Hair Colouring

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. 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. **The hair shaft is divided into four main distinct structures: cuticle, cortex, cell membrane complex (CMC) and the medulla**. 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.

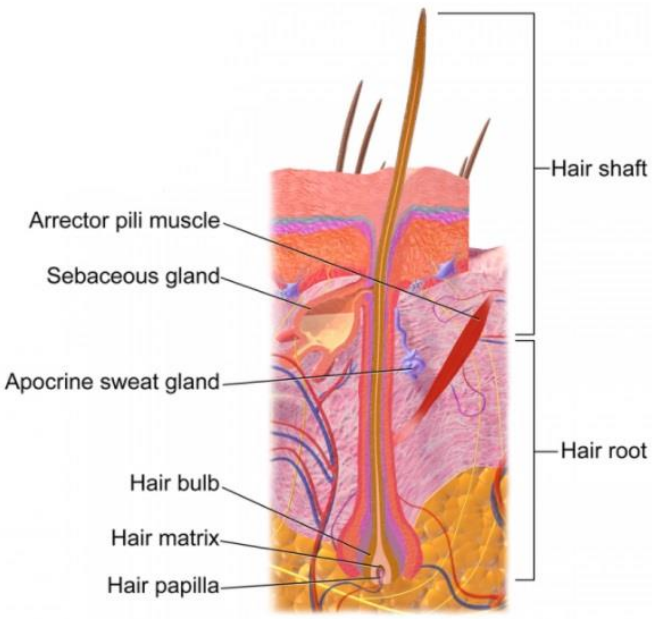

Figure 10.5.2 A hair follicle has a sebaceous gland and an arrector pili muscle.

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. 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. 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.

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. 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. 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.

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. 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.

1. 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

2. 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 nitroanthraquinone 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. 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.

3. 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 (H_2O_2). In demi-permanent dyeing, melanin is bleached to a lesser extent. This product utilises a small amount of monoethanolamine 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. 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. 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.

1.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.

2.Reaction modifiers/couplers

The modifiers are aromatic m-phenylenediamines, resorcinol, naphthol and other derivatives. 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. 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.

3.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.

4.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.

5.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).

6.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).

7.Vehicles

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

8.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).

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
Alkalizing 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), nitrophenyienediamines (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