

Review Article

Hair colouring: what a dermatologist should know?

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ABSTRACT

Hair is an important part of body and a major factor in self-image. A wide variety of hair cosmetic preparations are available and are used regularly by most of the world's population. Hair colouring is one of the commonly done procedure. However, any chemical treatment, normal grooming habits and environmental exposure can produce changes in hair texture or hair breakage. It is necessary for a dermatologist to know the basis of hair colouring, the procedure and the possible side effects it can cause. Also post colour care is also to be known about to prevent further damage to treated hair. This article explains the basic chemistry and mechanism involved in hair dyeing and the basic facts a dermatologist should know.

Keywords: Hair colouring, Paraphenylenediamine, Bleaching, Hair dye, Allergic contact dermatitis

INTRODUCTION

Hair is present in various colours and textures varying with race and ethnicity. Hair colour is determined by the melanocytes found only in the matrix area of the follicle at the base of the cortex directly above the follicular papilla. Eumelanin is the main pigment found in black/brown hair and pheomelanin is the predominant pigment found in blond/red hair. The hair shaft documents the history of the cosmetic practices of an individual.

Hair colouring is a procedure commonly used by both elderly people to conceal their grey hair and youth to achieve a new fashionable colour shade.

A wide variety of natural and synthetic hair-colouring agents is available. Vegetable and metallic dyes are natural colourants, but these have largely been replaced by synthetic dyes. Hair dyes can last longer on chemically treated hair as this hair is porous and unexpected colours can result on chemically treated hair.¹ Hair dyes are classified, non-oxidative and oxidative dyes. Non-oxidative coloration is further divided into two

groups, temporary and semi-permanent colorants. Oxidative colouring is also divided into three groups, permanent, demi permanent and auto-oxidation dyeing.

HAIR FIBRE

Hair consists of a long polymeric structure where peptide chains are held together by various chemical interactions such as covalent bonds (disulphide linkage), hydrogen bonds, ionic and hydrophobic interactions. Among them, disulphide linkage is particularly important for shaping the mechanical properties of the hair fibre.² The hair shaft is divided into four main distinct structures: cuticle, cortex, cell membrane complex (CMC) and the medulla.³

The cuticles are the most external part of the hair strand and keep its physical properties. They regulate the adsorption and diffusion of various active ingredients during bleaching, dyeing and hair treatments. It contains six to ten layers of overlapping cells and each cuticle cell contains an external thin membrane formed by a layer of fatty acid, responsible for the hydrophobic character of the fiber.⁴

The cortex forms the matrix where other proteins and keratin are located, and composes the larger part of the fibrous mass of human hair. They consist of cells filled with keratin and provides mechanical properties to the fibers.⁵ The cortical cells, adjacent to the cuticle, are flatter and contain less sulphur than the cells inside the cortex, which are rich in cystine, amino acids, lysine and histidine, in addition to the melanin granules.⁶ The consequently lower amount of disulphide crosslinks leaves non-keratinous proteins more labile and less resistant to chemical attack than the cystine rich keratinous components of the fibre.⁷

The matrix comprises the major structure of the hair and contains a high concentration of disulphide bonds. It presents considerable swelling when in contact with water. It exhibits keratin macro-fibrils aligned in the direction of the hair strand and melanin granules which are responsible for the hair colour and its photo protection. The CMC consist of cell membranes and adhesive material that “glue” or link the cortical and the cuticle cells. Chemically, CMC is composed of proteins, polysaccharides, and ceramides. It is also responsible for the hair’s natural moisture, making it bright, transparent, and hydrated.

The medulla is the innermost region and its presence along the hair is usually discontinuous or even absent and does not interfere with the hair structure.⁷ The medulla can be empty or filled with sponge keratin and has high lipid concentration, can serve as a pigment reservoir, and can contribute to the brightness of the hair.

TYPES OF HAIR COLOURING

Hair dying systems can be divided into two main categories, oxidative or non-oxidative, and also according to the colour durability after the application on hair strands: temporary, semipermanent, demi permanent and permanent.

Temporary hair colour

They are non-oxidative dyes, with high molecular weight and get deposited on the hair surface post colouring. As there is no oxidising agent, it doesn’t penetrate the cortex. They are anionic and hence highly water soluble and can be removed easily in first shampoo wash. It doesn’t bleach the hair and hence if the original hair colour is black, it is not usually seen and they do not have the power of whitening the hair strand. Because of high molecular weight, it covers only 15% of grey hair. These formulas are easy to use and carry little risk of contact dermatitis. However, these dyes readily stain the scalp and skin. The temporary non-oxidative formulations as single applications, present higher dye concentrations, ranging from 0.1% to 2.0% (w/w) and have the purpose of promoting a stronger dyeing effect. The formulation must get in contact with hair for about 30 min and results will occur immediately. It is suitable for those who wish

for fantasy colors. It resists from three to six washes when applied to bleached hair, like semipermanent dyeing. They are available in powder, shampoos and crayon formulation

Semi-permanent hair dye

They do not use oxidising agents like hydrogen peroxide. These formulations contain basic or cationic dyes with low molar mass, which has a high affinity for hair keratin and resists from three to six washes. Semi-permanent dyes consist of nitro aromatic amines or aromatic nitro-anthraquinone dyes that diffuse into the hair and bind to the hair, however do not attach firmly. Semi-permanent hair dyes are generally applied to freshly shampooed hair and allowed to remain on the hair for approximately 10-40 minutes and the hair is then rinsed with water. The product usually contains nitro-aromatic molecules sometimes mixed with inorganic pigments under neutral or slightly alkaline pH conditions. They penetrate slightly in the cortex, especially because of the high pH value of the product promotes the cuticles opening.⁸ They last for 5-6 shampoo washings and thus require a reapplication. They are, however, unable to lighten hair as they do not contain any bleach. Several products are available in the market: lotions, shampoos, mousses and emulsions. Cosmetic forms must have the ideal viscosity so that they do not flow during the application. These semi-permanent dyes have the potential to cause allergic contact dermatitis. They cause only minimum hair damage as it does not involve any harsh chemical processing.

Demi permanent hair dyes

They are more resistant to shampooing when compared to the semi-permanent dyes. They are applied with hydrogen peroxide or other demi permanent hair products are resistant for up to 20 washes because they consist of a mix of semipermanent molecules with oxidation dye precursors, applied with hydrogen peroxide (H₂O₂). In demi-permanent dyeing, melanin is bleached to a lesser extent. This product utilises a small amount of mono-ethanolamine as an alkaliser to get a pH level of 7-8. Because it doesn’t involve high level of melanin bleaching, it may offer superior hair quality. However, it gives very few colour shades and exhibits poor colour retention.

Permanent hair dyes

Majority in the market belong to this category. They cover up to 100% of white hair strands. Also, it is possible to have dark and light natural hair colour due to the combination of the oxidizing agents with the ammonia hydroxide.¹ They cause permanent dyeing, resistance to shampoo washes and other external factors, such as drying, friction, light, and others. The principal difference between the demi permanent hair dye in comparison with a permanent one is the alkalizing agent used because, in the first, mono-ethanolamine with low

color lightening power is used.⁹ Permanent dyes have the potential to damage the hair shaft. They utilize a series of chemical processes within a single application and all forms must be mixed with hydrogen peroxide before application, without which they are ineffective. The active ingredients penetrate the hair first and then react to form a new chromophore inside hair fibre.

FORMULATION OF HAIR DYE

The colour formation is based on a series of oxidation and coupling reactions and require four major components: the coupling bases; the reaction modifiers; an alkalizing compound; and an oxidizing agent.

Coupling bases

Bases are aromatic compounds derived from benzene, substituted by at least two electron donor groups such as NH₂ and OH in para or ortho positions for easy oxidation, acting as a colour developer.¹⁰

Reaction modifiers/couplers

The modifiers are aromatic m-phenylenediamines, resorcinol, naphthol and other derivatives.¹¹ They are aromatic compounds derived from benzene and substituted by groups such as NH₂ and OH in the meta position, which does not present easy oxidation by H₂O₂. They do not produce significant colour alone yield only feeble colouring through oxidation but can modify them when used with primary intermediaries and oxidants.¹⁰ determine the final shade of the colour after reaction with the oxidized form of the primary intermediate. Hydrogen peroxide oxidises the primary to a highly electrophilic intermediate which then couples with the coupler.

Alkalizing compound

This is necessary to promote the proper pH value for the beginning of the oxidation reaction. The most commonly alkalizing compounds used are ammonia (as ammonium hydroxide) and mono-ethanolamine (MEA) when the formulation contains water, or sodium silicate when it is in solid form (powder). When ammonia helps to remove the natural pigments present in hair as the melanin and in coverage of 100% of white hairs. After the formation of the coloured polymer in inner of cortex, its complete removal is not possible and hence its permanent. However, MEA does not oxidize melanin. Thus, products containing MEA instead of ammonia hydroxide are suitable for maintenance of similar shades or to dark hair.¹²

Oxidising agents

There are basically two types of oxidants used: hydrogen peroxide, when the vehicle is water, and sodium persulfate, when it is a powder.

Reducing agents

Reducing agents are added to oxidative dye formulations to retard the reaction between bases and reaction modifiers and to prevent the initiation of the reaction in the packaging tube during the storage time. e. g., sodium metabisulfite (MBS).

Antioxidants

Antioxidants are necessary to avoid the reaction beginning before the addition of the oxidant itself. A water-soluble antioxidant can prevent the manipulation of bases and initiation of oxidative reaction by reaction modifiers, which may interfere with the final colour of the product. E. g., erythorbic acid (AEB). An oil-soluble antioxidant is used as a vehicle for emulsion hair dyes because this avoids the yellowing of wax and the oxidation of bases and reaction modifiers. e.g., T-butyl quinone (TBQ).¹²

Vehicles

The oxidative dye is available as emulsion (most commonly used), gels, solutions (liquid), and powders.

Others

The peroxides are very unstable, requiring the use of stabilizers such as sodium stannate and the penta sodium pentetate. A mixture of surfactants and solvents is used to disperse dye molecules and ensure hair wetting.

Categories of contents commonly seen in hair dye (Table 1).

HAIR COLOUR FORMATION

To achieve a shade closer to hair colour, a single step process of hair dyeing is only needed. To achieve a light shade, a two-step process is done; bleaching with hydrogen peroxide and ammonium and potassium persulphate, and then dyeing is done.

Hair bleaching: It is commonly used by both elderly people to conceal their grey hair and youth to achieve a new fashionable colour shade. It is believed that the bleaching process begins with the gradual solubilisation of the melanin in hydrogen peroxide at high pH which may detach pigment grains from the hair proteins. The dissolved melanin is fairly easily broken down or depolymerised to carboxylate derivatives that are removed on rinse off.^{13,14} Bleaching can also lead to oxidation of protein components of the hair fibre. Oxidation of cystine cleaves disulphide linkage generating cystic acid. This alters the electrostatic properties of fibre and creates anionic sites which can subsequently lead to higher metal uptake. As the disulphide bond contributes to the tensile properties of the fibre, its cleavage leaves hair fragile and damaged.¹⁵

Bleached hairs showed apparent breaking and fracturing from the leading edge in the cuticle's scales. When the bleached hairs are re-treated with the bleaching agent, the cuticles were not only lifted but also removed from the hair surface. This is why bleached hair fibres present low tensile strength, high porosity and poor sensorial profile.^{16,17}

Table 1: Categories of contents in hair dye.

Oxidising agents	Hydrogen peroxide
Reducing agents	Sodium metabisulfite (MBS)
Stabilizers	Sodium stannate and the penta sodium pentetate
Alkalinizing compound	Ammonia (as ammonium hydroxide) and monoethanolamine (MEA)
Couplers	phenols, meta disubstituted phenylenediamines and phenyleneaminophenols, and various resorcinol (1,3-dihydroxybenzene) derivatives
Dyes	O-nitro anilines (gives yellow and orange shades), aminonitrophenols and their ethers (gives yellow and orange shades), Azo dyes (gives yellow and orange shades), nitrodiphenylamines (gives 'orange to red shades), nitrophenylenediamines (gives colour in the range red to violet), anthraquinone (Gives violet to blue shades).
Preservatives	Parabens, phenoxyethanol
Phot-Oprotectors	Homoxalate, Octinosate, Octocrylene, Oxybenzone
Surfactants	Sodium lauryl sulfate (SLS), sodium laureth sulfate (SLES), disodium laureth sulfosuccinate (DSLESS), disodium lauryl sulfosuccinate (DSLSS), capramidopropylbetaine, sodium lauroyl methyl isethionate (SLMI), cocamidopropyl betaine (CAPB), capryl/capamidopropyl betaine, sodium cocoamphoacetate
Emulsifiers	Oleth-23, cetaryl alcohol
Additives	Fragrance, avocado oil, sunflower oil, olive oil, Dimethicone (conditioning agent)
Solvents	Quaternium-80, benzyl alcohol, and glycols

During the permanent dyeing process, the mixture containing the primary intermediate (e. g., p-phenylenediamine) and the coupling agent (e.g., resorcinol) in alkaline medium (ammonia) is mixed with a hydrogen peroxide solution forming a paste with pH 9, 5. The mixture is applied to the hair and the precursors and hydrogen peroxide diffuse into the hair strand, where after specific chemical reactions a coloured compound

with a high molar mass is formed. The first step is the oxidation of primary to give a reactive intermediate. Under alkaline conditions in the presence of hydrogen peroxide, p-phenylenediamine is oxidised to give quinone diimine (QDI+). They react with the coupler, form the leuco dye (colourless). This is converted into the indoaniline dye within the hair strand. The intermediate compounds have similar sizes and, therefore, an easy and uniform penetration occurs inside the hair.¹⁸ The hair surface in untreated hair has a pH of 4.5 to 5.5. This acidic pH helps to keep the cuticular cells closely opposed to the cortex.¹⁹ The reaction occurs in an alkaline medium that promotes the opening of the cuticles that allows the penetration of the dyes' molecules into the cortex. Primaries are oxidised inside the hair to give reactive intermediates which then react with the couplers. This reaction yields a new chromophore imparting a new colour shade to the fibre. The new chromophore is bigger in size than the starting precursors and thus cannot diffuse out of the fibre easily. Part of the reaction also happens on the cuticles and the molecules are removed in the first washes. In the absence of a coupler, oxidation of the intermediate can form coloured polynuclear compounds generated by the reaction between the diimine and the original amine forming Bandrowski base. Beside oxidation of dye precursors, hydrogen peroxide bleaches naturally occurring melanin pigment inside hair fibre and its decomposition products are subsequently removed during rinse off.

Various parameters may affect the colour formation in the hair dyeing process, such as pH, pause time, hair keratin, and purity of the dye molecule, amongst others. The variation of the pH value directly influences the reaction rate because a more alkaline pH favours the reaction and facilitates the cuticle opening, allowing the penetration of molecules into the cortex.

The pause time is essential for a complete reaction between the bases and reaction modifiers to occur. According to the manufacturer's guidelines, the product must be in contact with the hair from 30 to 45 min after application because it is then possible to ensure colour reproduction and durability to washing.

There are other permanent hair-dye products which produce progressive hair colouration (by reacting with the sulphur of hair keratin) which are not formulated with oxidative hair dyes. They produce gradually a darkening of the hair. Lead acetate and bismuth citrate act as active ingredients in this type of products.²⁰

OTHER HAIR DYES

A number of herbal and ayurvedic dyes are available in India under various trade names such as Black Rose hair dye herbal, optima hair dye, khadi dye, vegetal etc. Though they claim herbal, many of them warrant for a sensitivity test prior to application and allergies have been noticed after application of the same.

Henna (*Lawsonia alba*), is a natural organic substance, and is the most widely used vegetable dye for hair, providing reddish orange shades. In some commercial products, it is mixed with other dyes to increase the range of colour. It consists of the dried leaves of the *Lawsonia alba* plant. Its colouring properties are due to the presence of the substance 2-hydroxy-1,4-naphthoquinone. Natural henna is mixed with tea water or coffee water overnight to make the colour more visible. *Indigofera tinctoria* is a natural dye that is available for commercial use as a green powder. It is mixed with water and applied the same way as henna; When mixed with henna, the colour results are superior.

Other natural dyes from walnut or logwood are used in Asian countries to blacken greying hair. Metallic dyes using the salts of silver, lead or bismuth were traditionally used by men, as the colour change occurs gradually and use is limited to darkening the hair.²¹ The metals are thought to interact with cysteine in the cuticle to form metal sulphides and the deposits gradually accumulate on the cuticle producing brittle, dull hair.

SIDE EFFECTS OF HAIR DYE

Hair colouring is a commonly done procedure; though not investigated fully, it is associated with a lot of side effects. Airborne contact dermatitis, irritant contact dermatitis, photo contact dermatitis, periorbital eczema, hand eczema, lichenoid lesions, and lichen planus pigmentosus-like pigmentary changes were the commonly observed clinical patterns of hair dye dermatitis. Paraphenylenediamine (PPD) is the major culprit responsible for most of the adverse effects. Contact leukoderma, contact urticaria, lymphomatoid papulosis, erythema multiforme-like or prurigo nodularis-like lesions, and anaphylaxis have also occurred with PPD.²²⁻²⁶ PPD intoxication results in multisystem involvement and can cause rhabdomyolysis and acute kidney injury (AKI), flaccid paralysis, severe gastrointestinal manifestations, cardiotoxicity and arrhythmias.²⁷ There are reports of increased risk of bladder carcinoma in women who use permanent dyes frequently and for long periods.²⁸ However, a case-control study conducted at a hospital in Spain with more than 300 women did not show an increased risk of developing bladder cancer related to the regular use of hair dyes.²⁹ It is also mentioned that use of permanent dyes can have a relevant impact on the risk of developing acute leukemia in adults.³⁰ Some dermatological and/or carcinogenic side-effects have been attributed to some chemicals used as hair dyes.³¹ Taylor et al described four cases of leukoderma caused by hair colors.³² In most of these cases, the cause of selective melanocytotoxicity is PPD, and depigmentation at patch test sites has also been reported after a few months of testing.³³ Primary sensitisation can be from sources other than hair dye. Today, PPD is permitted in the European union at a concentration of 6% and toluene-2,5-diamine is permitted at a concentration of 10%.³⁴

IF ALLERGIC TO PPD

A patch test is recommended. Dyes containing paratoluenediamine sulphate (PTDS) may be an option found in newer semi-permanent and permanent dyes and up to 50% may be able to tolerate it.³⁵

Open test: On a clean area behind the ear or on the forearm just below the elbow, the dye mix is applied with a cotton swab and allowed to dry. If there is no reaction in 48 to 72 hours, the dye mix can be safely used on the scalp.

Another hair colouring method has been followed by many, who are allergic to normal hair dye, includes, application of henna leaf paste (mixed with tea/coffee water and lemon juice) for 45-60 min followed by rinsing and then treating the hair with indigo powder paste (powder mixed in warm water) for few hours followed by rinsing. This gives a shade similar to black if done repeatedly. But indigo can stain hands and scalp, hence it is advised to apply only on hair shaft.

STYLES IN COLOURING

Highlighting is a process by which isolated sections of hair are either lightened or darkened. This is done by the 'foil method,' where strands of hair are separated by a comb and laid over an aluminium foil sheet, and then painted with a mixture of hydrogen peroxide and pigment. The foil is then folded, and the contact time depends upon the shade required.

Dip dyeing where only the tips of hair is dyed. Ombré is when a gradually increasing shade is applied from proximal to distal end of hair shaft.

POST COLOURING CARE

Shampoos with cationic surfactant is preferred post colouring.¹⁹ It is mandatory to use conditioners as they flatten the cuticles and seal the gaps that could expose the important cortex to environmental damage. Choosing the right surfactant system and conditioning agents are important for reducing the colour fade. Significantly faster colour fading was observed for sodium lauryl sulphate and sodium lauryl sulphate (surfactants). Sulphate-free surfactants showed statistically significant advantages for colour protection shampoos. A combination of silicone quaternium-22 microemulsion and silicone UV quat (poly-silicone-19) visibly improves the colour protection of shampoo formulations. An increasing level of Poly-silicone-19 correlates with increasing colour protection. An effective colour protection shampoo should be based on mild surfactants, conditioning agents for improved combability and feel of the hair and UV-filters for protection against fading induced by UV light.

To prevent serial fading of hair dye post colouring, it was found that polymers with hydrophobically modified and cationic functionalities are most effective in preventing hair dye dissolution in water. A primary example of a polymer within this category is a cationic terpolymer of vinylpyrrolidone, dimethylaminopropyl methacrylamide, and methacryloylamino propyl lauryl-dimonium chloride.³⁶

CONCLUSION

Hair colouring is getting common these days and people want to look young and trendy. However, it is associated with structural and systemic side effects. Hence, more developments should come in the field of hair colour to prevent the side effects and reduce structural side effects.

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