METHOD FOR COLORING HUMAN HAIR WITH POLYHYDROXIC AROMATIC COMPOUND, AROMATIC AMINE AND AN OXIDATION ENZYME

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This invention relates to coloring or dyeing hair and like keratinaceous substances by production of oxidation of a dark colored and natural appearing pigment in situ on or in the hair and, more particularly, to such hair coloring techniques conducted at a substantially neutral or, at least, not harshly alkaline pH and otherwise especially adapted for physically innocuous and non-deteriorative use and repeated re-use on growing human hair.

As noted or desired, the dyeing or coloring various keratinaceous substances such as animal hair or fur or wool, as well as human hair, has produced a wide variety of coloring or dyeing techniques using many different materials and chemical reactions for assuring binding or relatively permanent affixing of the pigment or dye or other coloring matter into or onto the hair fibers. As also well understood, notwithstanding the kindred chemical composition of growing human hair and other keratinaceous wool or hair or fur fibers, somewhat special problems are presented in the coloring of growing human hair because of a variety of peculiar physiological and other factors.

For example, the continued "growth" of human hair and continued proliferation or exposure of new lengths of fiber emerging from the hair follicles on the scalp necessitates relatively frequent repeated applications of whatever coloring technique is being utilized in order to achieve continuously the coloring effect desired. Thus a wide variety of coloring techniques generally or chemically available for reaction with keratinaceous materials are not useful or desirably useful in coloring human hair because of ancillary deleterious or undesired physiologically or harmful effects on human beings generally or specifically on the human beings.

Similarly, satisfactory utility for techniques or compositions for coloring human hair must meet, as a practical matter, certain fairly arbitrary, and quite human but non-technological, requirements superimposed by the users of such techniques or compositions. For example, a hair effecting technique which requires highly skilled manipulative treatment or a reaction time of perhaps several hours under controlled conditions with the hair being maintained in various reactive solutions or media may be said virtually completely to lack satisfactory utility from any commercial or practical standpoint, regardless of the technological or theoretical success with which a particular visual effect may be achieved. As will be understood, such extended manipulative or reaction time requirements are considered intolerable by the users (whether they be the person whose hair is being dyed or the cosmetician who is dyeing it) to such an extent that the process may be conclusively rejected by prospective users whether or not it achieves technologically a coloring effect of desired excellence, and, thus fails to provide satisfactory practical utility.

If it is attempted to avoid certain of the possible undesirable or intolerable physiological side reactions of the various materials which are theoretically capable of coloring keratinaceous fibers by utilizing only those materials which are naturally occurring (or closely chemically related to those naturally occurring), substantial difficulty may be experienced in obtaining the desired ultimate visible effect regarding suitability to dark hues or shades from the necessary chemical reactions within any reasonably practicable length of time. For example, assuming the natural coloring pigment in hair to be melanine and recognizing that such a natural type of pigment may be produced by the oxidation of histidines or other physiological substances or chemical compounds such as tyrosine, dihydrophenylalanine, etc., it will be found impossible to produce desired coloring results within any reasonable or tolerable limits acceptable to the user, regardless of the fact that a reasonably dark (or even black) pigmentation can ultimately be obtained by air oxidation (or other oxidation) of such materials.

Even the further recognition that the appropriate reaction rates can be substantially accelerated by superimposing a variety of reaction-accelerating conditions may not eliminate the ancillary difficulties peculiarly imposed on the treatment of growing human hair. Moreover, the coloring results or pigment formation and concentration may be substantially enhanced by increasing the harshness of the oxidizing environment (as by maintaining it in a highly alkaline peroxide medium) for obtaining acceptable and quite permanent results when attempting to dye various keratinaceous animal fibers such as deer furs or pelts, but the very harshness of such oxidation conditions may be deleterious for growing human hair especially when the same harsh treatment will have to be reapplied or repeated in a relatively short space of time to accommodate the new "growth" of hair exposing new lengths of fiber requiring coloring to maintain the desired effect.

Indeed, the vast majority of problems incident to attempting to provide satisfactory hair coloring techniques for purely cosmetic use on growing human hair may be related in one way or another to ancillary limitations rather than merely to the isolated or purely theoretical problem of coloring keratinaceous fibers or producing an oxidation pigment. As illustrative and quite commonly understood, it is theoretically possible to produce a variety of quite black colorations on human hair, many if not virtually all of which are widely considered unacceptable as producing a visual effect so different from normally black colored human hair as to be cosmetically or esthetically unacceptable, regardless of how easily they may be produced.

Similarly, various highly alkaline oxidation reactions utilizing materials such as paraphenylenediamine are widely used for darkening colorations of growing human hair, notwithstanding the well known fact that a certain proportion of human beings are highly sensitive to that material and react violently thereto in a number of toxic or disastrous manners. Even individuals who do not experience a physiological deleterious reaction to such materials when first applied, may gradually build up such hypersensitivity upon repeated applications as necessary in a desired program or regimen for continuous coloration of hair. The foregoing physiological difficulties may be readily avoided by utilizing other and more innocuous substances, but the visual results obtained thereby may fail to meet the esthetic or cosmetic standards demanded.

In this connection, and in considering the foregoing as well as the description which follows, it is to be understood that the "coloring" to which this invention relates involves producing a darker shade or hue of color on the hair; not bleaching or lightening the hair color. It can be understood that, despite the essentially artificial basis of the whole idea of coloring hair, completely satisfactory results are obtained primarily if the visual effect of the coloring technique is of a completely natural appearance and, preferably, undetectable as artificial coloring event or effect, except and to the extent that the results may be so obvious as to be transparent to the unaided eye. Thus, certain purely esthetic or idiosyncratic additional limitations are imposed on the evaluation of satisfactory
results which have, indeed, little bearing on either the chemical or the physiological considerations involved. It may, as well within the teachings now known to select or utilize a particular material or technique producing no deleterious physiological effects and visible within a relatively short reaction time, yet without satisfactory results as desired for the user if there is produced a coloring which is less dark or pigmented than desired or artificial appearing coloration, no matter how dark, such as a blue black hue or shade instead of the natural appearing brown black of human hair. Thus, satisfactory evaluations of hair coloring techniques and the results obtained thereby are subjected to purely non-chemical factors, consideration, i.e., the user's body chemistry, the degree or darkness of coloration particularly desired, and purely personal evaluation as to whether a certain colorometric black color is a "natural black" or an undesired artificial looking "patent leather" visual effect.

Of course, the rather subtle and personalized distinctions necessarily involved in the evaluation of the utility or satisfaction provided by hair coloring techniques might be made similarly as somewhat to matters of technological degree, but, as applied to the true practical or commercial evaluation of the teachings hereof, such distinctions, no matter how subtle, are quite realistically distinctions of kind. In the highly personal (and frequently secret) area of hair coloring, a technique which "just barely" fails to achieve the desired visual effect is categorically rejected as wholly unsatisfactory, in somewhat the same manner as a technique which has an adverse or deleterious physiological effect on "only a few" individuals may be rejected as wholly unacceptable by regulatory agencies if there exist an alternative and comparably satisfactory technique which delectitably affects no one.

According to this invention, then, there are provided hair coloring techniques and compositions for producing in situ on or in the hair, and substantially permanently bound or bonded thereon, pigmenting colorations of a wide and controllable variety of shades and hues of coloration, through the controlled oxidation of various quinone-forming compounds and mono or poly aromatic amines having the amino groups on the aromatic ring to form natural appearing pigments (having the appearance of melanin) on or in the hair fibers or under oxidation conditions which avoid harsh or alkaline treatments of the growing hair; and, as further features of this invention, the particular materials or compositions involved (either alone or under the conditions of use here) are selected to avoid recognized or undesirable physiological toxic or similar deleterious reactions, and whereby the oxidation reactions of applied materials to form the desired pigmentation or degree of coloration are accelerated at no higher than substantially a neutral pH by the synergistic utilization of a natural oxidation-enhancing or catalytic enzyme material.

With the foregoing and additional objects in mind, this invention will be explained in more detail, and other objects and advantages thereof will be apparent from the following description and the appended claims.

As essentially illustrative of this invention, one may note the utilization of organic compounds having a quinone structure and the reaction thereof in situ on the hair and under oxidizing conditions with an aromatic mono or poly amine to form a variety of possible reaction products of an essentially quinoid structure with nitrogen on the aromatic rings and of a pigment nature which readily bind with and remain substantially permanently affixed to the hair and provide a desired natural appearing pigmentation or coloration. Although a substantial variety of quinone or aromatic polyhydric or polyphenol type materials are available for reaction with a similarly wide variety of aromatic amines having the amino group directly on the aromatic ring, the various pigmentation products produced are all of a generally brown pigmentation character, despite the fact that possible cross linkages and tautomerism and other reactions result in a virtual infinitude of possible individual products. Nevertheless, all of such brownish pigments produced in accordance herewith produce on grey or blond or light colored hair, very natural colorations somewhat like natural melanin.

Thus, whether the desired intensity or hue of darkening coloration be merely that of auburn or even that of natural jet black, it is naturally achieved in accordance hereof merely or primarily by controlling the extent of the reaction, choice of reactants, and the amount and kind of brownish pigment produced.

As noted, and as will be understood, the production of one or more simple or polymeric or cross linked brownish pigments from the particular starting reactants hereof results from an oxidation reaction which, preferably, is merely air oxidation in a relatively short time as the reactants are exposed to react directly to the hair to be treated. Nevertheless, to achieve the particular results as desired satisfactorily in accordance hereof, it is preferred that such oxidation reaction be accelerated or catalyzed by the presence of some agent which, for example, in the hair of a natural oxidation enzyme such as tyrosinase, polyphenolase, catacolase, laccase, etc., and at a substantially neutral (or, at least, not harshly alkaline) pH.

Thus, this invention avoids or minimizes the various ancillary deleterious reactions which may arise from the use (or, more particularly, the repeated use) of harshly alkaline peroxide or other stringent oxidizing conditions previously required to produce, within any comfortably acceptable length of time, a sufficient pigment production for achieving desirably intense or permanent coloration or satisfactory results in coloring the hair to any desired degree beyond that which might be conventionally described as a mere tinting.

Thus, of the wide variety of starting materials available for achieving satisfactory results in accordance hereof, some may have been suggested in the prior art (or predictable from the teachings hereof) for an oxidation-type of reaction producing a dyeing or pigmentation possibly adapted for keratinous substances, yet having characteristics such that a fully hue or intense pigmentation is not achievable therewith in the absence of oxidizing conditions which are to be understood as being excessively harsh and destructive or destabilizing of the hair hereof as applied to realistically and commercially practicable hair coloring suitable or acceptable for modern cosmetic practice. Similarly, even though certain starting materials appropriate for use hereof have previously been known to engender an intense type of pigment formation when reacted under oxidizing conditions, such reactions are to be distinguished from the present teachings insofar as they required such harshly alkaline media as to produce some deleterious effect upon possible repeated re-use or produced unnatural looking pigmentation.

As will be understood, it is desired that the pigment producing oxidation reactions occur on the hair itself for the purpose of assuring satisfactorily permanent binding or bonding of the pigment. It is also desired that such oxidation be essentially air oxidation, rather than induced by harsher oxidants, and that the acceleration or control or catalyzing of the reaction be by natural enzymes and at a substantially neutral pH. Under such circumstances, the original starting reactants and the intermediate products may undergo a substantial number of reaction steps toward the ultimate pigment production. For purposes of this invention, and a wide variety of pigment combinations for building up various pigment effects in successive stages, the exact structure of all pigment products formed may not be known with certainty.
As generally illustrative of the type of reaction here with which satisfactory results are achieved, one may note basically as a repeating combining stage the combining of the nitrogen of an aromatic amine group with a reactive oxygen of a quinone to produce, with the elimination of $\text{H}_2\text{O}$, a preliminary pigment product. If the aromatic amine includes additional amino groups on the ring, these active groups are available for combining with additional quinones, hence, with additional and amine reactants to produce ultimately an extended chain or polymer-type of generally alternating or recurring quinone-amine linkages to form the desired pigment in situ or on the hair.

To achieve satisfactory results according to such a mechanism and within the other limits imposed in connection herewith (such as neutral $\text{pH}$, air oxidation, and short reaction time), it is preferred that the actual starting products be mono or poly hydric aromatic materials which are relatively stable in themselves initially, physiologically acceptable as to toxicity or sensitivity, and yet readily oxidized (at least in part) in the presence of an oxidation enzyme to a quinone structure available on the hair for the desired reaction or series of reactions with the aromatic amine component. Such readily oxidized mono or poly hydric aromatic materials are herein referred to as “quinone forming compounds” and satisfactorily include a wide variety of polynuclear aromatic materials in which the hydroxy groups directly on the aromatic ring and, preferably, on adjacent carbon atoms. As noted below, satisfactory results have been achieved utilizing, for the quinone forming compound in accordance herewith, such materials as catechol, adrenalin, pyrogallol, hydroquinone, etc., as materials which can be readily oxidized to the quinone structure initially and during reaction with an amine component.

Similarly, a variety of aromatic amine materials are available as the other principal starting reactant hereof, within the limits of the physiological and toxicity requirements incident to the utilization of this invention on human beings. Such materials have the available amino groups (preferably a plurality thereof) directly attached to the aromatic ring, and not in side chains. Satisfactory results have been achieved in accordance herewith utilizing as such amine reactant compounds such as aromatic amines, alkylated and unsubstituted aryl derivatives thereof, and such materials may satisfactorily include aminonitrophenols, phenyl-enediamines in ortho or meta or para configurations, aminophenols, aminonaphthoquinones, aminonitrophenols, aminoresorcinols, benzene triamines, nitrophenylaminoamines, variously alkylated amino toluenes, etc. As is apparent from the foregoing, a compound having both reactive hydroxy groups (or quinone structure) and amino groups directly on the aromatic nucleus may function satisfactorily as either the quinone component or the amine component in accordance herewith, although in each instance here it is preferred that the starting reactants be different compounds notwithstanding the fact that a particular material may function as either component in different applications of this invention.

Similarly, as apparent from the particular examples of combinations of materials and reactions noted below with which satisfactory results have been accomplished, the particular selection of individual reactants for use in any instance is to be made with due regard to the activity of the available active radicals, the quantity or manner thereof on each molecule of the starting materials or intermediates hereof, the necessary to accomplish the formation of the desired dark pigment under conditions of air oxidation, neutral pH, and as catalyzed by the noted oxidation enzymes, as well as with due regard to the physiological propensities of the particular materials. In this latter connection, however, the particular nature and conditions hereof have been found to diminish the apparent toxicity or physiological sensitization previously attributed to some of the available materials.

For example, the reduced reaction time of no more than 20 minutes or so for achieving satisfactory results in the controlled oxidation reactions in accordance with this invention may be so short as to permit the safe use of certain amine materials to which it would not be desired to apply directly to human skin for a longer period of contact. Also, the sensitizing effect of such material as paraphenylenediamine is found to be less marked or even negligible when used in accordance with this invention, apparently because the absence here of harsh alkaline oxidation conditions (such as with high $\text{pH}$ ammonia and peroxide oxidation media) avoids a principal alkaline attack on skin cells on the scalp which may sensitize the skin to deleterious attack by the paraphenylenediamine and catechol materials previously suggested in the prior art for hair coloring, thus indicating that a different pigmentation mechanism is occurring and, perhaps, also a chemical avoidance of the known physiological sensitizing toxicity of paraphenylenediamine.

As more specifically illustrative of the enhanced results in accordance with this invention, a variety of actual hair coloring trials were made and the results thereof noted in the following table, which also sets forth the particular materials and concentration of the quinone forming and amine starting reactants, as well as the pH of the reacting solutions. In order to provide comparable data for comparison in this disclosure, the various solutions as to which data are reported in the table were all prepared to include approximately equal volumes of the two starting reactants at substantially equal concentrations.

<table>
<thead>
<tr>
<th>Quinone Forming Compound</th>
<th>Amine</th>
<th>Undyed Color</th>
<th>Final Color</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catechol</td>
<td>2-Amino-4-nitrophenol</td>
<td>Blend...</td>
<td>Light brown, Light brown...</td>
<td>6.55</td>
</tr>
<tr>
<td>D...</td>
<td>...do...</td>
<td>do...</td>
<td>Reddish brown, Reddish brown...</td>
<td>6.55</td>
</tr>
<tr>
<td>D...</td>
<td>...do...</td>
<td>do...</td>
<td>Brown, Brown...</td>
<td>6.95</td>
</tr>
<tr>
<td>p-Phenylenediamine...</td>
<td></td>
<td>do...</td>
<td>Brown, Brown...</td>
<td>6.95</td>
</tr>
<tr>
<td>D...</td>
<td>...do...</td>
<td>do...</td>
<td>Brown...</td>
<td>6.55</td>
</tr>
</tbody>
</table>

The tabulated data were all obtained with a dying time of only 20 minutes to emphasize the enhanced results achieved here and as indicating a satisfactorily short dyeing time favorably comparable to the reaction times required for other hair coloring techniques. As substantiated by the following data, the neutral pH range in accordance herewith is about 7 up to 8.5, although most of the runs were actually fractionally below pH 7.
It is also to be noted that increasing the concentrations of the reactants in the solution (as by using initial concentrations of 3% of catechol and paraphenylenediamine instead of the 1% noted in the table) did not produce a substantial or even discernible change in the dyeing results obtained. Nor was there a change noted with increased concentrations of only one of the original reactants in order to provide an excess thereof in the reacting medium. Similarly, a trebling of the enzyme concentration produced no significant or appreciable change in the dyeing results.

Doubling or trebling or further increasing the reaction time (i.e., the time during which the reacting solution was allowed to remain on the hair prior to being rinsed therefrom) produced increasingly darker colorations, and also produced an appreciable decrease in the color difference between the results obtained with and without the presence of the enzyme. Thus, the extent of pigmentation and the darkening of coloration increases as the reaction is permitted to continue in air for longer periods. Nevertheless, a predetermined and desired dark coloration is achieved in much less time when the oxidation reaction is catalyzed by the small amount of enzyme in accordance herewith and to a quite graphic and unexpected extent of considerable commercial significance in the useful applicability of this invention in the practical coloring of growing human hair. For example, a reaction mixture including adrenal and paraphenylenediamine produced on blond hair in only 20 minutes a dark brown color when the enzyme tyrosinase was used in accordance herewith, whereas it required more than an hour of reaction time to achieve the same dark brown on the same blond hair with the same reaction mixture but without the enzyme.

Although the foregoing trials were conducted utilizing relatively pure or not previously reacted starting materials to achieve the noted colors as indicated in only 20 minutes, some acceleration of the extent of coloration or pigmentation is readily provided in accordance herewith by utilizing as starting materials components one or the other of which has previously been partially reacted through the successive reaction stages prior to application to the hair. For example, somewhat different results and more immediate or broader colorations may be noted within the same reaction time if the amine component, for example, already contains some reaction products prior to application to the hair, although, in view of the oxidation nature of the reaction involved, such situations may not be preferred in accordance herewith regarding any instances where the starting materials are to be stored prior to use for any length of time. Also, although the foregoing trials were conducted with only air oxidation, it is within the contemplation of this invention to accelerate the oxidation rate somewhat by the addition of a chemical oxidant (such as hydrogen peroxide) provided that a harshly alkaline or deleterious oxidizing situation is avoided. Such expedients, however, do not appear to be routinely necessary to achieve the ultimate of even a black pigmentation in the relatively short treatment times noted.

As will also be apparent from the foregoing, satisfactory results are achieved in accordance herewith in producing various different colors on the same blond or gray or brown hair by selecting different starting materials, rather than by attempting to alter the reaction time or other application or operating techniques. From the commercial standpoint, the foregoing is considered a desirable feature of this invention since it enables essentially the same technique and operating conditions to be employed, notwithstanding the fact that lighter or darker extents of coloration may be desired in a particular instance, with the choice of color or result being simply made or indicated merely by the choice of different starting materials. In this manner, a relatively inexperienced operator will achieve satisfactory results with this invention with a standard operating procedure simply by selecting a designated choice of starting materials depending upon the original color of the hair and the ultimate effect desired.

The factor, also, eliminates a large part of the operating criticality characteristic of many prior art hair coloring techniques. That is, although the length of reaction time has some bearing upon the extent of coloration, achieving a precise shade or hue is not directly dependent upon controlling the oxidation reaction precisely during the minute or otherwise under critical operating conditions which may easily go awry in practice and produce disastrously unsatisfactory results.

Because the reactions here involved are essentially oxidizing in nature, the starting reactant ingredients are preferably mixed together just prior to application to the hair. Similarly, because of the well-recognized natures of enzyme materials, it is preferred that the enzyme component be packaged or otherwise stored or made available in a substantially non-oxidizing atmosphere. With
the particular enzymes noted, however, the presence of the polyhydric or quinone forming compound appears to be necessary for the enzyme to function as an oxidation catalyst or accelerator, so that satisfactory results may be achieved by including the enzyme material in, for example, the amine component and separated from the quinone forming component prior to use, especially if the components are packaged in the absence of air and with appropriate pH control, etc., and/or, packaged as admixed with buffering agents, anti-oxidants, inert diluents or atmospheres, etc., as may be required for the particular conditions of storage, use, etc.

While the methods and compositions herein described constitute preferred embodiments of the invention, it is to be understood that the invention is not limited to these precise methods and compositions, and that changes may be made therein without departing from the scope of the invention which is defined in the appended claims.

What is claimed is:

1. A method for coloring hair and like keratinaceous substances by the formation in situ thereon of controlled pigment reaction products of controlled oxidation reactions conducted at a substantially neutral pH, comprising the steps of admixing on the hair an aromatic polyhydric material having the hydroxyl group directly on the aromatic ring and adapted for oxidation to a quinone structure and an aromatic amine with at least one amino group directly attached to the aromatic ring capable of reaction on said hair, subjecting said polyhydric material to air oxidation in the present of an oxidation enzyme at a pH within the range of about 7-8.5 forming as an oxidation product said quinone structure, reacting said quinone structure with the amino group of said aromatic amine under said conditions of air oxidation and substantially neutral pH in the presence of said enzyme for forming a pigment reaction product in said hair, and thereafter washing the reacted residues of said reaction from said hair providing thereon said desired coloring by said pigment reaction product formed during said reactions.

2. The method as recited in claim 1 in which said aromatic amine is an aromatic polyamine in which the reacting amine groups are directly on the aromatic nucleus.

3. The method as recited in claim 1 in which said oxidation reaction is maintained on said hair for a period of less than substantially one hour.

4. The method as recited in claim 3 in which said reaction is maintained for about twenty minutes.

5. The method as recited in claim 1 in which said substantially neutral pH is maintained below 7 during said reaction.

6. A method as recited in claim 1 in which said oxidation enzyme is selected from the group consisting of tyrosinase, polyphenolase, catalase, and laccase.

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