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REVIEW

Hair Cosmetics: Dyes☆

A. Guerra-Tapia,* E. Gonzalez-Guerra

Departamento de Medicina, Universidad Complutense de Madrid, Madrid, Spain

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Abstract Hair plays a significant role in body image, and its appearance can be changed relatively easily without resort to surgical procedures. Cosmetics and techniques have therefore been used to change hair appearance since time immemorial. The cosmetics industry has developed efficient products that can be used on healthy hair or act on concomitant diseases of the hair and scalp.

Dyes embellish the hair by bleaching or coloring it briefly, for temporary periods of longer duration, or permanently, depending on the composition of a dye (oxidative or nonoxidative) and its degree of penetration of the hair shaft. The dermatologist's knowledge of dyes, their use, and their possible side effects (contact eczema, cancer, increased porosity, brittleness) can extend to an understanding of cosmetic resources that also treat hair and scalp conditions.

PALABRAS CLAVE
Cosméticos capilares;
Tintes;
Eccema;
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Pelo;
Cuero cabelludo

Cosméticos capilares: tintes

Resumen El aspecto del cabello juega un papel significativo en la imagen corporal. Dado que se puede cambiar con relativa facilidad sin necesidad de recurrir a procedimientos quirúrgicos, los cosméticos y técnicas con dicho fin se usan desde tiempo inmemorial. La industria cosmética ha conseguido productos eficientes que actúan sobre el cabello tanto en estado de salud como para mejorar enfermedades del pelo y cuero cabelludo concomitantes.

Los tintes son cosméticos capilares decorativos que tienen como finalidad cambiar el color o decolorar el pelo de forma temporal, semipermanente, o permanente, en función de sus componentes (oxidativos o no) y de su penetración a diferentes niveles de la corteza del tallo. El conocimiento de los tintes, el modo de uso y los efectos secundarios posibles (eccema de contacto, cáncer, porosidad, fragilidad) proporciona al dermatólogo no solo conocimientos, sino herramientas terapéuticas coadyuvantes en la práctica tricológica diaria.

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* Corresponding author.
E-mail address: auroraguerratapia@gmail.com (A. Guerra-Tapia).

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Introduction

Hair is an important component of most mammal body coverings and helps create a barrier between an animal and its environment.[1] While it does not serve a vital biological function in humans, its psychological significance is considerable[1,2] owing to the fundamental role it plays in the development of body image and self-identification in both men and women.[3,4] Hair length, color, and style are especially important for physical appearance and self-perception, and can be modified according to how we wish to be perceived by others.[4] Unlike other physical attributes, these features are easily changed and do not require surgery.[2,3,5] Perhaps for this reason, since ancient times humans have developed products and techniques to change and improve hair appearance, color, texture, and style.[3]

The products in question are termed *hair cosmetics*. Trüeb defines them as ''preparations intended for placing in contact with the hair and scalp, with the purpose of cleansing, promoting attractiveness, altering appearance, and/or protecting them in order to maintain them in good condition.''[6] Hair cosmetics are used by men and women of all ages[7] to optimize hair appearance and repair hair damage, ironically caused in most instances by inappropriate exposure to hair cosmetics.[8] These products may sometimes be used as adjuncts to medical treatments for hair conditions.

Considering the above, dermatologists need to be aware of the principles of cosmetic hair care and of the formulations, application methods,[9] and side effects of different types of hair cosmetics.[10] The purpose is not only to diagnose and treat hair and scalp disorders, but also to ensure beneficial management of conditions with a serious psychological impact on the patient, for whom hair care advice can be as important as hope of a cure.[9] These principles will also assist in providing cosmetic guidance for those patients who merely wish to improve their appearance. Working together, dermatologists and the cosmetics industry have paved the way for better and increasingly convenient and effective products for regular grooming, repair, and maintenance.[8]

Hair Cosmetics: Definitions

Garrote and Bonet[11] define hair treatment cosmetics as ''the cosmetic products indicated for use when changes in the hair or scalp compromise its healthy appearance, lead to potential hair loss, or simply make the hair and hence the person look less attractive.''

Annex I to EU Directive No 76/768/EEC lists the following hair-care products[12]:

1. hair tints and bleaches
2. products for waving, straightening, and fixing
3. setting products
4. cleansing products (lotions, powders, shampoos)
5. conditioning products (lotions, creams, oils)
6. hairdressing products (lotions, lacquers, brilliantines)

Until recently, cosmetics were products used to enhance beauty whereas pharmaceuticals were used to cure disease. The boundaries are more blurred today, since the cosmetics industry uses physiologically active ingredients that form pharmacologically active compounds.[13]

We will classify hair cosmetics according to purpose:

- Hygiene: to remove dirt.
- Maintenance: to improve hair styling and protect the cuticle.
- Beauty: to change hair color or shape.
- Correction (or therapy): to contribute to medical or surgical treatment.

Hair Beauty Cosmetics: Hair Dyes

Hair beauty cosmetics are those that change hair color or shape. They include temporary setting products (such as hairspray, foam, or hair gel), permanent waving or straightening products, and hair dyes.

Hair dyes color hair either temporarily or permanently by removing part of the existing pigment and/or adding new pigment.[14]

Dyes are used by both men and women to alter natural hair color, postpone graying of hair, or restore pigmentation once graying has set in.[14,15] In developed countries, 70% of women dye their hair at least once, and many do so regularly.[14]

We will review certain key, basic concepts that should contribute to a better understanding of hair dyes and their use.

Hair Shaft: Structure

Hair is an appendage of the epidermis[2] comprising the hair follicle and hair shaft.[15] Beauty treatments do not affect the follicle cosmetically[2,15]; all changes involve the shaft.

The hair shaft, or hair fiber, comprises 3 layers: the cuticle, the cortex, and the medulla.[2,15] Chemically, the shaft consists of proteins, lipids, water, melanin, and trace elements.[16] A hair shaft can tell us about a person's hair care history,[17] and may feature signs of weathering, from the root to the tip.[15] The tip of the hair shaft, as the oldest part, exhibits the most cosmetic damage, whereas the root is probably less porous and has different chemical properties that affect its response and influence the cosmetic effects of treatments applied to this region.[17]

The hair shaft is a flexible structure that can be stretched to a considerable degree by applying traction. Breakage is thought to occur at loads ranging between 50 g and 100 g. This is relevant to prosthetic cosmetic practices, such as the application of hair extensions or of hair integration systems.[18]

Cuticle

The cuticle consists of 6 to 8 layers of overlapping scale-like cells arranged so that their free edges point toward the tip of the shaft.[16] It protects the cortex beneath and acts as a physical barrier against external insult.[2] It consists of 2 parts, the exocuticle and the endocuticle.

External to the cuticle is the F-layer, tightly joined to the cuticle by covalent bonds.[5] It consists of a single-molecule–thick layer of 18-methyl eicosanoic acid, a highly

hydrophobic branched-chain fatty acid,[5] considered by some to act as a natural hair protector or natural conditioner.[14]

Healthy cuticle is soft to the touch; reflects light, causing hair to shine; and limits shaft friction against other hair shafts.[16,19] It is responsible for the lustre and texture of hair.[10] What makes hair appealing to the sight and touch is chiefly the way the scale-like cuticle cells are arranged, allowing each hair shaft to slide gently over neighboring shafts.[1]

Friction from brushing and combing, application of alkaline products, and use of hair dryers all disrupt and damage the cuticle[5,10,20] and may compromise its protective role.[15]

Cortex

The cortex accounts for most of the keratinized hair shaft and is the main component responsible for its mechanical properties (hair strength and elasticity) and for hair color.[2,16] It is therefore the site of most cosmetic changes. Permanent hair coloring, waving, and straightening all cause physical and chemical changes to the cortex.[15]

The cortex is made up of densely packed elongated cortical cells containing keratin filaments that run parallel to the hair shaft[16] as well as an amorphous matrix of high-sulphur proteins in which the α-helical keratin chains are embedded.[19]

Keratins are a family of complex proteins.[2] Acidic keratin polypeptides pair with basic keratin polypeptides forming polypeptide chains of hard keratin known as protofilaments.[2,21] Multiple protofilaments make up a keratin strand with a large number of sulfur-containing cysteine residues[2,15] that form covalent disulfide bonds to adjacent chains, so that neighboring keratin chains are strongly crosslinked,[22] thus conferring high physical and chemical stability.[2]

These disulfide bonds are largely responsible for hair shape, stability, and texture,[15] and confer a degree of elasticity that allows hair wet with water to be stretched without damage up to 30% beyond its original length.[1]

Keratin chains are also more weakly bonded to each other by van der Waals forces, hydrogen bonds, and saline bonds.[22]

Medulla

Only terminal hairs can have a core medulla.[15] If present, the medulla may be a single core strand extending continuously through the shaft or only an intermittent strand.[19] The medulla is composed of specialized cells with intervening air spaces.[15] It either plays no cosmetic role at all[16] or a very minor one.[2]

Hair Shaft: Color

Hair color resides in the cortex. Though keratin, the main component of hair fibers, is colorless,[2] melanin, also found in the cortex, is responsible for characteristic hair color.[1,2] Melanin granules are formed in the melanocytes at the base of the hair follicle (the dermal papilla), which secrete melanosomes into keratinocytes.[14] In the anagen phase, melanosomes are transferred to cells in the cortex and the medulla,[21] but not the cuticle.[1] Melanin granules are spread throughout the cortex, more densely so in its outermost part,[14] yet do not enter the cuticle. Therefore, to alter natural hair color effectively, hair cosmetics need to get beyond the cuticle into the inner part of the hair shaft.[14]

Natural shades of hair are all created by 2 types of melanin: eumelanin and pheomelanin.[14] The relative amount of each of these 2 types, the total amount of melanin, and the size of the granules in each hair together determine hair color.[14,23] Whereas eumelanin is the predominant pigment in dark or black hair, pheomelanin prevails in blond or red hair, and overall melanin content is lower.[15]

Natural hair color tends to change from birth to old age[14]: children born with fair hair may have brown hair as adults.[14] Gray hair is a normal sign of aging.[15] Graying is usually a gradual and irreversible process[14] mostly caused by declining melanocyte function rather than a diminishing number of melanocytes.[14,23] Hair with no melanin looks white because it scatters light.[14]

Hair Dyes

Hair dyes are cosmetics used to change hair color. They require regular application to mask new hair growth.[14]

Hair dyes are classified as follows according to origin:

- Vegetable hair dyes (henna, chamomile, and cinchona). They change color hue, are nontoxic, and last only a short time.
- Mineral or metallic hair dyes (silver nitrate or lead salts). Requiring daily use, they darken or lighten hair gradually. They are potentially toxic and are incompatible with hydrogen peroxide. They may last for weeks or months.
- Synthetic hair dyes. These are classified according to wash fastness and degree of permanence as follows[14,15]:

a. Temporary hair dyes. Color remains in place for a few days. These dyes have a high molecular weight and remain on the surface of the cuticle.
b. Semipermanent hair dyes. Color persists for weeks. These dyes have a low molecular weight and achieve shallow penetration of the cortex.
c. Permanent dyes. Color persists indefinitely. These dyes have a very low molecular weight and penetrate the cortex deeply.
d. Hair bleaches.

Temporary Synthetic Hair Dyes

Temporary synthetic hair dyes, also known as color rinses, color glosses, or color glazes,[14] are typically used to add color highlights, remove yellowish hues from white hair, or cover up small amounts (<15%) of graying hair.[10]

The dye is weakly bonded to the hair, so it usually remains in place for a week and is easily removed by shampooing.[14,15] Products generally contain a combination of 2 to 5 coloring ingredients to achieve the desired hue.[24]

The dye is bonded to a cationic polymer to reduce its solubility and increase its affinity to hair. The resulting complex is dispersed in a base using surfactants to make the final product,[14] which may be marketed as a spray, lotion, foam, lacquer, or shampoo.[14]

These products easily stain the hair and scalp.[15]

Application Method

Temporary synthetic hair dyes are applied on clean hair. Shampoo-like products are rinsed in water whereas other cosmetic formulations (lacquers, sprays, and so on) remain in place until the hair is washed.

Semipermanent Synthetic Hair Dyes

Semipermanent synthetic hair dyes may be oxidative or nonoxidative.

Nonoxidative Semipermanent Synthetic Dyes

Nonoxidative semipermanent hair dyes are used to enhance color and to modify or soften the effect of gray hairs,[14,15] but cannot lighten hair color because no bleaching agents are included.[10] One salient characteristic is low molecular weight, which enables these products to diffuse into the middle layers of the cuticle without binding firmly to the hair protein itself.[14]

The most widely used semipermanent hair dyes are nonionic nitro dyes,[25] which are barely affected by the negative charges on the hair surface and also relatively small. They are thus able to get past the cuticle[14] with no oxidative reaction whatsoever.[15]

This type of dye is typically color-fast through 6 to 8 shampooings.[14] Washing opens up the cuticle and releases the dye, which is water soluble.[14]

Application Method. Nonoxidative semipermanent synthetic dyes are applied like shampoo, left on for 20 to 30 minutes, and then rinsed off with water.[14,15,26]

Oxidative Demipermanent Synthetic Dyes

Oxidative demipermanent synthetic dyes contain 2% hydrogen peroxide and low levels of alkalinizing agents (generally monoethanolamine rather than ammonia), so hair penetration is more efficient than with nonoxidative semipermanent dyes, but less so than with permanent dyes.[14] Owing to their greater coloring power, these dyes are used to enhance natural color, brighten it up, or cover up to 50% of gray hair, but have little hair-lightening potential.[14]

Application Method. Oxidative demipermanent synthetic hair dyes are applied like shampoo, left on for 20 to 30 minutes, and then rinsed in water.[14,15,26]

Permanent Synthetic Hair Dyes

Permanent synthetic hair dyes are the most widely used[15] and have the greatest commercial significance.[14] They are the most versatile, last longest, offer the widest range of hues,[14] and afford the highest gray-hair covering capacity (up to 100%), even with recalcitrant hair[14]; also, they can either darken or lighten natural hair color.[10]

They contain up to 6% peroxide and use ammonia as the alkalizing agent. This results in pH values ranging from 9 to 10.5, thus facilitating complete penetration through the hair cortex.[14]

Several chemical processes are involved in bringing about final hair color[14]:

1. Oxidation of melanin and of previously applied dye pigments. This lightens the underlying color. Melanin granules are dissolved and partially fragmented by oxidation, leaving a gap in the cortex.[14]

   Results are proportional to reaction time[24] and depend on the predominant type of melanin present in the hair shaft. Pheomelanins have been found to be more resistant than eumelanins to photobleaching, and probably to chemical bleaching as well.[27] Kojima et al.[28] have used nanoscale secondary ion mass spectrometry to demonstrate that the melanin granules found in black human hair are regions of great importance in oxidative hair dyeing.
2. Oxidation of dye precursors to form color-bearing chromophores.[29] Chromophores, typically p-diamines and p-aminophenols, are formed by the oxidizing action of hydrogen peroxide in the presence of several color couplers.[10,14] Typically used couplers are phenols, meta-aminophenols, or meta-diaminobenzenes, such as m-aminophenol, resorcinol, or 1-naphthol.[14]
3. Color change, usually in 3 stages[9]:

- Primary intermediates are oxidized to active imines; these imines are able to form black or brown complexes with multiple nuclei by reacting with their unoxidized counterparts.[14]
- With couplers or color modifiers present, the preferential reaction of the imines with the coupler molecules is at the most nucleophilic carbon atom in the molecule.[14]
- The compound formed by the coupling reaction is oxidized into a water-resistant dye.[14] The resulting complex color molecules are too large to diffuse back through the cuticle and be washed out, so dyeing is permanent and irreversible until new hair growth.[25,26]

Application Method

Application of permanent synthetic hair dyes requires mixing of separate product components[14]:

- Tint: dye precursors (an oxidant, usually hydrogen peroxide, and an alkalinizing agent, typically ammonia or monoethanolamine) in a surfactant vehicle. Generally available in cream or liquid form.[14]
- Developer: a stabilized solution of hydrogen peroxide,[14] generally in liquid form, to promote oxidation of the dye precursors.

The mixture is preferably applied to dirty hair so that the sebum can protect the scalp from aggressive compounds, and the product is allowed to act for 20 to 40 minutes before rinsing with water.[15]

Liquid tints are the easiest to mix, but less product loss occurs with tint creams.[14]

Dyeing must be repeated every 4 to 6 weeks to cover new hair growth.[10,14]

Adverse Effects of Temporary, Semi- or Demipermanent, and Permanent Dyes

Allergic Contact Dermatitis

While several studies indicate that the main allergens responsible for cosmetic-induced allergic contact dermatitis are methylisothiazolinones, p-phenylenediamine (PPD), and

fragrance mixtures, in that order, the main agent of allergic contact dermatitis in hair dyes is PPD.[30]

In a recent study of 2939 consecutive patients recruited from 12 dermatology care centers who were tested for contact reactions to dye components, 4.5% tested positive for PPD and 0.1% for resorcinol.[31]

The main agents of hair dye–triggered allergic contact dermatitis are para molecules, especially PPD and its derivatives o-nitro-p-phenylenediamine and para-toluenediamine,[32–34] which are highly sensitizing compounds. Darker dyes contain greater amounts of these substances.[35]

In normal hair-dyeing exposure, 1% of the PPD dose penetrates the skin, and 80% of that becomes monoacetyl-PPD and diacetyl-PPD by the action of *N*-acetyltransferase. Other derivative compounds bind to specific amino acids and form the complexes responsible for sensitization.[36]

Nevertheless, the published literature supports the inference that hair dyes cause very few adverse reactions (1 per million applications).[37,38]

Paradoxically, a number of studies show that the prevalence of allergic reactions to PPD seems to have been waning in recent years despite a worldwide increase in hair dye consumption.[39] In the European Union (EU), PPD was described as the fifth most frequent allergen in the years 1985 to 1990, but ranked fifteenth between 1991 and 1996.[40] This downward trend continued in subsequent years, and an overall reduction in prevalence was observed from 1969 to 2001.[34,41]

Contact dermatitis among professional hairdressers has also decreased, probably because neoprene gloves are used for protection.[42,43]

However, the rising fashion of body art, as well as the use of PPD-containing temporary tattoo products such as black henna, seem to be playing an important role in triggering allergic contact reactions to hair dyes.[44–47]According to the Cosmetic Ingredients Review Expert Panel, 2-amino-4-hidroxyethylaminoanisol and its salt, 2-amino-4-hidroxyethylaminoanisol sulfate, are safe when used in oxidative hair dyes as coupling agents, although they should not be used in cosmetic products in which they can form *N*-nitrous compounds.[48]

There are sporadic reports of allergic contact dermatitis caused by some components of temporary hair dyes, such as quinine.[49]

Eczema appears at the site of application and in sensitive nearby areas such as eyelids, and only in exceptional cases do patients experience severe and extensive symptoms such as facial edema or disseminated dermatitis.[14]

Cancer

The potential carcinogenicity of hair dye ingredients has drawn the attention of toxicologists and epidemiologists for decades, as oxidative hair dyes are formulated using compounds that belong to the large chemical family of arylamines, which includes several powerful human carcinogens (benzidine, 4-aminobiphenyl, and 2-naphthylamine).

However, an in-depth review by Nohynek et al.[39] of hair dye carcinogenicity studies conducted in humans and other mammals (including both laboratory studies and studies of occupational exposure) concluded that the combined findings strongly suggest that hair dyes do not pose a carcinogenetic risk. The absence of cancer risk to consumers arising from the use of oxidative hair dyes has been confirmed by the World Health Organization's International Agency for Research on Cancer as well as by the EU Regulatory Agency.[38,50]

However, a recent study by Couto et al.[51] in Brazil appears to confirm a possible link between exposure of pregnant women to hair dyes and straighteners and development of leukemia in their offspring up to the age of 2 years.

As to legislation regulating hair dyes in order to prevent adverse effects, Spanish Order No. SSI/771/2013 of May 6, 2013, which modifies Annexes II and III to Royal Decree No. 1599/1997 of October 17, 1997 on cosmetic products, changed both the number of products allowed and their concentration levels.[52]

The 1997 Royal Decree consolidated all extant Spanish legal rules on cosmetics into a single legislative text and enacted EU Council Directive No. 76/768/EEC of July 27, 1976 on the approximation of the laws of the Member States relating to cosmetic products, along with its later amendments. Subsequent EU-wide rules produced by the European Commission, EU member states, and industry stakeholders were implemented in Spain over the following years, and further Orders have amended the Annexes. According to the latest amended version, as of September 1, 2013 no cosmetic product may be sold or in any way transferred to a consumer unless it complies with the provisions of the Order.[52]

Hair Bleaches or Decoloring Agents

These products provide permanent hair lightening without the addition of another color.[14,15] Bleaching is the most effective method for lightening hair, whether naturally colored or dyed.[15] The process is the same as the first stage of dyeing with permanent synthetic dyes.

Hair bleaches contain hydrogen peroxide, ammonia, and persulfates to enhance their effectiveness and speed up the process.[10,14] Hydrogen peroxide is the oxidizing agent that releases oxygen from the hair shaft[15]; hair becomes lighter according to the amount of oxygen released.[10]

Bleaching agents oxidize existing melanin.[15] During complete bleaching, melanin granules are completely dissolved, leaving tiny gaps in the cortex.[14]

Dark hair requires longer bleaching time[15] and goes through a series of color stages: black to brown to red to orange to yellow to pale yellow to white.[9] This is why, particularly in very dark hair, partial bleaching may result in undesirable yellow or orange hues.[14]

Bleaching reactions are harder to achieve in red hair than in brown.[26] The color obtained is usually flat or dull and the results are hard to control,[35] so bleaching of red hair is frequently combined with special techniques or coloring dyes in order to accentuate the hair.[14,26]

Application Method

Hair bleaches are applied for a variable amount of time, according to existing color and to the degree of lightening sought. The bleaching agent is neutralized when the

intended amount of time has elapsed to prevent further toxicity to the hair fiber.

Adverse Effects of Hair Bleaches

Bleaches that contain persulfate salts (e.g. ammonium persulfate or potassium persulfate) may trigger immediate reactions such as rhinitis, asthma, contact urticaria, and even anaphylaxis. The underlying immune mechanism, however, is not known.[53]

Breakage of disulfide bonds has the following effects on hair:

- Increased cuticle porosity (porous hair).
- Increased hydrophilia of the shaft (swollen hair shaft).
- Increased brittleness due to porosity and swelling.

All these effects cause cosmetic changes that lead to styling difficulties and may mimic some intrinsic hair disorders, such as certain forms of alopecia in which appearance is consistent with hair shaft breakage near the scalp.

The detrimental effects of hair dyes may be minimized by using other hair cosmetics (maintenance cosmetics, which improve styling and protect the cuticle).

Conflict of Interest

The authors declare that they have no conflict of interest.

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