyl or ethyl, R<sub>23</sub> denotes a C<sub>1</sub>-C<sub>6</sub> lower alkyl group such as methyl or ethyl or a group corresponding to the formula: -R<sub>24</sub>-N(R<sub>22</sub>)<sub>2</sub>, R<sub>24</sub> representing a group -CH<sub>2</sub>-CH<sub>2</sub>-, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>- or -CH<sub>2</sub>-CH(CH<sub>3</sub>)-, R<sub>22</sub> having the meanings mentioned above.

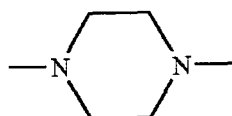
(7) The polymers derived from the N-carboxyalkylation of chitosan such as N-carboxymethyl chitosan or N-carboxybutyl chitosan.

(8) The amphoteric polymers of the -D-X-D-X- type chosen from:

a) The polymers obtained by the action of chloroacetic acid or sodium chloroacetate on the compounds containing at least one unit of formula:

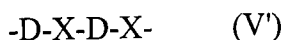


where D denotes a group

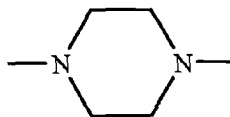


and X denotes the symbol E or E', E and E', which are identical or different, denote a bivalent group which is an alkylene group with a linear or branched chain containing up to 7 carbon atoms in the principal chain which is unsubstituted or substituted with hydroxyl groups and which may contain, in addition, oxygen, nitrogen or sulphur atoms, 1 to 3 aromatic and/or heterocyclic rings; the oxygen, nitrogen and sulphur atoms being present in the form of ether, thioether, sulphoxide, sulphone, sulphonium, alkylamine or alkenylamine groups, or hydroxyl, benzylamine, amine oxide, quaternary ammonium, amide, imide, alcohol, ester and/or urethane groups.

b) The polymers of formula:



where D denotes a group



and X denotes the symbol E or E' and, at least once, E'; E having the meaning indicated above and E' is a bivalent group which is an alkylene group with a linear or branched chain having up to 7 carbon atoms in the principal chain, which is unsubstituted or substituted with one or more hydroxyl groups and containing one or more nitrogen atoms, the nitrogen atoms being substituted with an alkyl chain optionally interrupted by an oxygen atom and necessarily containing one or more carboxyl functional groups or one or more hydroxyl functional groups and betainized by reaction with chloroacetic acid or sodium chloroacetate.

(9) The (C<sub>1</sub>-C<sub>5</sub>)alkyl vinyl ether/maleic anhydride copolymers partially modified by semiamidation with an N,N-dialkylaminoalkylamine such as N,N-dimethylaminopropylamine or by semiesterification with an N,N-dialkylaminoalkanol. These copolymers may also contain other vinyl comonomers such as vinylcaprolactam.

The preferred amphoteric film-forming polymers are those of the family (3) such as the copolymers whose CTFA name is Octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer such as the products sold under the names AMPHOMER<sup>®</sup>, AMPHOMER<sup>®</sup> LV 71 or LOVOCRYL<sup>®</sup> 47 by the company NATIONAL STARCH and those of the family (4) such as the butyl methacrylate/ N,N-dimethylcarboxyaminoethyl methacrylate copolymers.

The nonionic film-forming polymers which can be used according to the present invention may be chosen for example from:

- the homopolymers of vinyl acetate;
- the copolymers of vinyl acetate and acrylic ester;
- the copolymers of vinyl acetate and ethylene;
- the copolymers of vinyl acetate and maleic ester, for example dibutyl maleate;
- the copolymers of acrylic esters such as for example the copolymers of alkyl acrylates and alkyl methacrylates such as the products offered by the company ROHM & HAAS under the names PRIMAL<sup>®</sup> AC-261 K and EUDRAGIT<sup>®</sup> NE 30 D, by the company BASF under the name 8845, by the company HOECHST under the name APPRETAN<sup>®</sup> N9212;
- the copolymers of acrylonitrile and of a nonionic monomer chosen for example from butadiene and alkyl (meth)acrylates; there may be mentioned the products offered under

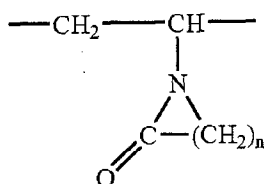
the name CJ 0601 B by the company ROHM & HAAS;

- the homopolymers of styrene;
  - the copolymers of styrene and alkyl(meth)acrylate such as the products MOWILITH<sup>®</sup> LDM 6911, MOWILITH<sup>®</sup> DM 611 and MOWILITH<sup>®</sup> LDM 6070 offered by the
  - 5 company HOECHST, the products RHODOPAS<sup>®</sup> SD 215 and RHODOPAS<sup>®</sup> DS 910 offered by the company RHODIA CHIMIE;
  - the copolymers of styrene, alkyl methacrylate and alkyl acrylate; the nonionic polyurethanes;
  - the copolymers of styrene and butadiene; the copolymers of styrene, butadiene and
  - 10 vinylpyridine;
  - the copolymers of alkyl acrylate and urethane;
  - the polyamides; and
  - the homopolymers and copolymers of vinylactam.
- 15 The alkyl groups of the nonionic polymers mentioned above preferably have from 1 to 6 carbon atoms.

According to the present invention, the film-forming polymers are preferably nonionic polymers, and better still nonionic polymers with vinylactam units. They are

20 described in particular in United States Patents 3 770 683, 3 929 735, 4 521 504, 5 158 762, 5 506 315 and in Patent Applications WO 94/121148, WO 96/06592, and WO 96/10593. They may be provided in pulverulent form or in the form of a solution or a suspension.

25 The homopolymers or copolymers with vinylactam units comprise units of formula:



in which n is independently 3, 4 or 5.

30 The number-average molecular mass of the polymers with vinylactam units is generally greater than about 5,000, preferably between approximately 10,000 and 1,000,000, and more preferably approximately between 10,000 and 100,000.

It is possible to use, in particular, as a film-forming polymer in the present invention, polyvinylpyrrolidones such as those marketed under the name Luviskol<sup>®</sup> K30 by the

35 company BASF; polyvinylcaprolactams such as those marketed under the name Luviskol<sup>®</sup> PLUS by the company BASF; poly(vinylpyrrolidone/vinyl acetate)

copolymers such as those marketed under the name PVPVA<sup>®</sup> S630L by the company ISP, Luviskol<sup>®</sup> VA 73, VA 64, VA 55, VA 37 and VA 28 by the company BASF; and poly(vinylpyrrolidone/vinyl acetate/vinyl propionate) terpolymers such as those marketed under the name Luviskol<sup>®</sup> VAP 343 by the company BASF.

5

It should be noted that, advantageously, the dry composition may comprise from 0.0001 to 80% by weight, preferably 0.01 to 40% by weight, and more preferably 0.1 to 20% by weight of the binder material, relative to the total weight of the composition.

10 Moreover, the dry composition useful in the present invention may comprise at least one additive. One or more additives may be used.

For example, the dry composition may comprise at least one plasticizer.

15 The plasticizers that are conventionally used in the field of the invention may be used in the dry composition. However, as more specific examples, there may be mentioned inter alia, urea, glycerine, sorbitol, mono- and/or disaccharides, dipropylene glycol, butylene glycol, pentylene glycol or polyethylene glycol, benzyl alcohol, or mixtures thereof.

20

Advantageously, the dry composition may comprise at least one formulation adjuvant and/or cosmetic active agent chosen for example from dispersing agents such as alkali metal lignosulphonates, antioxidants, pH-regulating agents, perfumes, silicones, and ceramides.

25

Usually, the content of the additive(s) in the dry composition may represent, for each, from 0.01 to 80% by weight, preferably 0.1 to 50% by weight, and more preferably 1 to 20% by weight; the total content of additives, if they are present, should not exceed 80% by weight of the dry composition.

30

The dry composition can be prepared by simply mixing at least one nitro dye or dyes as well as other ingredients such as at least one binder or binders. Any mixing means may be used for preparing the dry composition.

35 The dry composition in the form of a film may be prepared by:

- (i) preparing a mixture comprising at least one nitro dye mentioned above, at least one solvent, optionally at least one of said binder materials and/or said additives; and
- (ii) depositing said mixture on a heating plate so that the solvent therein is

40

evaporated.

The solvent preferably has a boiling point less than the vaporization or sublimation temperature of the nitro dye. Advantageously, the boiling point of the solvent is less than or equal to 110°C.

5

In the case that the dry composition comprises at least one binder mentioned above, the solvent entering into the mixture is preferably chosen from the compounds which solubilize or disperse at least the binder material. In the latter case, the binder materials are in the form of dispersions of solid or liquid particles of polymer (latex or pseudolatex). Moreover, the solvent furthermore has a boiling point less than the sublimation temperature of the dye and less than the degradation temperature of the binder material.

As examples of solvents which can be used in the present invention, there may be mentioned for example water, ethanol, acetone, isopropanol, ethyl acetate, dichloromethane, ethyl ether, and mixtures thereof.

Preferably, said mixture may comprise from 5 to 99.9% by weight of solvent.

The mixture may be deposited on an appropriate heating plate. As the heating plate, any plate with a heating device may be used. For example, a non-rough and horizontal heating plate can preferably used.

The mixture may be deposited in a conventional manner. Preferably, the mixture is deposited with an apparatus which makes it possible to obtain a substantially uniform film thickness.

It is preferable for the thickness of the mixture deposited to be relatively uniform. Moreover, the thickness of the mixture deposited is such that a film is obtained, preferably after the evaporation of solvent, which can be handled at room temperature. Without limitation, the thickness of the mixture deposited varies in general from 0.01 to 2 mm, preferably from 0.02 to 2 mm, and more preferably from 0.05 to 1 mm.

According to the present invention, the dry composition as described above is applied to keratin materials, in particular human keratin materials. A single type or two or more types of dry composition in combination may be used. The manner of the application is not limited, and any conventional manner of applying can be used. The dry composition may be applied to the keratin materials by using a hair brush, a comb, a glove, or a hand. Moreover, the dry composition may be placed on a support such as a film or sheet, and then the support is placed on the keratin materials such that the dry

40

composition directly contacts with the keratin materials.

After the dry composition is applied to the keratin materials, the composition and/or the keratin material is heated. The manner of the heating is not limited, and any  
5 conventional manner of heating can be used. Preferably, a source of heat is brought into contact with the dry composition and/or the keratin materials to be treated. It is preferable to apply a source of heat to the dry composition and/or the keratin material to be treated to cause the vaporization or sublimation of the nitro dye(s) comprised in the above-mentioned dry composition.

10 The source of heat may be provided in a conventional manner. As examples of such source of heat which can be used for the purpose of the present invention, there may be mentioned for example, a hair iron, hot air, hot steam, high frequency induction heating, microwave, infrared-light irradiation, UV light, visible light, ultrasonic wave, laser  
15 heating, and flash lamp irradiation, and the like.

The period for which the heat source is applied is such that the keratin material is not substantially degraded. More particularly, the physical and physicochemical properties of the keratin material are not substantially impaired. There is furthermore no  
20 substantial modification of their natural colour, or modification of their mechanical resistance properties.

Thus, the higher the temperature, the shorter the duration of treatment.

25 Advantageously, the heating temperature to cause the sublimation of the nitro dye according to the present invention may be between 100 and 600°C, preferably between 130 and 250°C, and more preferably between 140 and 220°C.

Moreover, the heating time to cause the sublimation of the nitro dye according to the  
30 present invention may be between 0.01 and 30 seconds, preferably between 0.1 and 10 seconds, and more preferably between 0.1 and 5 seconds.

Another embodiment of the present invention is a dry composition for thermal transfer  
35 process, which is used for dyeing keratin materials, in particular human keratin materials.

The expression "thermal transfer" is understood to mean, for the purposes of the present invention, the nitro dye(s) transfers from the dry composition to the keratin materials under heat. Preferably, the nitro dye(s) enters a gaseous state thereof from the solid  
40 state thereof in the dry composition under heat without passing through the liquid state

thereof, and the gaseous nitro dye(s) adhere(s) to or penetrate(s) into the keratin materials.

5 Such dry composition comprises at least one specific nitro dye as mentioned above. It is preferable that the nitro dye(s) is/are in a dispersed in the composition.

The dry composition for thermal transfer process according to the present invention may comprise at least one binder as mentioned above.

10 An another embodiment of the present invention is a laminated sheet, for a thermal transfer process, which can be used for dyeing keratin materials, in particular human keratin materials. The laminated sheet according to the present invention comprises:

- (i) a film comprising the dry composition described above; and
- (ii) a support.

15

The dry composition used in this embodiment is as explained above. A single type or two or more types of the dry compositions in combination may be used.

20 The support must be resistant to heat stimulus and be flexible to allow easy use for the coloration process. Thus, the support may advantageously be chosen from compounds which are not degraded under the conditions for carrying out the method. A single type or two or more types of supports in combination may be used.

25 The support may be chosen from compounds which do not become solubilized under the conditions for preparing said film. Thus, the support is not soluble in an aqueous medium.

Furthermore, the support may be chosen from compounds which conduct electricity or from compounds which are electrical insulators.

30

The water-soluble or water insoluble support may thus be made of a material chosen from polyurethanes, thermoplastic elastomers of the type including styrene-butadiene-styrene, styrene-ethylene-butadiene-styrene, ethylene-vinyl acetate, or coether ester, polyethylenes, polypropylenes, or silicones.

35

Such supports are sold in particular under the trade marks: BAYDUR<sup>®</sup>, DALTOFLEX<sup>®</sup>, UROFLEX<sup>®</sup>, HYPERLAST<sup>®</sup>, INSPIRE<sup>®</sup>, DESMOPAN<sup>®</sup>, ESTANE<sup>®</sup>, LASTANE<sup>®</sup>, TEXIN<sup>®</sup>, CARIFLEX<sup>®</sup>, KRATON<sup>®</sup>, SOLPRENE<sup>®</sup>, ELVAX<sup>®</sup>, ESCORENE<sup>®</sup>, OPTENE<sup>®</sup>, ARNITEL<sup>®</sup>, HYTREL<sup>®</sup>, or RITEFLEX<sup>®</sup>.

40



The material for the support may also be chosen from a paper, and a synthetic material with a high glass transition temperature such as polyester, polycarbonate, polyamide, polyimide, and polyaramid. A single type or two or more types of materials in combination may be used.

5

It would not be excluded to choose, as the support, an inorganic compound such as aluminum foil.

It is specified that the thickness of the support on which the dry composition is deposited preferably has a thickness which allows easy use for dyeing the keratin materials (easy folding, sufficient solidity to allow several applications with several foldings and unfoldings). Preferably, the thickness of the support may be between 0.001 mm and 2 mm, preferably 0.005 mm and 2 mm, and more preferably between 0.01 mm and 1 mm.

15

The laminated sheet according to the present invention can be prepared by:

- (i) preparing a mixture comprising at least one nitro dye of formula (I), at least one binder material, at least one solvent, and optionally at least one additive;
- (ii) depositing said mixture on an appropriate support; and
- (iii) heating the support so that the solvent in the mixture deposited on said support is evaporated.

20

At least one nitro dye, at least one binder material, at least one solvent, and at least one optional additive to be included in the mixture can be chosen appropriately from those specifically described above.

25

Once the mixture has been obtained, it is deposited on an appropriate support, such as a non-rough and horizontal support of the heating or non-heating bed or marble type.

Advantageously, the mixture is deposited directly on the support with which the mixture is intended to be used for dyeing, if such a variant is chosen.

30

The mixture may be deposited on the support in a conventional manner. Preferably, the mixture can be deposited with an apparatus which makes it possible to obtain a substantially uniform film thickness.

35

Furthermore, the thickness of the mixture deposited is such that a film of the dry composition can be obtained, preferably after evaporation of the solvent, which can be handled at room temperature (more particularly between 15 and 30°C). Without limitation, the thickness of the mixture deposited on the support is between 0.01 mm

40

and 2 mm, preferably between 0.02 mm and 1 mm, and more preferably between 0.05 mm and 0.5 mm.

5 After depositing the mixture on the support, the solvent is evaporated in a conventional manner to prepare a film comprising the dry composition.

In another embodiment of the present invention, the method for dyeing keratin materials, in particular human keratin materials, using said laminated sheet is provided. The method comprises the steps of:

- 10 (i) applying the laminated sheet described above to the keratin materials; and  
(ii) heating said laminated sheet and/or the keratin materials.

15 Preferably, the keratin materials are sandwiched by the laminated sheet. The laminated sheet can be then heated preferably by a source of heat so that the nitro dye comprised in the laminated sheet vaporizes or sublimates.

The heating may be performed in a conventional manner. Preferably, a source of heat may be applied to the laminated sheet and/or the keratin materials. By way of examples of such source of heat which can be used for the purpose of the present invention, there may be mentioned for example, a hair iron, hot air, hot steam, high frequency induction heating, microwave, infrared-light irradiation, UV light, visible light, ultrasonic wave, laser heating, and flash lamp irradiation, and the like.

25 Advantageously, the heating temperature to cause the sublimation of the nitro dye according to the present invention may be between 100 and 600°C, preferably between 130 and 250°C, and more preferably between 140 and 220°C.

30 Moreover, the heating time to cause the vaporization or sublimation of the nitro dye according to the present invention is between 0.01 and 30 seconds, preferably between 0.1 and 10 seconds, and more preferably between 0.1 and 5 seconds.

## EXAMPLES

35 The following examples are intended to further illustrate the present invention. They are not intended to limit the invention in any way. Unless otherwise indicated, the amounts indicated are weight percentages and are expressed relative to the total weight of the composition.

### 1. Preparation of a dyed film

40

A mixture with the following formulation was prepared by stirring the components shown in Table 1 for 20 minutes. The mixture was then deposited on a heating plate at 60°C, and the ethanol was evaporated to form a dry film.

5

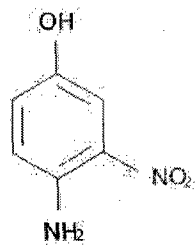
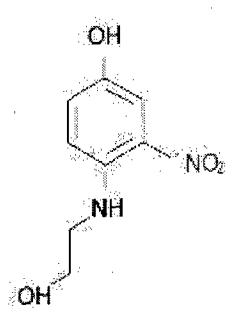
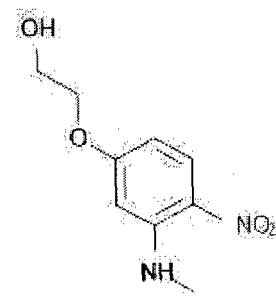
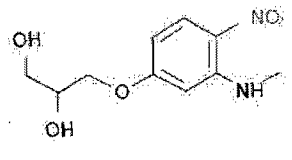
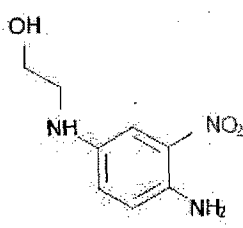
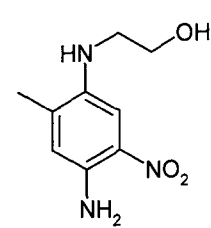
**Table 1**

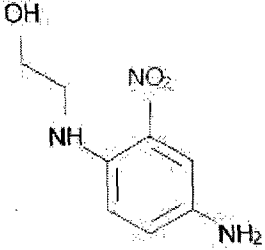
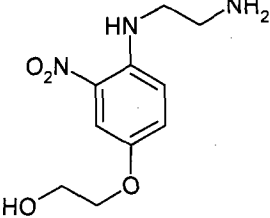
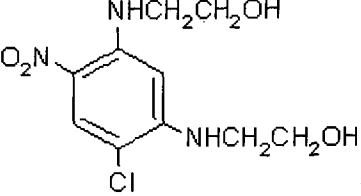
Components	Concentration
Dye	2%
Hydroxypropylcellulose (Klucel MF by the company Aqualon)	1.5%
Ethanol	qs 100%

The dye used was as follows.

10

**Table 2**

		
<b>DYE 1</b> 4-Amino-3-Nitrophenol	<b>DYE 2</b> 3-Nitro-p-Hydroxyethyl Aminophenol	<b>DYE 3</b> 3-Methylamino-4-Nitrophenoxyethanol
		
<b>DYE 4</b> 2-Nitro-5-Glyceryl Methylaniline	<b>DYE 5</b> 4-N-Hydroxyethyl-2-Nitro-1,4-Phenylenediamine	<b>DYE 6</b> 2-(4-Amino-2-Methyl-5-Nitrophenyl)aminoethanol

		
<p style="text-align: center;"><b>DYE 7</b> 4-Amino-2-Nitro-N-(Hydroxyethyl)aniline</p>	<p style="text-align: center;"><b>DYE 8</b> 1-(2-Aminoethyl)amino-4-(2-Hydroxyethyl)-Oxy-2-Nitrobenzene</p>	<p style="text-align: center;"><b>DYE 9</b> 1,5-Di(beta-Hydroxyethylamino)-2-Nitro-4-Chlorobenzene</p>

## 2. Hair dyeing

- The film obtained above was applied to a dry natural grey hair lock which is 90% white.
- 5 The hair lock was then covered with an aluminum foil.

The hair lock was thermally pressed by a hair iron with the condition of 220°C for 10 seconds. After this process, the hair lock was dyed and no rinsing was necessary.

- 10 The above hair dyeing process was performed in only a short period of time such as 10 seconds, and no solvent such as water or alcohol was used. Therefore, the above hair dyeing process was a quick and dry process. Further, since only the hair lock was dyed and no color transfer to other objects such as the hands was observed, the above hair dyeing process can realize clean coloring. Furthermore, since no rinsing is
- 15 necessary, the above hair dyeing process was environmentally friendly.

## 3. Colorimetric results ( $\Delta E$ evaluation)

- The color of the dyed hair was then measured using Minolta CM3600d
- 20 spectrophotometer (illuminant D65, angle 10°, SCI values) for the L\*, a\*, b\* colorimetric measurements.

- In this L\*, a\*, b\* system, L\* represents the intensity of the color, a\* indicates the green/red color axis and b\* indicates the blue/yellow color axis. The lower the value
- 25 of L, the darker or more intense the color. The higher the value of a\*, the redder the shade; the higher the value of b\*, the yellower the shade. The variation in coloring between the colored locks of natural white hair which is untreated (control) and after treatment are defined by  $\Delta E^*$  according to the following equation:

$$\Delta E^* = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2}$$

In this equation, L\*, a\* and b\* represent the values measured after dyeing the natural hair lock comprising 90% of white hairs and L<sub>0</sub>\*, a<sub>0</sub>\*, and b<sub>0</sub>\* represent the values measured for the untreated natural hair lock. The greater the value of ΔE\*, the greater the difference in color between the undyed lock and the dyed lock.

The value of ΔE\* for each dyed hair lock just after the dyeing process was determined. The results are shown in Table 3.

10

**Table 3**

	ΔE*
DYE 1	45
DYE 2	44
DYE 3	38
DYE 4	26
DYE 5	26
DYE 6	30
DYE 7	32
DYE 8	33
DYE 9	23

Hair lock for dye 1 was then washed with warm water and shampooed ten times. After being dried, ΔE\* value of the shampooed dyed hair was once again determined using the same method shown above. The results are shown in Table 4.

15

**Table 4**

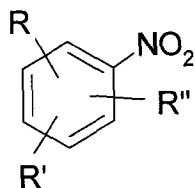
	ΔE*
DYE 1	45

20

By comparing the results of evaluation shown in Tables 3 and 4, it is apparent that the dyeing process according to the present invention was also very resistant toward post-washing operations.

## CLAIMS

1. A method for dyeing keratin materials, in particular human keratin materials, comprising the steps of:
- 5 (i) applying at least one dry composition comprising at least one nitro dye to said keratin materials; and
- (ii) heating said dry composition and/or said keratin materials to cause the vaporization or the sublimation of the nitro dye(s);
- wherein said nitro dye(s) corresponds to the following formula (I):



(I)

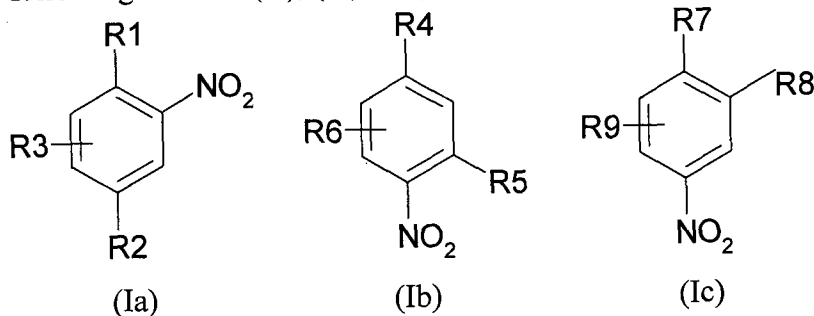
10 in which:

**R** represents -NH<sub>2</sub>, -NHC<sub>2</sub>H<sub>4</sub>OH, -NHC<sub>3</sub>H<sub>6</sub>OH, -NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>, -OC<sub>2</sub>H<sub>4</sub>OH, -NHCH<sub>3</sub>, or -OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH;

**R'** represents -OH, -OCH<sub>3</sub>, -N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>, -NH<sub>2</sub>, -NHC<sub>2</sub>H<sub>4</sub>OH, -OC<sub>2</sub>H<sub>4</sub>OH, -N(C<sub>2</sub>H<sub>4</sub>OH)(C<sub>2</sub>H<sub>5</sub>), -OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH, or -NHCH<sub>3</sub>; and

15 **R''** represents a hydrogen atom, a halogen atom, or an alkyl radical.

2. The method according to Claim 1, characterized in that the nitro dye corresponds to the following formula (Ia), (Ib), or (Ic):



wherein:

20 **R1** represents -NH<sub>2</sub>, -NHC<sub>2</sub>H<sub>4</sub>OH, -NHC<sub>3</sub>H<sub>6</sub>OH, or -NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>;

**R2** represents -OH, -N(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>, -NH<sub>2</sub>, -OC<sub>2</sub>H<sub>4</sub>OH, or -N(C<sub>2</sub>H<sub>4</sub>OH)(C<sub>2</sub>H<sub>5</sub>);

**R3** represents a hydrogen atom or an alkyl radical;

**R4** represents -OCH<sub>3</sub>, -OC<sub>2</sub>H<sub>4</sub>OH, -OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH, or -NHC<sub>2</sub>H<sub>4</sub>OH;

**R5** represents -NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>, -NHCH<sub>3</sub>, or -NHC<sub>2</sub>H<sub>4</sub>OH;

25 **R6** represents a hydrogen atom or a halogen atom;

**R7** represents -OH or -NHC<sub>2</sub>H<sub>4</sub>OH;

**R8** represents -NH<sub>2</sub> or -OCH<sub>3</sub>, and

**R9** represents a hydrogen atom or a halogen atom.

3. The method according to Claim 1 or 2, characterized in that the nitro dye is selected from the group consisting of 4-amino-3-nitrophenol,  
5 3-nitro-*para*-hydroxyethyl aminophenol, 3-methylamino-4-nitrophenoxyethanol, 2-nitro-5-glycerylmethylaniline, HC Red No. 7, HC Violet No. 1, HC Red No. 3, HC Orange No. 2, HC Yellow No. 10, and mixtures thereof.
- 10 4. The method according to any one of Claims 1 to 3, characterized in that the heating temperature is between 100 and 600°C, preferably between 130 and 250°C, and more preferably between 140 and 220°C.
- 15 5. The method according to any one of Claims 1 to 4, characterized in that the heating time is between 0.01 and 30 seconds, preferably 0.1 and 10 seconds, and more preferably 0.1 to 5 seconds.
6. The method according to any one of Claims 1 to 5, characterized in that the dry composition is in the form of a film.
- 20 7. The method according to any one of Claims 1 to 6, characterized in that the dry composition comprises at least one binder material.
- 25 8. The method according to Claim 7, characterized in that the binder material is selected from the group consisting of film-forming polymers; celluloses; plastics such as polyester, polystyrene, ketone resin, epoxy resin, terpene phenol resin, polyamide, polysulfone, polyethersulfone, polyvinyl butyral, acrylonitrile, styrene resin and polyacrylate; and waxes such as carnauba wax and paraffin wax.
- 30 9. A laminated sheet, comprising:
  - (i) a film comprising the composition according to any one of Claims 1 to 8; and
  - (ii) a support.
- 35 10. The laminated sheet according to Claim 9, characterized in that the support comprises at least one material selected from the group consisting of an aluminum foil, a paper, and a synthetic material with a high glass transition temperature such as polyester, polycarbonate, polyamide, polyimide, and polyaramid.
- 40

11. A method for dyeing keratin materials, in particular human keratin materials, comprising the steps of:
- (i) applying the laminated sheet according to Claim 9 or 10 to the keratin materials; and
  - 5 (ii) heating the laminated sheet and/or the keratin materials.
12. The method according to Claim 11, characterized in that the heating temperature is at a temperature between 100 and 600°C, preferably between 130 and 250°C, and more preferably between 140 and 220°C, and the heating time is between
- 10 0.01 and 30 seconds, preferably between 0.1 and 10 seconds, and more preferably between 0.1 and 5 seconds.



INTERNATIONAL SEARCH REPORT

International application No  
PCT/JP2011/075238

A. CLASSIFICATION OF SUBJECT MATTER  
INV. A61K8/41 A61Q5/06  
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)  
A61K A61Q  
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 practicable, search terms used)  
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

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Date of the actual completion of the international search  10 September 2012	Date of mailing of the international search report  20/09/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Yon, Jean-Michel

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International application No  
PCT/JP2011/075238

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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