



# Different Eras of Hair Coloring

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## ABSTRACT

Hair plays a significant role in body image, and its appearance can be changed easily. The cosmetic industry has gone through an innovative change over the last two decades. The focus has dramatically changed from cleaning to repair, reducing oxidative damage, and stimulating growth. Newer shorter procedures have evolved to make hair look naturally more lustrous, smooth, and manageable. Therefore, cosmetics have been used to change hair appearance since time immemorial. The cosmetics industry has developed efficient products that can be used on healthy hair, grey hairs or act on related hair and scalp diseases. Dyes beautify the hair by bleaching or coloring it briefly, for temporary periods, or permanently, depending on the dye composition (oxidative or nonoxidative) and its degree of penetration of the hair shaft. The story of hair coloring is influenced by the use of both natural and synthetic materials.

**Keywords – Hair structure, hair coloring, evolution, dye, pigments.**

## 1. INTRODUCTION

Hair is a unique character found in all mammals. In humans, it is a special feature, especially in females, but its main functions are in the protection of the skin. Eyebrows and eyelashes stop things from entering the eyes, while scalp hair prevents sunlight, cold, and physical damage to the head and neck.[1] The structure of hair contains cuticle, cortex, medulla, hair follicle, hair bulb, etc., The hair follicle is the structural unit responsible for the formation and production of hair fibres. Hair follicles are infoldings of the superficial epithelium enclosing a dermal part, the dermal papilla.[2] Hair growth is a cyclic event with stages of growth, and shedding, followed by the formation of new hair. In anagen (the growth phase), the hair fibres are produced from the hair bulb. Matrix cells are situated slightly above the dermal papilla in the bottom portion of the follicle, at the level of the midpart of the hair bulb. This germinative cell population is very active. The gross structure of the follicle also determines the shape of the hair produced. A straight follicle result in straight hair and a structurally curved follicle produces curly hair.[3]

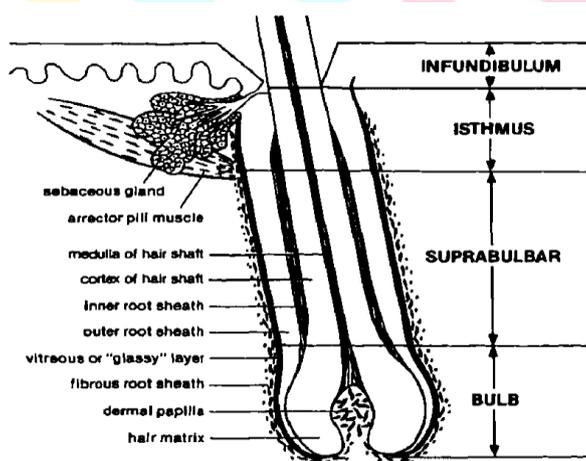


Figure 1: Diagram of hair.

Hairs are differentiated by their forms, types, and color, depending on the balance of different types of melanin (brown to black, indolic eumelanin, and yellow to reddish-brown, sulfur-containing pheomelanin); length; diameter; and cross-sectional shape. African, Asian, and European are the three traditional ethnic human categories according to which human hair is typically categorized.[4]

- **Types of hair color**

Different tone of hair color is due to melanin. Melanin is produced in a specific type of cell called melanocytes, which is found in the skin, eyes, and hair follicles. The type and amount of melanin and its distribution in cells create differences in hair, skin, and eye color. Eumelanin and pheomelanin are two types of melanin in our hair. Eumelanin is additionally referred to as the brown-black pigment, whereas pheomelanin is understood because of the red-orange pigment.[5]

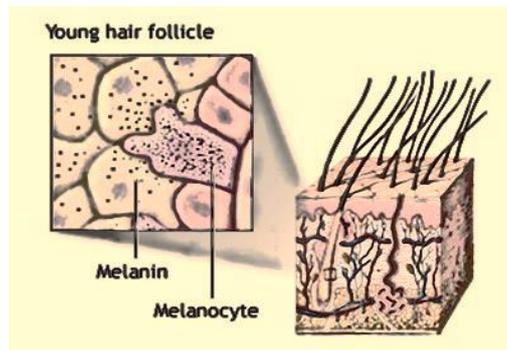


Figure 2: Melanin in hair.

- a) Human red hair: - In pheomelanin red hair, melanocytes contain pheomelanosomes and synthesize mostly pheomelanin. In other human red hair, melanocytes synthesize both eu- and pheomelanin's. A majority of melanocytes produce pheomelanosomes and also mosaic melanosomes. [6]



Figure 3: Human red hairs.

- b) Human blond hair: - Melanocytes produce eumelanosomes and synthesize both eu- and pheomelanin's. Melanosomes are not fully melanized and melanin granules are smaller and less numerous than in dark-haired subjects. Thus, the ultrastructural aspects suggests that the light color in blond hair is due to a quantitative decrease in the production and melanisation of melanosomes.[7]



Figure 4: Human blond hair.

- c) Human black and brown hair: - Follicular melanocytes produce typical eumelanosomes with ultrastructural characteristics identical to those of the epidermal melanosomes of Caucasoids and negroids. Lighter brown hair has smaller melanosomes.[8]



Figure 5: Human black hairs.



Figure 6: Human brown hairs.

- d) Grey and white hair: - Aging leads to "greying" and whitening of hair with high variability between individuals. Color changes are due to a decrease in the number of hair follicle melanocytes. In the melanocytic zone of the grey hair bulb, the number of melanocytes appears normal or slightly reduced, but the pigment cells contain very few melanosomes and appear to have little activity. In white hair, melanocytes are scarce and dopa-negative or entirely absent, and immunoreactive tyrosinase antigen cannot be detected in hair bulbs. However, as suggested by the detection of tyrosinase mRNA, amelanotic melanocytes may be present in the outer root sheath. This decrease in the number of hair follicle melanocytes, resulting in greying, might be linked to a defect in redox-regulated melanin synthesis. This defect might increase the auto-cytotoxicity of certain metabolic intermediates within the pigment cells. [8]



Figure 7: Human grey hairs.

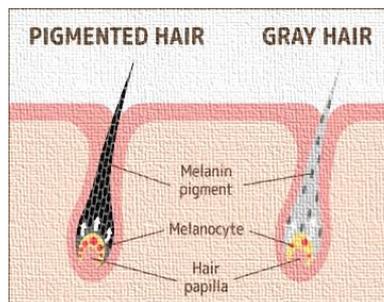


Figure 8: Melanin in grey hairs.

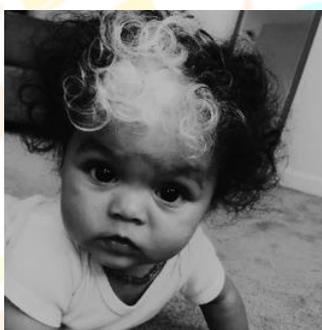


Figure 9: Human white hairs.

#### • Need of hair coloring [9]

- 1) The reason people color their hair is to cover grey. This process began centuries ago, with products using Heena, metallic- type powders, and other organic substances. The colors amplify or cover grey for natural, healthy results.
- 2) Colors produce natural-looking shade that not only enhance hair color; but skin tone as well.
- 3) Color produces many intensified and fashion tones that shine.
- 4) Colouring can make anyone's hair look thicker by correctly matching. Haircuts and hairstyles with color seem sculpted.
- 5) Psychological boosts are another reason people color their hair. People often need a change, just to give them a new outlook.

## 2. EVALUTION OF HAIR COLORING THROUGHOUT THE HISTORY

The history of hair coloring products is based on the use of naturally occurring materials. Which are obtained from plants, insects and metals. One of the first colorants was made from henna leaves. Which is widely used for long time in many areas from Egypt through the middle east to Asia. A large number of other plant-based materials have been used to color the hairs.[10] In ancient Greece, hair was made lighter by rinsing it in a potassium solution and rubbing in a pomade of yellow flower petals and pollen. Greek in 14th Century washing their hair with a special ointment made in Athens and then sitting in the sun to turn their hair golden. Ladies in 16th Century bleaching their hairs in the sun. In 1694, in that period to achieve black hair color the mixture of elderberries and wine was used. The use of radish extract to achieve an auburn shade, and a blend of ceruse, lime, and saffron or turmeric for blond hair. Gray hair was darkened by lead combs, which deposited lead particles on each strand. [11]

The first artificial dye was synthesized in the laboratory in 1856. In 1863, William Henry Perkin developed the first synthetic dye called Mauveine. Soon after, his chemistry professor August Hoffman derived a color changing molecule from Mauveine (called parphenylenediamine, or PPD), and it remains the foundation for most permanent hair dyes today. Eugene Schueller produced the first synthetic hair colorant in 1907. In 1920s the technique of permanent hair coloring was developed, involving oxidizing and alkalizing agent. [12]

## 3. SOURCES OF HAIR COLOUR

There are various ways of hair coloring in which different dyes/colors and pigments are used individually or in combination. The source of hair dye and color are classified as synthetic and natural. They are mentioned below:

## • Synthetic dyes

Many studies established the diffusion path of the dye molecule to the inner hair fibres. It involves the permeation of the molecules into inter-cuticular regions, passing through non-keratinized regions of the endocuticle and the intracellular cement. In later stages, it migrates to keratinized regions and, eventually, reaches the macro fibrils, before being incorporated into the matrix.[13] Because the dye molecule only interacts with the hair cuticles, the temporary and semipermanent non-oxidative dyes are based on colorful molecules and are called dye depositions. Semipermanent formulations have a minimal amount of molecular penetration into the hair cortex and can withstand up to six washes. The demi-permanent and permanent oxidative are based on precursors, named oxidation dyes, whose color characteristics are developed by means of the interaction with an oxidizing agent, and present longer-lasting color.[14] Synthetic hair dyeing systems can be divided according to the durability of color: temporary, semi-permanent, demi-permanent, and permanent:

### 1) Temporary non-oxidative hair dyes

It is synthetic hair dyes, also known as color rinses, color glosses, or color glazes, are typically used to add color highlights, and remove yellowish hues from white hair, or cover up small amounts (15%) of greying hair. Products generally contain a combination of 2 to 5 coloring ingredients to achieve the desired hue. The dye is attached to a cationic polymer to make it less soluble and increase its affinity to hair. The resulting complex is dispersed in a base using surfactants to make the final product, which may be marketed as a spray, lotion, foam, lacquer, or shampoo. Some formulations use two molecules to remove the yellowish effect in white hair and also four to five substances are mixed to reach the red, brown, and black shades.[15]



Figure 10: Temporary hair dye.



Figure 11: Temporary hair coloring.

### 2) Semi-permanent hair dyes

Semi-permanent dyes are synthetic, intrinsically colored, low molecular mass coal tar dyes and may also contain para dyes. They are used commonly at home to brighten a natural color or cover grey. This dyeing process involves no chemical oxidative reactions. The coloring mixture is blended with a compatible alkaline solution to reach a pH of 9–10 which enables the diffusion of the dye molecules into the cortex. It has great water solubility. Glycerine and certain solvents are employed to ensure their solubility not only in the formulation but also during application and product storage. These solvents include mixes of quaternary salts with high molecular weight, such as Quaternium-80, benzyl alcohol, and glycols. [16]



Figure 12: Semi-permanent hair dye.



Figure 13: Semi-permanent hair dye.

### 3) Demi-permanent oxidative hair dyes

Synthetic oxidative demi-permanent dyes contain 2% hydrogen peroxide and small amounts of alkalizing agents (usual monoethanolamine instead of ammonia), so they penetrate the hair more efficiently than non-oxidative semi-permanent dyes, but less than permanent dyes. Owing to their greater coloring power, these dyes are used to enhance natural color, brighten it up, or cover up to 50% of grey hair, but have little hair-lightening potential.[17]



Figure 14: Demi-permanent hair dye.



Figure 15: Demi-permanent hair dye.

#### 4) Permanent oxidative hair dyes

Permanent hair dyes are frequently used because this category provides greater potency of permanent dyeing, resistance to shampoo washes, and other external factors, such as light, friction, drying, and others. This category represents about 80% of the sold hair dyes and gets any shade, also covering up to 100% of white hair strands. Also, it is possible to have dark and light natural hair colors due to the combination of the oxidizing agents with the ammonia hydroxide.[18] It requires three main components. The first is an o- or p-substituted (hydroxy or amino) aromatic amine, referred to as the main intermediate, oxidation base, or developer (by way of analogy with color photography). Primary medial contain p-phenylenediamine, p-aminophenol, and their derivatives. The second component, the coupler, is typically an aromatic compound with electron-donating groups arranged meta to each other, containing m-phenylenediamines, resorcinol, naphthol's, and their derivatives.[19] These compounds alone do not produce significant colors by oxidation but modify the color when used with primary intermediates and oxidants. Couplers are classified into three groups, according to the color obtained in the fibre with the primary intermediates: yellow-green, red, and blue. The third component is the oxidant, almost nearly always hydrogen peroxide (although in special cases atmospheric oxygen can be used) with an alkali, typically ammonia. The oxidant serves two main purposes: to oxidize the primary intermediates and, in combination with ammonia, to lighten the natural hair color.[20]



Figure 16: Permanent hair dye.



Figure 17: Permanent hair dye.

- **Natural dyes**

Natural dyes are dyes or colorants derived from different parts of plants, insects and minerals etc., the majority of natural dyes are from plant sources like leaves, fruits, wood, flower. They are mentioned below:

##### 1) Plant-derived material

In ancient times dyes were typically obtained from plants such as henna, indigo, *cassia obovata*, turmeric, black walnut hulls, and red ochre. Archaeologists have discovered evidence that early man used minerals, plants, and even insects to appeal to or repel mates. Egyptians have used henna as a coloring agent as early as 1500 bc.[21]

##### a) Leaves (Heena and Indigo)

The first colorants were made from leaves. Heena is a very well-known herb, famous for its medical properties, applied to hair, nails, hands & feet at weddings, occasions, and festivals.[22] The plant *Lawsonia inermis*, also known as Heena, the henna tree, the mignonette tree, and the Egyptian privet, is the solitary species of the *Lawsonia* genus and the source of the dye known as henna. Henna has been used since antiquity. Powdered henna is usually made up into a paste with water just before use and then applied to the hair. On hair with a strong affinity for keratin, it gives a somewhat varied red/orange shade that is kept pretty well. It is believed that lawsone (2-hydroxy-1, 4-naphthoquinone), which is associated with glucosidic residues in the plant, is the substance that makes henna active. In order to produce different, darker shades indigo has been used as a hair coloring material sometimes in combination with henna. [23]

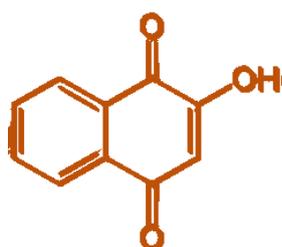


Figure 18: Structure of lawsone.



Figure 19: Henna.

Another example of hair dye found in leaves is Indigo. Indigo is found in the leaves of *Isatis tinctoria* or woad claimed to have been used by the ancient Britons to color themselves. *Indigofera Argenta*, which has been grown in Iran (Persia) since ancient times, is the primary source of indigo. The dried, powdered leaves are referred to as "reng." It is used as a blue dye. Indole is probably a product of indole-3-glycerol phosphate catabolism in *Isatis tinctoria*. It is oxidized into indoxyl and stored in young leaves as an indigo precursor. Further oxidation and dimerization of indoxyl produce indigoid pigments.[24]

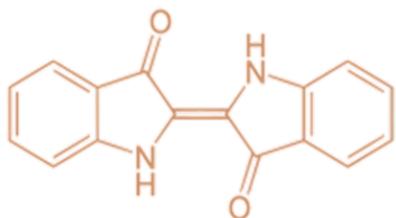


Figure 20: Structure of indigo.



Figure 21: Isatis Tinctoria.

#### b) Flower (Chamomile and Hibiscus)

Another vegetable dye commonly used for hair dye is flower to obtain yellow shades is chamomile which promotes greater light reflection. 1,3,4- trihydroxyflavone, is an active ingredient of a flower which is also called as apigenin. This plant has softening, moisturizing, and skin-soothing properties.[25]

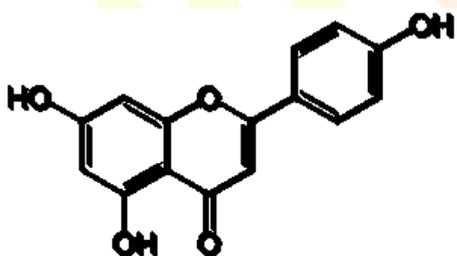


Figure 22: Structure of apigenin.



Figure 23: Chamomile.

The flower of *Hibiscus rosa-sinensis*, known as the Chinese hibiscus, China rose and shoe flower, is an evergreen flowering shrub native to East Asia. Pink-Red Hibiscus are common Hibiscus flower in India. Hibiscus flowers are used for hair care. It is used to blacken the hair and prevent it from greying. [26]

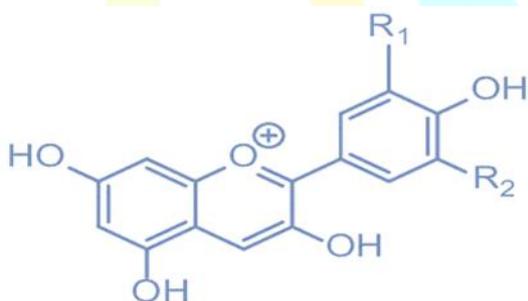


Figure 24: Structure of Anthocyanin



Figure 25: Hibiscus

#### c) Root (Madder and Turmeric)

Since ancient times, dyestuff made from the colorants derived from the roots of numerous plant species in the *genus Rubia* has been referred to as "madder" in general, although this actually represents different identified species from origins all over the world. The dyestuff was widely known to the dyers of the Egyptian, Greek, and Roman civilizations. Pedanius Dioscorides wrote about the effectiveness of madder in coloring red. Dyers were aware that the various sorts of madder could produce varied shades, but a knowledge of the cause for this was not available until the 19th century. The majority of 19th and 20th-century literature that followed similarly concluded that the major colorant present in extracts from *Rubica tinctorum* was alizarin, and purpurin is the primary color present in *Rubica cordifolia*.[27]

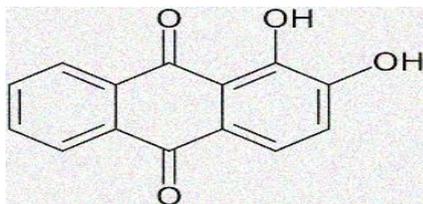


Figure 26: Structure of alizarin.

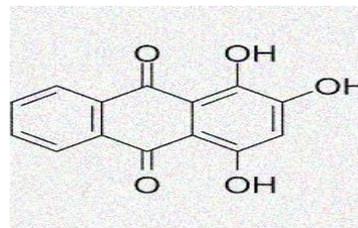


Figure 27: Structure of purpurin.



Figure 28: Rubica Tinctorium.



Figure 29: Rubica Cordifolia.

Turmeric (*Curcuma domestica*) is one of the found plants that has a high enough potential to be cultivated. The main components contained in turmeric are curcuminoids containing three components namely curcumin, desmetoksikurkumin, and bis-desmetoksikurkumin. The level of curcuminoid is 10% in turmeric. Curcuminoids are colour materials contained in turmeric, in yellow turmeric curcuminoids include yellow colour materials. The use of turmeric is to dye grey hair and produce a yellow black color. The pH value is of 7.2 which shows that turmeric can be used as a natural dye.[28]

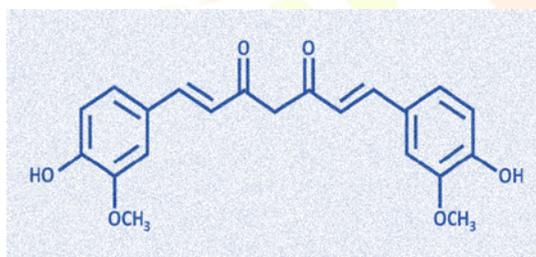


Figure 30: Structure of Curcuminoid



Figure 31: Turmeric

#### d) Wood (Brown catechu and Logwood)

Catechu Powder has long been used in hair care products to improve hair color, volume, and lustre. This hair conditioner leaves a lasting impression, unlike other hair conditioners. Using a regular Katha Powder act as a conditioner and will add volume and strength to your hair. The chief coloring component present in the catechu is catechin having the molecular formula  $C_{15}H_{14}O_6$ . The content of catechin in catechu varies from 4-7%. [29]

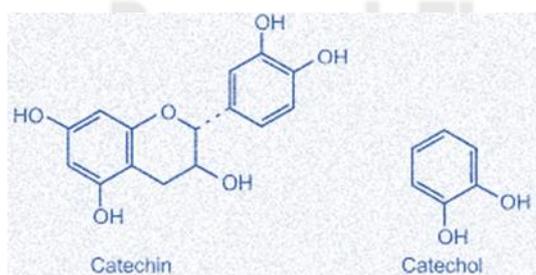


Figure 32: Structure of catechu.



Figure 33: Acacia catechu.

Logwood is used as natural dye. Haematoxylin, produced by heartwood extracts of the logwood tree *Haematoxylum campechianum*, oxidizes to hematein during isolation. chromium combined with the latter, which is red, results in colors of charcoal, grey, and black.

Logwood had become known as a source of dye. It had been known by the Spanish from the 1500s when they got to Campeche, and by the Mayans in the area from long before that.[30]

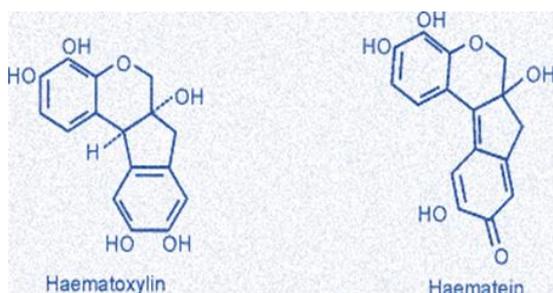


Figure 34: Structure of Haematoxylin and Haematein.



Figure 35: Logwood tree.

e) Fruit (Walnut and Amla)

Juglone (5-hydroxy-1,4-naphthoquinone) can be extracted from different parts of the Walnut tree. Juglone is an isomer of the more well-known lawsone (2-hydroxy-1,4-naphthoquinone), which colors Henna, and both are among the first hair dyes ever used. Leaves and hulls of walnut fruits are used for hair dyeing. Oleic acid, macadamia, linoleic acid, linolenic acid, methionine, cysteine, tryptophan, and threonine are among the substances found in walnuts. [31] 1,4-Benzoquinone is a small organic compound and, its low molecular weight makes it useful for semipermanent hair dye formulations. It can be considered a natural brown-dyeing source being it is found in young shoots of the pear (*genus Pyrus L.*), where it exhibits strong antibacterial activity. Walnut leaves are used in traditional medicine for external applications such as loss of hair, scalp itching, peeling, and dandruff. Walnut provides a link with the first commercially available products at the start of the 20th Century. Nutgalls are caused to form on the branches and leaves of the white oak tree (*Quercus infectoria or Lusitania*) by the penetration of the tissue by a parasitic wasp.[32]

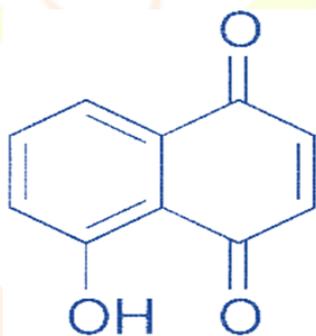


Figure 36: Structure of juglone.



Figure 37: Walnuts.

The fruit *Phyllanthus emblica Linn*, commonly known as Amla. Berries obtained from amla enhances the absorption of calcium, helping to make healthier hair. It maintains the hair color and prevents premature greying, strengthens the hair follicles. Amla is the most rich and concentrated form of Vitamin C along with tannins found among the plants. The vitamin C present in amla can help to stop premature greying and enhance natural hair color. [33]

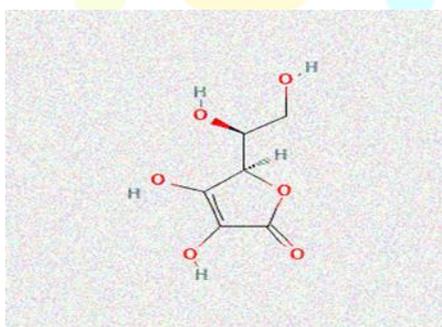


Figure 38: Structure of Ascorbic acid



Figure 39: Amla

## f) Soot (Kohl)

Kohl, used by the women of the East to give a "long, dark languish to the hairs as well as eyes," kohl used in the East, more akin to the Western product, is said to be made by burning almond shells and aromatic resins and collecting the soot. More complex recipe: they take out the inside of a lemon, fill it with plumbago and burnt copper, and put it on the fire until it turns carbonized. Then, they pound it in a mortar with coral, sandalwood, pearls, ambergris, a bat wing, and part of a chameleon's body after first burning the whole thing to cinders and moistening it with rosewater while it was still hot. Usually, a little brush or stick is used to apply it. It is removed from the hair by washing and used by stray grey hairs about the temples in the case of persons whose hair is naturally black.[34]



Figure 40: Kohl tube

## 2) Insects

In natural sources of hair dye insects are also used for hair coloring process. Insects are either fermented or crushed for their application. Here are few examples:

## a. Lac(laksa)

Lac, laksa insect meaning bright dye, was obtained from the resinous excretion deposited on the twigs of trees from female lac insect. It was an excellent dye used in India throughout the centuries starting from the late Vedic period. The resinous substance which is the source of dye has been described as both dark and red. Lac is used as a hair dye in ancient times. Laccaic acids are the principal components of lac insect body coloration.[35]

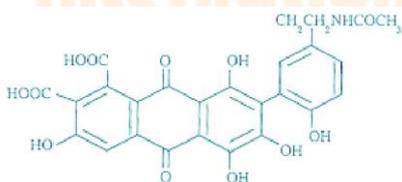


Figure 41: Structure of laccaic acid.



Figure 42: Lac insect.

## b. Cochineal

The use of cochineal insect dye goes back to the classic period. Cochineal means bright red or scarlet. Cochineal was one of the red dye-producing scale insects of the ancient world. The dye was extracted from the female body during the period of hatching. The real cochineal was a cactus feeding insect. Carminic acid is a red crimson anthraquinone coloring matter that occurs naturally in cochineal insects.[36]

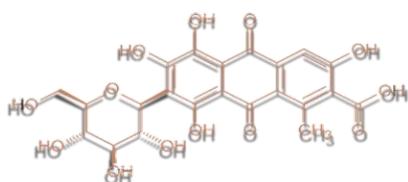


Figure 43: Structure of carminic acid.



Figure 44: Cochineal insect.

## c. Fermented leeches

In ancient Rome, to dye the hairs the Romans used all types of crazy methods. The strangest hair dye was a hair-blackening preparation made from leeches mixed with vinegar. The women would ferment this mixture; after two months they applied it to their hair and sat in the sun to bake.[37]



Figure 45: Leeches hair dye.



Figure 46: Leech.

There are so many improvements to see in hair coloring from history to present days. Protection of hair structure. Improvement of aesthetic best of the hair, brightness, bulk, combability, preferred appearance. Addition of antiseptics, antidandruff agents, antiseborrhea agents for the scalp, deodorants, etc. Addition of substances specific to operations other than dyeing, for example, film-formers, etc. [38]

The number of new dye precursors patented over the years, and examples of recent commercial success such as the diamino-N, N-dihydropyrazolones, suggest that the oxidative process in an optimized form will remain the dominant technology into the foreseeable future. The rapidly developing science of genetics and an emerging understanding of the molecular basis of hair pigmentation may be key elements in the development of systems encouraging natural, or semisynthetic hair re-pigmentation.[39]

#### 4. CONCLUSION

Hair coloring is the art of changing hair color. The main reason for these is to cover grey hairs to change to a color regarded as more fashionable. Throughout history, human beings have colored their hair for one-of-a-kind reasons. People colored their hair to signify one's elegance in society and as a part of beautification. At present people color their hair to cover up or blend grey hair to enhance existing hair color and create a fashion. Depending on our profession, lifestyle, current fashion, and age we can select one specific artificial hair color. These past few decades have witnessed significant growth in our understanding of the chemical and physical properties of hair structure, and of the mechanisms involved in the hair dyeing process. Hair coloring, whether it is indicated one's place in society, enhances existing hair color, changes the look for specific work, covers grey hair, or creates a new fashion artificial hair coloring was and still is a practical tool for enhancing the beauty of people.

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