

Formulation Aspect Of Hair Dyes

Anchal Kulte*, Ashish Sahu, Dhanshri Shripat**, Aryan Kande***

Abstract: Hair dye cosmetic products are used for colouring hair. These products are mainly classified into two categories according to their duration in the hair, i.e., temporary and permanent. This classification is in line with the type of active ingredients involved in the dyeing process and with the dyeing process itself, commonly known as non-oxidative and oxidative hair dye products. Owing to the different side effects described for these active cosmetic ingredients, some of them have been prohibited during the past years, whereas others have been restricted in the different legislations in force. The aim of this chapter is to familiarize the reader with the different compounds used as hair dyes and the legislation regulating these compounds, and especially to review the existing analytical methods for hair dye determination in cosmetic products.

Keywords: Hair Dye, Cometics, Amonia, Analytical Method, Hair Color

INTRODUCTION:

A variety of hair colours are observed between the people living in east and the people living in west. The agents that are responsible for variety of hair colours are only two which are pheomelanin and eumelanins. pheomelanin's impart different shades of red and yellow whereas, eumelanin imparts different shades of dark brown and black. A variety of hair colours are observed due to the following parameters.:

- The combination of pheomelanin and eumelanins.
- The quantity of the pigment present.
- The size of the granules of the pigments.
- The distribution of granules of the pigments.

Definition: Hair colourants are the cosmetic preparations which are used by men and women either to change the natural hair colour or to mask grey hair.

Properties:

1. The formulation of the hair colourant should be stable.
2. They should colour the hair evenly.
3. They should not lead to loss of the natural shine of hair.
4. The shaft of the hair must not be damaged.
5. The natural moisture of the hair must not be lost.
6. Must possess properties like non-irritant and non-sensitizing.
7. Must be non-toxic in nature. Must impart stable colour to the hair.

2.1 Classification of hair colourants :

1. Temporary hair colourants.
2. Semi-permanent hair colourants/Direct dyes,
3. Oxidative dyeing systems: It includes:
 - (A) Semi-permanent hair colourants.
 - (B) Permanent hair colourants.
4. Gradual hair colourants.
5. Natural dye

1. Temporary Hair Colorants: They are leave-in preparations. The hair is not rinsed after the application of the colorant. The colorant is easily removed with one wash using a shampoo because they are absorbed in to the cuticle and cannot enter into the cortex of the hair. They are rarely called as water rinses. Basically, temporary hair colorants consist of dye stuffs and acid. The different dye stuffs are acid dyes, basic dyes, metalized dye sand disperse dyes. Chemically the dye stuffs are azo dyes, anthraquinone dyes, benzoquinone mine dyes, triphenyl methane dyes, phenazine dyes and xanthenic dyes. The hair colourants are available in different formulations like powders, crayons, liquids, and shampoos.

(a) Powder Formulations: They are mostly used in theoretical make up and masquerades. The powder consists of dye stuff and acid like citric acid or tartaric acid. They are available in sachets.

Formula-1	Quantity for 100 g
Certified colour	5 g
Tartaric acid (buffer)	95 g

Application Technique: The powder is dissolved in 250 ml of water and this solution is applied on wet hair after shampooing.

(b) Crayon Formulations: These temporary hair colorants are applied between the applications of permanent hair colorants. They colour the new growing hair. They are available in many shades of colours. The composition of crayon is soap, waxes, dyes or pigments.

Formula-1	Quantity for 100 g
Stearic acid (anionic surfactant)	15 g

Triethanolamine (surfactant)	7 g
Beeswax (wax)	50 g
Carnauba wax(wax)	13 g
Ozokerite (wax)	7 g
Glyceryl mono stearate (surfactant)	6 g
Tragacanth (gum)	2 g
colour	q.s

Method: Triethanolamine, glyceryl monostearate and tragacanth are heated to 70°C. Stearic acid is incorporated in the above mixture and the mixture is heated to 75°C. Beeswax and carnauba wax are melted separately at 70--80°C. The molten waxes are added to the above mixture and stirred well. Colour is added and the mixture is stirred well. This mixture is then poured into the moulds.

Formula-2	Quantity for 100 g
Sodium stearate(thickener)	18 g
Gum Arabica (gum)	25 g
Glycerine (surfactant)	15 g
Color	17 g
Water(solvent)	25 g

Method: A mixture of water and glycerine is prepared and divided into two parts. Gum Arabica is added to one portion. Sodium stearate is added to the other portion and it is dissolved by warming. Both the portions are mixed and colour is added. This mixture is milled to form a paste. The paste is introduced into moulds and allowed to dry with the help of heat.

(c) Colour Shampoos: They develop a temporary tinge of colour. The base used in the preparation consists of sulphonated oils, anionic or non-ionic surfactants. They are available in only few colour shades.

Formula	Qty.For.100 g
Ammonium lauryl sulphate (surfactant)	30 g
Coco diethanolamine (pearlescent stabilizer)	2 g
Water (solvent)	To make up 100 g

2. Semi-permanent Hair Colourants / Direct Dyes: These colourants have a long lasting, colour retaining ability when compared to colour shampoos. The colour produced is stronger as well. Dark colours are obtained with the colourants though they do not contain H₂O₂. This offers an advantage that the melanin of the hair doesn't get bleached but is only masked with the colourant. The colour obtained on the grey hair is different than the black (pigmented) hair because of which the hairs are highlighted. The colourants are easily applied. This colour is not lost with one wash, but is gradually lost in 5 - 8 washes with shampoo. Fragrance may be added in the composition of the colourant.⁸

Ingredient: The semi-permanent hair colourants are composed of the following constituents.

- Dye
- Water
- Organic solvent like alcohol, derivatives of glycol.
- Fatty acid, fatty acid amide.
- Thickener.
- Surfactant
- Perfume
- Aliphatic primary amines which work as co-solvent and buffer., Example: 2 - amino, 2-methylpropanol.⁹

(a) Dyes: The action of the dye or dyes is observed on hair or white wool before proceeding for the colour preparation.

The following factors are of great concern during the use of the dyes.

- Aqueous solution of the dye.
- The pH effect on the dye.
- The composition of the base added.
- The effect of solvents added.

The dyes which impart different shades belong to the following categories:(i) O-nitro anilines. (Gives yellow and orange shades),(ii) Aminonitrophenols and their ethers (gives yellow and orange shades),(iii) Azo dyes (Gives yellow and orange shades),(iv) Nitrodiphenylamines (Gives 'orange to red shades), (v) Nitrophenylenediamines (Gives colour in the range red to violet).The semi-permanent hair colourants diffuse into and out of the hair which lead to off-shade fading. Therefore, colourants are selected which have a wide range of molecular sizes. This helps in,

- Even colouring of the hair.

- The properties of the dye like permeability and substantivity for porous tips of hair and undamaged root ends are compensated.

Demerits of Semi-permanent Hair Colourants: The hair ends get damaged which is referred as warm wearing. Large sized amino-containing molecules like Disperse Blue 1 and Disperse Violet 1 are used to prevent warm wearing of the ends. These molecules are easily washed off.

Formula	Quantity for 100 g
Quaternary ammonium compound (color)	10-12 g
Anionic surfactant (surfactant)	8-6 g
Acid (buffer)	6-8 g
Alkanolamide (surfactant)	4-6 g
Dye stuff (color)	1-2 g
Water (solvent)	To make a100 g

3. Oxidative Dyeing Systems: These dyes are also called as 'para dyes. At the time of application, these dyes are colourless but turn to a particular colour after undergoing chemical reactions on the hair. The chemical reactions include the following reactions in alkaline pH, which are oxidation and coupling and condensation.

Ingredients: The ingredients of these dyes which render the above reactions are bases, couplers, and oxidizing agent.

(a) Bases: They are primary intermediates. Chemically they are aromatic compounds.

(b) Couplers: They are aromatic in nature, and are referred as modifiers. They are the derivatives of benzene which show - NH₂ and - OH substitutions at meta position. Oxidation of couplers with hydrogen peroxide is difficult to achieve. Example: 2, 4-diaminoanisole, Resorcinol, m-chloro resorcinol, m-phenylene-diamine.

(c) Oxidizing Agents: Commonly used oxidizing agent is hydrogen peroxide. Formulation of Oxidative Dyeing Systems: The following factors are of great concern during the preparation of oxidation dyes.

1. Formulation bases
2. Dye components: It includes oxidation base and coupling agent.
3. Alkali.
4. Oxidizing agents
5. Antioxidant

1. Formulation Bases: They are used as vehicles for dyes (amino dyes) and modifiers. The vehicle is one which uniformly distributes the colourant mixture on the hair. Example: In amino dyes, a mixture of water (48-79.45%), ethyl alcohol (20-50%) glycerine (0.5 - 2%) is used because the amino dye has low aqueous solubility. If the preparation is an emulsion i.e., cream or lotion (rather than a solution) the distribution of the preparation on hair is more even. The formulation bases may be of the following kinds such as emulsion type, bleach-dye combination products, and powder preparations. The emulsion type preparations are of two types.

(a) Foaming-type Creams: They are emulsified using surfactants like monoethanolamine lauryl sulphate and ethylene glycol monostearate.

Formula	Quantity for 100g
Monoethanolamide lauryl sulphate(surfactant)	10 g
Ethylene glycol monostearate (surfactant)	1g
Preservative	q.s
Water(solvent)	To make 100g

(b) Non-Foaming-type Creams: They are emulsified by using mineral oil, cetyl alcohol and non-ionic emulsifier.

Formula	Quantity for 100 g
Mineral oil (emulsifying agent +emollient)	1.5 g
Cetyl alcohol (emulsifying agent +emollient)	5 g
Non-ionic emulsifier (emulsifying agent)	3-5 g
Preservative	q.s
Water (solvent)	To make 100g

Other additives like hydrous lanolin, lecithin, sequestering agent may be added to improve the formulation as a whole.

Bleach-dye Combination Products: They are used to bleach as well as colour the hair. Increased levels of ammonium hydroxide are used along with proportionate amounts of hydrogen peroxide Powder Preparation: It contains oxidizing agent such as sodium peroxide and alkali ammonium hydroxide. This powder preparation is made into a paste using water and is then applied.

2. Dye Components:

(a) Oxidation bases: By using varying concentrations of p-phenylene diamine or p-toluene diamine, a number of shades can be achieved.

(b) Coupling Agents: Instead of coupling agents, direct colouring agent can also be used, coupling agents modify the shade and stabilize it. The time required to develop color with different modifiers.

3. Alkali: The oxidation dyes work best in alkaline medium. Therefore, alkali is incorporated in their composition. The best alkali is ammonium hydroxide. It leaves no evidence of its presence on the hair. It is used in a concentration of 1 - 2% in the final preparation. Because of its odour, it is completely or partially replaced with ammonium carbonate, monoethanolamine, guanidine or arginine derivatives, diethanolamine, triethanolamine, alkanolamide etc,

4. Oxidizing Agent: On exposure to air, dyes such as amino dyes turn black. However oxidizing agent is added in its composition to achieve the desired colour. Examples are ferric chloride, potassium permanganate, potassium dichromate, hydrogen peroxide etc. Hydrogen peroxide is popularly used. It is used in a concentration of 5 - 6% solution which generates 20 volumes of oxygen. is responsible to develop colour on the hair. It is sold in a package containing two containers. One container contains dye and the other contains the developer.

5. Antioxidant: During the manufacturing of dyes, especially amino dyes, an atmosphere of nitrogen is maintained to prevent the darkening of the dye. Since dyes (amino dye) are darkened on exposure to air. Instead of maintaining nitrogen atmosphere, chemical antioxidant like sodium sulphite is included in the preparation. The total amount of base and the coupling agent used gives the amount of sodium sulphite to be used in the preparation. If darker shades are desired, then the amount of sodium sulphite is increased. The oxidative dyeing system consists of the semi-permanent hair colourants and the permanent hair colourants.

(A) Semi-permanent Hair Colourants: The semi-permanent and permanent hair colourants are the two classes of oxidation dyes or oxidative dyeing systems. They differ in the extent of giving light colour shades to the hair. The common constituents of both the classes are alkalizing agents, oxidants, dyes, solvents and surfactants.

(I). Alkalizing Agents: The alkalizing agents are added.

- To increase the pH of the formulation to an optimal level.
- To generate active oxidizers from hydrogen peroxide.
- To swell the hair fibres for absorption of dye.

Examples of alkalizing agents include ammonia, Monoethanolamine. The rate of bleaching of hair is based on the following factors and the rate of bleaching is directly proportional to the following factors.

- ph.
- Concentration of hydrogen peroxide.
- Amine added.

The rate of bleaching of different amines and ammonia is shown. Tertiary amine < secondary amine < primary amine < ammonia. It means ammonia is a strong alkalizing agent, which is used-widely. Instead of ammonia, high level of monoethanolamine is used alone or monoethanolamine and ammonia are used in combination. The semi-permanent products employ monoethanolamine alone, where a little bleaching is required, whereas hindered primary, secondary or tertiary amines are employed, when no bleaching is required.

(II). Oxidant: Oxidant is added in the composition of the colourants to generate active species (like p- phenylene diamine, benzoquinone monoamine) for coupling. Oxidants are used to bleach melanin present in the hair. Light colour shades are obtained when the grey and pigmented hair are coloured evenly by using semi-permanent colourants.

(III). Dye: Dyes are used to impart the desired colour shade to the hair.

(IV). Solvents: The constituents of the colourants which are not soluble in water, are dissolved by using solvents, so that a homogenous system is obtained.

(V). Surfactant: It reduces the surface tension between the different ingredients, to make a homogeneous preparation.

(B) Permanent Hair Colourants: The colour produced by these colourants last longer when compared to semi-permanent colourants. Actually, it is the precursor of dye which when applied undergoes chemical changes to form the colour rather than the dye itself. They are available in light colour shades to dark colour shades. It is the growth of hair more than fading of colour, which arises the need to re-dye. This results in stripped appearance of the hair. The oxidation dyes may cause allergic reactions in some individuals. According to the rules of drugs and cosmetics, the preparation must contain the caution in English, local and other regional languages on both the inner and outer labels.

Caution: "The preparation may cause irritation of skin in some individuals; therefore, it is advised to go for patch testing before using it on hair. The eyelashes and eyebrows are not dyed because it may cause blindness." Example: Metallic hair colourant / colour restorers.

4. Gradual colourant: it includes heavy metals in its composition. The hair is gradually coloured with several application of the colourant. The heavy metals used are lead or bismuth in their salt forms. The salts of the heavy metals are made into solutions and are used in the preparations. The preparation is applied many times because the colour develops gradually.

Demerit: since, the preparation includes heavy metals, it offer negative effects on the health. Therefore, the use of these colourants is declined.

5. Natural dyes: Since, antiquity, plant materials are looked upon as beneficial sources for various ailments and other purposes. The leaves are used as colourants:

(a) Henna: The leaves of henna are powdered and sold. The paste is formed by mixing the henna powder in hot water. The paste is directly applied on hair and a warm towel is wrapped around the head to enhance the colouring effect gives reddish colour to the hair. Henna is non-toxic and non-sensitizing. The active constituent of henna is lawsone, which is chemically 2-hydroxy-14 -

napthaquinone. It is responsible for imparting the color. Indigo leaves or synthetic indigo is added to henna to alter the colour. Apart from this, pyrogallic acid and metallic salts like copper sulphate are added. An increased level of pyrogallic acid added to henna, gives darker shades.

(a) Camomile: The flowers of camomile are used to obtain the colour. The flowers which contain the active principle are powdered. Its paste is made by mixing the powder with hot water and applied on the hair. A warm towel is wrapped over the head to enhance the colouring effect. The colour achieved is due to the navy-blue volatile oil obtained in the process. Either 2 parts of kaolin or 1 part of fuller's earth is added to camomile powder to form a cohesive composition. Henna is mixed with camomole in varying proportions, to modify the colours.¹⁰

2.2 Evaluation of hair colourant:

The following tests are carried out to evaluate hair colourants.

1. The sensitization tests

2. The toxic effect tests

1. The Sensitization Test: The test is carried out on animal skin. The colourants applied on the skin and is kept under observation for 24 hrs. If no reaction occurs, then the colourant is said to be non-sensitizing or non-irritant. Histopathological study is carried out as per requirements.

2. The Toxic Effect Test: Toxic effects are studied in animals to know about the long-term effects of the preparations.¹¹



Conclusion: The study says that first yearly day's hair color launched people think that 40 years above women. But present transformation yearly days to today hair color market growing in by 2700 cr due to the not only because of gray hair. The reason company targeted young generation towards variety Gray of styles in colouring hair and generally at present scenario increasing younger generation to middle generation grey hair. So, at present in India hair colorants market is 17% To fill that gap companies eventually concentrating variant in products. So Above report shows in analysis hair dye how the companies transformed up to know in Hair dye product in market and haircare industry.

References

1. Gaurav Kumar Sharma Text Book of cosmetic formulation
2. Birchall J, Brain KR. Microneedle arrays as transcutaneous delivery devices. In: Walters KA, Roberts MS, eds. Dermatologic, Cosmeceutic, and Cosmetic Development: Therapeutic and Novel Approaches. New York: Informa Healthcare, 2008:577–589
3. Barreiro-Iglesias R, Alvarez-Lorenzo C, Concheiro A. Incorporation of small quantities of surfactants as a way to improve the rheological and diffusional behavior of carbopol gels. *J ContrRel* 2001; 77:59–75.
4. .A-sasutjarit R, Sirivat A, Vayumhasuwan P. Viscoelastic properties of Carbopol 940 g els and their relationships to piroxicam diffusion coefficients in gel bases. *Pharm Res* 2005; 22:2134–2140.
5. Barry BW, *Dermatological Formulations, Percutaneous Absorption*. New York: Marcel Dekker, 1983.
6. www.nature.com/articles/3302375
7. <https://pubmed.ncbi.nlm.nih.gov/12413418/>
8. [.https://www.nature.com/articles/330237](https://www.nature.com/articles/330237)