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Review Article
Mechanism of Hair Dying and Their Safety Aspects: A Review

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Abstract

An original hair color change by application of chemical dye is a common practice among the men and women. Hair dyes are classified into the following category based on their color retention property, namely temporary, semi-permanent and demi-permanent and permanent. Temporary dyes are otherwise called as non-oxidative dyes, because coloring process was carried out without any oxidizing agent, it reduced stay time on the fiber, removing the hair during the first shampoo wash. Semi-permanent products consist of nitro aromatic amines or aromatic amino nitroanthroquinone dyes, which diffuse into the hair and bind to the hair, however do not attach firmly. Permanent hair dyes are called oxidation hair dyes, because of the oxidizing agent used for the color development. An active intermediate reacts further with coupler and provides the color to the hair and in general oxidation hair dyes provides shampoo resistant hair dyes. Some hair dyes can cause allergic reactions or sensitization that may result in skin irritation and hair loss. People can develop sensitivities with repeated exposure. Also, formulations may change over time. The primary toxicological concerns of hair dyes, primarily oxidation hair dyes, are with contact dermatitis and long-term "potential" systemic effects. The paradiamine oxidation derivative dyes reported to having more sensitizing potential when compared to other amine derivatives. P-Phenylenediamine is the major component of oxidation hair dyes and oxidation dyes are the most widely used of all hair dyes. Therefore PPD is the sensitizer of prime concern.

Key words: Hair dyes, coupler, bandrowski's base, temporary color, semi permanent color, para phenylenediamine (PPO)

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INTRODUCTION

Since the beginning of human civilization, humans are known to use cosmetics, combination of natural materials like herbal, animal fat substances etc.[1-3]. Original hair color changes by application of chemical/dye is a common practice among the men and women[4]. Natural dyes play a crucial role in human life[5]. Earlier days natural dyes are used for coloring the clothes, cosmetic, medicinal and another purpose[6] due to biodegradability and environmental concern, recent day's natural platform was very much pronounced. Natural dyes are having higher biodegradability, eco-friendly and safer to human. Nowadays, hair dyes are in the important phase of development and significant progress in discoveries and application of many new synthetic dyes has occurred. Hair dyes are classified into two categories, they are oxidative hair color and non-oxidative hair color. Classification based on the oxidation behavior of dyes. Some of the hair color/dyes directly deliver the color without any oxidizing agent and those category dyes/colors are called as "non-oxidative" dyes. Almost 90% of the market sold hair color are oxidative hair color category because these products were containing the oxygen release in the formula. The releasable oxygen will immense useful to oxidize the dye material and ignite the reaction mechanism and form a desired color to the hair[7]. Cream and lotion base hair colors are familiar with European market. Various types of oxidizing agent's available, liquid form of oxidizing agents are used for the cream and lotion base hair color and hydrogen peroxide is the best example of the liquid form of the oxidizing agent. The powder form of hair dyes also familiar in Asian countries, in Asian countries, they have added the dye material and other required chemicals in the henna base formula. The powder form of dyes diluted with water to make an applicable consistency. During the dilution time, the oxygen molecule released when the powder is reacted with water. The releasable oxygen further reacts with dye molecule and promotes the coloring mechanism. Barium peroxide, calcium peroxide, sodium perborate, potassium peroxide and sodium peroxide, etc., are the best example of the powder form of oxygen release. The concentrations of oxidizing agent play a crucial role in the reaction mechanism, higher concentration speed up the reaction mechanism and faster color delivery[7-10].

Some hair dyes can cause create allergic reactions to the sensitive people, that is results of skin irritation and hair loss issue. Continuous application of hair dyes builds sensitive with repeated exposure. So, it's possible to react even if you have dyed your hair in the past, without a problem. Clear user instruction was printed in every sachet, to follow before color application. That is the reason every time the consumer should clearly follow the user instruction, before hair color application. Hair dyes are classified into the following category based on their color resistance property, namely temporary, semi-permanent and permanent[11].

Temporary hair color: Temporary dyes are otherwise called as non-oxidative dyes, because coloring process was carried out without any oxidizing agent, it reduced stay time on the fiber, removing the hair during the first shampoo wash. Temporary coloring molecules have the high molecular weight and deposits on the hair surface only and not penetrate on the cortex[12]. Temporary hair color does not bleach the original hair strand i.e., it does not have the power of lightening/whitening the hair[13]. Temporary colors are applied for developing the fashion colors, usually used after one level lighter the original hair color, if the original color is black background, the color is not visually seen. Temporary colors are not useful to delivers the 100% gray coverage and used to hide or change the hair color tone[12]. A temporary color covers the 15% gray hairs only, because it does not penetrate to the cortex due to higher molecular weights. Temporary colors have the acid characteristics usually having the higher molecular weight and some commonly used temporary colors are listed in Table 1. Temporary colors have anionic characteristics and higher solubility in water, therefore, it was easily removed by first shampoo washing[13]. In general higher concentrations of temporary colors are used for delivers the desired color, because shampoo wash easily removes the excess amount of dye molecules. Temporary colors also used as a uniform color to achieve the optimum color delivery with continuous application. It is suitable for those wish to apply the fancy/fantasy colors to their hair[14] and some regularly used temporary colours are summarize in the Table 1.

Semi-permanent hair dye: The term semi permanent hair dye refers to those products that dye the hair lasting through 4-6 shampooing and does not use hydrogen peroxide to develop the hair color. Semi permanent products consist of nitro aromatic amines or aromatic amino

Table 1: Some temporary hair color examples

INCI name	CI number	CAS Number	Deliver color/shade
Acid yellow 23	CI19140	1934-21-0	Yellow
Acid orange No. 7	CI15510	633-96-5	Orange
Acid yellow No. 1	CI10316	846-70-8	Yellow
Acid red. 33	CI17200	3567-66-6	Red
Acid red 92	CI45410	4618-23-9	Red
Acid violet 43	CI60730	4430-18-6	Violet
Acid blue 9	CI42090	3844-45-9	Blue
Acid black 1	CI20470	1064-48-8	Black

nitroanthroquinone dyes that diffuse into the hair and bind to the hair, however do not attach firmly. Because these dyes are not tightly bound, they diffuse out of the hair after a few shampoo washing. Semi-permanent hair dyes are generally applied to freshly shampooed hair and allowed to remain on the hair for approximately 20 min and then hair is then rinsed with water. Often a "conditioner", packaged with the product, is applied and the hair is rinsed again and then dried. Robbins and Crawford[15] exclusively studied and confirmed this finding in a study of the diffusion of HC red 3 into the hair. These workers found that the weak binding bond formed between mononuclear dye and hair, that is the reason the shampoo washing easily removed it.

Demi-permanent hair color products are having the higher shampoo resistance pattern when compared to the semi-permanent dyes (resistance up to 20 washes), because demi-permanent dye molecules applied with hydrogen peroxide or other oxygen releasing agent without alkali solution. Robbins and Crawford[15] and Brown[16] exclusively studied the diffusion pattern of demi-permanent color and found that weak Van der Waals bonds formed between in demi-permanent coloring mechanism.

Frequently used semi permanent hair dyes are listed in Table 2.

Permanent hair dyes: Permanent hair dyes are called oxidation hair dyes, because of the oxidizing agent used for the color development. Permanent hair dyes were generally containing p-diamines and p-amino phenols that are oxidized in the presence of oxygen releases like hydrogen peroxide, barium peroxide, calcium peroxide, etc. and form active intermediates. An active intermediate reacts further with coupler and provides the color to the hair and in general oxidation hair dyes provides shampoo resistant hair dyes. Permanent hair dyes are otherwise called as an oxidative hair dye.

Corbett exclusively studied the review of the chemistry of oxidative dying mechanism. These reactions are usually carried out at alkaline pH, generally from 8-10[16-18]. By adjusting the proportions of pH, peroxide, precursors and couplers, the hair may be made lighter or darker in one process. Morel *et al.*[17], exclusively studied the permanent coloring mechanism and found that the color formation involves a tedious reaction between the precursors and the oxidizing agent. Precursors can be further classified into two categories: Oxidation basis or primary intermediaries and the couplers or reaction modifiers[16].

Table 2: Some Semi permanent hair color examples

INCI name	Deliver colour/shade
2-nitro-p-phenylenediamine	Red
4-nitro-o- phenylenediamine	Yellow orange
HC red No. 3	Red
HC yellow No. 2	Yellow
HC yellow No. 4	Yellow
HC blue No. 1	Blue
HC red No. 1	Red
HC orange No. 1	Orange
Disperse black 9	Black
Acid orange 3	Orange
Disperse violet 1	Violet

The pH of the dye mixture plays a crucial role in a permanent color mechanism, higher pH/alkaline medium promotes the opening the cuticle and it beneficial to the penetration of dye molecules into the cortex in a fast manner. However, the initial reaction was ignited by the oxidizing agent and the reaction occurs in the cortex of the hair. Some reaction also takes place in the outer layer of the hair i.e., cuticle and it was easily removed by the first washing with shampoo[19,20]. Oxidizing agent concentration also plays a crucial role in the coloring reaction mechanism. Ammonia hydroxide, amino ethyl propanol and ethanolamines are regularly used alkalizing agents. Similarly hydrogen peroxide, calcium dioxide, sodium perborate, barium peroxide is act as an oxidizing agent. Hydrogen peroxide directly releases the oxygen molecule. However, the powder form of oxidizing agents like sodium perborate, calcium peroxide, barium peroxide, etc., releases the oxygen molecule whenever it reacts with water. A small quantity of surfactants and solvents also used in hair color products, the solvents used for wetting the hair and also immensely useful for the dissolving the dye material. Surfactant helps to remove the excess amount of dye molecule/ unreacted species dye molecule in cuticle layer and also contributes to removing the stain on the scalp and forehead during the coloring time. Final product containing the reducing agent also, it will help to prevent the oxidation reaction between the dye material during the shelf life period, in general sodium sulphite, ascorbic acid, etc. act as a reducing agent, however higher concentration of reducing agent prevent the oxidation reaction, therefore the dosage of reducing agent is critical one. PPD undergo oxidation and form a various form of diamine and amine derivative and one of the hydrogen molecule moves and forms double bond structure and described in Fig. 1.

Couplers are aromatic compound and it derived from benzene, substituted by at least two electron donor groups such as NH_2 and OH in para or ortho positions to confer the property of easy oxidation, acting as a color developer[20].

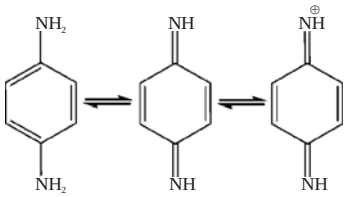

Fig. 1: Reaction mechanism of p-phenylenediamine

Table 3: Dye precursors and couplers

INCI name	Functions
4-amino-m-cresol	Dye precursors
1-hydroxyethyl-4-5-diaminophyrazole sulfate	Dye precursors
N,N, Bis [2-hydroxyethyl]-p-phenylene-di-amine sulfate	Dye precursors
Hydroxyethyl-p-phenylene-di-amine sulfate	Dye precursors
p-amino phenol	Dye precursors
p-methyl amino phenol sulphate	Dye precursors
p-phenylenediamine sulfate	Dye precursors
Tetra amino pyrimidine sulfate	Dye precursors
Toluene-2-5-diamine sulfate	Dye precursors
Resorcinol	Coupler
2-amino-3-hydroxypyridine	Coupler
4-amino-2-hydroxytoluene	Coupler
2-methyl-5-hydroxyethylaminophenol	Coupler
2-methyl resorcinol	Coupler
5-amino-6-chloro-o-cresol	Coupler
2-amino-4-hydroxyethylamino anisole sulfate	Coupler
1-napthol	Coupler
2,4,diaminophenoxy ethanol sulfate	Coupler
m-amino phenol	Coupler
Phenyl methyl pyrazolone	Coupler
4-chloro resorcinol	Coupler

Reaction modifiers/couplers: Reaction modifiers otherwise called as couplers, it containing the electron donating group in aromatic ring systems such as NH_2 and OH in the meta position and it does not undergo oxidation in the presence of oxygen release[18,20]. Coupler alone does not produce any significant color alone but it can modify when used along with primary intermediates and suitable oxygen release like hydrogen peroxide, barium peroxide, calcium dioxide, etc. Frequently used dye precursors and couplers are listed in Table 3.

Alkalizing agent: The alkalizing agent plays a significant role in hair dyeing mechanism, it promotes the pH level for the ignite the oxidation of primary dye intermediates. Ammonia/ammonium hydroxide (NH_4/NH_4OH) is a most commonly used alkalizer in hair colors[18,20]. The alkalizing agent also used for achieving the 100% gray hair coverage, because it is useful to remove the natural pigments in the melanin. In recent years ethanol amine derivative also used for the alkalizing agent i.e., mono ethanol amine, tri ethanol amine[18].

Bandrowski's base: Bandrowski's base has been pronounced from since 18th century onwards[10,12,13], it may be formed during the coloring process by the coupling of p-phenylenediamine (PPD) in the presence of oxidizing agent with higher pH. Higher pH (i.e., >9.0) value promotes the formation of Bandrowski's base. The molecular formula of Bandrowski's base is $C_{18}H_{18}N_6$ and CAS Number is 20048-27-5. Reaction step was explained in the Fig. 2.

In step 1, paraphenylenediamine undergoing oxidation to form a diamine derivatives further it reacts with resorcinol (Step 2) and forms an indophenol complex. In step 2, electrophilic species attacks a resorcinol anion, para to the phenolic group and forming the compound, which is under go oxidation and form an indo phenol complex in step 3. Indo phenol further reacts with another one indophenols complex form a brown polymeric poly indophenol derivatives, similarly indophenols react with paraphenylenediamine and form a trinuclear green pigment and it further reacts with another mole of indophenol and delivers a brown polymeric poly indophenols. Entire reaction mentioned above mechanism desired by the concentration of paraphenylenediamine, resorcinol, the oxidizing agent and pH. pH plays a crucial role in above mentioned chemical reaction[21].

Allergy and toxicology: The Scientific Committee on Cosmetic Products and Non food products of European Commission provides an opinion safety of each raw materials used in cosmetic manufacturer and formulator[3]. Now a day's certain hair coloring molecule, preservative and some fragrance ingredients are banned by the scientific council due to the toxic, carcinogenic and allergic reasons. Many scientists reviewed the general toxicology of hair dyes and mutagenicity-carcinogenicity of hair dyes and they have reported clinical observations of adverse reactions with hair dyes[22-25]. The primary toxicological concerns of hair dyes, primarily oxidation hair dyes, are with contact dermatitis and long-term "potential" systemic effects. The paradiamine oxidation derivative dyes are having more sensitizing potential when compared to other amine derivatives. P-Phenylenediamine is the major component of oxidation hair dyes and oxidation dyes are the most widely used of all hair dyes, therefore PPD is the sensitizer of prime concern.

Contact allergy to p-phenylenediamine (PPD) and other hair dyes materials have become an issue in Europe in nowadays[24,26].

Long-term toxicological risk from semi-permanent hair dyes is low, however, 2-nitro-p-phenylenediamine and 4-nitro-o-phenylenediamine are currently banned in Europe and United states because they have been tested exclusively and proved that both are having the higher potential of carcinogenicity.

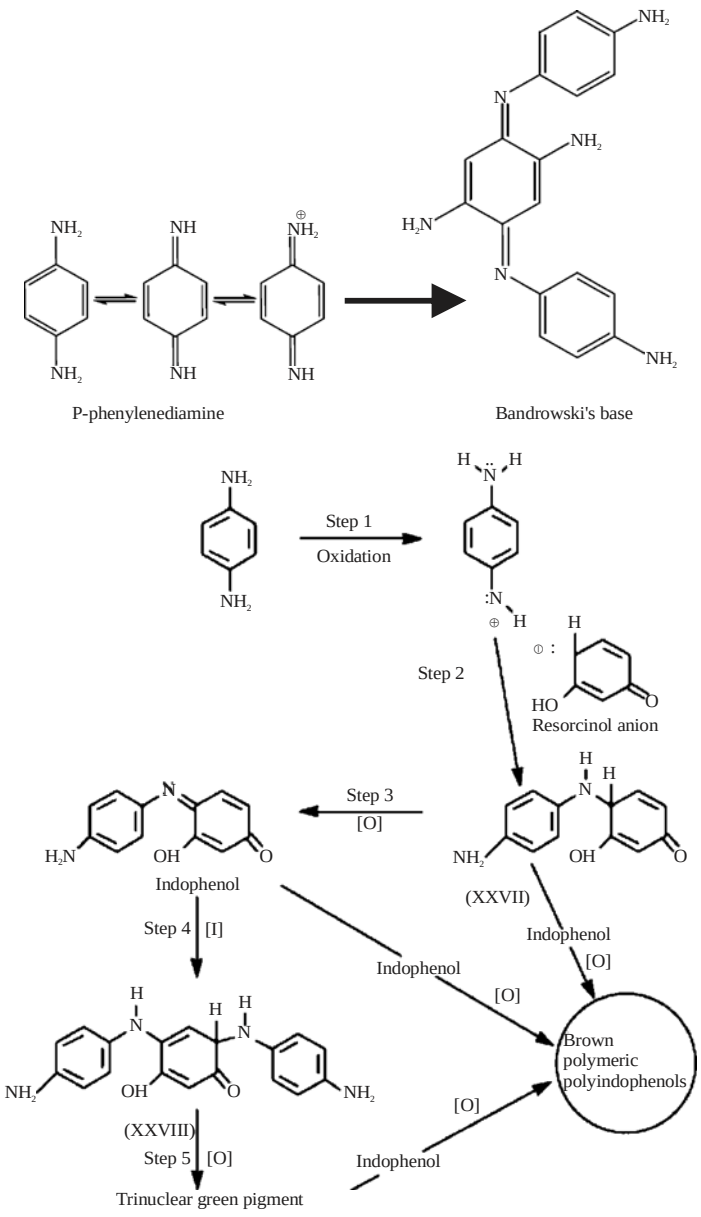

Fig. 2: Schematic diagram of paraphenylenediamine reaction resorcinol

The sensitization symptoms from oxidation dyes are noticed in discrete dermatitis at the periphery of the scalp and on the edges of the ears and itching scalp, occasionally, eruptions occur on the face, especially around the eyelids[25,26]. Usually symptoms appear several hours after the dyeing process and treatment of this allergic reaction caused by the oxidation of residual paradiamine with peroxide in saline solution and application of corticoid creams or lotions. Allergic response to temporary hair color rinses is rare, however, a few incidents of the allergic reaction to semi-permanent hair dyes have been reported[26-28].

CONCLUSION

An article deals with the various options of hair dyes concerning affinity of the hair and shampoo resistant pattern and they are permanent, semi-permanent, temporary and demi-permanent. Any types of hair color provide the satisfactory color delivery, gray coverage, less damage to the hair, more resistance to the shampoo wash. Alkaline medium act as a primary role in hair color mechanism, because the reaction occurs in an alkaline medium and it promotes the opening of the cuticles that allows the penetration of the dyes

molecules into the cortex. P-Phenylenediamine undergoes coupling reaction in the presence of oxidizing agent with higher pH and form a Bandrowski's base. Many articles revealed that the mutagenicity-carcinogenicity of hair dyes and their adverse reaction. Bandrowski's base contributes the carcinogenicity and other adverse effects. The main challenge is to identify the optimum pH to prevent the Bandrowski's base formation in reaction steps and also avoid other adverse effects.

SIGNIFICANCE STATEMENTS

This article provides the complete details of mechanism of hair coloring, its types and safety aspects. Article explains the reaction mechanism of self coupling para phenylene diamine and formation of Bandrowski's base. It reviews the previous knowledge on prominently used colour molecules and their mechanism. It is seen that powder hair dyes with herbal ingredients are prominently in use in south east Asia and it is getting acceptance in other developed markets like EU and Americas. It is observed that optimum pH of hair colour solution plays a crucial role in colour delivery mechanism since very higher pH promotes the formation of allergen like Bandrowski's base. Bandrowski base is reported to be linked with adverse effect. Hence this article would also act as reference literature for understanding safety aspects of powder coloring. Hair colour is dominating category in personal care industry. There are some safety concerns due to indivisual sensitivity to colour dyes like PPO.

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