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3,516,778

NAPHTHOQUINONE IMINE COMPOSITIONS AND METHOD FOR USING THE SAME

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No Drawing. Continuation-in-part of application Ser. No. 345,107, Feb. 17, 1964. This application June 9, 1964, Ser. No. 373,838

Int. Cl. A61k 7/12

U.S. Cl. 8—10.2 16 Claims

ABSTRACT OF THE DISCLOSURE

A method and a composition for dyeing living human hair on the head which involves a composition containing a tinctorial amount of a hair substantive naphthoquinone imine.

This application is a continuation-in-part of application Ser. No. 345,107, filed Feb. 17, 1964, now abandoned.

This invention relates to a method of dyeing hair and, more particularly, to a method for dyeing living human hair on the head. It also concerns novel hair dyeing compositions which are useful for this purpose and certain novel compounds that can be employed in formulating these compositions.

There are relatively few dyes which are known to be suitable for dyeing living human hair on the head by direct dyeing methods and 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 assistants, some of which irritate or cause staining of 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 into 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 herein 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.

The nitrophenylenediamine derivatives, which have been used for direct dyeing of the hair, generally give only weak dyeings which wash out readily and produce relatively light colors, such as yellows, reds, and at their deepest, violets. Hence, they are not satisfactory for making drab mixtures, nor dark browns nor blacks.

It has now been found that certain naphthoquinone imines can be used to dye human hair at temperatures which are below 40° C. It is not necessary to apply these derivatives as thick viscous pastes, and high concentrations of dye, surfactants, or solvents and other dyeing assistants are not necessary for obtaining proper dyeing of the hair. Furthermore, the naphthoquinone imine compositions of this invention do not stain or irritate the scalp or damage the hair.

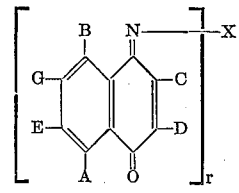
The dyes utilized in this invention are direct dyes which show a surprisingly high affinity for hair under aceptable conditions of application. They, therefore, give strong shades of a generally permanent nature. In general, they work over a wide range of pH and bath composition and give essentially uniform strengths on the various kinds of human hair, such as natural gray, permanent-waved and bleached. They are also generally stable in oxidizing dye baths (alkaline peroxide) and so can be used in combination with oxidation dyes. Their shade range includes the blue, varying from reddish blue to greenish blue. For

this reason they are suitable as a base for drab mixtures, and particularly, for dark browns and blacks.

The dyes employed in this invention have the further advantages over the known dyes in that they are, in general, stable on storage. This last advantage is of importance, since hair dyes are commonly marketed as aqueous compositions at pH's varying from about 3 to 10. Under storage conditions for long periods (say one year), and particularly in warm climates, the large majority of existing dyes undergo deterioration and show lower dye strength or a shade change when applied to hair.

The naphthoquinone imines that may be employed in accordance with the present invention are hair substantive naphthoquinone imines that are preferably water-soluble or water-dispersible and described by the formula:

I



and tautomeric forms thereof, wherein:

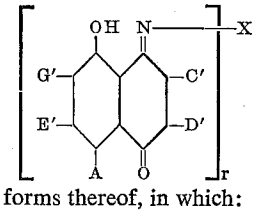
(1) X is selected from the group consisting of the monovalent radical —R and the divalent radical —R'—; wherein —R may be hydrogen, monovalent aliphatic, monovalent cycloaliphatic, monovalent aryl, monovalent aralkyl and monovalent heterocyclic radicals and wherein —R'—may be divalent aliphatic, divalent cycloaliphatic, divalent arylene, divalent aralkyl and divalent heterocyclic radicals.

(2) *r* is the number 1 or 2; *r* being 1 when X is monovalent, and *r* being 2 when X is divalent.

(3) A, B, C, D, E and G are selected from the group consisting of hydrogen, chlorine, bromine, sulfo, alkyl and the radical —HNR, in which R has the value ascribed to it above and wherein A and/or B may also be hydroxy.

In a more particular form of the invention, the naphthoquinone imines that may be employed are hair substantive naphthoquinone imines that are preferably water-soluble or water-dispersible and described by the formula:

II



and tautomeric forms thereof, in which:

(1) X and *r* have the same values ascribed to them above in connection with Formula I;

(2) A' is selected from the group consisting of hydroxy and the radical —HN—R in which R has the value ascribed to it above; and

(3) C', D', E' and G' are selected from the group consisting of hydrogen, chlorine, bromine, sulfo and alkyl.

In a preferred form of this invention C', D', E' and G' in Formula II is hydrogen.

As noted above, the radical X in Formulas I and II above may be a monovalent radical —R or a divalent radical —R'—. When reference is made herein to the monovalent character of the radical X, the term —R will be employed. On the other hand, the term —R'— will be used to designate the divalent aspects of radical X.

When —R in Formulas I or II above is a monovalent aliphatic radical, it may take various forms. Thus, for example, it may be an alkyl, monohydroxyalkyl, polyhy-

droxyalkyl, -(alkylene-NH)$_{n^1}$-alkylene-OH, wherein n^1 is a whole number from 1 to 3; -(alkylene-NH)$_{n^2}$-alkylene-NH_2, wherein n^2 is a whole number from 1 to 3, etc.

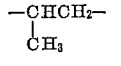
When —R in Formulas I or II above is alkyl, it may be a straight chain or branched chain alkyl radical which is preferably lower alkyl, e.g., having from 1 to 6 carbon atoms. By way of illustration the following alkyl groups may be mentioned as typical examples: methyl, ethyl, n-propyl, isopropyl, n-butyl, sec. butyl, tert. butyl, n-amyl, isoamyl, n-hexyl, and the like.

In the case where —R is a hydroxyalkyl radical in Formulas I and II, it may be a monohydroxy- or polyhydroxyalkyl radical. The alkyl chain is preferably a lower alkyl chain having from 2 to 6 carbon atoms. Typical mono and polyhydroxyalkyl radicals of this character are 2-hydroxyethyl; 3-hydroxypropyl; 2-hydroxypropyl; tris-(hydroxymethyl)methyl; 1,3 - dihydroxy-2-methyl-propyl; 2,3-dihydroxypropyl; 1,3-dihydroxy-2-propyl, etc.

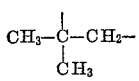
When —R in the Formulas I or II has the value -(alkylene-NH—)$_{n^2}$-alkylene-NH_2 or -(alkylene-NH)$_{n^1}$-alkylene-OH, the alkylene radicals are usually the same lower alkylene radicals which may be straight chained or branched, and ordinarily do not exceed 3 or 4 carbon atoms. In this case n^1 or n^2 is a number that ranges from 1 to 3. Typical alkylene radicals are the trimethylene radical (—CH_2—CH_2—CH_2—), the ethylene radical

(—CH_2—CH_2—)

the tetramethylene radical (—$CH_2(CH_2)_2$—CH_2—), the propylene radical



the isobutylene radical

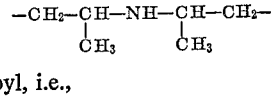


etc.

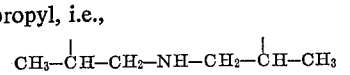
When the compounds of this invention take the form shown in Formula I or II, where X is the divalent radical —R'—, this divalent radical bridges two halves of the molecule, which are identical. —R'— may be a divalent alkylene, straight chained or branched, in which event it preferably is a lower alkylene radical having, e.g., from 2 to 6 carbon atoms. Typical examples are ethylene, trimethylene, tetramethylene, propylene, isobutylene, pentamethylene, etc.

In another case the divalent radical —R'— may be a hydroxyalkylene radical. In the preferred examples of this type this radical will have from 3 to 6 carbon atoms, such as 2-hydroxytrimethylene; 2-hydroxytetramethylene; 2,3-dihydroxytetramethylene; and hydroxyisobutylene.

—R'— may be constituted as the radical -(alkylene $NH)_{n^3}$-alkylene-, in which n^3 may have a value which is 1, 2 or 3, and the alkylene moiety is a lower alkylene radical, e.g., having 1 to 6 carbon atoms. Typical radicals of this character are as follows: 2,2'-iminodiethyl, i.e., —CH_2—CH_2—NH—CH_2—CH_2—; 3,3'-iminodipropyl, i.e., —CH_2—CH_2—CH_2—NH—CH_2—CH_2—CH_2—; 2,2'-iminodipropyl, i.e.,



iminodiisopropyl, i.e.,



—CH_2—CH_2—NH—CH_2—CH_2—NH—CH_2—CH_2—

—CH_2—CH_2—NH—CH_2—CH_2—NH—
CH_2—CH_2—NH—CH_2—CH_2—

—CH_2—CH_2—CH_2—NH—CH_2—CH_2—
CH_2—NH—CH_2—CH_2—CH_2—

—CH_2—$(CH_2)_5$—$NH(CH_2)_5CH_2$—

The radical —R may also be an aryl radical and preferably, a mono or a bicyclic aryl radical having up to 12 carbon atoms in the ring system. These will ordinarily take the form of substituted or unsubstituted phenyl, naphyl or biphenylyl radicals. The substituted radicals may contain any of a variety of substituents or combinations thereof. By way of example the following may be mentioned: alkyl, alkenyl, hydroxy, alkoxy, nitro, halogen, amino, alkylamino, dialkylamino, hydroxyalkylamino, bis-hydroxyalkylamino, acylamido, monohydroxyalkyl, polyhydroxyalkyl, carbalkoxy, carbamoyl, N-alkylcarbamoyl, N,N-dialkylcarbamoyl, cyano, sulfamoyl, N-alkylsulfamoyl, N,N-dialkylsulfamoyl, alkanoyl, mercapto, alkylthio, and alkylsulfonyl. In this case the alkyl moieties are also preferably lower alkyl. Moreover, the halogen may be chlorine, bromine, fluorine or iodine. Typical examples include phenyl; o-, m-, p-tolyl; 4-ethylphenyl; 2,4-xylyl; 4-alkylphenyl; 4 - isopropenylphenyl; 2 - ethoxyphenyl; 4-ethoxyphenyl; 2-methoxyphenyl; 3-methoxyphenyl; 4-methoxyphenyl; 4-hydroxyphenyl; 2-hydroxyphenyl; 3-hydroxyphenyl; 3-nitrophenyl; 2-chlorophenyl; 2-fluorophenyl; 3-bromophenyl; 4-iodophenyl; 3-aminophenyl; 4-methylaminophenyl; 4 - diethylaminophenyl; dimethylaminophenyl; 4-bis(hydroxyethyl)aminophenyl; 3 - acetamidophenyl; 4-acrylamidophenyl; 4-benzamidophenyl; 3-glycolylamidophenyl; 3-hydroxymethylphenyl; 4-(2-hydroxyethyl)phenyl; 4 - (2,3 - dihydroxypropyl)phenyl; 3 - carbethoxyphenyl; 4 - carbamoylphenyl; 3-(N-methylcarbamoyl)phenyl; 2-cyanophenyl; 3-cyanophenyl; 4-sulfamoylphenyl; 4-(N,N-bishydroxyethylsulfamoyl)phenyl; 3-acetylphenyl; 3-propionylphenyl; 4-methylmercaptophenyl; 3-methylsulfonylphenyl; 3-nitro-4-aminophenyl; 2-methyl-5-nitrophenyl; 3 - nitro-4-hydroxyphenyl; 2-chloro-5-nitrophenyl; 4-chloro-3-methoxyphenyl; 4-acetamido-2-methylphenyl; 4-acetamido-3-methoxyphenyl; 2 - carbamoyl-4-chlorophenyl; 2-methyl-5-sulfamoylphenyl; 2-chloro-5-cyanophenyl; 2 - hydroxy-5-sulfamoylphenyl; 3-nitro-4-hydroxyethylaminophenyl; 3-nitro - 4 - methylaminophenyl; 3-chloro - 5 - nitrophenyl; 2-hydroxy-5-nitrophenyl; 2-methoxy-5-nitrophenyl; 3 - nitro - 4 - dimethylaminophenyl; 2-hydroxy - 3 - chloro-5-sulfamoylphenyl; 7-hydroxy-2-naphthyl; 4-hydroxy-2-naphthyl; 6-sulfamoyl-2-naphthyl; 1 - methoxy-6-sulfamoyl-2-naphthyl; 4 - biphenylyl; 2-biphenylyl; 4'-acetamido-4-biphenylyl.

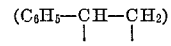
When X is a mono or bicyclic aryl radical in Formulas I and II, it preferably is a substituted radical of this character. It has been found that certain substituted aryl radicals, as hereinafter described, have a greater substantivity for hair than the unsubstituted aryl radicals.

When —R is an aralkyl radical in Formulas I or II above, it will be similar in general character to the aryl radical described above. It will, however, be bonded to the imino nitrogen of the naphthoquinone imine nucleus through its alkyl moiety. Examples of aralkyl radicals for the purpose are benzyl, p-chlorobenzyl; 3-methoxybenzyl; 2,4-dihydroxybenzyl; 2-phenylethyl; 1-phenylethyl; 1-phenylpropyl; 2-phenylpropyl; 2-naphthylmethyl, and the like.

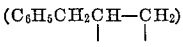
When —R is a cycloaliphatic radical, it may have up to 6 carbon atoms in the ring structure, the cyclohexyl or cyclopentyl being preferred. It may, in general, also carry the various substituents described above in connection with the substituted aryl radicals. As examples of suitable cycloaliphatic radicals, there may be mentioned: cyclopentyl; cyclohexyl; 2-hydroxycyclohexyl; 2-oxo-cyclohexyl; 3-methylcyclohexyl; 4-methylcyclohexyl; 3-chlorocyclohexyl; 4-methoxycyclohexyl, and the like.

When —R'— is a divalent arylene radical, it is preferably monocyclic or bicyclic in character, e.g., m-phenylene, p-phenylene, p-toluylene; 4,4'-biphenylene; 3,3'-dimethyl-4,4'-biphenylene; 3,3'-dichloro-4,4'-biphenylene, and the like. Substituted and unsubstituted arylene radicals are suitable, although generally the unsubstituted radical will be utilized.

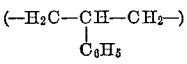
Similarly when —R'— is a divalent cycloaliphatic radical, it preferably contains up to 6 carbon atoms, the preferred radical being the divalent 1,2-; 1,3-; or 1,4-cyclohexylene radical. When —R'— is a divalent aralkyl radical the two valence bonds of the radical may both issue from the same alkyl moiety, as for example in the aralkyl radicals phenylethylene



3-phenylpropylene



and 2-phenyltrimethylene



or from different alkyl moieties, as in m- or p-phenylenedimethylene (—H_2C—C_6H_4—CH_2—), or one bond may issue from an alkyl moiety and the other from an aryl moiety, as in m- or p-phenylenemethylene

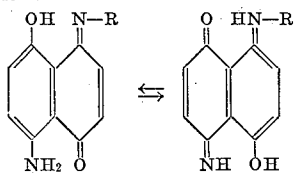
(—$C_6H_4CH_2$—)

When X is a heterocyclic radical in Formulas I or II above, it may take the form of the monovalent radical —R or divalent radicals —R'— or —R'—R'— in which each of R or —R'— is a heterocyclic ring structure containing up to and including three rings and 14 atoms in said ring structure. The heteroatoms of these ring structures may be selected from the group consisting of O, S, N or combinations thereof, and preferably each ring structure represented by —R or —R'— contains no more than 3 heteroatoms. When the divalent heterocyclic radical has the form —R'—R'—, the R's may be bonded to each other through a disulfide linkage, such as

—R'—S—S—R'—

In the case of the heterocyclic radicals, the substituents on the ring or rings of these radicals can vary considerably. These include one or more alkyl, hydroxy, nitro, halogen, amino, alkylamino, hydroxyalkylamino, alkoxy, monohydroxyalkyl, polyhydroxyalkyl, dialkylamino, bishydroxyalkylamino, cyano, carbamoyl, sulfamoyl, etc., or combinations thereof. In this case also the alkyl radical, and the alkyl moiety of the substituted alkyl radical are of the lower alkyl type. The halogen can be chlorine, bromine, fluorine or iodine. Typical examples of the heterocyclic radicals are 2-pyridyl, 3-pyridyl, 4-pyridyl, 6-amino-2-pyridyl, 2-methyl-4-thiazolyl, 4-quinolyl, 5-quinolyl, 7-quinolyl, 2-imidazolyl, 5-benzimidazolyl, 2-benzothiazolyl, 2-mercapto-5-benzothiazolyl, 2-naphtho-[1,2]thiazolyl, etc.

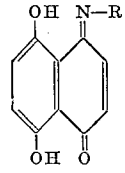
When C', D', E', G' and X of Formula II above are hydrogen, A' is amino and r is 1, the compound is one which is well-known in the prior art as "naphthazarin intermediate," hereinafter referred to as NI. This compound and compounds of like character exist in at least two tautomeric forms which may be expressed by the following equation:



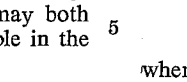
These are included in the present invention.

Embraced within the present invention are the naphthoquinone imines of the formula:

III



and tautomeric forms thereof wherein R has the value ascribed to it above. In a preferred form of these compounds, the radical R is an aminoalkylaminoalkyl radical of the formula



wherein alkylene is a lower alkylene radical and n is a number of 1 to 3. These are a novel group of compounds and are prepared by the condensation of an alkylenepolyamine—e.g.,

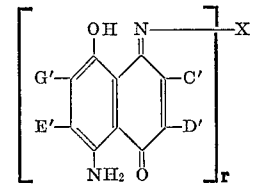
wherein n=1 to 3—and preferably a polyalkylenepolyamine of the formula

NH_2—alkylene—NH—alkylene—NH_2

with naphthazarin, i.e., 5,8-dihydroxy-1,4-naphthoquinone. The condensation is preferably carried out in an aqueous medium utilizing a large excess of the amine (e.g., 4 to 6 moles). The time of the condensation may vary between five minutes to several hours. However, best results are obtained in about 5 to 10 minutes. Similarly, the temperature may vary considerably between 40° to 100° C., but the optimum temperature is about 100° C.

The NI derivative which may be utilized in accordance with the present invention may be described by the general formula:

IV



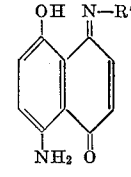
and tautomeric forms thereof wherein C', D', E', G', X, and r have the same value ascribed them in connection with Formula II. In those cases where X is a monovalent or divalent radical other than hydrogen, these compounds are prepared by condensing NI with a primary amine or diamine, preferably in the presence of an excess of the amine. The excess of amine will vary from a slight excess to a six-fold excess depending on the particular primary amine employed.

The reaction temperature and time will also vary with the particular reactants that are employed and the solvent system utilized. In general, however, the reaction will go at temperatures up to the reflux temperature of the reaction medium which will generally be in the neighborhood of about 80° C. to 100° C. Similarly, the reaction time may vary from 10 to 15 minutes up to about eight hours.

The solvent systems that can be employed will depend on the particular agents that are being condensed. These may be aqueous systems, as well as organic solvent systems. Particular solvents that have been employed include water, ethanol, isopropanol and glacial acetic acid.

With regard to NI reaction products generally illustrated in Formula IV above, it has been found that several classes of these compounds, which are noval, have particularly desirable properties as dyes for hair. One group of compounds of special interest are defined by the formula:

V

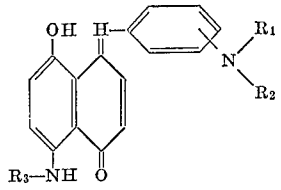


and tautomeric forms thereof wherein R'' is a hydroxyalkyl radical of 2 to 6 carbon atoms which may be monohydroxyalkyl or polyhydroxyalkyl or a hydroxyalkyl-

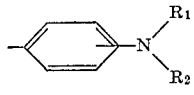
aminoalkyl radical. Such derivatives are generally characterized not only by a high degree of dispersibility in aqueous medium, but also by a surprisingly high affinity to various types of hair, particularly to bleached hair, as compared with the corresponding derivatives in which R'' is merely an alkyl group (e.g., ethyl). As examples of R'' which are in this novel and favorable class, there may be mentioned 2-hydroxyethyl; 3-hydroxypropyl; 2-hydroxypropyl; 2,3-dihydroxypropyl; tris(hydroxymethyl) methyl; 1,3-dihydroxy-2-methylpropyl; 1,3 - dihydroxy-2-propyl, as well as 2(2-hydroxyethylamino)ethyl; 3(2-hydroxyethylamino)propyl; 1(2 - hydroxyethylamino) - 2-propyl; 1(2-hydroxyethylamino)2-methyl-2-propyl; etc.

Another useful and novel class of NI derivatives are described by the formula:

VI



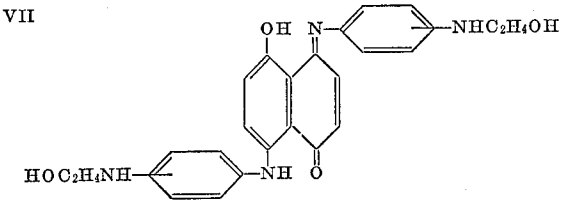
and tautomeric forms thereof in which R_1 and R_2 are selected from the group consisting of H, monohydroxyalkyl and polyhydroxyalkyl, at most one of R_1 and R_2 being hydrogen; and R_3 is selected from the group consisting of H and the radical



in which R_1 and R_2 have the same value ascribed to them above.

A typical group of compounds falling within Formula VI above is that wherein only R_1 and R_3 are hydrogen. Also of interest are compounds wherein R_3 is hydrogen, whereas R_1 and R_2 or both are hydroxyethyl; 2,3-dihydroxypropyl and the like. The case wherein both nitrogens carry organic substituents such as:

VII

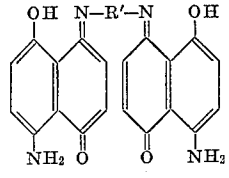


is also of interest.

Dyes of the class described by Formula VII are characterized by a generally high dispersibility and uniform affinity to a variety of hair when applied from a variety of media.

The condensation of two moles of NI with one mole of a diamine gives a derivative of NI that may be described by the general formula:

VIII



or tautomeric forms thereof wherein —R'— has the same value ascribed to it in connection with Formula II. Of particular interest and novelty are the compounds prepared from the aliphatic diamines, i.e., aliphatic compounds containing at least two primary amino groups. Typical examples of the alkylene radical —R'— which are suitable for this class are ethylene, trimethylene, tetramethylene, propylene, isobutylene, pentamethylene, etc. Also suitable for this class of dyes are those containing

the diradical -(alkylene $NH)_{n^3}$-alkylene-, such as 2,2-iminodiethyl; 2,2'-iminodipropyl;

$$—CH_2CH_2NHCH_2CH_2NHCH_2CH_2—$$

3,3'-iminodipropyl

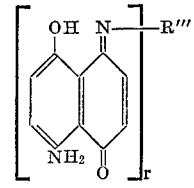
$$CH_3—\underset{|}{C}H—CH_2—NH—CH_2—\underset{|}{C}H—CH_3$$

$$—CH_2—CH_2—NH—CH_2—CH_2—NH—$$
$$CH_2—CH_2—NH—CH_2—CH_2—$$
$$—CH_2—CH_2—CH_2—NH—CH_2—CH_2—$$
$$CH_2—NH—CH_2—CH_2—CH_2—$$
$$—CH_2(CH_2)_5—NH—(CH_2)_5—CH_2—$$

and the like. These are prepared from the corresponding polyalkylenepolyamines, such as diethylenetriamine; triethylenetetramine; 2,2'-iminodipropylamine; 3,3'-iminodipropylamine; bis-hexamethylenetriamine and the like.

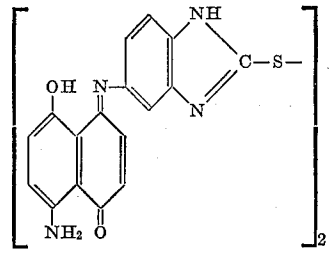
The reaction of NI with amino-substituted heterocyclic compounds produce a class of compound which is also worthy of special mention. More particularly, these can be defined by the formula:

IX



or tautomeric forms thereof in which R''' is a monovalent or divalent heterocyclic radical and r is 1 or 2, r being 1 when R''' is a monovalent radical, and r being 2 when R''' is a divalent radical. By way of example R''' may be 2-pyridyl, 3-pyridyl, 4-pyridyl, 6-amino-2-pyridyl, 2-methyl-4-thiazolyl; 4-quinolyl, 5-quinolyl, 7-quinolyl, 2-imidazolyl, 5-benzimidazolyl, 2-benzothiazolyl, 2-naphtho[1,2]thiazolyl.

When the heterocyclic reactant contains two reactive amino groups, the compound produced may contain a divalent heterocyclic moiety, in which each valence of said moiety is bonded to a NI nucleus through nitrogen. This might also result from the use of a heterocyclic amine which contains one amino group and one functional group capable of reacting with a functional group of another molecule of the same material to produce in effect a heterocyclic amine containing two amino groups. By way of illustrating the latter, the reaction of NI with 5-amino-2-mercaptobenzimidazole may give a compound having the following structure:



The naphthoquinone imines utilized in the present invention can be employed to prepare basic or acidic dye compositions and because of their stability, may be used in conjunction with oxidation dyes. Furthermore, they may likewise be included in hair dyeing compositions which contain other direct dyeing dyes that also may or may not contain an oxidation dye. A variety of direct dyeing dyes are known in the prior art which are useful for this purpose. They include nitro dyes, azo dyes, anthraquinone dyes, etc. By way of illustration, any of the nitro dyes disclosed in the following U.S. patents may be used in conjunction with the naphthoquinone imines: 2,750,326; 2,750,327; 3,088,877; 3,088,878 and 3,08,978.

The pH of the dye compositions of this invention can vary from about 2.5 to 11. In the acid range the pH of

about 3.5 to 6 is suitable. It is preferred, however, that the compositions be in the alkaline range and particularly at a pH of about 7.5 to 10. Any selected water-dispersable 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 dye and 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.

The alkalizing agent is selected so that it 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 to be applied to the keratinaceous material. A primary test of some selected alkalizing agent can be made to note its compatibility with the dye or to discover possibility of toxicity or injury.

Ammonium hydroxide because of its freedom from toxicity over a wide concentration range and its economy, is an acceptable alkalizing agent. However, there can be used in place of, or together with, ammonia any other compatible ammonia derivative as an alkalizing agent, such as an alkylamine, such as ethylamine, dipropylamine, or triethylamine, an alkanediamine, such as 1,3-diaminopropane, an alkanolamine, such as ethanolamine or diethanolamine, a polyalkylenepolyamine, such as diethylenetriamine, or a heterocyclic amine, such as morpholine.

Also, as alkalizing agent, any alkaline earth hydroxide, for example, calcium hydroxide or magnesium hydroxide, can be used up to the limit of its water solubility and at any concentration that fails to produce a precipitate with any of the components of the composition. The dissolved alkaline earth hydroxides are preferred over the alkali metal hydroxides, such as sodium hydroxide, or potassium hydroxide, or carbonates, such as sodium carbonate and bicarbonate, any of which can also be used so long as their ultimate concentration in the final dyeing solution is below that which might possibly irritate the scalp.

The alkalizing component of choice, however, is 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) primary aliphatic diamines, such as ethylenediamine; 1,2-diaminopropane; 1,3-diaminopropane; diethylenetriamine; triethylenetetramine; 2,2'-iminodipropylamine; 3,3'-iminodipropylamine; and bis-hexamethylenetriamine; (B) alkanolamines, such as ethanolamine; isopropanolamine; diethanolamine; di-isopropanolamine; triethanolamine; triisopropanolamine; N-methyldiethanolamine; diisopropylethanolamine; dimethylisopropanolamine; 2-amino-2-methylpropane-1,3-diol; tris(hydroxymethyl)methylamine and the like, which may also have a phenyl substituent, e.g., N-(2-hydroxyethyl)aniline; N-methyl-N-(2-hydroxyethyl)aniline; N,N-bis(2-hydroxyethyl)aniline; and (C) heterocyclic amines, such as morpholine, N-methylmorpholine, N-ethylmorpholine, N-hydroxyethylmorpholine, N-phenylmorpholine, piperidine, N-hydroxyethylpiperidine, and piperazine.

The pH of the composition may be adjusted with any inorganic or organic acid or acid salt which is compatible with the composition and will not introduce toxicity under its conditions of use, especally when acid compositions are desired. 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.

Water-soluble surface active agents can also be employed in the dyeing compositions utilized in this invention. These can be anionic, non-ionic or cationic. Illustrative of the various types of water-soluble surface active agents there can be mentioned: higher alkylbenzenesulfonates; alkylnaphthalenesulfonatess; sulfonated esters of alcohols and polybasic acids; taurates; fatty alcohol sulfates; sulfates of branched chain or secondary alcohols; alkyl dimethylbenzyl 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 isothionate; 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.

A thickening agent can also be incorporated in the present dyeing composition which 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.

Tinctorially effective quantities of the naphthoquinone imines in the compositions of this invention can vary over a wide range, such as that of 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 dyeing compositions of this invention are preferably aqueous compositions. The term "aqueous composition" is used herein in its usual generic sense as embracing any water-containing composition embodied in the invention. This includes true solutions of the dye in an aqueous medium, either alone or in conjunction with other materials, which are also dissolved or dispersed in the aqueous medium. The term "aqueous composition" also encompasses any mixture of dye with the aqueous medium either alone, or together with other ingredients. The dye may be colloidally dispersed in the medium or may merely be intimately mixed therein.

The term "aqueous medium" as used herein, includes any medium which contains water. Thus, the aqueous medium may be an aqueous alkaline or aqueous acid medium. Moreover, the aqueous medium may comprise water and a solvent, e.g., ethanol. The latter may be employed as a common solvent to enhance the solution of the dye or some other organic material.

The aqueous compositions of this invention may take many forms. Thus, they may be thin or thick flowable liquids, pastes, gels, etc.

Typical dyeing compositions of the various classes described above are set forth below:

(1) ALKALINE COMPOSITIONS

	General range	Preferred range
Dye, percent	0.01–5	0.01–2
Surface active agent, percent	0.25–5	0.25–1
Alkali, percent	0.1–10	0.25–5
Thickening agent, percent	0.1–20	0.5–3
Acid, pH	7–11	7.5–9.5
Water to 100%.		

Any of the dyes, surface active agents, alkalies, thickening agents, acids and combinations thereof set forth

above may be used in the proportions specified in the table immediately above.

(2) ACID COMPOSITIONS

The acid compositions are similar to the above alkaline compositions, except that the alkali is omitted, and the acid is added to a pH of 2.5–7, preferred 3.5–6. The surfactant may be anionic, cationic or non-ionic or suitable mixtures of these, and any of these mentioned above may be used. The choice of thickener is somewhat more limited, to alkylcellulosics, such as methylcellulose, and inorganics. In certain cases the surfactant, itself, acts as a thickener.

(3) OXIDATION DYE COMPOSITIONS

The naphthoquinone imines utilized in this invention are generally compatible with oxidation dyes. Accordingly, they can be used in oxidation dye compositions. Suitable compositions contain 1–5% ammonia, 2–3% hydrogen peroxide or urea peroxide; 0.005% to 2% oxidation dye components; 0.001% to 3% naphthoquinone imine as defined above, as well as surfactants, thickeners, etc. By way of illustration in this connection the following oxidation dye components can be utilized in formulating this composition: o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, p-toluenediamine, nitro-p-phenylenediamine, 4-nitro-o-phenylenediamine, p-aminodiphenylamine; 4,4'-diaminodiphenylamine; 4,6-dinitro-2-aminophenol; 4-nitro-2-aminophenol; 2,4-diaminoanisole, hydroquinone, resorcinol, p-aminophenol; 1,2,4-trihydroxybenzene; 1,2,4-triacetoxybenzene.

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 suspending the dye in water in 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 at temperatures varying from 40° C. to 110° C., either before dilution with water or afterwards.

When the dye used in the compositions of this invention is "naphthazarin intermediate," it may be employed in the crude state, directly as obtained from its preparative medium. The preparation of NI is well-known and is accomplished by the reduction of 1,5-dinitronaphthalene by means of S_2O_3 (sulfur dissolved in sulfuric acid or oleum). When the reaction mixture is poured on ice, and the aqueous solution clarified and neutralized, NI is precipitated, and after recovery may be used without further purification in hair dyeing compositions.

However, it is an aspect of this invention to provide a novel purification method for NI, which then surprisingly enhances its properties in hair dyeing compositions. This purification method consists of heating NI with a 10–20% aqueous solution of a secondary or tertiary alkanolamine, such as diethanolamine or triethanolamine or a morpholine, at about 100° C., for brief periods (10 minutes to one hour). The NI is then recovered by dilution with brine, filtration, and washing with brine. The alkanolamines which may be used, besides diethanolamine and triethanolamine, are such, for example, as: diisopropanolamine, triisopropanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, diisopropylethanolamine, dimethylisopropanolamine, N-hydroxyethylmorpholine, and N-hydroxyethylpiperidine. Also suitable are morpholines, such as morpholine, N-methylmorpholine and N-ethylmorpholine.

The NI so purified shows the following advantages over the original crude NI: more soluble in water; gives clearer and brighter shades on hair, wool and nylon; its dyeing compositions show greater storage stability. The prior methods of purifying NI show considerable deficiencies over the method of this invention. Thus, recrystallization from glacial acetic acid gives low recovery of NI, as well as contamination with insoluble self-condensation products. The purification through the leuco compound leads to the reprecipitation of many of the impurities, and poor quality of the NI so obtained.

The following examples are further illustrative of the present invention. It is to be understood, however, that the invention is not limited thereto.

In the example below reference is made to various dyeing procedures. These procedures are identified as follows:

PROCEDURE I

Hair dyed from an alkaline bath

A mixture as follows was diluted with 50 ml. of water, and the whole heated at 60° C. for one hour:

	G.
Dye	0.25
Ethanol	0.35
Ethanolamine	4.0
Sodium N - methyl - N - oleoyltaurate (Igepon T–33)	0.5
Sodium carboxymethylcellulose	3.0

The mixture was then further diluted with water to a volume of 100 cc., 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 remain for 20 minutes at 30° C. Afterwards, the hair was rinsed in clear water and dried in air.

PROCEDURE I(a)

In this procedure the same dyeing steps and mixture utilized in Procedure I was employed. However, this mixture, before any dilution, was heated at 110° C. for 10 minutes. Then 50 ml. of water was added, the mixture was heated at 60° C. for one hour, and the volume was adjusted to 1000 ml.

PROCEDURE II

Hair dyed from an acid bath

A mixture was prepared as follows:

	G.
Dye	0.3
Ethanol	0.35
Nonylphenoxypoly (ethyleneoxy) ethanol (Igepalco–730)	1.0
Methylcellulose	2.0
Water to 100 ml.	
Lactic acid to pH 3.5—ca. 0.25 g.	

This composition was poured on normal gray, permanent-waved, and bleached hair and left in contact for 20 minutes at 30° C.

PROCEDURE III

Hair dyed from peroxide bath

The following composition was prepared:

	G.
Dye	0.75
Isopropanol	2.5
Oleic acid	35.0
Polyoxyethylene sorbitan monooleate (Tween 80)	10.0
Isooctyl phenyl polyethoxy ethanol (Triton X–100)	3.5
Ethylenediamine tetracetic acid	0.25
28% ammonia—10.0 ml.	
Water to 100 ml.	

A 30-ml. aliquot of this composition was mixed with 30 ml. of 6% hydrogen peroxide and the mixture poured on natural gray hair and allowed to remain there for 40 minutes at 30° C. The hair was then rinsed with clear water, and shampooed.

Example 1

Hair dyed with NI from alkaline baths.—Procedure I above was followed in which 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine (NI) was used as the dye. All hair was dyed a strong level reddish blue shade, fast to shampooing and rubbing; the various types of hair being similar in shade and strength of dyeing.

When NI was used in Procedure I(a) described above, this gave a greenish blue shade on hair of similar fastness.

When in the composition of Procedure I, triethanolamine was used in place of ethanolamine, the shade obtained on hair was a blue, not as reddish as obtained with ethanolamine.

Example 2

Hair dyed with NI from an acid bath.—Procedure II above was followed using 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine (NI) as the dye. When this composition was poured on normal gray, permanent-waved and bleached hair and left in contact for 20 minutes at 30° C., as described in the procedure, all was dyed a reddish blue shade, stable to rinsing, shampooing, and rubbing.

Example 3

Hair dyed with NI from peroxide bath.—Procedure III above was followed using 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine (NI) as the dye. This dyed the hair a bright blue shade of excellent levelness, fast to rubbing.

Example 4

Purification of NI by treatment with alkanolamines.—A sample of "naphthazarin intermediate" was prepared by a known method as follows:

In 540 g. 100% sulfuric acid (monohydrate) was dissolved 20 g. sulfur powder at 90–95° C. Then, at this temperature range, was added 40 g. 1,5-dinitro-naphthalene portionwise over a period of one hour, and the mixture heated for another hour. An additional 68 g. monohydrate was added, and the mixture was finally heated for one-half hour at 95° C. The batch was allowed to cool and to stand at room temperature for about 16 hours. It was then poured onto 2000 g. ice, the solution clarified, and the sulfur residue washed with 500 ml. water. The combined filtrates were neutralized with ammonia to a pH of 7, while keeping the temperature below 10° C. The precipitate of NI was filtered off, washed with 1000 ml. water, pressed dry, and dried in air at 80° C. The crude NI thus obtained was used in the subsequent purification procedure as follows:

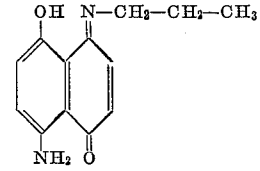
A mixture composed of 40 g. of crude "naphthazarin intermediate" and 50 g. of diethanolamine in 300 g. of water was heated at 100° C. for 30 minutes. The dye dissolved completely, and the solution on cooling was poured into 500 ml. of 20% brine. At this point 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine repricipitated and was recovered by filtration, washing with brine and then with water, and drying. When the dye so obtained was compared with the dye not treated with diethanolamine, it was considerably more soluble in water, and gave clearer and brighter dyeings on hair. Moreover, its dyeing composition, prepared according to the method of Procedure I, and stored at 50° C. showed no loss in strength or change in shade when the dyeing was repeated after three months. In comparison the crude NI was less soluble, gave duller shades on hair, and its dyeing composition prepared according to Procedure I, on being stored for 3 months at 50° C., and then re-applied to the hair showed a change in shade toward the brighter, and a loss of 50% in dye strength.

When the above experiment was repeated using triethanolamine instead of diethanolamine, similar improvements in solubility, dyeability of hair and storage stability were observed.

(A) CONDENSATION OF NI AND ALIPHATIC AMINES

Example 5

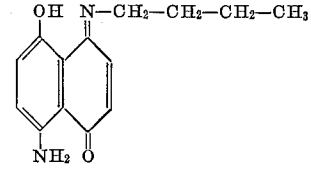
Preparation of N-propyl NI derivative.—A mixture of 14 g. (0.075 mole) of 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine and 20 g. (0.34 mole) n-propylamine in 60 ml. water was heated at 80° C. for 10 minutes. The reaction mixture was diluted with 600 ml. of 10% brine, filtered after cooling, and the cake was washed with 10% brine, and finally dried at 85° C. The product has the structure indicated below according to the elementary analysis and infra-red spectrum. It is a black powder.



When applied to normal gray hair by the method of Procedure I, the alkyl derivative of this example gave a level grayish blue coloration which was fast to shampooing and rubbing.

Example 6

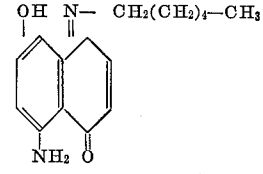
Following the same synthesis procedure described in the first paragraph of Example 5, utilizing the same molar proportions of NI and alkylamine, but substituting n-butylamine for the propylamine, the corresponding N-butyl compound is obtained which may be described as:



When applied to gray hair in accordance with Procedure I, it gave the hair a grayish blue color.

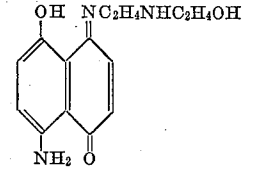
Example 7

Following the same synthesis procedure described in the first paragraph of Example 5, utilizing the same molar proportions of NI and alkylamine, but substituting n-hexylamine for the propylamine, the N-hexyl product is obtained, which may be described as:



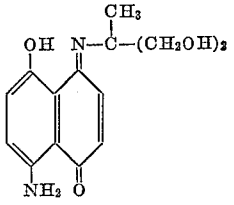
Example 8

Preparation of N-hydroxyethylaminoethyl NI derivative.—A mixture of 20 g. naphthazarin intermediate and 24 g. N-(2-hydroxyethyl)ethylenediamine in 200 ml. water was heated 10 minutes at 85° C. After cooling, the reaction slurry was diluted with 100 ml. 20% brine, and the dye was precipitated with 100 ml. 40% zinc chloride solution. After filtering and washing with brine the dye was dried at 80° C. The dye had the structure indicated below. It is a black powder which decomposes at 235° C. and dyes natural gray and bleached hair in shades of gray when applied by Procedure I.



Example 9

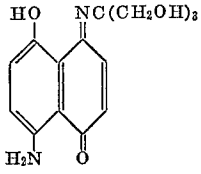
Preparation of N-substituted polyhydroxyalkyl NI derivative.—A mixture of 14 g. naphthazarin intermediate and 20 g. 2-amino-2-methyl-1,3-propanediol in 150 ml. water was heated 10 minutes at 100° C. and poured into 200 ml. 20% brine. After 3 hours stirring, the dye was filtered off and washed with 20% brine until free of excess amine and dried. The dye had the structure indicated below. This is a black powder that decomposed at 265° C. Nitrogen calculate, 9.87%; found, 9.10%.



When the dye of this example was applied to normal gray hair by the method and with the adjuvants of Procedure I, it gave a reddish blue hue which was uniform and fast to washing and rubbing. When applied to gray or bleached hair with triethanolamine in place of ethanolamine as the alkalizing agent, it gave a clear blue shade of good rub and shampoo fastness.

Example 10

A mixture of 40 g. 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine and 120 g. tris(hydroxymethyl)methylamine in 300 ml. water was heated at 80° C. Then 200 ml. ethanol was added, and the dye dissolved completely. The solution was boiled for 4 hours under reflux conditions. After this time the alcohol was distilled off, and the slurry was diluted with 2000 ml. of brine (20%). After cooling, the dye was filtered, washed with 5% brine and dried. Its structure is:



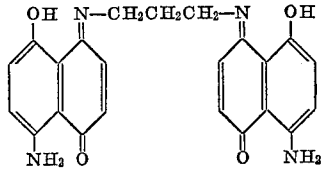
Analysis.—Calc'd for $C_{14}H_{17}N_2O_5$: N, 9.90%. Found: N, 9.53%.

When applied to gray hair in accordance with Procedure I, it dyes hair reddish blue in good strength. When triethanolamine is used in place of the ethanolamine of Procedure I, this composition dyes gray hair blue.

(B) CONDENSATION OF NI AND ALIPHATIC POLYAMINES

Example 11

Preparation of trimethylene derivative of NI

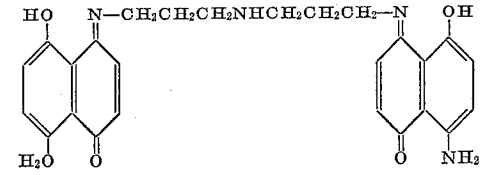


A mixture of 24 g. (0.32 mole) 1,3-diaminopropane and 24 g. (0.13 mole) 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine in 80 ml. water was heated at 85° C. for 10 minutes. After cooling, the slurry was diluted with 600 ml. 20% brine, filtered, and the cake was washed with 20% brine until free of the excess of 1,3-diaminopropane. The filter cake was dried at 80° C. The product had the formula above. Nitrogen calculated, 13.4%; found, 12.9%.

When the product was applied to normal gray hair by the methods of Procedures I and I(a) above, it gave a strong bluish gray coloration, fast to shampooing and rubbing.

Example 12

Preparation of 3,3'-iminodipropyl derivative of NI

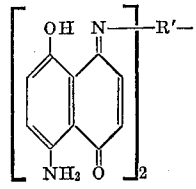


A mixture of 25 g. (0.136 mole) of 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine and 25 g. (0.191 mole) of 3,3'-iminodipropylamine in 100 ml. water was heated for 15 minutes at 100° C. After cooling, the product was precipitated by the addition of 250 ml. of 20% brine, filtered off, washed with brine, and dried in air. It had the above designated structure. Nitrogen calculated, 14.8%; found, 15.1%.

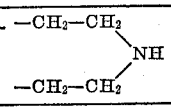
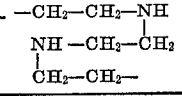
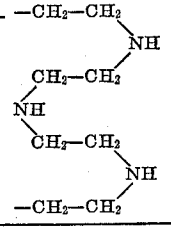
When the dye was applied to hair by Procedure I, it showed a strong greenish blue shade on natural gray, bleached and permanent-waved hair. When applied to hair by Procedure I(a), the shade was bluish gray.

When these compositions containing the dye were stored at 50° C. for 3 months and the dyeing on hair repeated, there was no diminution in dye strength and no change in shade.

Following the same synthesis procedure described above in paragraph 1 of Example 12 and utilizing the same molar proportions, unless otherwise indicated, the polyamines and NI are reacted as indicated in column 3 below. The compounds produced may be described by the formula:



wherein —R'— is a divalent radical as appears in column 2.

Example No.	—R'—	Preparation
13		NI plus diethylenetriamine; excess of amine, 4 to 6 moles; solvent water; time 5 to 10 min.; temp. 100° C.
14	—CH_2—CH_2—	NI plus ethylenediamine.
15		NI plus triethylenetetramine.
16		NI plus tetraethylenepentamine.

The dyeing results obtained with the products of this type are given in the table below. The product used is

identified by the diamine employed in the condensation reaction.

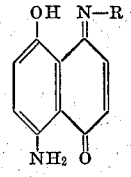
Diamine	Dyeing of gray hair as per— Procedure I	Procedure I(a)
Diethylenetriamine	Bluish gray	Bluish gray.
Triethylenetetramine	Grayish blue	Grayish blue.
Tetraethylenepentamine	Bluish gray	Grayish blue.

(C) CONDENSATION OF NI WITH HYDROXY OR ALKOXY AROMATIC AMINES

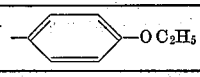
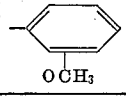
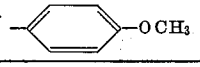
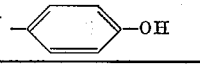
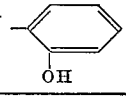
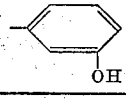
Example 17

A mixture of 188 g. (1 mole) NI and 137 g. (1 mole) o-phenetidine were heated with stirring for 4 hours in 1000 ml. 80% acetic acid with the addition of 140 g. sodium acetate (anhydrous). The color of the batch after 2 hours changed from reddish blue to greenish blue. After cooling the dye was filtered off and washed with brine, then with a little water and dried. The product was 5-amino-8-hydroxy-1,4-naphthoquinone-1-(o-ethoxyphenyl)imine. It dyed gray and bleached hair in level blue shades when applied by Procedures I and II.

Following the same synthesis procedure described in Example 17, unless otherwise indicated, NI was reacted with the hydroxy or alkoxy aromatic amine as indicated in column 3 below. The compounds produced may be described by the general formula:



wherein R is a monovalent radical as appears in column 2.

Example No.	Constitution R=	Preparation
18		NI plus p-phenetidine.
19		NI plus o-anisidine.
20		NI plus p-anisidine.
21		NI plus p-aminophenol; 4 hrs. boiling in glacial acetic acid.
22		NI plus o-aminophenol; 4 hours boiling in glacial acetic acid.
23		NI plus m-aminophenol.

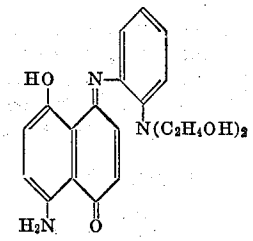
The product of Example 21 when used in Procedure I gave to gray hair a blue color. When triethanolamine was used in place of the ethanolamine in Procedure I, gray hair was also dyed a blue color.

The product of Example 23 gave gray hair a grayish blue color when applied by Procedure I.

(D) CONDENSATION OF NI WITH HYDROXYALKYLPHENYLENEDIAMINE DERIVATIVES

Example 24

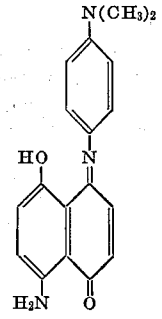
A mixture of 5.65 g. of NI, 6.3 g. N,N-bishydroxyethyl-o-phenylenediamine and 10.0 g. anhydrous sodium acetate was heated for 2 hours at 90° C. in 250 ml. 75% acetic acid. The batch was filtered warm to remove insolubles and the filtrate was neutralized with ammonia to a pH of 6.8 to 7.0. The precipitated dye was filtered off and dried. The product had the following structure:



When applied to gray hair by Procedures I, II and III, it showed level blue coloration. The same procedure with N,N-bishydroxyethyl-p-phenylenediamine gave a dye with similar properties on hair.

(D-1) CONDENSATION OF NI WITH DIALKYLAMINO AROMATIC AMINES

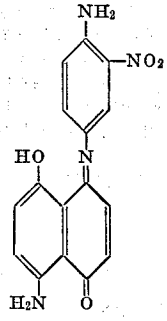
Example 24A



A solution of 4.2 g. (0.031 mole) N,N-dimethyl-p-phenylenediamine in 75 cc. glacial acetic aid was added to 5.7 g. (0.03 mole) naphthazarin intermediate in 100 cc. glacial acetic acid at reflux. The mixture was heated at reflux for one hour, filtered and the filtrate poured into 500 cc. 20% brine. The pH was adjusted to neutral by means of ammonia in order to precipitate the dye. The precipitate was filtered off, redissolved in boiling dioxane. The solution was clarified and added to 20% brine. The precipitated dye was washed with water and dried. The product dyed hair greenish blue by Procedure I, and somewhat bluer in shade by Procedure II and had the structure shown above.

(D-2) CONDENSATION OF NI WITH NITROANILINES

Example 24B

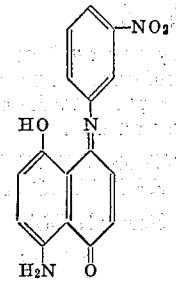


A solution of 4.8 g. (0.031 mole) nitro-p-phenylenediamine in 50 cc. glacial acetic acid was added dropwise to a refluxing solution of 5.7 g. (0.03 mole) naphthazarin intermediate in 100 cc. glacial acetic acid and refluxing was continued for one hour. The hot mixture was filtered and the filtrate poured into 600 cc. 20% brine and the precipitated product was filtered off. The dried precipitate was heated in 75 cc. dioxane at reflux, the hot mixture filtered, and the filtrate added to 500 cc. 20% brine. The precipitated material was filtered off, washed with water and dried. The product

was a dark blue powder having the above designated structure. It dyed hair greenish blue when applied by Procedure I.

When in the above example, the nitro-p-phenylenediamine was replaced by a molecular equivalent of 4-amino-2-nitro-phenol, there was obtained as product 5-amino-8-hydroxy-1, 4 - naphthoquinone-1-(4-hydroxy-3-nitrophenyl)-amine, which had a similar shade and affinity on hair.

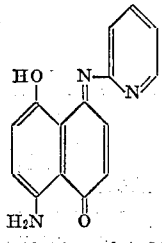
Example 24C



A solution of 6.3 g. (0.045 mole) m-nitro-aniline in 90 cc. glacial acetic acid was added dropwise to refluxing solution of 5.7 g. (0.03 mole) naphthazarin intermediate in 90 cc. glacial acetic acid and the mixture refluxed for one hour. The mixture was filtered hot and the filtrate poured into 600 cc. 20% brine whereupon the precipitated material was filtered off. The dried precipitate was reprecipitated from hot dioxane solution by the addition of 20% brine. The dye was filtered off, washed salt-free with water and dried. The product had the structure designated above and dyed hair greenish blue when applied by Procedure I.

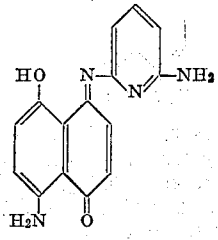
(E) CONDENSATION OF NI WITH HETEROCYCLIC AMINES

Example 25



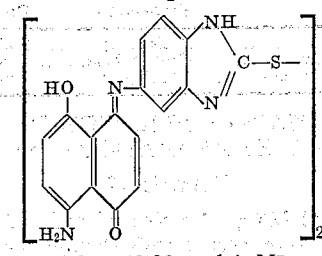
A mixture of 5.7 g. (0.03 mole) NI and 2.9 g. (0.034 mole) 2-aminopyridine in 75 ml. glacial acetic acid was heated at reflux for four hours. The cooled batch was diluted with 300 ml. 20% brine to precipitate the product, which was filtered off and washed free of acetic acid with 20% brine. Then, it was washed free of salt with a small quantity of water and dried. The product was a dark blue powder having the above designated structure, and dyed hair by Procedures I and II a strong shade of blue.

Example 26



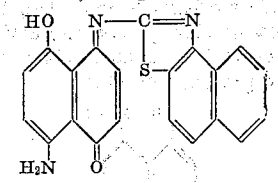
A mixture of 5.7 g. (0.03 mole) NI and 3.4 g. (0.031 mole) 2,6-diaminopyridine was heated at reflux in 75 ml. glacial acetic acid for 4 hours. After cooling, the solution was diluted with 300 ml. 20% brine and the precipitated product was filtered off. The dye was washed free of acetic acid with 20% brine, then washed salt-free with water and dried. The product had the structure designated above. Hair was dyed greenish blue by this product applied by Procedures I and II.

Example 27



A mixture of 5.7 g. (0.03 mole) NI and 5.0 (0.0302 mole) 5-amino-2-marcaptobenzimidazole was heated in 100 ml. 80% acetic acid for 4 hours at 90° C. The batch was filtered hot and the filter-cake washed with isopropanol and dried. The product, which has the structure drawn above, dyed hair a green shade blue, fast to rubbing and shampooing, when applied by Procedures I and II.

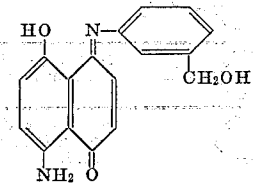
Example 28



A mixture of 5.7 g. (0.03 mole) NI, 6.4 g. (0.032 mole) 2-amino-naphthol[1,2]thiazole and 10 g. anhydrous sodium acetate in 250 ml. 80% acetic acid was heated for 4 hours at 90° C. The batch was filtered from insoluble impurities at 70° C., and the filtrate neutralized with ammonia while cooling to pH 7.0. The precipitate was filtered off, washed with water and dried. The product had the structure indicated above. It dyed hair by Procedures I and II in greenish blue shades of good shampoo fastness.

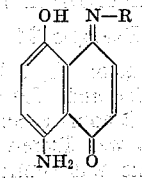
(F) CONDENSATION OF NI WITH AMINOBENZYL ALCOHOLS

Example 29

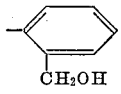
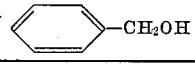


A mixture of 2.5 g. (0.0133 mole) NI, 5.0 g. (0.04 mole) m-aminobenzyl alcohol and 5.0 g. anhydrous sodium acetate was heated while stirring for 2 hours at 90° C. The reaction slurry was poured into 1500 ml. water and the mixture left to stand overnight and filtered. The filter-cake was washed with water and dried, giving a product having the above designated structure.

Following the same synthesis procedure described in Example 29, NI was reacted with the aminobenzyl alcohols, as indicated in column 3 below. The compounds produced may be described by the general formula:



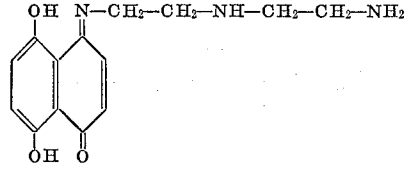
wherein R is the monovalent radical as appears in column 2 below.

Example No.	Constitution R=	Preparation
30		NI plus o-aminobenzyl alcohol.
31		NI plus p-aminobenzyl alcohol.

(G) CONDENSATION OF NAPHTHAZARIN WITH AMINES

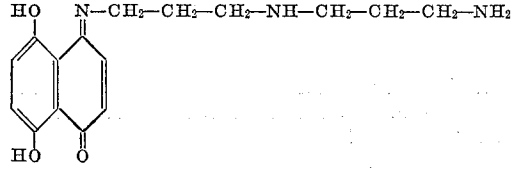
Example 32

In 30 ml. water, 4 g. (0.02 mole) sublimed naphthazarin and 10 g. (0.09 mole) diethylenetriamine were heated at the boil for five minutes. The solution was poured into 50 ml. 20% brine and the product precipitated with 50 ml. of 40% zinc chloride solution. The precipitate was filtered off, washed with brine, then with a little water and dried. The precipitation of the dye can also be performed by means of sodium chloride, potassium chloride or sodium sulfate in place of the zinc chloride, but the yield is lower. The product dyed natural gray and bleached hair a strong gray color when applied by Procedures I and II. The product may be described by the following formula:



Example 33

The procedure of Example 32 was followed, except that in place of the diethylenetriamine, 3,3'-iminodipropylamine was employed. The product obtained can be described by the following formula:



When applied to natural gray and bleached hair by Procedures I and II, it gave very strong bluish gray colors.

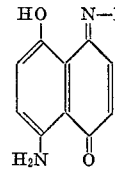
Example 34

Sulfonated naphthazarin intermediate.—A solution of 5.65 g. 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine (NI) in 58 g. 20% oleum was prepared by gradually adding the naphthoquinone imine powder to the oleum while keeping the temperature at about 25–30° C. The solution was then heated at 100.110° C. for 2 hours, or until a test sample was completely soluble in water. The mixture was poured onto 200 g. ice and 40 g. sodium chloride added. The precipitated 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine monosulfonic acid sodium salt was recovered by filtration, washing with 20% brine, then with a minimum of cold water to remove salt, and drying at 80° C. in air.

The product was applied to normal gray hair and bleached hair by Procedure I giving a moderately strong reddish blue dyeing. When triethanolamine was substituted for ethanolamine in Procedure I, the dyeings were somewhat greener blues. When applied by Procedure II, the dyeings were greenish blue. In all cases the dyeings were level, and uniform as between gray and bleached hair, and fast to rubbing. The compositions stored at 50° C. for 3 months gave similar dyeings on hair with no change in shade and strength compared to the initial dyeings.

Example 35

Dyeing hair with alkyl and aryl derivatives of NI from acid bath



Procedure II above is followed using a series of derivatives of the general structure above, in which R has the value shown in column 1 below.

The results are as follows:

R	Color on gray hair	Color on bleached hair
$-CH_2CH_2NHC_2H_4OH$	Gray	Gray.
$-C(CH_2OH)_3$	Blue	Blue.
$-C(CH_2OH)_2CH_3$	do	Do.
n-Propyl	Grayish blue	Grayish blue.
n-Butyl	do	Do.
p-Hydroxyphenyl	Blue	Blue.

Example 36

Dyeing hair with bis-NI derivatives from acid baths.—The dye prepared by the reaction of diethylenetriamine with two molar equivalents of 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine was incorporated into an acidic hair dyeing composition of Procedure II and dyed on hair. There was obtained a slate blue coloration of normal gray hair, permanent-waved hair and bleached hair, fast to shampooing and rubbing.

Similarly, the dyes prepared using other diamines in place of diethylenetriamine, showed the following dyeings:

Diamine:	Color on gray hair
Triethylenetetramine	Grayish blue.
Tetraethylenepentamine	Slate gray.
1,3-diaminopropane	Bluish gray.

EXAMPLES OF OTHER DYE BATH COMPOSITIONS

Example 37

A mixture was prepared of the following components by stirring them together thoroughly at about 50° C.:

	G.
The dye, 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine (wet with 0.5 ml. isopropanol)	0.2
Diisopropanolamine	3.5
Polyoxyethylated nonylphenol	3.0
Sodium carboxymethyl cellulose	2.0
Water to make 50 ml.	

When the mixture was homogeneous, it was cooled to room temperature, diluted to 100 ml. and the pH adjusted to 9.0 by addition of citric acid.

The composition so prepared was poured on natural gray hair, on bleached hair, and on permanent-waved hair, and allowed to remain in contact with the hair for 20–25 minutes at about 30° C. Afterwards, the hair was removed, shampooed and dried. The various kinds of hair were all dyed a level greenish blue of fairly similar shade, fast to rubbing and shampooing. When the above described composition was stored at 50° C. for 3 months and another dyeing on hair performed, there was no loss of strength or shade change compared with the original dyeing.

In the above composition, in place of the dye 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine there may be sub-

stituted an equal weight of any of the following dyes, with the dyeing results as indicated below:

5-amino-8-hydroxy-1,4-naphthoquinone-1-n-butylimine—bluish gray of uniform shade on the various kinds of hair

Product of Example 9—blue; uniform on the various kinds of hair

Product of Example 13—grayish blue; uniform on the various kinds of hair

In the above composition, in place of the diisopropanolamine there may be substituted an equal weight of morpholine, N-methylmorpholine or N-ethylmorpholine, with similar dyeing results.

In the above composition in place of the polyoxyethylated, nonylphenol there may be substituted an equal weight of polyoxyethylene lauric ester or of glyceryl stearate, with similar dyeing results.

Example 38

The following composition was prepared by mixing the ingredients at about 50° C.

	G.
The dye, $N^1,N^{1\prime}$-trimethylene-bis-5-amino - 8 - hydroxy-1,4-naphthoquinone-1-imine (product of Example 11) (wet with 0.5 ml. ethanol)	0.15
Diethylenetriamine	3.0
Sodium N-coconut acid N-methyl taurate	3.0
Methylcellulose	3.0
Water to make 50 ml.	

When the mixture was homogeneous, it was cooled, the volume adjusted to 100 ml. by the addition of water, and the pH adjusted to 9.0 by the addition of acetic acid. It was then poured on gray hair, bleached hair, and permanent-waved hair, where it was allowed to remain for 30 minutes at 30° C. The hair was shampooed and dried. The various kinds of hair were all dyed a strong level shade of grayish blue, fast to shampooing and rubbing.

In the above composition, in place of the above-named dye, there may be substituted an equal weight of the following dyes, with the dyeing results as indicated:

Product of Example 10—strong blue shade on various kinds of hair; composition stable on storage for 3 months at 50° C.

N^1-p-acetamidophenyl-5-amino - 8 - hydroxy - 1,4 - naphthoquinone-1-imine—blue on the various kinds of hair

N^1-benzyl - 5 - amino - 8 - hydroxy-1,4-naphthoquinone-1-imine—greenish blue on the various kinds of hair

In the above compositions, in place of the sodium N-coconut acid N-methyl taurate, there may be substituted an equal weight of sodium dodecylbenzenesulfonate, sodium lauryl sulfate, or the dioctyl ester of sodium sulfosuccinate. The dyeing results are similar.

In the above compositions the methyl cellulose may be omitted. The compositions are then freely flowing fluids instead of having the viscous consistency of the above compositions. The dyeing effects on hair, however, are similar.

Example 39

The following composition was prepared by mixing the ingredients thoroughly at about 50° C. until homogeneity was achieved.

	G.
The dye, $N^1,N^{1\prime}$ - (3,3'-iminodipropyl)bis-5-amino-8-hydroxy-1,4-naphthoquinone - 1 - imine (product of Example 12) (wet with 0.5 ml. isopropanol	0.15
N-phenyldiethanolamine	3.0
Lauric diethanolamide	3.0
Sodium alginate	1.0
Water to make 50 ml.	

After cooling, the volume was adjusted to 100 ml., and the pH to 9.5 by addition of tartaric acid. This mixture was poured on natural gray, waved, and bleached hair where it was allowed to remain for 30 minutes at 30° C., whereupon the hair was removed, shampooed, and dried. The various kinds of hair were all dyed a greenish blue shade of good strength which was fast to shampooing and rubbing. When the above composition was stored at 50° C. for 3 months, and the dyeing repeated, there was essentially no difference, either in shade or strength from the initial dyeings.

In the above composition, in place of the dye therein mentioned, there may be substituted an equal weight of any of the following dyes, with the dyeing results as indicated:

Product of Example 15—bluish gray shades on all kinds of hair

5-amino-8-hydroxy - 1,4 - naphthoquinone - 1 - cyclohexylimine—bluish gray of moderate strength

N^1(p-carbamoylphenyl) - 5 - amino - 8 - hydroxy - 1,4-naphthoquinone-1-imine—greenish blue on all kinds of hair

In the above composition, in place of the phenyldiethanolamine, there may be substituted an equal weight of diethanolamine, N-methyldiethanolamine, or dimethylisopropanolamine with essentially the same results in the dyeings.

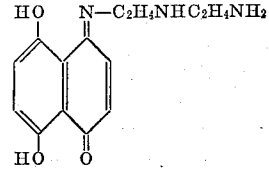
In the above composition, in place of the lauric diethanolamide, there may be substituted an equal weight of myristic diethanolamide, polyoxyethylated fatty alcohol or lauric isopropanolamide with essentially the same dyeing results.

Example 40

The following composition was prepared:

The dye,

G. 0.1



Ethyleneglycol monostearate	2.0
Polyacrylic acid	1.0
Water to make 50 ml.	
Citric acid to pH 4.	

This mixture was poured on natural gray, permanent-waved, and bleached hair, and allowed to remain in contact with the hair for 30 minutes at 30° C. Afterwards, the hair was shampooed and dried. All specimens of hair were dyed a strong shade of gray, level, and uniform as among the various types of hair, and fast to shampooing and rubbing. When the composition was stored for 3 months at 50° C. and the dyeing repeated, there was no change in shade or strength compared with the original dyeings.

In the above composition in place of the dye mentioned, there may be substituted the following dyes, with dyeing results as indicated:

N^1(p-hydroxyphenyl)-5-amino - 8 - hydroxy-1,4-naphthoquinone-1-imine—blue on the various types of hair

N^1-tris(hydroxymethyl)methyl - 5 - amino - 8 - hydroxy-1,4-naphthoquinone-1-imine—strong blue on the various types of hair

N^1[p-(N,N - bishydroxyethylamino) - phenyl]-5-amino-8-hydroxy-1,4-naphthoquinone-1-imine—blue on hair of various types

In the above composition, in place of the ethyleneglycol monostearate, there may be substituted an equal weight of oleic ethanolamide, a fatty alcohol polyglycol ether,

cetyl pyridinium bromide, or dodecylbenzyl trimethyl ammonium chloride, with essentially the same dyeing results.

In the above composition the polyacrylic acid may be omitted, giving a much less viscous mixture which is otherwise similar in dyeing properties.

Example 41

The following composition was prepared:

	G.
The dye, product of Example 17 (wet with 0.5 ml. isopropanol)	0.25
Isopropanolamine	3.0
Mixed fatty acid monoethanolamide	4.0
Water to make 100 ml.	
Citric acid to pH 7.5.	

This composition was allowed to remain in contact with normal gray, permanent-waved, and bleached hair for 20 minutes at 32° C., and the hair was then removed and shampooed. All these types of hair were dyed a similar shade of level blue of high strength, which was fast to shampooing the rubbing. The composition was stored at 50° C. for 3 months, then gave dyeings similar in strength and shade to the original dyeings.

Example 42

A mixture was prepared of the following components:

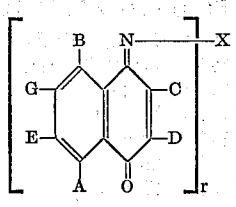
	G.
The dye, product of Example 10	0.060
p-Phenylenediamine	0.060
m-Aminophenol	0.025
Nitro-p-phenylenediamine	0.010
4-nitro-o-phenylenediamine	0.045
Resorcinol	0.100
Isopropanol	2.5
Sodium lauryl sulfate	1.00
Propylene glycol	10.00
Polyethoxylated octylphenol	15.00
Ammonia 28%—10.0 ml.	
Water to make—100 ml.	

To 30 ml. of this composition was added 30 ml. 6% hydrogen peroxide, and this mixture was poured at once on natural gray hair where it was allowed to remain for 45 minutes at 30° C. The hair was then rinsed and shampooed. The hair was dyed a light brown shade which was level and fast to rubbing and shampooing.

Although the invention has been described with reference to specific forms thereof, it will be understood that many changes and modifications may be made without departing from the spirit of this invention.

What is claimed is:

1. A method for dyeing living human hair on the head which comprises impregnating said hair with a tinctorial amount of a hair substantive naphthoquinone imine selected from the group consisting of:



and tautomeric forms thereof wherein:

(1) X is selected from the group consisting of the monovalent radical —R and the divalent radical —R'—, wherein —R may be hydrogen, alkyl having 1 to 6 carbon atoms, hydroxyalkyl having 2 to 6 carbon atoms in the alkyl chain and up to 3 hydroxy groups, -(alkylene-NH)$_{n'}$-alkylene-OH wherein n' is a number from 1 to 3 and alkylene has up to 4 carbon atoms, -(alkylene-NH)$_{n^2}$-alkylene-NH$_2$ wherein n^2 is a number from 1 to 3 and alkylene has up to 4 carbon atoms, monovalent cycloalkyl having up to 6 carbon atoms in the ring, said cycloalkyl may be substituted with a group selected from the class consisting of hydroxy, oxo, methyl, chloro and methoxy monovalent aryl, monovalent aralkyl and monovalent heterocyclic radicals; and wherein —R'— may be divalent alkylene having 3 to 6 carbon atoms, divalent hydroxyalkylene radicals containing from 3 to 6 carbon atoms and up to 2 hydroxy groups, -(alkylene-NH)$_{n^3}$-alkylene- in which n^3 is from 1 to 3 and the alkylene moiety has from 1 to 6 carbon atoms, divalent cycloalkyl having up to six carbon atoms in the ring divalent arylene, divalent aralkyl and divalent heterocyclic radicals;

(2) r is a whole number from 1 to 2: r being 1 when X is monovalent, and r being 2 when X is divalent; and

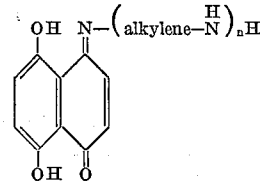
(3) A, B, C, D, E and G are selected from the group consisting of hydrogen, chlorine, bromine, sulfo, alkyl and the radical —HNR in which R has the value described to it above and wherein the radicals selected from the group consisting of A and B may also be hydroxy; said aryl and aralkyl radicals being monocyclic or bicyclic having up to 12 carbon atoms in the respective ring systems and said heterocyclic radical being selected from the group consisting of 2-pyridyl, 3 - pyridyl, 4 - pyridyl, 6-amino - 2 - pyridyl, 2-methyl-4-thiazolyl, 4-quinolyl, 5-quinolyl, 7-quinolyl, 2-imidazolyl, 5-benzimidazolyl, 2-benzothiazolyl, 2-mercapto-5-benzthiazolyl and 2-naphtho[1,2] thiazolyl.

2. A method according to claim 1 wherein the naphthoquinone imine is naphthazarin intermediate.

3. A method according to claim 1 wherein said naphthoquinone imine is 5-amino-8-hydroxy-1, 4-naphthoquinone-1-imine or tautomers thereof.

4. A method according to claim 1 wherein said tinctorial amount is in the range of from about .01 to 5% by weight.

5. A method according to claim 1 wherein naphthoquinone imine is of the group:



and tautomeric forms thereof in which n is a whole number from 1 to 3 said alkylene radical having up to 4 carbon atoms.

6. A method according to claim 12 wherein the radical

$$\left(\text{—alkylene—}\overset{H}{\underset{|}{N}}\right)_n H$$

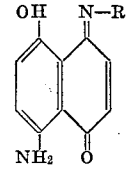
is selected from the group consisting of

—CH_2—CH_2—NH—CH_2—CH_2—NH_2

and

—CH_2—CH_2—CH_2—NH—CH_2—CH_2—CH_2—NH_2

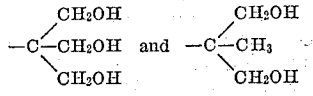
7. A method according to claim 1 wherein the naphthoquinone imine is of the group:



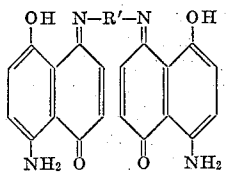
and tautomeric forms thereof wherein R is a radical selected from the group consisting of polyhydroxyalkyl and hydroxyalkylaminoalkyl radicals in which the alkyl chain contains from 2 to 6 carbon atoms and from 1 to 3 hydroxy groups.

8. A method according to claim 7 wherein R is selected from the group consisting of

$$-CH_2-CH_2-NH-CH_2-CH_2-OH$$



9. A method according to claim 1 wherein the naphthoquinone imine is of the group consisting of:



and tautomeric forms thereof wherein —R'— is a divalent radical selected from the group consisting of alkylene and the radical (-alkylene-NH)$_{n^1}$-alkylene-, wherein n^1 is a whole number from 1 to 3.

10. A method according to claim 9 wherein —R'— is selected from the group consisting of

$$-CH_2-CH_2-NH-CH_2-CH_2-$$

$$-CH_2-CH_2-CH_2-NH-CH_2-CH_2-CH_2-$$

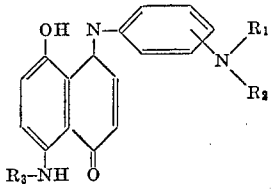
$$-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-$$

$$-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-$$

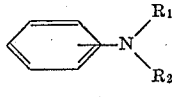
and

$$-CH_2-CH_2-CH_2-$$

11. A method according to claim 1 wherein the naphthoquinone imine is of the group consisting of:

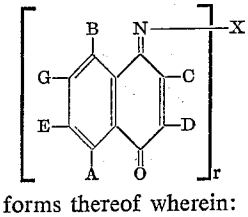


and tautomeric forms thereof wherein R_1 and R_2 are selected from the group consisting of H, and hydroxyalkyl having up to 3 carbon atoms and 2 hydroxy groups, at most one of R_1 and R_2 being hydrogen; and R_3 is selected from the group consisting of H and the radical



in which R_1 and R_2 have the same values ascribed to them above.

12. An aqueous hair dyeing composition containing from .01 to 5% by weight of a hair substantive naphthoquinone imine dye and from 0.1% to about 10% by weight of the composition of an alkalizing agent to impart thereto an alkaline pH, said dye being selected from the group consisting of:



and tautomeric forms thereof wherein:

(1) X is selected from the group consisting of the monovalent radical —R and the divalent radical —R'—, wherein —R may be hydrogen, monovalent cycloalkyl having up to 6 carbon atoms in the ring, said cycloalkyl may be substituted with a group selected from the class consisting of hydroxy, oxo, methyl, chloro and methoxy, alkyl having 1 to 6 carbon atoms, hydroxyalkyl having 2 to 6 carbon atoms in the alkyl chain and up to 3 hydroxy groups, -(alkylene-NH$_{n'}$-alkylene-OH wherein n' is a number from 1 to 3 and alkylene has up to 4 carbon atoms, -(alkylene-NH)$_{n^2}$-alkylene-NH-$_2$ wherein n^2 is a number from 1 to 3 and alkylene has up to 4 carbon atoms, monovalent aryl, monovalent aralkyl and monovalent heterocyclic radicals and wherein —R'— may be divalent alkylene having 3 to 6 carbon atoms, divalent hydroxyalkylene radicals containing from 3 to 6 carbon atoms and up to 2-hydroxy groups, -(alkylene-NH)$_{n^3}$-alkylene- in which n is from 1 to 3 and the alkylene moiety has from 1 to 6 carbon atoms, divalent cycloalkyl having up to six carbon atoms in the ring, divalent arylene, divalent aralkyl and divalent heterocyclic radicals;

(2) r is a number from 1 to 2, r being 1 when X is monovalent, and r is 2 when X is divalent; and

(3) A, B, C, D, E and G are selected from the group consisting of hydrogen, chlorine, bromine, sulfo, alkyl and the radical —NHR in which R has the value ascribed to it above and wherein radicals selected from the group consisting of A and B may also be hydroxy; said aryl and aralkyl radicals being monocyclic or bicyclic having up to 12 carbon atoms in the respective ring systems and said heterocyclic radical being selected from the group consisting of 2-pyridyl, 3-pyridyl, 4-pyridyl, 6-amino-2-pyridyl, 2-methyl-4-thiazolyl, 4-quinolyl, 5-quinolyl, 7-quinolyl, 2-imidazolyl, 5-benzimidazolyl, 2-benzothiazolyl, 2-mercapto-5-benzthiazolyl and 2-naphtho[1,2] thiazolyl.

13. A hair dyeing composition according to claim 12 wherein the pH is in the range of about 7.5 to 10.

14. A hair dyeing composition according to claim 12 wherein the alkalizing agent is an organic amine .

15. A hair dyeing composition according to claim 12 wherein the alkalizing agent is selected from the group consisting of monoalkanolamines, dialkanolamines and trialkanolamines.

16. A composition according to claim 15 wherein the dye is 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine or tautomers thereof.

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ALBERT T. MEYERS, Primary Examiner

D. R. ORE, Assistant Examiner

U.S. Cl. X.R.

8—10, 10.1, 11

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,516,778 June 23, 1970

Walter H. Brunner

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 17, "primary" should read -- preliminary --. Column 26, line 3, after "methoxy" insert a semicolon; lines 17 and 18, "described" should read -- ascribed --; line 50, "claim 12" should read -- claim 5 --. Claim 10, insert a semicolon (;) at the end of lines 3, 4, 5 and 7 respectively of this claim.

Signed and sealed this 19th day of January 1971.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents