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3,251,744

NAPHTHAZARIN HAIR DYEING COMPOSITION AND METHOD

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This invention relates to compositions and methods for the dyeing of human hair with naphthazarin, i.e., 5,8-dihydroxy-1,4-naphthoquinone.

There are only a relatively few dyes which are known to be suitable for dyeing living human hair on the head by direct dyeing methods which give strong permanent coloration to the hair at temperatures which are comfortably tolerated by the body, e.g. temperatures of less than about 40° C. Most hair dyes require various peroxides for the development of color, or the use of various dyeing assistance some of which irritate or stain the skin. The direct dyes which have been proposed for dyeing human hair either give only surface coloration to the hair without sufficient penetration of the dye in the hair shaft and thus rinse off or rub off easily, or they stain the scalp, or require various assistants in obtaining good dyeing. By direct dye is meant a dye which will penetrate into the hair shaft and give coloration to the hair without subsequent or simultaneous additional manipulations such as reaction with peroxides.

Disperse dyes, which are non-ionic, generally have very low affinity for hair. Those few which are used for direct dyeing of the hair, for example nitrophenylenediamine derivatives, give weak dyes which wash out readily.

In particular, naphthoquinones have little value as dyes for hair. Thus, 1,2-naphthoquinone and 1,4-naphthoquinone have only poor affinity for normal gray hair under various conditions of dyeing. Henna, whose principal color component is 2-hydroxy-1,4-naphthoquinone, has long been used for dyeing hair. However, it is effective only when applied from acid medium, and then gives an unstable reddish tint which darkens progressively on wearing, giving an unpredictable shade. Juglone, which is 5-hydroxy-1,4-naphthoquinone, gives only transient shades on hair, and is now rarely used.

More recently the use of quinones broadly have been described for use in hair dyeing compositions, as in U.S. Patent No. 3,041,244. However, those quinone hair dyeing compositions need to contain a high concentration of the dye; they are viscous pastes at temperatures about 40° C. and therefore are undesirable; further, they require large quantities of surfactants or solvents, and in most cases require a combination of these techniques to give any satisfactory dye uptake.

It has now been found that naphthazarin has good affinity for human hair at temperatures which are below 40° C. when applied in suitable compositions. It is not necessary to apply naphthazarin as a thick viscous paste, and the high concentration of dye, surfactants, or solvents and other dyeing assistants are not necessary to obtain proper dyeing of the hair. Naphthazarin does not stain or irritate the scalp nor damage the hair. It gives a strong purple shade of a permanent nature, which does not change on wearing, and is fast to rubbing and shampooing. The shade is substantially uniform on various kinds of human hair such as natural gray, permanent waved, and bleached hair. It is produced by direct dyeing without the use of developing agents such as peroxides.

The compositions of this invention can contain the conventional adjuvants of hair dyeing compositions in addition to the naphthazarin such as water soluble surface active agents, thickening agents and alkalizing agents. Tintorially effective quantities of naphthazarin in the compositions can vary over a wide range such as that of

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about 0.01% to greater than about 5%, e.g. 10%, by weight of the composition and preferably from about 0.01% to about 2% by weight. The water content of the composition is ordinarily the major constituent and can vary over a wide range dependent in large measure on the quantity of other additives. Thus, the water content can be as little as 10% and preferably from about 70% to 99%.

The water soluble surface active agents employed in the compositions can be anionic, non-ionic or cationic. Illustrative of the various types of water soluble surface active agents there can be mentioned: higher alkyl benzene sulfonates; alkyl naphthalene sulfonates; sulfonated esters of alcohols and polybasic acids; taurates; fatty alcohol sulfates; sulfates of branched chain or secondary alcohols; alkyl dimethyl benzyl ammonium chlorides; and the like. Illustrative of specific surfactants there can be mentioned: lauryl sulfate; polyoxyethylene lauryl ester; myristyl sulfate; glyceryl monostearate; sodium salt of palmitic methyl taurine; cetyl pyridinium chloride; lauryl sulfonate; myristyl sulfonate; lauric diethanolamide; polyoxyethylene stearate; stearyl dimethyl benzyl ammonium chloride; dodecyl benzene sodium sulfonate; nonyl naphthalene sodium sulfonate; dioctyl sodium sulfosuccinate; sodium n-methyl-n-oleoyl taurate; oleic acid ester of sodium isethionate; sodium dodecyl sulfate; the sodium salt of 3,9-diethyl tridecanol-6-sulfate; and the like. The quantity of water soluble surface active agent can vary over a wide range such as that of from about 0.25% to 15% and preferably from about 0.25% to 10% by weight of the composition.

The thickening agent may be one or several of those commonly used in hair dyeing, such as sodium alginate or gum arabic, or cellulose derivatives such as methylcellulose, or the sodium salt of carboxymethylcellulose, or acrylic polymers, such as polyacrylic acid sodium salt, or inorganic thickeners such as bentonite. The quantity of thickening agent can vary over a wide range such as that of from about 0.1% to 20% and preferably from about 0.5% to 5% by weight of the composition.

The pH of the composition can vary from about 2.5 to about 11, but it is preferred that the compositions be in the alkaline range and particularly at a pH of about 7.5 to 10. Any selected water dispersible compatible alkalizing agent, if it is desired to have the compositions in the alkaline range, can be used to give the desired pH. The quantity of the alkalizing agent employed can vary over a wide range depending on the particular alkalizing agent employed and the desired pH. Illustratively, the alkalizing agent can vary from less than about 0.1% to about 10% and preferably from about 0.25% to about 5% by weight of the composition.

Any water-soluble alkalizing agent that will not interfere (i.e., is compatible) with the dye employed, and will not precipitate the dye or introduce any possibility of toxicity under the conditions of use, or injure the scalp, at its ultimate concentration in the composition can be used. However, it is preferable to use any compatible ammonia derivative alkalizing agent such as an alkanolamine such as mono-, di-, or triethanolamine, isopropanolamine, N-methyl ethanolamine, 2,3-dihydroxypropylamine, or 2-amino-2-methyl-1,3-propanediol, or an alkyl amine such as monoethylamine, diethylamine, propylamine, dipropylamine or triethylamine or a heterocyclic amine such as morpholine, N-ethylmorpholine, piperidine, N-ethylpiperidine, 2-pipecoline, or piperazine.

The alkalizing component is preferably a water-soluble organic amine of low volatility (B.P. higher than about 50° C.) having less than about 12 carbon atoms, such as n-propylamine, isobutylamine, 2-ethylbutylamine, diethylamine, triethylamine. Particularly suited as the alkalizing agent are the following: (a) aliphatic diamines

or polyamines, such as ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, diethylenetriamine, triethylenetetramine, dipropylentriamine and N(2-aminoethyl) morpholine; (b) alkanolamines, such as ethanolamine, isopropanolamine, diethanolamine, and triethanolamine, which may also have a phenyl substituent, e.g. an arylalkanolamine, such as N-phenyldiethanolamine.

The acid employed for adjusting the pH can be any inorganic or organic acid or acid salt which is compatible with the composition and will not introduce toxicity under its conditions of use. Illustrative of acids or acid salts there can be mentioned: sulfuric, formic, acetic, lactic, citric or tartaric acid, or ammonium sulfate, sodium dihydrogen phosphate, or potassium bisulfate.

The dyeing compositions of this invention can be prepared by the conventional methods used in the hair dyeing art. Thus, they can be prepared by dissolving or dispersing the dye in water of the desired concentration. Water miscible organic solvents can be employed to facilitate solution of the dye; in this event, the dye can be dissolved first in the solvent and then diluted with water. The dispersion of the various ingredients can also be facilitated by heating the composition.

The dyeing compositions can be applied to living human hair on the head by the conventional techniques known in the art. Illustratively they can be poured over the hair or applied with a brush, sponge, or other means of contact until the hair is properly impregnated. The time of contact of the dyeing composition with the hair is not critical and can vary over the wide range used in the hair dyeing art, such as periods of about 5 minutes to 2 hours or more, and preferably from about 10 to 60 minutes. As mentioned hereinabove, the dyeing on live hair is preferably effected at temperatures below 40° C. such as those from 15° C. to 40° C. and preferably at ambient room temperatures such as those of about 20° C. to 35° C.

The following examples are illustrative of a preferred form of the invention:

Example 1

A mixture consisting of the following ingredients was heated at 50° C. for ten minutes with occasional stirring to effect a homogeneous dispersion:

Naphthazarin	-----g--	0.25
Ethanol	-----g--	0.35
Diethylenetriamine	-----g--	4.0
Sodium N-methyl-N-oleoyltaurate (Igepon T-33)	-----g--	0.5
Sodium carboxymethylcellulose	-----g--	3.0
Water	-----ml.	50.0

The above dispersion was then further diluted with water to a volume of 100 ml., and citric acid was added to give a pH of 9.9. The dye composition so obtained was poured on natural gray hair, permanent waved hair and bleached hair, and allowed to impregnate the hair for 20 minutes at 30° C. Afterwards the hair was rinsed in clear water and dried in air. All hair was dyed a strong purple coloration.

When the above composition and methods, except for the substitution of an equal quantity of triethanolamine in place of the diethylenetriamine, was used to dye hair, the shade obtained was similar.

Example 2

A mixture of the following materials was heated at 50° C. for ten minutes with stirring until they were effectively dispersed:

Naphthazarin	-----g--	0.40
Ethanol	-----g--	0.35
N-phenyldiethanolamine	-----g--	3.0
Isocetyl phenyl polyethoxy ethanol (Triton X-100)	-----g--	1.0
Methylcellulose	-----g--	3.0
Water	-----ml.	50.0

When the dispersion was homogeneous it was further diluted, to 100 ml., and the pH was adjusted to 9.5 by the addition of citric acid. The dye composition so obtained was poured on natural gray hair, on permanent waved hair, and on bleached hair, and allowed to remain on the hair for 20 minutes at 38° C. Finally, the hair was rinsed in clear water and dried. All the types of hair were dyed to an approximately equal strength of purple color, which was fast to rubbing and shampooing.

When, in this example, 1,3-diaminopropane was substituted for the N-phenyldiethanolamine, in equal amount, all hair was dyed a similar shade of equal fastness.

The dyeing compositions of this invention can be aqueous dispersions in the usual generic sense as embracing true solutions of the dye and the other ingredients in water or in any aqueous medium within the bounds of the invention as well as intimate admixtures of the dye or the other ingredients in the aqueous medium. The aqueous medium also includes the aqueous alkaline or acid medium or for example, a sufficient amount of a compound, e.g. ethanol, employed as a common solvent to enhance the solution of the dye or some other organic material. The dyeing compositions of this invention can be formulated as pastes, gels, or flowable liquids.

It is to be understood that the foregoing examples are intended only to illustrate and in no sense to limit the invention to the specific dyeing compositions, or manipulative techniques employed therein. The invention can be practiced broadly within the description thereof set forth hereinabove, and it is to be understood that any modifications or equivalents that would occur to one skilled in the art are to be considered as lying within the scope of this invention.

What is claimed is:

1. A method for dyeing living human hair on the head with naphthazarin which comprises impregnating the hair with an aqueous dispersion consisting essentially of a tinctorially effective amount of naphthazarin and an organic amine alkalizing agent having less than about 12 carbon atoms, said dispersion having a pH of about 7.5 to 11.

2. The method of claim 1 wherein the aqueous dispersion contains an organic amine alkalizing agent selected from the class of aliphatic diamines and polyamines, alkanolamines, and arylalkanolamines.

3. The method of claim 2 wherein the hair is dyed at a temperature below about 40° C.

4. A hair dyeing composition consisting essentially of an aqueous dispersion containing: (a) a tinctorially effective amount of naphthazarin; (b) a water-soluble surface active agent; (c) a thickening agent and (d) an organic amine alkalizing agent having less than about 12 carbon atoms, said composition having a pH between about 7.5 and 11.

5. A hair dyeing composition consisting essentially of an aqueous dispersion containing: (a) from about 0.01% to about 10% of naphthazarin; (b) from about 0.25% to about 15% of a water-soluble surface active agent; (c) from about 0.1% to about 20% of a thickening agent; and (d) a sufficient quantity of an organic amine alkalizing agent having less than about 12 carbon atoms to impart a pH of about 7.5 to 11 to the aqueous dispersion.

6. A hair dyeing composition consisting essentially of an aqueous dispersion containing: (a) from about 0.01% to about 5% of naphthazarin; (b) from about 0.25% to about 10% of a water-soluble surface active agent; (c) from about 0.5% to about 10% of a thickening agent; and (d) a sufficient quantity of an organic amine alkalizing agent having less than about 12 carbon atoms to impart a pH of about 7.5 to about 10 to the dispersion.

7. A hair dyeing composition consisting essentially of an aqueous dispersion containing: (a) from about 0.01%

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to about 5% of naphthazarin; (b) from about 0.25% to about 10% of a water-soluble surface active agent; (c) from about 0.5% to about 10% of a thickening agent; and (d) a sufficient quantity of an organic amine alkalizing agent selected from the class of aliphatic diamines and polyamines, alkanolamines, and aryldialkanolamines to impart a pH of about 7.5 to about 10 to the dispersion, said organic amine alkalizing agent having less than about 12 carbon atoms.

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