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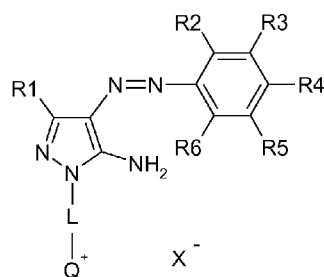
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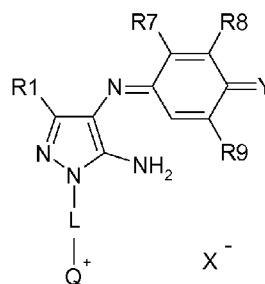
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(54) Title: NEW COSMETIC COMPOSITIONS COMPRISING CATIONIC DYES AND PROCESS FOR DIRECT DYEING OF KERATIN FIBERS



(I)



(II),

(57) Abstract: The present invention relates to new compositions for dyeing keratin fibers comprising, in a medium suitable for dyeing, one or more cationic dye of general formula (I) or (II), or a physiologically tolerated adduct thereof with an acid: (II), as well as to a process for dyeing keratin fibers comprising one or more cationic dye of general formula (I) or (II), or a physiologically tolerated adduct thereof with an acid.

NEW COSMETIC COMPOSITIONS COMPRISING CATIONIC DYES AND PROCESS FOR DIRECT DYEING OF KERATIN FIBERS

Technical field of the invention

The invention relates to new compositions for dyeing or for lightening and dyeing keratin fibers, and in particular human keratin fibers such as the hair, comprising at least one cationic direct dye. The present invention also relates to the
5 process for direct dyeing of keratin fibers using these compositions.

Background of the invention

Throughout the years, there has been a desire to alter the color of synthetic and natural fibers. In particular, coloring of human hair has been sought in view of changing styles and fashion.

10 The coloring of hair is currently subject to the most varied trends. Whereas in the past hair was colored primarily to cover gray hair, today there is an increasing demand for integrating the hair color into current fashion as an expression of personality.

Now as before, two established methods of hair coloring are broadly
15 applied.

One is the oxidative system, which has attained cosmetic significance. Keratin fibers, and in particular human hair, are dyed with dye compositions containing dye precursors, so called primary intermediates and couplers. Primary intermediates are in particular para-phenylenediamines and para-aminophenols,
20 which are generally referred to as oxidation bases. Couplers are selected in particular from meta-dihydroxybenzenes, meta-aminophenols and meta-phenylenediamines to provide a wide range of different color nuances. The cosmetic composition containing the oxidation bases is normally activated by the addition of hydrogen peroxide, which give rise to colored compounds by a process
25 of oxidative condensation.

Another dye system which is non-oxidative is the semi-permanent system which offers the opportunity of coloring hair with colorants containing direct dyes (often referred to as toners).

Conventional non-oxidative colorants are advantageous particularly when
5 customers want to change the color shades more frequently and at the same time want to avoid a deterioration of hair quality from frequent exposure to oxidants. In the case of tints the colorations can be weakened gradually with every hair washing, such colorations normally withstand at the most 5 to 10 hair washings, depending on the product used and the kind of hair. Customers often make use of
10 precisely these deficiencies so that they can later apply a new color shade to achieve a different coloring result.

Whenever customers do not want to use the permanent system and do not want to accept the inconveniences of the semi-permanent system either, no alternative available on the market based on direct dyes which has the performance
15 and durability of the oxidative system; as the term "semi-permanent" already indicates the resistance to everyday conditions is very limited. Single dyes which have been developed may fulfill some fastness criteria; however, they are often suffering from incompatibilities with other dyes or have spectral inconveniences so that they were not useful for setting up an entire dye system with a broader shade
20 palette.

The majority of conventional semi-permanent colorants are based on the family of nitro dyes. These dyes which are derivatives of nitro-p-aminophenol and nitro-p-phenylenediamine are widely used.

Another type of dyes for direct coloring are cationic dyes, for example, the
25 widely used "Arianor®-Dyes". However, also these dyes are suffering from various deficiencies; so for instance the dyes are standardized and components may vary from one batch to another.

Nitro dyes and Arianor® dyes have different dye uptake properties on

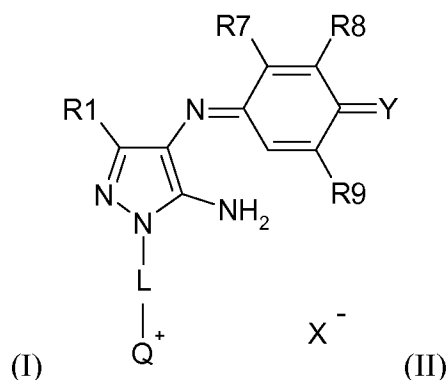
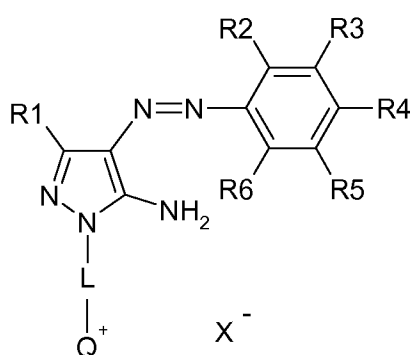
keratin fibers depending on the degree of hair damage. Normally nitro dyes show stronger dye uptake on the root areas whereas cationic dyes show stronger dye uptake on the lengths. Numerous compositions available on the market consist therefore of quite complex compositions of nitro and Arianor® dyes to provide
 5 more even color results.

However, the individual dyes of the above described types have the drawback that they produce irregularities when used on hair that has been damaged to different degrees or lead to quite uneven colorations; further, the endurance of the coloration is insufficient, i.e., fastness in particular with respect to shampoos;
 10 after each washing the color result becomes weaker so that the natural hair color is re-obtained after five to ten washes, depending on the individual hair type.

There is also the need of compositions for dyeing keratin fibers able to produce a broad range of colors and therefore there is still strong need for dyes which fulfill these requirements.

15 Summary of the invention

The present invention relates to new compositions for dyeing keratin fibers comprising, in a medium suitable for dyeing, one or more cationic dye of general formula (I) or (II), or a physiologically tolerated adduct thereof with an acid:



20

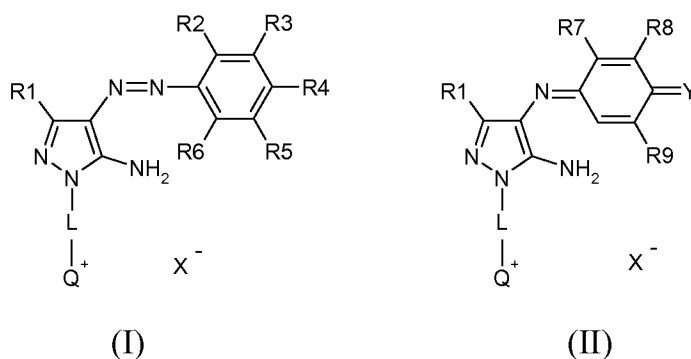
wherein the substituents are as defined below.

The invention also relates to a process for dyeing keratin fibers comprising one or more cationic dye of general formula (I) or (II), or a physiologically

tolerated adduct thereof with an acid.

Detailed description of the invention

One subject of the invention is a composition for dyeing keratin fibers, and in particular human keratin fibers such as the hair, comprising, in a medium
5 suitable for dyeing, one or more cationic direct dye of general formula (I) or (II), or a physiologically tolerated adduct thereof with an acid:



10 wherein

R1 is hydrogen, a straight-chain or branched (C1-C6)-alkyl group, a (C1-C4)-hydroxyalkyl group, a (C1-C4)-aminoalkyl group, a (C1-C8)-alkylamino group, a di-(C1-C8)-alkylamino group, a (C1-C4)-alkylamino-(C1-C4)-alkyl group or a di(C1-C4)-alkylamino-(C1-C4)-alkyl group,
15 a benzyl group, an aryl group or a heteroaryl group;

R2 to R6 are, equal or different independently from each other, selected from hydrogen, a straight-chain or branched (C1-C6)-alkyl or -alkoxy group, a (C1-C4)-hydroxyalkyl or -hydroxyalkoxy group, a methoxymethyl group, a nitro group, a halogen atom selected from chlorine, bromine, iodine and fluorine, a
20 trifluoromethyl group, a cyano group, an acetamino or an amino group;

R7 is a hydrogen atom, a methyl or an ethyl group, a hydroxy group, an amino group, a hydroxy-(C2-C3)-alkylamino group or a methoxy group;

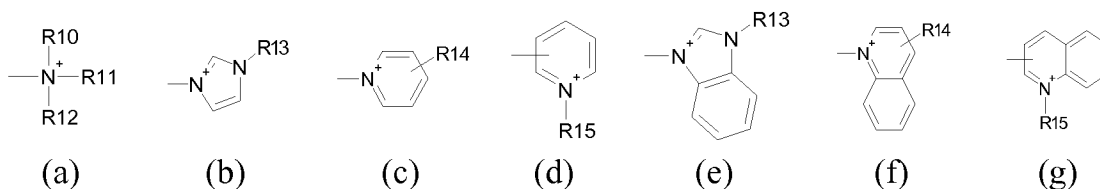
R8 is a hydrogen atom, a halogen atom selected from chlorine, bromine, iodine and fluorine or a methyl group;

R9 is a hydrogen atom, an amino group, a (C1-C6)-alkyl group, a (C1-C6)-alkoxy group or a (C2-C3)-hydroxyalkoxy group;

Y is an oxygen atom or an NR group wherein R is (C1-C4)-alkyl, (C2-C4)-hydroxyalkyl; or the NR group is bonded to R9 to form a benzoxazine system;

5 L is a bridging group between the pyrazole ring and the quaternary group and consists of a phenylene diradical or a (C1-C3)-alkylene diradical;

Q^+ is a saturated cationic group selected from formula (a) or an unsaturated or aromatic cationic group selected from formula (b) to (g):



10 wherein

R10 to R12 are, equal or different and independently of each other, selected from a straight-chain or branched (C1-C6)-alkyl group, a (C2-C4)-hydroxyalkyl group, a (C3-C6)-dihydroxyalkyl group, a (C3-C6)-polyhydroxyalkyl group or a (C1-C6)-alkoxy-(C1-C4)-alkyl group; or
 15 two of the groups R10 to R12 together with the nitrogen atom to which they are linked form a five-membered or six-membered heterocycle, optionally containing one or more other heteroatoms (for example O, N, S) and other substituents [for example F, Cl, Br, I, OH, NH₂ or a straight-chain or branched (C1-C6)-alkyl group, a straight-chain or branched (C1-C6)-alkoxy group, a (C1-C6)-alkoxy-(C1-
 20 C4)-alkyl group or a hydroxyethyl group];

R13 is a straight-chain or branched (C1-C8)-alkyl group, a hydroxyethyl group or a benzyl group;

R14 is hydrogen, a straight-chain or branched (C1-C9)-alkyl group, an amino group, a mono-(C1-C6)-alkylamino group, a di-(C1-C6)-alkylamino group
 25 or a pyrrolidino group;

R15 is a (C1-C4)-alkyl radical, which may be substituted with a hydroxy radical;

X^- is a monovalent or polyvalent anion, which may be selected from the group comprising chloride, bromide, methylsulfonate or methylsulfate, arylsulfonate, hydrogen sulfate, sulfate, phosphate, acetate or hydroxysuccinate ion.

The dyes may also be isolated as adduct with an acid, in particular with an inorganic acid such as hydrochloric acid or hydrobromic acid.

Preferred are cationic dyes of general formula (I) or (II) wherein:

10 R1 is hydrogen;

R2 to R6 are, equal or different independently from each other, selected from hydrogen, a methyl or methoxy group, a (C1-C2)-hydroxyalkyl group, a (C2-C3)-hydroxyalkoxy group, a methoxymethyl group, a nitro group, a chloro atom, or a trifluoromethyl group;

15 R7 is a hydroxy group, an amino group, a hydroxyethylamino group or a methoxy group;

R8 is a hydrogen atom, a chloro atom or a methyl group;

R9 is a methyl group, a methoxy group or a hydroxyethoxy group;

20 R10 to R12 are, equal or different and independently of each other, selected from a methyl group, ethyl group or hydroxyethyl group; or two of the R10 to R12 groups together with the nitrogen atom to which they are linked form a pyrrolidino group, morpholino group or N-methylpiperazino group;

R13 is a methyl group or a hydroxyethyl group;

25 R14 is hydrogen, a methyl group, p-dimethylamino group or p-pyrrolidino group;

R15 is a methyl, ethyl or hydroxyethyl group;

Y is O or NH;

X^- is a chloride, bromide or methylsulfate;

L is a (C1-C3)-diradical;

Q^+ is a (C3-C9)-trialkylammonium radical, a N-methylimidazolium radical or a N-methylpyridinium radical.

Most preferred are the cationic dyes of general formula (I) or (II) wherein:

5 R1 is hydrogen;

R2-R6 are, equal or different independently from each other, selected from hydrogen, a methyl or methoxy group, a (C1-C2)-hydroxyalkyl group, a hydroxyethoxy group, a methoxymethyl group, a nitro group, or a chloro atom;

R7 is a hydroxy group, an amino group or a hydroxyethylamino group;

10 R8 is a hydrogen atom or a methyl group;

R9 is a methyl group, a methoxy group or a hydroxyethoxy group;

R10 to R12 are, equal or different and independently of each other, selected from a methyl group, ethyl group or hydroxyethyl group; or two of the R10 to R12 groups together with the nitrogen atom to which they are linked form a pyrrolidino group, morpholino group or N-methylpiperazino group;

R13 is a methyl group;

R14 is hydrogen, a methyl group, p-dimethylamino group or p-pyrrolidino group;

R15 is a methyl, ethyl or hydroxyethyl group;

20 Y is O or NH;

X^- is a chloride, bromide or methylsulfate;

L is a methylene diradical;

Q^+ is an N-methyl pyridinium moiety.

Manufacturing of the cationic direct dyes of the present invention is based on commonly known chemical methods. As an example, the synthesis of dyes of the present invention is illustrated in the following part. Selected was a starting pyrazole, substituted at the pyrazole-N1 atom with a pyridine-3-yl-methyl radical, which leads to dyes containing the substitution pattern (d).

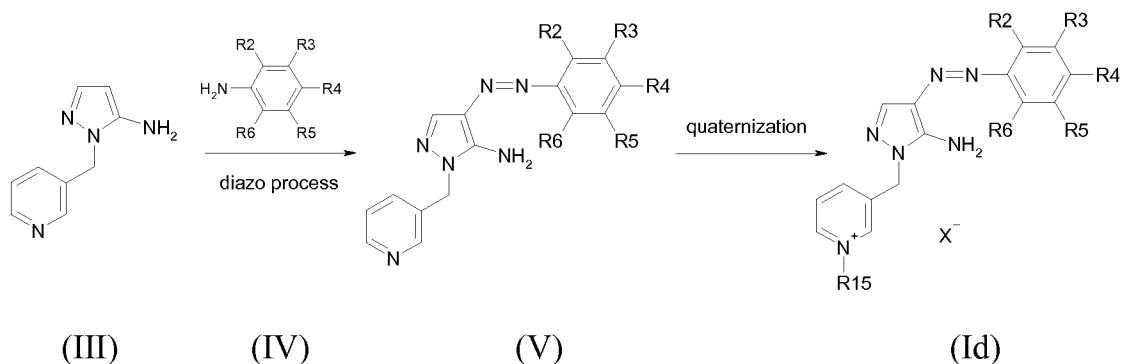
The synthesis of numerous 5-amino pyrazoles, useful for synthesis of the cationic dyes of the current invention, was described by H. Höhn, Z. Chem., 10, 386 (1970). Selected from this literature was for illustration of the current invention 1-(pyridin-3-ylmethyl)-1H-pyrazol-5-amine (III). Synthesizing the dyes of the invention is especially economical if the same 5-amino-pyrazole intermediate is used for manufacturing dyes of formula (I) and formula (II).

As shown by Scheme 1, diazotation of an aromatic amine (IV) and coupling with the 5-aminopyrazole (III) gives the azo compound (V) which in the following is then quaternized to give the cationic dyes of formula (Id).

A huge number of aromatic amines of structure (IV) are commercially available and can be used for preparing the dyes of general formula (I). Therefore, the examples given in the following represent a few samples of a wide range of possible products.

The diazo process is carried out according to known methods, which are for instance described in "Methoden der Organischen Chemie (Houben Weyl)", Band X/3, Georg Thieme Verlag, Stuttgart, 1965, pp. 1-212 for the diazotation of aromatic amines, and pp. 213ff for the azo coupling.

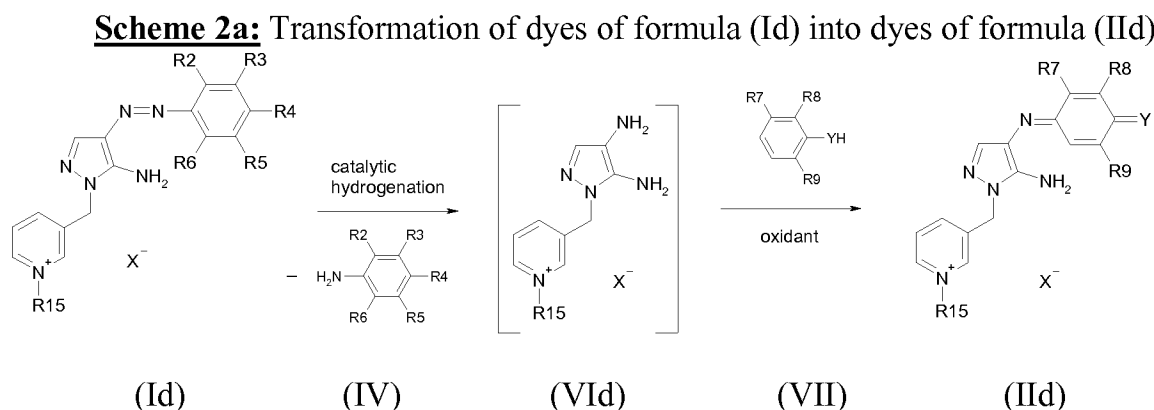
Scheme 1: Synthesis of cationic dyes of formula (I) starting from 1-(Pyridin-3-ylmethyl)-1H-pyrazol-5-amine



Some of the cationic dyes of formula (Id) are appropriate intermediates to be converted into the cationic dyes of formula (IId). In this case preferred are dyes

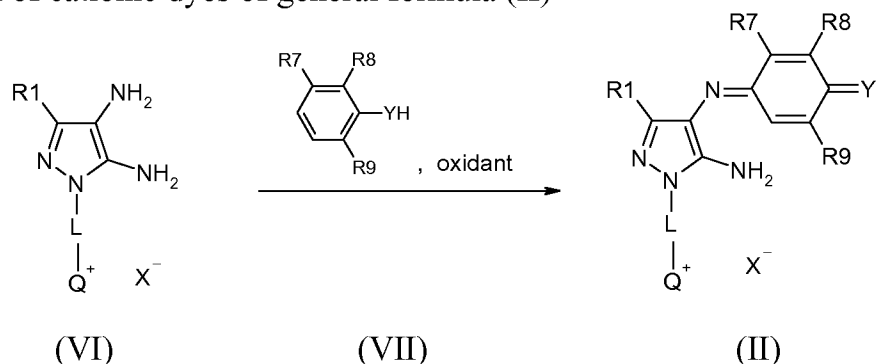
in which the groups R2 to R6 are sufficiently inert to the treatments described in the following.

By cleaving the azo group of cationic dyes of formula (I), selected for illustration was formula (Id), preferentially by catalytic hydrogenation, the aniline (IV) is split off and the 4,5-diaminopyrazole intermediate (VIId) is obtained. Isolation of the pyrazole is not required; preferentially the pyrazole is generated in situ and directly reacted with common hair dye couplers (VII) or other meta-donor substituted benzenes in presence of an oxidant whereby cationic dyes of the general formula (IIId) are obtained. Chemistry of the dye transformation process is illustrated in Scheme 2a.



Cationic pyrazole dyes of the general formula (II) can also be obtained by oxidative coupling of the isolated quaternized 4,5-diaminopyrazole; in this regard reference is expressly made to US7462204B2 where the synthesis and the isolation of quaternized 4,5-diaminopyrazoles is reported.

Scheme 2b: Coupling of quaternized 4,5-diaminopyrazoles (VI) and formation of cationic dyes of general formula (II)



By using coupling components of structure (VII) the cationic dyes of general formula (II) are obtained, which are brilliant orange to deep violet.

The cationic chromophores can be combined with various anions. The type of anion is normally the result of the selected reagents used in the process, such as
5 the alkylating agents or agents added to the dye in order to exchange the anion. The latter can be necessary for practical reasons, for instance to improve the crystallization properties of the dyes.

In some cases it can be favorable to isolate the dyes as adduct with an acid, for instance as a 1:1 adduct with hydrochloric acid or with hydrobromic acid.

10 Furthermore, some of the dyes can contain crystal water.

According to a preferred embodiment of the present invention, the pyrazole azo dyes of general formula (I), which can be used, for example, in the compositions in accordance with the invention, may be selected from the group comprising:

15 3-{[5-Amino-4-(phenyldiazenyl)-1*H*-pyrazol-1-yl]methyl}-1-methylpyridinium chloride;

3-({5-Amino-4-[(4-methylphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

20 3-({5-Amino-4-[(4-methylphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium bromide;

3-({5-Amino-4-[(3-methylphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(2-methylphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

25 3-[(5-Amino-4-{[4-(hydroxymethyl)phenyl]diazenyl}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium bromide;

3-[(5-Amino-4-{[3-(hydroxymethyl)phenyl]diazenyl}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium bromide;

3-[(5-Amino-4-{[2-(hydroxymethyl)phenyl]diazenyl}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium bromide;

3-({5-Amino-4-[(4-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

5 3-({5-Amino-4-[(2-methyl-4-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium methyl sulfate;

3-({5-Amino-4-[(2-methyl-3-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

10 3-({5-Amino-4-[(4-methyl-2-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

3-[(5-Amino-4-{[2-(methoxymethyl)-4-nitrophenyl]diazenyl}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium methyl sulfate;

3-[(5-Amino-4-{[4-(trifluoromethyl)phenyl]diazenyl}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium chloride;

15 3-[(5-Amino-4-{[3-(trifluoromethyl)phenyl]diazenyl}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium chloride;

3-[(5-Amino-4-{[2-(trifluoromethyl)phenyl]diazenyl}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium chloride;

20 3-({5-Amino-4-[(4-methoxyphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(3-methoxyphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(2-methoxyphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

25 3-({5-Amino-4-[(4-chlorophenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(3-chlorophenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(2-chlorophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(2-chloro-4-methylphenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

5 3-({5-Amino-4-[(5-chloro-2-methylphenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(4-chloro-2-methylphenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

10 3-({5-Amino-4-[(5-chloro-2-methoxyphenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(3-chloro-4-fluorophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(2-chloro-4-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

15 3-({5-Amino-4-[(2-chloro-5-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(4-chloro-2-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

20 3-({5-Amino-4-[(4-chloro-3-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(5-chloro-2-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(2-cyano-4-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

25 3-({5-Amino-4-[(2,4-dichlorophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(2,5-dichlorophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(2,4-dimethylphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(2,5-dimethylphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

5 3-({5-Amino-4-[(4-(methoxycarbonyl)phenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium methyl sulfate;

4-{{5-Amino-4-(phenyldiazenyl)-1*H*-pyrazol-1-yl}methyl}-1-methylpyridinium chloride;

10 4-{{5-Amino-4-[(4-methylphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl}-1-methylpyridinium chloride;

4-{{5-Amino-4-[(3-methylphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl}-1-methylpyridinium chloride;

4-{{5-Amino-4-[(2-methylphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl}-1-methylpyridinium chloride;

15 4-[(5-Amino-4-{{4-(hydroxymethyl)phenyl}diazenyl}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium bromide;

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20 4-[(5-Amino-4-{{2-(hydroxymethyl)phenyl}diazenyl}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium bromide;

4-{{5-Amino-4-[(4-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl}-1-methylpyridinium chloride;

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10 4-{[5-Amino-4-[(4-methoxyphenyl)diazanyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

4-{[5-Amino-4-[(3-methoxyphenyl)diazanyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

4-{[5-Amino-4-[(2-methoxyphenyl)diazanyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

15 4-{[5-Amino-4-[(4-chlorophenyl)diazanyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

4-{[5-Amino-4-[(3-chlorophenyl)diazanyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

20 4-{[5-Amino-4-[(2-chlorophenyl)diazanyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

4-{[5-Amino-4-[(2-chloro-4-methylphenyl)diazanyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

4-{[5-Amino-4-[(5-chloro-2-methylphenyl)diazanyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

25 4-{[5-Amino-4-[(4-chloro-2-methylphenyl)diazanyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

4-{[5-Amino-4-[(5-chloro-2-methoxyphenyl)diazanyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

4-{{[5-Amino-4-[(3-chloro-4-fluorophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

4-{{[5-Amino-4-[(2-chloro-4-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

5 4-{{[5-Amino-4-[(2-chloro-5-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

4-{{[5-Amino-4-[(4-chloro-2-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

10 4-{{[5-Amino-4-[(4-chloro-3-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

4-{{[5-Amino-4-[(5-chloro-2-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

4-{{[5-Amino-4-[(2-cyano-4-nitrophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

15 4-{{[5-Amino-4-[(2,4-dichlorophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

4-{{[5-Amino-4-[(2,5-dichlorophenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

20 4-{{[5-Amino-4-[(2,4-dimethylphenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

4-{{[5-Amino-4-[(2,5-dimethylphenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

4-({[5-Amino-4-[(4-(methoxycarbonyl)phenyl)diazenyl]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium methyl sulfate.

25 According to another preferred embodiment of the present invention, the pyrazole dyes of general formula (II), which can be used, for example, in the compositions in accordance with the invention, may be selected from the group comprising:

3-({5-Amino-4-[(2-amino-3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)amino]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

3-{[5-Amino-4-({2-[(2-hydroxyethyl)amino]-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene} amino)-1*H*-pyrazol-1-yl]methyl}-1-methylpyridinium chloride;

5 3-({5-Amino-4-[(2-amino-4-imino-5-methylcyclohexa-2,5-dien-1-ylidene)amino]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

3-({5-Amino-4-[(2-amino-4-imino-5-methoxycyclohexa-2,5-dien-1-ylidene)amino]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

10 3-{[5-amino-4-({2-[(2-hydroxyethyl)amino]-4-imino-5-methoxycyclohexa-2,5-dien-1-ylidene} amino)-1*H*-pyrazol-1-yl]methyl}-1-methylpyridinium chloride;

3-[(5-Amino-4-{[2-amino-5-(2-hydroxyethoxy)-4-iminocyclohexa-2,5-dien-1-ylidene]amino}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium chloride;

3-({5-amino-4-[(5-hexyl-2-hydroxy-4-oxocyclohexa-2,5-dien-1-ylidene)amino]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

15 4-({5-Amino-4-[(2-amino-3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)amino]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

4-{[5-Amino-4-({2-[(2-hydroxyethyl)amino]-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene} amino)-1*H*-pyrazol-1-yl]methyl}-1-methylpyridinium chloride;

20 4-({5-Amino-4-[(2-amino-4-imino-5-methylcyclohexa-2,5-dien-1-ylidene)amino]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

4-({5-Amino-4-[(2-amino-4-imino-5-methoxycyclohexa-2,5-dien-1-ylidene)amino]-1*H*-pyrazol-1-yl} methyl)-1-methylpyridinium chloride;

4-{[5-amino-4-({2-[(2-hydroxyethyl)amino]-4-imino-5-methoxycyclohexa-2,5-dien-1-ylidene} amino)-1*H*-pyrazol-1-yl]methyl}-1-methylpyridinium chloride;

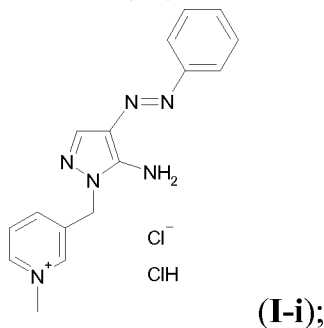
25 4-[(5-Amino-4-{[2-amino-5-(2-hydroxyethoxy)-4-iminocyclohexa-2,5-dien-1-ylidene]amino}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium chloride.

The dyes may also exist in one or more tautomeric forms.

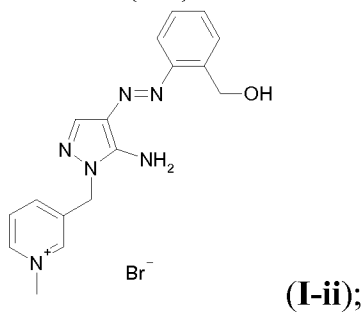
Most preferred cationic dyes of general formula (I) or (II), obtainable from

the pyrazole intermediate (III), may be selected from the group comprising:

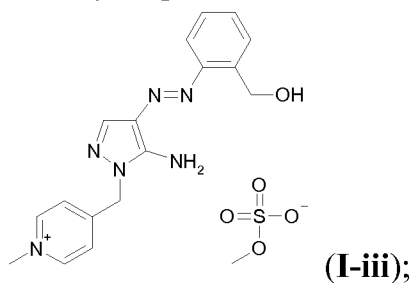
3-{[5-Amino-4-(phenyldiazenyl)-1H-pyrazol-1-yl]methyl}-1-methylpyridinium chloride hydrochloride (**I-i**)



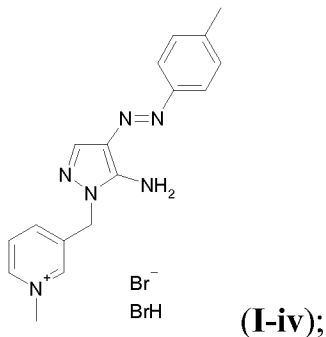
5 3-[(5-Amino-4-{[2-(hydroxymethyl)phenyl]diazanyl}-1H-pyrazol-1-yl)methyl]-1-methylpyridinium bromide (**I-ii**)



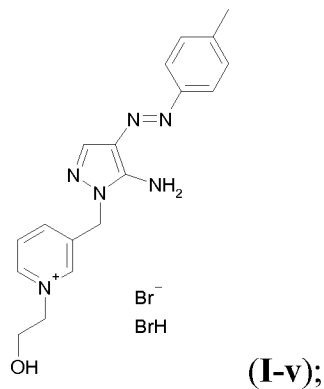
4-[(5-Amino-4-{[2-(hydroxymethyl)phenyl]diazanyl}-1H-pyrazol-1-yl)methyl]-1-methylpyridinium methylsulphate (**I-iii**)



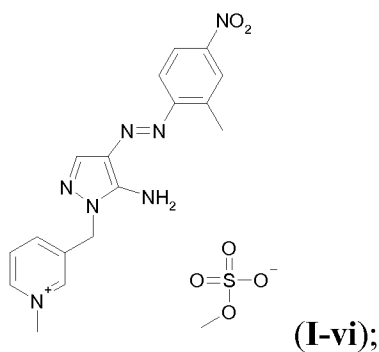
10 3-({5-Amino-4-[(4-methylphenyl)diazanyl]-1H-pyrazol-1-yl}methyl)-1-methylpyridinium bromide hydrobromide (**I-iv**)



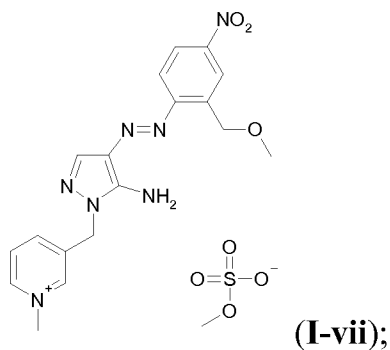
3-({5-Amino-4-[(4-methylphenyl)diazenyl]-1H-pyrazol-1-yl}methyl)-1-(2-hydroxyethyl)pyridinium bromide hydrobromide (**I-v**)



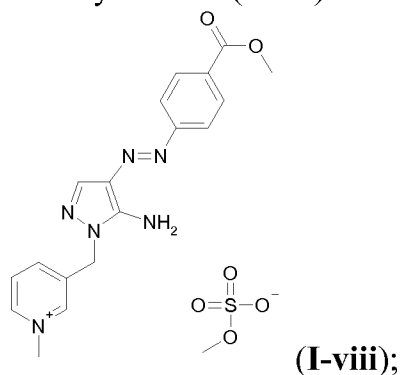
5 3-[(5-Amino-4-{[2-methyl-4-nitrophenyl]diazenyl}-1H-pyrazol-1-yl)methyl]-1-methylpyridinium methyl sulfate (**I-vi**)



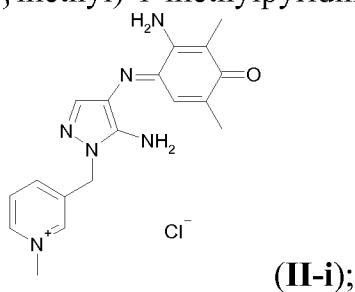
10 3-[(5-Amino-4-{[2-methoxymethyl-4-nitrophenyl]diazenyl}-1H-pyrazol-1-yl)methyl]-1-methylpyridinium methyl sulfate (**I-vii**)



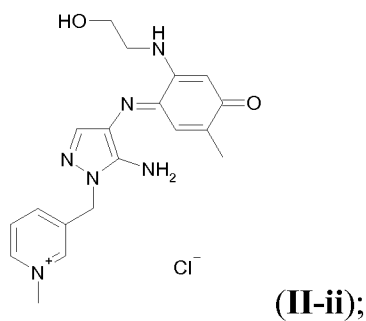
3-(5-Amino-4-[(4-(methoxycarbonyl)phenyl)diazenyl]-1H-pyrazol-1-yl)methyl)-1-methylpyridinium methyl sulfate (**I-viii**)



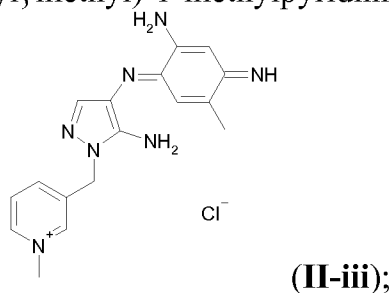
3-(5-Amino-4-[(2-amino-3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)amino]-1H-pyrazol-1-yl)methyl)-1-methylpyridinium chloride (**II-i**)



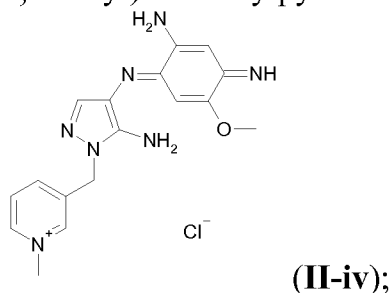
3-[5-Amino-4-({2-[(2-hydroxyethyl)amino]-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene}amino)-1H-pyrazol-1-yl)methyl]-1-methylpyridinium chloride (**II-ii**)



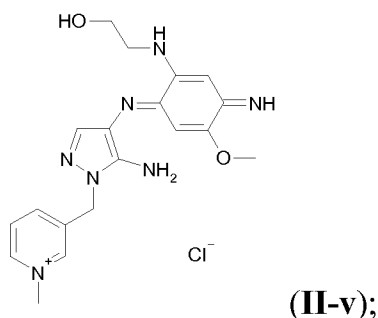
3-(5-Amino-4-[(2-amino-4-imino-5-methylcyclohexa-2,5-dien-1-ylidene)amino]-1H-pyrazol-1-yl)methyl)-1-methylpyridinium chloride (**II-iii**)



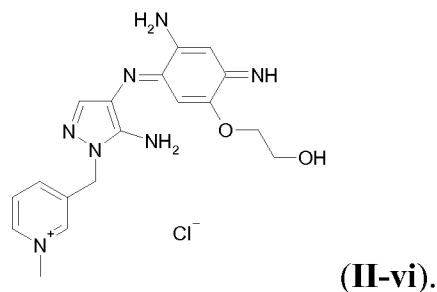
3-({5-Amino-4-[(2-amino-4-imino-5-methoxycyclohexa-2,5-dien-1-ylidene)amino]-1H-pyrazol-1-yl}methyl)-1-methylpyridinium chloride (**(II-iv)**)



3-([5-amino-4-({2-[(2-hydroxyethyl)amino]-4-imino-5-methoxycyclohexa-2,5-dien-1-ylidene}amino)-1H-pyrazol-1-yl]methyl)-1-methylpyridinium chloride (**(II-v)**)



3-[(5-Amino-4-{[2-amino-5-(2-hydroxyethoxy)-4-iminocyclohexa-2,5-dien-1-ylidene]amino}-1H-pyrazol-1-yl)methyl]-1-methylpyridinium chloride (**(II-vi)**)



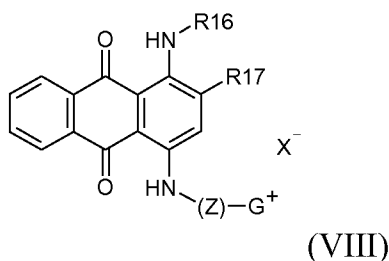
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15

According to a preferred embodiment, the compositions of the invention comprising, in a medium suitable for dyeing, one or more cationic dye of general formula (I) or (II), as defined above, may further comprise one or more known conventional direct dye(s), different from those of general formula (I) and (II). The color range of the cationic direct dyes of general formula (I) and (II) can be extended, for example, by the addition of one or more conventional cationic direct

dye which is a cationic direct blue dye. Surprisingly it was found that cationic anthraquinone blue dyes of the general formula (VIII) are highly compatible with the dyes of general formula (I) and (II) and fulfill the requirements in an outstanding manner:

5



wherein

R16 is a hydrogen atom, a C1-C6 alkyl group which may be substituted by one or two hydroxy groups, a di-(C1-C2)alkylamino-(C2-C3)alkyl group, a phenyl or a tolyl group;

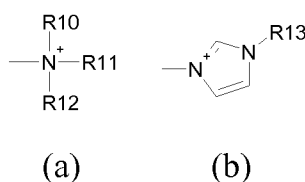
10

R17 is a hydrogen atom, a methyl or a methoxy group;

Z is a (C2-C3)-alkylene diradical;

G⁺ is a cationic group selected from formula (a) or (b) wherein R10-R12 and R13 are as defined for general formula (I) and (II);

15



X⁻ is an anion as defined for general formula (I) and (II), preferably it is chloride, bromide, methylsulfonate or methylsulfate.

The anthraquinone dyes of general formula (VIII) HC Blue 16 and HC Blue 17 (INCI names) are the most preferred.

20

The cationic dye(s) of general formula (I) or (II) according to the invention are preferably used in a concentration of from 0.001 to 10% by weight, and even more preferably from 0.05 to 5% by weight, relative to the total weight of the

ready-to-use composition.

Although combinations of the cationic dyes of general formula (I) and (II) and optionally (VIII) are able to produce a broad range of colors further conventional direct dyes may be added, which may be cationic, nonionic or anionic or mixtures thereof.

Cationic direct dyes which can be used in combination with cationic dyes of general formula (I) or (II) are for instance the dyes Basic Yellow 57, Basic Brown 16, Basic Brown 17, Basic Red 76, Basic Red 118, and Basic Blue 99.

Further cationic dyes are for instance described in EP658095B1, Basic Yellow 87, Basic Orange 31 and Basic Red 51.

Useful cationic dyes of the triphenylmethane type are for instance Basic Violet 2 and Basic Blue 77.

Non ionic dyes which may be used in combination with cationic dyes of general formula (I) or (II) are of the nitro dye type which can be selected from 2-Amino-3-nitrophenol; 2-[(2-Hydroxyethyl)amino]-1-methoxy-5-nitrobenzene; 1-(2-Hydroxyethoxy)-3-methylamino-4-nitrobenzene; 2,3-(Dihydroxypropoxy)-3-methylamino-4-nitrobenzene; 1-[(2-Ureidoethyl)amino]-4-nitrobenzene; 4-[(2-Hydroxyethyl)amino]-3-nitro-1-methylbenzene; 1-[(2-Hydroxyethyl)amino]-2-nitrobenzene (HC Yellow No. 2); 1-(2-Hydroxyethoxy)-2-[(2-hydroxyethyl)amino]-5-nitrobenzene (HC Yellow No. 4); 1-Amino-2-[(2-hydroxyethyl)amino]-5-nitrobenzene (HC Yellow No. 5); 4-[(2,3-Dihydroxypropyl)amino]-3-nitro-1-trifluoromethylbenzene (HC Yellow No. 6); 3-[(2-Aminoethyl)amino]-1-methoxy-4-nitrobenzene hydrochloride (HC Yellow No.9); 1-Chloro-2,4-bis-[(2-hydroxyethyl)amino]-5-nitrobenzene (HC Yellow No. 10); 2-[(2-Hydroxyethyl)amino]-5-nitrophenol (HC Yellow No. 11); 1-Chloro-4-[(2-hydroxyethyl)amino]-3-nitrobenzene (HC Yellow No. 12); 4-[(2-Hydroxyethyl)amino]-3-nitro-1-trifluoromethyl-benzene (HC Yellow No. 13); 4-[(2-Hydroxyethyl)amino]-3-nitro-benzonitrile (HC Yellow No. 14); 4-[(2-

Hydroxyethyl)amino]-3-nitro-benzamide (HC Yellow No. 15); 1,4-diamino-2-nitrobenzene; 1,4-Bis[(2-hydroxyethyl)amino]-2-nitrobenzene; 2-Amino-4,6-dinitro-phenol; 4-Amino-3-nitrophenol; 1-Amino-5-chloro-4-[(2-hydroxyethyl)amino]-2-nitrobenzene; 4-[(2-Hydroxyethyl)amino]-3-nitrophenol;

5 1-[(2-Aminoethyl)amino]-4-(2-hydroxyethoxy)-2-nitrobenzene (HC Orange No. 2); 4-(2,3-Dihydroxypropoxy)-1-[(2-hydroxyethyl)amino]-2-nitrobenzene (HC Orange No. 3); 2-[(2-Hydroxyethyl)amino]-4,6-dinitro-phenol; 4-Ethylamino-3-nitrobenzoic acid; 2-[(4-Amino-2-nitrophenyl)amino]-benzoic acid; 2-Chloro-6-ethylamino-4-nitrophenol; 2-Amino-6-chloro-4-nitrophenol; 4-[(3-

10 Hydroxypropyl)amino]-3-nitrophenol; 2,5-Diamino-6-nitropyridine; 1,2,3,4-Tetrahydro-6-nitroquinoxaline; 4-Amino-2-nitro-diphenylamine (HC Red No. 1); 4-Amino-1-[(2-hydroxyethyl)amino]-2-nitrobenzene (HC Red No. 3); 1-Amino-4-[(2-hydroxyethyl)amino]-2-nitrobenzene (HC Red No. 7); 1-Amino-5-chloro-4-[(2,3-dihydroxypropyl)amino]-2-nitrobenzene (HC Red No. 10); 5-Chloro-1,4-

15 [di(2,3-dihydroxypropyl)amino]-2-nitrobenzene (HC Red No. 11); 1-Amino-4-[di(2-hydroxyethyl)amino]-2-nitrobenzene hydrochloride (HC Red No. 13); 7-Amino-3,4-dihydro-6-nitro-2H-1,4-benzoxazine (HC Red No. 14); 1-Amino-3-methyl-4-[(2-hydroxyethyl)amino]-6-nitrobenzene (HC Violet No. 1); 1-(3-Hydroxypropylamino)-4-[di(2-hydroxyethyl)amino]-2-nitrobenzene (HC Violet

20 No. 2); 1-(2-Hydroxyethyl)amino-2-nitro-4-[di(2-hydroxyethyl)amino]-benzene (HC Blue No. 2); 1-Methylamino-4-[methyl-(2,3-dihydroxypropyl)amino]-2-nitrobenzene (HC Blue No. 6); 1-[(2,3-Dihydroxypropyl)amino]-4-[ethyl-(2-hydroxyethyl)amino]-2-nitrobenzene hydrochloride (HC Blue No. 9); 1-[(2,3-Dihydroxypropyl)amino]-4-[methyl-(2-hydroxyethyl)amino]-2-nitrobenzene (HC

25 Blue No. 10); 4-[Di(2-hydroxyethyl)amino]-1-[(2-methoxyethyl)amino]-2-nitrobenzene (HC Blue No. 11); 4-[Ethyl-(2-hydroxyethyl)amino]-1-[(2-hydroxyethyl)amino]-2-nitrobenzene hydrochloride (HC Blue No. 12); 2-((4-Amino-2-nitrophenyl)amino)-5-dimethylaminobenzoic acid (HC Blue No. 13).

Anionic dyes in combination with cationic dyes of general formula (I) or (II) and optionally (VIII) may be used to obtain very specific effects; such as, for example, Acid Yellow 1, Acid Yellow 23, Acid Red 52, Acid Red 92 and Acid Violet 43.

5 Further cationic dye(s) different from those of general formula (I), (II) and (VIII), nonionic dyes and anionic dyes are preferably used in a concentration of from 0.001 to 5% by weight, and even more preferably from 0.05 to 2.5% by weight, relative to the total weight of the composition.

The compositions for dyeing keratin fibers in accordance with the invention
10 can be in various forms, such as in form of a liquid, a cream, a gel, a liquid able to produce foam, or in any other form which is appropriate for dyeing keratin fibers, in particular human hair.

The compositions for dyeing keratin fibers can therefore comprise various adjuvants used conventionally in compositions for dyeing hair, such as solvents,
15 fatty alcohols, fatty acids, cationic, nonionic, anionic, amphoteric surfactants or mixtures thereof, cationic, nonionic, anionic, amphoteric polymers or mixtures thereof, inorganic or organic thickeners, inorganic or organic acids and bases for adjusting the pH to the desired range, buffers, penetrating agents, sequestering agents, dispersing agents, film-forming agents, preserving agents, opacifiers and
20 fragrances.

The medium which is suitable for dyeing in accordance with the invention generally comprises water or a mixture of water and at least one organic solvent in order to dissolve the compounds in case they are not sufficiently soluble in water. The organic solvent may be, for example, an alcohol such as ethanol and
25 isopropanol; glycerol; glycols and glycol ethers such as 2-butoxy-ethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and monomethyl ether; and an aromatic alcohol such as benzyl alcohol or phenoxyethanol, and mixtures thereof.

The solvents can be present in a concentration preferably ranging from approximately 1 to approximately 40% by weight relative to the total weight of the composition, and even more preferably from approximately 2 to approximately 20% by weight relative to the total weight of the composition.

5 Fatty alcohols may be aliphatic alcohols usually consisting of a chain of 8 to 22 carbon atoms, but can also contain 36 or more carbon atoms. Fatty alcohols usually have even number of carbon atoms and a single hydroxy group attached to the terminal carbon. Some are unsaturated and some are branched.

10 Examples are for instance cetyl alcohol, myristyl alcohol, stearyl alcohol, isostearyl alcohol, lanolin alcohol, lauryl alcohol, oleyl alcohol, behenyl alcohol, and mixtures thereof.

Amongst various surfactants which can be used, the preferred surfactants will ensure maximum compatibility of the cosmetic medium with the variety of dyes, optionally added oxidizing agents, conditioning materials typically present in
15 such compositions.

Suitable anionic surfactants for the hair colorants according to the invention are any anionic surface-active substances suitable for use on the human body. Such substances are characterized by a water-solubilizing anionic group such as, for example, a carboxylate, sulfate, sulfonate or phosphate group and a lipophilic alkyl
20 group containing around 10 to 22 carbon atoms. In addition, glycol or polyglycol ether groups, ester, ether and amide groups and hydroxyl groups may also be present in the molecule. The following are examples of suitable anionic surfactants - in the form of the sodium, potassium and ammonium salts and the mono-, di- and trialkanolammonium salts containing 2 or 3 carbon atoms in the alkanol group:

- 25
- linear fatty acids containing 10 to 22 carbon atoms (soaps),
 - ether carboxylic acids corresponding to the formula $R-O-(CH_2-CH_2O)_x-CH_2-COOH$, in which R is a linear alkyl group containing 10 to 22 carbon atoms and $x=0$ or 1 to 16,

- acyl sarcosides containing 10 to 18 carbon atoms in the acyl group,
 - acyl taurides containing 10 to 18 carbon atoms in the acyl group,
 - acyl isethionates containing 10 to 18 carbon atoms in the acyl group,
 - sulfosuccinic acid mono- and dialkyl esters containing 8 to 18 carbon
- 5 atoms in the alkyl group and sulfosuccinic acid monoalkyl polyoxyethyl esters containing 8 to 18 carbon atoms in the alkyl group and 1 to 6 oxyethyl groups,
- linear alkane sulfonates containing 12 to 18 carbon atoms,
 - linear α -olefin sulfonates containing 12 to 18 carbon atoms,
 - α -sulfofatty acid methyl esters of fatty acids containing 12 to 18
- 10 carbon atoms,
- alkyl sulfates and alkyl polyglycol ether sulfates corresponding to the formula $\text{RO}-(\text{CH}_2-\text{CH}_2\text{O})_x-\text{SO}_3\text{H}$, in which R is a preferably linear alkyl group containing 10 to 18 carbon atoms and x is 0 or 1 to 12,
 - esters of tartaric acid and citric acid with alcohols in the form of
- 15 addition products of around 2 to 15 molecules of ethylene oxide and/or propylene oxide with fatty alcohols containing 8 to 22 carbon atoms.

Preferred anionic surfactants are alkyl sulfates, alkyl polyglycol ether sulfates and ether carboxylic acids containing 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule and, in particular, salts of

20 saturated and, more particularly, unsaturated C8-C22 carboxylic acids, such as oleic acid, stearic acid, isostearic acid and palmitic acid.

Zwitterionic surfactants are surface active compounds which contain at least one quaternary ammonium group and at least one $-\text{COO}^{(-)}$ or $-\text{SO}_3^{(-)}$ group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines,

25 such as N-alkyl-N,N-dimethyl ammonium glycinate, for example cocoalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, cocoacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in

the alkyl or acyl group and cocoacylaminoethyl hydroxyethyl carboxymethyl glycinate. A preferred zwitterionic surfactant is the fatty acid amide derivative known by the CTFA name of Cocamidopropyl Betaine.

Ampholytic surfactants are surface-active compounds which, in addition to
5 a C₈₋₁₈ alkyl or acyl group, contain at least one free amino group and at least one —COOH or —SO₃H group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkyl aminobutyric acids, N-alkyl iminodipropionic acids, N-hydroxyethyl-N-alkyl amidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines,
10 2-alkyl aminopropionic acids and alkyl aminoacetic acids containing 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkyl aminopropionate, cocoacyl aminoethyl aminopropionate and C12-C18 acyl sarcosine.

Nonionic surfactants contain, for example, a polyol group, a poly-alkylene
15 glycol ether group or a combination of polyol and polyglycol ether groups as the hydrophilic group. Examples of such compounds are:

- products of the addition of 2 to 30 moles of ethylene oxide and/or 0 to 5 moles of propylene oxide onto linear fatty alcohols containing 8 to 22 carbon atoms, onto fatty acids containing 12 to 22 carbon atoms and onto alkylphenols
20 containing 8 to 15 carbon atoms in the alkyl group,
- C12-C22 fatty acid monoesters and diesters of products of the addition of 1 to 30 moles of ethylene oxide onto glycerol,
- C8-C22 alkyl mono- and oligoglycosides and ethoxylated analogs thereof,
- 25 - products of the addition of 5 to 60 moles of ethylene oxide onto castor oil and hydrogenated castor oil,
- products of the addition of ethylene oxide onto sorbitan fatty acid esters,
- products of the addition of ethylene oxide onto fatty acid

alkanolamides,

- cationic surfactants.

Examples of cationic surfactants suitable for use in compositions according to the invention are, in particular, quaternary ammonium compounds. Preferred are ammonium halides, such as alkyl trimethyl ammonium chlorides, dialkyl dimethyl ammonium chlorides and trialkyl methyl ammonium chlorides, for example cetyl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, lauryl dimethyl ammonium chloride, lauryl dimethyl benzyl ammonium chloride and tricetyl methyl ammonium chloride; in some cases the anion of the cationic surfactant may be different and consists of an alkylsulfate anion. Other cationic surfactants suitable for use in accordance with the invention are for instance the quaternized protein hydrolyzates.

Also suitable for use in accordance with the invention are cationic silicone oils such as, for example, the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethyl silyl amodimethicone), Dow Corning 929 Emulsion (containing a hydroxylamino-modified silicone which is also known as Amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethyl siloxanes, Quaternium-80);

alkyl amidoamines, particularly fatty acid amidoamines, such as the stearyl amidopropyl dimethyl amine obtainable as Tego Amid®S 18, are distinguished not only by their favorable conditioning effect, but also and in particular by their ready biodegradability;

quaternary ester compounds, so-called "esterquats", such as the methyl hydroxyalkyl dialkoyloxyalkyl ammonium methosulfates marketed under the trade name of Stepantex® and the products marketed under the trade name of Dehyquart® - such as Dehyquart® AU-46 and Dehyquart® L-80 - are also readily

biodegradable. The esterquats are the particularly preferred surfactants for the purposes of the invention.

One example of a quaternary sugar derivative suitable for use as a cationic surfactant is the commercially available product Glucquat®100 (CTFA name: 5 Lauryl Methyl Gluceth-10 Hydroxypropyl Dimonium Chloride).

The compositions of the present invention may further comprise one or more thickeners in an amount sufficient to provide the composition with the required viscosity so that it can be readily applied to the hair without unduly dripping off the hair. Preferred for use are salt tolerant thickeners, such as xanthan, 10 guar, hydroxypropyl guar, scleroglucan, methyl cellulose, ethyl cellulose (available as AQUACOTE™), hydroxyethyl cellulose (NATROSOL™), carboxymethyl cellulose, hydroxypropylmethyl cellulose, microcrystalline cellulose, hydroxybutylmethyl cellulose, hydroxypropyl cellulose (available as KLUCEL™), hydroxyethyl ethyl cellulose, cetyl hydroxyethyl cellulose (available 15 as NATROSOL™ Plus 330), N-vinylpyrrolidone (available as POVIDONE™), Acrylates/Ceteth-20 Itaconate Copolymer (available as STRUCTURE™ 3001), hydroxypropyl starch phosphate (available as STRUCTURE™ ZEA), polyethoxylated urethanes or polycarbamyl polyglycol ester (e.g. PEG-150/Decyl/SMDI copolymer (available as ACULYN™ 44), PEG-20 150/Stearyl/SMDI copolymer available as ACULYN™ 46), Acrylates/Beheneth-25 Methacrylate Copolymer (available as ACULYN™ 28), Acrylates/Vinyl Neodecanoate Crosspolymer (available as ACULYN™ 38), Acrylates/Steareth-20 Methacrylate Crosspolymer (available as ACULYN™ 88), PEG-150 Distearate (available as ACULYN™ 60), trihydroxystearin (available as THIXCIN™), 25 acrylates copolymer (e.g. available as ACULYN™ 33) or hydrophobically modified acrylate copolymers (e.g. Acrylates/Steareth-20 Methacrylate Copolymer (available as ACULYN™ 22), non-ionic amphophilic polymers comprising at least one fatty chain and at least one hydrophilic unit selected from polyether urethanes

comprising at least one fatty chain.

Typically, the added amount may be at least 0.05%, preferably at least 0.5% to 1%, by weight of thickener relative to the total weight of the composition. When the composition is obtained by mixing several components, the thickener may be present in any of the components.

The composition may further optionally comprise a cationic polymer or a combination of cationic polymers. Preferred cationic polymers are Polyquaternium-7, Polyquaternium-22, Polyquaternium-37 and Polyquaternium-87. Particularly preferred are Polyquaternium-22 and Polyquaternium-37 and mixtures thereof. The compositions of the present invention may comprise at least about 0.05%, preferably from about 0.5% to 2% by weight of the composition of a cationic polymer.

Besides the cationic polymers which have conditioning properties, the compositions of the present invention may also comprise conditioning agents. Conditioning agents suitable for use may be selected from silicone materials, amino silicones, polymeric resins, polyol carboxylic acid esters, cationic surfactants, water-insoluble oils, oil derived materials and mixtures thereof.

Useful silicone conditioning materials can be selected from polyalkylsiloxane oils, linear polydimethylsiloxane oils containing trimethylsilyl or hydroxydimethylsiloxane end groups, polymethylphenylsiloxane polydimethylphenylsiloxane or polydimethyldiphenylsiloxane oils, silicone resins, organofunctional siloxanes having in their general structure one or a number of organofunctional group(s), the same or different, attached directly to the siloxane chain. Said organofunctional group(s) are selected from polyethyleneoxy and/or polypropyleneoxy groups, (per)fluorinated groups, thiol groups, substituted or unsubstituted amino groups, carboxylate groups, hydroxylated groups, alkoxylated groups, quaternium ammonium groups, amphoteric and betain groups. The silicone can either be used as a neat fluid or in the form of a pre-formed emulsion.

The conditioning agent may generally be used at levels of from about 0.05% to about 20% by weight of the composition, preferably of from about 0.1% to about 15%, more preferably of from about 0.2% to about 10%, even more preferably of from about 0.2% to about 2%.

5 Particularly preferred are phosphate-based conditioning and emulsifying wax comprising a mixture of cetearyl alcohol (mixture of cetyl alcohol and stearyl alcohol), dicetyl phosphate and ceteth-10 phosphate (e.g. available as CRODAFOS™ CES). Another useful raw material may be beheneth 30 phosphate, cetostearyl alcohol, mono and dicetyl phosphate (e.g. available as CRODAFOS™
10 BES-70).

The preferred amount of such materials is at least 0.1%, preferably from 0.1% to about 20%, preferred for the current application is an amount between 0.5% and 5% by weight.

The compositions may further comprise ingredients which have antistatic or
15 film forming properties such as polyamines, for example PEG-15 Cocopolyamine and Chitosan.

The compositions may also comprise extracts, for instance plant extracts or vegetable oils, for example in amounts from 0.1 to 5%, more preferably from 0.5 to 2.5% by weight.

20 The pH of the composition may generally range from approximately 2 to approximately 12, preferably the pH is from 7 to 11. The pH can be adjusted to the desired value using acidifying or basifying agents usually used in the dyeing of keratin fibers.

Acidifying agents may be inorganic or organic acids such as hydrochloric
25 acid, phosphoric acid, carboxylic acids such as malic acid, citric acid or lactic acid, and sulphonic acids.

Basifying agents may be, for example, aqueous ammonia, alkaline carbonates, alkanolamines such as monoethanolamine (MEA) and triethanolamine,

1-amino-2-propanol, 2-amino-2-methyl-propanol (AMP), 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol and tris(hydroxymethyl)-aminomethane (tromethamine, Tris), sodium hydroxide, potassium hydroxide or mixtures thereof.

- 5 The amount of basifying agents can range between 0.1 and 10% by weight, preferably between 1 and 5% by weight.

It may be the consumers desire to obtain a more fashioned shade by using a ready-to-use composition containing at least one cationic dye of general formula (I) or (II) optionally (VIII).

- 10 In such a case it may be required to lighten the naturally pigmented hair which for instance can be achieved by the addition of an oxidizing agent; in some cases it may be favorable that the ready-to-use composition also contains an ammonium salt such as ammonium chloride.

- 15 The oxidizing agent present in the composition may be selected from oxidizing agents used conventionally in oxidation dyeing and preferably from hydrogen peroxide, urea peroxide, alkali metal bromates and persalts such as a percarbonate salt, a bromate salt, a perborate salt or a persulfate salt. Hydrogen peroxide is particularly preferred.

- 20 The ready-to-use compositions in accordance with the invention lead from weakly colored to intense, from colorations of low chromaticity to chromatic colorations. Therefore the compositions according to the invention are useful to provide natural shades as well as fashioned shades. Besides the chromatic properties the ready-to-use compositions show very good evenness and excellent properties of resistance with respect to atmospheric factors such as light and bad
25 weather and with respect to perspiration and the various treatments to which the hair may be subjected (washing, blow-drying, combing, or permanent-waving).

Another object of the invention is a process for dyeing keratin fibers, and in particular human keratin fibers such as the hair, using a ready-to-use composition

as defined above.

According to this process, the ready-to-use composition is applied to the hair fibers and is left on them for an exposure time preferably ranging from approximately 3 to approximately 40 minutes, more preferably from approximately 10 to approximately 30 minutes, after which the fibers are rinsed, optionally washed with shampoo, rinsed again and dried.

The examples which follow further illustrate the invention.

EXAMPLES

Example 1: Preparation of {[5-amino-4-(aryldiazenyl)-1H-pyrazol-1-yl]methyl}-1-methylpyridinium salts of structure I

Step 1: General procedure for the preparation of 4-(aryldiazenyl)-1H-pyrazol-5-amine intermediates

100 mmol of the corresponding arylamine is added to 50 ml a 1:1 (v/v) mixture of water and hydrochloric acid 35%. The mixture is stirred for 15 min at room temperature to obtain a solution or a fine suspension, respectively, and then the mixture is cooled in an ice bath. At 0-5°C a solution of 7.25 g (105 mmol) of sodium nitrite in 20 ml water is added within 30 min; stirring is continued for 1 hour. The obtained diazonium salt solution is then added to a mechanically stirred solution of the corresponding 5-amino-1H-pyrazole (100 mmol) and 20.5g (250 mmol) sodium acetate dissolved in 150 ml water/methanol 2:1 (v/v). The spontaneously obtained orange-yellow, fine dye suspension is stirred for 1h; then the product is filtered off, washed with water and dried.

According to the general procedure the following compounds were obtained from 1-(pyridin-3-ylmethyl)-1H-pyrazol-5-amine:

Example 1a: 4-(Phenyldiazenyl)-1-(pyridin-3-ylmethyl)-1H-pyrazol-5-amine

Arylamine: aniline

Yield: 91%

m.p.: 164°C

CHN Analysis (C₁₅H₁₄N₆; MW = 278.32):

	<u>%C</u>	<u>%H</u>	<u>%N</u>
Calculated:	64.73	5.07	30.20
Found:	64.4	5.0	30.5

5 **Example 1b: 4-[(4-methylphenyl)diazenyl]-1-(pyridin-3-ylmethyl)-1H-pyrazol-5-amine**

Arylamine: p-toluidine

Yield: 98%

m.p.: 163-164°C

10 **Example 1c: Methyl 4-{[5-amino-1-(pyridin-3-ylmethyl)-1H-pyrazol-4-yl]diazenyl}benzoate**

Arylamine: methyl p-aminobenzoate

Yield: 96%

m.p.: 158°C

15 **Example 1d: 4-[(2-methyl-4-nitrophenyl)diazenyl]-1-(pyridin-3-ylmethyl)-1H-pyrazol-5-amine**

Arylamine: 2-methyl-4-nitroaniline

Yield: 96%

m.p.: 198-199°C

20 **Example 1e: 4-{[2-(methoxymethyl)-4-nitrophenyl]diazenyl}-1-(pyridin-3-ylmethyl)-1H-pyrazol-5-amine**

Arylamine: 2-methoxymethyl-4-nitroaniline

Yield: 88%

m.p.: 187-189°C (dec.)

Example 1f: (2-{[5-amino-1-(pyridin-3-ylmethyl)-1H-pyrazol-4-yl]diazeryl}phenyl)methanol

Arylamine: 2-aminobenzylalkohol

Yield: 77%

5 m.p.: 158°C

By the same procedure is obtained from 1-(pyridin-4-ylmethyl)-1H-pyrazol-5-amine:

Example 1g: (2-{[5-amino-1-(pyridin-4-ylmethyl)-1H-pyrazol-4-yl]diazeryl}phenyl)methanol

10 Arylamine: 2-aminobenzylalkohol

Yield: 82%

m.p.: 180-182°C

Step 2: Quaternization of the Intermediates from Step 1

Example 2a: 3-{[5-Amino-4-(phenyldiazenyl)-1H-pyrazol-1-yl]methyl}-1-methylpyridinium chloride hydrochloride (I-i)

15 4-(Phenyldiazenyl)-1-(pyridin-3-ylmethyl)-1H-pyrazol-5-amine (example 1a, 20mmol, 5.57g) is heated to reflux in acetonitrile (50ml) whereby an orange-red solution is obtained. Then dimethylsulfate (22mmol, 2.77g) is added and heating is continued. After approximately 4 hours the reaction mixture is allowed to cool. At room temperature hydrochloric acid is added with stirring whereby the product precipitates out. Stirring is continued for 1h; then the product is filtered off and dried to give 6.63g (86.5% of th.) orange, fine powdery solid.

The dye crystallizes out as hydrochloride and contains one equivalent of crystal water.

25 CHN Analysis (C₁₆H₁₇N₆.Cl x HCl x H₂O, MW = 383.28)

	% C	% H	% N
Calculated:	50.14	5.26	21.93
Found:	49.9	5.2	21.9

Example 2b: 3-[(5-Amino-4-{[2-(hydroxymethyl)phenyl]diazenyl}-1H-pyrazol-1-yl)methyl]-1-methylpyridinium bromide (I-ii)

(2-{[5-Amino-1-(pyridin-3-ylmethyl)-1H-pyrazol-4-yl]diazenyl}phenyl)methanol (70 mmol, 21.58 g) is stirred in 3-methoxypropionitrile (100 ml) and heated to 60°C. At this temperature dimethylsulfate (73.5 mmol, 9.27 g) is added within 30 min. A clear red solution is obtained after the addition was complete. Stirring is continued for another 30 min. The reaction mixture is allowed to cool to room temperature, then the solvent is evaporated. The viscous residue is dissolved in water (80 ml), then ammonium bromide solution (73.5 mmol, 7.2 g dissolved in 30 ml water) is added and stirring at room temperature is continued. Shortly after the addition the dye precipitates out. The solid is filtered off and recrystallized from water (60ml). After filtration and drying 15.88 g (56.3% of th.) yellow solid is obtained.

CHN Analysis (C₁₇H₁₉N₆O.Br; MW = 403.28)

	% C	% H	% N
Calculated:	50.63	4.75	20.84
Found:	50.77	4.80	21.07

¹H-NMR (DMSO-d₆): δ = 8.95 (signal overlap, 2H); 8.38 (d, ³J = 8.1 Hz, 1H); 8.15 (dd, ³J = 8.9 Hz, ³J = 2.6 Hz, 1H); 7.97 (s, 1H); 7.54 (m, 2H); 7.44 (s, broad, 2H); 7.32 (m, 2H); 5.48 (s, 2H); 5.21 (s, broad, 1H); 4.86 (s, 2H); 4.37 ppm (s, 3H).

Example 2c: 4-[(5-amino-4-{[2-(hydroxymethyl)phenyl]diazenyl}-1H-pyrazol-1-yl)methyl]-1-methylpyridinium methyl sulfate (I-iii)

To a stirred suspension of (2-{[5-amino-1-(pyridin-4-ylmethyl)-1H-pyrazol-4-yl]diazenyl}phenyl)methanol (3.08 g, 10 mmol) in 3-methoxypropionitrile (30 ml) dimethylsulfate is added (1.32 g, 10.5 mmol). The mixture is heated to 60°C and a clear solution is obtained. After 2 hours the reaction mixture is allowed to cool whereby the product crystallizes out. Filtration and drying gives 3.87 g (89.1

% of th.) orange-yellow product.

The product on TLC is uniform and shows the expected characteristics of a cationic dye.

TLC (silica 0.25 mm), isopropanol (4)/water (5.5)/acetic acid (0.5): R_f starting material = 0.81; R_f cationic dye = 0.58.

Example 2d: 3-({5-Amino-4-[(4-methylphenyl)diazenyl]-1H-pyrazol-1-yl}methyl)-1-methylpyridinium bromide hydrobromide (I-iv)

4-[(4-Methylphenyl)diazenyl]-1-(pyridin-3-ylmethyl)-1H-pyrazol-5-amine (example 1b, 120mmol, 35.08g) is heated to reflux in 350ml acetone. Then dimethylsulfate (126mmol, 15.89g) is added over a 30min period and heating is continued for another 3h. The reaction mixture is evaporated, then the residue is dissolved in 150ml ethanol and 25ml of an ammonium bromide solution (180mmol, 17.63g) is added followed by the addition of a solution of hydrobromic acid with external cooling (33% in acetic acid, 132mmol, 32.37g). Precipitation occurs and a thick suspension is obtained. The mixture is diluted with 50ml ethanol and stirring is continued at room temperature for another hour. The solid is filtered off and recrystallized from 450ml ethanol/water 9:1 (v/v). Filtration and drying gives 34.72g (57.4% of th.) orange needles.

The dye crystallizes out as hydrobromide and contains two equivalents of crystal water.

CHN Analysis (C₁₇H₁₉N₆.Br x HBr x 2H₂O, MW = 504.22)

	% C	% H	% N
Calculated:	40.50	4.80	16.67
Found:	40.67	4.73	16.66

Example 2e: 3-({5-Amino-4-[(4-methylphenyl)diazenyl]-1H-pyrazol-1-yl}methyl)-1-(2-hydroxyethyl)pyridinium bromide hydrobromide (dye I-v)

A mixture of 4-[(4-Methylphenyl)diazenyl]-1-(pyridin-3-ylmethyl)-1H-pyrazol-5-amine (example 1b, 100mmol, 29.24g) and 2-bromoethanol (500mmol,

65.77g) is heated to 100°C in 350 ml 3-methoxypropionitrile for 6 hours. After this period, the obtained solution is allowed to cool to room temperature and the solvent is evaporated. The residue is then dissolved in 100ml ethanol. With mechanical stirring and cooling in an ice bath a solution of hydrobromic acid 33% in acetic acid (100mmol, 24.5g) is added carefully whereas a fine suspension is formed. After the addition is complete, stirring is continued for another half hour. The solid is filtered off and dried to give 39.88g (80.0% of th.) orange-red powder.

CHN Analysis (C₁₈H₂₁N₆O.Br x HBr, MW = 498.22)

	% C	% H	% N
Calculated:	43.39	4.45	16.87
Found:	42.88	4.86	16.30

Example 2f: 3-({5-Amino-4-[(2-methyl-4-nitrophenyl)diazenyl]-1H-pyrazol-1-yl}methyl)-1-methylpyridinium methyl sulfate (I-vi)

4-[(2-methyl-4-nitrophenyl)diazenyl]-1-(pyridin-3-ylmethyl)-1H-pyrazol-5-amine (example 1d, 37.1g, 110mmol) is heated in 330ml 3-methoxypropionitrile to 75°C; a thick suspension is obtained. At this temperature dimethylsulfate (14.5g, 115mmol) is added and stirring is continued for 2 hours whereby an easily stirrable suspension is obtained. The heating bath is removed, then at 50°C 100ml acetone is added and stirring is continued for an additional hour. Filtration of the dye and drying gives 46.9g (92% of th.) bright orange solid.

¹H-NMR (DMSO-d₆): δ = 8.97 (signal overlap, 2H); 8.41 (d, ³J = 8.1 Hz, 1H); 8.22 (d, ⁴J = 2.6 Hz, 1H); 8.15 (dd, ³J = 8.1 Hz, ³J = 6.5 Hz, 1H); 8.10 (dd, ³J = 8.7 Hz, ⁴J = 2.6 Hz, 1H); 8.03 (s, 1H); 7.75 (s, 2H); 7.70 (d, ³J = 8.7 Hz, 1H); 5.50 (s, 2H); 4.39 (s, 3H); 3.38 (s, 3H); 2.61 ppm (s, 3H).

Example 2g: 3-[(5-Amino-4-{[2-(methoxymethyl)-4-nitrophenyl]diazenyl}-1H-pyrazol-1-yl)methyl]-1-methylpyridinium methyl sulfate (I-vii)

4-{[2-(Methoxymethyl)-4-nitrophenyl]diazenyl}-1-(pyridin-3-ylmethyl)-

1H-pyrazol-5-amine (140 mmol, 51.43 g) is dissolved in N-methyl-2-pyrrolidone (150 ml) and heated to 60°C. Then dimethylsulfate (154 mmol, 19.42 g) is added within 10 min. The mixture is stirred at 60°C for 1 h; then temperature is increased to 80°C. After 2 h another dimethylsulfate (15.4 mmol, 1.94g) is added to
5 complete the reaction. After 3 h another temperature is raised to 100°C for an additional hour. Heating is stopped, and the mixture is diluted with N-methyl-2-pyrrolidone (50 ml). The solution is filtered warm, then at approximately 60°C, acetone (250 ml) is carefully added whereas the dye precipitates out and a fine suspension is formed. After stirring for 30 min the suspension is cooled in an ice
10 bath and the solid is filtered off. The dye is washed with acetone and dried. Yield: 48.87 g orange solid (70.7% of th.).

1H-NMR (DMSO-d₆): δ = 8.95 (signal overlap, 2H); 8.41 (d, ³J = 8.1 Hz, 1H); 8.34 (d, ⁴J = 2.6 Hz, 1H); 8.22 (dd, ³J = 8.9 Hz, ⁴J = 2.6 Hz, 1H); 8.14 (dd, ³J = 8.1 Hz, ³J = 6.5 Hz, 1H); 8.05 (s, 1H); 7.82 (s, broad, 2H); 7.76 (d, ³J = 8.9 Hz,
15 1H); 5.48 (s, 2H); 4.86 (s, 2H); 4.37 (s, 3H); 3.41 (s, 3H); 3.5-3.3 ppm (signal overlap, 3H and water).

Example 2h: 3-({5-Amino-4-[(4-(methoxycarbonyl)phenyl)diazenyl]-1H-pyrazol-1-yl}methyl)-1-methylpyridinium methyl sulfate (dye I-viii)

Methyl 4- {[5-amino-1-(pyridin-3-ylmethyl)-1H-pyrazol-4-yl]diazenyl}benzoate (example 1c, 6.6g, 19.6mmol) is suspended in 100ml 3-methoxypropionitrile and heated to 100°C. Dimethylsulfate (2.6g, 20.6mmol) is added over a 15 min period whereby a red solution is obtained. Stirring is continued for an additional hour; then the reaction mixture is allowed to cool to room temperature. The solution is concentrated to a volume of 20-30ml, then an
20 identical volume of isopropanol is added to precipitate the dye. After stirring for 30 min the dye is filtered off, washed with isopropanol and dried to give 7.8g (86% of th.) mustard-yellow solid.

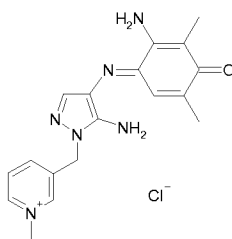
1H-NMR (DMSO-d₆): δ = 8.95 (signal overlap, 2H); 8.38 (d, ³J = 8.1 Hz,

1H); 8.14 (dd, $^3J = 8.1$ Hz, $^3J = 6.1$ Hz, 1H); 8.05 (d, $^3J = 8.8$ Hz, 2H); 7.97 (s, 1H); 7.84 (d, $^3J = 8.8$ Hz, 2H); 7.62 (s, 2H); 5.49 (s, 2H); 4.38 (s, 3H); 3.87 (s, 3H); 3.38 ppm (s, 3H).

Example 3: Synthesis of the Cationic dyes of Structure (II)

5 General method: In a flask are placed 35ml ethanol and 5ml water. With stirring, 3-[(4,5-diamino-1H-pyrazol-1-yl)methyl]-1-methylpyridinium methylsulfate dihydrochloride (10mmol, 3.88g) and the corresponding coupler (11mmol) are added and the pH of the mixture is adjusted to 9 by the addition of ammonium hydroxide 28%. Then aqueous hydrogen peroxide solution of 9%
10 strength (30mmol, 11.34g) is added; within a few minutes the color of the reaction mixture changes to deep red. After stirring for 16h at room temperature a red-brown dye suspension is obtained. The solid is filtered off, washed with ethanol and dried.

Example 3a: 3-({5-Amino-4-[(2-amino-3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)amino]-1H-pyrazol-1-yl}methyl)-1-methylpyridinium chloride (II-i) is obtained from 3-amino-2,6-dimethylphenol (3.34g, 89% yield).



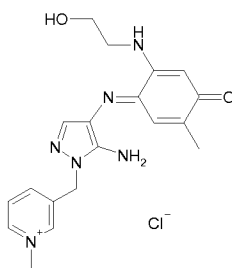
1H-NMR (DMSO- d_6): $\delta = 8.98$ (s, 1H); 8.95 (d, $^3J = 6.1$ Hz, 1H); 8.35 (d, $^3J = 8.0$ Hz, 1H); 8.13 (dd, $^3J = 8.0$ Hz, $^3J = 6.1$ Hz, 1H); 7.85 (s, 1H); 7.17 (d, $^4J = 1.2$ Hz, 1H); 7.02 (s, 2H); 6.32 (s, broad, 2H); 5.48 (s, 2H); 4.37 (s, 3H); 1.93 (d, $^4J = 1.2$ Hz, 3H); 1.76 ppm (s, 3H).

The same dye is obtained if, in an autoclave, a solution of 3-[[5-amino-4-(phenyldiazenyl)-1H-pyrazol-1-yl]methyl]-1-methylpyridinium chloride
25 hydrochloride (example 2a, 36.53 g, 0.1 mol) in 350 ml ethanol/water 2:1 (v/v) is

hydrogenated at 9 bar of hydrogen pressure for 3 hours using 3.6 g of Pd/C (10%). Then, under nitrogen atmosphere, the catalyst is filtered off. To the obtained filtrate 3-amino-2,6-dimethylphenol (13.72 g, 0.1 mol) is added. With stirring, the pH is adjusted to 9 by the addition of ammonium hydroxide 28% followed by the addition of hydrogen peroxide 9% (95g, 0.25 mol). Within a few minutes the color of the solution changes to deep red. Stirring is continued at room temperature for 16 hours. The obtained mixture is neutralized by the addition of hydrochloric acid 10%. At a rotavapor the mixture is concentrated to approximately 50% of the volume followed by cooling in an ice bath; the precipitated dye is filtered off. Washing with ethanol and drying gives 21.14 g (56.7 % of th.) dark red-brown solid.

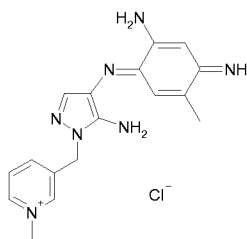
The compound is identical with the reference manufactured by the general method.

Example 3b:3-{{5-Amino-4-({2-[(2-hydroxyethyl)amino]-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene}amino)-1H-pyrazol-1-yl]methyl}-1-methylpyridinium chloride (II-ii) is obtained from 2-methyl-5-hydroxyethylaminophenol (1.59g, 39.5% yield).



¹H-NMR (DMSO-d₆): δ = 9.01 (s, 1H); 8.96 (d, ³J = 5.9 Hz, 1H); 8.35 (d, ³J = 8.1 Hz, 1H); 8.13 (dd, ³J = 8.1 Hz, ³J = 5.9 Hz 1H); 7.88 (s, 1H); 7.36 (t, ³J = 6.2 Hz, 1H); 7.22 (d, ⁴J = 1.3 Hz, 1H); 7.18 (s, 1H); 5.51 (s, 2H); 5.26 (s, 2H); 4.37 (m, signal overlap, 4H); 3.53 (t, ³J = 6.2 Hz, 2H); 3.18 (dt, ³J = 6.3 Hz, ³J = 6.2 Hz, 2H); 1.92 ppm (d, ⁴J = 1.3 Hz, 3H).

Example 3c: 3-({5-Amino-4-[(2-amino-4-imino-5-methylcyclohexa-2,5-dien-1-ylidene)amino]-1H-pyrazol-1-yl}methyl)-1-methylpyridinium chloride (II-iii) is obtained from 2,4-diaminotoluene (3.28g, 92% yield).

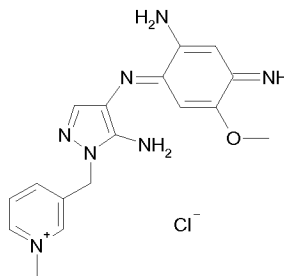


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$^1\text{H-NMR}$ (DMSO- d_6): δ = 9.08 (s, 1H); 8.98 (d, 3J = 6.0 Hz, 1H); 8.45 (d, 3J = 8.1 Hz, 1H); 8.19 (s, 1H); 8.14 (dd, 3J = 8.1 Hz, 3J = 6.0 Hz, 1H); 8.07 (s, broad, 5H); 7.27 (d, 3J = 0.9 Hz, 1H); 5.88 (s, 1H); 5.57 (s, 2H); 4.37 (s, 3H); 2.13 ppm (d, 3J = 0.9 Hz, 3H).

10

Example 3d: 3-({5-Amino-4-[(2-amino-4-imino-5-methoxycyclohexa-2,5-dien-1-ylidene)amino]-1H-pyrazol-1-yl}methyl)-1-methylpyridinium chloride (II-iv) is obtained from 2,4-diaminoanisole sulfate (3.29g, 88% yield).



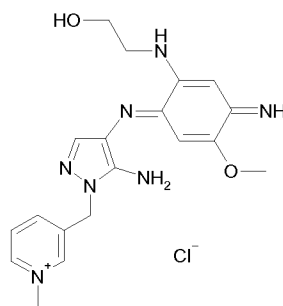
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$^1\text{H-NMR}$ (DMSO- d_6): δ = 9.08 (s, 1H); 9.0-8.8 (s, broad, 1H); 8.98 (d, 3J = 6.0 Hz, 1H); 8.45 (s, broad, 2H); 8.42 (d, 3J = 8.2 Hz, 1H); 8.14 (dd, 3J = 8.2 Hz, 3J = 6.0 Hz, 1H); 8.00 (s, 1H); 7.93 (s, broad, 2H); 6.38 (s, 1H); 5.92 (s, 1H); 5.56 (s, 2H); 4.37 (s, 3H); 3.91 ppm (s, 3H).

20

Example 3e: 3-{[5-amino-4-({2-[(2-hydroxyethyl)amino]-4-imino-5-methoxycyclohexa-2,5-dien-1-ylidene}amino)-1H-pyrazol-1-yl]methyl}-1-methylpyridinium chloride (II-v) is obtained from 2-amino-4-hydroxyethylaminoanisole sulfate (3.6g, 86% yield).

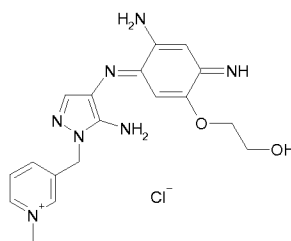
5



1H-NMR (DMSO-d₆): δ = 9.09 (s, 1H); 9.0-8.7 (m, signal overlap, 2H); 8.41 (d, 3J = 8.0 Hz, 1H); 8.3-7.9 (s, broad, 3H); 8.14 (dd, 3J = 8.0 Hz, 3J = 6.1 Hz, 1H); 7.98 (s, 1H); 6.44 (s, 1H); 5.88 (s, 1H); 5.57 (s, 2H); 5.3-4.8 (s, broad, 1H); 4.37 (s, 3H); 3.92 (s, 3H); 3.60 (t, 3J = 5.7 Hz, 2H); 3.5-3.0 ppm (m, signal overlap, 2H and water).

Example 3f: 3-{[5-Amino-4-{2-amino-5-(2-hydroxyethoxy)-4-iminocyclohexa-2,5-dien-1-ylidene]amino}-1H-pyrazol-1-yl)methyl}-1-methylpyridinium chloride (II-vi) is obtained from 2,4-diaminophenoxyethanol 2HCl (2.95g, 73% yield).

15



1H-NMR (DMSO-d₆): δ = 9.16-9.11 (m, signal overlap, 2H); 9.01 (d, 3J = 6.1 Hz, 1H); 8.53 (s, broad, 2H); 8.45 (d, 3J = 8.0 Hz, 1H); 8.14 (dd, 3J = 8.0 Hz, 3J = 6.1 Hz, 1H); 8.02 (s, broad, 2H); 7.96 (s, 1H); 6.37 (s, 1H); 5.95 (s, 1H); 5.61 (s, 2H); 5.28 (t, 1H); 4.38 (s, 3H); 4.08 (t, 2H); 3.73 ppm (m, unstructured, 2H).

20

Examples 4-7 (Single Dyes in Liquid Compositions)

Colorants are prepared by dissolving the dyes of formula (I) and/or (II) in the following composition:

	10.0 %	Ethanol
5	5.0 %	Plantacare 818 UP
	3.0 %	Ammonia, 28% w/w in water
	0.2 %	Hydroxyethylcellulose
	0.5 %	Dyestuff according to Table 1
	81.3 %	<u>Water or hydrogen peroxide 6% according to Table 1.</u>
10	100.0 %	

The colorant which is in form of a gel is applied to white Yak hair. After a processing time of 30 min at 30°C, the hair is washed with water and dried. The colors are of intense, vivid shades as indicated in Table 1.

Table 1: Dye-outs of single dyes

15

Example	Dyestuff	Water / Hydrogen peroxide	Visual Aspect	L*a*b* values		
4	(I-ii)	Water	yellow	79.11	-8.12	71.83
	(I-ii)	Hydrogen peroxide	yellow	79.39	-6.84	73.41
5	(I-vi)	Water	orange- yellow	58.39	36.50	66.61
	(I-vi)	Hydrogen peroxide	orange yellow	60.50	39.95	70.98
6	(II-i)	Water	orange- red	30.75	51.98	22.65
	(II-i)	Hydrogen peroxide	orange- red	33.13	52.98	26.34
7	(II-vi)	Water	red-violet	22.19	40.39	4.79
	(II-vi)	Hydrogen peroxide	red-violet	23.51	39.63	4.28

Examples 8-15 (Compositions in Gel Form)

Stock solutions were prepared by separate dissolving dyes of formula (I) and (II) and conventional dyes in the following composition:

	10.0 %	Ethanol
5	5.0 %	Plantacare 818 UP
	3.0 %	Ammonia, 28% w/w in water
	0.2 %	Hydroxyethylcellulose
	1.0 %	Dyestuff compositions according to Table 2
	<u>80.8 %</u>	Water
10	100.0 %	

The stock solutions containing the dyes are prepared with the proportions indicated in the Table 2 (numbers in grams). The obtained colorants are applied to white Yak hair in a sufficient amount. After a processing time of 30 min at 30°C, the hair was washed with water and dried. The nuances are as indicated in Table 2.

15

20

25

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Table 2: Colorants containing dyes of Structure (I) and (II)

Dye solutions 1.0%	Examples							
	8	9	10	11	12	13	14	15
Stock solutions								
(I-ii)	1.0	1.0						
(I-v)				2.0				
(I-vi)			1.0					
(II-i)			1.5		2.2	1.0		1.0
(II-ii)		1.5		0.1			1.1	
(II-iii)					1.0			
HC Blue 16	1.0	1.0				2.0		2.0
HC Blue 17			0.5				1.2	
Basic Yellow 57			0.15				0.07	
Basic Red 76				0.05				
Basic Red 51					0.2			
4-Hydroxypropylamin o-3-nitrophenol				0.06				
2-Chloro-6-ethylamino-4-nitrophenol					0.15			
2-Amino-6-chloro-4-nitrophenol			0.1					
Acid Violet 43						0.5		
Hydrogen peroxide 6%	2.0	10.0			3.5		2.0	4.0
Water		10.0	3.0	12.5		3.0	2.0	2.0
Nuance	green	light brown	copper brown	orange	bordeaux	dark brown	medium brown	neutral grey

Example 16, Cream Composition

	9.00 %	Crodafos CES
	5.00 %	Propylene glycol
5	1.00 %	Merquat 550 (Polyquaternium-7 from Lubrizol)
	5.00 %	Ammonia, 28% w/w in water
	0.25 %	dye (I-i)
	0.25 %	dye (II-i)
	0.02 %	dye (II-iii)
10	0.30 %	HC Blue 16
	<u>79.18 %</u>	Water
	100.00 %	

The cream composition is mixed 1:1 (w/w) with hydrogen peroxide 6% and applied to hair swatches of different degree of damage. The hair fibers were

- 50% human grey hair, untreated, and
- light blond human hair, additionally bleached.

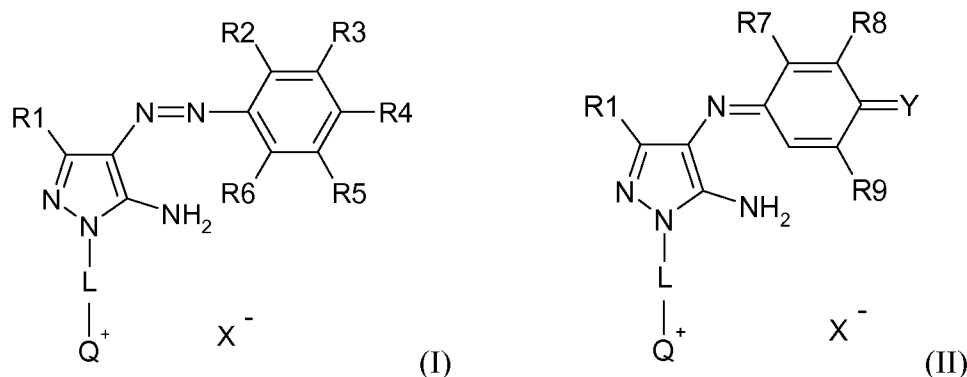
5 The standard processing time was 30 min at 30°C. The hair swatches were rinsed with warm water, shampooed and dried. In both cases the color result was identical, medium brown.

The grey coverage, which was 100%, was evaluated by means of the 50% human grey hair swatch.

CLAIMS

1. A composition for dyeing keratin fibers comprising, in a medium suitable for dyeing, one or more cationic dye of general formula (I) or (II), or a physiologically tolerated adduct thereof with an acid:

5



wherein

R1 is hydrogen, a straight-chain or branched (C1-C6)-alkyl group, a (C1-C4)-hydroxyalkyl group, a (C1-C4)-aminoalkyl group, a (C1-C8)-alkylamino group, a di(C1-C8)-alkylamino group, a (C1-C4)-alkylamino-(C1-C4)-alkyl group or a di(C1-C4)-alkylamino-(C1-C4)-alkyl group, a benzyl group, an aryl group or a heteroaryl group;

R2 to R6 are equal or different independently from each other selected from hydrogen, a straight-chain or branched (C1-C6)-alkyl or -alkoxy group, a (C1-C4)-hydroxyalkyl or -hydroxyalkoxy group, a methoxymethyl group, a nitro group, a halogen atom selected from chlorine, bromine, iodine and fluorine, a trifluoromethyl group, a cyano group, an acetylamino or an amino group;

R7 is a hydrogen atom, a methyl or an ethyl group, a hydroxy group, an amino group, a hydroxy-(C2-C3)-alkylamino group, or a methoxy group;.

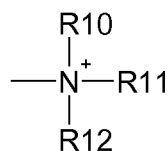
R8 is a hydrogen atom, a halogen atom selected from chlorine, bromine, iodine and fluorine or a methyl group;

R9 is a hydrogen atom, an amino group, a (C1-C6)-alkyl group, a (C1-C6)-alkoxy group or a (C2-C3)-hydroxyalkoxy group;

Y is an oxygen atom or an NR group wherein R is (C1-C4)-alkyl, (C2-C4)-hydroxyalkyl; or the NR group is bonded to the R9 to form a benzoxazine system;

L is a bridging group between the pyrazole ring and the quaternary group and consists of a phenylene diradical or a (C1-C3)-alkylene diradical;

5 Q^+ is a saturated cationic group selected from formula (a):



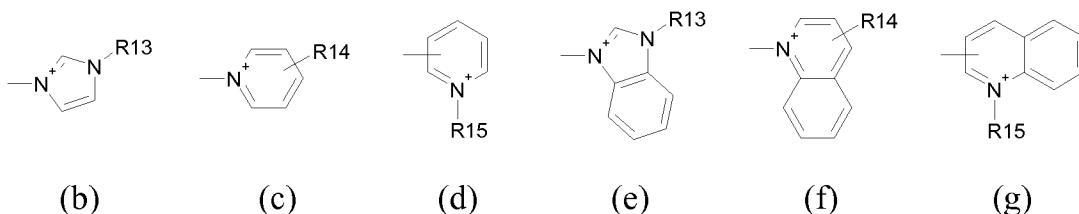
(a)

wherein

R10 to R12 can bear equal or different and independently of each other substituents selected from a straight-chain or branched (C1-C6)-alkyl group, a (C2-
10 C4)-hydroxyalkyl group, a (C3-C6)-dihydroxyalkyl group, a (C3-C6)-polyhydroxyalkyl group or a (C1-C6)-alkoxy-(C1-C4)-alkyl group; or two of the groups R10 to R12 together with the nitrogen atom to which they are linked forming a five-membered or six-membered heterocycle optionally containing one or more other heteroatoms and other substituents selected from F, Cl, Br, I, OH,
15 NH₂ or a straight-chain or branched (C1-C6)-alkyl group, a straight-chain or branched (C1-C6)-alkoxy group, a (C1-C6)-alkoxy-(C1-C4)-alkyl group or a hydroxyethyl group;

or Q^+ is an unsaturated or aromatic cationic group which is selected from formula (b) to (g):

20



wherein

R13 is a straight-chain or branched (C1-C8)-alkyl group, a hydroxyethyl

group or a benzyl group;

R14 is a hydrogen atom, a straight-chain or branched (C1-C9)-alkyl group, an amino group, a mono-(C1-C6)-alkylamino group, a di-(C1-C6)-alkylamino group or a pyrrolidino group;

5 R15 is a (C1-C4)-alkyl radical which may be substituted with a hydroxy radical;

X⁻ is a monovalent or polyvalent anion and is selected from chloride, bromide, methylsulfonate or methylsulfate, arylsulfonate, hydrogen sulfate, sulfate, phosphate, acetate or hydroxysuccinate ion.

10 2. A composition according to claim 1, wherein

R1 is hydrogen;

R2 to R6 are, equal or different independently from each other, selected from hydrogen, a methyl or methoxy group, a (C1-C2)-hydroxyalkyl group, a (C2-C3)-hydroxyalkoxy group, a methoxymethyl group, a nitro group, a chloro
15 atom, or a trifluoromethyl group;

R7 is a hydroxy group, an amino group, a hydroxyethylamino group or a methoxy group;

R8 is a hydrogen atom, a chloro atom or a methyl group;

R9 is a methyl group, a methoxy group or a hydroxyethoxy group;

20 R10 to R12 are, equal or different and independently of each other, selected from a methyl group, ethyl group or hydroxyethyl group; or two of the R10 to R12 groups together with the nitrogen atom to which they are linked form a pyrrolidino group, morpholino group or N-methylpiperazino group;

R13 is a methyl group or a hydroxyethyl group;

25 R14 is hydrogen, a methyl group, p-dimethylamino group or p-pyrrolidino group;

R15 is a methyl, ethyl or hydroxyethyl group;

Y is O or NH;

X^- is a chloride, bromide or methylsulfate;

L is a (C1-C3)-diradical;

Q^+ is a (C3-C9)-trialkylammonium radical, a N-methylimidazolium radical or a N-methylpyridinium radical.

5 3. A composition according to claim 1, wherein

R1 is hydrogen;

R2-R6 are, equal or different independently from each other, selected from hydrogen, a methyl or methoxy group, a (C1-C2)-hydroxyalkyl group, a hydroxyethoxy group, a methoxymethyl group, a nitro group, or a chloro atom;

10 R7 is a hydroxy group, an amino group or a hydroxyethylamino group;

R8 is a hydrogen atom or a methyl group;

R9 is a methyl group, a methoxy group or a hydroxyethoxy group;

R10 to R12 are, equal or different and independently of each other, selected from a methyl group, ethyl group or hydroxyethyl group; or two of the R10 to R12 groups together with the nitrogen atom to which they are linked form a pyrrolidino group, morpholino group or N-methylpiperazino group;

R13 is a methyl group;

R14 is hydrogen, a methyl group, p-dimethylamino group or p-pyrrolidino group;

20 R15 is a methyl, ethyl or hydroxyethyl group;

Y is O or NH;

X^- is a chloride, bromide or methylsulfate;

L is a methylene diradical;

Q^+ is an N-methyl pyridinium moiety.

25 4. A composition according to claim 1, wherein the cationic dye of general formula (I) or (II) is selected from the group consisting of:

3-{[5-Amino-4-(phenyldiazenyl)-1H-pyrazol-1-yl]methyl}-1-methylpyridinium chloride hydrochloride;

3-[(5-Amino-4-{[2-(hydroxymethyl)phenyl]diazenyl}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium bromide;

4-[(5-Amino-4-{[2-(hydroxymethyl)phenyl]diazenyl}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium methylsulphate;

5 3-({5-Amino-4-[(4-methylphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium bromide hydrobromide;

3-({5-Amino-4-[(4-methylphenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-(2-hydroxyethyl)pyridinium bromide hydrobromide;

10 3-[(5-Amino-4-{[2-methyl-4-nitrophenyl]diazenyl}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium methyl sulfate;

3-[(5-Amino-4-{[2-methoxymethyl-4-nitrophenyl]diazenyl}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium methyl sulfate;

3-({5-Amino-4-[(4-(methoxycarbonyl)phenyl)diazenyl]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium methyl sulfate;

15 3-({5-Amino-4-[(2-amino-3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)amino]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

3-{[5-Amino-4-({2-[(2-hydroxyethyl)amino]-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene}amino)-1*H*-pyrazol-1-yl]methyl}-1-methylpyridinium chloride;

20 3-({5-Amino-4-[(2-amino-4-imino-5-methylcyclohexa-2,5-dien-1-ylidene)amino]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

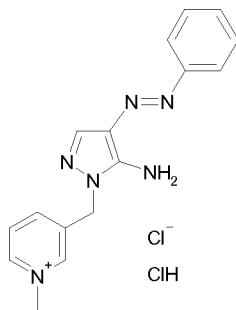
3-({5-Amino-4-[(2-amino-4-imino-5-methoxycyclohexa-2,5-dien-1-ylidene)amino]-1*H*-pyrazol-1-yl}methyl)-1-methylpyridinium chloride;

3-{[5-amino-4-({2-[(2-hydroxyethyl)amino]-4-imino-5-methoxycyclohexa-2,5-dien-1-ylidene}amino)-1*H*-pyrazol-1-yl]methyl}-1-methylpyridinium chloride;

25 3-[(5-Amino-4-{[2-amino-5-(2-hydroxyethoxy)-4-iminocyclohexa-2,5-dien-1-ylidene]amino}-1*H*-pyrazol-1-yl)methyl]-1-methylpyridinium chloride.

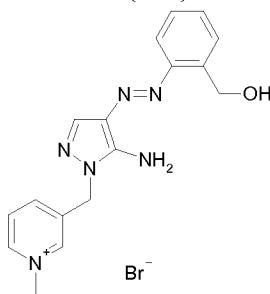
5. A composition according to claim 1, wherein the cationic dye of general formula (I) or (II) is selected from the group consisting of:

3-{[5-Amino-4-(phenyldiazenyl)-1H-pyrazol-1-yl]methyl}-1-methylpyridinium chloride hydrochloride (**I-i**)



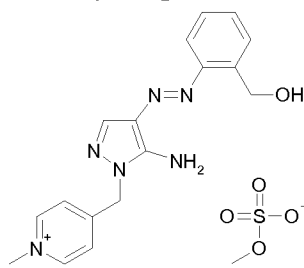
(**I-i**);

5 3-[(5-Amino-4-{[2-(hydroxymethyl)phenyl]diazanyl}-1H-pyrazol-1-yl)methyl]-1-methylpyridinium bromide (**I-ii**)



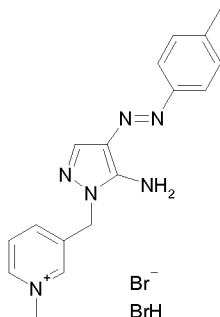
(**I-ii**);

4-[(5-Amino-4-{[2-(hydroxymethyl)phenyl]diazanyl}-1H-pyrazol-1-yl)methyl]-1-methylpyridinium methylsulphate (**I-iii**)



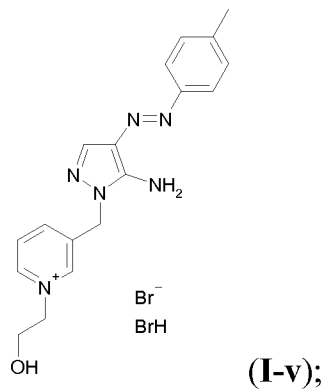
(**I-iii**);

10 3-({5-Amino-4-[(4-methylphenyl)diazanyl]-1H-pyrazol-1-yl}methyl)-1-methylpyridinium bromide hydrobromide (**I-iv**)

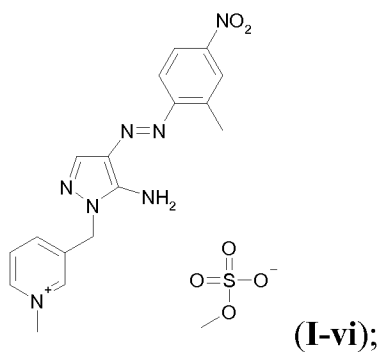


(**I-iv**);

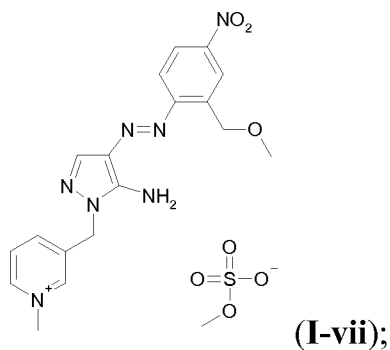
3-({5-Amino-4-[(4-methylphenyl)diazenyl]-1H-pyrazol-1-yl}methyl)-1-(2-hydroxyethyl)pyridinium bromide hydrobromide (**I-v**)



5 3-[(5-Amino-4-{[2-methyl-4-nitrophenyl]diazenyl}-1H-pyrazol-1-yl)methyl]-1-methylpyridinium methyl sulfate (**I-vi**)

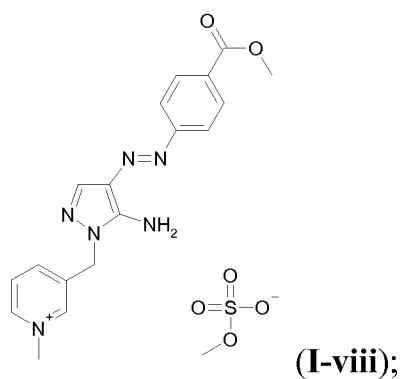


10 3-[(5-Amino-4-{[2-methoxymethyl-4-nitrophenyl]diazenyl}-1H-pyrazol-1-yl)methyl]-1-methylpyridinium methyl sulfate (**I-vii**)



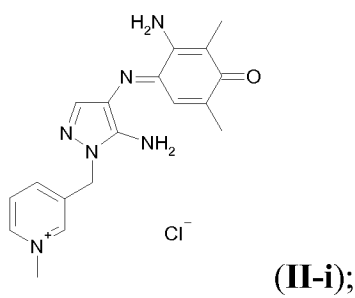
3-({5-Amino-4-[(4-(methoxycarbonyl)phenyl)diazenyl]-1H-pyrazol-1-yl}methyl)-1-methylpyridinium methyl sulfate (**I-viii**)

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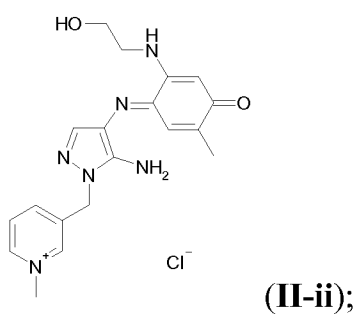


3-({5-Amino-4-[(2-amino-3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)amino]-1H-pyrazol-1-yl}methyl)-1-methylpyridinium chloride (**II-i**).

5



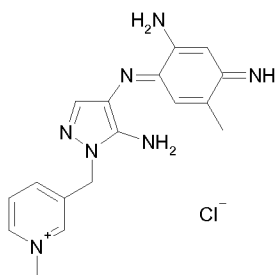
3-{{5-Amino-4-({2-[(2-hydroxyethyl)amino]-5-methyl-4-oxocyclohexa-2,5-dien-1-ylidene}amino)-1H-pyrazol-1-yl}methyl}-1-methylpyridinium chloride (**II-ii**)



10

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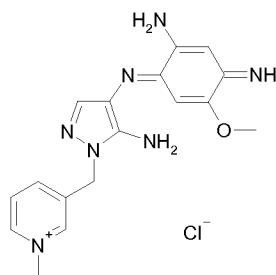
3-({5-Amino-4-[(2-amino-4-imino-5-methylcyclohexa-2,5-dien-1-ylidene)amino]-1H-pyrazol-1-yl} methyl)-1-methylpyridinium chloride (**II-iii**)



5

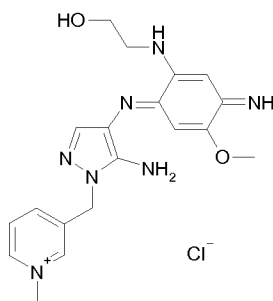
(**II-iii**);

3-({5-Amino-4-[(2-amino-4-imino-5-methoxycyclohexa-2,5-dien-1-ylidene)amino]-1H-pyrazol-1-yl} methyl)-1-methylpyridinium chloride (**II-iv**)

(**II-iv**);

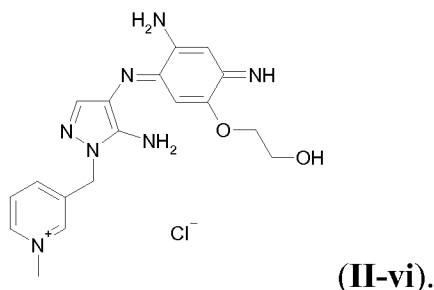
10

3- { [5-amino-4- ({2-[(2-hydroxyethyl)amino]-4-imino-5-methoxycyclohexa-2,5-dien-1-ylidene} amino)-1H-pyrazol-1-yl] methyl } -1-methylpyridinium chloride (**II-v**)

(**II-v**);

15

3-[(5-Amino-4-{[2-amino-5-(2-hydroxyethoxy)-4-iminocyclohexa-2,5-dien-1-ylidene]amino}-1H-pyrazol-1-yl)methyl]-1-methylpyridinium chloride (**II-vi**)

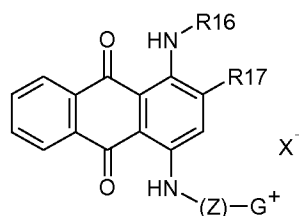


6. A composition according to claims 1-5, wherein said one or more cationic dye of general formula (I) or (II) as defined in claims 1-5 is present in a concentration ranging from of 0.001 to 10% by weight relative to the total weight of the composition.

7. A composition according to claims 1-6, wherein the composition has a pH ranging from of 2 to 12, preferably from 7 to 11.

8. A composition according to claims 1-7, further comprising one or more cationic direct blue dyes.

9. A composition according to claim 8, wherein the one or more cationic direct blue dye has the general formula (VIII):



(VIII)

wherein

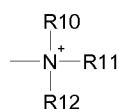
R16 is a hydrogen atom, a C1-C6 alkyl group which may be substituted by one or two hydroxy groups, a di(C1-C2)alkylamino-(C2-C3)alkyl group, a phenyl or a tolyl group;

R17 is a hydrogen atom, a methyl or a methoxy group;

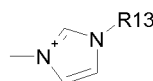
Z consists of a (C2-C3)-alkylene diradical;

G⁺ is a cationic group selected from formula (a) or (b) wherein R10-R12 and R13 are as defined in claims 1-3 for formula (I) and (II);

5



(a)



(b)

X⁻ is an anion as defined above for general formulae (I) and (II), preferably it is selected from chloride, bromide, methylsulfonate or methylsulfate.

10. A composition according to claim 9, wherein the one or more cationic direct blue dyes of general formula (VIII) is selected from HC Blue 16 and HC Blue 17.

11. A composition according to claims 1-10, further comprising one or more conventional direct dyes.

12. A composition according to claims 1-11, wherein the one or more conventional direct dye is selected from nonionic, cationic or anionic dyes, or mixture thereof.

13. A composition according to claims 1-12, further comprising at least one oxidizing agent.

14. A composition according to claim 13, wherein the at least one oxidizing agent is selected from the group consisting of hydrogen peroxide, urea peroxide, a percarbonate salt, a bromate salt, a perborate salt or a persulfate salt.

15. A composition according to claims 1-14, further comprising compounds independently selected from the group consisting of anionic, neutral or cationic thickeners; anionic, nonionic or cationic emulsifying waxes; neutral or cationic silicones; cationic polymers.

16. A ready-to-use composition according to claims 1-15, which is in the form of a liquid, a cream, a gel, a foamable liquid or a foam.

17. Process for dyeing keratin fibers comprising:
- applying to the fiber a composition according to claims 1-16,
 - allowing an exposure time of 10 to 45 minutes at 20 to 40°C,
 - rinsing said fibers with water, and optionally with a shampoo and rinsing
- 5 again, and then drying them.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/062997

A. CLASSIFICATION OF SUBJECT MATTER

INV. A61K8/49 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, 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.
A	WO 2005/051918 A1 (WELLA AG [DE]; GOETTEL OTTO [CH]; HAYOZ ANDRE [CH]; MORAND EMMANUEL [C] 9 June 2005 (2005-06-09) page 2, paragraph 2; claims; examples -----	1-17
A	WO 95/01772 A1 (CIBA GEIGY AG [CH]; MOECKLI PETER [CH]) 19 January 1995 (1995-01-19) cited in the application claims; examples -----	1-17
A	FR 1 391 408 A (GEIGY AG J R) 5 March 1965 (1965-03-05) example 3 -----	1-17
A	US 2006/005327 A1 (GREAVES ANDREW [FR] ET AL) 12 January 2006 (2006-01-12) page 27, left-hand column; claims ----- -/-	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search

30 April 2014

Date of mailing of the international search report

21/05/2014

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/062997

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 308 205 A (BATTISTI RUGGERO ET AL) 29 December 1981 (1981-12-29) claims -----	1-17
A	FR 2 925 052 A1 (OREAL [FR]) 19 June 2009 (2009-06-19) claims -----	1-17
A	EP 2 246 038 A1 (OREAL [FR]) 3 November 2010 (2010-11-03) claims -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/062997

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005051918	A1	09-06-2005	BR PI0416810 A 09-01-2007
		DE 10354584 A1 30-06-2005	
		EP 1687280 A1 09-08-2006	
		JP 2007511550 A 10-05-2007	
		US 2007056120 A1 15-03-2007	
		WO 2005051918 A1 09-06-2005	
WO 9501772	A1	19-01-1995	AU 687849 B2 05-03-1998
		BR 9405500 A 08-09-1999	
		CA 2142091 A1 19-01-1995	
		CN 1111444 A 08-11-1995	
		DE 69428096 D1 04-10-2001	
		DE 69428096 T2 02-05-2002	
		EP 0658095 A1 21-06-1995	
		ES 2161775 T3 16-12-2001	
		JP 3281386 B2 13-05-2002	
		JP H08501322 A 13-02-1996	
		MX 206700 B 12-02-2002	
		US 5733343 A 31-03-1998	
		WO 9501772 A1 19-01-1995	
FR 1391408	A	05-03-1965	NONE
US 2006005327	A1	12-01-2006	NONE
US 4308205	A	29-12-1981	BE 860920 A1 17-05-1978
		DE 2750952 A1 18-05-1978	
		ES 464207 A1 16-07-1978	
		FR 2371490 A1 16-06-1978	
		GB 1595235 A 12-08-1981	
		IT 1067981 B 21-03-1985	
		JP S5363434 A 06-06-1978	
		NL 7712429 A 19-05-1978	
		US 4308205 A 29-12-1981	
FR 2925052	A1	19-06-2009	FR 2925052 A1 19-06-2009
		WO 2009077390 A2 25-06-2009	
EP 2246038	A1	03-11-2010	EP 2246038 A1 03-11-2010
		FR 2945041 A1 05-11-2010	
		JP 2010260860 A 18-11-2010	
		US 2010275390 A1 04-11-2010	