

Chapter 7

Dyeing Human Hair

Abstract The different types of dyes described for human hair include, permanent or oxidation dyes, semipermanent dyes, temporary dyes or color rinses and other types of dyes either proposed for or used on human hair. The mechanism of oxidative dyeing of human hair is presented in detail describing a large number of different dye precursors and couplers and how they combine to form different dye species. Hydrogen peroxide and the new peroxymonocarbonate oxidative systems are presented. Different matrix compounds used in hair dyeing are also included. Regulatory activities related to oxidation hair dyes, described in this chapter, focus on the European community which has been the most active in the regulation of oxidation dye ingredients and provides periodic updates on the COLIPA website for safe and banned hair dye substances. Because of the increase in the aging population and the global sale of hair dye products to the graying population, a review of the initiation of hair graying including the age at which graying begins for different populations, the incidence of graying versus age in 5 year increments for different populations and graying among different geo-racial groups are also presented.

7.1 Introduction

Because of the increase in the aging population and the resultant graying of hair for all peoples of the world, the global sale of hair dye products has been increasing at a faster rate than many other hair care products. Therefore, a review of the incidence of hair graying, graying versus age and graying among different geo-racial groups is presented at the end of this chapter. Other areas of new research for this edition described in this chapter include a means to minimize hydroxyl radical in oxidative hair dyeing, a new oxidative system and photoprotection of hair proteins. Fading of artificial hair colors and effects of photofilters on fading, regulatory methods, hair shine effects and dyeing, and a novel method for producing permanent dyed hair using dye-metal ion complexes have also been included.

There are three ways to modify the color of hair: it may be made lighter by bleaching (see Chap. 5); artificial colors may be added to the hair; or a combination of both of these methods may be employed. Adding color is the subject of this chapter. Hair coloring has been carried out for more than 2,000 years [1, 2] using various vegetable, mineral, and animal substances as coloring agents. Most of the dyes considered for human hair may be described as oxidation dyes, ionic dyes, metallic dyes, natural based hair colors, or reactive dyes.

The classification used for discussion in this chapter consists of four groups:

Permanent or oxidation dyes

Semipermanent dyes

Temporary dyes or color rinses

Other dyes

Oxidation dyes are often referred to as permanent hair dyes and are the most important of the commercial hair dyes. Permanent hair dyes generally consist of p-diamines and p-aminophenols that are oxidized by hydrogen peroxide to active intermediates [3]. These active intermediates then react inside the hair with color couplers to provide shampoo-resistant dyes.

Semipermanent products consist of nitroaromatic amines or aromatic amino nitroanthraquinone dyes [4, 5] that diffuse into and bind to the hair but do not bind firmly. Since these dyes are not firmly bound, they diffuse out of the hair with water and shampooing and can be nearly completely removed after a few (4–6) shampoos. Temporary dyes or color rinses are acid dyes [6–8] similar to those used in wool dyeing. However, because color rinses are used at room temperature, the dyes do not diffuse into the hair or bind firmly and they may be removed by a single shampooing.

Other dyes developed and described in the literature for hair include basic dyes [9], metallic dyes, reactive dyes, vegetable dyes [2], and natural-based hair colors discussed in the last part of this chapter. Wool dyeing is very different from hair dyeing because of the high temperatures involved in the former. In fact, low temperature dyeing in wool is 80–85°C. Solvent assist dyeing permits wool to be dyed at 60–70° still too high a temperature for dyeing human hair. Prototype systems have been developed based on chemistry related to that of natural melanin pigment formation [10]. These developmental systems may one day become commercial.

Most hair dyeing processes are diffusion-controlled reactions and therefore provide a “ring dyeing” effect, see Figs. 7.1 and 7.2. The ring dyeing in Fig. 7.1 was produced after 18 h reaction with methylene blue at high pH, a relatively complete dyeing process. Most commercial dyeing of hair provides a ring dyeing effect, but to a lesser extent, more like that of Fig. 7.2 produced by cetrimonium chloride for 1 h at pH 9 and stained with Rubine dye.

For forensic or commercial evaluations, light microscopy can determine whether or not hair of unknown history has been dyed with a permanent hair dye or has recently been dyed with a semipermanent dye. Human scalp hair does not generally contain pigment in the cuticle. Therefore, a light microscopic evaluation of fiber

Fig. 7.1 Ring dyeing effect. Fibers treated with methylene blue (18 h at pH 9). Some of fibers show complete penetration, while others show incomplete ring dyeing. Note some of the fine fibers are less completely dyed than some of the coarser ones

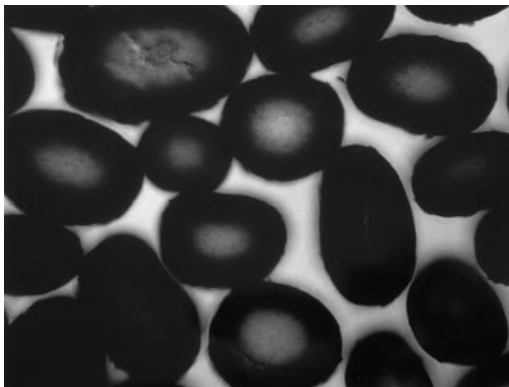
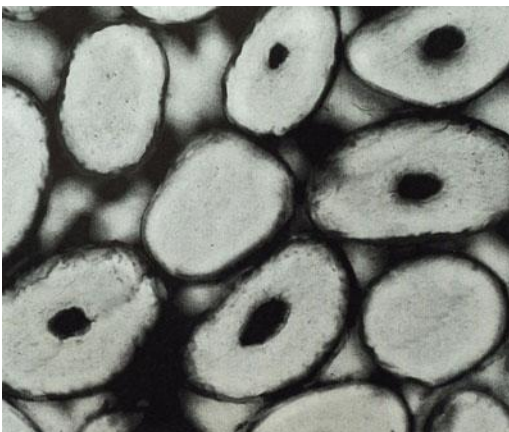


Fig. 7.2 Another illustration of “ring dyeing”. Cross-sections of hair fibers treated with cetrimonium chloride (1 h pH 9) and then stained with Rubine dye after sectioning. The stain shows where the cationic surfactant has penetrated into the hair



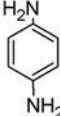
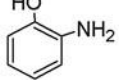
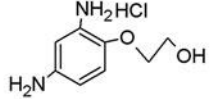
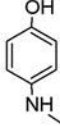
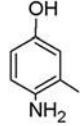
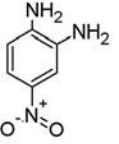
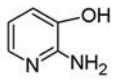
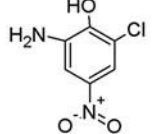
cross-sections or even an optical section can reveal whether or not the hair in question has been treated with a commercial hair dye by determining if there is dye in the cuticle. The basic physical chemistry of the interactions of ionic dyes with hair is related to that of ionic surfactants and is described in Chap. 6, including definitions for diffusion coefficients, ion affinities and experimental procedures to determine these parameters of physical chemistry.

7.2 Oxidation Dyes or Permanent Hair Dyes

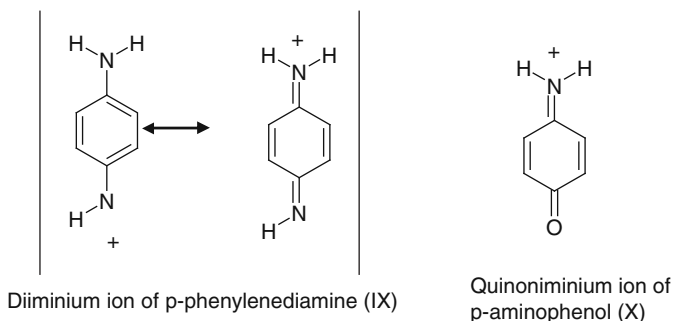
7.2.1 Compositions and Dyeing Conditions

Oxidation hair dyes consist of dye precursors that form active intermediates, dye couplers that condense with the active intermediates, an oxidizing agent (hydrogen

Table 7.1 Some oxidation dye precursors

	
p-phenylenediamine (I)	o-amino phenol(II)
	
2,4 di-amino phenoxy-ethanol HCl (III)	4-methylamino phenol (IV)
	
4-amino-m-cresol (V)	4-nitro-o-phenylenediamine
	
2-amino-3-hydroxy-pyridine	2-amino-6-chloro-4-nitrophenol

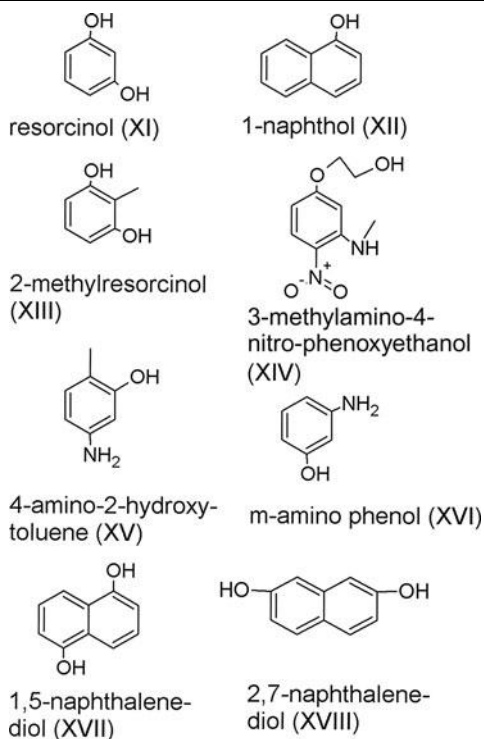
peroxide), and matrix compounds consisting of surfactants, preservatives, and additives for pH adjustment and ingredients for conditioning. These reactions are usually carried out at alkaline pH, generally from 8 to 10 [2, 11–14]. By adjusting the proportions of oxidant, precursors, and couplers, the hair may be made lighter or darker in one process. Oxidation dye precursors are derivatives of aniline (see Table 7.1). Precursors are difunctional ortho- or para-diamines or aminophenols that are capable of oxidizing to diiminium (IX) or quinoniminium (X) ions, proposed by Corbett [3] as the active intermediates of this process.



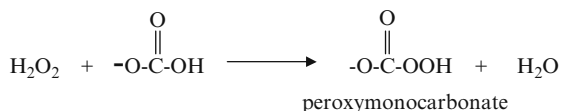
This paper [3] by Corbett is an excellent review of the chemistry of oxidative dyeing. Oxidation dye couplers are electron-rich aromatic species. They are commonly substituted resorcinols or meta-phenylenediamines, usually containing a vacant position para to the amine or phenolic group (see Table 7.2). Oxidation dye precursors, when oxidized in the absence of couplers, form colored compounds, usually gray or brown-black shades. On the other hand, couplers themselves usually produce little or no color, but in the presence of precursors and oxidizing agent, they modify the color formed by the precursor. The ingredients above are described in [2, 14–19] and on product ingredient labels.

Most oxidation dye formulations contain two or three or more ingredients that act as either dye precursors or couplers. Therefore, several reactions are involved, and multiple dye products are formed for each hair color formulation. As indicated before, hydrogen peroxide is usually the oxidizing agent of choice for oxidative hair dyeing. However, peracids [3], and autoxidation [19] or air oxidation of the highly electron-rich dye precursors or oxidation with a mixture of ammonium carbonate with hydrogen peroxide and glycine [20] have also been used. This latter system is believed to function by the formation of peroxy monocarbonate and offers some advantages [20].

Table 7.2 Some oxidation dye couplers



^aThese and other couplers are described in References 2 and or 14–19 and on product labels



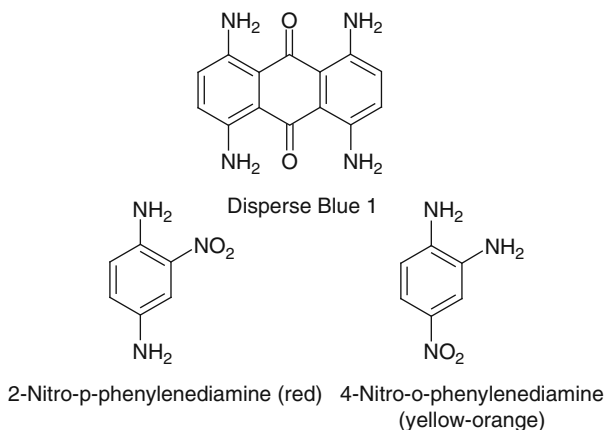
Oxidation by hydrogen peroxide in oxidation dyes is generally performed at a pH of 10 ± 0.2 . This pH involves the hydroperoxide anion as the primary active oxidizing species. However, Marsh et al. [21] have shown that when redox metals such as copper or iron are present in the hair or the water supply, free radical reactions can also occur involving the very active and destructive hydroxyl radical. These same scientists also demonstrated that some of the oxidative damage by the hydroxyl free radical can be reduced by including certain chelants in the oxidative system [21]. For a more comprehensive discussion of the effects of oxidation reactions on hair see Chap. 5.

Another advantage offered by the peroxymonocarbonate system is that similar hair lightening to that of hydrogen peroxide at pH 10 can be achieved by significantly lower pH's because of peroxymonocarbonate's lower pKa (3.8 and 10.3 [22]) versus 11.75 for hydrogen peroxide [23]. The higher pH required for hydrogen peroxide is because the active species in its reactions is likely the hydroperoxide anion which is only 50% of the peroxide at its PKa, whereas the monoanionic peroxymonocarbonate species is active and it is essentially fully ionized at pH 8 and higher. Furthermore the peroxymonocarbonate system has been shown to provide maximum lightening between pH 9 and 9.5 and it decreases with further increasing pH. This effect is most likely due to the formation of the dianion (pKa 10.3) which is a less effective oxidizing agent for hair pigments.

Even though hydrogen peroxide or peroxymonocarbonate are the oxidizing agents of choice for oxidative dyeing, peracids [3], and autoxidation [19] or air oxidation of highly electron-rich dye precursors have also been used. The nature of the autoxidation process must be analogous to the self-condensation reactions described for dye precursors in the next section. Internal cyclization of the dinuclear indo dye will also occur frequently [19]. A few trisubstituted benzene derivatives and analogous naphthalenes [19, 24] and quinolines have also been described along with some of the dye products for autoxidative dyeing, but this is clearly not a preferred process.

Modern oxidation dyes sometimes contain coloring agents in addition to dye precursors and couplers; for example, direct dyes like disperse blue 1 and nitrophenylenediamines are sometimes included.

One might predict that these ingredients could enter into oxidation dye reactions, but because the strong electron-withdrawing nitro or anthraquinone groups are present, these groups should decrease the rates of oxidation and coupling of these species below that of oxidation dye reactants. Thus, these dyes probably function primarily as direct color modifiers.



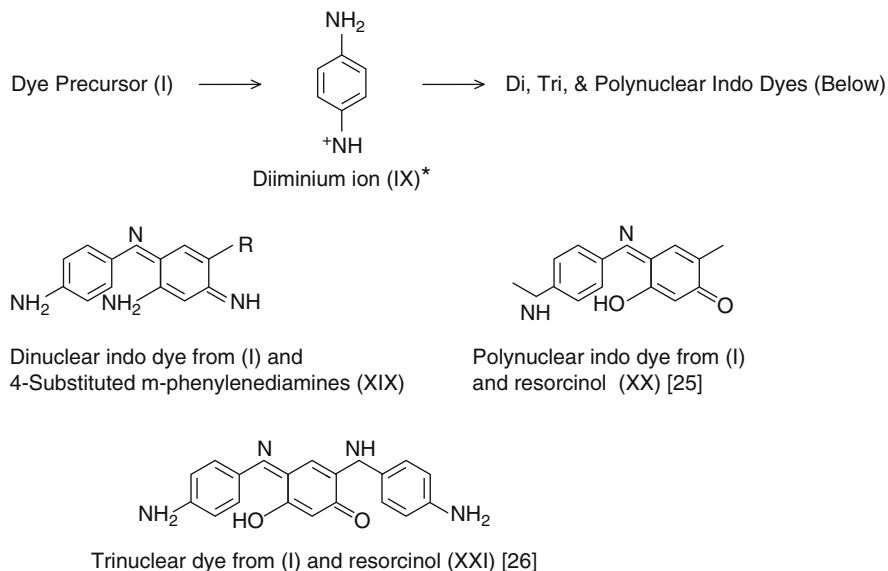
Tables and data describing the colors formed by reaction of many of the precursors and couplers that are shown in Tables 7.1 and 7.2, as well as related ingredients, have been compiled by Wall [2], Tucker [8], and Corbett [3, 19].

7.2.2 Summary of the Reactions of Oxidation Dyes

Table 7.3 summarizes a scheme for formation of oxidation dyes and provides some examples of the types of dyes that have been isolated from these reactions.

This scheme shows that a dye precursor (e.g., p-phenylenediamine) is oxidized to its corresponding diiminium ion (IX). This active intermediate then condenses with an electron-rich dye coupler, forming a dinuclear product that is oxidized to an indo dye. This reaction may stop at the dinuclear dye stage, or additional condensation-oxidation reactions may occur, forming trinuclear or even polynuclear dyes and pigments [3, 25]. More detailed mechanisms describing the formation of these and other indo dye products are presented in the next section.

Because most oxidation dye products contain 5–7 or more ingredients capable of acting as either dye couplers or precursors, mixtures of di-, tri-, and polynuclear indo dyes are formed in these reactions. In addition, it is conceivable that nucleophilic groups in hair might even add to the indo dyes, covalently bonding dye molecules to the hair. Penetration of the dye precursors and the couplers can occur, but penetration must be limited to the outer regions of the hair, since the condensation reactions that occur are relatively fast compared with diffusion, and the larger condensation products (at least in the hair) are resistant to shampooing.

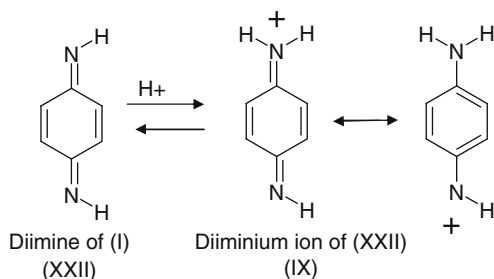
Table 7.3 Scheme and examples of indo dyes formed in oxidative hair dyeing

^aOf the several possible resonance forms of (IX), this one is shown in the next few sections because it enables one to visualize the mechanisms proposed to explain the products which are intended as tools for structure prediction rather than as descriptions of the molecular actions

7.2.3 Mechanisms for Oxidation Dye Reactions

7.2.3.1 The Active Intermediates in Oxidation Dye Reactions

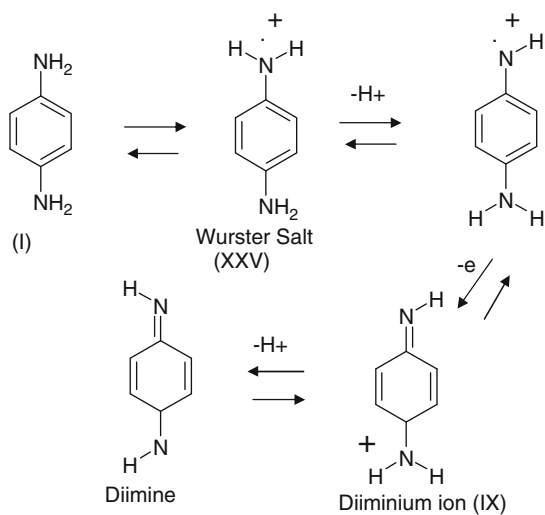
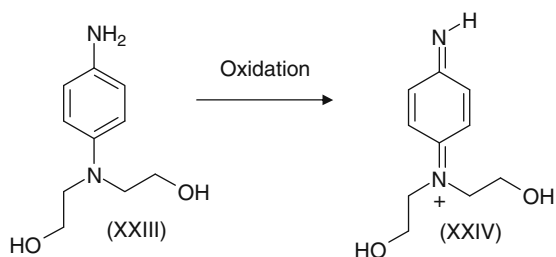
The diimine (XXII) has been described as a vital intermediate in oxidative hair dyeing [26]. Subsequently, Corbett [3] described the protonated diimine (IX) as the reactive species that actually attacks dye coupling agents, ultimately forming indo dyes.



Certainly diiminium ions are more electrophilic and are therefore more capable of serving as the active species in these reactions than diimines. As such, diiminium ions are described as the active intermediates in the mechanisms considered in the

subsequent discussions. By analogy, quinoniminium ions, such as (X), would be the active intermediates formed from ortho- and para-aminophenols. If one assumes that diimines are formed by two one-electron transfer reactions [27, 28] with the loss of two protons, and that the entire sequence occurs stepwise, then a diiminium ion is formed before diimine.

Although diimines may form in these interactions, they are not necessary intermediates for forming the di-, tri-, and polynuclear indo dyes that have been shown to form. For example, compound (XXIII), an *N,N*-dialkyl-substituted *p*-phenylenediamine, has been used in several commercial hair dyes in the past. This species should be capable of forming a diiminium ion (XXIV), although it cannot form a corresponding diimine. One might speculate that (XXIII) functions only as a dye coupler; however, related *N,N*-dialkyl *p*-phenylenediamines have been used with common dye couplers (in the absence of unsubstituted *p*-phenylenediamines). This finding suggests that this type of species does act as a dye precursor in oxidative hair dyeing [8, 29, 30].

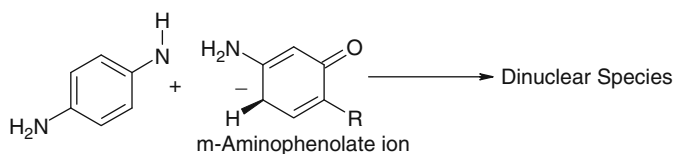


Mechanisms may also be written involving Wurster salts (XXV) to provide the di-, tri-, and polynuclear indo dyes for these reactions. Lee and Adams [31] generated the Wurster salt of p-phenylenediamine by electrochemical oxidation in buffered media. Above pH 6, the radical stability decreases rapidly, indicating the low stability of these species under hair-dyeing conditions. Therefore, the diiminium ion is more likely the active intermediate in actual hair dyeing.

For the following discussion, a five-step reaction mechanism explains the formation of di-, tri-, and polynuclear indo dyes that have been isolated from oxidation dye reactions.

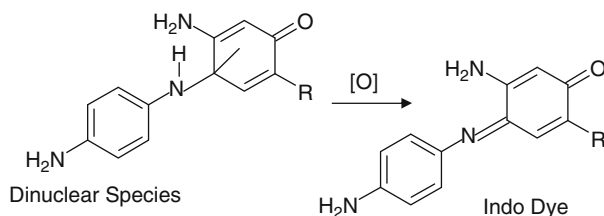
Step 1: Formation of the diiminium ion from the dye precursor.

Step 2: The diiminium ion attacks a coupler (generally para to an amino or phenolic group), forming a dinuclear species.



Step 3: Oxidation of the dinuclear species to a dinuclear indo dye then occurs. If the 4 position of the indo dye is blocked (bears a substituent other than hydrogen), the reaction tends to stop at this step.

Step 4: Dye precursor or another molecule of indo dye may add by 1, 4 addition across the indo dye, forming a trinuclear or polynuclear species (see Table 7.3).



Step 5: Oxidation of trinuclear or polynuclear species to higher indo dyes occurs.

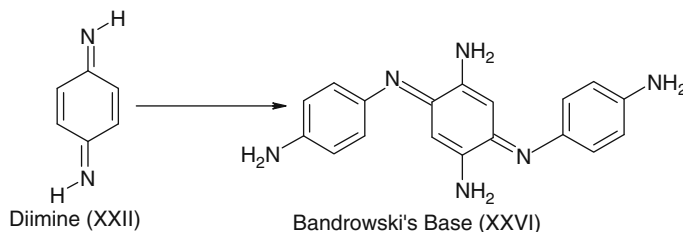
Steps 4 and 5 may be repeated, forming higher polymeric dyes.

7.2.3.2 Some Products Formed in Oxidation Dye Reactions

Bandrowski's Base

Several years ago it was proposed [14, 32] that p-phenylenediamine diffuses into the fibers and is oxidized to diimine (XXII). This diimine can then condense with p-phenylenediamine to form Bandrowski's base (XXVI) a brown-black indo dye. A great deal of discussion and work concerning the actual chemical structure

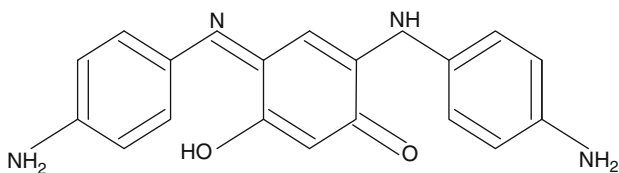
[33–35] and importance of Bandrowski's base to oxidative dyeing has taken place [33, 34]. Altman and Rieger [33] and Dolinsky et al. [34] independently provided evidence that the structure shown (XXVI) represents the correct tautomer, in contrast to the structure proposed earlier by Bandrowski [35]. Altman and Rieger also suggested that Bandrowski's base is probably the end product of an undesirable side reaction in hair dyeing but is not the main colorant of hair dyed with *p*-phenylenediamine. Corbett [3] confirmed this conclusion by showing that modern dye couplers are several orders of magnitude more reactive to diiminium ion than is *p*-phenylenediamine. These facts preclude the formation of significant quantities of Bandrowski's base in modern oxidation dyes.



The formation of Bandrowski's base may be described by a mechanism consistent with the general scheme described in the previous section.

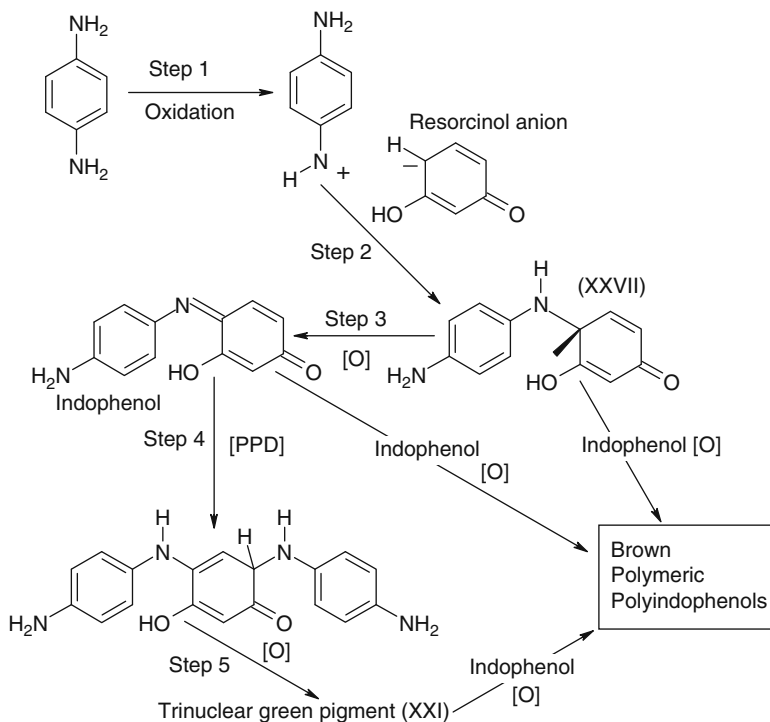
7.2.3.3 Polyindophenols from Resorcinol and *P*-Phenylenediamine

Resorcinol is one of the components of many oxidation dyes, and as such is probably the most commonly used oxidation dye coupler. Brody and Burns [25] have shown that *p*-phenylenediamine, in the absence of hair and phenols, is oxidized to Bandrowski's base. However, when resorcinol is present, polyindophenols (XX) are formed, and the formation of Bandrowski's base is effectively prevented [25]. These brown polymeric polyindophenol pigments have been identified by elemental analysis, acetyl values, and hydrolysis to *p*-phenylenediamine. Low-molecular-weight di- and trinuclear species were not detected by Brody and Burns. However, Shah et al. [36] isolated a green pigment from hair dyed with mixtures of *p*-phenylenediamine and resorcinol and identified this pigment as the trinuclear indophenol (XXI).



Trinuclear green pigment from *p*-phenylenediamine & resorcinol (XXI)

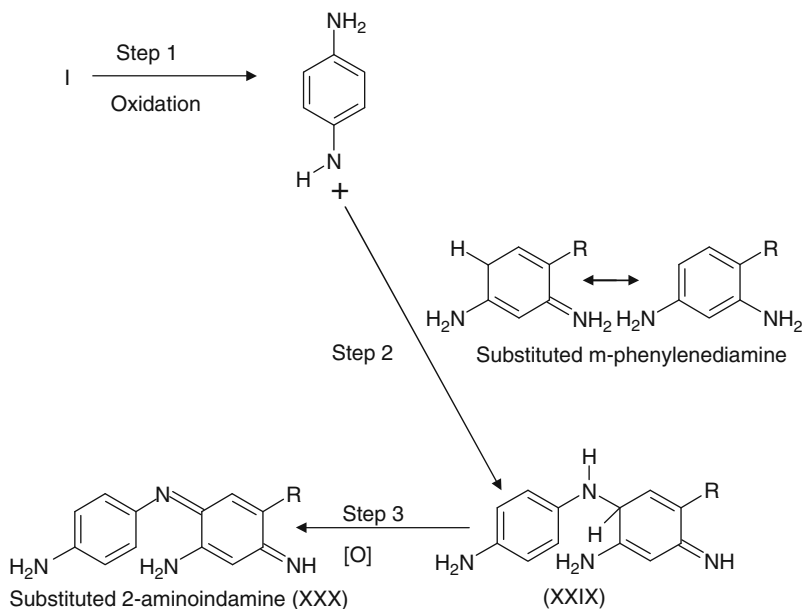
The following scheme describes the formation of the trinuclear green pigment and polyindophenols from (I) and resorcinol and is consistent with the general mechanism described earlier. This scheme suggests that the diiminium ion (IX) is the active species, and its formation has already been described. In Step 2, this electrophilic species attacks a resorcinol anion, para to the phenolic group, forming (XXVII), which is oxidized to indophenol in Step 3.



In Step 4, p-phenylenediamine adds to the indophenol in a 1,4 manner [28, 37], producing the trinuclear species (XXVIII), which is then oxidized to the trinuclear green pigment (XXI). Several routes exist for formation of polymeric indophenols. All of these routes are analogous to steps 4 and 5. Repetition of these steps results in the formation of higher polymers. Because most oxidation dyes contain both p-phenylenediamine and resorcinol, the formation of these tri- and polynuclear pigments is important to the oxidative dyeing of human hair.

7.2.3.4 Indamines from M-Phenylenediamines

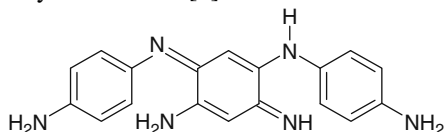
In addition to resorcinol, 4-methoxy m-phenylenediamine has been an important dye coupler, and is representative of the class of m-phenylenediamine coupling agents.



This type of dye coupler reacts with dye precursors to give blue-violet dyes that have been shown to be 2-aminoindamines [38]. Mechanistically, the formation of 2-aminoindamines is related to the formation of indophenols and fits the general scheme described earlier.

When the R group of structure (XXX) is methoxy, it represents the structural formula for the 2-aminoindamine of p-phenylenediamine and 4-methoxy m-phenylenediamine, which is a relatively stable dye. Other, less frequently used m-phenylenediamines form unstable blue dyes that cyclize internally at high humidities, forming red 2,8-diaminophenazines [3].

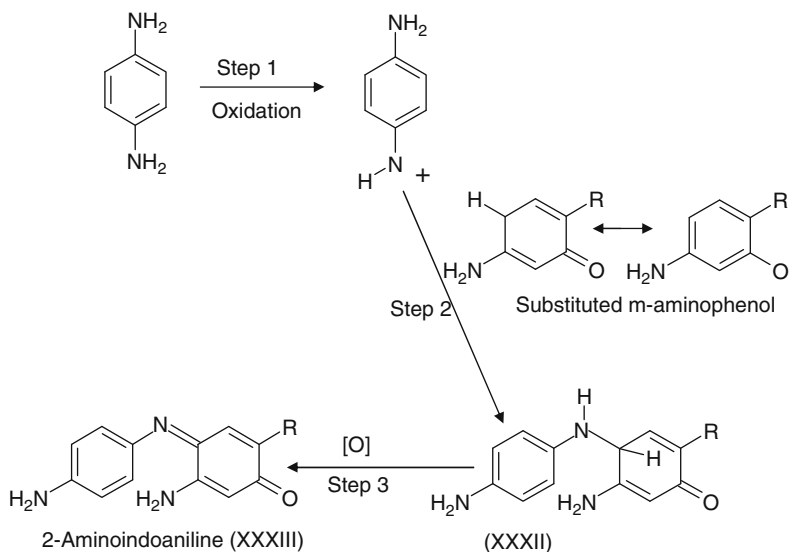
The parent compound m-phenylenediamine reacts with (I) to produce a trimer (XXXI) analogous to the trinuclear green pigment that has been isolated from resorcinol and p-phenylenediamine [3].



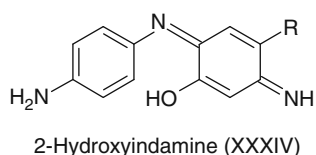
Trimer of p-phenylenediamine and m-phenylenediamine (XXXI)

7.2.3.5 Indo Dyes from M-Aminophenols

The reactions of m-aminophenols with p-phenylenediamine are similar to those described for m-diphenols and m-diamines and are summarized by the reaction scheme below.

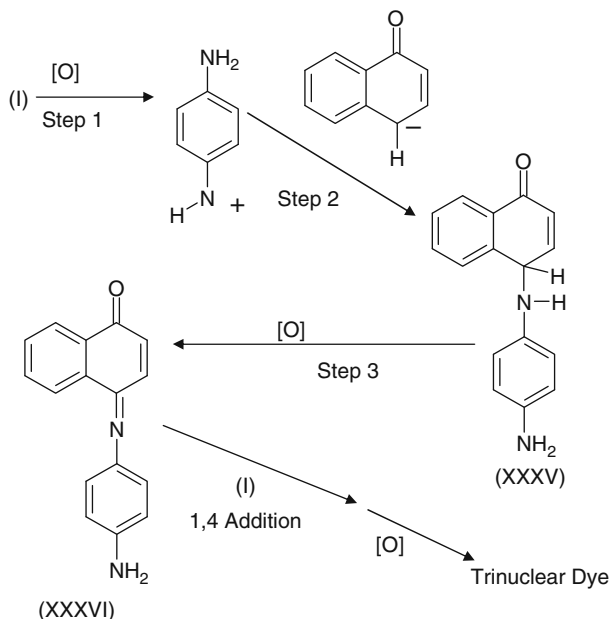


Once again (I) is oxidized to the electrophilic diiminium ion (IX) that attacks the aminophenol para to the phenolic group, forming (XXXII). This species is then oxidized to the dimeric indo dye (XXXIII) [3], analogous to indophenol. If the R substituent of (XXXII) is (almost anything but hydrogen), the reaction generally stops at the dimer stage. However, if R is hydrogen, it adds another molecule of (I) at the 4 position and is oxidized to a trimeric indo dye [3], analogous to the trimeric pigment of (I) and resorcinol; see structure (XXI). If the position para to the phenolic group is blocked, then the diiminium ion attacks para to the amino group, giving 2-hydroxyindamines [3]; see structure (XXXIV).



7.2.3.6 Speculation About Dye Products Formed with Other Common Coupling Agents

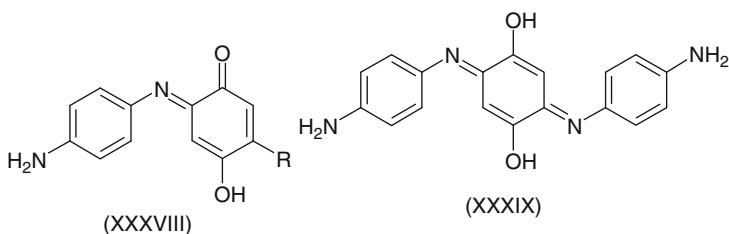
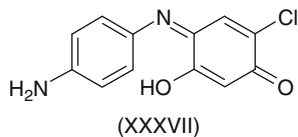
1-Naphthol is a commonly used dye coupler, and its reactions in oxidative dyeing are probably similar to those described in the previous sections; that is, the active diiminium ion attacks para to the naphthol group, forming (XXXV). Oxidation of (XXXV) should provide the indonaphthol (XXXVI).



Reaction may stop at this stage, or 1, 4 addition and oxidation may occur, producing a trinuclear dye analogous to that from resorcinol and p-phenylenediamine.

Schematic reactions similar to those for resorcinol and diiminium ions can be written for pyrogallol and diiminium ions, suggesting di-, tri-, and polynuclear indophenolic dyes from the reaction of this species with dye precursors.

4-Chlororesorcinol, in the presence of diiminium ions, probably tends to stop at the dimeric stage, forming (XXXVII), since the positioning of the chloro group would tend to inhibit 1,4 addition.



Hydroquinones probably form dinuclear dyes analogous to (XXXVIII) and then stop at this stage, whereas the parent compound (unsubstituted hydroquinone) probably forms analogous dinuclear species and even trinuclear dyes (XXXIX) analogous to Bandrowski's base.

7.3 Matrix Compounds

Matrix compounds in hair dyeing consist of surfactants, emulsifiers, preservatives, conditioning agents and additives for pH control/adjustment. They are essentially non-color additives that are functional in hair dyes, see Table 7.4. Vincent et al. [39] described a procedure for the extraction of matrix compounds from oxidation hair dyes to allow for the clean chromatographic separation of hair dye compounds for analysis. These same three scientists [40] have provided a reference method to allow for the identification and quantification of hair dye forming agents. This method was developed to be used for the European regulatory enforcement of these types of products.

7.4 The Formulation of Permanent Hair Dyes

Permanent hair dyes should be formulated with two different compositions or parts. The first composition is a precursor-coupler base containing surfactants (to help dissolve the precursors and couplers, to assist in spreading the dye evenly over the hair, and to help thicken the product so it does not run down the face during use), alkalinity (to facilitate the oxidation reaction), a low concentration of a reducing agent (to inhibit oxidation of the precursors by air), the precursors and couplers, and water. The second composition is an oxidizing base containing oxidizing agent, stabilizer (for the peroxide), and sometimes surfactant (for thickening during use), see Table 7.5.

To formulate the foregoing hair precursor-coupler bases, add the sulfonate and neodol to water with stirring at room temperature. Add the sodium sulfite (reducing agent-stabilizer) and then the dye precursors and couplers, stirring until they

Table 7.4 Some matrix compounds in hair dyeing

Ingredient	Function
Oleic acid	Surfactant/emulsifier
Triethanol amine	pH control
Sodium lauryl sulfate	Surfactant
Nonoxynol-12	Surfactant/emulsifier
Sodium sulfite	Antioxidant
Methyl paraben	Preservative
BHT	Antioxidant/preservative

Table 7.5 Precursor-coupler base^a

Ingredient	Percent of ingredient for desired hair color			
	Dark brown	Light brown	Red	Black
<i>Dodecyl benzene Sulfonate</i>	14	14	14	14
Cocodiethanolamide	9	9	9	9
Neodol 91-2.5	6	6	6	6
<i>Ammonium Hydroxide</i>	6	6	6	6
Sodium sulfite	0.3	0.3	0.3	0.3
p-Phenylenediamine	0.4	–	–	0.4
o-Aminophenol	0.3	0.4	–	0.2
p-Aminophenol	–	0.4	0.4	–
4-Methyl-5-aminophenol	–	–	0.4	–
m-Aminophenol	–	–	–	0.2
Water	64	63.9	63.9	63.9

^aThe colors listed can be achieved when starting with naturally light blonde hair. The actual shade achieved depends on the starting hair color, the hair condition, and reaction time

Table 7.6 Oxidizer base

Ingredient	Percentage
Hydrogen peroxide (30%)	50
Dodecyl benzene sulfonate (50%)	33
Phosphoric acid	1
Water	16

dissolve completely. Then, add the alkalinity, followed by the amide, whereupon the product will thicken. The oxidizer base is detailed in Table 7.6. In some cases, the dye precursors and couplers should be dissolved in the amide and then the other ingredients added as above.

To formulate the oxidizer base, dissolve the sulfonate in water with stirring at room temperature. Add the phosphoric acid to the peroxide separately. Lastly, add this mixture slowly to the detergent in water with stirring.

7.5 Usage Instructions

Use of this type of product consists of three steps: the allergy test, the strand test, and application to the hair on the head.

7.5.1 The Allergy Test

Wash a small area inside the arm at the elbow. Apply a few drops of dye solution with a cotton swab to that area. Leave this area of skin uncovered for 24 h. If any itching, redness, burning, or any other allergic symptom is noticed, do not use the product. However, if there is no allergic reaction, apply the product.

7.5.2 *The Strand Test*

Snip a small strand of hair about $\frac{1}{4}$ in. wide (~0.6 cm), cutting it close to the scalp. Apply tape to the cut ends to hold the hairs together during treatment. Mix a small amount (1 tsp.) of precursor-coupler base and oxidizer base. Apply the dye solution to the strand of hair and wait 20 min. Then wipe the dye from the strand to check the color. If the desired shade is not dark enough, apply more dye and recheck. Continue until the desired depth of shade is achieved.

Now the consumer is ready to use the product. Mix 100 g of the precursor-coupler base with 75 g of the oxidizer base and spread it through the hair, allowing the reaction to proceed for 10–20 min or the time indicated by the strand test before rinsing thoroughly with water.

7.6 Regulatory Activities Related to Oxidation Hair Dyes

The European community has been the most active region with respect to the regulation of oxidation dye ingredients. In the late 1980s more than 150 oxidation dye couplers and precursors combined were listed for use in the European Cosmetic Directive. As of this writing, a proposal by COLIPA (Comite de Liaison Europeen de Industrie de la Parfumarie de Produits Cosmetiques et de Toilette) contains only 25 of these, see Table 7.7 and more than half of these ingredients require further testing to actually remain on this list permanently.

COLIPA has a website (www.colipa.eu/hair-dyes.html) that is worth following for anyone in the hair dye industry. On this website at the bottom of the page is a link to hair dyes that contains several important objectives and lists for those concerned with hair dyes. There is an *Assessment Strategy for Hair Dyes Safety*, and a *List of 44 positively assessed hair dye substances by the SCCP* (updated: January 2009), a *List of provisionally allowed substances* (62) (Updated: November 2006), a *List of 117 hair dye substances with an updated safety file* (Updated: November 2006), a *List of 135 banned hair dye substances* (Updated: September 2007), a *List of 49 hair dye substances proposed for ban* (Updated: September 2007), and *Guidance Document to the Commission Directive 2007/54/EC of 29 August 2007 (ban of 85 hair dyes)*.

One concern however is the lack of solidarity that exists in Europe concerning regulatory matters. For example, 1-nitro-p-phenylenediamine is banned in Italy, but it is listed by COLIPA as safe, see Table 7.7. Another example of the independence of many European countries in regulatory matters is one that created confusion in the surfactant arena just a few years ago. For example, there were labeling requirements for LAS (linear alkyl benzene sulfonate) in Scandinavia, but not for the remainder of Europe. These labeling requirements created problems for marketing Pan-European products containing surfactants. Hopefully such emotional and independent decision making will not prevail in hair dyes too. The status of the

Table 7.7 Oxidation dye ingredients proposed for the future positive hair dye list by COLIPA

A. Sufficient testing done	B. Additional testing required
p-Phenylenediamine	4-Chlororesorcinol
Resorcinol	1-Naphthol
o-Aminophenol	1,5-Naphthalenediol
m-Aminophenol	2,7-Naphthalenediol
1,4-Diaminophenoxyethanol HCl	4-Methylamino phenol
2-Methylresorcinol	Hydroxybenzomorpholine
4-Amino-m-cresol	4-Amino-2-hydroxytoluene
1-Methoxy-2-amino-4-B-hydroxyethylamino benzene	6-Amino-m-cresol
6-Amino-o-cresol	3,4-Diaminobenzoic acid
Hydroxyethyl-3,4-methylenedioxyaniline HCl	3,4-Methylenedioxyphenol
2-Aminomethyl-p-aminophenol HCl	Hydroxyethyl-p-phenylenediamine sulfate
2-Nitro-p-phenylenediamine ^a	2,4-Diamino-5-methylphenetol HCl
	2,4-Diamino-5-methylphenoxyethanol HCl

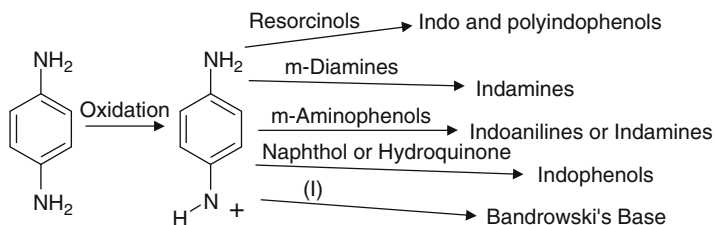
^aBanned in Italy, but listed as safe by COLIPA

regulatory process for hair dyes in Europe is worth following especially for any company concerned with the global marketing of hair dyes.

7.7 Synopsis of Oxidation Dyeing of Human Hair

Oxidative dyeing consists of treating hair with an oxidizing system and dye precursors and couplers. Up to this time, the primary oxidizing agent is hydrogen peroxide with alkalinity (ammonia or ethanolamine) and the dye precursors and couplers. The pH of these systems is about 10 ± 0.2 . The oxidizing system has two functions: One is to decolorize the hair pigments and thus lighten the hair in preparation for the colors. Second, the oxidizing system oxidizes the dye precursors to diiminium ion active ingredients as described in the previous sections. Bleaching of the hair pigments is critical to the coloring process especially for lighter or blonde shades. But, bleaching can produce damage to the hair proteins and lipids see Chap. 5.

The literature on the interactions of oxidation dyes shows that dye precursors and dye couplers are both involved. Dye precursors are oxidized to active intermediates, probably diiminium or quinoniminium species. These active intermediates react with resorcinol to form polyindophenols, trinuclear and polynuclear dyes, with m-diamines to form indamines, with m-aminophenols to form indamines; and with naphthol and hydroquinone to form indophenols. Bandrowski's base is a trinuclear species, the product of a side reaction that does not occur to a significant extent in oxidative dyeing.



Since most oxidation dyes contain three to seven components capable of acting as either dye precursors or couplers, and most contain p-phenylenediamine and resorcinol, several di-, tri-, and polynuclear colored species of this general type are formed in these reactions.

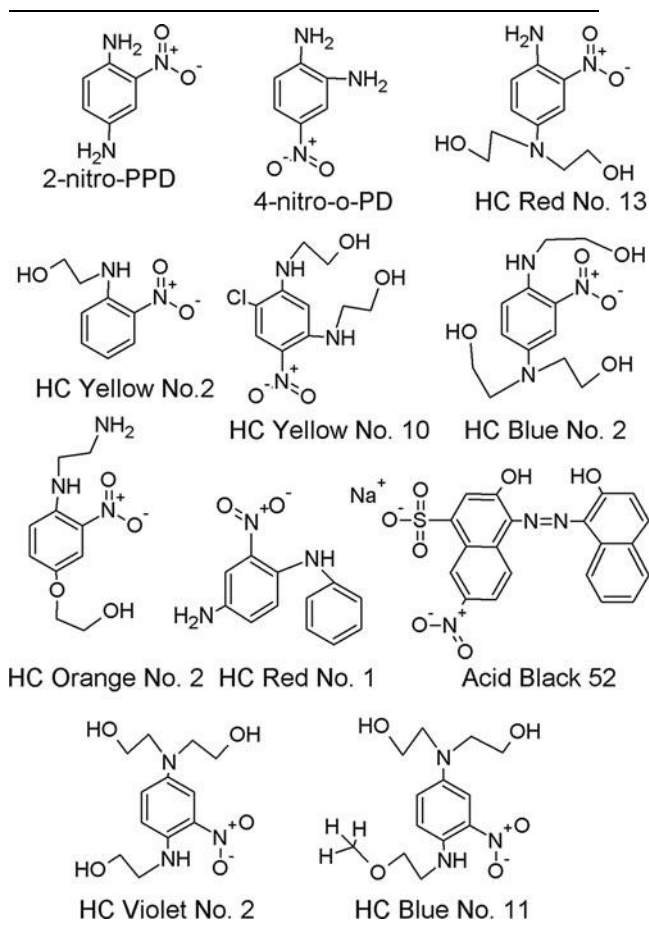
7.8 Semipermanent Hair Dyes

The term “semipermanent hair dye” refers to those products that dye the hair lasting through four to six shampoos. These products do not use hydrogen peroxide to develop the hair color [5]. For this type of product, preformed hair dyes are required. Table 7.8 depicts chemical structures of some dyes currently used in semipermanent hair dye products. To achieve the desired shade, each product contains a combination of up to as many as 18 hair dyes [41, 42] similar to those described in Table 7.8. Other ingredients in these products are matrix compounds, such as, solvents (primarily water and glycols or glycol derivatives), surfactant(s), amide, fragrance and acid or alkali for pH adjustment.

Semipermanent hair dyes are generally applied to freshly shampooed hair and allowed to remain on the hair for approximately 20 min. The hair is then rinsed with water. Often a “conditioner,” is packaged with the product. After application of the dye and rinsing the conditioner is added and the hair rinsed again and dried generally without shampooing.

7.8.1 Formulation of Semipermanent Hair Dyes

To formulate the dye products described in Table 7.9, first dissolve the sulfate in water, and then add the sulfonate, the neodol and the amide while stirring. Add the dyes and stir until they are completely dissolved. Alternatively, the dyes may be dissolved in the amide and/or the neodol and then added to the anionic surfactants in water.

Table 7.8 Examples of some dyes used in semipermanent hair dye products**Table 7.9** Formulated semipermanent hair dyes^a

Ingredients	Percent of ingredients for desired hair color		
	Light brown	Dark brown	Red-auburn
Cocodiethanolamide	10	10	10
NaDodecylbenzene sulfonate	4	4	4
Neodol 91-2.5	6	6	6
Sodium lauryl sulfate	2.5	2.5	2.5
2-Nitro-p-phenylenediamine	0.4	0.4	0.4
HC Red No. 3	0.2	0.2	–
HC Yellow No. 2	0.2	0.2	0.2
HC Blue No. 2	–	0.1	–
Water	76.7	76.6	76.9

^aThese colors can be achieved starting with naturally blonde hair. The actual shade will depend on the starting hair color, the condition of the hair, and the time permitted for reaction

7.8.2 Usage Instructions for Semipermanent Hair Dyes

There are three basic steps to the usage instructions for this type of product: first, the allergy test; second, the strand test (both are described under the formulation of permanent hair dyes); and third, the actual application of the product to the hair. To apply a semipermanent hair dye, first shampoo the hair, rinse, and towel dry. Thoroughly saturate the hair with the product, using plastic gloves, being careful to minimize contact of the dye solution with the scalp. Allow the product to react with the hair for about 30 min or the time indicated by the strand test. After rinsing, a crème rinse/conditioner may be added to the hair, which is then lathered and rinsed. On the other hand, the hair may be rinsed thoroughly with water, but not shampooed. It is then set and styled as usual.

In summary, semipermanent hair dyes are products that last through four to six shampoos. They are mixtures of preformed dyes generally with 10–18 dyes mixed to achieve the desired shade. These dyes are generally mononuclear, dinuclear, or trinuclear species and are usually aromatic amines, amino nitrobenzenes, or anthraquinone derivatives. These dyes generally diffuse into hair and are retained by weak polar and Van der Waals attractive forces. Therefore, the affinity of the dyestuff generally increases with increasing molecular size. Peroxide is not used to develop the color. Therefore, no “major” chemical changes occur to the fibers during this type of dyeing.

7.8.3 Color Fading and Light Fastness of Permanent and Semipermanent Dyes

7.8.3.1 Semipermanent Dyes and Rinse-Out

The hair dyes of Table 7.8 generally consist of neutral aromatic amine, nitro aromatic amine, or anthraquinone derivatives. They are all highly polar ingredients and can be classified as mono-, di-, or trinuclear (ring) dyes. Wong [43] studied the kinetics of dye removal from hair for this type of hair dye. He concluded that under all conditions the larger, trinuclear dyes rinse more slowly from hair than the smaller, mononuclear dyes.

For both bleached and unbleached hair, Wong [43] showed that dye rinse-out for small dye molecules (corresponding to the mononuclear species) of semipermanent hair dyes is diffusion controlled with relatively weak dye-to-hair interactions. Han et al. [44] confirmed this finding in a study of the diffusion of HC Red 3 (Table 7.8) into and out of hair. For a discussion of techniques to determine diffusion coefficients, see Chap. 6. These workers found essentially no hysteresis in the adsorption vs. desorption kinetics, suggesting weak binding between this mononuclear dye and hair. Han et al. [44] indicated that HC Red 3 has a pK_a of 3.7. Therefore, this dye is not positively charged under hair-dyeing

conditions, but is neutral. Thus charge-charge interactions are not involved in the binding of this dye to hair. This factor helps to explain the weak binding found between this dye and hair.

Wong [43] also found that the larger trinuclear dyes, analogous to those of Table 7.8, have a higher affinity for hair than the simple mononuclear dyes undoubtedly arising from a larger number of polar and Van der Waals binding sites between dye and hair.

The principles of this study by Wong are being utilized today in semipermanent hair dye products in the following manner. It is well known that diffusion into hair and removal of dye are faster in weathered tip ends than in the root ends [5]. Thus, blends of dyes are used not only to obtain the right blend at root and tip, but to provide a more even wash fastness in both root and tip ends. For example, blends of single ring dyes diffuse more readily into and are retained more readily in root ends, whereas blends of dinuclear and trinuclear dyes are retained more readily in tip ends [45]. Thus the proper blending of mononuclear and dinuclear with trinuclear dyes will provide a more even wash fastness to both root and tip regions of hair.

Han et al. [44] further found that the diffusion coefficient of the mononuclear HC Red 3 increased with pH, with dye concentration (1.0–5.0 g/l), and with increasing temperature (25–60°C). When the dye bath solvent was changed from water to 50 volume percent aqueous ethanol dye uptake decreased. However, the diffusion coefficients remained similar in magnitude. The pH effect can be explained by increased swelling of the hair. The dye concentration and temperature effects are consistent with expectation for a diffusion-controlled interaction. The solvent effect occurs because the dye is more soluble in the ethanol-water system than in water alone, thereby increasing the affinity of dye for the solvent phase relative to the keratin, causing more of the dye to partition into the aqueous-ethanol phase and less into the hair.

Blankenburg and Philippen [46], using a scanning photometer microscope, studied the reaction of this same dye with hair. These scientists demonstrated maximum absorption of dye near the fiber exterior. Whereas at longer dyeing times the dyestuff concentration in the center of the fiber increased. In all cases, ring dyeing was observed; see Figs. 7.1 and 7.2. These results are consistent with a diffusion-controlled process.

Wong [43] found that for the smaller mononuclear dyes, bleaching increased the rate of dye rinse-out. However, for the larger dyes, the rinse-out rate decreased with a small amount of bleaching, and went through a minimum until the rinse-out rate began to increase with bleaching. Wong suggested that with a small amount of bleaching the larger dyes are able to reach more hindered positions in the hair substrate. Therefore, with a small amount of bleaching the dyes bind more firmly and are more difficult to remove with rinsing. However, with additional bleaching, the hair becomes more penetrable, and the rinse-out rate of the larger dyes increases but never approaches the rinse-out rates for smaller dyes.

7.8.3.2 Dye Color and Light Stability of Semipermanent Dyes

Corbett [45] related dye color and light stability of some semipermanent hair dyes to dye structure. With regard to light-fastness, Corbett demonstrated that for monosubstituted nitrobenzene dyes, the ortho-substituted dyes are the most stable to light and the para-substituted the least light-stable. For nitrobenzene dyes containing two electron-donating substituents, those with 2,5 substitution are the most light stable, while those with 2,4 and 3,4 substitution are less stable to light.

7.8.3.3 The Mechanism of Fading of Highly Colored Indo Dyes

Although this phenomenon has not been studied at length, Corbett [3] proposed that fading of indo dyes most likely involves the addition of aromatic moieties to dinuclear indo dyes, together with hydrolytic degradation to p-diamines and hydroxybenzoquinones that further degrade.

7.8.3.4 Fading of Permanent Hair Dyes by Shampoos and Light

Red or auburn hair dyes have been shown to fade more than other shades. Pyrazole derivatives such as 1-hydroxyethyl-4,5-diamino pyrazole sulfate produce the most vivid red colors although non-pyrazole red dyes are generally based on 4-amino-2-hydroxy toluene or 2-methyl-1-naphthol as red couplers [47]. Furthermore, color fading has been shown to be greatest by UVB and least by IR. For example, the color fading order is: UVB > UVA > Visible > IR [44]. However, these relative fading effects in actual practice have been found to be very different from this ranking because of the differences in the relative intensities of the various portions of natural sunlight in different parts of the world. As a result, the contributions of UVB and UVA depends on radiation time (63% at 16 h and 27% at 48 h), and the greatest effect is from visible light [48]. Therefore blocking UV light can produce a significant decrease in color fading but will not completely suppress color loss.

Locke and Jachowicz [49] demonstrated that greater fading or color loss is produced by a combination of shampooing and light radiation versus light radiation alone. Furthermore, these scientists concluded that color fading is related to the type of hair used. For example, the greatest fading occurs with natural white or bleached hair compared with brown hair. Furthermore, they calculated that use of a UVB photofilter such as octyl methoxy cinnamate on hair at a level as high as 30 mg/gm hair will absorb less than 25% of the total UV radiation, but UVA absorbers will absorb about 40% of UV at the same high concentration.

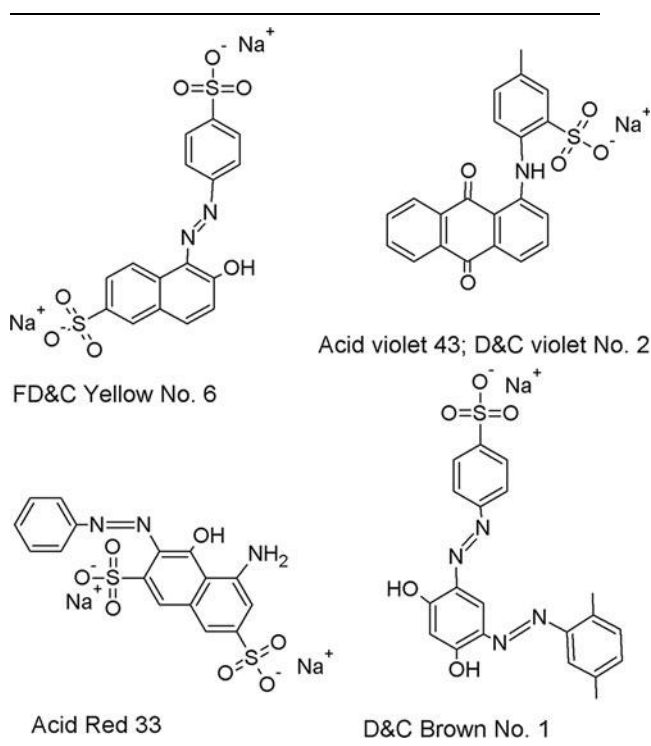
7.8.4 Analysis of Semipermanent Hair Dyes

Several scientific studies have been concerned with the application of high-performance liquid chromatography for analysis of direct dyes in semipermanent hair coloring products primarily for quality control purposes [42, 50]. This technique has been used successfully for the complete separation of 18 dyes in a standard mixture. It has also been applied to the separation and analysis of these dyes in eight commercial hair coloring products.

7.9 Temporary Hair Dyes or Color Rinses

The objective of temporary hair dyes is to provide color to the hair; color that is capable of being shampooed out of the hair with a single shampooing. Table 7.10 depicts structures for a few hair-coloring ingredients used in today's hair rinses. A large number of hair color ingredients previously used in color rinses are described in the article by Wall on hair dyes [51]. Each color rinse product consists

Table 7.10 Some hair color ingredients used in color rinse products



of a mixture of color additives, either among those described in Table 7.10 or similar FD&C or D&C colors. Generally two to five color ingredients are mixed to achieve the desired shade [51], because a single ingredient generally will not provide the desired color to the hair. Two dyes are sometimes used to provide tints for gray hair; four to five dyes are generally mixed to achieve reds, browns, or black.

These products are usually applied to freshly shampooed hair and combed through. An alternative is to spray the product onto the hair and comb it into the hair to achieve even distribution of the dyes. The hair is then set and dried without rinsing to minimize penetration of dyes into the fibers. The dyes used in color rinses are generally larger molecular species than those used in semipermanent hair dye products. Color rinse dyes are generally anionic or acid dyes, see Table 7.10, and are similar to those used in wool dyeing. These dye ingredients are selected to provide maximum water solubility and minimum penetration so they can be shampooed out of the hair. Wool dyeing is very different from hair dyeing primarily because of the temperatures employed. In fact, low temperature dyeing in wool is 80–85°C. Solvent assist dyeing permits dyeing wool at 60–70°C, which is still too high for human hair. For a more complete discussion of the dyeing of wool fiber, see the book *Wool Dyeing* edited by D.M. Lewis [52].

Some other dyes used in this type of product are direct black 51, direct red 80, acid black 2, D&C yellow No. 10, and other FD&C and D&C dyes.

7.9.1 Formulation of Color Rinses

Temporary hair dye products frequently contain thickeners, a surfactant, sometimes a hair-setting polymer, and a buffer or acid such as tartaric, acetic, or citric to provide an acidic medium for application of the dyes to the hair. To make the hair rinses described in Table 7.11, first hydrate the hydroxyethylcellulose (0.7 g) with 49 g of water by stirring. Next, add the neodol and the nonoxynol. Then add the remaining water followed by the buffer. Next, slowly dissolve the dyes in the product with stirring. Finally, add the cetrimonium chloride and stir until it is completely dissolved.

7.9.2 Usage of Color Rinses

First shampoo the hair with a good cleaning shampoo. Rinse the hair thoroughly and towel dry. Thoroughly saturate the hair with the product, using plastic gloves if desired, being careful to minimize contact with the scalp. Dry the hair and style as desired.

Table 7.11 Prototype hair rinse formulations^a

Ingredients	Percent of ingredients for desired hair color		
	Brown	Red	White
Nonoxynol-9	1.0	1.0	1.0
Hydroxyethylcellulose(HHR)	0.7	0.7	0.7
Cetrimonium chloride	0.6	0.6	0.6
Neodol 91-2.5	0.5	0.5	0.5
Citric acid trihydrate	0.5	–	0.5
Trisodium phosphate	–	0.3	–
Direct black 51	0.5	0.01	–
Acid violet 43	0.04	0.03	–
Direct red 80	0.03	0.05	–
Acid orange 24	0.04	0.02	–
External D&C violet 2	–	–	0.03
D&C red 33	–	–	0.01
FD&C yellow 6	–	–	0.005
D&C yellow 10	–	–	0.005
Water	96.54	96.79	96.65

7.10 Other Dyes for Hair

7.10.1 *Metallic Dyes*

Salts of several metals including lead, silver, bismuth, cobalt, copper, iron, and mercury have been used in the past for dyeing hair [53]. Among these metallic dyes, lead dyes are the only ones in commercial use today. Lead dyes contain lead acetate and sulfur and react with hair to darken it slowly, presumably forming lead-sulfur complexes in the cuticle layers. The listing of lead acetate as a hair color additive in cosmetics is described in this Federal Register listing [54]. These products are popular among men because of the slow gradual buildup of color (Table 7.12). However, shades are limited for lead dyes, and the dye can react if treated subsequently with bleaches, permanent waves, and even with certain other hair dyes [16] (Table 7.12).

7.10.2 *Formulation of a Lead Acetate-Sulfur Hair Dye*

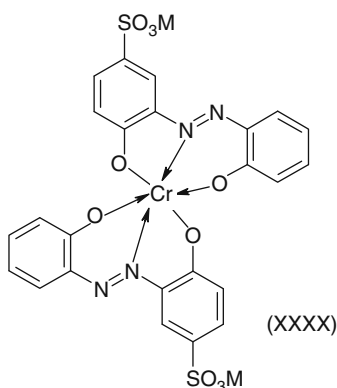
Dissolve the lead acetate in water with stirring. Disperse the sulfur in propylene glycol and add this dispersion to the lead acetate in water while stirring vigorously. Continue to stir while adding the fragrance and preservative that is previously dissolved in alcohol and the surfactant.

Another form of metallic dye is called premetalized dyes. These compounds are metal complexes of anionic dyes with chromium, cobalt, or some other metal,

Table 7.12 Lead acetate-sulfur hair dye

Ingredient	Percentage
Sulfur (finely divided)	1.0
Lead acetate	1.0
Nonoxynol-9	0.8
Denatonium benzoate	0.5
Fragrance	0.2
Propylene glycol	20.0
Ethanol	3.0
Water	73.5

generally in a ratio of 1:2 (metal:dye); see structure (XXXX) [55–57]. Some trade names are Irgalan, Cibalan, Lanasyne, Carbolan, and Isolan. Premetalized dyes have been patented and described for use with hair [58, 59]. Premetalized dyes are often classified as acid dyes rather than as metallic dyes, even though from substantivity and bonding considerations they are probably more like metallic dyes. The use of premetalized dye in the presence of an alcohol (benzyl or amyl) is called solvent assist dyeing [56]. Solvent assist dyeing is an interesting technique that produces a larger uptake of dye relative to a pure aqueous solvent and has been described in patents on human hair.

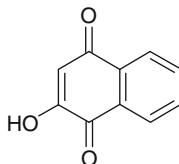


7.10.3 Novel Permanent Dye Using a Dye-Metal Ion Complex

Ochiai et al. [60] reported that permanent dyes can be developed in hair using dye-metal ion complexes. These scientists used aluminum chloride as the metal ion which was allowed to penetrate into the hair so that the aluminum ion could complex with the acid dyes in the hair. Benzyl alcohol and ethanol were employed as penetration enhancers to provide for deeper penetration of the dyes. The advantage to this type of system, if it is effective, is that it would appear to provide color permanence to the hair without oxidative damage.

7.10.4 Vegetable Dyes

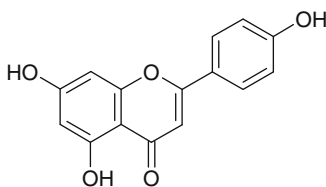
Natural organic substances from plants are the earliest known hair dyes. But, of the many substances of this type that have been tried over the years, only henna and camomile are currently used to a significant commercial extent [2]. The active coloring material of henna (Lawsone) is 2-hydroxy-1, 4 naphthaquinone. The structure of this active dye ingredient was established by Tommasi [59] and Cox [61].



2-Hydroxy-1, 4-naphthaquinone (henna)

This substance is the principal dyeing agent of the shrub henna, known as Egyptian privet. Henna has been used for dyeing hair and staining nails since ancient times in Egypt [1]. This dye is found in the leaves of the plant and is usually extracted with aqueous sodium bicarbonate. Henna produces yellow to reddish shades in proteins and is normally applied in acidic media. The nonionized (acid) form of henna is yellow while the ionized form is reddish-orange. Although the more deeply colored form of henna is available at higher concentrations at alkaline pH, henna dyes hair better at acidic pH. Amro et al. [62] proposed that protonated groups on the hair fiber complex with lawsone anions. Therefore, acidic pH is optimal to create a higher concentration of protonated sites on the hair to attach to the ionized lawsone in solution. When the ionized form of lawsone is removed from solution, additional lawsone ionizes to maintain equilibrium and thus to dye hair the reddish shade characteristic of henna dyed hair.

The active coloring substance from camomile flowers is a polyhydroxy flavone, 4',5,7-trihydroxy flavone [2]. This substance is also found in parsley; and its common name is apiginin [63].



4',5,7-Trihydroxy flavone (camomile)

Other polyhydroxy flavones exist in plants [59]. These flavones are usually combined as glucosides or rhamnosides and are generally yellow. These materials have been used for dyeing cloth and hair. For dyeing cloth, these dyes are usually

mordanted with chromium, tin, or iron salts. This mordanting process changes the color as well as the binding character of the dye.

These two dyestuffs, henna and camomile, are chemically related by the alpha-, beta-unsaturated grouping. This group is capable of undergoing 1,4 addition reactions with free amino or other nucleophilic groups of the side chain residues of hair proteins. The review by Wall [2] describes vegetable dyes in greater detail, including their history, sources, active ingredients, and even dyeing conditions.

7.10.5 Natural-Based Oxidative Hair Coloring

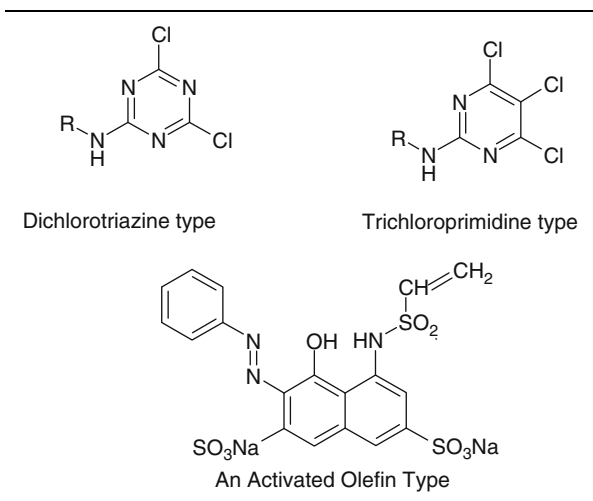
Natural hair dyeing processes have been described in the literature based on 3,4-dihydroxyphenylalanine (dopa) [10]. Natural pheomelanin type dyes begin with the oxidation of DOPA to dopaquinone which then reacts with cysteine, a nucleophile to ultimately form the natural red hair pigments. Brown et al. [10] found that by beginning with the oxidation of DOPA and incorporating sulfur-containing nucleophiles in the process, a wide range of shades can be produced on hair that are acceptable for hair dyeing. Oxidants such as atmospheric oxygen work, although the combination of hydrogen peroxide and iodide ions appears to be more effective [64–66].

An intense black eumelanin type pigment is produced by reacting DOPA with controlled amounts of potassium ferricyanide. 8-Hydroxy-1,4-dihydrobenzothiazine or thio substituted catechols which are simple analogs of intermediates of the melanic pathways when oxidized with different at specific pH conditions provide different colors similar to those of permanent hair dyes [10]. Sometimes when these catechol or benzothiazine intermediates are oxidized in the presence of oxidation dye nucleophiles they provide permanent hair dye colors. These systems are still developmental and have not been commercialized, but do appear to offer promise for the future.

7.10.6 Fiber Reactive Dyes

A fiber-reactive dye binds to the hair or wool through covalent bonds. These reactions generally involve either nucleophilic displacement by amino, guanidino, hydroxyl, or sulfhydryl groups of the keratin on a dyestuff containing either a labile halogen or sulfate grouping. In addition, nucleophilic addition onto a dyestuff containing an activated olefinic linkage can also be used for permanent binding. Fiber reactive dyes have not been used commercially for dyeing human hair. Nevertheless, these dyes offer a novel approach to permanent dyeing. A few examples of this type of dye are described in Table 7.13. Fiber-reactive dyes will react with unreduced keratin. However, prior reduction provides additional

Table 7.13 Some examples of fiber-reactive dyes used in wool dyeing



mercaptan groups for reaction with the dye and therefore enhances dyeing. For additional information, see the articles by Brown [13], Stead [55], and by Shansky [67] and the references therein.

7.11 Photoprotection of Hair by Hair Dyes

Pande et al. [68] demonstrated that hair dyes (both oxidation and semi-permanent) grant a photoprotective effect to hair proteins providing a significant decrease in cortical damage as shown by tensile testing. This reduction in damage is greater the darker the dyes used. The fact that this effect can be seen in the tensile properties proves that this photo-protection effect of hair dyes extends down into the cortical proteins.

7.12 Hair Dyeing and Luster

Hair shine is basically a ratio of specular to diffuse light scattering. Dark hair usually appears shinier than lighter hair. This is because part of the light is reflected at the fiber surface, and part enters the fiber. The light entering the fiber is scattered by reflecting off irregularities of the interior. When the light reemerges from the fiber interior, the diffuse component is increased decreasing hair shine. If the fiber is colored or dyed, some of this diffuse component is absorbed before reemerging,

reducing it. In this manner hair that has been dyed makes the fibers shinier [69]. See the section on hair luster or shine in Chap. 10 for additional details on hair shine.

Keis et al. [69] studied the effect of natural hair pigmentation on hair luster (shine) using a goniophotometer. This study confirmed that increasing hair color reduces light scattering and increases luster. These same scientists also examined dyed hair and found a similar but more complicated picture. Dye composition, concentration and penetration depth must be taken into consideration to account for the results. In addition, the luster of hair of different colors is perceived differently by the human eye adding further complications. However, Lefaudeux et al. [70] described a method for hair luster based on polarization imaging that they suggest is consistent for different hair colors.

7.13 Safety Considerations for Hair Dyes

Corbett has reviewed the general toxicology of hair dyes [5, 71]. Mutagenicity-carcinogenicity of hair dyes has been reviewed by Kirkland [72]. Bergfeld [73], Ishihara [74], and Bourgeois-Spinasse [75] reported clinical observations of adverse reactions with hair dyes. See also the section entitled, *Regulation of oxidation hair dye intermediates* earlier in this chapter. This discussion consists of a synopsis of these toxicological reviews and reports.

As described earlier in the section on regulation of oxidation dyes, the European community has been the most active region in the world with respect to the safety and regulation of oxidation dye ingredients. COLIPA (Comite de Liaison Europeen de Industrie de la Parfumarie de Produits Cosmetiques et de Toilette) is a very active group in Europe that is dealing with the regulation and safety testing requirements for permanent hair dye ingredients. Anyone concerned with manufacturing and marketing hair dyes should be aware and keep aware of the writings and conclusions of this group (see the discussion on COLIPA earlier in this chapter for details).

The primary toxicological concerns of hair dyes, primarily oxidation hair dyes, are with contact dermatitis and long-term “potential” systemic effects [5]. Of all hair products, the most sensitizing are the paradiamine oxidation dyes [75]. Furthermore, the most sensitizing ingredients of these products are p-phenylenediamine, p-toluenediamine sulfate, and o-chloro-p-phenylenediamine, although other related aromatic amines have been shown to provide some sensitizing potential [74].

Since p-phenylenediamine is the major component of oxidation hair dyes and oxidation dyes are the most widely used of all hair dyes, p-phenylenediamine is the sensitizer of prime concern. Corbett [5] pointed out that while p-phenylenediamine is a strong allergin, the incidence of allergic reactions by oxidation dyes is of low frequency and the reaction when observed is generally mild. Corbett suggests that this low incidence of sensitization is due to the rapid reaction and decreasing concentration of this reactive ingredient during actual hair dyeing [5].

The sensitization symptoms from oxidation dyes are a discrete dermatitis at the periphery of the scalp and on the edges of the ears. Itching scalp, and occasional eruptions occur on the face, especially around the eyelids [74]. Eruptions on the trunk and limbs are rare [74].

Usually symptoms appear several hours after the dyeing process has begun. Treatment of this allergic reaction consists of oxidation of residual paradiamine with peroxide in saline solution. This treatment should be followed by application of corticoid creams or lotions [75]. Allergic reaction to hair color rinses is rare [67]; however, a few incidents of allergic reaction to semipermanent hair dyes have been reported [71].

Misra et al. [76] provided data to suggest that the skin toxicity of p-phenylenediamine might relate to its interaction with lipophilic biomolecules and the subsequent biotransformation products. Gagliardi et al. [77] examined the alleged claim that exposure to vapors of p-phenylenediamine in hair dressing salons might cause lung allergies. Their results and conclusions suggest that this is not the case. They conclude that it is unreasonable to consider that hairdressers are at risk to p-phenylenediamine-induced asthma.

Long-term toxicological risk from semipermanent hair dyes is low [5, 71]. However, 2-nitro-p-phenylenediamine and 4-nitro-o-phenylenediamine currently used in Europe in semipermanent hair dyes, but not in the U.S; have been tested extensively for potential carcinogenicity. This latter dye was shown to be non-carcinogenic in animal feeding studies. But, the former diamine caused adenomas in rats, but only at the highest feeding level. At moderate and low feeding levels, this dye did not produce adenomas [71].

Several hair dye ingredients, primarily permanent hair dye components, have been tested for potential carcinogenicity [5, 72]. The impetus for this testing arose from the finding several years ago that some aromatic diamines provide a positive reaction as mutagens [5, 71] in the Ames bacterial screening assay against the bacterium *Salmonella typhimurium* [76].

Corbett summarized the details of the mutagenicity screening of oxidation dye components. He concluded that the Ames test for aromatic diamines does not correlate as well with results of carcinogenicity in animal feeding studies, as for other chemical types [5]. Both Corbett [5] and Kirkland [72] summarized the results of several common hair dye ingredients in in-vitro mutation tests, in dominant lethal animal testing, and in epidemiological studies. One of these testing programs consisted of a CTFA study involving more than 35 oxidation dye components and 34 textile dyes used in temporary hair color products. From this work and other studies, the FDA determined (in October 1979) that all hair dye products containing 2,4-diamino anisole must bear a cancer-warning label [77–79]. Industry responded by removing this ingredient from oxidation hair dyes.

Corbett concluded that “all animal studies completed to date have shown hair dyes to be safe for their intended use.” Kirkland [72] concluded that “epidemiological and human monitoring studies have not detected any such risk (carcinogenicity) in exposed human populations.” However, Kirkland suggested that more controlled epidemiological studies and more extensive monitoring of exposed populations are in order.

7.14 Gray Hair and Graying of Human Hair

Gray hair is described in this Chapter on hair dyeing because the gray hair audience is one of the largest groups that dye their hair. It is unfortunate that so little is known about the physical and chemical properties and distinctions between gray hair and highly pigmented hair fibers. For a discussion on the current status of this subject see the section entitled, *Hair Pigment Structure and Chemical Oxidation*, in Chap. 5.

Nevertheless, data on the incidence of graying versus age and some of the background and speculation on possible causes of graying in this Chapter should be useful to those involved in research and development of hair dyes. This section begins with a discussion on the formation of gray hair followed by the incidence of gray hair by sex, age, and geo-racial group. Next, the relationship between gray hair and other important hair parameters such as diameter and hair density is presented. Finally, the reactivity of gray hair and the phenomenon of sudden graying are described.

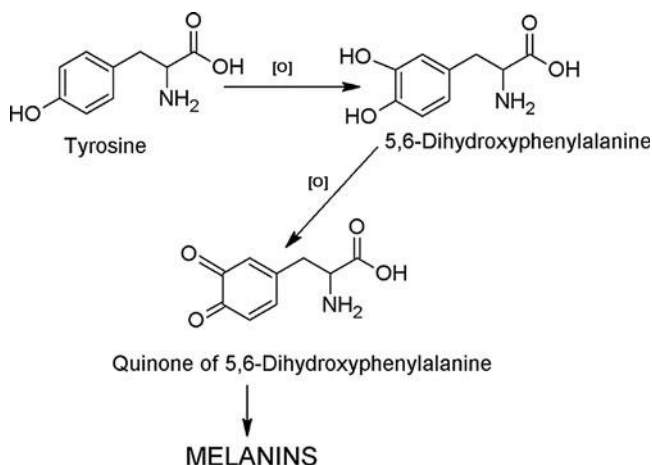
7.14.1 *The Process of Graying of Scalp Hair*

Gray hair relates to the size and distribution of the melanin granules as well as the types of pigments in the fibers; see Chap. 5 for additional details on hair pigments. The medulla does seem to play some role in gray hair, as suggested by Nagase et al. [80] by scattering light through a change in refractive index at the air to hair interface of medullary “pores”. This effect is analogous to the phenomenon that occurs in the genetic abnormality of pili annulati also known as ringed hair that provides the appearance of bands or rings of silver or gray and dark regions along the fiber axis, see Chap. 1 for additional details.

Gray hair is dependent on the production of less pigment in the individual hairs with advancing age. It is usually associated with middle age; however, graying can begin in one’s early 20’s as described later in this chapter. Graying generally begins in the temple region and then spreads to the vertex or crown and finally to the remainder of the scalp usually affecting the occipital region (back of the skull) last. The formation of hair pigments takes place in the melanocytes (pigment producing cells) in the bulb of the follicle starting with the amino acid tyrosine as described in Chap. 5. The melanin type pigments are incorporated into the hair fiber as large granules in the zone of keratinization, see Chap. 1.

Biochemical control of the graying process is still not completely understood; however, Kukita [81] suggested that gray hair is produced by a gradual decrease in the function of melanin producing cells. Tobin and Paus [82] suggested that melanocytes in the region of the hair bulb function through 7–15 different hair cycles to produce pigmented hairs for up to four decades or longer. Each group of melanocytes in each follicle functions independently of melanocytes in neighboring

hairs. Graying results from a decrease and the eventual termination of the activity of the enzyme tyrosinase in the lower bulb [81, 82]. This enzyme is involved in the reaction scheme called Raper's scheme for the formation of 5, 6-dihydroxyphenylalanine and then its quinone from the amino acid tyrosine. These species then react further to produce the melanin pigments.



Kukita [81] demonstrated that the onset of tyrosinase activity coincides with the appearance of melanocytes during anagen. Its activity increases rapidly with increasing numbers of melanocytes. Tobin et al. [83] summarized the regulation of coat color in hairy mammals by POMC-derived peptides (α -melanocyte stimulating hormone, adrenocorticotrophic hormone and β -Endorphin). The expression of these peptides and the melanocyte-1 receptor (MC-1R) are confined to specific regions of the hair follicle and are adjusted or controlled in their effectiveness during the hair growth cycle. β -Endorphin has also been shown by Tobin et al. [83] to play a role in the regulation of human hair pigmentation.

Commo et al. [84] studying hair follicles of pigmented hair, gray hair and white hair determined that the loss of hair shaft melanin is associated with a decrease in both hair bulb melanin content and hair bulb melanocytes population density. Arck et al. [85] suggested a free radical theory of graying involving high oxidative stress and apoptosis in the graying process. This hypothesis suggests that radiation, inflammation and psycho-emotional stresses are involved in graying. Therefore, increases in any of these stresses will speed up the graying process. On the other hand, any reduction in these stresses should lead to delaying the graying process. This hypothesis seems to fit the suggestion by Tobin and Paus [82] that the initiation of graying begins about 5 years later for Asians and even later for Africans compared with Caucasians, because darker pigmentation in skin and hair surrounding the hair bulb should provide some protection against sunlight radiation effects or stress.

Tobin and Paus [82] suggested that the active melanocytes in the hair bulb are replaced with "seedlings" seven to fifteen times in a human lifetime. Therefore, a

small number of melanocytes in the hair bulb function for up to 10 years at an exceptionally high melanogenic activity. This intense oxidative activity generates large amounts of reactive oxygen species (ROS). If these ROS are not actively removed over time, then DNA (nuclear and mitochondrial) damage results producing mutations that induce de-pigmentation or graying.

7.14.2 The Onset and Incidence of Graying

Tobin and Paus [82] predicted that the average age of the onset of gray hair for Caucasians is in the mid-30s, while for Asians it is in the late 30s and for those of African descent it occurs in the mid-40s. These scientists are talking about the age of the onset of complete graying rather than the age of onset of a few gray hairs which occurs earlier than these specified ages.

Keogh and Walsh [86] conducted a large study on the incidence of graying in 1965 in Australia. This study included subjects from ages 25 to 60 plus. These scientists found no significant difference in the graying of hair of males versus females, so they combined the male and female data and separated the data into 5 year age increments. This study contained a total of 8,720 persons including 6,653 men and 2,067 women. This paper did not specify racial characteristics of the group. However, the data is from Victoria, Australia, therefore it likely consists largely or totally of Caucasians.

Keogh and Walsh included persons who had dyed their hair and those who had not dyed it. When the hair had been dyed or suspected of being dyed they relied on the subject's own statement regarding the true color and degree of grayness prior to dyeing because preliminary trials showed the observers to be in substantial agreement with ratings by trained observers.

7.14.3 The Effect of Hair Color on the Perception of Graying

The data of Table 7.14 summarizes the data of Keogh and Walsh [86] comparing % any gray and % complete gray versus the "true color of the hair" categorized as Fair, Medium and Dark. Significant differences were observed in the ability to see graying of these three hair color types.

For the data of Table 7.14, the numbers of subjects are all relatively large especially in the three lowest age groups. Each of these groups contains more than 300 subjects. The data of age groups 42.5 through 52.5 are all 205 subjects or larger and for age group 57.2, the number of subjects is 137 or greater. But, in age group 62.5 the number of subjects in each hair color group is only 26 or fewer. Therefore, the data of this oldest age group are the least reliable.

These authors [86] analyzed the data by logistic regression and concluded that at approximately age 49 (48.6%) about 50% of this population has 50% gray hair. This

Table 7.14 Age and graying of Caucasian scalp hair; calculated by means polynomial modeling from data by Keogh and Walsh [86]

% Any detectable gray				% Total or completely gray			
Age	Fair	Medium	Dark	Age	Fair	Medium	Dark
27.5	3.4	9.4	27.7	27.5	0.4	0	0.0
32.5	19.4	34.0	47.4	32.5	0.6	0	0.5
37.5	39.2	54.1	63.9	37.5	0.9	2.2	0.54
42.5	60.1	70.0	77.3	42.5	4.6	3.3	2.6
47.5	79.1	82.1	87.2	47.5	8.9	7.0	7.4
52.5	93.6	90.7	94.1	52.5	23.9	17.4	13.8
57.5	100	96.1	97.7	57.5	42.3	30.1	18.6
62.5	97.8	98.6	98.2	62.5	50.0	23.3	16.8

The following model equations were used to calculate the above values from the Keogh and Walsh data for % any gray. All models contain $R^2 = 0.99$ or greater and $p < 0.0001$

$$\% \text{ Any gray (fair)} = -102.446 + 3.832\text{Age} - 0.0632(\text{Age}-45)^2 - 0.0037(\text{Age}-45)^3$$

$$\% \text{ Any gray (medium)} = -36.80 + 2.518\text{Age} - 0.07342(\text{Age}-45)^2$$

$$\% \text{ Any gray (dark)} = -8.013 + 2.013\text{Age} - 0.0641(\text{Age}-45)^2$$

For % completely gray higher order polynomial models were used, but were not effective for extrapolating to zero gray. An effective model could not be constructed for fair hair; therefore, the Keogh and Walsh data were used. For both medium and dark hair $R^2 = 0.99$ and $p < 0.02$

$$\% \text{ completely gray (medium)} = -26.69 + 0.6917\text{Age} + 0.1116(\text{Age}-45)^2 + 0.00699(\text{Age}-45)^3 - 0.0002867(\text{Age}-45)^4 - 2.316e-5(\text{Age}-45)^5$$

$$\% \text{ completely gray (dark)} = -39.165 + 0.9749\text{Age} + 0.0511(\text{Age}-45)^2 - 0.001606(\text{Age}-45)^3 - 0.0001277(\text{Age}-45)^4$$

statement has been widely quoted and mis-quoted to apply to all populations. It would appear that the age of 49 for 50% gray hair should apply to Caucasian populations. If the conclusion of Tobin and Paus [82] is correct about graying in other geo-racial groups, one would expect it to be about 5 years later for Asians and 10 years later for those of African descent.

Chi Square analysis shows significant differences between fair and medium to dark haired groups. In contrast to little graying, this perception of complete graying appears earlier in the fair haired group than in the other two hair color groups especially after age 40. This effect likely arises because a few dark hairs will stand out more readily against a light background of gray hair than a few light hairs against a light gray background.

7.14.4 The Age that Graying Begins

To test at what ages the detection of graying begins, the Keogh and Walsh [86] data for the three classes of hair color were examined because these data started at age 25. Plots were made of the mid-point age of each age group versus the % any gray, providing the % any gray data of Table 7.14. The graphical data were clearly not linear, but displayed a distinct curvature. JMP statistical software from SAS was used to provide the best fitting polynomial models for all three hair color types (fair,

medium and dark). Graphs were constructed from the prediction data of the best equations with the smoothest-least interrupted curves in the lower age groups and predictions made to as low an age as feasible.

From this analysis, the detection of any gray hair for the dark haired persons begins at about age 21–22, for the medium color hair persons it begins at about age 25 and for the fair haired persons the detection of graying begins at about age 26. deBerker et al. [87] have described where graying occurs at earlier ages than suggested by these data. This, “premature graying” has been defined as the “onset of graying before 20 years of age” [87] in Caucasians, before 30 years of age in people of African descent [82, 87] and before 25 years of age in Asians [82, 87]. This definition agrees well with the conclusions from the statistical equations to predict the beginning of graying in Caucasians. The conditions of premature graying are generally related to diseases [87] such as pernicious anaemia, hyperthyroidism and certain autoimmune diseases or even premature cardiovascular disease as shown by Eisenstein and Edelstein [88].

7.14.5 A Second Large Study of Graying of Hair

Another large data pool of graying versus age is from the Copenhagen city heart study by Schnohr et al. [89]. The authors of this study do not specify racial characteristics of the subjects. Because of the location I assume that the subjects are largely or totally Caucasians. One advantage to the Copenhagen study is that it contained such large numbers (5,837 men and 7,163 women (13,000 total subjects)). The disadvantages of this study are that the age groups were in 10 year increments and it did not include any subjects younger than 30 years of age. In addition, the authors separated out those subjects who dyed their hair and did not determine grayness on those subjects. The Copenhagen study separated all subjects into those with no gray hair, those with little gray hair, moderate gray hair and total gray/white hair and also those with dyed hair and those with wigs.

To determine if the data from these two large studies could be combined, I assumed that the percentage of gray haired subjects in the dyed hair group was the same as in the non-dyed group and added the two together. With this assumption and combining the data of men and women, the data of % any gray and % total or complete gray corresponded well with the data of Keogh and Walsh [86], that is the differences were generally within plus or minus 2%.

7.14.6 Best Estimates of % Little Gray, % Moderate Gray and % Completely or Total Gray in 5 Year Age Increments

Data from all three hair color types of the Keogh and Walsh [86] study were combined with the data of men and women in the Copenhagen study. The Keogh

and Walsh study went down to age 25 while the Copenhagen study [87] only to age 35 (30–39). The Keogh and Walsh study used few subjects at age 55 and above; whereas the Copenhagen study used many more subjects in the higher age groups. So, where possible, the Keogh and Walsh data were used for ages 20–30 and the Copenhagen study was used for ages 60–70. Means of the combined studies were used for ages 35–55. The data of Table 7.15 summarizes the analyses of these combined studies on the incidence of graying with additional explanations as part of that table.

No comparable data on graying of hair versus age based on large numbers of Asians or Africans could be found in the literature. Therefore, assuming that these conclusions of Tobin and Paus [82] are correct: that graying begins with Asians and Africans about 5 years and 10 years later than with Caucasians and that once graying begins the rate of graying is the same for these three geo-racial groups, then one can approximate the incidence of graying versus age for Asians and Africans by examining the data of n–14 and 7–15 and moving each data point back 5 years for Asians and 10 years (to older ages) for Africans. Until sufficient data can be obtained for large numbers of Asians and those of African descent these approximations should be useful.

Table 7.15 Percent little gray, percent moderate gray and percent total gray of the scalp hair of Caucasians at different ages; calculated by polynomial modeling from data by Keogh and Walsh [86] and Schnohr et al. [89]

Age	% little gray	% moderate gray	% total gray (Eqn)	% any gray (Eqn)
20	0	0	0	0
25	6.3	0 ^a	0	6.3
30	22.5	0.6 ^a	0	23.1
35	43.5	3.7	0.5	42.8
40	52.3	9.3	2.7	61.4
45	54.7	16.4	6.0	76.2
50	52.2	22.7	10.3	86.0
55	46.2	30.1	15.7	90.9
60	38.0	33.7	22.2	92.4
65	29.1	36.8	29.8	93.3
70	20.8	37.5	38.5	98.0

% little gray is from a cubic equation for the Copenhagen study data of ages 35–70 and for ages 20–30 by subtraction. For the cubic model $R^2 = 0.99$, $p = 0.0015$ and the root mean square error = 2.157: % little gray = $47.74 + 0.1569\text{Age} - 0.1046(\text{Age}-43.98)^2 + 0.001867(\text{Age}-43.98)^3$

% moderate gray was obtained by subtraction of % total gray + % little gray from % any gray

% total gray is from a quadratic equation of data combined from the Keogh and Walsh and Copenhagen studies where $R^2 = 0.994$, $p < 0.0001$ and root mean square error is 1.167. The equation is: % total gray = $-28.35 + 0.7625\text{Age} + 0.0215(\text{Age}-45)^2$

% any gray is from a quartic model from data of Keogh and Walsh and the Copenhagen studies combined where $R^2 = 0.996$ and $p < 0.0001$ and the root mean square error is 2.8799. Equation: % any gray = $-35.58 + 2.484\text{Age} - 0.103(\text{Age}-45)^2 - 0.0007748(\text{Age}-45)^3 + 9.267 \cdot 10^{-5}(\text{Age}-45)^4$

^aThis data point was from linear regression analysis and extrapolation from ages 35 to 70

7.14.7 *Hair Graying and Hair Fiber Diameter*

There is conflicting evidence in the literature as to whether gray hairs are coarser or finer than highly pigmented hairs. Nevertheless, current evidence appears to favor that gray-white hairs are coarser than highly pigmented hairs, but the evidence is not overwhelming. This subject is covered in detail in Chap. 5 in the section entitled, *Hair Pigment Structure and Chemical Oxidation*. For leading references into this area see the papers by Hollfelder et al. [90], Gao and Bedell [91] and Van Neste [92] which are summarized in that section in Chap. 5.

7.14.8 *Hair Graying and Scalp Hair Density Versus Age*

This is area with a major GAP and requires investigation. My conclusion is that not considering diseases like alopecia areata (described later), hair density in gray areas should differ very little from those in areas with highly pigmented hairs on the same scalp. Consider that Graying begins in the temple region in the early 20s (as mentioned above) and yet the temple region is one of the last scalp regions to be affected by male pattern alopecia (MPA). Graying does not appear to be affected by female pattern alopecia (FPA). Therefore, MPA and FPA appear independent of graying therefore I would conclude that there is little difference in scalp hair density of gray and pigmented hair. I offer the caution that this is a conclusion, not a fact, and needs to be either confirmed or denied by additional research.

7.14.9 *Sensitivity of Gray Hair to Light Radiation and Free Radical Reactions*

Less pigmented hairs, e.g., gray hairs, blonde hair or bleached hairs are also more sensitive to light radiation than heavily pigmented hairs [48, 91]. Therefore, lightly pigmented gray hairs when exposed to ultraviolet radiation for a sufficient period will show lower levels of cystine and correspondingly higher levels of cysteic acid particularly in their outer layers as compared to heavily pigmented hairs. In addition ultraviolet or free radical damage to tryptophan, as shown by McMillen and Jachowicz [93], and other amino acids occurs at a faster rate in lightly pigmented gray hairs versus heavily pigmented hair. Pande et al. [68] showed that dyed hair when exposed to ultraviolet light provides higher tensile properties than non-dyed hair. This experiment demonstrates that hair pigments provide photochemical protection to hair. Therefore gray hairs will show greater damage to sunlight and ultraviolet light compared with more highly pigmented hairs (see Chaps. 5, 9 and 10 for additional information).

7.14.10 Sudden Graying–Whitening of Hair

Jelinek [94] reviewed several historical and literary reports of sudden graying of hair. The one that this author has heard most frequently is that of Sir Thomas More, whose hair was reported to have turned white the night before his execution. A note in the *British Medical Journal* [95] on the subject of “sudden whitening of hair” relates this condition to alopecia areata. Sabouraud [96] reported that white hairs are often retained in patches of alopecia areata. This report [96] attributes sudden whitening to a disease process related to alopecia areata. Sudden graying-whitening involves the entire scalp, wherein the dark hairs are shed over a short time period, but most of the white or gray hairs are retained providing the appearance of sudden graying.

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