Abstract:

A substantive and photostable dye suitable for cosmetic applications is provided by encapsulating a dye in substantive microspheres, binding to keratin. The microspheres protect the dye against detrimental effect of light and UV radiation, and ensures binding of the dye to the hair or other keratinaceous substance.
SUBSTANTIVE PHOTOSTABLE DYES AND METHOD FOR THE PRODUCTION THEREOF

Description

Technical field

The invention concerns improvements in hair dyes and more specifically though not exclusively in semi-permanent hair dyes. More generally, the present invention concerns dyes suitable for cosmetic applications and dye compounds for compositions useful in cosmetic applications.

Background art

Hair dyeing is accomplished with substances that absorb some wavelengths and transmit others. Dyes are compounds of different types, added to cosmetic formulations for both attractive and corrective purposes (C. Zviak (Ed.) The Science of Hair Care, Marcel Dekker Inc., New York, 1987).

The colorants or dyes usable in cosmetic applications are defined by local laws and regulations. For example, colorants or dyes approved by Italian law are listed, according to their Color Index classification, in Annex IV to Law 713/86 and subsequent updates. They fall into four categories of application according to their toxicological and physical properties:

1) Coloring agents allowed in all cosmetic products;
2) Coloring agents allowed in all cosmetic products, except those intended to be applied in the proximity of the eyes, in particular eye make up and eye make-up remover;
3) Coloring agents allowed exclusively in cosmetic products intended not to come into contact with mucous membranes;
4) Coloring agents allowed exclusively in cosmetic products intended to come into contact only briefly with the skin.

Regarding hair dyes, they can be distinguished into three categories:

1) Oxidative colorants (or "permanent")
2) Direct colorants (or "semi-permanent")
3) Temporary colorants (or "highlights").

The previous classification is based on the stability and duration of the color, on the quality of the results and the variety of shades obtainable.
Therefore three types of hair dyes can be identified according to the duration of the color on the hair (after the operation has been carried out) and the type of chemicals employed:

- permanent hair dyes
- semi-permanent hair dyes
- temporary hair dyes

The "permanent hair dyes" allow a durable change of the natural hair colour, through an oxidation reaction carried out with colorless bases and therefore not listed in Annex IV but in Annex III of the above mentioned Italian Law. As a result of such reaction the oxidized molecules on the hair are transformed into colored compounds, the so-called oxidative dyes.

This coloration is resistant to shampooing and other external factors, but is sensible to light, that can modify the color, and can often cause contact allergic dermatitis, due mainly to compounds such as like para-phenylenediamine, nitro-ortho-phenylenediamine and nitro-para-phenylenediamine used in the oxidative process.

The "semi-permanent hair dyes", also called "direct", employ true dyes, the application of which takes place without involving oxidation. This coloration resists to 4-5 shampooing, with slow and uniform bleaching, because the dyes used have a good affinity for hair keratin, are resistant to the light (a function of the type of molecule used), and to the mechanical action of the comb, therefore the color is progressively reduced after repetitive washings. These products are useful to partially mask white hairs, add highlights to a natural color or to make grey hair more attractive.

Semi-permanent coloration does not need any preliminary or simultaneous modification of the keratin or oxidation processes of the melanin of the hair.

The dyes used in semi-permanent colorations are mainly nitroanilines, nitrophenylenediamines, nitroaminophenols, azo- e anthra-quinones derivatives.

The presence of a nitro-group, as a chromophore, confers the molecule its color properties (M.L. Schlossman (Ed.), The Chemistry and Manufacture of Cosmetics, Kobo Products Inc. 2000).

The "temporary hair dyes", also called "highlights", provide only
temporary changes and add light and brightness, while keeping the natural colour; this provides only a slight change in the natural hair color. In this case the colour can be removed during the first shampoo.

The temporary dyes can therefore only improve or correct an existing shade, add a slight shade or confer improved brightness. The dyes employed act by depositing colorants on the cuticle of the hair without being absorbed, due to their high molecular weight, and can be easily removed with the first shampooing.

Hair dyes represented from several years one of the cosmetic products most used by both women and men.

The most common reasons for dyeing the hair are to change the natural color, to dye white hair, to add a nuance or enliven the natural color.

The indiscriminate use of dyes can produce dermatological and in some cases toxicological effects, due to percutaneous penetration of the dyes.

The new technologies introduced in the fields of dyes, together with more creative methods of coloration, have contributed to a worldwide increased interest in this field. Recent studies have been aimed at increasing the safety of hair dyes, extending the duration of the coloration, improving the efficacy of the products.

In the attempt to improve the safety of the formulations and to protect the coloring substances, the latter have been encapsulated in liposomes or niosomes, as disclosed for example in WO-A-2005/120444 ("Colorants containing vesicles for keratin fibres") or in FR-A-2.648.132. Direct or oxidative dyes have been absorbed, incorporated or encapsulated in vesicles, in particular liposomes and niosomes, to obtain a more intense coloring, and colorant penetration in the skin, which can be limited, but which is however always present. In Japan several hair dye compositions have been prepared for long lasting colors, as disclosed e.g. in WO-A-2005/120446 ("Hair dye compositions for long lasting coloros"). All these formulations contain free dyes, which are for this reason less stable and less safe with respect to those encapsulated. In Germany in 2005 Wella (see WO-A-2005/1 7816) proposed the use of cationic dyes ("Cationic quinoxaline thiazole azo dye-containing colorants"). This invention regards cationic dyes
for keratin fibers, contained in a formulation of a product without oxidative agents. Also in this case the coloring substances are not encapsulated in delivery systems.


Some oxidative hair dyes have been encapsulated in microcapsules, as reported in WO-A-2006/24334 ("Microencapsulated oxidative hair dyes"), but all the formulations disclosed therein contain oxidative agents.

Microcapsules containing water soluble direct dyes have been disclosed in US-A-2006/171,909 ("Cosmetic compositions comprising colorants with low free dye") to be used on the skin, hair and nails.

The patent literature, therefore, clearly shows an increasing interest in dyes endowed with color stability and substantive properties for keratin (the term "substantive properties" refers to the capacity to bond with keratin).

Summary of the invention

The present invention concerns substantive photostable dyes for semi-permanent or direct hair coloring. In particular this invention concerns microencapsulated dyes and dye compositions using said microencapsulated dyes. According to the invention, the dye is microencapsulated in substantive microspheres, i.e. microparticles, which are stable to light, long lasting and without negative effects, for example as far as bio-compatibility and safety are concerned.

"Substantive" is understood in the context of the present description and attached claims, as a substance which is suitable to bind with keratin or a keratinaceous substance. More specifically, a substantive microsphere is one which forms a non-covalent bond with keratin or a keratinaceous substance, such as for example hair, nails or other human tissues containing keratin.

The microspheres are preferably cationic microspheres.

The dye-encapsulating microspheres are suitable for direct hair coloring. Moreover, they can give a uniform, long lasting, coloration stable to UV radiation and safe for the skin. Encapsulation or micro-encapsulation of dyes in the microspheres protects the dye from damages and alterations
induced e.g. by UV or visible light radiation. The substantive nature of the microspheres allows the dye to be indirectly bound to the hairs or other keratinaceous substances.

The present invention also concerns methods for obtaining substantive microspheres for direct hair coloration or for other uses, specifically cosmetic uses, such as for the production of dye compositions for nails, skin and other keratin-containing substances. Preferably the method of the invention provides for the manufacturing of cationic substantive microspheres containing direct, i.e. semi-permanent, hair dyes. According to some embodiments, the microspheres are manufactured by solvent evaporation (emulsification/evaporation) technique. According to other embodiments, the microspheres are manufactured by spray drying technique.

According to some embodiments the substantive microspheres contain dyes for the above mentioned applications, where a methacrylic polymer (as EUDRAGIT® RS 12,5, RS 30D, RS 100, RS PO, RL 12,5, RL 30D, RL 100, RL PO, RD 100, E12,5, E100, EPO) or any natural and synthetic cationic polymers and the dye are dispersed in a volatile solvent and then the obtained phase is emulsified with a continuous dispersing phase. After evaporation of the solvent, the microspheres thus obtained are harvested by filtration, washed and finally dried under vacuum.

Advantageously a stabilizing agent can be added to the emulsion to avoid droplet coalescence.

In some embodiments a cationic polymer (e.g. a methacrylic polymer), stearate magnesium and dye are dispersed in an organic solvent (for example acetone). The organic phase thus obtained is dispersed under stirring in a lipophilic solvent (for example mineral oil) or immiscible with the dispersed phase containing the cationic polymer. The resulting product is thus emulsified.

A further subject of the invention is a process for the production of substantive microspheres containing dyes, wherein the polymer (e.g. a cationic polymer) and the dye are dispersed in a suitable solvent and the solution or dispersion obtained is nebulized using a spray-dryer. The temperature is suitably set based on the solvent used.

The dye can be selected from the group including: HC RED n. 3;
BASIC RED 51, HC BLUE n. 2, BASIC BROWN 16 and BASIC BROWN 17 and all suitable dyes for direct hair coloring, natural or/and synthetic dyes included or not included in Annexes in accordance with EU Cosmetic Directive, excluded dyes listed in Annex II (forbidden substances).

Substantive cationic microspheres have been obtained, resistant to light and thermostable, that confer to the hair a uniform and long lasting coloration.

The microencapsulated dyes in these cationic microspheres are stable and preserve their chemical-physical, organoleptic and functional properties, that make them suitable for their use.

The microspheres according to the invention easily bind to the hair, having high physical-chemical affinity for keratin ("substantive" microspheres).

Brief description of the drawings

The invention will be better understood by the following description of preferred embodiments, reference being made to the attached photographs, wherein

Figs. 1-6 show scanning electron microscope images of microspheres obtained by an emulsification/evaporation method;

Figs. 6-10 show scanning electron microscope images of microspheres obtained by the solvent evaporation technique and spray-drying.

Detailed description of the invention

Experimental

The microparticles microspheres have been prepared by two methods:- the solvent evaporation (emulsification/evaporation) method and the spray-drying method.

According to the first method, a natural or synthetic substantive polymer (e.g. a cationic polymer and more specifically a methacrylic polymer, for instance) and a dye or a dyes mixture are dispersed in a volatile solvent and then the obtained (dispersed) phase A is emulsified with a continuous (dispersing) phase B. Since the two phases are immiscible, a stable emulsion is formed thanks to the presence of a droplets stabilizer preventing droplets coalescence during solvent evaporation.
After evaporation of the solvent, the microspheres are harvested by filtration, washed a suitable number of times, typically 4-5 times with a suitable solvent and finally dried under vacuum.

Some examples of this preparation method are set forth here below:

Example 1
Cationic methacrylic polymer, magnesium stearate and HC RED No 3 (N'-hydroxyethyl-2-nitro-p-phenylenediamine) dye supplied by Jos. H. LOWENSTEIN & Sons, Inc. (New York - U.S.A.) (in concentrations from about 1% to about 90% preferably from about 10% to about 50%) are dispersed in an organic solvent (acetone).

The organic phase A is dispersed under stirring in a phase B, constituted by a lipophilic solvent (for example mineral oil or paraffin oil).

The dispersing phase B must not dissolve the polymer and must be immiscible with the dispersed phase A.

The system is emulsified with a turboemulsifier at speeds from about 200 to about 9000 rpm preferably from about 600 to about 2000 rpm for a few minutes, until an emulsion and the formation of the microparticles is obtained.

Example 2
The same preparation as Example 1 using BASIC RED 51 (2[(4-(dimethylamino)phenyl)azo]-1,3-dimethyl-1H-imidazolium chloride) dye supplied by Jos. H. LOWENSTEIN & Sons, Inc. (New York - U.S.A.) and analogous conditions.

Example 3
The same preparation as Example 1 using HC BLUE No. 2 (N^1,N^4,N^4-tri(hydroxyethyl)-2-nitro-p-phenylenediamine) dye supplied by SIGMA-ALDRICH (Milano - ITALY) and analogous conditions.

Example 4
The same preparation as Example 1 using BASIC BROWN 16 (8-[(4-aminophenyl)diazenyl]-7-hydroxy-N,N,N-trimethyl-naphthalen-2-ammonium chloride) dye supplied by LCW SENSIENT COSMETIC TECHNOLOGIES (Saint Ouen L’Aumone - France) and analogous conditions.

Example 5
The same preparation as Example 1 using BASIC BROWN 17 (8-[(4-
amino-3-nitrophenyl)azo]-7-hydroxy-2-naphthyltrimethyl-ammonium chloride) dye supplied by LCW SENSIENT COSMETIC TECHNOLOGIES (Saint Ouen L'Aumone - France) and analogous conditions.

The second method for obtaining the microspheres is the so-called spray drying method. Said method is based on nebulizing a polymer solution or dispersion containing the dye or a dyes mixture through a dessiccating chamber of a spry-dryer. The solvent is rapidly evaporated by a stream of heated air transforming the small droplets in solid microparticles.

Microparticles obtained are usually organic solvent free with respect to other preparation methods.

Some examples using this second preparation method are set forth here below.

**Example 6**

Polymer and Unipure Yellow LC124 dye supplied by LCW SENSIENT COSMETIC TECHNOLOGIES (Saint Ouen L'Aumone - France) (in concentrations from 0.1% to 50%) are dispersed in a suitable organic solvent (dichloromethane, acetone...). The dispersion obtained is nebulized at temperature higher than that of solvent boiling point.

The microspheres containing the dye are obtained after evaporation of organic solvent.

**Example 7**

The same preparation as Example 6 using HC RED No 3 dye (N'-hydroxyethyl-2-nitro-p-phenylenediamine) and analogous conditions.

**Example 8**

The same preparation as Example 6 using Basic Brown 16 (8-[(4-aminophenyl)diazzenyl]-7-hydroxy-N,N,N-trimethyl-naphthalen-2 ammonium chloride) dye supplied by LCW SENSIENT COSMETIC TECHNOLOGIES (Saint Ouen L'Aumone - France) and analogous conditions.

**Morphological and size analysis - Substantivity evaluation**

The microspheres have been observed under a scanning electronic microscope (SEM) in order to determine their morphology and particle size.

The attached figures show some of such morphologies with a relative dimensional range (0.1-500 micrometers, preferably from about 1 to about 150 micrometers, more preferably from about 1 to about 50 micrometers)
obtained with the two methods described above.

More specifically, Figs. 1-6 show microspheres prepared by emulsification/evaporation method and Figs. 5-10 show microspheres prepared by spray-drying method.

The microspheres prepared by the solvent evaporation technique and spray-drying have been analyzed spectrophotometrically to determine their loading (the dye percentage obtained). The data obtained show a good encapsulation efficacy (between 50% and 95%) for all dyes tested.

Substantivity of the microspheres i.e. the capability of the microspheres to bind to keratin or keratinaceous substances, has been measured to hair keratin as described here below. Natural hair pigmented with different colors (from white to dark brown) has been used as a substrate.

The residual dye percentage on the hair has been evaluated spectrophotometrically:

a) after application of a lipophilic or hydrophilic gel containing the dye free or included in the microspheres;

b) after application of an aqueous solution or dispersion of dye free or included in microspheres followed by five washing with shampooing.

Spectrophotometrical analyses, performed on native hair have shown that, under the experimental conditions, the hair does not release substances able to interfer with the measurements.

Substantivity evaluation using method a)

The lipophilic or hydrophilic gel was spread on the hair. After 15 minutes of contact the hair was washed with water and after that extracted by ethanol. The solution was analysed spectrophotometrically. The substantivity of HC RED No 3 dye is about 68% in the case of free dye, while the dye microencapsulated in the microspheres showed a substantivity of about 94%.

Substantivity evaluation using method b)

The results have shown that substantivity in general can vary from 30% to 90% before washing, and that after 5 washings with shampooing, the residual amount of dye on the hair is from about 1 to about 40 times preferably from about 1 to about 10 times higher when using dyes microencapsulated in microspheres with respect to free dye.
The substantivity of HC RED No. 3 dye, evaluated after 15 minutes of contact of the hair with the aqueous dye solution, is 35%, while microencapsulated dye in microspheres showed a substantivity of 70%.

In all cases the better results are obtained when the dyes are dissolved or dispersed in a base that contains a thickener so the product stays on the hair without running or dripping. Application time of 10 to 40 minutes is common after which time the product is rinsed off.

The free dye stability has been compared with that of microencapsulated dye irradiating the samples with a solar simulator equipped of Xenon lamp and irradiating for to 10, 20 and 30 MED (corresponding to 300, 600 and 900 mJ/cm²).

The spectrophotometrical data obtained from the analysis of the samples indicate (during irradiation time corresponding with the maximum irradiated power) that the free dye is photodegraded from 10% to 98% according to case, while only 1.5% to 9% of the same dye was degraded when microencapsulated in the microparticle system. Therefore as a result of microencapsulation the degradation of dye is very low and consequently there is no discoloration of semi-permanent coloring for exposure of hair to UV ray.

The micro-particles, i.e. microspheres according to the present invention can be included in various cosmetic vehicles suitable for application on the hair (mono-, bi-, three- phase systems): powders, lotions, gels, shampoos-in formulations, mousses, oils, emulsions O/W, W/O, W/S, multiple emulsions, paste, spray, etc.

They could be further included in hair cosmetic formulations providing more durable effects. They consist of the conventional semipermanent dyes blended with oxidative dye precursors, which in conjunction with oxidant produces longer lasting color moieties. Such products are occasionally referred to as "demipermanents". Often included in the semipermanent category are also the vegetable dyes that are permitted to be used in EU.

Though the main and at present preferred and most advantageous application of the invention in cosmetics is addressed to hair dyeing, other possible applications of dyes encapsulated in substantive microspheres are not excluded. Uses of microspheres according to the invention can be
foreseen in compositions, such as cosmetic compositions, for skin and nail applications, choosing suitable dyes allowed under current regulations for those specific applications.
Claims

1) A dye composition including at least a dye encapsulated in microspheres, characterized in that said microspheres are substantive microspheres.

2) A dye composition according to claim 1, wherein said microspheres are cationic microspheres.

3) A dye composition according to claim 1 or 2, wherein said microspheres are made of a methacrylic polymer.

4) A dye composition according to one or more of the preceding claims, wherein said at least one dye is a direct, natural or synthetic dye.

5) A dye composition according to one or more of the preceding claims, wherein said at least one dye is a dye suitable for direct hair coloring.

6) A dye composition according to one or more of the preceding claims, wherein the dye is chosen from the group consisting of: HC RED n.3, BASIC RED 51, HC BLUE N°2, BASIC BROWN 16 and BASIC BROWN 17 or a combination thereof.

7) A dye composition according to one or more of the preceding claims, wherein the microspheres are used in a mono-, bi- or three-phase systems.

8) A dye composition according to one or more of the preceding claims, further including other dyes or oxidative dye precursors in presence of oxidizing agents.

9) A dye composition according to one or more of the preceding claims, in the form of a cosmetic composition, preferably a cosmetic composition for changing the appearance of keratinaceous substances, and even more preferably a hair dye composition.

10) A dye composition according to one or more of the preceding claims, including two or more dyes

11) A method for the preparation of substantive microspheres as components for a dye composition, said microspheres encapsulating at least one dye or a mixture of dyes, said method including the steps of: dispersing a polymer and a dye in a volatile solvent; emulsifying the phase so obtained with a continuous dispersing phase; and harvesting the microspheres so obtained by evaporation and filtration; washing and drying said microspheres
under vacuum.

12) Method according to claim 11, wherein a stabilizing agent is added to avoid droplet coalescence of the emulsion.

13) Method according to claim 11 or 12, wherein said solvent is an organic solvent.

14) Method according to claim 11 or 12 or 13, wherein the polymer is dispersed in said solvent together with magnesium stearate and the dye, and the phase so obtained is emulsified by dispersing under stirring in a lipophilic solvent immiscible with the phase comprising the polymer.

15) A method for the preparation of substantive microspheres as components for a dye composition, said microspheres encapsulating at least one dye or a mixture of dyes, said method including the steps of: dissolving or dispersing a polymer and at least a dye in a volatile solvent; nebulizing the phase so obtained in a spry-dryer; evaporating the solvent.

16) Method according to one or more of claims 11 to 15, wherein the polymer is a cationic polymer.

17) Method according to one or more of claims 11 to 16, wherein the polymer is a methacrylic polymer.

18) Dye-encapsulating microparticles as components for a dye composition, characterized in that said microparticles are substantive microspheres, binding to a keratinaceous substance.

19) Microcaspheres according to claim 18, formed by a cationic polymer and preferably a methacrylic polymer.
Fig. 8