

A BRIEF INTRODUCTION TO THE COLOUR OF HAIR

THE STRUCTURE OF HAIR

To understand the chemistry of hair, we first must look at the structure of our hair.

The hair is made of 95% Keratin, a hard, fibrous protein, which is insoluble in water, thus ensuring impermeability and protection for the hair [1]. The hair shaft is comprised of three layers (Figure 1). The inner layer is the Medulla, the second layer is the Cortex and the outer layer is the Cuticle. The Cortex makes up the majority of the hair shaft. The Cuticle is a tightly formed structure made of shingle-like overlapping scales. The pigments, which are protein granules, are stored in the Cortex of the hair beneath the scaly cuticle layer. It is both the Cortex and the Medulla that holds the hair's pigment, giving it its colour.

Around 18 amino acids can be found in the hair, such as Proline, Threonine, Leucine and Arginine [1]. Chemically, human hair contains approximately 95% Keratin with the rest being made up of water, lipids (fats), disulphide bridges (e.g the sulfurated amino acid cystine), and low concentrations of trace minerals (e.g. iron, zinc, copper...).

Cystine is responsible for adding rigidity and resistance to the entire structure.

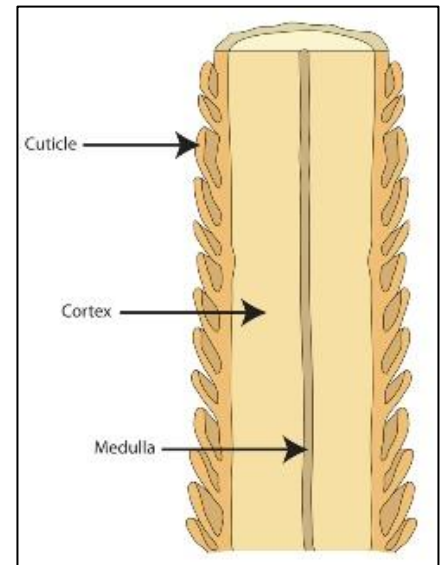


Figure 1 | Schematic cross section of a strand of hair.[1]

WHAT DETERMINES HAIR COLOUR?

There are two types of Melanin protein found in the hair: Eumelanin, which is responsible for hair shades from black to brown, and Pheomelanin, which is responsible for red and yellow-ish colours [2]. Absence of pigment results in white or grey hair. The melanin type and granule size determine the colour of hair, while the density of distribution of these pigment granules determines how light or dark the hair is.



Figure 2 | Colour pigments in hair. [2]

HOW DO HAIR DYES PENETRATE THE HAIR?

There are two main chemical ingredients in hair dyes, hydrogen peroxide (H_2O_2) and ammonia (NH_3). Hydrogen peroxide (also known as the developer or oxidizing agent), helps to initiate the colour-forming process and creates longer-lasting colour. It oxidizes the natural melanin pigments in hair, removing some of the conjugated double bonds that lead to their colour, and making their molecules colourless. Peroxide breaks chemical bonds in hair, releasing sulfur, which also accounts for the characteristic odour of hair colouring products [7]. As the melanin is decolourized, a new permanent colour is bonded to the hair cortex. The larger the volume of the developer, the greater the amount of sulfur is removed from the hair. Loss of sulfur causes hair to harden and lose weight. Hydrogen peroxide is generally kept at 30% volume or lower.

The other chemical, ammonia, acts as a catalyst when the permanent hair colour comes together with the peroxide. Ammonia causes the dye molecules to after pass into the hair and induce more permanent colouring (**Figure 3**). It also helps lighten the natural hair colour in the presence of hydrogen peroxide.

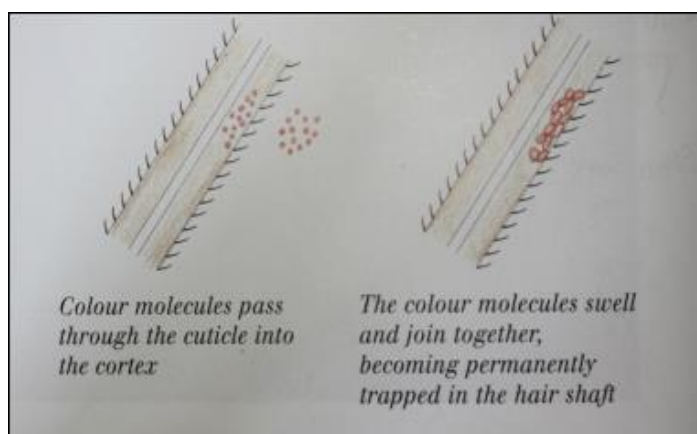


Figure 3 | The swelling of the cuticles allowing pigment molecules (granules) to pass through. Once through they bind together and become trapped in the cortex.

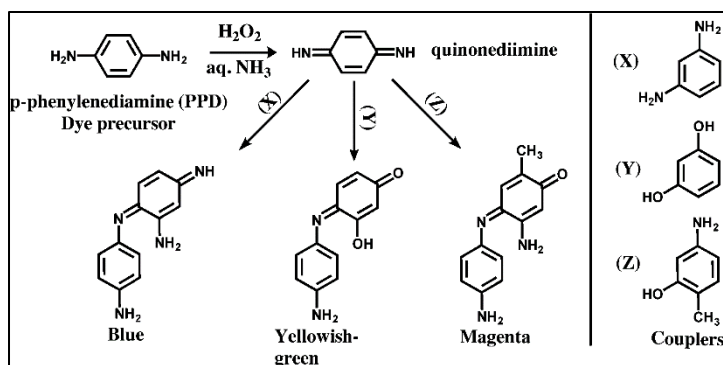


Figure 4 | Reaction schemes for dye synthesis. [3]

Other properties of the hair, such as the degree of damage and porosity, will also affect dye penetration. A high pH (usually about 10) causes the hair to swell and aids penetration, giving longer-lasting or 'permanent' colouring effects that are more resistant to washing.

The scheme beside (**Figure 4**) shows the reaction of a common dye intermediate, 1,4-diaminobenzene, with three different couplers in the presence of an oxidizer at pH 9-10.

HOW DO DYES PRODUCE A COLOUR?

The colourant contains two types of molecule known as the dye intermediate and the coupler, while the developer contains the oxidizing agent (generally hydrogen peroxide).

One commonly used primary intermediate, paraphenylenediamine (PPD) becomes very reactive and produces dye molecules when exposed to an oxidizing agent. However, the PPD itself can only produce a dark brown colour. To result in different colours, couplers, or coupling agents, are added to the hair dye mixture.

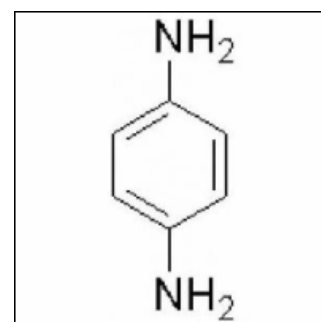


Figure 5 | The paraphenylenediamine (PPD) molecule. [4]

As with most organic dyes, they don't appear to be coloured by themselves, but once reacted with the primary intermediate molecules, they can produce a wide range of hair dye colours.

The concentration of the couplers is responsible for determining the intensity (lightness/darkness) of a given colour.

The twenty starting molecules [7], based on aromatic rings, are not coloured. The main groups that are substituted onto the benzene ring are electron-rich groups, e.g. amino (-NH₂) and hydroxyl (-OH) groups. These electron-rich groups 'repel' the electrons into the ring system to form a delocalised cloud above and below the annular plane [5].

The two types of starting molecules, primaries and couplers are generally ortho- or para-substituted benzene rings and meta-substituted benzene rings respectively (**Figure 6**).

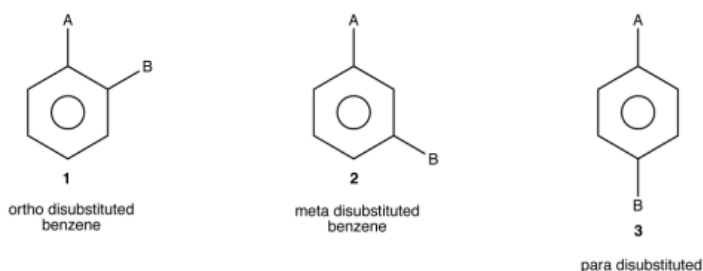


Figure 6 | Ortho, Meta & para substituted benzene rings.

The reason why any molecule appears coloured is that they absorb energy within the visible part of the electromagnetic spectrum. The discrete frequencies absorbed is determined by the unique electronic structure of that material. Different conjugated systems will exhibit different discrete energy levels for which they can absorb photons corresponding to the gaps separating them.

The quantised energy of the photons which are absorbed corresponds to a wavelength (or frequency) of light ($E=h\nu$). When a colour is absorbed from a light source, the reflected/transmitted colour will be complementary to that (e.g. a substance absorbing strongly in the orange part of the spectrum will exhibit the complementary colour – blue, **Figure 7**).

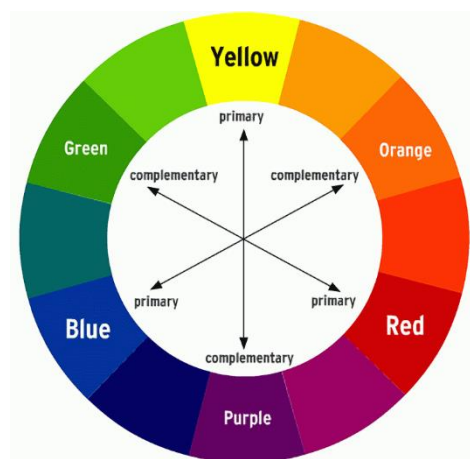


Figure 7 | The colour wheel, demonstrating the complimentary pair principle. [6]

By varying the number of double bonds on the types of groups substituted on the benzene rings, controls the energy of photons absorbed and hence the colour. Due to the starting molecules only possessing 3 double bonds, these molecules absorb light in the UV regime (beyond the visible spectrum), and therefore don't appear to be coloured. When the developer is mixed with the tint, the hydrogen peroxide initiates an oxidation reaction. This results in the loss of electrons from the starting molecules, allowing the benzene rings to react to form larger compounds. These larger compounds contain either two or three benzene rings, and therefore numerous double bonds. The greater the number of double bonds, the more likely a delocalised electron structure is formed which has energy levels that can allow for absorption within the visible part of the spectrum. The dyes now show a colour.

3 COUPLING AGENTS



Figure 8| Coupling agents to create different colours of hair dye. [7]

REFERENCES

- [1] Design Essentials Suriname, "Hair Structure," 2014. [Online]. Available: <http://designessentials.nl/hair-structure>.
- [2] Karen Welch, Chelsea S., "Toning Blonde Hair," SoZo HAIR Salon, 2016. [Online]. Available: <http://sozohair.net/toning-blonde-hair/>.
- [3] Amit Delori,*a Andrew J. Urquhart*b and Iain D. H. Oswald*a, "Supramolecular hair dyes: a new application of cocrystallization†," *CrysEngComm*, no. 28, 2016.
- [4] G. J. Nohynek, "Toxicology of Hair Dyes," *The Science of Hair Care*, 2005.
- [5] Frank Harris, Fave Waistnidge, Mark Gale, Mutlu Cukorva, "Salters Advanced Chemistry for OCR B," 4 ed., Oxford, Cambridge and RSA (OCR), pp. 296-298.
- [6] R. Sahu, "CHAPTER(3) - Coordination chemistry - Artist's Colour Wheel," *Chemquiries*, April 2019. [Online]. Available: <https://www.chemquiries.com/2019/04/artists-colour-wheel.html>.
- [7] CompoundChem, "The Chemistry of Permanent Hair Dyes," CompoundChem, 2015.