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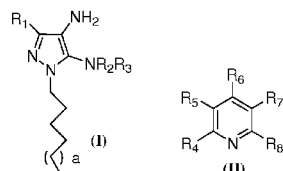
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(54) Title: OXIDATIVE DYEING COMPOSITIONS COMPRISING AN 1-HEXYL/HEPTYL-4,5-DIAMINOPYRAZOLE AND A PYRIDINE AND DERIVATIVES THEREOF



(57) Abstract: A composition for the oxidative dyeing of keratin fibers, in particular human keratin fibers, comprising (A) a 1-hexyl/heptyl-4,5-diaminopyrazole compound of the general formula (I), its physiologically compatible water-soluble salt, or mixtures thereof; (B) a pyridine compound of the general formula (II), its physiologically compatible water-soluble salt, or mixtures thereof; and (C) an oxidizing agent, wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 and R_8 are as defined herein and $a = 1$ or 2.

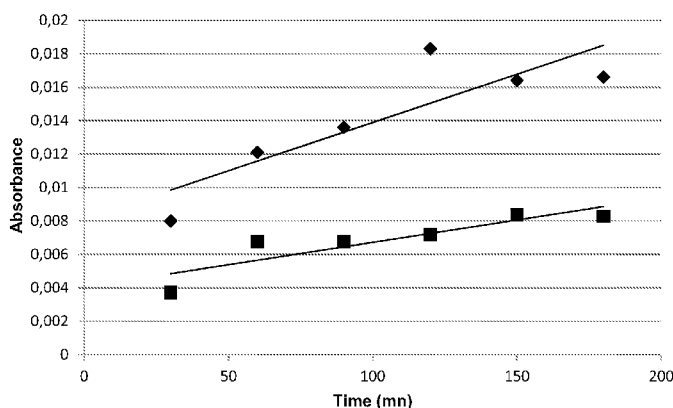


Fig. 1



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OXIDATIVE DYEING COMPOSITIONS COMPRISING AN 1-HEXYL/HEPTYL-4,5-
DIAMINOPYRAZOLE AND A PYRIDINE AND DERIVATIVES THEREOF

FIELD OF THE INVENTION

The present invention relates to a composition for the oxidative dyeing of keratin fibers,
5 in particular human keratin fibers, comprising (A) a 1-hexyl/heptyl-4,5-diaminopyrazole
compound as defined in formula (I) hereafter, its physiologically compatible water-soluble salt,
or mixtures thereof, (B) a pyridine compound of the general formula (II) as defined hereafter, its
physiologically compatible water-soluble salt, or mixtures thereof, and (C) an oxidizing agent.

BACKGROUND OF THE INVENTION

10 The oxidative dyeing of hair is one of the most extensively used methods to color hair. In
this process oxidative hair coloring precursors are used in combination with an oxidizing agent,
commonly a peroxy oxidizing agent. The precursors are generally small molecules capable of
diffusing into hair, generally comprising primary intermediates and couplers. A wide variety of
primary intermediates and couplers have been employed in such oxidative hair coloring
15 compositions. Selections of specific combinations of couplers and primary intermediates allow
reaching the desired nuance of hair color.

Besides providing the desired color, the dye precursors used for oxidative hair dyeing
have to also meet some additional requirements. Indeed, the combination of couplers and primary
intermediates used should deliver the desired intensity together with good wash and bleeding
20 fastness and be acceptable from a toxicological and dermatological point of view.

Pyrazole compounds have been disclosed as oxidative dye precursors. A colorant for
keratin fibers comprising a pyrazole derivative (I), a *m*-aminophenol derivative (II) and a
pyridine derivative (III) is known. See for example EP 1166748A2.

The compositions of the prior art comprising pyrazole compounds are not satisfactory
25 especially in terms of intensity, wash fastness and bleeding.

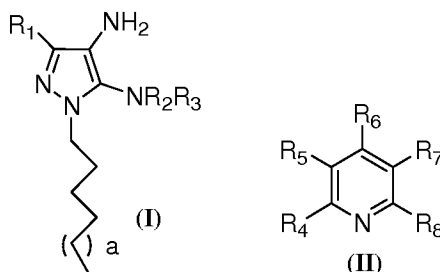
Furthermore, these disclosures do not disclose an example with a selection of a C6/C7
straight chain alkyl substituent on the N-1 position of a 4,5-diaminopyrazole.

The invention provides novel dye compositions that overcome known drawbacks of
pyrazole compounds. In particular the invention provides good hair color intensity together with
30 good wash and bleeding fastness. Indeed, it has surprisingly been found that the modification of

the pyrazole ring system on the N-1 position by a C6/C7 straight alkyl chain combined with pyridine couplers provides excellent properties of resistance to the various treatments which keratinous fibers may undergo.

SUMMARY OF THE INVENTION

The present invention relates to a composition for the oxidative dyeing of keratin fibers, in particular human keratin fibers comprising (A) a 1-hexyl/heptyl-4,5-diaminopyrazole compound of the general formula (I), its physiologically compatible water-soluble salt, or mixtures thereof; (B) a pyridine compound of the general formula (II), its physiologically compatible water-soluble salt, or mixtures thereof; and (C) an oxidizing agent.



wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 and R_8 are as defined in the claims and $a = 1$ or 2 .

The present invention also relates to a method of dyeing hair comprising the steps of applying this composition to hair, and to a kit comprising: (i) a tint component comprising at least (a) a 1-hexyl/heptyl-4,5-diamino pyrazole compound of the general formula (I), its physiologically compatible water-soluble salt, or mixtures thereof, (b) a pyridine compound of the general formula (II), its physiologically compatible water-soluble salt, or mixtures thereof, and (ii) a developer component comprising (c) an oxidizing agent.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a graph demonstrating the Solution Diffusion Testing results of a 1-pentyl- and 1-hexyl-4,5-diamino pyrazole with 2,6-dimethoxypyridine-3,5-diamine (compound of formula (II.2)).

Figure 2 shows a graph demonstrating the Solution Diffusion Testing results of a 1-pentyl- and 1-hexyl-4,5-diamino pyrazole with 2,6-dimethoxypyridine-3,5-diamine and 2,5-toluenediamine sulfate (DTS).

DETAILED DESCRIPTION OF THE INVENTION

Definitions

As used herein, the term “composition for the oxidative dyeing of keratin fibers” means a

ready-to-use composition in a suitable carrier medium for dyeing keratin fibers, in particular human hair, comprising oxidative dye precursors (primary intermediates and couplers) and an oxidizing agent. These compositions can typically be the result of a mixture of two compositions namely a tint component comprising the dye precursors and usually an alkalizing agent such as ammonia and/or monoethanolamine and a developer component comprising the oxidizing agent.

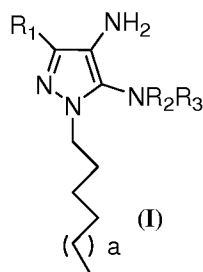
As used herein, the term "keratin" refers to a scleroprotein found in epidermal tissues and modified into hard structures such as horns, hair, and nails. As used herein, the term "hair" refers to keratinous fibers on a living, e.g. a person, or non-living body, e.g. in a wig, hairpiece, or other aggregation of non-living keratinous fibers. Mammalian, preferably human, hair is preferred. Notably, hair, wool, fur, and other keratinous fibers are suitable substrates for coloring by the compounds and compositions described herein.

As used herein, the term "dye precursors" refers to compounds that may be used in the composition to act as primary intermediates, couplers, or both, in order to provide color to keratinous fibers.

It is to be understood that when this development refers to a particular structure, all of the reasonable additional tautomeric structures are included. In the art, tautomeric structures are frequently represented by one single structure and the invention follows this general practice.

Pyrazole compound

The 1-hexyl/heptyl-4,5-diaminopyrazole compound of the invention is of the general formula (I), its physiologically compatible water-soluble salt, or mixtures thereof:



wherein a is equal to one or two;

wherein R₁ is selected from the group consisting of:

(a) C-linked substituents selected from the group consisting of:

(i) substituted or unsubstituted, straight or branched or cyclic, saturated or unsaturated, aliphatic or heteroaliphatic substituents, in particular alkyl or hydroxy substituted alkyl,

(ii) substituted or unsubstituted, mono- or poly- unsaturated aromatic or heteroaromatic substituents, in particular aryl or heteroaryl,

wherein said C-linked substituents comprise from 1 to 6 carbon atoms and from 0 to 5 heteroatoms selected from the group consisting of O, F, N, P and Si;

5 (b) S-linked substituents selected from the group consisting of SA^1 , SO_2A^1 , SO_3A^1 , SSA^1 , SOA^1 , $SO_2NA^1A^2$, SNA^1A^2 , and $SONA^1A^2$;

(c) O-linked substituents selected from the group consisting of OA^1 , ONA^1A^2 ;

(d) N-linked substituents selected from the group consisting of NA^1A^2 ; $(NA^1A^2A^3)^+$, NA^1SA^2 , NO_2 ; NA^1A^2 ;

10 (e) halogens selected from the group consisting of F, Cl, Br, and I; and

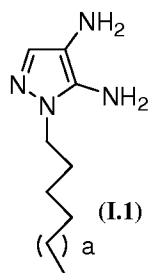
(f) hydrogen;

wherein A^1 , A^2 , and A^3 are independently selected from the group consisting of hydrogen; substituted or unsubstituted, straight or branched or cyclic, saturated or unsaturated, aliphatic or heteroaliphatic or aromatic or heteroaromatic substituents, preferably substituted or unsubstituted
15 alkyl, or A^1 and A^2 together with nitrogen atoms to which they are bound form a ring; wherein said substituents or ring comprise from 1 to 6 carbon atoms and from 0 to 5 heteroatoms selected from the group consisting of O, S, N, P, and Si;

R_2 and R_3 are selected independently of each other from the group consisting of a hydrogen atom; a C1-C6 alkyl substituent; a trifluoromethyl substituent; a C1-C6 aminoalkyl substituent; a C1-C6 hydroxyalkyl substituent; C1-C6 an alkoxyalkyl substituent.
20

Suitable salts of formula (I) are for example chlorides, bromides, sulfates, malates, tartrates, lactates and acetates. Of particular interest is the hemisulfate salt, which can provide a better stability during storage than other salts such as chloride or sulfate.

In a preferred embodiment the 1-hexyl/heptyl-4,5-diaminopyrazole compound (I) is a
25 compound with formula (I.1):



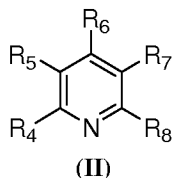
wherein a is equal to one or two.

The 1-hexyl/heptyl-4,5-diaminopyrazole compounds of formula (I) are combined with a

pyridine compound of formula (II) in order to provide a resulting hair color with excellent washfastness, bleeding fastness, and intensity.

Pyridine compound

The pyridine compound of the invention is according to the general formula (II) below,
5 or a physiologically compatible water-soluble salt:



wherein R₄, R₅, R₆, R₇ and R₈ are substituents selected independently of each other from the group consisting of:

(a) C-linked substituents selected from the group consisting of:

10 (i) substituted or unsubstituted, straight or branched or cyclic, saturated or unsaturated, aliphatic or heteroaliphatic substituents, in particular alkyl or hydroxy substituted alkyl,

(ii) substituted or unsubstituted, mono- or poly- unsaturated aromatic or heteroaromatic substituents, in particular aryl or heteroaryl,

15 wherein said C-linked substituents comprise from 1 to 6 carbon atoms and from 0 to 5 heteroatoms selected from the group consisting of O, F, N, P and Si;

(b) S-linked substituents selected from the group consisting of SA¹, SO₂A¹, SO₃A¹, SSA¹, SOA¹, SO₂NA¹A², SNA¹A², and SONA¹A²;

(c) O-linked substituents selected from the group consisting of OA¹, ONA¹A²;

20 (d) N-linked substituents selected from the group consisting of NA¹A²; (NA¹A²A³)⁺, NA¹SA², NO₂; NA¹A²;

(e) halogens selected from the group consisting of F, Cl, Br, and I; and

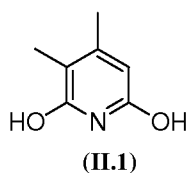
(f) hydrogen;

wherein A¹, A², and A³ are independently selected from the group consisting of hydrogen;
25 substituted or unsubstituted, straight or branched or cyclic, saturated or unsaturated, aliphatic or heteroaliphatic or aromatic or heteroaromatic substituents, preferably substituted or unsubstituted alkyl, or A¹ and A² together with nitrogen atoms to which they are bound form a ring; wherein said substituents or ring comprise from 1 to 6 carbon atoms and from 0 to 5 heteroatoms selected from the group consisting of O, S, N, P, and Si.

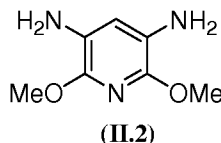
Suitable salts of formula (II) are for example chlorides, bromides, sulfates, malates, tartrates, lactates and acetates.

In preferred embodiments, R₄, R₅, R₆, R₇ and R₈ are independently selected from hydrogen, hydroxyl, C1-C6 alkyl, C2-C6 hydroxyalkyl, amino, C1-C6 alkylamino, C2-C6 hydroxyalkylamino, C1-C6 alkoxy and mixtures thereof. Preferred pyridine derivatives of formula (II) are 3,4-dimethylpyridine-2,6-diol, pyridine-2,6-diamine, 2,6-dimethoxypyridine-3,5-diamine, 6-methoxy-N2-methylpyridine-2,3-diamine, and 2-aminopyridin-3-ol.

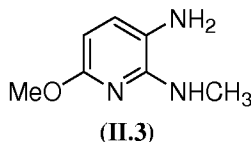
In a more preferred embodiment the pyridine derivative (II) is a compound with formula (II.1):



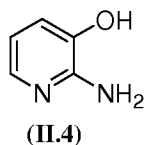
In a preferred embodiment the pyridine derivative (II) is a compound with formula (II.2):



In a preferred embodiment the pyridine derivative (II) is a compound with formula (II.3):

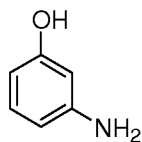


In a preferred embodiment the pyridine derivative (II) is a compound with formula (II.4):



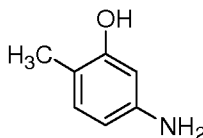
The hair dyeing composition of the present invention further may be comprised of an auxiliary coupler. In a preferred embodiment the auxiliary coupler is a compound with formula (III.1):

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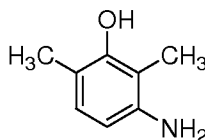
(III.1)

In a preferred embodiment the auxiliary coupler is a compound with formula (III.2):



(III.2)

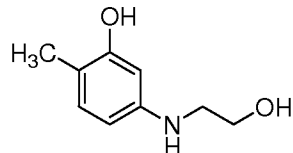
In a preferred embodiment the auxiliary coupler is a compound with formula (III.3):



(III.3)

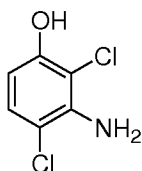
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In a preferred embodiment the auxiliary coupler is a compound with formula (III.4):



(III.4)

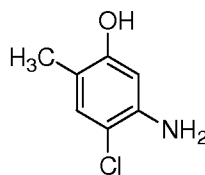
In a preferred embodiment the auxiliary coupler is a compound with formula (III.5):



(III.5)

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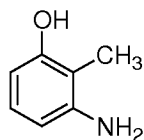
In a preferred embodiment the auxiliary coupler is a compound with formula (III.6):



(III.6)

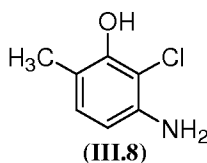
In a preferred embodiment the auxiliary coupler is a compound with formula (III.7):

8



(III.7)

In another preferred embodiment the *m*-aminophenol compound (III) is a compound with formula (II.8):



(III.8)

5 It has surprisingly been found that the modification of the pyrazole ring system in N-1-position by a C6/C7 straight alkyl chain provides a dye precursor which couples with a pyridine compound to give excellent properties of resistance to the various treatments which keratinous fibers may undergo, in particular washfastness and resistance to bleeding.

Oxidizing Agent

10 The compositions of the invention comprise an oxidizing agent. Typical suitable oxidizing agents for the oxidative dyeing of keratin fibers may be selected from hydrogen peroxide, sodium periodate, urea peroxide, melamine peroxide, perborates, percarbonates, perphosphates, persilicates, persulfates, oxidizing enzymes such as uricases, oxidases, and peroxidises, and mixtures thereof. Hydrogen peroxide, perborates, or percarbonates may be
15 preferred.

Another potential oxidizing agent for use herein is a source of peroxymonocarbonate ions. Preferably, such a source is formed in situ from a source of hydrogen peroxide and a hydrogen carbonate ion source. Such an oxidizing agent has been found to be particularly effective at a pH of up to and including 9.5, preferably from about 7.5 to about 9.5 more
20 preferably about pH 9. Moreover, this system is also particularly effective in combination with a source of ammonia or ammonium ions.

Accordingly, any source of these peroxymonocarbonate ions may be utilized. Suitable sources for use herein include sodium, potassium, guanidine, arginine, lithium, calcium, magnesium, barium or ammonium salts of carbonate, carbamate and hydrocarbonate ions and
25 mixtures thereof. In particular, sodium carbonate, sodium hydrogen carbonate, potassium carbonate, potassium hydrogen carbonate, guanidine carbonate, guanidine hydrogen carbonate,

lithium carbonate, calcium carbonate, magnesium carbonate, barium carbonate, ammonium carbonate, ammonium hydrogen carbonate and mixtures thereof may be preferred. Percarbonate salts may also be utilized to provide both the source of carbonate ions and as an oxidizing agent. Preferred sources of carbonate ions, carbamate and hydrocarbonate ions are sodium hydrogen carbonate, potassium hydrogen carbonate, ammonium carbonate, ammonium carbamate, and mixtures thereof.

The hair dyeing composition may usually comprise from about 1% to about 15% by total weight of the composition, typically from about 1.5% to about 10% by weight, and more typically from about 2% to about 8% by weight of the oxidizing agent relative to the total weight of the composition.

The oxidizing agent may be provided in a developer component which is mixed to a tint component to obtain the composition of the invention. The developer component may be based on any desired formulation chassis, including any commercial product, for example an oil-in-water emulsion. Typical developer components comprise about 6% or about 9% of H₂O₂ by total weight of the composition. A commercial example is the Welloxon® Emulsion with respectively about 6% and about 9% H₂O₂, marketed by Wella and comprising as INCI ingredients: Water, Hydrogen Peroxide, Cetearyl Alcohol, Cetareth-25, Salicylic Acid, Phosphoric Acid, Disodium Phosphate, Etidronic Acid.

The hair dyeing composition of the invention may be formed as thick liquid, cream, gel, emulsion, foam, aerosol mousse or as a solid form to which water is added to generate the oxidant and form a thickened vehicle suitable for hair coloring. They may comprise in addition to the ingredients indicated above further ingredients in order to further enhance the properties of the composition, including but not limited to: solvents; oxidative dyes, direct dyes; oxidizing agents; radical scavengers; thickeners and or rheology modifiers; chelants; pH modifiers and buffering agents; carbonate ion sources; peroxy monocarbonate ion sources; anionic, cationic, nonionic, amphoteric or zwitterionic surfactants, or mixtures thereof; anionic, cationic, nonionic, amphoteric or zwitterionic polymers, or mixtures thereof; fragrances; enzymes; dispersing agents; peroxide stabilizing agents; antioxidants; natural ingredients, e.g. proteins and protein compounds, and plant extracts; conditioning agents including silicones and cationic polymers, ceramides, preserving agents; and opacifiers and pearling agents (such as titanium dioxide and mica). Some adjuvants referred to above, but not specifically described below, which are suitable are listed in the International Cosmetics Ingredient Dictionary and Handbook, (8th ed.; The Cosmetics, Toiletry, and Fragrance Association). Particularly, vol. 2, sections 3 (Chemical

Classes) and 4 (Functions) are useful in identifying specific adjuvants to achieve a particular purpose or multipurpose. A few of these ingredients are discussed hereinbelow, whose disclosure is of course non-exhaustive.

Alkalizing agent

5 The composition for the oxidative dyeing of keratin fibers may further comprise, generally in the tint component, an alkalizing agent as known in the art. Any alkalizing agent known in the art may be used such as ammonia, alkanolamines for example monoethanolamine, diethanolamine, triethanolamine, monopropanolamine, dipropanolamine, tripropanolamine, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-methyl-1-propanol, and 2-amino-2-hydroxymethyl-
10 1,3-propanediol, guanidium salts, alkali metal and ammonium hydroxides such as sodium hydroxide, alkali metal and ammonium carbonates, and mixtures thereof. Typical alkalizing agents are ammonia and/or monoethanolamine.

Typically, the compositions for the oxidative dyeing of keratin fibers comprise from about 0.1% to about 10%, preferably from about 0.5% to about 6%, more preferably from about
15 1% to about 4% by weight of the alkalizing agent relative to the total weight of the composition.

Primary intermediates

In addition to the pyrazole compounds of the invention, the hair dyeing compositions of the invention may comprise further primary intermediates. Suitable primary intermediates for use in the compositions described herein include, but are not limited to: toluene-2,5-diamine, p-
20 phenylenediamine, *N*-phenyl-p-phenylenediamine, *N,N*-bis(2-hydroxyethyl)-p-phenylenediamine, 2-hydroxyethyl-p-phenylenediamine, hydroxypropyl-bis-(*N*-hydroxyethyl-p-phenylenediamine), 2-methoxymethyl-p-phenylenediamine, 2-(1,2-dihydroxyethyl)-p-phenylenediamine, 2,2'-(2-(4-aminophenylamino)ethylazanediyl)diethanol, 2-(2,5-diamino-4-methoxyphenyl)propane-1,3-diol, 2-(7-amino-2H-benzo[b][1,4]oxazin-4(3H)-yl)ethanol, 2-
25 chloro-p-phenylenediamine, p-aminophenol, p-(methylamino)phenol, 4-amino-m-cresol, 2-methoxy-p-phenylenediamine, 2,2'-methylenebis-4-aminophenol, 2,4,5,6-tetraminopyrimidine, 2,5,6-triamino-4-pyrimidinol, 1-hydroxyethyl-4,5-diaminopyrazole sulfate, 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-ethylpyrazole, 4,5-diamino-1-isopropylpyrazole, 4,5-diamino-1-butylpyrazole, 4,5-diamino-1-pentylpyrazole, 4,5-diamino-1-benzylpyrazole, 2,3-diamino-6,7-
30 dihydropyrazolo[1,2-a]pyrazol-1(5H)-one dimethosulfonate, salts thereof (for example chlorides, bromides, sulfates, malates, tartrates, lactates and acetates) and mixtures thereof.

Of particular interest are toluene-2,5-diamine, p-phenylenediamine, 2-hydroxyethyl-p-phenylenediamine, 2-methoxymethyl-p-phenylenediamine, 2-(2,5-diamino-4-methoxyphenyl)propane-1,3-diol, 2-chloro-p-phenylenediamine, 2-methoxy-p-phenylenediamine, 2-((2-(4-amino-phenylamino)-ethyl)-(2-hydroxyethyl)-amino)-ethanol, their salts thereof (for example chlorides, bromides, sulfates, malates, tartrates, lactates and acetates) and combinations.

Typically, the compositions for the oxidative dyeing of keratin fibers comprise from about 0.1% to about 10%, preferably from about 0.3% to about 6%, more preferably from about 0.5% to about 4% by weight of the primary intermediates relative to the total weight of the composition.

Couplers

In addition to the pyridine compounds of the invention, the hair dyeing compositions of the invention may comprise other couplers to obtain various shades. Suitable couplers for use in the compositions described herein include, but are not limited to: resorcinol, 4-chlororesorcinol, 2-chlororesorcinol, 2-methylresorcinol, 4,6-dichlorobenzene-1,3-diol, 2,4-dimethylbenzene-1,3-diol, *m*-aminophenol, 4-amino-2-hydroxytoluene, 2-methyl-5-hydroxyethylaminophenol, 3-amino-2,6-dimethylphenol, 3-amino-2,4-dichlorophenol, 5-amino-6-chloro-*o*-cresol, 5-amino-4-chloro-*o*-cresol, 6-hydroxybenzomorpholine, 2-amino-5-ethylphenol, 2-amino-5-phenylphenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 2-amino-5-ethoxyphenol, 5-methyl-2-(methylamino)phenol, 2,4-diaminophenoxyethanol, 2-amino-4-hydroxyethylaminoanisole, 1,3-bis-(2,4-diaminophenoxy)-propane, 2,2'-(2-methyl-1,3-phenylene)bis(azanediyl)diethanol, benzene-1,3-diamine, 2,2'-(4,6-diamino-1,3-phenylene)bis(oxy)diethanol, 3-(pyrrolidin-1-yl)aniline, 1-(3-(dimethylamino)phenyl)urea, 1-(3-aminophenyl)urea, 1-naphthol, 2-methyl-1-naphthol, 1,5-naphthalenediol, 2,7-naphthalenediol or 1-acetoxy-2-methylnaphthalene, 4-chloro-2-methylnaphthalen-1-ol, 4-methoxy-2-methylnaphthalen-1-ol, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dimethoxy-3,5-pyridinediamine, 3-amino-2-methylamino-6-methoxypyridine, 2-amino-3-hydroxypyridine, 2,6-diaminopyridine, pyridine-2,6-diol, 5,6-dihydroxyindole, 6-hydroxyindole, 5,6-dihydroxyindoline, 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one, 1,2,4-trihydroxybenzene, 2-(benzo[d][1,3]dioxol-5-ylamino)ethanol (also known as hydroxyethyl-3,4-methylenedioxyaniline), and mixtures thereof.

When the composition is obtained by mixing a tint component and a developer component, additional primary intermediates and couplers may be preferably incorporated in the

tint component.

Typically, the compositions for the oxidative dyeing of keratin fibers comprise from about 0.1% to about 10%, preferably from about 0.3% to about 6%, more preferably from about 0.5% to about 4% by weight of the couplers relative to the total weight of the composition.

5 **Direct Dyes**

The compositions of the present invention may also comprise compatible direct dyes, in an amount sufficient to provide additional coloring, particularly with regard to intensity. Typically, such an amount will range from about 0.05% to about 4%, by weight of the direct dyes relative to the total weight of the composition. When the composition is obtained by mixing a tint
10 component and a developer component, the direct dyes are usually incorporated in the tint component.

The following direct dyes are commonly used: Acid dyes such as Acid Yellow 1, Acid Orange 3, Acid Black 1, Acid Black 52, Acid Orange 7, Acid Red 33, Acid Yellow 23, Acid Blue 9, Acid Violet 43, HC Blue 16, Acid Blue 62, Acid Blue 25, Acid Red 4, Basic Dyes such
15 as Basic Brown 17, Basic Red 118, Basic Orange 69, Basic Red 76, Basic Brown 16, Basic Yellow 57, Basic Violet 14, Basic Blue 7, Basic Blue 26, Basic Red 2, Basic Blue 99, Basic Yellow 29, Basic Red 51, Basic Orange 31, Basic Yellow 87, 4-(3-(4-amino-9,10-dioxo-9,10-dihydroanthracen-1-ylamino)propyl)-4-methylmorpholin-4-ium-methylsulfate, (*E*)-1-(2-(4-(4,5-dimethylthiazol-2-yl)diazenyl)phenyl)(ethylamino)ethyl)-3-methyl-1H-imidazol-3-ium chloride,
20 (*E*)-4-(2-(4-(dimethylamino)phenyl)diazenyl)-1-methyl-1H-imidazol-3-ium-3-yl)butane-1-sulfonate, (*E*)-4-(4-(2-methyl-2-phenylhydrazono)methyl)pyridinium-1-yl)butane-1-sulfonate, N,N-dimethyl-3-(4-(methylamino)-9,10-dioxo-4a,9,9a,10-tetrahydroanthracen-1-ylamino)-N-propylpropan-1-aminium bromide, Disperse Dyes such as Disperse Red 17, Disperse Violet 1, Disperse Red 15, Disperse Violet 1, Disperse Black 9, Disperse Blue 3, Disperse Blue 23,
25 Disperse Blue 377, Nitro Dyes such as 1-(2-(4-nitrophenylamino)ethyl)urea, 2-(4-methyl-2-nitrophenylamino)ethanol, 4-nitrobenzene-1,2-diamine, 2-nitrobenzene-1,4-diamine, Picramic acid, HC Red No. 13, 2,2'-(2-nitro-1,4-phenylene)bis(azanediyl)diethanol, HC Yellow No. 5, HC Red No. 7, HC Blue No.2, HC Yellow No. 4, HC Yellow No. 2, HC Orange No. 1, HC Red No. 1, 2-(4-amino-2-chloro-5-nitrophenylamino)ethanol, HC Red No. 3, 4-amino-3-nitrophenol, 4-(2-hydroxyethylamino)-3-nitrophenol,
30 2-amino-3-nitrophenol, 2-(3-(methylamino)-4-nitrophenoxy)ethanol, 3-(3-amino-4-nitrophenyl)propane-1,2-diol, HC Yellow No. 11, HC Violet No. 1, HC Orange No. 2, HC Orange No. 3, HC Yellow No. 9, HC Red No. 10, HC Red No. 11,

2-(2-hydroxyethylamino)-4,6-dinitrophenol, HC Blue No. 12, HC Yellow No. 6, HC Yellow No. 12, HC Blue No. 10, HC Yellow No. 7, HC Yellow No. 10, HC Blue No. 9, 2-chloro-6-(ethylamino)-4-nitrophenol, 6-nitropyridine-2,5-diamine, HC Violet No. 2, 2-amino-6-chloro-4-nitrophenol, 4-(3-hydroxypropylamino)-3-nitrophenol, HC Yellow No. 13, 6-nitro-1,2,3,4-tetrahydroquinoxaline, HC Red No. 14, HC Yellow No. 15, HC Yellow No. 14, N2-methyl-6-nitropyridine-2,5-diamine, N1-allyl-2-nitrobenzene-1,4-diamine, HC Red No. 8, HC Green No.1, HC Blue No. 14, and Natural dyes such as Annato, Anthocyanin, Beetroot, Carotene, Capsanthin, Lycopene, Chlorophyll, Henna, Indigo, Cochineal.

Thickeners

10 The hair dyeing compositions of the present invention may comprise a thickener in an amount sufficient to provide the composition with a viscosity so that it can be readily applied to the hair without unduly dripping off the hair and causing mess. Typically, such an amount will be at least 0.05%, preferably at least 0.5%, more preferably at least 1%, by weight of thickener relative to the total weight of the composition. When the composition is obtained by mixing
15 several components, the thickener may be present in any of the components.

Preferred for use herein are salt tolerant thickeners, including but not limited to: xanthan, guar, hydroxypropyl guar, scleroglucan, methyl cellulose, ethyl cellulose (available as AQUACOTE(TM)), hydroxyethyl cellulose (NATROSOL(TM)), carboxymethyl cellulose, hydroxypropylmethyl cellulose, microcrystalline cellulose, hydroxybutylmethyl cellulose,
20 hydroxypropyl cellulose (available as KLUCEL(TM)), hydroxyethyl ethyl cellulose, cetyl hydroxyethyl cellulose (available as NATROSOL(TM)) Plus 330), N-vinylpyrrolidone (available as POVIDONE(TM)), Acrylates/Ceteth-20 Itaconate Copolymer (available as STRUCTURE(TM) 3001), hydroxypropyl starch phosphate (available as STRUCTURE(TM) ZEA), polyethoxylated urethanes or polycarbamyl polyglycol ester (e.g. PEG-150/Decyl/SMDI
25 copolymer (available as ACULYN(TM) 44), PEG-150/Stearyl/SMDI copolymer available as ACULYN(TM) 46), Acrylates/Beheneth-25 Methacrylate Copolymer (available as ACULYN(TM) 28), Acrylates/Vinyl Neodecanoate Crosspolymer (available as ACULYN(TM) 38), Acrylates/Steareth-20 Methacrylate Crosspolymer (available as ACULYN(TM) 88), PEG-150 Distearate (available as ACULYN(TM) 60), trihydroxystearin (available as
30 THIXCIN(TM)), acrylates copolymer (e.g. available as ACULYN(TM) 33) or hydrophobically modified acrylate copolymers (e.g. Acrylates/Steareth-20 Methacrylate Copolymer (available as ACULYN(TM) 22), non-ionic amphiphilic polymers comprising at least one fatty chain and at least one hydrophilic unit selected from polyether urethanes comprising at least one fatty chain.

Also preferred for use herein are thickeners based on lamellar gel network systems, comprising at least one surfactant or amphophile having an HLB of 6 or less and a melting point of at least 30 °C, preferably selected from fatty alcohols comprising from 14 to 30 carbon atoms, or oxyethylenated fatty alcohols comprising from 16 to 30 carbon atoms and 2 units or less of ethylene oxide, and further comprising at least one ionic or nonionic surfactant, preferably selected from:

- anionic surfactants selected from C8-C30 alkyl sulfates, preferably C12-C18 alkyl sulfates,

- anionic surfactants according to the formula R_nX_mYM , wherein R is independently selected from alkyl, alkenyl or alkylaryl groups having from 8 to 30 carbon atoms, X is independently selected from polar groups comprising at least one carbon atom and at least one oxygen or nitrogen atom, Y is an anionic group selected from carboxylates, sulfates, sulfonates or phosphates, n and m are independently 1 or 2, and M is hydrogen or a salt forming cation and mixture thereof, most preferably selected from C8-C30 alkyl ether phosphates having from 1 to 20, preferable 2 to 10 ethylene oxide units (e.g. available as CRODAFOS(TM) CES),

- non-ionic surfactant comprising one or more polyethyleneoxide chains, preferably each polyethyleneoxide chain has on average at least 50 ethylene oxide units and most preferably 100 to 200 ethylene oxide units (e.g. available as VOLPO(TM) S200),

- cationic surfactants selected from quaternary ammonium salts or amido-amines having at least one fatty chain, preferably comprising at least 16 carbon atoms and most preferably at least 20 carbon atoms,

- and mixture thereof.

Examples of such lamellar gel network systems are disclosed in EP1,832,273 and EP2,103,299.

The composition preferably comprises a mixture of ceteryl alcohol and dicetyl phosphate and ceteth-10 phosphate (e.g. available as CRODAFOS(TM) CES).

Chelants

The compositions of the present invention may comprise chelants in an amount sufficient to reduce the amount of metals available to interact with formulation components, particularly oxidizing agents, more particularly peroxides and percarbonates. Typically, such an amount range from at least 0.15%, preferably at least 0.25%, by weight of the chelants relative to the

total weight of the composition. Suitable chelants for use herein include but are not limited to: diethylenetriamine-N,N',N''-polyacids, diethylenetriaminepentaacetic acid (DTPA), diethylenetriaminepenta(methylene phosphonic acid) (DTPMP), diamine-N,N'-dipolyacid, monoamine monoamide-N,N'-dipolyacid, and N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid chelants (preferably EDDS (ethylenediaminedisuccinic acid)), carboxylic acids (preferably aminocarboxylic acids), phosphonic acids (preferably aminophosphonic acids) and polyphosphoric acids (in particular straight polyphosphoric acids), their salts and derivatives. When the composition is obtained by mixing a tint component and a developer component, the chelants may be incorporated in the tint component or in the developer component or in both. A chelant is usually present in developer components for stability reason.

pH Modifiers

The compositions of the present invention may comprise in addition to the alkalizing agent discussed above a pH modifier and/or buffering agent in an amount that is sufficiently effective to adjust the pH of the composition to fall within a range from about 3 to about 13, preferably from about 8 to about 12, more preferably from about 9 to about 11.

Radical Scavengers

According to the present invention, the compositions may comprise a radical scavenger. As used herein the term radical scavenger refers to a species that can react with a radical, to convert the radical species by a series of fast reactions to an unreactive or less reactive species. The radical scavenger is also preferably selected such that it is not an identical species as the alkalisng agent and is present in an amount sufficient to reduce the damage to the hair during the coloring /bleaching process. The compositions of the present invention comprise a radical scavenger from about 0.1% to about 10%, preferably from about 1% to about 7% by weight of the radical scavenger relative to the total weight of the composition. Suitable radical scavengers for use herein may be selected from the classes of alkanolamines, amino sugars, amino acids, esters of amino acids and mixtures thereof. Suitable compounds include 3-substituted-pyrazol-5-ones, 3-carboxy-1H-pyrazol-5-one, 3-methyl-1-phenyl-pyrazol-5-one, 3-methyl-1-p-tolyl-pyrazol-5-one, 3-methyl-1-(4-sulfophenyl)-pyrazol-5-one, 3-methyl-1-(4-sulfoamidophenyl)-pyrazol-5-one, 3-methyl-1-(3-sulfophenyl)-pyrazol-5-one, 3-methyl-1-(3-sulfoamidophenyl)-pyrazol-5-one, 3-methyl-1-(2-chloro-5-sulfophenyl)-pyrazol-5-one, 3-methyl-1-(2,5-dichloro-4-sulfophenyl)-pyrazol-5-one, 3-methyl-1-(4-chlorophenyl)-pyrazol-5-one, 3-methyl-1-(4-carboxyphenyl)-pyrazol-5-one, 3-carboxy-1-phenyl-pyrazol-5-one, 3-carboxy-1-(4-

sulfophenyl)-pyrazol-5-one, 1,3-diphenyl-pyrazol-5-one, methyl pyrazol-5-one-3-carboxylate, 3-amino-1-propanol, 4-amino-1-butanol, 5-amino-1-pentanol, 1-amino-2-propanol, 1-amino-2-butanol, 1-amino-2-pentanol, 1-amino-3-pentanol, 1-amino-4-pentanol, 3-amino-2-methylpropan-1-ol, 1-amino-2-methylpropan-2-ol, 3-aminopropane-1,2-diol, glucosamine, N-acetylglucosamine, glycine, arginine, lysine, proline, glutamine, histidine, sarcosine, serine, glutamic acid, tryptophan, or mixtures thereof, or the salts, such as the potassium, sodium, or ammonium salts, or mixtures thereof. In some embodiments, the inventive compositions may comprise glycine, sarcosine, lysine, serine, 2-methoxyethylamine, glucosamine, glutamic acid, morpholine, piperidine, ethylamine, 3-amino-1-propanol, or mixtures thereof.

10 **Method of hair dyeing**

In order to use the dyeing composition, the tint component and developer components are usually mixed immediately prior to use and a sufficient amount of the mixture is applied to the hair, according to the hair abundance, generally from about 60 to about 250 grams. Upon such preparation the composition is applied to the hair to be dyed and remains in contact with the hair for an amount of time effective to dye the hair. Typically, the hair dye composition is allowed to act on the hair from about 2 to about 60, preferably about 15 to about 45, more preferably about 30 minutes, at a temperature ranging from 15 °C to about 50 °C. Thereafter, the hair is rinsed with water to remove the composition and dried. If necessary, the hair is washed with a shampoo and rinsed, e.g., with water or a weakly acidic solution, such as a citric acid or tartaric acid solution, and dried. Optionally, a separate conditioning product may also be provided.

The method of dyeing hair with the composition may therefore comprise the steps of:

(i) providing a tint component comprising (a) a 1-hexyl/heptyl-4,5-diaminopyrazole compound of the general formula (I) as defined in claim 1, its physiologically compatible, water-soluble salt, or mixtures thereof and, (b) a pyridine compound of the general formula (II) as defined in claim 1, its physiologically compatible water-soluble salt, or mixtures thereof;

(ii) providing a developer component comprising (c) an oxidizing agent;

(iii) mixing the tint component and the developer component to obtain a composition for the oxidative dyeing of keratin fibers according to the composition of the invention;

(iv) applying said composition for the oxidative dyeing of keratin fibers onto the hair.

The method may further comprise waiting a period of time, typically between 2 minutes and 60 minutes, and then rinsing the composition from the hair.

The compositions can be applied on hair via applicator bottle or brush. It can be used on full head or partly on single strands (highlight application) as common highlight applicator foils, caps and special applicators can be used, but also freehand techniques such as balayage, with brush and/or combs can be possible. The composition can also be applied as a mousse via a manual spray, a pressurized container or an aerosol mousse.

The composition may be dispensed as a solid form to which water is added to generate the oxidant and form a thickened vehicle suitable for hair coloring.

The dye combination of the invention may also be used in three components system. See for example disclosed US2010/0223739A2 assigned to L'Oreal. Such a process and kit for lightening or dyeing keratin fibers may comprise the following composition applied to the hair fibers: an aqueous cosmetic composition (A) comprising at least one fatty substance and at least one surfactant; a cosmetic composition (B) comprising at least one alkaline agent and the oxidative dyes of the invention and if present direct dyes and other oxidative dyes, a cosmetic composition (C) comprising at least one oxidizing agent, wherein the amount of the at least one fatty substance in composition (A) is greater than 20% by weight relative to the total weight of composition (A).

Methods of making - Kit

The composition, and its tint component and developer component, may be manufactured by conventional processes known in the art for manufacturing oxidative dyeing products, and admixing the ingredients of each component composition in suitable vessels, followed by packaging in appropriate individual containers. The components may be for example packaged in plastic or aluminium bottles.

In particular, the present invention may be provided as a kit comprising different components to be mixed by the consumer or salon stylist to obtain a hair dyeing composition according to the invention. Such a kit may comprise:

- (i) a tint component comprising (a) a 1-hexyl/heptyl-4,5-diaminopyrazole compound of the general formula (I) as defined above, its physiologically compatible water-soluble salt, or mixtures thereof, and (b) a pyridine compound of the general formula (II) as defined above, its physiologically compatible water-soluble salt, or mixtures thereof, and
- ii) a developer component comprising an oxidizing agent.

The kit may be presented in a single package comprising separate containers for the tint component, the developer component, and optionally a conditioner, a color refresher or other hair treatment product, instructions for use, gloves. The instructions for use include the steps of the method described above and optionally provide visual cues or pictures for the desired steps of the method. Kits are usually sold in retail products with enough material in each component for preparing a hair dyeing composition for one use.

The composition may be dispensed as a foam using for example manually-actuable, non-aerosol dispenser such as a pump or squeeze foamer, aerosol mousse. See for example EP 613,728 B1, WO 97/013585 A1, EP 1,716,933A1, US 3,709,437, US 3,937,364, US 4,022,351, US 4,147,306, US 4,184,615, US 4,615,467 and FR 2,604,622. One particular example of a squeeze foamer useful herein is able to dispense from an upright or inverted position such as the one discussed in US 6,604,693 assigned to Taplast, and more specifically, at column 2, line 65, through column 4, line 67 of that patent.

The composition may be dispensed as a solid form to which water is added to generate the oxidant and form a thickened vehicle suitable for hair coloring

EXAMPLES

The following are non-limiting examples of the compositions of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention, which would be recognized by one of ordinary skill in the art. All concentrations are listed as weight percent, unless otherwise specified.

The compositions tested were formulated by mixing a tint component according to the formulation below with a developer component in a 1:1 ratio. The developer component is a commercially available Welloxon developer at 6% (20 vol) peroxide concentration. In all the tests, white hair was used (1.5g tress). 3 g tint component + 3 g developer component were applied for each switch for 30 minutes at 30 °C. The tresses were rinsed for 2 minutes including 30 seconds shampoo.

Table 1: Tint Formulation:

Ingredients	Weight %
Lanolin alcohol	2.0
Glyceryl Stearate	5.5
Glycol Distearate	2.0

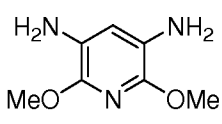
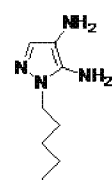
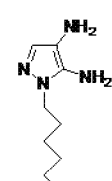
Cetearyl alcohol and SLS	17.5
Sodium cocoyl isethionate	0.46
Sodium laureth sulfate	4.0
Ascorbic acid	0.3
Sodium sulfate	0.001
Sodium sulfite	0.4
Disodium EDTA	0.1
Alkyl (C5, C6 or C8) Pyrazole salts (%)	X
Coupler (%)	Y
Ammonia, 28.3% in water	6.43
Fragrance	0.25
Reverse osmosis water	QS to 100% Total Wt

X and Y were calculated dependent upon the alkyl pyrazole and coupler type to reach a final molar concentration of ca. 0.075 M in the tint component formulation.

Color intensity

After mixing with the tint component indicated with the developer component, the resulting mixture was applied to white hair and rinsed. The resulting color was measured using a colorimeter and characterized by the L* value. An L* of 100 is considered white and L* of 0 is considered black, therefore the higher the L* value the lower the color intensity. The measured L* values for the different primary dye combinations are summarized in Table 2 below.

Table 2: Comparison of L* values

	 (II.2)
C5 	16.35
C6 	16.44

20

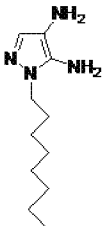
C8	
	18.18

Table 2 demonstrates that the L^* values of hair tresses dyed with the C8 alkyldiaminopyrazole combined with 2,6-dimethoxypyridine-3,5-diamine are significantly higher compared to the other alkyldiaminopyrazoles with 2,6-dimethoxypyridine-3,5-diamine. As the C8 alkyldiaminopyrazole combined with 2,6-dimethoxypyridine-3,5-diamine clearly does not give the desired color intensity, it will not be further analyzed or compared to the present invention.

Wash Fade test

The wash fade measures the fading of the color after repeated wash cycles (up to 24). In this test, five hair tresses are dyed and the initial color measurements are obtained, one is retained for reference. Shampoo is then applied according to this procedure. The four remaining hair tresses are thoroughly wet for 30 sec. 0.1 g of a conventional shampoo per gram of hair (*e.g.* 0.1 g shampoo for each 1.0 g tress) is applied. The shampoo is applied with a syringe using a zigzag action down the length of the hair. The shampoo is milked into hair for 30 secs, ensuring even application, at a speed of less than 30 strokes/60 seconds (for example-1 stroke every 2 seconds) using a '2 fingers and thumb' action.

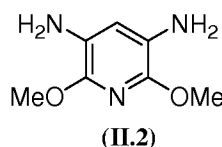
The shampoo is then rinsed according to this procedure: the rinse water temperature is set to $37\text{ }^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and flow-rate to $4 \pm 0.5\text{ l/min}$. The sprayer is held at an angle to the tresses and the tresses are rinsed for 30 seconds while gently stroking the shampoo out of the hair (20 strokes total). Multiple tresses may be rinsed at the same time, as long as water is running over all tresses. A total time of 30 seconds and a total of 20 strokes should be used for multiple tresses. After rinsing, starting at the top of the tress, the tress is squeezed between fingers to remove excess water (one stroke).

The tresses are then dried according to the procedure: the tresses are laid onto a clean paper towel and blotted gently. The tresses are held 10 cm from a blow dryer (set to high heat) and dried 1.5 min while using fingers to separate the hair. If needed, the hair is brushed gently

twice. The tresses are turned over and dried 1.5 min while using fingers to separate the hair. If needed, hair is brushed gently twice. Between washings, hair tresses are kept out of light; either wrapped in aluminum foil or stored in a drawer.

This procedure is repeated on the remaining four hair tresses for each dye sample. Color readings are taken at the 3rd, 6th, 9th, 12th, 15th, 18th, 21st and 24th shampoo/rinse/dry cycle washing intervals. At the 6th, 12th, 18th and 24th shampoo/rinse/dry cycle one hair tress was retained for color measurements and visual assessments.

For the present experiment, C5 and C6 alkyldiaminopyrazoles were tested in combination with a pyridine derivative of formula (II.2):



The starting value (0 wash cycle) for each combination of dyes was taken as a reference and the delta $\Delta E^* = \sqrt{((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)}$ values were calculated for each cycle relative to it $\Delta E_x^* = \sqrt{((L_x^* - L_0^*)^2 + (a_x^* - a_0^*)^2 + (b_x^* - b_0^*)^2)}$. The results are summarized in the Table 4 below:

Table 3: Wash fade testing result.

Cycle	C6	C5
0	0	0
6	1.33	1.41
12	1.33	1.59
18	1.97	2.30
24	1.63	3.90

As can be seen on Table 3, this experiment demonstrates a higher rate of loss of color from hair tresses dyed in the following order C5 > C6.

Diffusion testing

The diffusion testing protocol measures the ability for the dye to stay within the hair when the fibers are wet. In this test, dyed tresses of hair were prepared as indicated above and then separately immersed in a 1 litre beaker containing 900.0 g water. The beaker was placed in the center of a stir plate and the tress attached to a clamping device that was used to lower the tress into the beaker. When in the beaker, the tress remained above the stir bar in the center of the beaker. The tress was lowered until the water line was at the top of the hair tress. The stir plate was turned on so that the stir bar would spin at approximately 100 rpm. All tresses were tested at

the same spin rate. The tress was left in the beaker with stir bar rotating for three hours. After the three hours, the tresses were removed. The absorbance spectrum of the remaining solution was measured using a UV-vis spectrophotometer to characterize the amount of dye that diffused out of the hair into the solution. A full absorbance spectrum from 400 to 700 nm was measured and the absorbance at the peak maximum was measured for each case. The absorbance values for the C5 and C6 alkyldiaminopyrazole combinations are normalized and account for differences in starting dye concentrations in the hair fibers.

Figure 1 demonstrates the rate of increase of absorbance values after following the diffusion testing protocol with hair tresses dyed with the indicated combination of C5 or C6 alkyldiaminopyrazole with 2,6-dimethoxypyridine-3,5-diamine.

1. ♦ a C5 alkyl diamino pyrazole in combination with 2,6-dimethoxypyridine-3,5-diamine.

2. ■ a C6 alkyl diamino pyrazole in combination with 2,6-dimethoxypyridine-3,5-diamine.

Equations for lines on graph:

$$\text{C5 } y = 6\text{E-}05x + 0.0081$$

$$\text{C6 } y = 3\text{E-}05x + 0.004$$

The C6 alkyldiaminopyrazole consistently leaches less dye materials into solution than the C5 alkyldiaminopyrazole. This implies that less color diffuses from the hair tresses containing the C6 relative to the C5 alkyldiaminopyrazole.

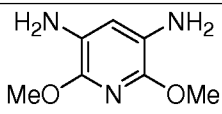
Towel Bleeding

A consumer relevant measure of the ability to see differences in washfastness is to assess how much color from wet dyed hair tresses transfers to a white cloth, such as a white wash cloth. The amounts of towel bleeding resulting from washed tresses dyed with a C5 alkyldiaminopyrazole and C6 alkyldiaminopyrazole with compound of formula (II.1) were measured using conventional ΔE^* measurements. The testing method is summarized below:

After washing a dyed hair switch by the method described above, place the switch on a white cloth (50% cotton, 50% polyester) with an average color reading of $L^*=95.8$, $a^*=-1.40$ and $b^*=0.89$. Fold the cloth in half over the hair switches. Place a 2.27 kg weight on the folded cloth for 5 min. Upon removal of the hair, visual inspection shows a larger and more intense stain for the C5 alkyldiaminopyrazole compared to the C6 alkyldiaminopyrazole compound. The

noticeability of the stain on the fabric was calculated using the ΔE measurements for C5 and C6 relative to the fabric. (see ΔE^* values below). A higher ΔE^* value shows more color transfer to the cloth (bleeding).

Table 4: Towel bleeding results

	C5	C6
 (II.2)	$\Delta E = 3.66$	$\Delta E = 2.94$

- 5 It was found that the C6 alkyldiaminopyrazole dye had a stain intensity of almost 50% less noticeable than the C5 alkyldiaminopyrazole dye after one wash cycle.

Additional examples

- The Color Intensity, Diffusion Testing, and Towel Bleeding test as indicated above were conducted under the same conditions with a tint component comprising 2,5-toluenediamine sulfate (DTS) as a further primary intermediate as indicated in Table 5 below.
- 10

Table 5: Tint Formulation with DTS

Ingredients	Weight %
Lanolin alcohol	2.0
Glyceryl stearate	5.5
Glycol Distearate	2.0
Cetearyl alcohol and SLS (9:1)	17.5
Sodium cocoyl isethionate	0.46
Sodium laureth sulfate	4.0
Ascorbic acid	0.3
Sodium sulfate	0.001
Sodium sulfite	0.4
Disodium EDTA	0.1
Sodium chloride	0.292
C5 pyrazole salt Or C6 pyrazole salt Or C8 Pyrazole salt	0.869 Or 0.925 Or 1.042
2,6-dimethoxypyridine-3,5-diamine	1.211
2,5-toluenediamine sulfate (DTS)	0.220

Ammonia, 28.3% in water	6.43
Fragrance	0.25
Reverse osmosis water	QS to 100% Total Wt

The combined amount of pyrazole and DTS represents a total molar concentration of about 0.050M for these primary intermediates.

The results are as indicated below.

Color intensity

5

Table 6: Comparison of L^* values with DTS

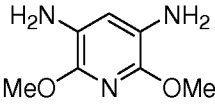
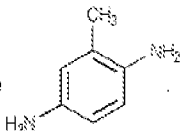
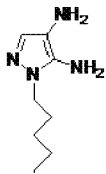
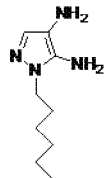
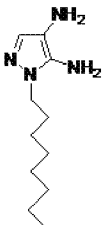
	 (II.2)  H_2SO_4
C5	 17.43
C6	 17.54
C8	 18.99

Table 6 demonstrates that the L* values of hair tresses dyed with the C8 alkyldiaminopyrazole combined with 2,5-toluenediamine and 2,6-dimethoxypyridine-3,5-diamine are significantly higher compared to the other alkyldiaminopyrazoles with 2,5-toluenediamine and 2,6-dimethoxypyridine-3,5-diamine.

Diffusion testing

The same testing as described above was performed and results shown in Fig. 2 for:

1. ♦ a C5 alkyl diamino pyrazole in combination with 2,6-dimethoxypyridine-3,5-diamine and DTS.

5 2. ■ a C6 alkyl diamino pyrazole in combination with 2,6-dimethoxypyridine-3,5-diamine and DTS.

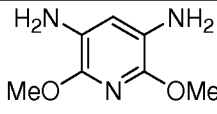
Equations for lines on graph

$$\text{C5 } y = 5\text{E-}05x + 0.0079$$

$$\text{C6 } y = 3\text{E-}05x + 0.0019$$

10 **Towel Bleeding**

Table 7: Towel bleeding results

	C5	C6
 (II.2)	$\Delta E = 5.58$	$\Delta E = 3.46$

Concluding remark

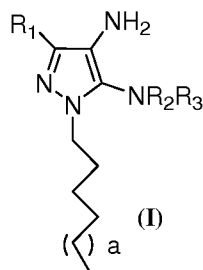
15 The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 mm” is intended to mean “about 40 mm.”

CLAIMS

What is claimed is:

1. A composition for the oxidative dyeing of keratin fibers, in particular human keratin fibers, comprising:

- (A) a 1-hexyl/heptyl-4,5-diamino pyrazole compound of the general formula (I), a physiologically compatible water-soluble salt thereof, or mixtures thereof,



wherein a is equal to one or two;

wherein R₁ is selected from the group consisting of:

(a) C-linked substituents selected from the group consisting of:

(i) substituted or unsubstituted, straight or branched or cyclic, saturated or unsaturated, aliphatic or heteroaliphatic substituents, in particular alkyl or hydroxy substituted alkyl,

(ii) substituted or unsubstituted, mono- or poly- unsaturated aromatic or heteroaromatic substituents, in particular aryl or heteroaryl,

wherein said C-linked substituents comprise from 1 to 6 carbon atoms and from 0 to 5 heteroatoms selected from the group consisting of O, F, N, P and Si;

(b) S-linked substituents selected from the group consisting of SA¹, SO₂A¹, SO₃A¹, SSA¹, SOA¹, SO₂NA¹A², SNA¹A², and SONA¹A²;

(c) O-linked substituents selected from the group consisting of OA¹, ONA¹A²;

(d) N-linked substituents selected from the group consisting of NA¹A²; (NA¹A²A³)⁺, NA¹SA², NO₂; NA¹A²;

(e) halogens selected from the group consisting of F, Cl, Br, and I; and

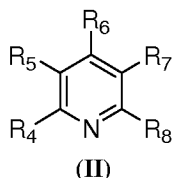
(f) hydrogen;

wherein A¹, A², and A³ are selected independently of each other from the group consisting of hydrogen; substituted or unsubstituted, straight or branched or cyclic, saturated or unsaturated, aliphatic or heteroaliphatic or aromatic or heteroaromatic substituents, preferably substituted or unsubstituted alkyl, or A¹ and A² together with nitrogen atoms to which they are bound form a

ring; wherein said substituents or ring comprise from 1 to 6 carbon atoms and from 0 to 5 heteroatoms selected from the group consisting of O, S, N, P, and Si;

R_2 and R_3 are selected independently of each other from the group consisting of a hydrogen atom; a Cl-C6 alkyl substituent; a trifluoromethyl substituent; a Cl-C6 aminoalkyl substituent; a Cl-C6 hydroxyalkyl substituent; Cl-C6 an alkoxyalkyl substituent;

- (B) a pyridine compound of the general formula (II), a physiologically compatible water-soluble salt thereof, or mixtures thereof,



wherein R_4 , R_5 , R_6 , R_7 and R_8 are substituents selected independently of each other from the group consisting of:

(a) C-linked substituents selected from the group consisting of:

(i) substituted or unsubstituted, straight or branched or cyclic, saturated or unsaturated, aliphatic or heteroaliphatic substituents, in particular alkyl or hydroxy substituted alkyl,

(ii) substituted or unsubstituted, mono- or poly- unsaturated aromatic or heteroaromatic substituents, in particular aryl or heteroaryl,

wherein said C-linked substituents comprise from 1 to 6 carbon atoms and from 0 to 5 heteroatoms selected from the group consisting of O, F, N, P and Si;

(b) S-linked substituents selected from the group consisting of SA^1 , SO_2A^1 , SO_3A^1 , SSA^1 , SOA^1 , $SO_2NA^1A^2$, SNA^1A^2 , and $SONA^1A^2$;

(c) O-linked substituents selected from the group consisting of OA^1 , ONA^1A^2 ;

(d) N-linked substituents selected from the group consisting of NA^1A^2 ; $(NA^1A^2A^3)^+$, NA^1SA^2 , NO_2 ; NA^1A^2 ;

(e) halogens selected from the group consisting of F, Cl, Br, and I; and

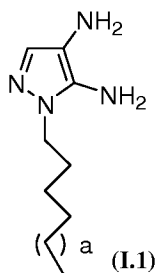
(f) hydrogen;

wherein A^1 , A^2 , and A^3 are selected independently of each other from the group consisting of hydrogen; substituted or unsubstituted, straight or branched or cyclic, saturated or unsaturated, aliphatic or heteroaliphatic or aromatic or heteroaromatic substituents, preferably substituted or unsubstituted alkyl, or A^1 and A^2 together with nitrogen atoms to which they are bound form a

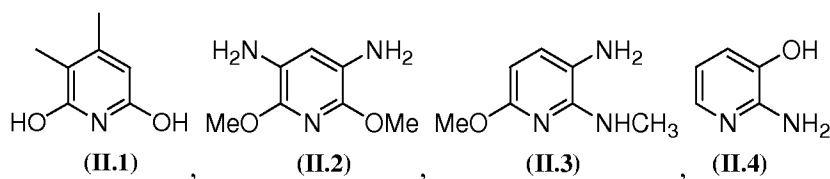
ring; wherein said substituents or ring comprise from 1 to 6 carbon atoms and from 0 to 5 heteroatoms selected from the group consisting of O, S, N, P, and Si; and

- (C) an oxidizing agent.

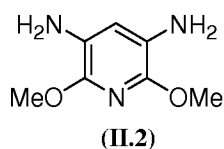
2. A composition according to claim 1, wherein the 1-hexyl/heptyl-4,5-diamino pyrazole compound **(I)** is a compound with formula **(I.1)**:



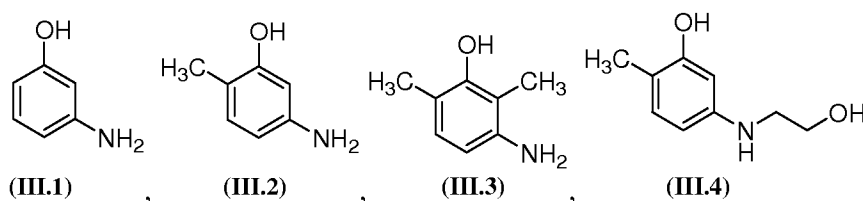
3. A composition according to claim 1 or 2, wherein the pyridine compound **(II)** is selected from compounds with formula **(II.1)** to **(II.4)**:

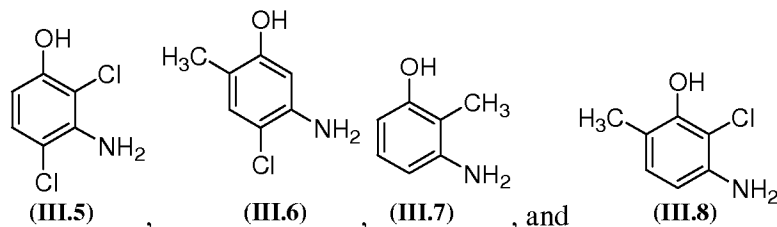


preferably



4. A composition according to any one of the preceding claims further comprising an auxiliary coupler, preferably wherein said auxiliary coupler is an aminophenol compound selected from the group consisting of:





5. A composition according to any of the preceding claims, further comprising a primary intermediate selected from toluene-2,5-diamine, p-phenylenediamine, 2-hydroxyethyl-p-phenylenediamine, 2-methoxymethyl-p-phenylenediamine, 2-(2,5-diamino-4-methoxyphenyl)propane-1,3-diol, 2-chloro-p-phenylenediamine, 2-methoxy-p-phenylenediamine, 2-((2-(4-amino-phenylamino)-ethyl)-(2-hydroxyethyl)-amino)-ethanol, salts thereof and combination thereof.

6. A composition according to any one of the preceding claims further comprising at least one additional component selected from the group consisting of alkalizing agents, auxiliary primary intermediates, auxiliary couplers, direct dyes, thickeners, chelants, pH modifiers and/or buffering agents, radical scavenger systems and mixtures thereof.

7. A composition according to any of the preceding claims, further comprising fatty alcohols comprising from 14 to 30 carbon atoms, or oxyethylenated fatty alcohols comprising from 16 to 30 carbon atoms and 2 units or less of ethylene oxide.

8. A composition according to claim 7, further comprising at least one ionic or nonionic surfactant selected from:

- anionic surfactants selected from C8-C30 alkyl sulfates, preferably C12-C18 alkyl sulfates,

- anionic surfactants according to the formula R_nX_mYM , wherein R is independently selected from alkyl, alkenyl or alkylaryl groups having from 8 to 30 carbon atoms, X is independently selected from polar groups comprising at least one carbon atom and at least one oxygen or nitrogen atom, Y is an anionic group selected from carboxylates, sulfates, sulfonates or phosphates, n and m are independently 1 or 2, and M is hydrogen or a salt forming cation and mixture thereof, most preferably selected from C8-C30 alkyl ether phosphates having from 1 to 20, preferable 2 to 10 ethylene oxide units;

- non-ionic surfactant comprising one or more polyethyleneoxide chains, preferably each polyethyleneoxide chain has on average at least 50 ethylene oxide units and most preferably 100 to 200 ethylene oxide units;
 - cationic surfactants selected from quaternary ammonium salts or amido-amines
5 having at least one fatty chain, preferably comprising at least 16 carbon atoms and most preferably at least 20 carbon atoms; and
 - mixtures thereof.
9. A composition according to claim 8 comprising a mixture of cetearyl alcohol and dicetyl phosphate and ceteth-10 phosphate.
- 10 10. A composition according to any of the preceding claims further comprising a chelant selected from the group consisting of: diethylenetriamine-N,N',N''-polyacids, diethylenetriaminepentaacetic acid (DTPA), diethylenetriaminepenta(methylene phosphonic acid) (DTPMP), diamine-N,N'-dipolyacid, monoamine monoamide-N,N'-dipolyacid, and N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid chelants
15 (preferably EDDS (ethylenediaminedisuccinic acid)), carboxylic acids (preferably aminocarboxylic acids), phosphonic acids (preferably aminophosphonic acids) and polyphosphoric acids (in particular straight polyphosphoric acids), their salts and derivatives .
11. A composition according to any of the preceding claims wherein said oxidizing agent is
20 selected from the group consisting of hydrogen peroxide, sodium periodate, urea peroxide, melamine peroxide, perborates, percarbonates, perphosphates, persilicates, persulfates, oxidizing enzymes such as uricases, oxidases, and peroxidases, a source of peroxymonocarbonate ions and mixtures thereof.
12. A composition according to any of the preceding claims, wherein said composition is
25 dispensed as a foam.
13. A method of dyeing hair comprising the steps of:
- (i) providing a tint component comprising (a) a 1-hexyl/heptyl-4,5-diaminopyrazole compound of the general formula (I) as defined in claim 1, a physiologically compatible water-soluble salt thereof or mixtures thereof and, (b) a pyridine compound of the general

formula (II) as defined in claim 1, a physiologically compatible water-soluble salt thereof or mixtures thereof;

(ii) providing a developer component comprising (c) an oxidizing agent;

5 (iii) mixing the tint component and the developer component to obtain a composition for the oxidative dyeing of keratin fibers according to any of the preceding claims;

(iv) applying said composition for the oxidative dyeing of keratin fibers onto the hair.

14. An oxidative hair dyeing kit comprising: (i) a tint component comprising (a) a 1-hexyl/heptyl-4,5-diamino pyrazole compound of the general formula (I) as defined in claim 1, a physiologically compatible water-soluble salt thereof or mixtures thereof and,
10 (b) a pyridine compound of the general formula (II) as defined in claim 1, a physiologically compatible water-soluble salt thereof or mixtures thereof, and ii) a developer component comprising an oxidizing agent.
15. A tint component comprising (a) a 1-hexyl/heptyl-4,5-diaminopyrazole compound of the general formula (I) as defined in claim 1, a physiologically compatible, water-soluble salt thereof or mixtures thereof and; (b) a pyridine compound of the general formula (II) as
15 defined in claim 1, a physiologically compatible water-soluble salt thereof or mixtures thereof.

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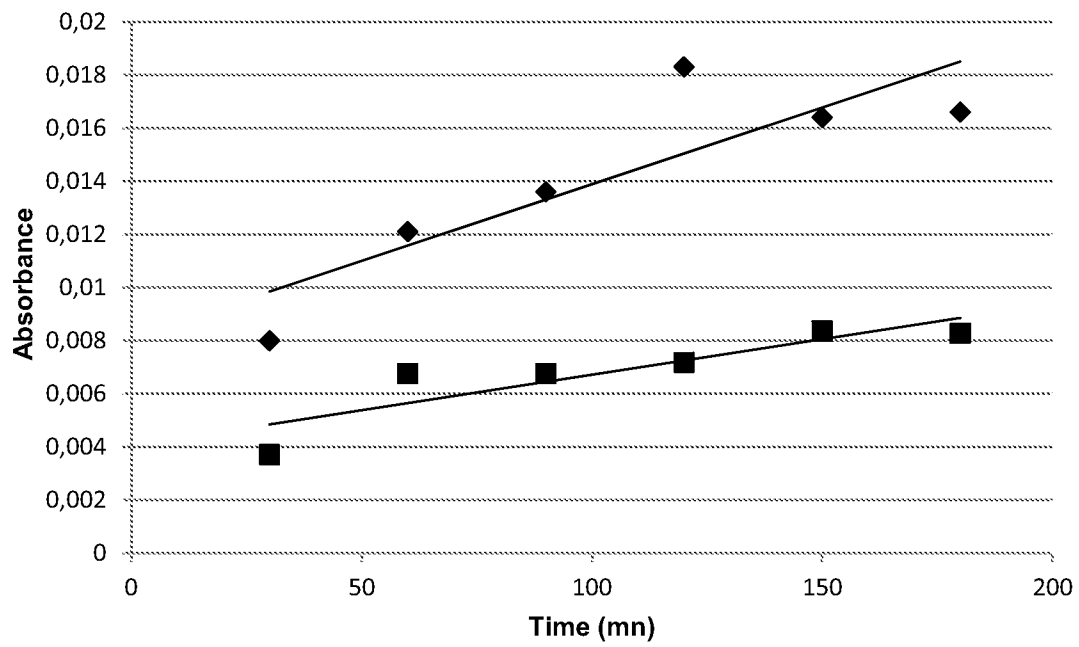


Fig. 1

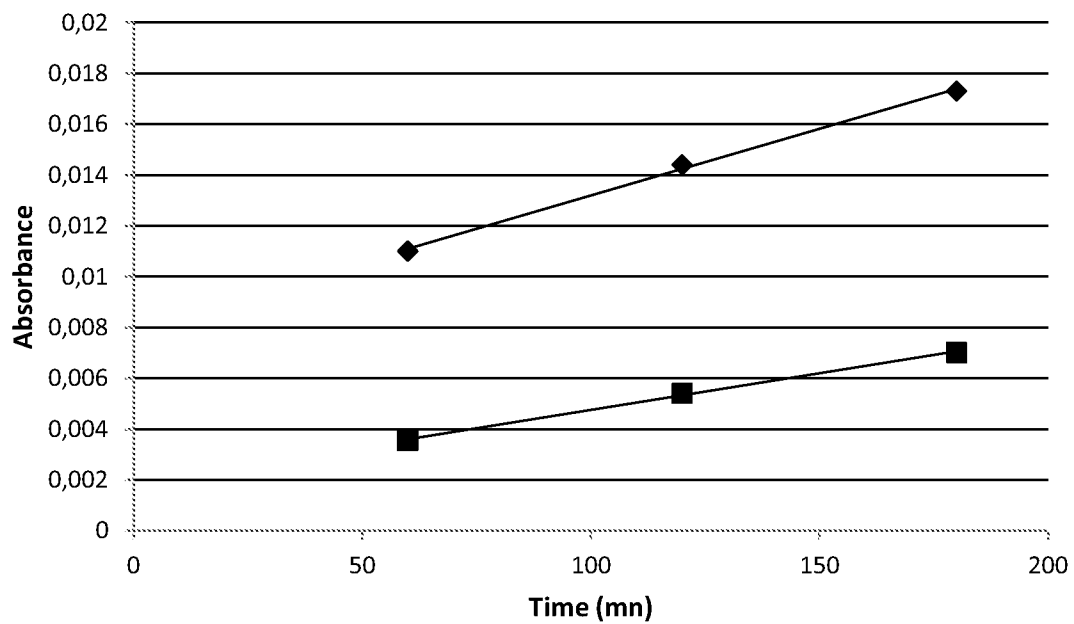


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/025367

A. CLASSIFICATION OF SUBJECT MATTER INV. A61Q5/10 A61K8/49 A61K8/66 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, CHEM ABS Data, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 488 783 A1 (OREAL [FR]) 22 December 2004 (2004-12-22) paragraphs [0001], [0015]; claims; examples -----	1-15
Y	DE 10 2008 033875 A1 (HENKEL AG & CO KGAA [DE]) 7 May 2009 (2009-05-07) paragraphs [0001], [0006] - [0008], [0010] - [0036], [0054] - [0056]; claims; examples -----	1-15
Y	EP 1 787 632 A1 (HENKEL KGAA [DE]) 23 May 2007 (2007-05-23) paragraphs [0001], [0006] - [0009], [0034], [0035]; claims; examples -----	1-15
<div style="display: flex; justify-content: space-between; align-items: center;"> <div> <input type="checkbox"/> Further documents are listed in the continuation of Box C. </div> <div> <input checked="" type="checkbox"/> See patent family annex. </div> </div>		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search <div style="text-align: center; font-size: 1.2em;">24 June 2013</div>	Date of mailing of the international search report <div style="text-align: center; font-size: 1.2em;">03/07/2013</div>	
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 <div style="text-align: center; font-size: 1.2em;">Pregetter, Magdalena</div>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/025367

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1488783	A1	22-12-2004	AT 345771 T 15-12-2006
		DE 602004003290 T2	24-05-2007
		DK 1488783 T3	19-02-2007
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		EP 1787632 A1	23-05-2007
