Section III

Adornment

Part 1: Colored Facial Cosmetics

Chapter 22: Facial foundation

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BASIC CONCEPTS

- Facial foundation places a pigment over the skin surface to camouflage underlying defects in color and contour.
- Facial foundations must be developed to match all ethnicities and facial needs.
- New optic technologies have allowed modern facial foundations to create a flawless facial appearance more effectively.
- Facial foundations impact skin health because they are worn daily for an extended period.

Introduction

Complexion makeup is anything but a trifling subject. The practice is deeply rooted in human history. It has evolved along with civilizations, fashions, scientific knowledge, and technologies to meet the various expectations depending on mood, nature, culture, and skin color. A prime stage to beautifying the face, complexion makeup creates the "canvas" on which coloring materials are placed. Women consider it as a tool to even skin color, modify skin color, or contribute to smoothing out the skin surface. To fulfill these different objectives, substances extracted from nature took on various forms over time until formulation experts developed a complex category of cosmetics including emulsions, poured compacts, and both compact and loose powders. These developments have improved the field of skin care providing radiance, wear, and sensory effects.

It remains a challenge to adequately satisfy the varying makeup requirements of women from different ethnic origins, who do not apply products in the same way and do not share the same diverse canons of beauty. It is therefore necessary to gain a thorough understanding of the world's skin colors.

Finally, as a product intended to be in intimate contact with the skin, facial foundations must meet the most strenuous demands of quality and safety. This has motivated evaluation teams to develop methods for assessing product performance.

Complexion makeup – an ancient practice

Modifying one's self-appearance by adding color and ornament to the skin of the face and body skin is hardly a recent trend [1–3]. From Paleolithic times, man has decorated himself with body paint and tattoos for various ritual activities. In the Niaux Cavern (Ariège, France), the cave of Cougnac (Lot, France), and the Magdalenian Galleries of le Mas d'Azil (Ariège), the past ages have left evidence of these practices. Along with the flint tools in the Magdalenian Galleries at le Mas d'Azil ochre nodules were found that look like "sticks of makeup" as well as grinding instruments, jars, spatulas, and needle-like "rods" 8–11 cm long, tapered at one end and spatula-shaped on the other end, suitable for applying body paint.

From the earliest of ancient civilizations, there are cosmetic recipes containing a variety of ingredients which are often closer to magic than to rational chemistry, aimed particularly at modifying the complexion. Usually used exclusively by high dignitaries, cosmetics were intended to whiten the complexion.

Ancient Mesopotamia (2500 BC)

The queen and the princes of Ur used cosmetics consisting of a mixture of mineral pigments based on Talak (from which the word "talc" is derived). Nowadays such cosmetics are still commonly used in some parts of the Middle East.

Ancient Egypt (3rd millennium BC)

The priests used plaster to cover their faces. It was also desirable for women to exhibit very white skin without blemishes, as these were indications of a privileged life of leisure.

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The complexion was whitened with mixtures of plaster, calcium carbonate, tin oxide, ground pearls, and lead carbonate (ceruse) mixed with animal grease, waxes, and natural resins. Evidence of the complexity of the ancient recipes has been determined by chemical analyses carried out jointly by the Centre National de la Recherche Scientifique, L'Oréal's Recherche department, the Research Laboratory of the Museums of France, and the European Synchrotron Radiation Facility on the content of cosmetic flasks found in archeologic excavations [4]. The earliest cosmetic formulary is attributed to Cleopatra – *"Cleopatrae gyneciarum libri."*

Ancient Greece

In Ancient Greece, the white, matte complexion symbolizing purity was obtained through generous application of plaster, chalk, kaolin (*gypsos*), and ceruse (*psimythion*), but Plato was already denouncing the harmfulness of these cosmetics.

Ancient Rome

Ancient Rome raised the use of makeup to the level of an art form. In addition to cosmetics that enhance the beauty of face and body, cosmetics were applied to improve appearance and hide flaws, notably those caused by the aging process.

Women of the upper classes "coated" their face with complex mixtures with recipes reported in Ovid's *Cosmetics* or in Pliny the Elder's *Natural History*. For instance, hulled barley, powdered stag antlers, narcissus bulbs, spelt, gum, and honey were the components of a mixture to make the face shiny. Dried crocodile excrement, ceruse, vegetal extracts, as well as lanolin or suint (also known as *oesype*) were used to whiten the complexion.

Recently, an analysis was made of an ointment can, christened *Londinium*, discovered in London when excavating a temple dated at the middle of the 2nd century AD. It contained glucose-based polymers, starch, and tin oxide. The white appearance of the cream reflects a certain level of technological refinement [5].

From the Middle Ages to the 19th century

In Europe, from the Middle Ages up to the middle of the 20th century, good breeding and good manners were associated with a white complexion. In the Middle Ages, makeup was based on water, roses, and flour, which did not prevent ceruse from making a strong comeback in the Renaissance. It was then subsequently mixed with arsenic and mercury sublimates to give the complexion a fine silver hue.

Toxic effects of these cosmetics, however, was beginning to worry the authorities. In 1779, following the onset of a number of serious cases, the manufacture of "foundation bases" was placed under the control of the Société Royale de Médicine, which had just been set up in 1778. The toxic components were then removed. This measure seems to have made them disappear from the market, but it was not until 1915 that the use of ceruse was officially prohibited.

In 1873, Ludwig Leichner, a singer at the Berlin Opera, sought a way to preserve his skin tone by creating his own foundation base from natural pigments. In 1883, Alexandre Napoléon Bourjois devised the first dry or pastel foundation. Bourjois was about to launch his first dry blush, Pastel Joue.

With the birth of the cosmetics industry, products were widely distributed. Modern manufacturing techniques with production on an industrial scale coupled with the beginning of mass consumer use started at the beginning of the 20th century.

20th century: the industrial era and diversification

In the 20th century, fashionable powders for the complexion became more sophisticated [6,7]. Market choice extended with the launch of new brands such as Gemey, Caron, and Elizabeth Arden.

The 1930s saw the development of trademarks such as Helena Rubinstein and Max Factor created by professional movie and Hollywood makeup artists. The products were suited to the requirements of the movie studios. Extremely opaque, tinted with gaudy colors, they were compact and difficult to apply. After the success of Max Factor's Pancake and Panstick cosmetics, use of the word "makeup" became widespread. Initiated by Chanel in 1936, the fashion in Europe and the USA began to switch from white to a tanned complexion.

Even though women were more inclined to wear cosmetics, makeup was still not part of everyday life. Pancake makeup, a mixture of stearate, lanolin, and dry powders, was not easy to apply. Technical advances gradually made products more practical. The box of loose powder was equipped with a sieve in 1937 (Caron). In 1940, Lancôme launched Discoteint, a creamy version of its compact. Coty micronized its powder (Air Spun) in 1948. Yet, it was not until the 1950s that a real boom occurred in the number of products on the market. Compact makeup was made available in creamy form; foundation became a fluid cream (Gemey, Teint Clair Fluide, 1954). It was the start of a great diversification of formulations: fluids, dry or creamy compacts, sticks, and powders. Makeup became multifaceted, with more sophisticated effects, including moisturizing, protection from damaging environmental factors, and other skincare properties in addition to providing color.

Since then, complexion makeup has followed the continuous changes in regulations and advances in biologic knowledge, especially in the area of skin physiology. Over the last decades, it has benefitted from technologic progress in the field of raw materials, as well as from enhanced understanding and gains in optics and physical chemistry. Finally, makeup was enriched with the diversity of cultures from all over the world prompted by globalization. The beginning of the 21st century opens a new era of visual effects, sensory factors, and multiculturalism.

Formulation diversity

Women expect foundations to effect a veritable transformation that hides surface imperfections, blemishs, discolorations, and wrinkles, while enhancing a dull complexion and making shiny skin more satiny. Whereas making up the eyes and the lips is generally done playfully, the complexion receives more attention. It is in this area that women display their greatest expertise and are the most demanding. Women have high expectations for their foundation including:

- Guaranteed evenness and concealment of flaws;
- Hiding of wrinkles and pores;
- Good adherence to the skin;
- Matting of lustrous skin;
- Excellent wear all day long;
- Unaltered color over time;
- Pleasant, easy application; and
- Appropriate for sensitive skin.

Variety of formulations

In order to satisfy diverse demands, a large number of products types and forms have been developed (Figure 22.1):

- Fluid foundations;
- Compact, easy-to-carry foundations with adjustable effects; and
- Powders to be used alone or in combination with a fluid foundation.

Fluid foundations: emulsions

Fluid foundations include both oil-in-water (O/W) and water-in-oil (W/O) emulsions. Until the 1990s, most foundations were O/W emulsions. Generally intended for mixed to oily skin, they are characterized by:

- Very rapid drying, which can complicate even application;
- Poor coverage;
- Reduced wear;
- Appropriate for mixed to oily skin with their external aqueous continuous phase, which makes them feel fresh on the skin.

Figure 22.1 Diversity of textures: from fluid emulsion to paste dispersion.

In the 1990s, the first W/O formulations revolutionized the foundation market. The external oil continuous phase gives textures with longer drying times more suitable for perfect product application. The progressive coating of pigments has improved their dispersion in the oil phase and helped to stabilize the emulsion.

Throughout the years, the oil phase has been diversified mainly as a result of introducing silicone oils, first in conventional then in volatile forms. Silicone oils have dramatically changed the cosmetic attributes of facial foundation. Foundation no longer has to be spread evenly over the face. Its slickness makes it slide on the skin evenly with a single stroke without caking. The use of volatile oils, siliconated or carbonated, gave rise to the design of long-lasting foundations. As the volatile phase evaporates, the tinted film concentrates on the skin. Adhering during drying on the skin surface, the tinted film withstands friction and does not stain clothes.

Thus, the “non-transfer” facial foundation was born.

In the 21st century, combining volatile oils with different volatilities will lead to novel cosmetic attributes; the oily phase gradually evaporates accompanying finger strokes during application. Today, 90% of the foundations on the market are water/silicone/oil emulsions. Over the past few years, the chemistry of the emulsifying agents have also expanded as new functionalized emulsifiers become available. Either endowed with moisturizing effects or able to enhance optical properties, they contribute to the comfort and the performance of facial foundations.

Compact foundations

Compact foundations are made up of waxes and oils in which powders and pigment phases are dispersed under heat, but compact foundations can be greasy, heavy, and streaky. The more recent use of esters and siliconated oils has made it possible to lighten the texture and improve application qualities. Volatile oils also help the facial foundation film remain unaltered for a longer time and provide long-lasting coverage. Compact foundations display the advantage of being adjustable with a sponge, which is ideal for concealing localized defects. Packaging the foundation in compact cases makes it practical for touching up during the day.

Waterpacts are a special compact type that contain water. They consist of W/O or O/W emulsions rich in waxes that are poured into the compact under heat. The water content makes it necessary to use waterproof packaging. These solid emulsions are difficult to manufacture and preserve, but they have the huge advantage of making the compact fresh as well as practical in use.

Compacts can also be packaged as sticks for more precise and localized strokes, such as around the eyes.

Powders

Compact powders are distinct from loose powders as they represent the "portable to go" version of loose powders. They are composed of fillers and pigments. A binder containing 10% oils and grease ensures the compact powder particle cohesion, while also providing comfort and ease of application. To make a high-quality powder a suitable milling procedure must be used in order to disperse the pigments finely and evenly throughout the powder phase.

Loose powders

A loose powder is characterized by weak particle cohesion. It does not contain binder or may contain just enough to provide a degree of cohesion that controls the final product volatility. Loose powders are generally applied with a puff, but manufacturers are developing tricks for easy application by using more finely tuned application brushes. Unlike with a puff, the powder does not scatter.

Compact powders

There are different kinds of compact powders:

- Finishing powders provide sheer coverage and are used for touch-up during the day. They are usually applied with a sponge over a foundation to mask facial shine. The fillers used in these powders tend to be organic, because they are more transparent. They also have the advantage of absorbing sebum while still leaving a natural look. The formulation challenge is to find a good balance between texture quality and the ease in placing the proper amount of powder on the applicator.
- Powder foundations are compact or loose powders whose covering power is equivalent to that of a foundation (i.e. better than a finishing powder). They can be used instead of foundation, for instance by women who dislike fluid textures. The loose powder version known as mineral makeup is currently enjoying considerable success.
- Two-way cakes, which are available in compact form, can be used either wet or dry. This kind of powder is popular with Japanese women. Using it dry gives the same kind of makeup as a powder foundation, while using it wet gives more even coverage. This dual usage requires the vast majority of the fillers to be hydrophobic. Treated fillers, coated with silicone oils that cannot be wetted, are mostly used. In this way, the compact remains unaltered after contact with water and does not cake. These two-way cakes are formulated to provide fuller coverage than powder foundations. They give a very matte appearance that will not wear off in hot, humid conditions such as in the Asiatic climate.

Figure 22.2 The four iron oxides used in foundations.

The main drawback of all powders is a certain discomfort relative to foundation, mainly because of the absence of any moisturizing effect (Table 22.1).

Color creation

At the core of foundation formulations there is a combination of colored powders that must be:

- As finely dispersed as possible with optimal stability; and
- Able to create a natural-looking tinted film once smeared over the skin.

To achieve this end, the formulator has available various colorants that comply with the different cosmetics legislations (positive lists) and are thus certified to be harmless, chemically pure, and microbiologically clean. These are inorganic pigments such as metallic oxides – yellow, red, and black iron oxides – to which colored and uncolored pearls can be added to give a lustrous effect. To brighten foundations (especially the darkest ones) blue pigment can be substituted for black.

For improved pigment dispersion and formula stability, the process of pigment coating has gradually become the standard. In water/silicone emulsions, a silicone coating is most frequently used. Coating with an amino acid aims at developing products for sensitive skin.

Pigments and coverage

The amount of titanium oxide pigment in the product is an indication of its ability to cover skin flaws (i.e. the level of coverage provided). A foundation is characterized by theoretical coverage on a scale from 7 (natural effect) to 50

Table 22.1 Products categories overview.

Skin type target	Formulations characteristics	Name of category	Main objectives
All types of skin but adapted to Asian routine	Uncolored formulations To be applied under foundation	Foundation base	Application: Lasting effect – spreadability Moisturizing effect – matt finish
All types of skin	Weakly colored	Tinted creams	Strong skincare attributes
All types of skin	Weakly colored but pearly	Bronzers Highlighters	Healthy "glow" effect, suntan color
All types of skin	Greens, purples, blues, apricot	Complexion correctors	Correction of discoloration (red spots by green tints) Complexion freshener (apricot – blue)
All types of skin	Low to full coverage	Fluid foundations	Wear – matt finish Antiaging – radiance
Normal to oily skin	Low to full coverage	Compacted powders, such as two-way cakes (adapted to Asian routine)	Matt finish – complexion evenness
Normal to dry skin	Medium to full coverage	Compact foundation	Evenness – adjustability of the result. Comfort – mobility
Normal to oily skin	Weak to medium coverage	Waterpacts (poured emulsions)	Same properties as compacts, plus freshness and hydrosoluble actives
Eye contour	Medium to full coverage	Concealers	Hides dark circles under the eyes
All types of skin	Transparent to opaque (mineral makeup)	Loose powders	Matt finish and adhesion – evenness

(corrective makeup). However, this ignores the optical properties of the product, which may also be able to mask skin defects through a soft focus effect [8]. It also does not take into account the influence of texture, which will determine how transparent or opaque the colored deposit is according to the ability of the product to spread evenly as a thin layer over the skin.

Importance of fillers

Fillers are all the non-pigment powders introduced in the product to provide:

- Covering power;
- The ability to absorb sebum and sweat so as to make the skin velvety and fix the color to the skin;
- Fineness and smoothness, which enhances cosmetic qualities of the textures; and
- Spreadability, which makes application easier.

Both form and chemical nature govern the final qualities of fillers (Figures 22.3a–c). Talc is an example of a spreadable, lamellar powder that is widely used for its extreme softness and absorbing power. Kaolin, starches, and calcium carbonate used to be widely employed but they have now been superseded by:

- Different varieties of silica, sometimes porous forms;
- Polymers such as nylon and polymethylmethacrylate (PMMA); and
- Mica platelets that can also be coated.

Not only are these powders essential to the basic properties of a product, but they also contribute to its optical properties. Transparent or opaque, lustrous, matte, or soft focus, they help to achieve the desired finish on the skin.

Facial foundation application

Most women usually apply their facial foundation first when applying cosmetics. They may choose to modify their complexion color or make it more glowing and even without changing the color. Whatever effect is desired, makeup is used to recreate an ideal of color and finish peculiar to each individual according to ethnic and cultural practices. It must also be adapted to suit the woman's routine: application of a single product, use over a base or under a powder, stroked on by finger or by sponge.

There is a great diversity in the use of complexion makeup. The formulator must address several issues. Being familiar

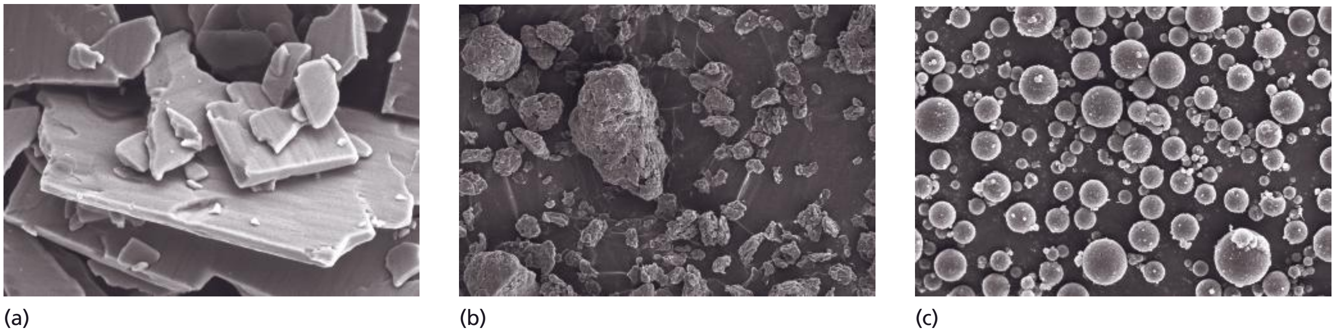

Figure 22.3 Shape variety of fillers (a–c).

with the various skin color characteristics is a primary requisite for recreating the shades that closely match the ethnic origin of the user. For any given product, this is a necessary prerequisite for creating a range of shades that will likely satisfy the women throughout the world, whether Caucasian, Hispanic, African, or Asian.

A large study carried out on a widely representative panel demonstrated significant differences in the colorimetric characteristics of skin color of six ethnic groups living in nine different countries [9,10]. The recorded measurements enabled the definition of a wide color space showing the various color spectra typical of each ethnic group's skin color mesh and overlap (Figure 22.4).

Further studies showed that the variety of makeup routines reflected the ethnic origin and cultural heritage which determines whether a woman feels positive toward her natural skin color. For many women, skin color is a major factor in their cultural identity. Complexion makeup is the easiest way to achieve even skin color by erasing surface color variations or correcting color unevenness. Some women wish to appear more deeply "tanned" than their natural color. This behavior is commonly found in Caucasian and Hispanic women. Japanese women, however, desire their makeup to give them a lighter complexion (Figure 22.5) [10].

The formulator works within this defined scope to develop shades matching natural skin colors. To meet women's expectations, it is necessary to analyze how women self-perceive their complexion. By identifying skin colors within a definite color range and precisely identifying the makeup habits of women over the world, it is now possible to formulate a variety of shades that match up with the wishes of all women.

Emphasis on quality, safety and confirmed performance

Complexion makeup creates an intimate relationship between the skin and a complex formulation that is left on for hours. Before being marketed, every product has to undergo a battery of tests to confirm its safety and performance. There are several steps in this process.

Design stage

The formulator must ensure high quality ingredients are used by defining specifications and analytical controls and carrying out screening for the non-toxicity of the ingredients with *in vitro* tests on reconstructed skin models. Each raw material used must be cleared for safety and have a proper toxicologic dossier.

Formulation stage

It is necessary to:

- Evaluate stability by subjecting products to thermal cycles to accelerate aging.
- Confirm the level of microbiologic preservation of the formulas using challenge tests. The selected method of preservation and the nature of the preservatives depend on the technology involved (powder emulsion, anhydrous compact). The risk of microbiologic contamination increases with the water content. It also depends on the packaging; a pump bottle provides better protection than a jar.
- Check it is harmless through using alternate methods: *in vitro* testing and including tests run on reconstructed skin model, e.g. (EpiSkin®, L'Oréal Episkin SNC, Lyon, France); clinical tests (simple patch test [SPT] and repeated patch test [RPT]); and, finally, user tests under dermatologic controls, carried out on the product's targeted skin types, particularly on sensitive skins and using wide ranging, representative panels. Use testing under ophthalmologic controls is carried out systematically on products intended to mask under-eye rings.

Performance stage

The performance of the product must be studied to ensure that it complies with consumer wishes and to obtain an unbiased opinion on advertising claims and consumer complaints. Sensorial analysis tests provide qualitative and quantitative assessments of a product's features by a trained panel of experts, as well as by untutored panels performing the tests under the formula's normal user conditions.

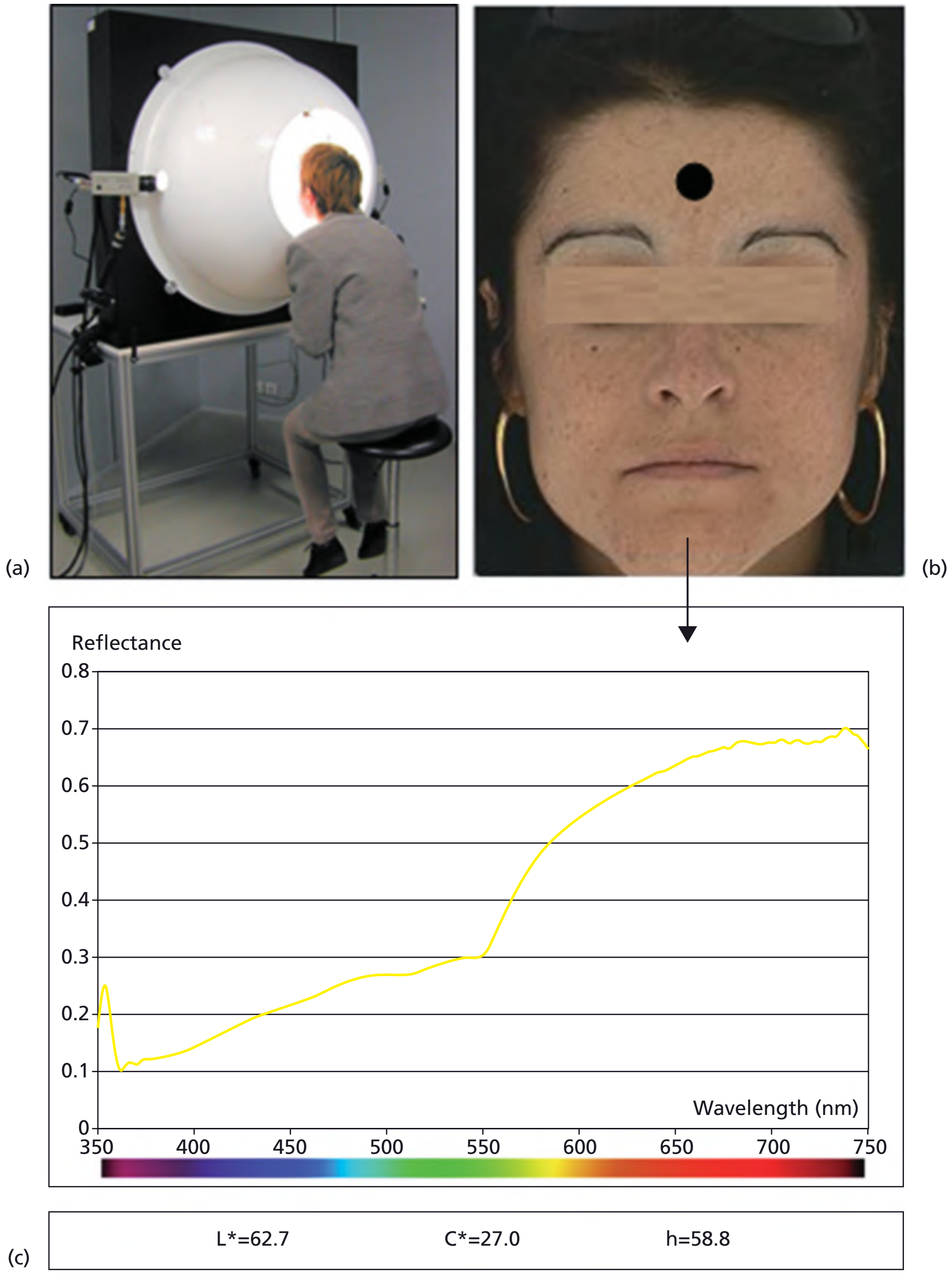

Figure 22.4 (a) The color of the forehead was measured using a spectroradiometer inside a Chromasphere™. (b) The volunteer placed her face into the Chromasphere. A standardized camera was used to acquire pictures of the face. (c) A spectroradiometer measured the reflectance of forehead in the visible field 400–700 nm every 4 nm. The recorded spectrum was expressed in the CIE 1976 standard colorimetric space L*C*h D65/10° where each color is described through three coordinates that reflect perception by human eye. h, Hue angle (angular coordinate); C*, chroma (radius coordinate); L*, lightness (*z* axis).

Additionally, a complexion product can be tested with the conventional methods used for skincare cosmetics:

- Measurement of moisturizing effects using SkinChip® (L'Oréal, Chevilly-Larue, France) or Corneometer® (Courage & Khazaka, Köln, Germany);
- Effects on skin firmness with using the Dermal Torque Meter® (Dia-Stron Ltd, Andover, UK);
- Image analysis on skin imprints or, even better, projection of light fringes involving no contact with skin (i.e. skin in real conditions with makeup as applied) to assess antiwrinkle performance.

Also specific tests:

- Color appraisal using the Chromasphère® (L'Oréal, Chevilly-Larue, France): the difference in the color of the skin before and after applying makeup quantifies the improvement in color evenness and change in color effect. Moreover, it makes it possible to monitor both. As a result, the manufacturer can claim that its makeup effects last a given number of hours.
- Evaluation of the matt finish with a suitable device (Samba® [Bossa Nova Technologies, Venice, CA, USA]).

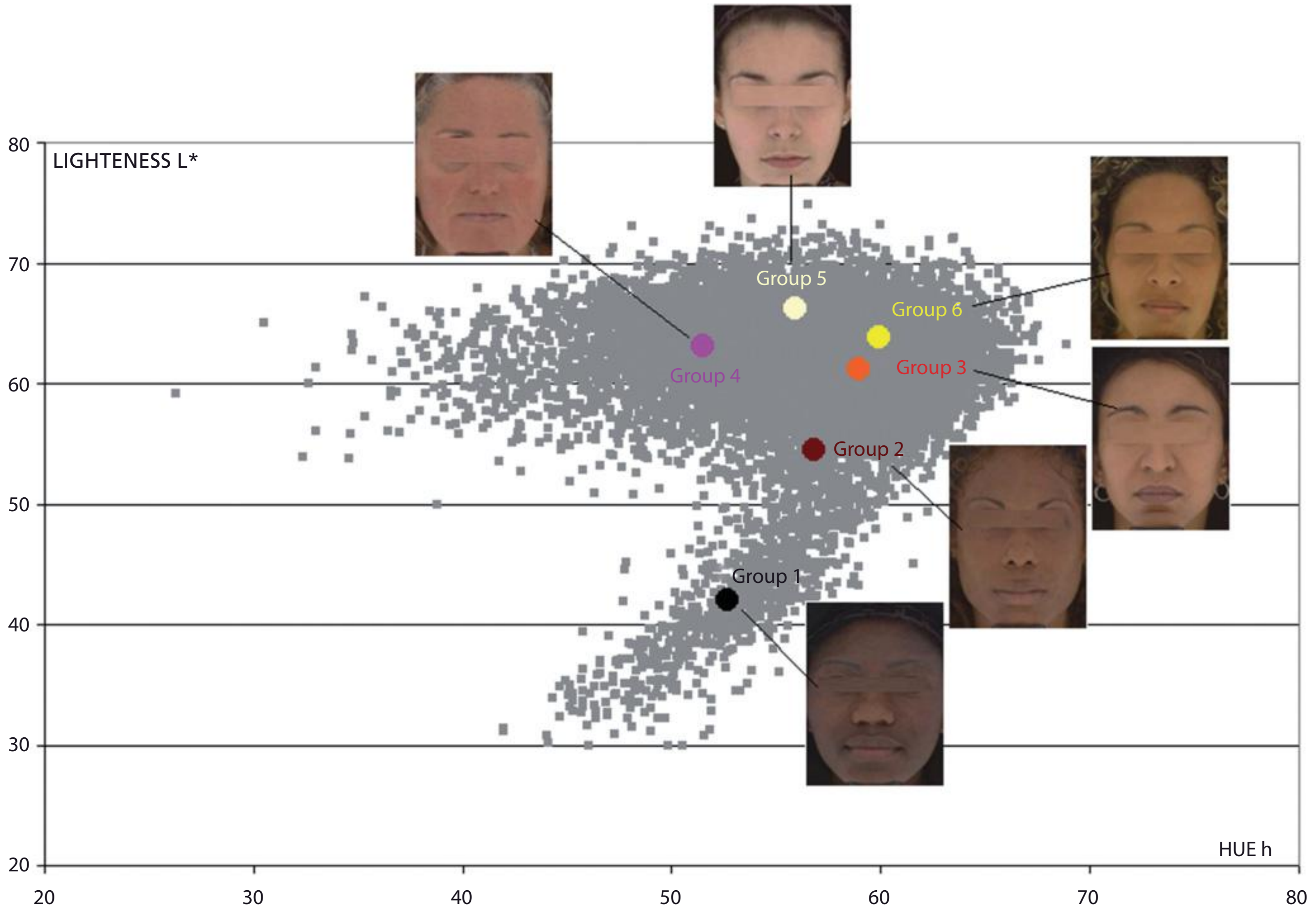

Figure 22.5 The worldwide skin color space depicted in (h, L*) and split in six groups of skin tones that reflect the color diversity.

Conclusions and prospects

Beauty is diverse. Textures, tones, matte or lustrous results, play time, and sensoriality must all come together to give a woman a simple means to recreate her ideal complexion. Complexion makeup products today benefit from knowledge of physical chemistry, resulting in better understanding of the relationships between chemical composition, texture, and application behavior. Facial foundations benefit from technologic advances in optics, which has generated formulations that are sheer, glowing, matte, able to provide soft focus concealment of flaws, while simultaneously giving shades that mirror the natural hues of the skin.

Complexion makeup products have been expanded to deliver multisensory effects and address ethnic diversity issues. From simple emulsions applied by finger, facial foundations have evolved into mousses, creamy compacts, and soft powders that can be applied by brush or sponge, and layered. Facial foundations contribute to beauty of the face respecting the women's own skin, but also addressing their culture and ethic diversity [11,12]. New forms, new optical effects, and new application methods will permit users to attain their ideal complexion irrespective of origin or own canons of beauty.

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Chapter 23: Camouflage techniques

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BASIC CONCEPTS

- Camouflage makeup is used to cover facial defects of contour and color.
- Camouflage makeup must be artistically applied to achieve an optimal result.
- Camouflage techniques can improve quality of life.
- Camouflage therapists can train patients in the proper application techniques for cosmetics.

Introduction

Camouflage techniques can be helpful in patients who do not achieve complete or immediately attractive results from dermatologic therapy. Because appearance is one of the pivotal factors influencing social interactions, facial blemishes and disfigurements are a psychosocial burden in affected patients leading to low self-esteem and poor body image. Camouflage makeup can normalize the appearance of skin and improve quality of life. Training in camouflage techniques is essential because the application is different from regular foundations. This chapter discusses the use of camouflage cosmetics.

Definitions

Camouflage cosmetics were introduced more than 50 years ago to improve the appearance of World War II pilots who had sustained burns. The products provided an opaque cover over the damaged skin areas. Modern high quality camouflage products provide a excellent coverage, but with a more natural appearance (Figure 23.1).

There are several brands of camouflage makeup on the market. They aim to conceal skin discoloration and scars and to impart a natural, normal appearance. Camouflage products differ from makeup products purchased over the counter. They contain up to 25% more pigment, as well as fillers endowed with optical properties. Camouflage makeups are waterproof and designed to cover and mask a problem, but must be mixed to match the patient's skin tone. The goals of camouflage cosmetics are to provide [1]:

1 *Color:* Camouflage makeup must match all skin tones as it should blend into the color of the area on the face it is intended to cover evenly.
2 *Opacity:* Camouflage makeup must conceal all types of skin discoloration, yielding as natural and normal an appearance as possible.
3 *Waterproof:* Camouflage makeup must be rain and sweat-resistant, remaining unaltered with athletics (e.g. swimming).
4 *Holding power:* Camouflage makeup must adhere to skin without sliding off.
5 *Longer wear:* Camouflage makeup must provide the assurance of long wear with easy reapplication, if necessary.
6 *Ease of application:* Camouflage makeup must be easy to apply. Too many steps and color applications may create patient confusion.

There are several different types of camouflage cosmetics:

1 *Full concealment:* A method referring to complete coverage of the damaged skin and extending beyond the boundaries of the injured area. High coverage foundation creams or cover creams should be used for full concealment.
2 *Pigment blending:* A method that involves selection of a cover cream that matches the color of patient's foundation.
3 *Subtle coverage:* A light application of foundation cream that conceals only moderately.

Contouring is used to minimize areas of hypertrophy or atrophy present in facial scars, using highlighting or shading to create the illusion of smoothness.

Camouflage makeup application procedures

It is important to remember that camouflage makeup is most effective when applied over skin with color abnormalities or

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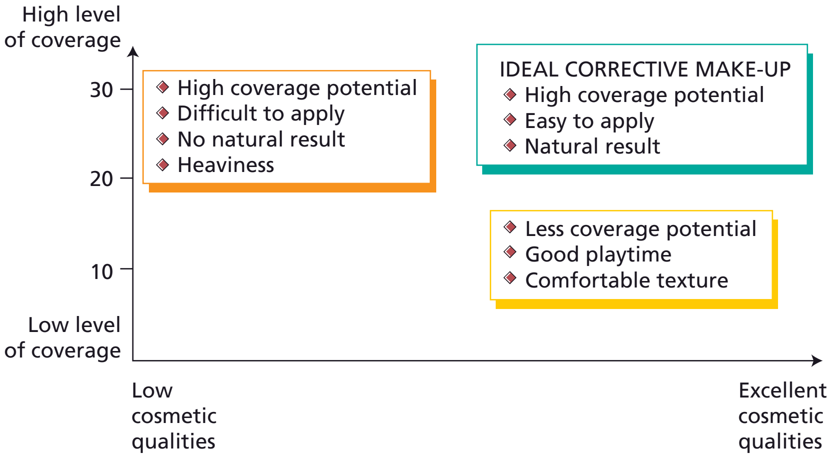


Figure 23.1 Ideal corrective makeup: a compromise between coverage and cosmetic qualities. After Sylvie Guichard, L'Oreal Recherche.

discoloration. The size of the defect is immaterial, because it is as easy to cover a large blemish as a smaller one. However, the camouflage of texture abnormalities is more challenging. Rough scars are more difficult to conceal than smooth scars because unevenness is exaggerated after camouflaging [2].

This section of the chapter presents the steps necessary to complete a camouflage makeup application procedure for a given patient. First, patients should be asked about prior experience in attempting to camouflage their lesions with or without medical makeup. If they have no experience, the necessary steps should be discussed in detail. Second, the patient's skin should be cleansed with a product selected according to patient's skin type. For an optimal camouflage result, the skin should be well exfoliated and moisturized. If using a camouflage product without sun protection factor (SPF) protection, a sunscreen-containing moisturizer should be selected otherwise a bland moisturizer can be used.

Third, the camouflage product must be selected to match the patient's skin. The camouflage therapist should identify the underlying tones that contribute to skin color: haemoglobin produces red, keratin produces yellow, and melanin produces brown [3]. Thinner skin possesses more red tones while thicker skin appears more yellow. For this reason, it is almost impossible to mimic natural skin color with only one shade.

Fourth, the camouflage therapist must understand color. There are three color coordinates: hue, value, and intensity.

1 *Hue* is the coordinate for the pure spectrum colors commonly referred to as "color name" – red, orange, yellow, blue, green, violet – which appear in the hue circle or rainbow. Each different hue is a different reflected wavelength of light. White light splitting up through a prism has seven hues: red, orange, yellow, green, blue, indigo, and violet.

2 *Value* is defined as the relative lightness or darkness of a color. Adding white to a hue produces a high value color, often called a tint. Adding black to a hue produces a low value color, often called a shade.

3 *Intensity*, also called chroma or saturation, refers to the brightness of a color. A color is at full intensity when not mixed with black or white – a pure hue. The intensity of a color can be altered, making it duller or more neutral by adding gray to the color.

Matching a color from one manufacturer to another one is a very difficult procedure because of the variety of shades that can be produced by combining various colors and the tints of the color that can be made by varying the amount of white. Judgment of color should always be made on the skin and never in the container because what seems to be the same shade may appear quite different on the skin.

The use of neutralizers in camouflaging is somewhat controversial. Some experts think it is possible to neutralize undesirable skin discoloration [2]. For example, green undertoner neutralizes a red complexion and lavender undertoner negates a yellow complexion. Other authors think that makeup undertoners do nothing but create a third color [4]. They consider that when two colors are mixed, the result is a third color. Mixing opposite colors on the color wheel (e.g. green and red or yellow and purple) will result in an unattractive gray–brownish color that must be concealed with a color that matches the skin, which adds an extra step and thickness to the makeup.

For contouring, several products have to be applied. Hypertrophic scars appear lighter than surrounding skin, and have to be camouflaged applying a darker product than to surrounding skin. Atrophic scars, however, appear darker than surrounding skin, and have to be corrected using lighter product.

Once the shades have been selected, the camouflage therapist should apply them to the back of the hand as a painter uses a palette to warm and soften the product (Figure 23.2a,b). The warm skin makes the product more malleable so it will apply more easily. Camouflage products are best

Figure 23.2 Camouflage makeup technique. (a) Remove a small amount of the corrective makeup. (b) Warm the product on the back of the hand. (c) Apply over the imperfection to be covered. (d) Blend in round the edges. (e) Generously apply the powder. (f) Remove any surplus with a brush.

applied with a sponge in a patting motion but can also be applied with the fingertips (Figure 23.2c). The patting motion applies the product to the surface of the skin and does not clog pores, which allows the skin to retain its natural characteristics. Distinct borders are eliminated by blending the edges (Figure 23.2d).

A camouflage product often is not used over the entire face like a regular facial foundation, but the surrounding skin must be matched as closely as possible. Patients have to be reminded that skin color on the hands does not really correspond to skin color of the face. The application is generally followed up with an application of powder which sets and waterproofs the camouflage product (Figure 23.2e,f). The setting powder used should be translucent so that the camouflage product does not change color. For patients with very dry skin, it is not necessary to use a powder as the oils are quickly absorbed into the skin.

Many patients may prefer using only one shade even when the color match is not perfect. Men may not wish to mix colors. It might be of interest to show the patient the coverage with one shade and the coverage using more than one shade while demonstrating that color blending is relatively easy and worthwhile.

For men, common skin flaws must be reproduced in order to prevent a “mask-like” appearance [5]. Beard stubble can be recreated by using different sponges and a brown or black pigment that mimics surface irregularities. Other colored powdered blushes can be used on the cheeks to simulate the natural glow of youth and around the eyes and mouth to attract the attention on other parts of the face [6]. Pictures should be taken before and after the application to document the cosmetic results.

Finally, the cosmetics must be removed each evening prior to bed. Removing camouflage makeup is more difficult than regular makeup. Alcohol or acetone-based removers are too irritating for sensitive skin, thus it is better to use water-soluble cream-type makeup remover. The remover is applied generously to emulsify the makeup followed by wiping with cotton pads. The face is then rinsed with tepid water and patted dry [7].

Other camouflage therapies

A few other options than camouflage makeup therapies have been suggested. Dihydroxyacetone, the main ingredient in self-tanning creams, has been proposed for camouflaging in patients with vitiligo [8]. It may be a cheap, safe, and effective alternative especially for the hands and the feet as cover creams are waterproof but not rubproof.

Medical tatooing under local anesthesia has also been tried to create the appearance of hair in hairless areas [9]. The pigment used is made of ferrous oxide, glycerol, and alcohol. A test on a small area should be performed to evaluate the outcome. The needle should be introduced into the dermis similarly to the natural hair pattern of the patient.

Medical indications for camouflage makeup

There are various medical indications for camouflage makeup. The lesion requiring camouflage can be permanent or temporary. The best results are obtained with macules, but papules, nodules, or scars can also be camouflaged. Macular lesions for camouflaging include pigmentary disorders such as vitiligo (Figure 23.3), chloasma (Figure 23.4), lentigenes, postinflammatory hypopigmentation or hyperpigmentation (Figure 23.5); hypervascular disorders such as telangiectasia (Figure 23.6) and angioma (Figure 23.7); and tattoos. Papulonodular lesions for camouflaging include discoid lupus, acne, dermatosis papulosa nigra, and facial scars.

After a graft for oncologic surgery, or for other postsurgical scars, there may be variation in pigmentation and/or relief and corrective cosmetics may be of interest. Depending on the skin's ability to heal, camouflage therapy can be applied 7–10 days after most surgical procedures. However, the premature use of makeup following epidermal damage may cause a secondary infection or tattooing effect.

There may be transient injuries or lesions of the skin that can be camouflaged with makeup. An injury may produce hematoma and oedema that should be concealed for occupational reason or social event. Corrective makeup can also be used after medical procedures such as laser resurfacing, peels, and microdermabrasion to camouflage erythema. After filler injections, redness may also appear. Laser hair removal will induce temporary redness, but following some lasers the skin may become purpuric. Camouflage makeup optimizes the patient's postprocedure appearance. Indeed, if the patient knows he or she will be red, he or she will require an appointment at the end of the day or of the week. With corrective makeup, patients are able to go back straight to work. Similarly, after filler or botulinum toxin injections, hematomas may appear which can be camouflaged with corrective makeup.

Beginning a camouflage clinic

It is important to offer patients camouflaging makeup knowledge [6]. In general, the dermatologist will delegate this activity to a staff member. Many physicians find that a camouflage therapist can bring an added value to the practice by enhancing patient recovery.

The room for teaching camouflaging techniques should contain a table with a mirror and fluorescent bulbs to provide adequate light. A chair should be placed in the room tall enough to allow the camouflage therapist to stand. Several camouflage products should be available in various shades to match the different skin colors.

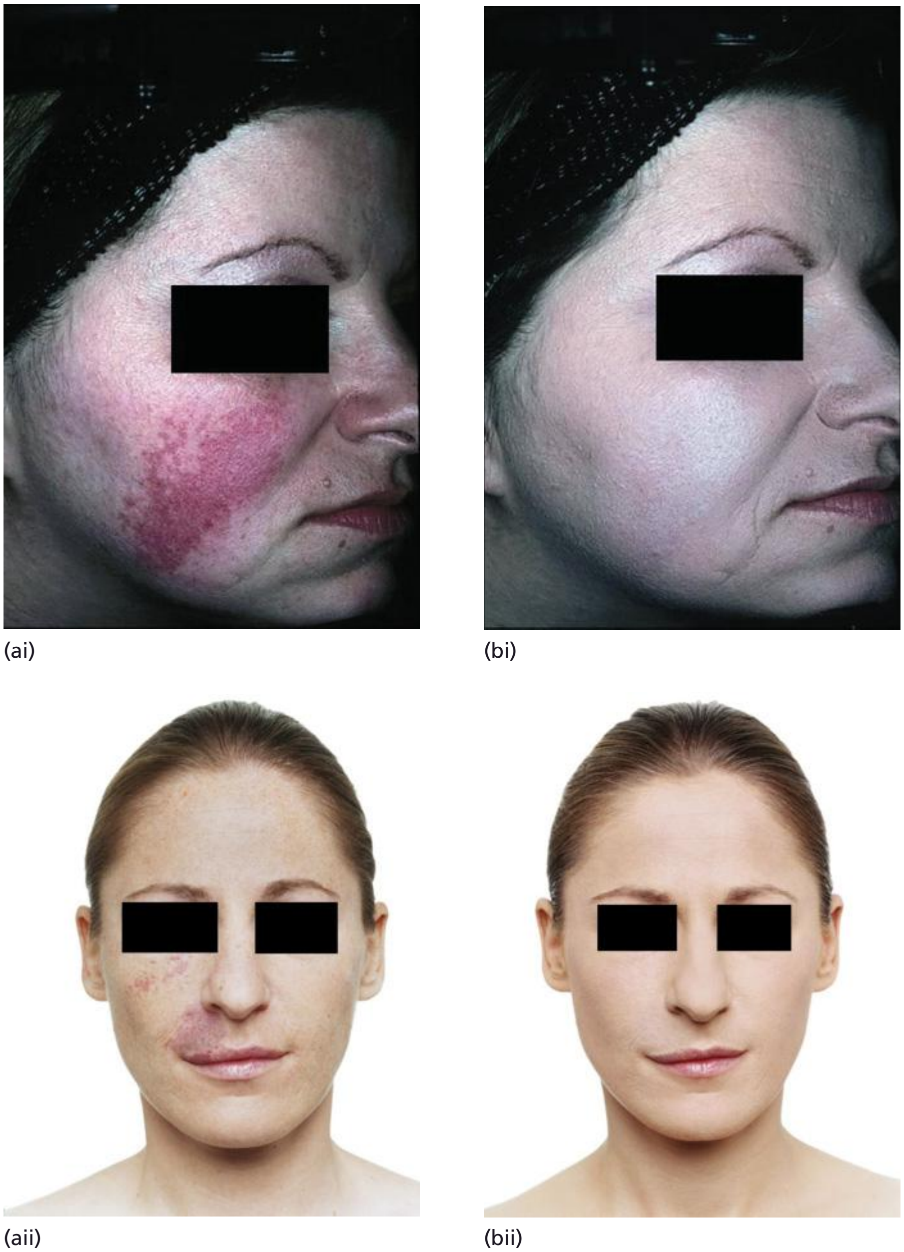
Figure 23.3 Periorbital hyperpigmentation: (a) before and (b) after camouflage.


(ai) (bi) (aii) (bii)

Figure 23.4 Vitiligo: (a) (i & ii) before and (b) (i & ii) after camouflage.


(a) (b)

Figure 23.5 Melasma: (a) before and (b) after camouflage.



(ai) (bi) (aii) (bii)

Figure 23.6 Vascular malformation: (a) (i & ii) before and (b) (i & ii) after camouflage.

The camouflage therapist

In the USA, camouflage therapists are state-licensed and medically trained skincare professionals, with both clinical knowledge and therapeutic skill [5]. They do not treat patients but educate them by providing information on the best way to go about applying camouflage makeup. In other countries of the world such a degree does not exist. Camouflage therapists should obtain appropriate training and education. They should be trained to select and apply cosmetics beyond the application of standard cosmetics. Their training should include the study of facial anatomy, highlighting and contouring techniques, and prosthetic makeup techniques similar to those used in the stage and motion picture industry.

The camouflage therapist should be a good communicator to teach patients how to apply various products, which the patient can easily reproduce without assistance. Camouflage therapists should be genuinely interested in the patient's

Figure 23.7 Telangiectasia: (a) before and (b) after camouflage.

well-being. Therefore, they should be mature enough to work with people who have a severely damaged appearance.

The camouflage therapist must record the patient's history and identify needs based on the patient's perception of the problems. Because of the clinical knowledge and personal qualities required, a trained nurse would be an ideal camouflage therapist [7,10].

The camouflage therapist can design a cosmetic treatment plan. During the interview four issues should be addressed [5]:

1. The ability of the patient to follow simple instructions.
2. The patient's social activities and job environment.
3. The patient's prior makeup experience.
4. The financial status of the patient.

Camouflage makeup and quality of life

Psychosocial aspects of skin disease has important implications for optimal management of patients. The presence of abnormal visible skin lesions may result in significant psychologic impairment. Health-related quality of life (QOL) is a measurement method to describe physical, social, and psychologic well-being and to assess the burden of disease on daily living. Several general measures have been developed [11]. Surprisingly, women who used facial foundation reported a poorer QOL than those who did not. This was interpreted to mean that more severely impacted patients are more likely to hide the disorder using camouflage cosmetics, albeit inadequately. Yet, wearing makeup may improve appearance and looking better translates into feeling better. Those who feel better show signs of higher self-esteem.

Many studies have been performed in order to demonstrate the effects of corrective makeup on patients' QOL [12–14] and remove misconceptions that the use of cosmetics can be tedious and difficult for ordinary people. A wide range of facial blemishes and disfigurements such as pigmentary disorders, vascular disorders, scars, acne, rosacea, lupus, lichen sclerosus, and keratosis pilaris have been included in these studies. QOL questionnaires were completed before the first application and after applying corrective makeup. Results show that corrective cosmetics are well-tolerated and patients report high satisfaction rates. There is an immediate improvement in skin appearance and no significant adverse effects. Corrective cosmetics rapidly improve QOL, which persists with continued use. There was no difference in QOL according to the type of facial disfigurement or the size of the affected area. Not only were patients improved with pigmentary or vascular disorders, but also with scars.

Camouflage therapy can help patients cope with skin disorders that affect appearance. The cosmetics can be used long-term without difficulty. Camouflage therapy is of great help to patients who cannot be medically improved.

Conclusions

Camouflage techniques help affected patients cope with the psychologic implications of facial blemishes or disfigurements. Covering visible signs of the disease minimizes stigmatization. Today's high quality camouflage products provide excellent good coverage with a natural appearance. Many physicians find that a camouflage therapist can bring an added value to the practice by enhancing patient recovery.

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Chapter 24: Lips and lipsticks

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BASIC CONCEPTS

- The lips possess a complex anatomy consisting of mucosa and skin.
- Lipsticks are designed to enhance the appearance of the lips.
- Lipstick is an anhydrous paste of oils and waxes in which pigments are dispensed along with other coloring agents.

Introduction

Lip makeup is an essential element in seduction and women frequently use lipsticks to make their faces more attractive. The lips are muscular membranous folds surrounding the anterior part of the mouth. This tissue is both mucosa and skin and has a complex anatomy. Labial tissue has a dense population of sensory receptors, is very sensitive to environmental stress, can present pigmentation defects, and is modified during aging. Lipstick formulations are most widely used to enhance the beauty of lips and to add a touch of glamour to women's makeup. The lipstick that we know today is a makeup product composed of anhydrous pastes such as oils and waxes in which are dispersed pigments and other coloring agents designed to accentuate the complexion of the lips. This chapter draws together our knowledge of the biology of this special tissue, and gives detailed information on the formulation elements of lipsticks.

Lip anatomy

The lips are muscular membranous folds surrounding the anterior part of the mouth. The area of contact between the two lips is called the stomium and forms the labial aperture. The external surfaces of the lips are covered by skin, with its hair follicles, sebaceous glands, and sweat glands; the inner surface is covered by the labial mucosa, a non-stratified, non-keratinized epithelium bearing salivary glands. The transitional zone between these two epithelia is the red vermilion border of the lips (Figure 24.1). It has neither hair follicles nor salivary glands, but sebaceous glands are present in about 50% of adults [1]. The red area is also keratinized, with rete ridges more marked than in the neighboring cutaneous zone.

Several studies have identified an intermediate area between the vermilion zone and the mucosa that does not contain a cutaneous annex; it is covered by a stratified epithelium that lacks a stratum granulosum but does have a thick parakeratin surface layer. This intermediate zone increases with age [2–4].

The deeper region of this soft tissue forming the lips is made up of a layer of striated muscle, the orbicularis orbis muscle, and loose connective tissue. The muscle makes a hooked curve towards the exterior at the edge of the vermilion area which gives the lips their shape.

Immediately above the transition between the skin and the vermilion zone is the Cupidon arch, a mucocutaneous ridge, also called a white roll, or the white skin roll. Its physical appearance and lighter color seem to be essentially caused by the configuration of the underlying muscle [5]. This region is rich in fine, unpigmented, "vellous" hairs that may influence the appearance of this zone.

The lips have great tactile sensitivity. Labial tissue has a dense population of sensory receptors, including Meissner corpuscles, Merkel cells, and free nerve endings. The sensitivity of the lips is somewhere between that of the tongue and the fingertips [6].

Labial epidermis

The epidermis of the vermilion region is twice as thick (180 μm) as the adjacent skin [4,7,8]. It still has the markers of cutaneous epidermis differentiation, even though it has fewer keratinized layers than the skin [9]. Barrett *et al.* [4] found that the distribution of cytokeratins (CK) differed from that of the intermediate zone, with a loss of the skin cytokeratins CK1 and CK10 and the presence of the mucosal cytokeratins CK4, CK13, and CK19. CK5 and CK14 were still present in the basal layer and occasionally in the suprabasal layer. CK8, CK18, and CK20 were found only in Merkel cells. Involucrin was present in all the zones, but its

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Cosmetic Dermatology: Products and Procedures. Edited by Z.D. Draelos.

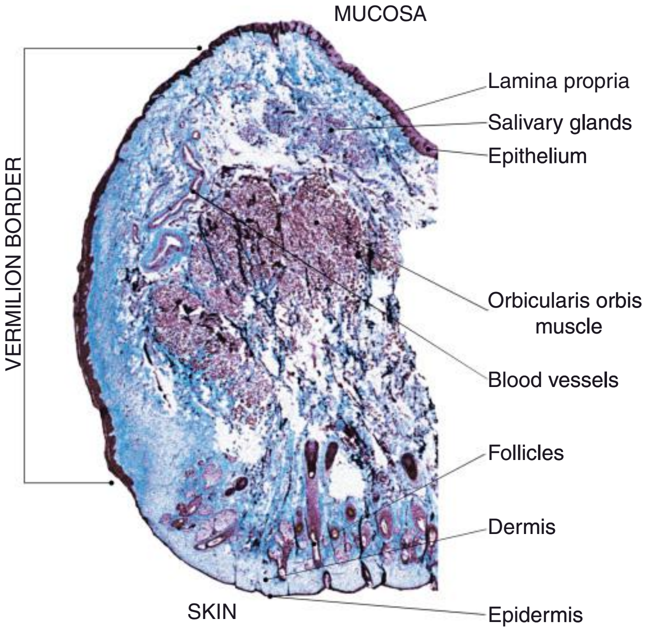

Figure 24.1 Lip histology.

restricted distribution in the stratum granulosum of the skin extended to the stratum spinosum and the parabasal keratinocytes of the lip zone and the mucosa. Loricrin, profilaggrin, and filaggrin were found in the stratum granulosum of the orthokeratinized zones but not after the junction between the vermilion zone and the intermediate zone.

The corneocytes in the mucosa are flat, smooth cells. In contrast, most of the corneocytes on the surface of the vermilion border are seen to have microvilli on all their internal surfaces when examined under the high power microscope [10]. These projections are rarely seen on the corneocytes of the adjacent skin [11]. The cell turnover of the epidermis of the vermilion border seems to be more rapid than that of the adjacent skin cells. The vermilion border also appears to lose water three times as fast as the cheeks and to have only one-third the conductance. Thus, the lips function as a barrier but their capacity to retain water is much poorer than that of facial skin [1].

Hikima *et al*. [11] showed that the surface of the lips, like the surface of the skin, has cathepsin D-like activity and chymotrypsin-like activity. These enzymes are involved in the hydrolysis of corneodesmosomes, and hence in the release of corneocytes from the skin surface.

Like the skin, the vermilion border epithelium contains melanocytes and there is melanin in the cytoplasm of basal cells [4]. However, as the melanin pigmentation is light and associated with reduced keratinization, the color of the hemoglobin is seen more clearly. There are also Langerhans cells in this zone [8]. Cruchley *et al*. [12] used immunodetection of CD1a to show that there were more Langerhans cells per unit area of the lips than in abdominal skin.

Sallette *et al*. [13] recently showed that there is more neuropeptide-type neurotransmitter in the epidermis of the lips than in the eyelids, which seems to indicate that the lips are better innervated.

Lip dermis and lamina propria

The epithelium of the vermilion border lies on a layer of connective tissue, which ensures the continuity of the cutaneous dermis and the lamina propria. This tissue is composed of collagen fibers and a network of elastic fibers.

There is a thin layer of fatty tissue between the muscle and the dermis in the cutaneous part of the lips with many attachments between the muscle and the skin [14]. The deep part of the lamina propria of the mucosa lies above the hypodermis of the subcutaneous zone. The invaginations at the junction between the epithelium and the connective tissue of the vermilion border are higher than those of the skin [15]. These papillae contain blood capillaries. The capillary loops in the vermilion border are higher than those of the skin, which accentuates the red color of the lips because of the hemoglobin in them [16].

The lymph drainage of the red border is not uniform; it flows towards the cutaneous system on the external side of the lips and towards the mucosal system on the inner side [17].

Lip topology

The description of lip topology first interested legal medicine because each individual has a different organization, much like fingerprints. The study of lip prints is called cheiloscopy. The development of kiss-proof lipsticks led legal medicine to develop protocols for revealing latent prints at a crime scene [18]. Lip prints can be classified in several ways and their distributions in populations have been quantified [19–22].

Sensitivity of lips to the environment

As the lips have little cornified tissue or melanin they are very sensitive to chemical, physical, or microbial damage. Their prolonged exposure to sunlight, particularly for fair-skinned people, may lead to the appearance of actinic cheilitis and even spinocellular carcinoma [23]. Pogoda and Preston-Martin [24] suggested that frequent applications of sunscreen can have a positive protective effect. Smoking has also been found to be a major risk factor for lip cancers.

Aging of the lips

The esthetic consequences of aging of the superficial lip tissues (sagging, distension, and ptosis) are aggravated by changes in the shape of the bone and dental infrastructure and the aging of the underlying muscles and adipose tissue. The orientation of the labial aperture changes with a drooping of the lateral commissures: from a concave curve in newborns and children to a horizontal line in adults, and then to an inverted curve in the elderly. In profile, the lips, particularly the lower lip, recede with age. The upper lip becomes lower and enlarged [3,22]. Tissues become less extensible and elastic because of repeated mechanical stresses and the weakening of the orbicularis orbis muscle with age [3,25].

The vermilion border becomes larger, longer, and thicker at the corners of the mouth [2]. While wrinkles develop in the skin around the lips with age, the outline of the lips themselves becomes sunken [22]. The depth and organization of the lips varies greatly from one person to another and some young people have deep furrows. Both the spatial resolution and the tactile sensitivity of the lips decrease with age [3,6,25,26]. There may also be histologic signs of solar elastosis. The superficial microcirculatory network (both papillary and mucosal) may become smaller and less dense (reticular and mucosal), together with an apparent thinning of the lips in older people who have lost their teeth [15].

Cosmetic surgery can be used to “refresh” and to fill the tissue to rejuvenate the lips. This might involve reducing the upper lip or recovering the shape of a young lip by a series of interventions to reinforce the shape and projection of the lips and restructure the Cupid’s bow, better define the lip outline, and lift the corners of the mouth. This surgery is accompanied by a rejuvenation of the perioral region, including removal of peribuccal wrinkles, peeling, laser resurfacing, and dermabrasion [27–30].

Lip plumpness and cheilitis

Cheilitis can be caused by a cold or dry environment, repeated pressure on the lips – as it can develop in players of wind instruments – or by defective dental work. It can also occur in people taking oral retinoids, or from a lack of dietary vitamin B_{12} (riboflavin), B_6 (pyridoxine), nicotinic acid, folic acid, or iron [31].

Hikima *et al.* [11] reported that the corneocytes at the edges of dried out lips become flattened and their surface area increased. This suggests that the turnover of these cells is slowed in dried out lips. The degree of visible dryness is also correlated with a reduction in cathepsin D, one of the enzymes involved in desquamation, but the chymotrypsin-like activity remains unchanged.

The upper lip seems to dry out less than the lower lip as it is less exposed. While the hydration measured by the capacitance does not seem to change with age, the loss of water via the lips decreases [25]. Clinically assessed drying out increases with age [22].

Defects of lip pigmentation

Pigmentation defects, particularly ephelides and lentigos, may also occur. The lips of some populations, like those from Thailand, may become dark because of the accumulation of melanin in the basal layer of the epidermis without any increase in the number of melanocytes [32]. This disorder may be congenital, caused by smoking, or an allergic reaction to a topical compound. Smoking can also increase pigmentation of the buccal mucosa in darker-skinned people (Africans, Asians, Indians) [33].

Lipsticks

Lipstick, a symbol of feminine beauty and sensuality and a method of attracting attention, has a very long history. The red color and bloom (lively, plump) of the lips was first accentuated in the ancient world. Today, a woman uses lipstick to highlight her individuality, character, and seductive capacity and to underline her smile [34]. It is everything but an empty gesture; it reflects the image that the woman has of herself and what she wants to project in society.

In the 18th century, people distinguished between the red coloring used for the lips and the rouge used for the cheeks. Many rather toxic substances have been used in the past. The red coloring material used can be of animal, vegetable, or mineral origin. It could be obtained from the cochineal beetle imported from Mexico, the purple dye extracted from molluscs, red sandalwood from Brazil, or the orcanette root. The minerals most frequently used were lead oxide (minium), mercuric sulfate (cinnabar), and antimony.

The popularity of lipstick exploded in the 20th century with the use of lip makeup based on a colored paste made from grapes and sold in little jars. These were deep colors. The mouth became much fuller with the arrival and spread of talking movies in the 1930s. The first “indelible” or “kiss-proof” lipstick was the lipstick Rouge Baiser sold by the French chemist Paul Baudecroux in 1927. Red, pouting lips became all the rage in the 1950s, while in the 1990s lip gloss or brilliant was produced as a paste rather than a stick.

Lipstick formulation

The lipstick that we know today is a makeup product composed of anhydrous pastes in which are dispersed pigments and other coloring agents designed to accentuate the complexion of the lips. It is formed into a stick by pouring the hot material into a mould. A classic lipstick formula is:

- Wax (about 15%) which is solid at room temperature. It provides hardness and creaminess when applied;
- Waxy paste (20%) helps lubricate the lipstick after application;
- Oil (30%) for dispersing the pigments;
- Texturing agents (about 10%) to improve the texture;
- Coloring agents, pigments, and/or pearls (20%) to give color;
- Preserving agents and antioxidants (1%) to stabilize the formulation;
- Perfume (1%);
- Active ingredients including UV filters to improve long-term benefit.

Table 24.1 Waxes.

Origin	Wax	Properties	Source	Appearance
Animal	Beeswax	Composed of fatty acids and alcohols Thickener	Bees	Relatively solid, give a lustrous appearance
Plant	Carnuba wax	Harder than bees wax Very slightly acid, but brittle Often used mixed with bees wax	From the leaves of the carnuba palm (Brazil)	Relatively hard, and give a lustrous appearance
	Candelilla wax	Very hard wax	From the candelilla plant	Matte appearance
Mineral	Paraffin Ozokerite	Non-stick Non-polar White, fairly transparent and odorless	Paraffin is obtained from oil refining	More malleable

Table 24.2 Waxy pastes.

Origin	Name	Properties	Source	Appearance
Synthetic	Polybutene	Adherence Brilliance Extremely hydrophobic	Synthesis from ethylene	Very viscous transparent, viscous liquid
Synthetic	Methyl hydrogenated rosinate			

Waxes

The wax may be of vegetable, animal, or synthetic origin. They are solid at room temperature and must be melted for use. They create a crystalline network within the formulation that gives the lipstick its shape. The wax is chosen to give the stick a suitable hardness so that it does not break during application. They also give the lipstick a rather matte appearance (Table 24.1).

Lipsticks are currently made using specific fractions of wax that provide specific fusion points. These refined fractions are whiter and more odorless than the original waxes, which were a complex mixture of natural lipids.

Waxy pastes

They are called pastes because they are semi-solid forms of wax at room temperature (Table 24.2). They contribute to the cosmetic function of the lipstick by helping to keep the color on the lips. They can do this because they are sticky and because their fusion point is close to the temperature of the lips, thus enabling the stick to melt during application.

Oils

These hydrophobic liquids are solvents for the coloring agents that allow them to diffuse so as to develop their color. The oils provide comfort, lubrication during application, and contribute greatly to the cosmetic effect. They may also provide brilliance and subtlety (Table 24.3). Castor oil has been used for many years but is now less often utilized. It has excellent pigment-dispersing properties because of its polarity; its main inconvenience is its unpleasant taste and odor (caused by oxidation). It is gradually being replaced by stable, odorless, fatty acid esters.

Table 24.3 Oils.

Name	Properties	Source	Appearance
Di isostearylmalate	Emollient Not oxidized Colorless Odorless	Synthetic	Colorless liquid
Trimethylolpropane Triisostearate	Emollient Comfort	Synthetic	Colorless, viscous liquid
Polyglyceryl-2 Triisostearate	Emollient Comfort Dispersant	Synthetic	Transparent pale yellow liquid

Texturing agents

These components can be very different; they provide moisturizing, brightness, and subtlety. For example, polyamide

Table 24.4 Pigments and coloring agents.

Component	Origin
Titanium (IV) oxide – mica	Mineral
Ferrous oxide (II)	Mineral
Ferric oxide (III)	Mineral
DC Red 33	Organic
DC Red 27	Organic
DC Red 21	Organic
DC Red 7	Organic
DC Red 6	Organic
DC Red 28	Organic
DC Red 30	Organic

powders bring softness, silica beads provide subtlety and a matte finish, titanium dioxide flakes give a soft-focus effect, while bismuth oxychloride gives a satin, shimmering effect.

Pigments

Pigments are synthetic substances or of mineral origin. They are fine powders when dry and are used because they are very opaque and have great coloring properties (Table 24.4).

The solid powders are suspended and dispersed in oil. The covering property of a lipstick depends on its pigment content; these pigments can hide the underlying lip color. International regulations strictly limit the use of pigments. Only a restricted number can be used on the face because of the risk of ingestion. The pearly and metallic effects are obtained with composite materials, often multilayered. These are interference pigments because they create long wavelength interference patterns in natural light. Holographic effects may be obtained by liquid crystals (cholesterol derivatives) or multilayer plastic slabs (terephthalates).

Antioxidants and preserving agents

The most frequently used antioxidants are the β-carotenes (provitamins A), ascorbic acid, and tocopherol, which are all powerful, natural antioxidants. The preserving agents are used to control bacterial proliferation. There are few preserving agents (phenoxyethanol mainly) in anhydrous products such as lipsticks.

Perfume

Perfume provides the desired smell to the lipstick. It is generally used as an oil-based concentrate that is miscible with the other oils in the formulation.

Active ingredients

These are used to provide their specific properties to the finished product and often permit claims of antiaging or moisturizing. They must be included at the considered concentration to be effective. Vitamin A, as β-carotene, vitamin E (tocopherol), and vitamin C are classically used in lipstick. Sunscreen can be used to protect the lips against UV rays for an antiaging quality.

Lip glosses and brilliances

A lip brilliance is a makeup product that generally has low covering qualities but reflects light and gives the lips a shiny appearance. A brilliant lipstick has a gloss effect. So, by extension, the term lip gloss includes lip brilliants.

Lip glosses nourish the lips and give them a light, wonderfully supple appearance and a long-lasting sparkle. Their crystalline effect is brought about by their ultra-brilliant, transparent base. They may be used over a lipstick to give a new sparkle to the lipstick color, or simply provide the lips with a very pure, superfine color. Its formulation differs from that of lipstick only in the quantity and nature of the components classically used in lipsticks.

Lip glosses are frequently sold in small flasks and are applied with a special applicator. They are not applied directly to the lips, so they do not need to have a solid structure like a lipstick. The wax content is lower and the content of waxy paste higher.

Conclusions

Lipsticks and lip glosses are essential to a women's makeup, and have a key role in the affirmation of her personality and well-being. These skin surface products – thanks to their simple formula that contains a limited number of constituents – are usually well accepted and adverse reactions are very rare.

Pink, purple, even blue, the colors follow the fashion trends, and, most of the time, they are coordinated with clothes and nail polishes. The shapes and textures that women appreciate remain quite classic. Indeed, if raw materials are constantly evolving, cosmetic regulations worldwide lay down some new restrictions to the manufacturers of the beauty sector. Nevertheless, these regulatory evolutions still allow the creation of ever more innovative and qualitative products.

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Chapter 25: Eye cosmetics

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BASIC CONCEPTS

- Mascara is intended to darken, thicken, and lengthen the lashes to make them more noticeable. Careful selection of mascara film materials and new applicator technologies are enhancing women's abilities to accentuate these characteristics quickly and effectively.
- Other eyelash products, beyond mascara, such as lash perms and lash tints are becoming more prevalent and are beginning to gain mainstream acceptance. These new products are changing the way women think about eyelash beauty.
- Eyeshadow is color applied to the upper eyelids that is used to add depth and dimension to the eyes, thus drawing attention to the eye look or eye color.
- Eyeliner is used to outline the eyelids, serving to define the eyes and to make the eye look more bold or to give the illusion of a different eye shape.
- New eye cosmetic products are being introduced that feature enhanced long wear, new applicator surfaces, novel color effects, sustainable natural materials, improved application, and even lash growth.

Introduction

This chapter gives a broad introduction to eye cosmetics. Mascara, eyeshadows, and eyeliners are presented along with the physiology of eyelashes and future trends.

Eye cosmetic history

Cosmetics have been used to decorate the eyes for thousands of years. In Ancient Egypt materials such as charcoal and kohl were mixed with animal fat to create ointment for darkening the lashes and eyelids. They used eye cosmetics for the same reasons that we do now: in youth to attract by accentuating and drawing attention to the eyes, and in age to preserve beauty as it starts to fade [1,2].

Moving forward to more modern times, in the 18th and 19th centuries, men would condition their hair and mustaches with a touch-up product for graying hair called Mascaro. This was also used in stage makeup as both an eyelash and brow cosmetic. In the 19th century women darkened their lashes with lamp black, which they could collect simply by holding up a plate to catch the soot above a lamp or candle flame. They also used cake mascara (soap, wax, and pigment wetted with a moistened brush) to darken their lashes, or they could plump their lashes with petroleum jelly. Since then a wide variety of innovations have changed both the way we decorate eyes and the penetration of these products into daily use by the majority of women [3].

The first half of the 20th century saw a range of new product forms emerge including liner pencils, melted wax dripped onto lashes, eyelash curlers, eyebrow pencils, lash dye, cream mascara (toothpaste style tube with brush), false lashes, liquid drops, and even turpentine-based waterproof mascara. As the century progressed, more and more women were using eye cosmetics, driven in part by the makeup of the popular actresses in the Hollywood movies and also because of new distribution systems, such as Maybelline's mail order mascara and availability at local stores. By the late 1930s, the majority of women applied cosmetics around their eyes [4].

In 1957, Helena Rubenstein launched the first modern day mascara – a tube of mascara cream with the applicator stored inside the tube. No longer was the mascara applicator separate from the mascara formulation. This efficient and more sanitary design took off quickly and, by the 1960s, became the standard form of mascara. Once this new product form was established, the applicator quickly changed from a simple grooved aluminum rod to the ubiquitous twisted wire brush applicator that is the predominant applicator today [3].

By the 1970s, waterproof mascaras were more appealing than the past turpentine-based versions because of the availability of purified petroleum-based volatile solvents [4]. Fibers were introduced into mascaras for a "lengthening" benefit. Eyeshadows were available in a broad range of

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Cosmetic Dermatology: Products and Procedures. Edited by Z.D. Draelos.

matte and sparkling colors, partly because of the growth of iridescent pigments in the 1960s. By the 1980s and into the 1990s, the rapidly improving performance of polymers resulted in more durable eye cosmetics that would glide on with ease and maintain their effect for hours [5].

Eyelash physiology

Eyelashes are terminal hairs growing from follicles around the eye. Like all hair, the eyelash is a mixture of dead cells that have been keratinized, binding material, melanin granules, and small amounts of water. The outer surface is comprised of a series of overlapping, transparent scales called cuticle cells that protect the inside, called the cortex. The cortex contributes to the eyelash's shape, mechanical properties, and color. Eyelashes vary by ethnicity and, as a result, can have an elliptical or circular cross-section with an average diameter of 60–120 µm, tapering to a fine, barely pigmented tip [6–8]. Figure 25.1 is a series of scanning electron micrographs that show the shape, cross-section, and surface morphology of an eyelash.

While hair over the body is likely there for thermal insulation and proximity sensation, eyelashes protect the eye from debris and signal the eyelid to close reflexively when something is too close to the eye. Chemically, eyelashes are the same as scalp hair, and across ethnicities the chemistry of lashes is the same. Eyelashes have a substantially shorter, slower growth phase than scalp hair, hence their shorter length, and they typically last for 5–6 months before falling out. An active follicle, during the anagen (growth) cycle, will typically produce a lash at approximately 0.15 mm/day, half the growth rate of scalp hair. If a lash if plucked from the hair follicle, a new hair can begin growing in as little as 8–10 weeks [6–7,9].

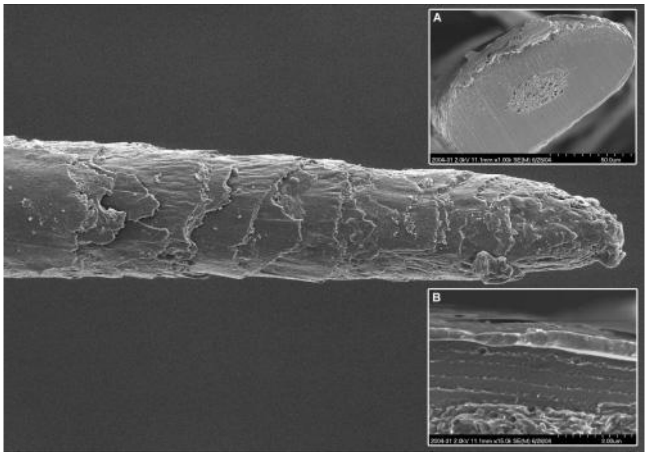

Figure 25.1 Scanning electron microscope images of the eyelash. The eyelash tapers to a fine tip. The cross-section may be circular or elliptical (A), and the surface is composed of overlapping cuticle cells (B).

The direction that the eyelash protrudes from the eyelid is based on the follicle's position in the skin. The curvature of the lash is derived from the shape of the follicle. As the lash forms inside the follicle, and the protein strands are bonded together, the lash shape that is formed corresponds to the shape of the follicle they are formed within. Eyelashes are arranged around the eye in a narrow band 1–2 mm wide. Lashes are longer (8–12 mm) and more numerous (90–200) on the upper eyelid, while lower eyelid lashes number 30–100 and are typically 6–8 mm long [8].

There are a number of ailments to which the eyelashes are prone, the most common of which are listed in Table 25.1.

Mascara

Over half of women who wear cosmetics wear mascara. In fact, mascara is a product that women tend to be passionate about. When asked which cosmetic they would choose if they could only choose one, over 50% of women would choose mascara.

Mascara is intended to darken, thicken, and lengthen the lashes to make them more noticeable. Through careful selection of materials, mascara films can be produced to accentuate these characteristics. Mascara formulations can be roughly divided into two different types: water-resistant and waterproof.

Table 25.1 Common eyelash ailments.

Ailment	Description
Madarosis, or hypotrichosis	Thinning, or loss, of eyelid and eyebrow hairs. Can be caused by aging, physical trauma, burns, X-ray therapy, overuse of glued false lashes, and trichotillomania (impulse to pull out one's hairs, including eyelashes)
Stye	A stye can be caused, among other things, from a bacterial infection of the eyelash follicle's sebaceous glands, leading to an inflammation of skin tissue around the eyelash follicle
Poliosis	Lashes losing their pigmentation with age, caused by less melanin granules being present in the lashes. Gray lashes are pigmented, just with less pigment than those of a younger person. Completely unpigmented lashes are white
Trichiasis	This is the abnormal growth of lashes directed towards the eyeball, causing irritation and possibly leading to infection

Mascara composition

Water-resistant mascaras typically deliver a combination of waxes, polymers, and pigments in a water-based emulsion to the lashes. The water helps contribute to the enhanced lash attributes by absorbing into the lash, bloating its diameter by as much as 30% and in many cases forcing the lashes to curl. The waxes are emulsified into the water creating a thick, creamy texture that glides onto the lashes in a thick film that resists fading, abrasion, and flaking throughout the day, but is still easily removed with warm water and soap. Polymers are often included to bind the mascara to itself as well as to the lashes. Advances in polymer technology over the last 20 years have led to very substantive films that last throughout the day, even though they are delivered to the lash in an aqueous medium.

Consumers who desire the longest lasting mascara will select the anhydrous waterproof formulations which contain little to no water and deliver very durable, but difficult to remove films. Waterproof mascaras usually use hydrocarbon solvents and anhydrous raw materials. They provide a long-wearing film on the lashes, which is very resistant to water, smudging, and smearing. Its anhydrous nature makes it more difficult to both apply and remove, and it may have more eye irritation potential. A list of common water-resistant and waterproof mascara ingredients and their functions can be found in Table 25.2.

Additional ingredients can be added to a formulation to enhance particular eyelash characteristics. A common method for producing lengthening mascara is to include fibers in the formulation so that, when applied, the fibers will extend beyond the natural ends of the eyelashes. Similarly, large, lightweight, hollow particles may be incorporated into the mascara film to create a thicker film for bolder lashes. Synthetic or natural polymers with novel properties can also be incorporated to induce a curling effect on the lashes.

Other forms of mascara are available such as clear mascaras, waterproofing topcoats, pearlescent topcoats, and lash primers. This breadth of cosmetic options gives consumers many choices to groom and decorate their lashes.

Mascara applicator technology

Consumers will typically judge a better mascara applicator as one that creates more clumps of lashes that are uniformly spaced apart [10]. However, different consumers apply their mascara for different end looks – some aspiring for only a few (spiky) clumps of lashes, others working towards well-separated lashes. The twisted wire brush has been the mainstay mascara applicator for 50 years. As seen in Figure 25.2, it is simply a metal wire bent back upon itself into two parallel wires. Bristles, typically made of nylon, are inserted between the bent wire and it is twisted around to form a

Table 25.2 Water-resistant and waterproof mascara ingredients and function.

Class	Material type	Examples	Function
Water-resistant solvent	Carrier fluid	Water, propylene glycol	Deliver mascara ingredients to lashes in liquid vehicle
Waterproof solvent	Carrier fluid	Isododecane, cyclomethicone, petroleum distillates	Deliver mascara ingredients to lashes in liquid vehicle
Film former	Polymers/binder	Cellulosic polymers, acrylates co-polymer/xanthan or acacia gum	The main constituent of the mascara film and serves to bind the other ingredients together in the wet and dried film
Structurant	Waxes/clays	Beeswax, carnauba wax/bentonite clay	Provides body and structure to the mascara film during application and wear
Surfactant or emulsifier	Anionic/non-ionic, etc.	Sodium laureth sulfate/TEA soap, polysorbates	In a formulation with two immiscible substances, an emulsifier stabilizes the two dissimilar parts of the formulation, preventing separation
Colorant	Pigments	Iron oxides, mica, ultramarines	Provides color to the mascara film
Care or attribute	Hair treatment/ lengthening, etc.	Panthenol, keratin/nylon or silk fiber	An ingredient included for a specific effect in the mascara film
Preservatives	Antimicrobial/pH adjuster/chelator	Parabens, potassium sorbate/citric acid/EDTA	Prevents contamination of harmful microorganisms such as bacteria, mold, and fungus

helical arrangement of bristles. The bristles are very effective at depositing mascara onto lashes, but the inconsistent spacing between bristles on the brush can lead to excessively large clumps of lashes, uneven lash separation, and the need for compensatory grooming of the lashes.

The skill of the consumer plays a large part in achieving her desired look in a timely manner, and the twisted wire applicator has seen many adjustments over the years to make mascara application easier and quicker for consumers to achieve their desired lash appearance. Innovations include tapering the end of the applicator, curving the brush, hollow bristles, changing the diameter or length of the applicator, and even cutting shapes out from the applicator's profile to create channels within the collection of bristles. Despite the wide variety of twisted wire applicator innovations, the bristles all converge around a central shaft and the spacing between adjacent bristles is highly variable. This limits the consistency of both lash clump size and gaps between clumps of lashes.

Figure 25.2 Twisted wire brush mascara applicators.

In the last 5 years, technology advancements have enabled a whole new category of molded mascara applicators to emerge. The precisely engineered surfaces of a molded applicator, shown in Figure 25.3, give control over the placement, number, and physical properties of bristles or other grooming surfaces. The result is consistent gaps between bristles, enabling the bristles to penetrate deeper into the lashes for increased mascara transfer and more efficient and regular separation of lashes. In addition, the varieties of colors, shapes, and textures that can be created are almost limitless and offer new opportunities to delight consumers. A few examples of these are shown in Figure 25.4.

Other eyelash treatments

The ability to change the appearance of eyelashes extends beyond mascara. False eyelashes may be applied as entire strips or as individual groups of lashes. They are adhered to the eyelid with a non-permanent adhesive. This allows easy application and removal at the end of the day.

Lash tinting involves application of a semi-permanent dye for color that lasts about a month. This is a two part product, just like permanent coloring for scalp hair. An oxidative cream is mixed with an oxidizing agent and then applied

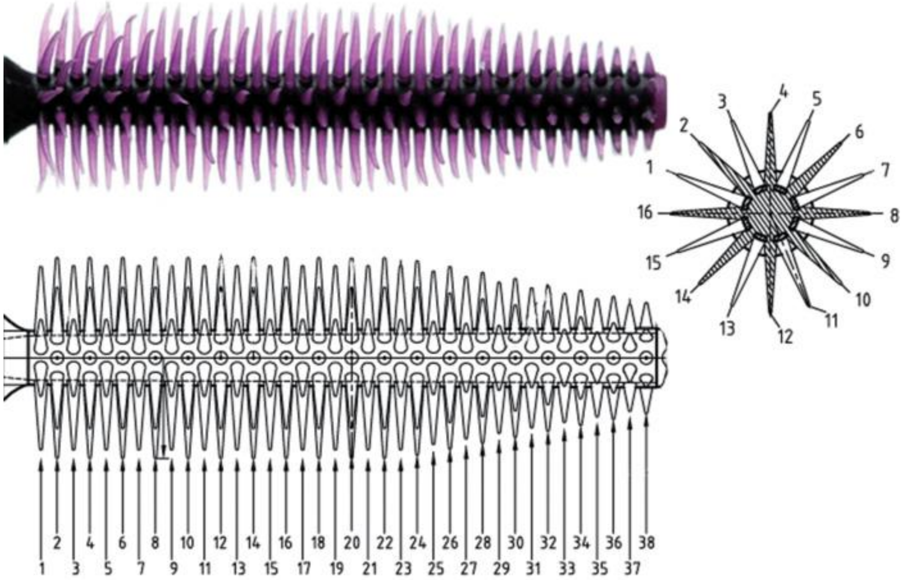

Figure 25.3 Molded mascara applicator with precisely engineered, parallel bristles.

Figure 25.4 Various molded mascara applicator designs showing the wide range of possibilities that are possible with this emerging applicator type.

onto the lashes and left for 15–20 minutes. The dye forms while it is penetrating into the lashes.

Lash perming is achieved by rolling the lashes of the top eyelid around a thin cotton tube. The lashes are then coated with a high pH gel that penetrates into the lashes and breaks disulfide bonds holding together keratin protein strands in the cortex. After about 15 minutes, a second neutralizing coat is applied to the lashes to neutralize the high pH and reform bonds between protein strands to hold the lash in its new shape after the cotton cylinder is removed.

Eyelash extensions are synthetic fibers that are bonded to individual lashes, usually with a cyanoacrylate adhesive. Typically, 30–80 lashes per eyelid will have eyelash extensions applied, and they typically last 1–2 months.

Eyelash transplants involve relocating scalp follicles to the eyelids. Small incisions are made in the top and bottom eyelids into which are placed the transplanted follicles. Manual curling and trimming is necessary because the scalp follicles will continue to grow hair for years in a relatively straight direction.

Blepharopigmentation, or eyelid tattooing, involves application of pigmentation into skin at the edges of the eyelid to simulate either eyeliner or the appearance of lashes. This is permanent but can be reversed with laser surgery.

Over the past 3 years, a number of products have launched with claims that suggest physiologic stimulation of lash growth for darker, thicker, longer, and curlier lashes. Most of these make use of prostoglandin analogs that are typically used for treating glaucoma, but are known to have the above (beneficial) side effects [11].

Eyeshadow

Eyeshadow is color applied to the upper eyelids. It is used to add depth and dimension to the eyes, thus drawing attention to the eye look or eye color. The predominant form is powder, both pressed and loose, but eyeshadow is also available in other forms, such as creams, sticks, and liquids. Eyeshadows are very similar to blushes and pressed powder in terms of their key ingredients (Chapter 22). They are usually comprised of pigments and pearls, and fillers bound together with a volatile or non-volatile binder. They may also contain other powder particles such as boron nitride or polytetrafluoroethylene to improve slip and pay-off on application.

Eyeliners

Eyeliner is used to outline the upper and lower eyelids. This serves to define the eyes against the backdrop of the face. Eyeliner can also be used to make the eye look more bold or to give the illusion of a different eye shape. They are typically available in liquid form and wood or mechanical pencils. Wood pencils excel at creating a softer, more natural look. Mechanical pencils tend to be a bit bolder, and the gel forms are good for gliding easily across the eyelid. Liquid liners can create a distinctively defined eye and provide longer wear but can be difficult to apply correctly. Most eye pencils are comprised of colorants dispersed in a waxy matrix for ease of application and to help the color adhere to the skin. Liquid liners, although not as popular as the pencil form, contain colorants that are dispersed in volatile solvents so they can be applied with a brush or pen-like applicator.

Product application

Eyeshadow application techniques vary according to the look you are trying to achieve but, generally, an appealing look can be achieved using three complementary shades in light, medium, and dark. The lightest shade highlights the area below the eyebrow, the medium shade is applied to the creased area, and the darkest shade is reserved for the area immediately above the upper eyelashes. Matte, silky shadows tend to blend nicely and are better for mature eye skin than iridescent or sparkly shades which can highlight fine lines or puffiness.

Generally, eyeliner is applied to the outer two-thirds of the lower lid below the lashes and to the entire upper lid above the lashes in a thin line. An angled brush can be used to gently soften the look. Although dark liners draw a lot of attention to the eyes, softer shades of brown, especially in the daytime, can be used to avoid looking too harsh.

Curling the lashes with an eyelash curler prior to mascara application will make the eyes seem more wide open and bright. Usually, mascara is applied generously to upper lashes and to a lesser extent to the lower lashes. Color choice of mascaras can change the look obtained. For instance, on light-haired individuals brown mascara can be used for a softer, more natural look. Black or brown–black is best for deeper skin tones or for a more dramatic look. Figure 25.5 shows the effect of applying eye cosmetics.

Safety and regulatory considerations for eye area cosmetics

Most countries or regions regulate cosmetics to a varying degree of complexity, largely because of safety considerations. Because cosmetics touch and interact directly with the human body, the various regulations are in place to ensure that consumers are not exposed to materials that may be harmful. This stems from various safety incidents that have occurred with personal care products. For instance, consumers can have allergic reactions to lash dyes, which were becoming a popular product in the 1930s. In one case, an allergic reaction to a lash dye led to one consumer becoming blind [4]. Ultimately this was one of many cases in the USA that led to Food and Drug Administration (FDA) overseeing of cosmetics. In particular, it led to a positive list of colorants that could be used for eye area cosmetics [12]. In later years, other regulatory bodies, such as the European Commission, adopted similar restrictions to the FDA's on colorants for use in the eye area [13].

Because of their intimate contact with the human body, all cosmetics should be adequately preserved from microbiologic insults. This is especially true for eye cosmetics where contact with a contaminated product could lead to an eye area infection and the possibility of more serious complications.

The future of eye cosmetics

For a mature category such as eye cosmetics, it is surprising how much potential still exists for product innovation. New products are being introduced that feature enhanced long wear, new applicator surfaces, novel color effects,

Figure 25.5 The impact of eye cosmetics on eye beauty. (a) Before. (b) After.

Figure 25.6 Digital simulations of lashes aid cosmetic scientists in visualizing potential lash looks for product design.

sustainable natural materials, improved application, and even lash growth.

The mascara application experience is being improved with automated applicators that use vibrating or rotating brushes to take away some of the skill necessary to achieve beautiful lashes. These applicators can be held up against the lashes while they work for the consumer by exposing more of the applicator surface to the lashes, encouraging more deposition of mascara and more grooming of the lashes.

Products are coming onto the market that claim to actually stimulate and enhance lash growth. While there are regulatory considerations that make these products controversial, if approved for consumer use they may negate the need of some women to use mascara to achieve beautiful lashes.

Scientists around the world are even starting to tap in to virtual modeling to peel back the individual factors of eye beauty, and to design looks not yet achievable with today's products. Three-dimensional modeling and simulation are being exploited to mimic consumers' real eyelashes, and then simulate how those lashes may be made more beautiful. For the first time we can explore both the true limits of eye beauty and the individual impacts of single lash variables (e.g. lash separation, thickness, lift, color, curl) on beauty. An optimized digital representation of a consumer's lashes can be used to design a formula and applicator to deliver the right personalized lash look for them. Figure 25.6 shows several related simulations where only lash clumping is adjusted [14].

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Part 2: Nail Cosmetics

Chapter 26: Nail physiology and grooming

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BASIC CONCEPTS

- Knowledge of nail unit anatomy and physiology and an understanding of nail plate growth and physical properties are important prerequisites for understanding nail cosmetics.
- Disruption and excessive manipulation of certain nail structures, such as the hyponychium and eponychium/cuticle, should be discouraged during nail cosmetic procedures and nail salon services.
- In addition to beautifying natural nails, nail cosmetics are beneficial in camouflaging unsightly medical and infectious nail problems, especially during the lengthy treatment period.
- Some nail cosmetics provide a protective coating for fragile, weak, and brittle nails.
- Proper nail grooming is crucial for maintaining nail health.
- Although most nail cosmetics are used safely, it is important to be aware of potential complications associated with nail cosmetic materials and application processes.

Introduction: Nail physiology

Nail unit anatomy

Understanding nail unit anatomy is an essential first step to comprehending the complexity of nail cosmetics use, including pathology induced by cosmetic materials and procedures. The nail unit is composed of the nail matrix, proximal and lateral nail folds, the hyponychium, and the nail bed (Figure 26.1).

Table 26.1 lists common nail signs and definitions relevant to nail cosmetics.

Nail matrix

The nail matrix is comprised of germinative epithelium from which the nail plate is derived (Figure 26.2). The majority of the matrix underlies the proximal nail fold. The distal portion of the nail matrix is the white lunula visible through the proximal nail plate on some digits. It is hypothesized that the white color of the lunula can be attributed to both incomplete nail plate keratinization and loose connective tissue in the underlying dermis. The proximal nail matrix generates the dorsal (superficial) nail plate, while the distal nail matrix generates the ventral (inferior) nail plate. This concept is crucial to understanding nail pathology. Preserving and protecting the matrix during nail cosmetic processes is essential for proper nail plate formation. Significant damage to the nail matrix can result in permanent nail plate dystrophy.

The nail plate is derived from the nail matrix and composed of closely packed, keratinized epithelial cells called onychocytes. Cells in the matrix become progressively flattened and broadened and lose their nuclei as they mature into the nail plate. The nail plate is curved in both the longitudinal and transverse planes, allowing for adhesion to the nail bed and ensheathment by in the proximal and lateral nail folds. Longitudinal ridging may be present on both the dorsal and ventral surface of the nail plate. Mildly increased longitudinal ridging on the dorsal nail plate is considered a normal part of aging. Ridging on the ventral surface of the nail plate is caused by the structure of the underlying nail bed and vertically oriented blood vessels. The composition and properties of the nail plate are further discussed below.

Nail folds

The nail folds surround and protect the nail unit by sealing out environmental irritants and microorganisms through tight attachment of the cuticle to the nail plate. The cuticle is often cut or pushed back during cosmetic nail procedures which can allow moisture, irritants, bacteria, and yeasts under the nail fold, resulting in infection or inflammation of the nail fold, termed paronychia (Figure 26.3). Chronic

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Table 26.1 Common nail signs associated with or helped by nail cosmetics.

Nail sign	Definition	Association
Onycholysis	Separation of the nail plate from the nail bed	Vigorous cleaning of hyponychium exacerbates. Polish hides
Onychorrhexis	Increased longitudinal ridging	Associated with aging, distal notching. Polish may help
Onychoschizia	Lamellar splitting of the free end of the nail plate	
Paronychia	Inflammation of the nail fold	
Dyschromia yellow	Staining of the surface of the nail plate yellow from the dye in nail polish	
Green/black discoloration	*Pseudomonas* is a bacteria that generates a green–black pigment that discolors the nail plate	
Nail bed changes as in psoriasis, onychomycosis		

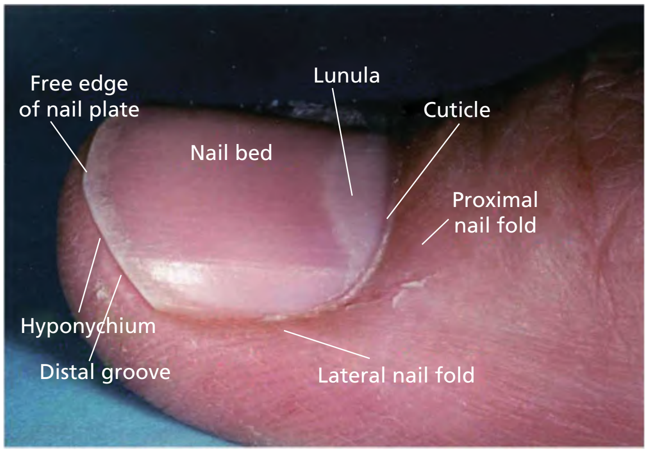

Figure 26.1 Nail unit with lines indicating important structures.

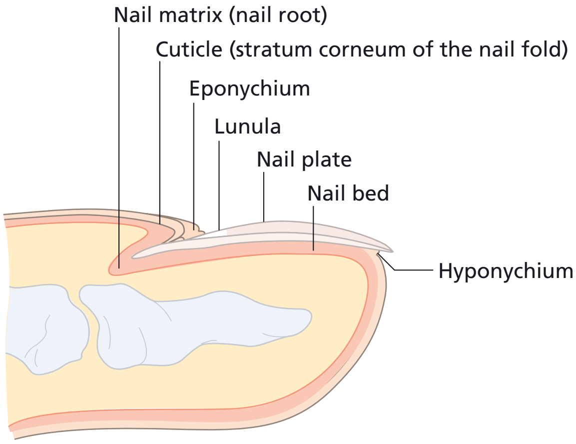

Figure 26.2 Diagram of the nail unit.

Figure 26.3 Paronychia.

paronychia may disrupt the underlying nail matrix and subsequently lead to nail plate dystrophy.

Hyponychium

The hyponychium is the cutaneous margin underlying the free edge of the nail plate. The nail bed ends at the hyponychium. It is contiguous with the volar aspect of the fingertip.

The hyponychium has a similar function as the cuticle and acts as an adherent seal to protect the nail unit. The hyponychium should not be overmanipulated during nail grooming to avoid onycholysis, or separation of the nail plate from the nail bed. This space created between the nail plate and bed retains moisture and establishes an environment for potential pathogens, such as yeast, bacteria, or fungi.

Nail bed

The nail bed is thin, 2–5 cell layer thick epithelium that underlies the nail plate. It extends from the lunula to the hyponychium. The nail bed is composed of longitudinal, parallel rete ridges with a rich vascular supply which is responsible for the pink coloration of the bed, as well as longitudinal ridges on the ventral surface of the nail plate. In chronic onycholysis the nail plate is separated from the nail plate for an extended duration, the nail bed epithelium may become keratinized, form a granular layer, and lead to permanent onycholysis (Figure 26.4).

Other structures

The distal phalanx lies immediately beneath the nail unit. The extensor tendon runs over the distal interphalangeal joint and attaches to the distal phalanx 12 mm proximal to the eponychium. Given that there is little space between the nail unit and distal phalanx, minor injury to the nail unit may extend to the periosteum and lead to infection.

Nail growth

Normal nail growth has been cited to vary from less than 1.8 mm to more than 4.5 mm per month. Average fingernail growth is 0.1 mm per day, or 3 mm per month. This information is useful when determining the duration of nail pathology. For example, if splinter hemorrhages are located 6 mm from the proximal nail fold, it can be estimated that they occurred from injury approximately 2 months prior. Based on this growth rate, fingernails grow out completely in 6 months. Toenails grow at one-third to half of the rate of fingernails and take 12–18 months to grow out completely.

Several factors affect nail growth. Nail growth peaks at 10–14 years and declines after 20 years. Nail growth is proportional to finger length, with fastest growth of the third fingernail and slowest growth of the fifth fingernail. Nails grow slower at night and during the winter. Other factors causing slower nail plate growth include lactation, immobilization, paralysis, poor nutrition, yellow nail syndrome, antimitotic drugs, and acute infection. Faster nail growth has been noted during the summer and in the dominant hand. Pregnancy, psoriasis, and nail biting are other factors linked to faster nail growth. Table 26.2 summarizes factors influencing nail growth.

Physical properties of nails

Nail composition

The nail plate is composed mainly of keratin, which is embedded in a matrix of non-keratin proteins. There is wide variation in reported percentage of inorganic elements found in the nail plate. Several elements, including sulfur, calcium, iron, aluminum, copper, silver, gold, titanium, phosphorus, zinc, and sodium, are constituents of the nail plate. Of these elements, sulfur has the greatest contribution to nail structure and comprises approximately 5% of the nail plate. Nail plate keratin is cross-linked by cysteine bonds, which contain sulfur. Some studies attribute brittle nails to decreased cysteine levels.

There is a popular misconception that calcium content is responsible for nail hardness. This idea likely stems from knowledge that bone density is related to calcium intake. Calcium comprises less than 1% of the nail plate by weight. No evidence supports that decreased calcium is linked to brittle nails and that calcium supplementation increases nail strength. In fact, kwashiorkor, a nutritional deficiency caused by insufficient protein intake, is manifested by soft, thin nails and demonstrates increased nail plate calcium.

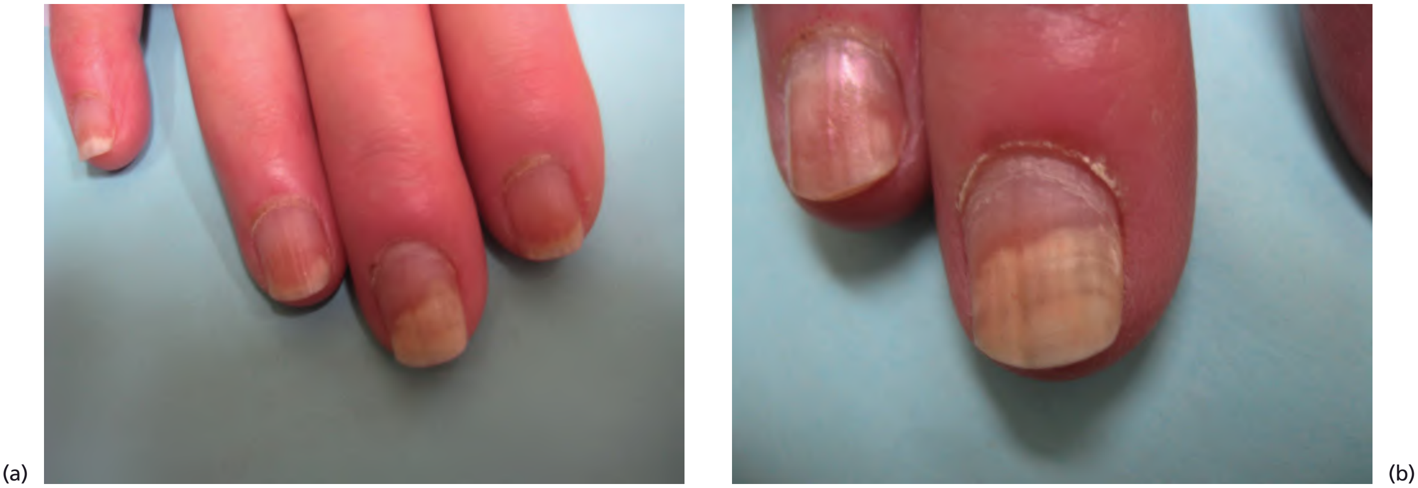

Figure 26.4 (a & b) Onycholysis.

Table 26.2 Nail cosmetic products: ingredients and uses.

Product	Ingredients	Application procedures	Benefits of use	Potential complications
Nail polish	Film former: nitrocellulose Thermoplastic resin: (toluene sulfonamide formaldehyde resin) Plasticizer: dibutyl pthalate Solvents and pigments	Polish is applied in several coats with a small brush and allowed to dry by evaporation	Provides an attractive glossy smooth decorative surface and camouflages nail defects Protects nail from dehydration and irritants	Yellow staining of nail plate. Potential for allergy to toluene sulfonamide formaldehyde resin and other ingredients
Nail hardener	May contain formaldehyde in a nail polish base, also may have fibers that reinforce the nail	Application similar to nail polish which is applied in several coats	Forms several layers of protection on the nail plate	Potential allergy to formaldehyde and possible brittleness
Acrylic nail extensions	Acrylic monomer, polymer, polymerized to form a hard shell attached to the nail plate or to a plastic tip glued to the nail	Monomer (liquid) and polymer (powder) mixed to form a paste and polymerized with a catalyst to a harden the product	Cover unsightly nail defects, may help manage onychotillomania and habit tic disorder	Possible allergy to acrylates, inflexibility of artificial nail may cause injury to nail unit
Cuticle remover	Contains potassium hydroxide or sodium hydroxide plus humectants	Applied to cuticle for 5–10 minutes to soften cuticle adhered to nail plate	Gently removes dead skin attached to the nail plate without mechanical trauma	Over removal of cuticle and result in the potential for paronychia and secondary bacteria and *Candida* infections. Can soften the nail plate
Nail polish remover	Acetone, butyl acetate, ethyl acetate, may also contain moisturizer such as lanolin or synthetic oils	Wiped across nail plate with cotton or tissue to remove nail polish	Removes polish smoothly without removing layers of nail plate	May dehydrate the nail plate and periungual tissue

Water content of the normal nail plate is reported to range between 10% and 30%. The most commonly accepted value is 18% water content in normal nails and 16% in brittle nails. However, a study aimed at confirming this demonstrated no statistically significant difference between normal and brittle nails [1]. In addition, this study showed lower water content than previously thought, with a mean water content of 11.90% in normal nails and 12.48% in brittle nails. Some limitations in this study were noted, including analysis of only the distal nail plate. In addition, the time between sample collection and analysis was variable, with an average of 24 hours, and a subanalysis demonstrated loss of water content varied significantly between those samples analyzed at 1 and 24 hours.

Lipids, including squalene and cholesterol, are also constituents of the nail plate and comprise 5% of the nail plate by weight. These lipids are thought to diffuse from the nail bed to the nail plate.

Nail flexibility

Most references to nail strength and hardness actually refer to nail flexibility. A flexible nail will bend and conform to physical force, whereas a hard nail will break and become brittle. Nail flexibility is aided by plasticizers, which are liquids that make solids more flexible. Examples of nail plasticizers are water and lipids. Flexibility is decreased by solvents, such as nail polish removers, which remove both water and lipids, and detergents, which remove lipids.

Nail brittleness is caused by loss of flexibility. Brittle nails are a common complaint and are found in 20% of the general population and more commonly in females (Figure 26.5). Brittleness encompasses several nail features including onychoschizia which is lamellar peeling of distal nail plate (Figure 26.6), splitting and notching sometimes associated with ridges, and fragility of the distal nail plate, lamellar splitting of the free end of the nail plate. Several attempts have been made to define brittleness with objective measurements, including Knoop hardness, which evaluates indentation at a fixed weight; modulus of elasticity, which describes the relationship between force/area and deformation produced; tensile strength; and a brittleness grading system.

Although there are systemic and cutaneous conditions that may cause brittle nails, exogeneous causes are more

Figure 26.5 (a–c) Brittle nails.

Figure 26.6 Onychoschizia, distal lamallar peeling of the nail plate.

Figure 26.7 (a) Manicure; (b–d) Pedicure.

common. These include mechanical trauma, exposure to solvents and extraction of plasticizers, and repeated hydration and drying of nails.

Nail thickness

Thickness of the nail plate is determined primarily by matrix length and rate of growth. Measurements of distal plate thickness demonstrate greatest thickness in the thumbnail, followed by the second, third, fourth, and fifth fingernails. Thickness also is influenced by sex, with males having an average nail plate thickness of 0.6 mm, compared to 0.5 mm in females.

Nail grooming principles

Nail care

Several principles of nail care should be observed during nail grooming to maintain normal nail structure.

Manicure and pedicures are the process of grooming the fingernails and toenails respectively at home or in a nail salon (Figure 26.7). The procedure involves soaking the nails to soften prior to trimming and shaping the nail plate. Excess cuticle is removed from the nail plate using a chemical cuticle remover and often a metal implement. The nails are then finished with a shiny, smooth coat of nail enamel, commonly called nail polish, sandwiched between a base coat and top coat, or the nails may be buffed to a soft luster.

Other procedures such as acrylic gel or silk wrap enhancements may be added to the basic manicure. These nail extension procedures involve applying product to the natural nail or to a plastic tip glued to the nail. The material are applied and shaped before curing or polymerizing to form a hard surface.

Nail trimming

Most nail experts advocate shaping nails with an emery board rather than clipping or cutting nails. Filing should be carried out with the file exactly perpendicular to the nail surface to avoid inducing onycholysis. Proper filing of the free edge of nail plate reduces sharp edges that may catch and cause nail plate tearing. If nails must be clipped or cut, this should be performed after they have been hydrated which maximizes nail flexibility and prevents breakage during trimming. Nails should also be kept as short as possible. Long nails, especially those that are brittle, may act as a lever and create onycholysis.

Nail buffing and filing

The dorsal nail plate surface is often filed to remove shine from the natural nail plate at nail salons prior to application of nail products or artificial nails. Care must be taken to avoid excessive filing, especially with electric drills. The nail plate is approximately 100 cell layers thick. If filing must be done, only 5% of the nail plate thickness, or approximately five cell layers, should be removed which is just enough to remove the shine of the dorsal nail plate in order to facilitate adherence of the product to the nail plate. Limited buffing to reduce nail ridging is acceptable, but excessive buffing thins the nail plate and should be avoided.

Care for brittle nails

Brittle nails should be treated by avoiding nail trauma and increasing flexibility. Nails should be kept short. This prevents lifting of the nail plate, disruption of the hyponychium, and onycholysis. In addition, nails should be trimmed after they have been hydrated and are the most flexible. Moisturizing the nail plate increases flexibility and helps avoid brittle nails. Some experts recommend moisturizing up to four times daily. Avoiding solvents and frequent hydration and dessication of nails also helps maintain flexibility. There is controversy regarding avoidance of nail cosmetics in the management of brittle nails. Some believe that nail polish is protective and seals the moisture in the nail plate by preventing rapid evaporation. Nail polish also protects the nail plate from some environmental irritants. There is some concern that overuse of nail polish remover will dehydrate the nail and exacerbate brittleness.

Biotin has also been advocated for brittle nails, but results are inconclusive. The recommended dose is 2.5–5 mg/day, which is 100–200 times the recommended daily allowance. Given that biotin has relatively few side effects, most experts recommend its use, in addition to the above grooming recommendations.

Adverse effects from nail grooming

Nail cosmetics are safely used by millions of people worldwide. In addition to enhancing the appearance of normal nails, cosmetics are useful for improving the appearance of unsightly nail dystrophy caused by medical disease, such as psoriasis (Figure 26.8), onychomycosis (Figure 26.9), or trauma. Although nail cosmetics rarely cause problems, it is important to be aware of possible adverse effects related to procedures or to materials used in nail cosmetics (Figure 26.10).

Figure 26.8 Psoriasis: salmon patch oil drop discoloration.

Figure 26.9 Onychomycosis.

Allergic reactions to nail cosmetic ingredients

The most common allergen in nail polish is toluene sulfonamide formaldehyde resin with sensitization occurring in up to 3% of the population. Other potential allergens are cyanoacrylate nail glue, formaldehyde in nail hardeners, and ethylmethacrylate in sculptured nails. Allergic contact dermatitis from nail cosmetics is seen on periungual skin, as well as the eyelids, face, and neck, caused by touching these areas with freshly polished fingernails (Figure 26.11).

Irritant reactions

Common nail products that cause irritant reactions include acetone or acetate nail polish removers and cuticle removers

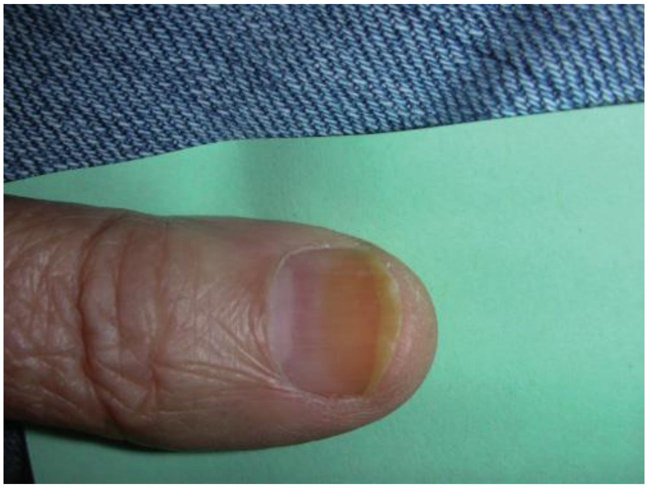

Figure 26.10 Yellow staining from nail polish.

with sodium hydroxide. Reactions are manifested as an irritant dermatitis of the periungual skin and as brittle nails, including onychoschizia. Prolonged use of nail polish induce keratin granulations on the nail plate. This commonly is seen when fresh coats of nail enamel are applied on top of old enamel for several weeks. These granulations cause superficial friability of the nail plate (Figure 26.12).

Nail cosmetic procedures

Several nail problems, including paronychia, onycholysis, and thinning of the nail plate, may be mechanically induced by cosmetic procedures. Paronychia, or inflammation of the proximal nail fold, is often caused by cutting or pushing back the cuticle, leading to separation of the proximal nail fold and the nail plate. Sharp manicure instruments used to clean under the nail plate may induce onycholysis and create an environment for secondary bacterial and

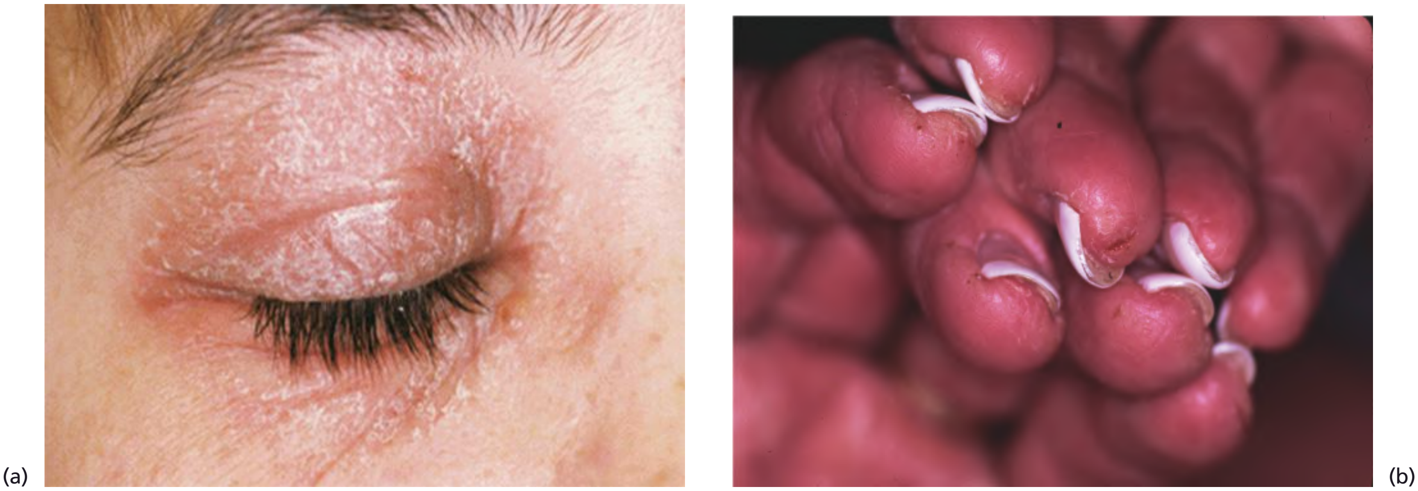

Figure 26.11 Allergic contact dermatitis from nail cosmetics. (a) On the eyelid. (b) On periungual skin caused by acrylates.

Figure 26.12 (a & b) Keratin granulations.

Figure 26.13 Infection caused by *Pseudomonas*.

fungal infection. Onycholysis may be exacerbated by long artificial nails because of increased mechanical leverage. Nail drills or excessive filing and buffing may lead to thinning of the nail plate and brittle nails. Breaks in the integrity of the nail unit allow access of microorganisms such as *Candida* and *Pseudomonas* (Figure 26.13) and result in exacerbation of paronychia and onycholysis. Some basic principles for safe use of nail cosmetics are outlined in Table 26.3.

Conclusions

Nail cosmetics is a multibillion dollar industry which continues to grow. Thorough knowledge of nail anatomy and physiology is essential for the safe use and development of nail cosmetics.

Table 26.3 Information for patients for safe nail cosmetic use. After Rich [2].

- Be sure that the salon sterilizes instruments, preferably with an autoclave. Some salons offer instruments for clients to purchase
- Stinging, burning, or itching following a nail salon treatment may be signs of an allergic reaction to a cosmetic ingredient. Remove the product and seek medical evaluation by a dermatologist
- If using artificial nail extensions, keep them short. Long nails can cause mechanical damage to the nail bed. Remove extensions at the first sign of onycholysis and avoid enhancements until the nail is reattached
- Do not allow nail technician to cut or clip cuticles. Cuticles serve an important function and should not be cut. They may be pushed back gently with a soft towel after soaking the nails or bathing

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Chapter 27: Colored nail cosmetics and hardeners

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BASIC CONCEPTS

- Nail lacquers contain resins that create a thin, resistant film over the nail plate.
- Adding color to the nail plate surface is accomplished with a variety of nail lacquers including a basecoat, color coat, and topcoat.
- Nail hardeners cross-link nail protein to increase strength, but overuse may contribute to brittle nails.
- Nail lacquers are resistant to contamination and cannot spread nail infectious disease.

Introduction

The use of colored nail polish and nail hardeners has increased among consumers with the rise of the manicure industry. With nail salons found in almost every strip mall, painting nails is a very popular service for the customers of the professional manicurist. The use of nail cosmetics is well rooted in history. Ancient Chinese aristocrats colored their nails red or black with polishes made with egg white, bees wax, and gelatin. The Ancient Egyptians used henna to dye the nails a reddish brown color (J. Spear, editor of *Beauty Launchpad*, Creative Age Publications, Van Nuys, CA, personal communication). In the 19th and early 20th centuries, "nail polish" was a colored oil or powder, which was used to rub and buff the nail, literally polishing and coloring the nail simultaneously. Modern nail polish was created in the 1920s, based on early nitrocellulose-based car paint technology [1].

The term "nail polish" is somewhat of a misnomer for modern products, because no actual polishing is involved in its application. The product is composed of dissolved resins and dries to a hard, glossy coat, so the technically correct name is "nail lacquer." However, the terms "nail polish," "nail enamel," "nail varnish," "nail paint," and "nail lacquer" are used interchangeably. Several specialty products have developed from nail lacquer, including basecoats, topcoats, and hardeners. A newer technology involves pigmented UV-curable resins. This chapter discusses the current use of these modern formulations (Table 27.1).

Application techniques

These nail products are applied by painting the nail with a brush. In best manicuring practices, old nail lacquer is removed with a solvent followed by application of a basecoat, two coats of colored nail lacquer, and a topcoat allowing sufficient time for drying between coats. The basecoat increases the adhesion of the colored nail lacquer to the nail while the topcoat increases the chip-resistant characteristics of the colored nail lacquer. These products are applied on both natural and artificial nails. Nail hardener is only applied to natural nails, either as a basecoat or a stand alone product. UV-curing nail "lacquers" are hardened with a UV light after application; no evaporation is necessary. In all cases, best practice dictates that the products be kept off the skin. Failure to do so can result in eventual, irreversible sensitization and allergic contact dermatitis [2].

Proper nail cosmetic application dictates the maintenance of excellent hygiene in the nail salon. Unsanitary procedures may result in medical problems [3]. Nail technicians must use cleaned, disinfected, or disposable nail files and tools. Clipping or cutting the cuticles before applying nail lacquer can also lead to infection. Infections with staphylococcus [4] and herpetic whitlows [5] have been attributed to unsanitary manicures. Nail technicians should not perform services on diseased nails.

Lacquers, topcoats, and basecoats

Nail lacquers contain six primary ingredients: resins, solvents, plasticizers, colorants, thixotropic agents, and color stabilizers. By law, all ingredients must be disclosed on the

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Figure 27.1 Lacquered nails. Reproduced by permission of OPI Products, Inc.

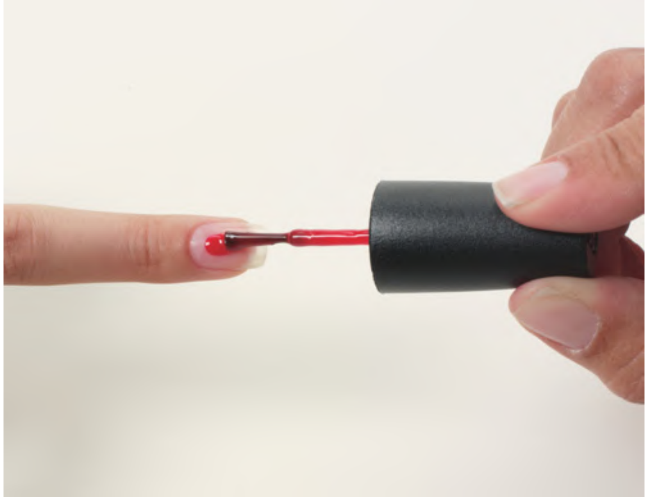

Figure 27.2 Painting a nail. Reproduced by permission of OPI Products, Inc.

Figure 27.3 Be careful with the cuticle. Reproduced by permission of OPI Products, Inc.

Table 27.1 Overview of product types.

Product class	Nail lacquer	Basecoat	Topcoat	Nail hardener	UV curable
Coating created by	Solvent evaporation	Solvent evaporation	Solvent evaporation	Mainly solvent evaporation; some polymerization of formalin may occur	Polymerization
Resin type or mix	Balanced	Biased toward adhesion	Biased towards glossiness, hardness	Balanced or biased towards adhesion	Balanced; resin formed by reacting directly on nail
Pigment	Yes	Little or none	Little or none	Usually none	Yes
Removal	Easily dissolves in solvent	Easily dissolves in solvent	Easily dissolves in solvent	Easily dissolves in solvent	Soften by acetone soak, then peel
Benefits	Attractive color; can be applied over natural nails or enhancements	Helps color coat last longer; protects natural nail from staining	Helps color coat last longer; some contain optical brighteners or UV protectants	Strengthens natural nail by cross-linking proteins; may be used as a basecoat	Attractive color; tough cured-in-place resin protects nail

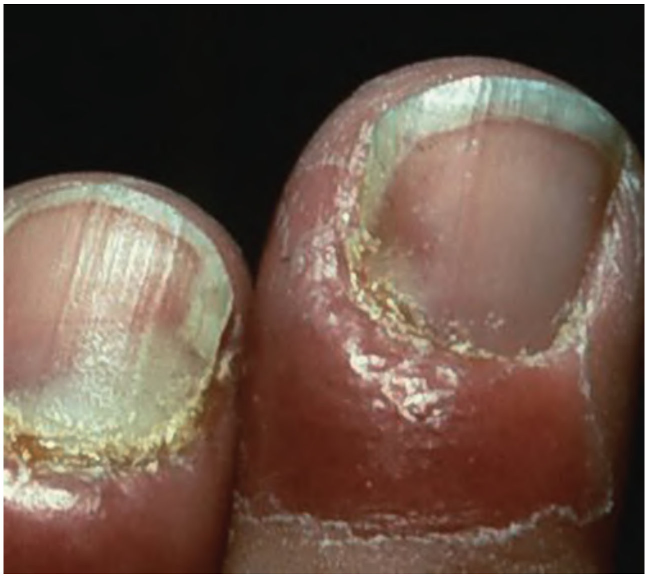

Figure 27.4 Infected nail. Reproduced by permission of *Nails Magazine*.

product packaging, usually by means of the International Nomenclature for Cosmetic Ingredients (INCI) names. Understanding the chemistry nomenclature is important for isolating the causes of allergic contact dermatitis. Each of these ingredients is discussed in detail.

Resins

Resins hold the ingredients of the lacquer together while forming a strong film on the nail. Chemically, the resins are polymers – long-chain molecules – that are solid or gummy in their pure state. Two types of resins are used. Hard, glossy resins give the lacquered nail its desired appearance; these include nitrocellulose and the methacrylate polymers or co-polymers (usually labeled by their generic INCI name, "acrylates co-polymer"). Topcoat formulations have a higher percentage of these harder resins. Softer, more pliable resins, which enhance adhesion and flexibility, include tosylamide/formaldehyde resin, polyvinyl butyral, and several polyester resins. Basecoats incorporate a higher proportion of pliable resins. Of all the resins, tosylamide/formaldehyde resin is the most commonly implicated in allergic reactions [6] affecting not only the fingers, but other parts of the body by transfer [7].

Solvents

Solvents are the carriers of the lacquer. They must dissolve the resin, suspend the pigments, and evaporate leaving a smooth film. The drying speed must be controlled to prevent bubbling and skinning, thus faster drying is not necessarily better. Optimum drying speed requires a careful blend of solvents. Ethyl acetate, n-butyl acetate, and isopropyl alcohol are common solvents, other acetates and alcohols are also occasionally employed. All solvents have a dehydrating and defatting action on the skin, but this usually occurs during the removal of the lacquer, not its application.

Figure 27.5 Dermatitis on the finger. Reproduced by permission of *Nails Magazine*.

Formerly, toluene was a commonly used solvent, but the industry trend is to move away from it in response to expressed health concerns. Research indicates that toluene exposure for a nail technician and consumer is far below safe exposure limits [8]; however, consumer perceptions are negative for toluene, necessitating its replacement. A related chemical, xylene, has already virtually vanished from the industry. Ketones such as acetone or methyl ethyl ketone are not amenable to suspension of pigments and are therefore used at low levels, if at all, in lacquers, although these substances will dissolve the resins effectively and therefore are useful as lacquer removers.

A few water-based nail lacquers are now on the market. Because of their much slower drying time they are unlikely to replace solvent-based products in the foreseeable future. If they are ever perfected, they will completely take over the industry, because water is cheaper, non-flammable (which reduces shipping costs), and odorless.

Plasticizers

Plasticizers keep the resins flexible and less likely to chip. Camphor and dibutyl phthalate (DBP) have long been used for this purpose; however, the EU maintains its 2004 ban of DBP, despite authoritative findings regarding its safety in nail lacquer [9]. Because many manufacturers sell globally, DBP has largely been replaced by other plasticizers, including triphenyl phosphate, trimethyl pentanyl diisobutyrate, acetyl tributyl citrate, ethyl tosylamide, and sucrose benzoate.

Colorants

Colorants are selected from among various internationally accepted pigments. They are mostly used in the "lake" form,

Figure 27.6 Nail lacquer. Reproduced by permission of OPI Products, Inc.

meaning that the organic colorants have been adsorbed or co-precipitated into inorganic, insoluble substrates such as the silicates, oxides, or sulfates of various metals. A shimmer effect is created by minerals such as mica, powdered aluminum, or polymer flakes. Guanine from fish scales is falling out of favor but is still occasionally used.

Following INCI convention, most colorant materials are labeled by their international "Color Index" (CI) numbers. This is a convenient way to identify colors, which have different national designations. Labeling colorants by their CI numbers is either legal or *de facto* accepted by most regulatory agencies around the world; even so, out of deference to local custom, colors are often declared binonially (e.g. CI 77891/Titanium Dioxide).

However, because of space limitations, lacquer manufacturers may declare only the CI numbers on the bottle – often on a small peel-off sticker at the bottom of the bottle. This can pose a problem as few nail lacquer users are aware that, for example, "CI 60725" means the same as "D&C Violet #2" (USA) or "Murasaki 201" (Japan). Fortunately, the full designations of the colors are usually listed on the box (which has more space than the bottle) and/or the Material Safety Data Sheet (MSDS). If these are unavailable, a web search or a phone call to the manufacturer is usually sufficient to obtain this information.

Another difficulty with international designations is that some closely related colorant chemicals and their lakes are lumped under one CI number. An example is the ubiquitous CI 15850, which covers D&C Red #6, D&C Red #7, and all the various lakes of both. Normally, the manufacturer can provide more specific information if needed.

Colorants sometimes cause staining of the nail. Although uncommon, it is more often seen with colors at the red end of the spectrum. It can usually be prevented by using a basecoat between the lacquer and the natural nail [10]. Topcoats can also cause apparent yellowing, but this is usually the product rather than the natural nail – as can be easily seen by removing the product [10].

Thixotropic agents

Thixotropic agents provide flow control and keep the lacquer colorants dispersed. They are usually clay derivatives such as stearalkonium bentonite or stearalkonium hectorite. Most topcoats and basecoats are uncolored and do not require these additives. Silica is also sometimes used as a thickener.

Color stabilizers

Color stabilizers, such as benzophenone-1 and etocrylene, are added to prevent color shifting of the lacquer on exposure to UV light. These substances are better known as sunscreens, but their use in nail lacquer is to protect the color. Some specialty topcoats have a high level of UV protectants, for application over colored nail lacquer to prevent fading during tanning booth use.

Minor ingredients

Minor ingredients may include vitamins, minerals, vegetable oils, herbal extracts, or fibers such as nylon or silk. Some companies may include adhesion-enhancing agents in lacquers or basecoats, or other proprietary ingredients whose functions they elect not to disclose (Table 27.2).

Antifungal agents

Antifungal agents may be added to nail lacquer for therapeutic purposes. However, as of this writing, there is only one prescription US Food and Drug Administration (FDA) approved antifungal nail lacquer, a topical solution of 8% ciclopirox (Penlac®, Sanofi-Aventis, Bridgewater, NJ, USA). According to *FDA Consumer Magazine*, "There are no approved nonprescription products to treat fungal nail infections … fungal infections of the nails respond poorly to topical therapy … the agency ruled that any OTC product labeled, represented or promoted as a topical antifungal to treat fungal infections of the nail is a new drug and must be approved by FDA before marketing" [11]. Furthermore, the FDA's policy is to "prohibit claims that nonprescription topical antifungals effectively treat fungal infections of the scalp and fingernails" [12].

Preservatives

Preservatives are not present in nail lacquer. Regulatory authorities inquired if microbial cross-contamination could occur when the same nail lacquer bottle and brush are used on multiple clients. In response, a series of experiments was performed to investigate microbe survival in nail lacquer. The results indicate that nail lacquers do not support micro-

Table 27.2 Common ingredients of nail lacquer and related products.

Ingredient category and examples	Function
Hard resins	
Nitrocellulose	Gloss
Acrylates co-polymer	Toughness
Soft resins	
Tosylamide/formaldehyde resin	Flexibility
Polyvinyl butyral	Adhesion
Solvents	
Ethyl acetate	Carrier for the resin and pigment
Butyl acetate	Removing lacquer
Isopropyl alcohol	Soaking and removing UV-cured colors
Acetone (removers only)	
Monomers and oligomers	
Polyurethane acrylate oligomer	Hardens to hold color on nail
Hydroxypropyl methacrylate	Only in UV-curable colors, not standard lacquer
Various other acrylates and methacrylates	
Photoinitiators	
Benzoyl isopropanol	Initiates the light cure reaction
Hydroxycyclohexyl phenyl ketone	Only in UV-curable colors, not standard lacquer
Colorants	
FDA/EU approved colorant	Esthetic
Mica	
Plasticizers	
Camphor	Keeps resin flexible to prevent chipping
Dibutyl phthalate (formerly)	
Thixotropic agents	
Stearalkonium hectorite	Controls flow
Stearalkonium bentonite	Suspends pigment until use
UV stabilizers	
Benzophenone-1	Prevents light-induced color fading
Etocrylene	
Hardeners	
Formalin	Hardens nail protein by cross-linking
Dimethyl urea	Only in hardener products
Hydrolyzed proteins	
Keratin	Thought to bond with formalin and nail protein
Wheat, oats, etc.	Usually used in hardeners

bial growth in the laboratory or salon (OPI Products Inc., and Nail Manufacturers Council, unpublished data) [13]. The solvents are sufficiently hostile to microbes that no preservative is required. This does not apply to water-based products, because water is required for microbial growth. Although solvent-based water-free lacquer is hostile to microbes, it would be a mistake to assume that it has any curative value for nail fungus or other infections.

Nail hardeners

Modern nail hardeners are quite a contrast to an antique method of nail hardening which used fire. On the early American frontier, the combat sport called "rough and tumble" or "gouging" allowed fingernails to be used as weapons, and expert "gougers" hardened their nails by heating them over candles [14]. The heat of the candle flame caused cross-linking of the nail proteins.

Modern nail hardeners contain a chemical cross-linking agent. Otherwise, their composition is similar to ordinary nail lacquer. As with lacquers, care must be taken to avoid skin contact during application to avoid allergic sensitization, particularly to the most common hardener, formalin (which is mistakenly equated with "formaldehyde" under current labeling rules.) Formalin cross-links proteins primarily by reacting with their nitrogen-containing side groups, forming methylene bridges [15]. Overuse causes too many cross-links, reducing the flexibility of the protein and causing brittleness, yellowing, and cracking of the nails. Manufacturers generally recommend avoiding overuse by cycling the products, alternating between the hardener and a non-hardening topcoat every week or two.

Other hardeners include dimethyl urea (DMU), which is does not cross-link as aggressively as formalin. It is also less allergenic [16]. Glyoxal, a relative of formaldehyde, is larger and less able to penetrate the skin, also contributing to reduced allergenicity. Hydrolyzed proteins are common additives in hardeners and may chemically bond to the formalin. Many nail hardeners are simply clear lacquers with no cross-linking agents at all. These products rely on the strength of the resins to protect the nails. Until DMU or some other alternative proves itself, the most effective nail hardeners will likely continue to rely on formalin.

Figure 27.7 Brittle nail. Reproduced by permission of *Nails Magazine*.

Formaldehyde issues

Formalin, formaldehyde, and tosylamide/formaldehyde resin warrant some additional discussion. True formaldehyde is a highly reactive gas. Obviously, it cannot be a part of nail products in that form. It is therefore combined with water to make a product traditionally called "formalin." Formalin contains water and a reaction product of water and formaldehyde, properly known as methylene glycol. Published literature [17] on the hydration of formaldehyde reveals a chemical equilibrium constant for this reaction, which confirms the near complete conversion of formaldehyde to methylene glycol. This chemical equilibrium constant yields the presence of 0.0782% free formaldehyde in formalin. A nail hardener that is 1.5% formalin, the typical upper limit, therefore contains less than 0.0012% or 12 parts per million of formaldehyde. This is not to dismiss "formaldehyde allergy", which causes significant suffering to some patients, but it would be more accurately known as methylene glycol or formalin allergy (Figure 27.8).

Unlike formaldehyde, methylene glycol is non-volatile; this explains why a California study showed that formaldehyde gas levels in nail salons were not above the normal background levels found in other settings such as offices [8]. This is significant because the only identified cancer risk associated with formaldehyde exposure results from inhalation in industrial settings [18], not cosmetic skin or nail exposure.

Tosylamide/formaldehyde resin is also a cause for controversy solely because of the word "formaldehyde" in its name. It is an inert macromolecule, created by reacting tosylamide and formaldehyde. However, the formaldehyde is consumed in the reaction, and any leftover formaldehyde is hydrated to methylene glycol by the water molecules generated in the reaction. Hence the formaldehyde content of the resin is essentially nil. However, allergies nevertheless occur; it has been speculated that trace formaldehyde is

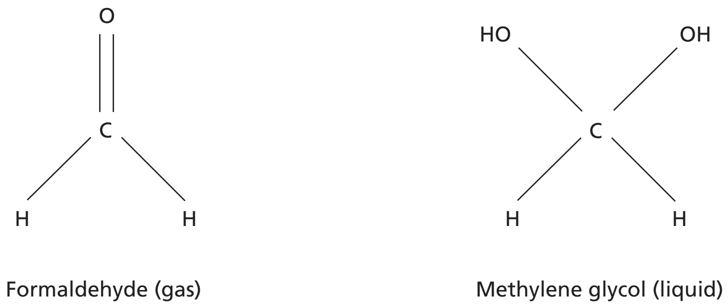

Figure 27.8 Formaldehyde versus methylene glycol. Reproduced by permission of OPI Products, Inc.

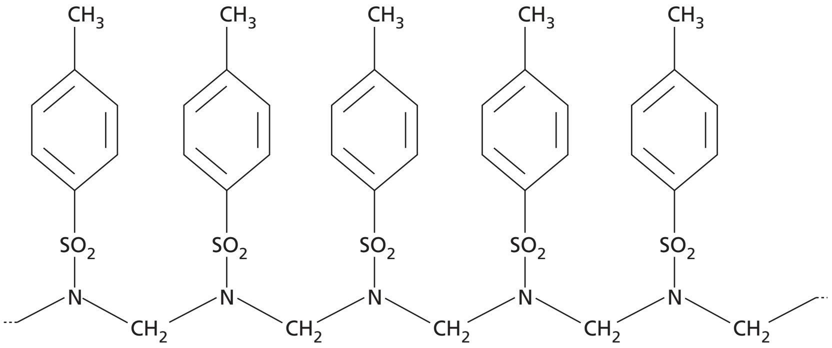

Figure 27.9 Tosylamide formaldehyde resin. Reproduced by permission of OPI Products, Inc.

responsible but sensitization to tosylamide/formaldehyde resin can occur in the absence of formaldehyde sensitization [19,20], and tests indicate that side products of the synthesis reaction can be responsible for the resin allergies [21] (Figure 27.9).

A final concern occasionally raised regarding formaldehyde is its absence. Because formaldehyde-releasing agents have a long history as preservatives in other forms of cosmetics, it is sometimes mistakenly assumed that formaldehyde was added to nail lacquer for preservative purposes. As a result, publicity regarding "formaldehyde-free" products has inspired fears of microbial cross-contamination via nail lacquer brushes. As noted above, experiments have shown that solvent-based nail lacquer is hostile to microbes and needs neither formaldehyde nor any other preservative.

UV-cured "lacquers"

UV-cured nail enhancements are discussed elsewhere (Chapter 28); however, a relatively new class of UV-curing nail "lacquers" merits mention here. The same pigments are used as in standard nail lacquer but instead of a solvent/resin base, curable methacrylate or acrylate oligomers and monomers are used. A photoinitiator causes polymerization of the monomers on exposure to UV light, leaving a polymer/pigment coat. Unlike the products to create nail enhancements, these curable colored products are not used to sculpt nails, but are designed to apply as a thin coat of color, resembling conventional lacquer.

Allergic sensitization may result from repeated skin exposure to uncured or incompletely cured monomers; the fully cured coat is inert. Good manicuring technique can mitigate this risk, but once an allergy is established it is irreversible. Allergies to the photoinitiators and pigments are also possible. The low-power UVA lamps used to activate the photoinitiator are comparable to summer sunshine [10], so the 1–3 minute curing time poses no hazard to healthy skin (Table 27.3).

Table 27.3 Common health effects of nail color ingredients.

Ingredients	Health concerns
Resins	Possible allergies, particularly to tosylamide/formaldehyde resin
Solvents	Dehydration and defatting of skin and nails Irritant dermatitis
UV-curable acrylates/methacrylates	Allergy after repeated exposure to uncured monomer or oligomer
Photoinitiators	Possible allergies Possible photosensitization
Colorants	Occasional staining Occasional allergies
Plasticizers	Possible allergies Camphor exposure is contraindicated for some patients with fibromyalgia
Thixotropic agents	None known
UV stabilizers	Possible allergies
Hardeners (cross-linkers)	Formalin sensitization and allergies are common Overuse may cause brittleness or splitting of nail Not recommended for nails that are already brittle
Hydrolyzed proteins	Possible allergies May trigger gluten sensitivity via transfer to mouth

Nail lacquer removers

In contrast to nail enhancements for nail elongation purposes, no polymerization takes place during the drying of nail lacquer; the resin is simply deposited on the nail as the

Figure 27.10 UV curing lamp. Reproduced by permission of OPI Products, Inc.

solvent evaporates. Therefore, removing nail lacquer is easy: it can be redissolved and wiped off with a solvent-soaked cloth pad, tissue, or cotton ball. Any solvent that dissolves the resin, and is safe for skin exposure, can be successfully used. Although UV-curable nail colors are polymerized, they are far less cross-linked than enhancements, and can be removed with a short acetone soak.

Acetone, chemically known as dimethyl ketone or 2-propanone, is the preferred solvent, because it is the least physiologically hazardous. Other removers are based on ethyl acetate or methyl ethyl ketone (MEK). Ethyl acetate has the advantage of not damaging acrylic nails, so it is used for removing lacquer from nail elongation enhancements. However, because of air quality regulations in California, ethyl acetate, MEK, and most other acetone alternatives are prohibited for nail lacquer removers, and other states and countries are considering similar actions. Acetone is exempt because its atmospheric breakdown produces less photochemical smog than almost any other solvent. One other “clean air” solvent, methyl acetate, is allowed in California, but has been avoided by most manufacturers because of toxicity concerns; those who use it add an embittering agent to deter accidental ingestion. Other hazardous solvents such as methanol and acetonitrile are seldom used, and are not California-compliant (Figure 27.11).

All solvents can have significant drying and defatting effects on the skin, leading to irritation. This can be mitigated by using a lacquer remover with added moisturizers, or by using lotion afterwards. Drying and cracking of the nail can also result; oiling the nail is the most common way to counteract this. Some removers contain fragrances or botanical additives, which may pose allergy risks.

Low-odor, non-volatile removers have been created based on methylated vegetable oils and/or various dibasic esters. As with water-based nail lacquer, however, the slow speed of nail polish removal with these products prevents them from finding general marketplace acceptance. These products are less damaging to the skin barrier.

Figure 27.11 Polish remover in action. Reproduced by permission of OPI Products, Inc.

Conclusions and future developments

Arguably the largest potential for future improvement lies in cleaner application techniques, not new products. As more cases of manicure-transmitted infection are publicized, customers and governments will demand that nail technicians practice proper sanitation and disinfection.

Most manufacturers are looking to develop “greener” products, whether in perception or reality. The trends away from toluene and DBP will surely continue, as will efforts to find a functional substitute for formalin. As for removers, most likely only acetone will survive the regulatory concerns. Water-based and UV-cured products have the potential to reduce solvent emissions, but still have unresolved disadvantages compared to traditional lacquers. Research continues in realm of nail polish as adding nail color is commonly practiced form of adornment.

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Chapter 28: Cosmetic prostheses as artificial nail enhancements

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BASIC CONCEPTS

- Artificial nail enhancements are commonly used to address malformed fingernails.
- The major forms of artificial nail enhancements include nail wraps, liquid and powder, or UV gels.
- Methacrylate monomer liquid systems remain the most widely used type of artificial nail enhancement.
- Proper application of artificial nail enhancements can avoid infection and sensitization.

Introduction

The natural nail plate can not only be cosmetically elongated and enhanced to beautify the hands, but also to effectively address discolored, thin, and weak or malformed fingernails. When used properly, these cosmetic products and services provide great value and enhance self-esteem. Artificial nails not only add thickness and strength to the nail plate, they extend its length, typically 0.25–0.75 inches. A skilled nail technician can closely mimic the length and shape of the final product to create natural-looking artificial nails. Certain techniques utilizing custom blending of colored products allow the appearance of the nail bed to be extended beyond its natural boundary, which can dramatically lengthen the appearance of the fingers (Figure 28.1).

A typical nail salon client wears artificial nail products to correct problems they are having with their own natural nails such as discoloration, splitting, breaking, unattractive or deformed nails (i.e. median canal dystrophy or splinter hemorrhages). There are several basic types from which to choose: nail wraps, liquid and powder, or UV gels. An overview of each type is given in Table 28.1.

Liquid and powder

Liquid and powder systems ("acrylic nails") were the original artificial nail enhancements. These systems were similar to certain dental products made from methacrylate monomers and polymers. Methacrylates are structurally different from acrylates, have different safety profiles, and should not be confused with one another. The literature frequently confuses methacrylates with acrylates and/or incorrectly suggests they are a single category (i.e. [meth] acrylate). The first structure shown in Figure 28.2 has a branching methyl group (–CH3) attached to the double bond of ethyl methacrylate. The branching changes both the size (10% larger) and shape of the methacrylate molecule, which reduces the potential for skin penetration. This helps explain why methacrylate monomers are less likely to cause adverse skin reactions than homologous acrylate monomers (i.e. ethyl acrylate and ethyl methacrylate). It is also one important reason why artificial nails containing acrylates are more likely to cause adverse skin reactions than those based solely on methacrylate monomers [1].

Methacrylate monomer liquid systems remain the most widely used type of artificial nail enhancement in the world. The "liquid" is actually a complex mixture of ethyl methacrylate (60–95%) and other di- or tri-functional methacrylate monomers (3–5%) that provide cross-linking and improved durability, inhibitors such as hydroquinone (HQ) or methyl ether hydroquinone (MEHQ) (100–200 p.p.m.), UV stabilizers, catalysts such as dimethyl tolyamine (0.75–1.25%), flexibilizing plasticizers and other additives. The "powder" component is made from poly methyl and/or ethyl methacrylate polymer beads (approximately 50–80 µm), coated with 1–2% benzoyl peroxide as the polymerization initiator, colorants, opacifiers such as titanium dioxide, and other additives.

Liquid and powder systems are applied by dipping a brush into the monomer liquid, wiping off the excess on the inside lip of a low volume container (3–5 mL) called a dappen dish. The excess monomer is removed by wiping the brush on the edge of the dappen dish. The tip of the brush is drawn through the polymer powder, also in a dappen dish, and a small bead or slurry forms at the end of the brush. Three to

Cosmetic Dermatology: Products and Procedures. Edited by Z.D. Draelos.

Table 28.1 The three main types of artificial nail enhancements.

Type	Chemistry	Also known as	Hardener
Nail wraps	Cyanoacrylate monomers	Fiberglass wraps, resin wraps, no-light gels, silk or paper wraps	Spray, drops, powder, or fabric treated with an tertiary aromatic amine
Liquid and powder	Methacrylate monomers and polymers	Acrylic, porcelain nails, solar nails	Polymer powder treated with benzoyl peroxide; monomer liquid contains tertiary aromatic amine
UV gels	Urethane acrylate or urethane methacrylate oligomers/monomer	Gel nails UV gels Soak-off gels	Low-power UVA lamp to activate the photoinitiator and tertiary aromatic amine catalyst

Figure 28.1 The use of custom-blended colored powders with methacrylate monomers to "illusion sculpt" and extend the apparent length of a short nail bed while also correcting a habitually splitting nail plate. (Courtesy Creative Nail Design, Inc., Vista, CA, USA.)

six beads are normally applied and smoothed into shape with the brush. Pink powders are applied over the nail bed and white powders are used to simulate the free edge of the nail plate. The slurry immediately begins to polymerize and hardens on the nail within 2–3 minutes. Over 95% of the polymerization occurs in the first 5–10 minutes, but complete polymerization can take 24–48 hours [2]. After hardening, the nail is then shaped either by hand filing or with an electric file to achieve the desired length and shape. The finished nail can be buffed to a high shine or nail color applied.

Length is added to the nail plate in one of two ways:

1 Adhering an ABS plastic nail tip to the nail plate with a cyanoacrylate adhesive, coating the tip with the liquid and powder slurry, and filing as described above. This technique is called "tip and overlay."

2 A non-stick (Mylar© or Teflon© coated paper) form is adhered underneath the free edge of the natural nail and used as a support and guide to which the liquid and powder slurry is applied, then shaped and filed. This technique is called "nail sculpting."

Proper preparation of the natural nail's surface is the key to ensuring good adhesion. Before the service begins, natural nails should be thoroughly scrubbed with a clean, disinfected, soft-bristled brush to remove contaminants from the service of the nail plate as well as underneath the free edge (Figure 28.3). This removes surface oil and debris that can block adhesion. The nail is then lightly filed with a low grit abrasive file (180–240 grit) to increase surface area for better adhesion. Nail surface dehydrators containing drying agents such as isopropyl alcohol are applied to remove surface moisture and residual oils. Adhesion promoting "primers" are then applied to increase surface compatibility between the natural nail and artificial nail product. These adhesion promoters contain proprietary mixtures of hydroxylated monomers or oligomers, carboxylic acids, etc. In the past, methacrylic acid was frequently used but has fallen out of favor because of its potential as a skin and eye corrosive [3].

UV gels

Products that cure under low intensity UVA lights, typically 435–325 nm, to create artificial nails are called "UV gels." UVB and UVC are not used to create UV gel nails [4]. Unlike liquid and powder systems, UV gels are not mixed with

Ethyl methacrylate

$C_6H_{10}O_2$

Molecular weight 114 Daltons

Ethyl acrylate

$C_5H_8O_2$

Molecular weight 100 Daltons

Figure 28.2 Chemical structure differences between methacrylates and acrylates.

Figure 28.3 Equipment used to create liquid and powder artificial nails. 1, Nail scrub brush; 2, dappen dishes containing liquid and powder; 3, Mylar nail form; 4, abrasive files; 5, nail enhancement application brush; 6, ABS preformed nail tips; 7, plastic-backed cotton pad; 8, Nitrile gloves; 9, N-95 dust mask. (Courtesy Paul Rollins Photography, Inc. Laguna Niguel, CA, USA.)

another substance to initiate the curing process. Historically, UV gels have been blends of polymerization photoinitiators (1–4%), urethane acrylate oligomers, and durability improving, cross-linking monomers (approximately 75–95%), and catalysts such as dimethyl tolyamine (0.75–1.25%). Newer formulations using urethane methacrylate oligomers and monomers lower the potential for adverse skin reactions.

Rate of cure is a hindrance for UV-curable artificial nails. Slow cure rates allow atmospheric oxygen to prevent curing of the uppermost layers of UV gel products. This layer can also be observed with certain types of liquid monomers: "odorless" products that utilize hydroxyethyl or hydroxypropyl methacrylate as the main reactive monomer. This residual sticky surface layer is called the "oxygen inhibition layer" [5].

UV gels can be clear, tinted, or heavily colored. The natural nail is cleaned, filed, dehydrated, and coated with adhesion promoters. The UV gel is then applied to the nail, shaped, and finished in the same fashion as two-part liquid and powder systems and produces very similar looking results. In most cases, the same equipment used to create other types of artificial nails is used (Table 28.2). A notable exception is UV gel curing achieved by placing the artificial nail under a UVA lamp for 2–3 minutes per applied layer. Because UVA does not efficiently penetrate more than a few millimeters into the UV gel, these products are applied and cured in several successive layers. UV gels are also applied over ABS nail tips or non-stick nail forms to lengthen the appearance of the natural nail.

Nail wraps

Methyl and ethyl cyanoacrylate monomer is used not only for adhering ABS nail tips to the natural nail, but also to create artificial nail coatings called "nail wraps." This technique is not widely used, but accounts for at least 1% of the worldwide market [6].

The natural nail is precleaned, shaped, and filed as described above, but the cyano functional group provides tremendous adhesion to the natural nail plate, eliminating the need for adhesion-promoting primers (Figure 28.4). Nail enhancements relying on cyanoacrylate monomers do not contain other cross-linking monomers and therefore are inherently weaker than cross-linking artificial nail enhancement systems. To improve durability and usefulness, a woven fabric (silk, linen, or fiberglass) is impregnated with cyanoacrylate monomer and adhered to the nail plate. Even so, these types of coatings are not strong enough to be sculpted on a non-stick nail form and cannot be extended beyond the free edge of the natural nail plate, unless the

Table 28.2 Specialized equipment used to create artificial nail enhancements.

Item	Description
Brush	Natural or synthetic hair brush for application, spreading, and shaping of monomer and oligomers products on the nail plate
Dappen dish	Small containers that hold liquid artificial nail monomer, oligomers, or polymer powders during the application process
Manual files	Wooden or plastic core boards coated with abrasive particles (e.g. silicon nitride, aluminium oxide or diamond) used to shape, shortening, smooth, thin, or buff both natural and artificial nails
Electric files	Handheld, variable speed, rotary motors that securely hold barrel-shaped abrasive bits and are use for the same purposes as manual files
Nippers	Small clippers sometimes used to remove old artificial nail product from the nail plate
Wood stick	A thin, pencil-shaped, plastic implement used to remove cuticle tissue from the nail plate
Buffers	Block shape, high grit abrasive buffers use for shape refining (180–240 grit) or buffing to a high shine (>1000 grit)
UV lamp	Electrical device that holds either 4 or 9 W UVA producing bulbs and is used to cure UV gel nail products
Cotton pads	Disposable pads or balls used to remove old nail polish and/or dusts after filing
Scrub brush	Soft bristle, disinfectable brushes used to clean natural and artificial nails
Nail forms	Mylar© or Teflon© coated paper used as a support and guide to extending artificial nails beyond the natural nail's free edge
Nail tips	Preformed ABS plastic tips adhered to the natural nail to support artificial nail products and create nail extensions beyond the nail's free edge
Wrap fabric	Loosely woven silk, linen, or fibreglass strips adhered to the natural nail plate with cyanoacrylate monomer to create nail wraps
Droppers	Used to transfer product from larger containers into dappen dishes or to apply nail wrap curing accelerators
Scissors	Slightly curved blades use for trimming or cutting natural nails and wrap fabrics
Disinfectant container	Containers designed to hold EPA registered disinfectants needed to properly disinfectant tools and implements
Remover bowl	Container that holds solvents (e.g. acetone) for artificial nail removal

nail wrap is applied over an ABS nail tip, as previously described. Usually, cyanoacrylate monomers are very low viscosity, mobile liquids, but they are sometimes thickened with polymers (e.g. polymethyl methacrylate) and used without a reinforcing fabric. Such systems are referred to as "no-light gels."

Cyanoacrylate monomers are applied without the use of a brush, directly from the container's nozzle and will cure upon exposure to moisture in the nail plate, but the process can be greatly hastened by solvent mixtures containing a tertiary aromatic amine such as dimethyl tolylamine (0.5–1%), which is either sprayed on, applied with an dropper, or impregnated into the woven fabric. After curing (5–10 seconds), the nail wrap coating can be shaped and buffed to a high shine or nail color applied. This technique is also used to mend cracks or tears in the nail plate, by using the

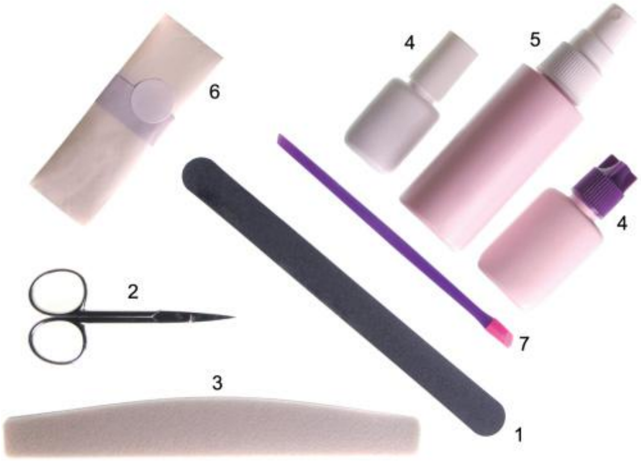

Figure 28.4 Materials needed to apply nail wraps. 1, Abrasive file for nail preparation and final shaping; 2, scissors for cutting fabric; 3, block buffer for high-shining; 4, cyanoacrylates; 5, spray-on catalyst; 6, silk fabric; 7, pusher to gently remove skin from the nail plate. (Courtesy Paul Rollins Photography, Inc. Laguna Niguel, CA, USA.)

cyanoacrylate monomer to adhere a small piece of fabric over the broken or damaged area of the plate.

Artificial nail removal

Improper removal of artificial nails can lead to nail damage; however, they can be safely removed if the proper procedures are followed. Acetone (dimethyl ketone) is the preferred remover for artificial nail products, but methyl ethyl ketone (MEK) is also used. The artificial nails are placed in a small bowl and immersed in solvent. Nail wraps are the easiest to remove because they are not cross-linked polymers and have lower solvent resistance. They usually require less than 10 minutes immersion for full removal. Liquid and powder products are cross-linked polymers and can take 30–40 minutes to remove. UV gels are also cross-linked and these urethane acrylate or methacrylate based artificial nails have inherently greater solvent resistance so removal can take 45–60 minutes. The removal process is greatly accelerated by prefiling to remove the bulk of the artificial nail. Improper removal can cause significant damage to the nail plate. Prying or picking off the artificial nails can lead to onycholysis [7]. A common myth is that artificial nail should be regularly removed to allow nails to “breathe”; in reality they should only be removed when there is a need. Frequent removal is not advised.

Rebalancing

As the natural nail grows, the artificial nail advances leaving a small space of uncoated nail plate. Every 2–3 weeks the nail technician will file the artificial nail down to one-third its thickness, reapply fresh product, and reshape the artificial nail, thereby covering the area of new growth. This process is called “rebalancing” and is essential to maintaining the durability and appearance of the artificial nail.

“Soak-off gels” are highly plasticized, which softens the coating, making it more susceptible to solvent removal. This type of artificial nail often has low durability and therefore must be frequently removed and replaced, which can lead to excessive nail damage.

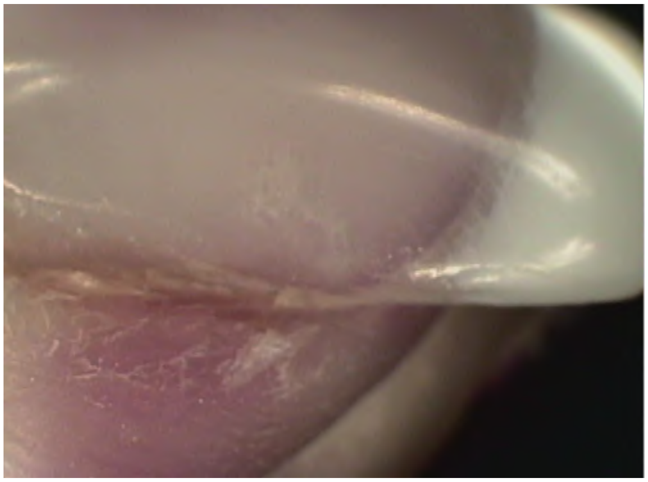

Figure 28.5 Example of an adverse skin reaction caused by repeated contact to the skin. (Courtesy Paul Rollins Photography, Inc. Laguna Niguel, CA, USA.)

Adverse reactions

Both nail technicians and those wearing artificial nails can develop adverse skin reactions if steps are not taken to avoid prolonged and/or repeated skin contact with artificial nail products. For example, the product should be applied to the nail plate in such a manner that skin contact is avoided (i.e. a tiny free margin left between the eponychium and artificial nail). Typically, reactions are a result of many months of overexposure to eponychium, hyponychium, or lateral side walls (Figure 28.5).

Reactions can appear as paronychia, itching of the nail bed and, in extreme cases, paresthesia and/or loss of the nail plate [8,9]. Onycholysis can be a result of allergic reactions, but the nail plate is resistant to penetration from external agents and this condition is more likely to be caused by overly heavy handed, aggressive filing techniques with coarse abrasives or overzealous manicuring of the hyponychium area [10]. Allergic contact dermatitis can affect the chin, cheeks, and eyelids as a result of touching the face with the hands [11]. Filings and dusts may contain small amounts of unreacted monomers and oligomers, because it can take

24–40 hours for the artificial nails to finish the curing process.

Nail technicians should be instructed to wash their hands thoroughly before touching the face or eye area. They should be warned to avoid contact with the dusts and filings, especially the oxygen inhibition layer created on the surface of UV gels and odorless monomer liquid systems (see above), which can contain substantial amounts of unreacted ingredients. Gloves (nitrile) and/or plastic-backed cotton pads should be used to remove the oxygen inhibition layer as skin contact should be avoided. The UV bulbs in the curing lamps should be changed every 2–4 months (depending on usage) to ensure thorough cure and lessen the amount of unreacted ingredients, thereby lowering the potential for adverse skin reactions. For liquid and powder systems, it is common for technicians to use excessive amounts of liquid monomer, creating a wet consistency bead. Nail technicians should avoid applying beads of product with a wet mix ratio because this can lower the degree of curing and increase the risk of overexposure to unreacted ingredients. Nail technicians should be instructed to avoid all skin contact with uncured artificial nail products or dusts and not to touch them to client's skin prior to curing.

Nail damage and infection

Avoiding the use of heavy grit abrasives (<180 grit) or electric files directly on the nail plate will lessen the potential for damage and injury (e.g. onycholysis). Plate damage can occur when nail technicians aggressively file the natural nail, rather than use safer, smoother abrasive files (>180 grit). These gentler methods also increase the surface area for better adhesion, but without overly thinning or damaging the nail plate.

Methyl methacrylate (MMA) monomer is sometimes used illegally in artificial nail monomer liquids because of its low cost when compared to better alternatives (e.g. ethyl methacrylate [EMA]). MMA has very poor adhesion to the natural nail plate so technicians who use these liquid monomers frequently abrade away the uppermost layers of the natural nail plate to achieve significantly more adhesion by allowing for deposition into the more porous layers underneath. However, this poor technique can compromise the nail plate's strength and durability, so liquid monomer MMA containing products should be avoided [12]. The other artificial nail systems described in this chapter have improved adhesion and do not require technicians to heavily abrade the nail plate in order to achieve proper adhesion.

Infections can occur underneath the artificial nail to produce green or yellow stains (Figure 28.6). Several types of bacteria and dermatophytes can cause such infections (*Pseudomonas aeruginosa, Staphylococcus aureus, Trichophyton rubrum*). To avoid this, state regulations require nail technicians to properly clean and disinfect all implements in an Environmental Protection Agency (EPA) registered disinfectant to avoid transmission of pathogenic organisms, and to dispose of all single-use items. Clients should wash their hands, scrubbing under the nails with a clean and disinfected, soft-bristled brush before receiving any services.

Figure 28.6 Example of an nail infection growing underneath an artificial nail. (Courtesy Paul Rollins Photography, Inc. Laguna Niguel, CA, USA.)

Education

Almost every US state requires specialized nail training and education, typically 300–750 hours depending on the state, to obtain a professional license and some states have continuing education requirements. The textbooks teach a surprisingly wide range of topics including anatomy and physiology of the skin and nails, product chemistry, an overview of common nail related diseases and disorders, contamination and infection control and universal precautions, safe working practices, as well as manicuring, pedicuring, and the artificial nail techniques described in this chapter [13–15].

Multilingual information sources for proper use and other safety information can be found from a wide range of sources, including the EPA [16] and Nail Manufacturers Council [17].

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Part 3: Hair Cosmetics

Chapter 29: Hair physiology and grooming

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BASIC CONCEPTS

- The hair follicle is a complex structure that produces an equally complex structure, the hair fiber.
- Human hair keratins consist of at least 19 acidic and basic proteins which are expressed in various compartments of the hair follicle.
- The science behind modern shampoos and conditioners has led to the development of rationally designed products for normal, dry, or damaged hair.

Definitions

The use of hair cosmetics is ubiquitous among men and women of all ages. Virgin hair is the healthiest and strongest but basic grooming and cosmetic manipulation cause hair to lose its cuticular scale, elasticity, and strength. Brushing, combing, and shampooing inflict damage on the hair shaft, much of which can be reversed with the use of hair conditioners. In this chapter, the physiology of hair, grooming techniques including the science and use of shampoos and conditioners, are reviewed.

Physiology

Hair follicle

The hair follicle is a complex structure that demonstrates the ability to completely regenerate itself – hair grows, falls out and then regrows. Plucked hairs can regrow. Important cells for the development of hair follicles include stem cells in the bulge region and dermal papilla cells [1]. Hair follicle stem cells are described as being present just below the entrance of the sebaceous duct into the hair follicle. The hair follicle's complexity is further appreciated when examining the organization of follicles in the scalp and the complexity of its vascular complex and nerve innervation. Scalp hair follicles present in groups of one, two, three, or four follicular units (Figure 29.1).

The hair follicle is defined histologically as consisting of several layers (Figure 29.2). It is the interaction of these layers that produces the hair fiber. The internal root sheath consists of a cuticle which interdigitates with the cuticle of the hair fiber, followed by Huxley's layer, then Henle's layer. Henle's layer is the first to become keratinized, followed by the cuticle of the inner root sheath. The Huxley layer contains trichohyalin granules and serves as a substrate for citrulline-rich proteins in the hair follicle. The outer root sheath has specific keratin pairs, K5–K16, characteristic of basal keratinocytes and the K6–K16 pair characteristic of hyperproliferative keratinocytes, similar to what is seen in the epidermis. Keratin K19 has been located in the bulge region [2,3].

The complexity of the hair follicle is further demonstrated by the fact the follicle cycles from the actively growing phase (anagen), through a transition phase (catagen), and finally a loss phase (telogen). The signals associated with the transition from anagen, catagen to telogen are the subject of current research activities in this field.

Product of the hair follicle: the hair fiber

The hair follicle generates a complex fiber which may be straight, curly, or somewhere in between. The main constituents of hair fibers are sulfur-rich proteins, lipids, water, melanin, and trace elements. The cross-section of a hair shaft has three major components, from the outside to the inside: the cuticle, the cortex and the medulla [4].

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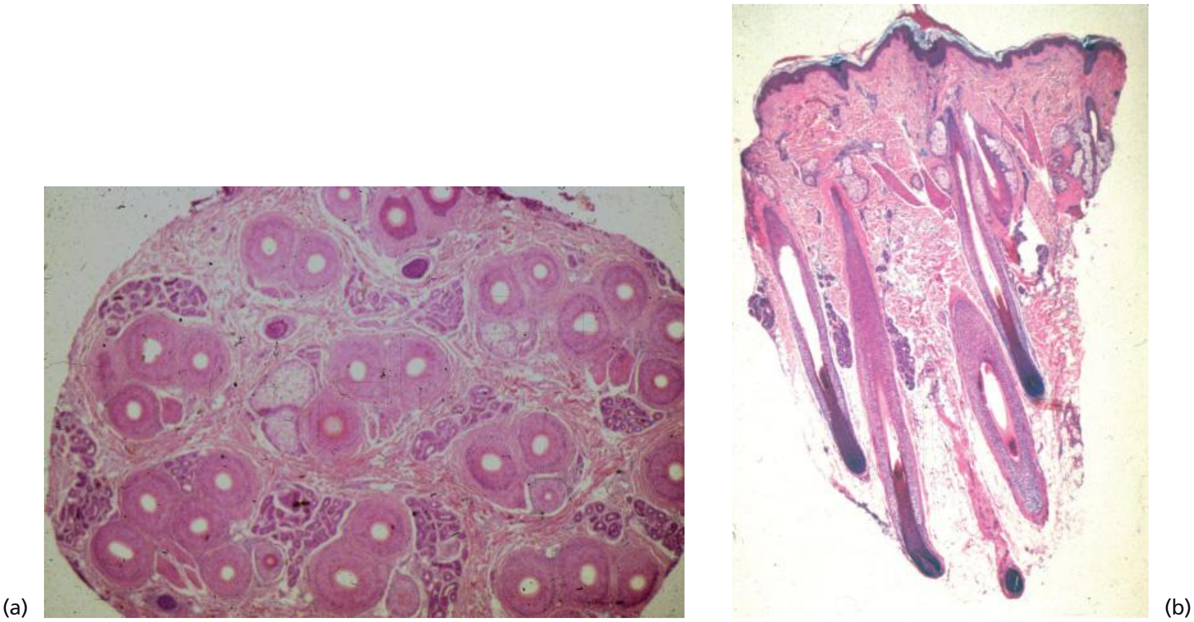

Figure 29.1 (a) Horizontal section of a 4 mm scalp biopsy specimen demonstrating follicular units containing 1, 2, 3, or 5 anagen follicles. (b) Vertical section of a 4-mm scalp punch biopsy specimen from a normal, healthy Caucasian female in her early twenties.

Fibers can be characterized by color, shaft shape – straight, arched, or curly – as well as microscopic features. The cuticle can be defined by its shape – smooth, serrated, or damaged, and whether or not it is pigmented. The cortex can be described by its color and the medulla by its distribution in fibers. It can be absent, uniform, or randomly distributed. Lastly, fibers can be abnormal and present with structural hair abnormalities such as trichoschisis or trichorrhexis nodosa. Both of these structural abnormalities can commonly be seen in patients with hair fiber injury related to routine and daily cosmetic techniques including application of high heat, frequent perming as well as from weathering, the progressive degeneration from the root to the tip of the hair initially affecting the cuticle, then later the cortex [3].

The cuticle is also composed of keratin and consists of 6–8 layers of flattened overlapping cells resembling scales. The cuticle consists of two parts: endocuticle and exocuticle. The exocuticle lies closer to the external surface and comprises three parts: b-layer, a-layer, and epicuticle. The epicuticle is a hydrophobic lipid layer of 18-methyleicosanoic acid on the surface of the fiber, or the f-layer. The cuticle protects the underlying cortex and acts as a barrier and is considered to be responsible for the luster and the texture of hair. When damaged by frictional forces or chemicals and subsequent removal of the f-layer, the first hydrophobic defense, the hair fiber becomes much more fragile.

The cortex is the major component of the hair shaft. It lies below the cuticle and contributes to the mechanical properties of the hair fiber, including strength and elasticity. The cortex consists of elongated shaped cortical cells rich in keratin filaments as well as an amorphous matrix of sulfur proteins. Cysteine residues in adjacent keratin filaments form covalent disulfide bonds, which confer shape, stability, and resilience to the hair shaft. Other weaker bonds such as the van der Waals interactions, hydrogen bonds and coulombic interactions, known as salt links, have a minor role. These bonds can be easily broken just by wetting the hair. It is the presence of melanin in the cortex that gives hair color; otherwise, the fiber would not be pigmented [4].

The medulla appears as continuous, discontinuous, or absent under microscopic examination of human hair fibers. It is viewed as a framework of keratin supporting thin shells of amorphous material bonding air spaces of variable size [4]. Fibers with large medullas can be seen in samples obtained from porcupines or other animal species. Other than in gray hairs, human hairs show great variation in their medullas.

Human hair keratins

Human hair keratins are complex and, until recently, research suggested that the hair keratin family consisted of 15 members, nine type I acidic and six type II basic keratins, which exhibited a particularly complex expression pattern in the hair-forming compartment of the follicle (Figure 29.2). However, recent genome analyses in two laboratories has led to the complete elucidation of human type I and II keratin gene domains as well as a completion of their complementary DNA sequences revealing an additional small hair keratin subcluster consisting of genes *KRT40* and *KRT39*. The discovery of these novel genes brought the hair keratin family to a total of 17 members [3].

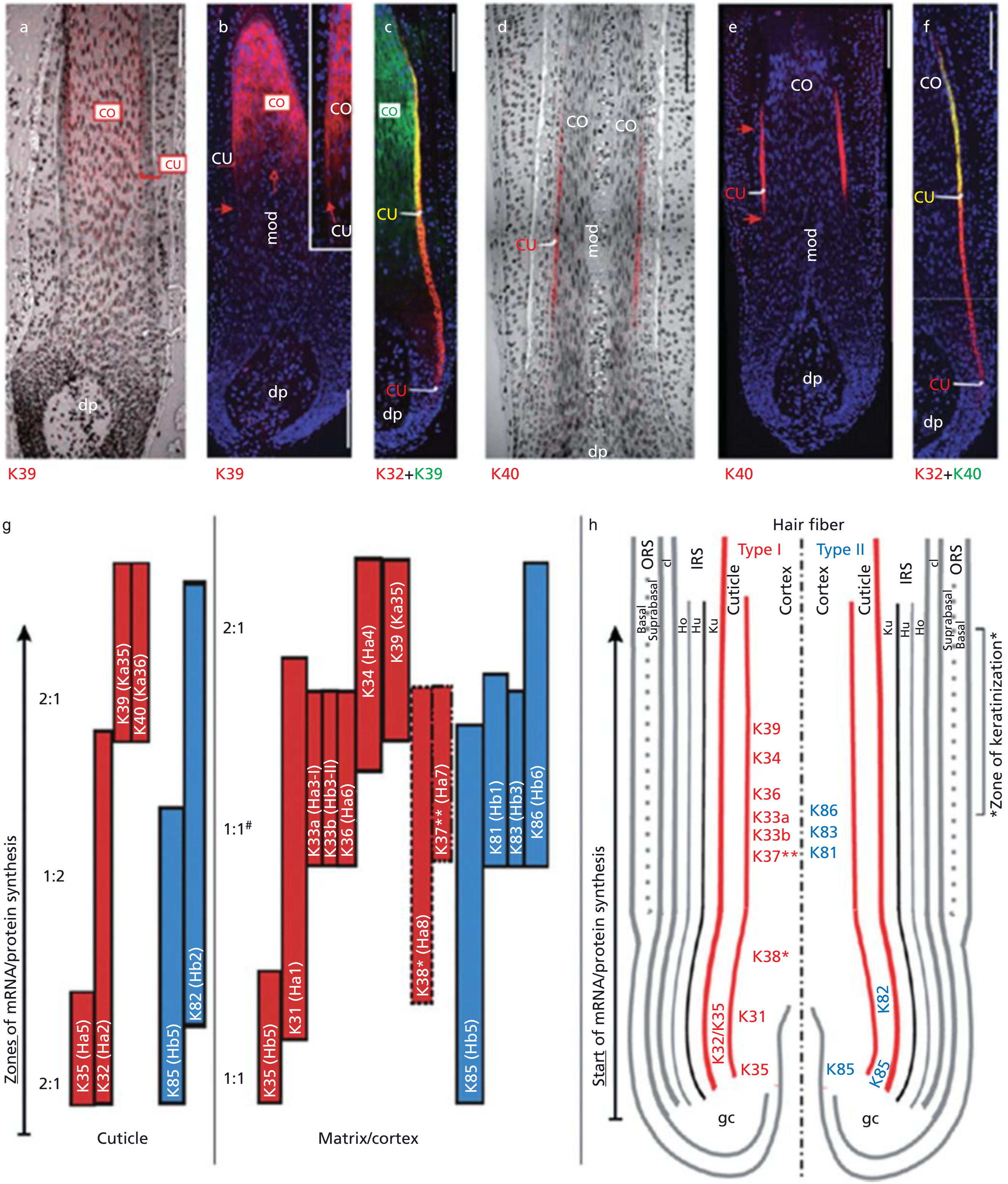

Figure 29.2 Schematic presentation of the complex pattern of hair keratin expression in the human hair follicle. (Reprinted by permission from Macmillan Publishers Ltd, *J Invest Dermatol* 127, 1532–5, 2007.)

The human type II hair keratin subfamily consists of six individual members which are divided into two groups. Group A members hHb1, hHb3, and hHb6 are structurally related, while group C members hHb2, hHb4, and hHb5 are considered to be rather distinct. Both *in situ* hybridization and immunohistochemistry on anagen hair follicles have demonstrated that hHb5 and hHb2 are present in the early stages of hair differentiation in the matrix (hHb5) and cuticle (hHb5, hHb2), respectively. Cortical cells simultaneously express hHb1, hHb3, and hHb6 at an advanced stage of differentiation. In contrast, hHb4, has been undetectable in hair follicle extracts and sections, but has been identified as the most significant member of this subfamily in cytoskeletal extracts of dorsal tongue [3].

Grooming

Shampoos: formulations and diversity

Cleaning hair is viewed as a complex task because of the area that needs to be treated. The shampoo product has to also do two things – maintain scalp hygiene and beautify hair. A well-designed conditioning shampoo can provide shine to fibers and improve manageability, whereas a shampoo with high detergent properties can remove the outer cuticle and leave hair frizzy and dull.

Formulations

Shampoos contain molecules with both lipophilic and hydrophilic sites. The lipophilic sites bind to sebum and oil-soluble dirt and the hydrophilic sites bind to water, permitting removal of the sebum with water rinses. There are four basic categories of shampoo detergents: anionics, cationics, amphoterics, and non-ionics (Table 29.1). A typical shampoo will typically have two detergents. Anionic detergents have a negatively charged hydrophilic polar group and are quite good at removing sebum; however, they tend to leave hair rough, dull, and subject to static electricity. In contrast, ampotheric detergents contain both an anionic and a cationic group allowing them to work as cationic detergents at low pH and as anionic detergents at high pH. Ampotheric detergents are commonly found in baby shampoos and in shampoos designed for hair that is fine or chemically treated [5].

Table 29.1 Four categories of shampoo detergents.

1. Anionics
   Lauryl sulfate
   Laureth sulfates
   Sarcosines
   Sulfosuccinates
2. Cationics
3. Amphoterics
   Betaines such as cocamidopropyl betaine
   Sultaines
   Imidazolinium derivatives
4. Non-ionics

The number of shampoo formulations on the market can be overwhelming but when the chemistry behind those marketed for "normal hair" or "dry hair" is understood, recommending the best product becomes easier (Table 29.2). Shampoos for "normal" hair typically have lauryl sulfate as the main detergent and provide good cleaning of the scalp. These are best utilized by those who do not have chemically treated hair. Shampoos designed for "dry hair" primarily provide mild cleansing but also excellent conditioning. An addition to shampoo categories has been the introduction of conditioning shampoos which both clean and condition. The detergents in these types of shampoos tend to be amphoterics and anionics of the sulfosuccinate type. These work well for those with chemically damaged hair and those who prefer to shampoo frequently. For individuals with significant sebum production, oily hair shampoos containing lauryl sulfate or sulfosuccinate detergents can work well but can by drying to the hair fiber.

Hydrolyzed animal protein or dimethicone are added to conditioning shampoos, also commonly called 2-in-1 shampoos. These chemicals create a thin film on the hair shaft to increase manageability and even shine. For individuals with tightly kinked hair, conditioning shampoos with both cleaning and conditioning characteristics that are a variant of the 2-in-1 shampoo can be beneficial. These shampoos can be formulated with wheatgerm oil, steartrimonium hydrolyzed animal protein, lanolin derivatives, or dimethicone and are designed for use either weekly or every 2 weeks.

Conditioners

Conditioners can be liquids, creams, pastes, or gels that function like sebum, making hair manageable and glossy appearing. Conditioners reduce static electricity between fibers following combing or brushing by depositing charged ions on the hair shaft and neutralizing the electrical charge. Another benefit from conditioners is improved hair shine

Table 29.2 Categories of shampoos are available for the following hair types.

Normal hair

Dry hair

Oily hair

Tightly kinked hair

Table 29.3 Categories of hair conditioners.

Category	Primary ingredient
Cationic detergent	Quaternary ammonium compounds
Film-former	Polymers
Protein-containing	Hydrolyzed proteins
Silicones	Dimethicone
	Cyclomethicone
	Amodimethicone

which is related to hair shaft light reflection. Conditioners may also improve the quality of hair fibers by reapproximating the medulla and cortex in frayed fibers [5,6].

There are several hair conditioner product types including instant, deep, leave-in, and rinse. The instant conditioner aids with wet combing; the deep conditioner is applied for 20–30 minutes and works well for chemically damaged hair. A leave-in conditioner is typically applied to towel dried hair and facilitates combing. A rinse conditioner is one used following shampooing and also aids in disentangling hair fibers.

There are at least four conditioner categories, summarized in Table 29.3. The quaternary conditioners are cationic detergents. The film-forming conditioners function by coating fibers with a thin polymer layer. Protein-containing conditioners contain small proteins with a molecular weight of 1000–10 000 Da. These penetrate the hair shaft and are thought to increase fiber strength temporarily. Silicone conditioners form a thin film on the hair shaft and, by doing so, reduce static electricity and friction. Dimethicone is the most common form of silicone used.

Conclusions

The hair follicle is recognized as being a complex structure consisting of at least 17 different keratins as well as lipids, water, melanin, and trace elements. The follicle produces an equally complicated structure, the hair fiber which may be straight, wavy, or curly. Hair is cited as a factor contributing to attractiveness and is frequently styled to convey cultural affiliations [4].

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Chapter 30: Hair dyes

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BASIC CONCEPTS

- Hair dyes are a cosmetic product category that can be traced back thousands of years. Modern hair dyes have been developed since the late 19th century and are now available in a broad range of products delivering a variety of color results and usage conditions.
- Hair dyes constitute a large product category – over 70% of women in the developed world color their hair at least once, and many do so regularly. Psychologic aspects of color transformation should not be underestimated; especially dyeing gray hair can contribute significantly to the confidence and self-perceived attractiveness of many people.
- Within the category, permanent or oxidative hair dyes represent the largest market share with around 80% of all products. A combination of hydrogen peroxide and an alkalizing agent (typically ammonia) form the basis to lighten the natural hair color while at the same time depositing oxidatively coupled dyes inside the hair shaft.
- Disadvantages of using particularly permanent hair dyes regularly include a high maintenance routine, and changes to the hair structure which require special care and attention.
- Because of the complex chemistry of hair dyes, safety and regulatory criteria are important aspects of modern hair dyes. Special emphasis needs to be put on proper safety and use instructions to further minimize a potential allergy risk.

Introduction

Modern hair dyes offer a broad range of products and a variety of color results. They constitute a large category – over 70% of women in the developed world color their hair at least once, and many do so regularly. The number one reason for dyeing hair is to cover gray hair and look younger. Within the category, permanent or oxidative hair dyes represent the largest market share with around 80% of all products. A combination of hydrogen peroxide and an alkalizing agent (typically ammonia) form the basis to lighten the natural hair color while at the same time depositing wash-resistant color complexes inside the hair shaft. Because of the complex chemistry of hair dyes, safety and regulatory criteria are important aspects of modern hair dyes. Special emphasis needs to be put on proper safety and use instructions to further minimize a potential allergy risk.

Definitions

Natural hair color manifests itself in a vast multitude of shades and tones – from the lightest blonde and warmest brunette to the most vibrant red and deepest black. Yet, for thousands of years humans have attempted to enhance or change their natural hair color, initially with the help of natural preparations such as kohl and henna [1], nowadays with modern products which offer anything from subtle results to dramatic changes.

Hair dyes can be defined as products that alter the color appearance of hair temporarily or permanently, by removing some of the existing color and/or adding new color. They constitute a significant category in the cosmetics market – it is estimated that over 70% of women in the developed world have used hair color, and a large proportion of those do so regularly [2]. Consumers have the choice between home hair dye kits, and having their hair dyed professionally at a salon. While each woman may have a very individual reason for coloring her hair, covering gray can be considered a universal key motivator. Other desired performance aspects include enhancing the existing color, wanting a different color from the one given by nature, or achieving a more striking looking appearance.

Product subtypes

- Temporary hair dyes.
- Semi-permanent hair dyes.
- Permanent (oxidative) hair dyes.
- Hair bleaching.

A wide range of products for changing the color of hair is available to consumers. Today's hair dyes can remove (lift)

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Table 30.1 Overview of hair dye product types.

Hair dye product types	Dye technology	Level of lastingness
Temporary	Preformed FD&C and D&C dyes	Wash out (with one wash)
Semi-permanent	Preformed HC and disperse dyes	Wash out (with 6–8 washes)
Demi-permanent	Oxidative dyes, reduced peroxide concentration	Wash out (with up to 24 washes)
Permanent	Oxidative dyes	Permanent (grows out)
Bleaching	Oxidative bleaching, no dye deposition	Permanent (grows out)

D&C, dyes to be used in drugs and cosmetics; FD&C, dyes allowed to be used in food, drugs and cosmetics; HC, dyes to be used in hair colorants.

natural hair color, add (deposit) new artificial color, or indeed do both at the same time. They offer a variety of results, from a subtle color refresher to a significant change in the natural hair color, based on very different dye technologies. The classification of hair dyes is based on the permanency of the induced color change (Table 30.1). It should be noted that home and salon hair dyes are based on the same technologies, while there are key differences in shade and application variety.

Temporary dyes

Temporary dyes or color rinses are usually formulated with high molecular weight acid or dispersed dyes, which have little affinity for hair and are quite soluble in the dye base. The dye is complexed with a cationic polymer to decrease solubility and increase affinity for hair, and the complex dispersed in the dye base by surfactants. The complex coats the hair and excess can be rinsed off [3]. The binding forces between hair substrate and dyes are low so color is easily washed out after the first shampoo.

Each product contains a mixture of generally two to five color ingredients to achieve the desired shade [4]. Typical product forms include shampoos and sprays. While color results are very limited (no lightening, no grey coverage), temporary dyes may be a good option to test colors or refresh dyed hair.

Semi-permanent dyes

Semi-permanent hair dyes use a combination of preformed (direct) dyes to obtain results that last up to 6–8 shampoos. The dyes are generally characterized by their low molecular weight, allowing them to diffuse into the outer cuticle layers without binding firmly to the hair protein (Figure 30.1).

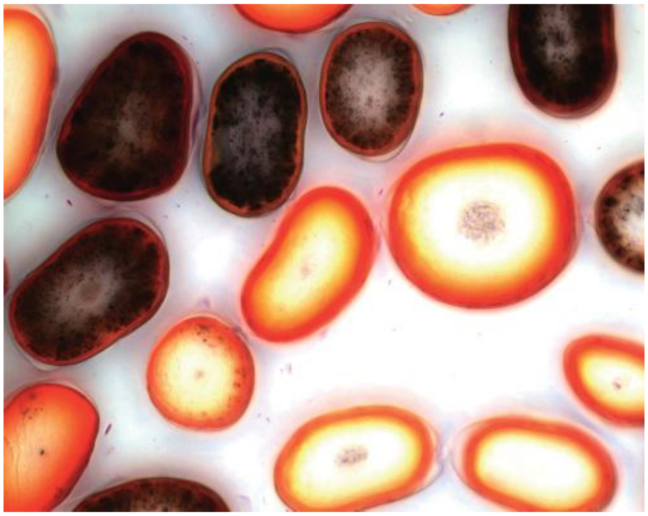


Figure 30.1 Hair cross-section showing color penetration after semi-permanent dyeing.

Nitro-dyes are the most important group of dyes used in semi-permanent colorants [5]. These uncharged (non-ionic) dyes are barely influenced by negative charges on the surface of the hair. As a result, and because of their relatively small size, they are able to penetrate into the hair cuticle. Washing hair opens the cuticle, allowing color to escape over time because of the solubility of the dyes in water.

The products contain a mixture of preformed dyes and are usually on the hair for approximately 20–30 minutes. Color results are limited (no lightening, blend away first grays).

Demi-permanent and permanent dyes

Demi-permanent and permanent hair dyes involve oxidative chemistry, requiring different product components to be mixed just before they are applied. Oxidative dyes are the most frequently used and commercially most relevant hair dyes. Within this category we differentiate two product groups: permanent and demi-permanent dyes. The primary distinctions between those two are the type and level of alkalizing agent and the concentration of peroxide, which result in different color results with regard to lastingness, gray coverage, and lightening performance.

Demi-permanent colors typically use 2% hydrogen peroxide (concentration on head) and low levels of alkalizer (usually monoethanolamine, not ammonia), leading to a less efficient dye penetration (ring dye effect; Figure 30.2). They wash out in up to 24 shampoos. While they can be used to enhance and brighten natural color and blend or cover up grays up to 50%, they have little or no lightening potential.

Permanent colorants use up to 6% peroxide (concentration on head) and contain ammonia as alkalizer to bring the pH of the final product to 9.0–10.5. This allows complete penetration across the cortex (Figure 30.3). They are the

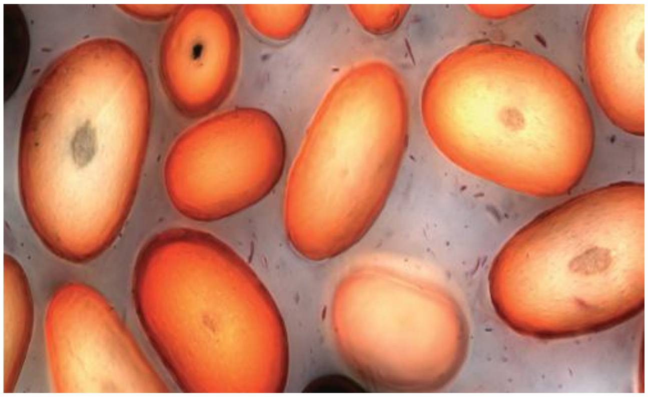


Figure 30.2 Hair cross-section showing color penetration after demi-permanent dyeing.

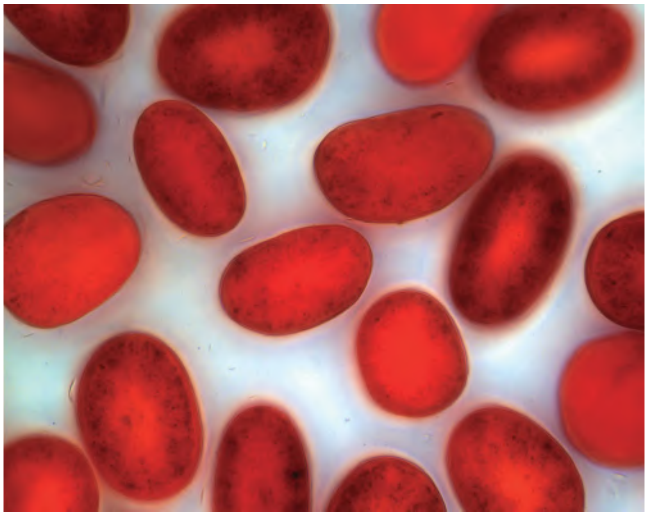


Figure 30.3 Hair cross-section showing color penetration after permanent dyeing.

most versatile and long-lasting hair dyes and are also available in the widest spectrum of shades. Permanent dyes can lighten hair significantly, change color in subtle or dramatic ways, and provide 100% gray coverage, even on resistant grays. Reapplication is required every 4–6 weeks to avoid a noticeable regrowth at the root line.

Bleaches

Hair bleaches are products that lighten hair without adding a new color. In addition to hydrogen peroxide and ammonia they contain persulfates to boost and accelerate the bleaching efficacy. Bleaching is the most efficient method of lightening natural and precolored hair. In the case of a partial bleaching, especially on very dark hair, the results can be an unwanted yellow to orange-colored shade.

Bleaches can lift the natural hair color most significantly and are often used with special techniques to apply highlighting effects to hair. Just as with permanent dyes, regular reapplication is needed to prevent visible regrowth of the naturally darker hair.

Chemistry

Natural hair pigmentation

The natural coloration of hair is caused by the presence of melanin in the cortex of the hair shaft, which occurs in the form of minute pigment granules. All natural hair color shades are created by just two types of melanin: the more common brownish black eumelanin, and the less common reddish yellow pheomelanin. The final color of hair is determined by the amount of melanin it contains, by the size of the pigment granules, and by the ratio between the two melanin types [6]. Black hair contains eumelanin in high concentration, whereas we find less pigment overall – and higher ratios of pheomelanin – in blonde and red hair.

Despite clear differences in molecular size and general properties, the two melanin types are biogenetically related and develop from a common metabolic pathway involving dopaquinone as a key intermediate [7]. The pigments are present as oval or spherical granules, generally in the range 0.2–0.8 μm in length, and constitute less than 3% of the total hair mass [4]. Production of the pigment particles is located in specialized cells, the melanocytes, deep within the hair follicle. Melanocytes are hidden in the dermal papilla of the hair bulb where they secrete tiny packages called melanosomes into the surrounding keratinocytes.

Natural hair color changes are often observed over the years from birth to old age. Many fair-haired children gradually become darker and by middle age have brown hair. Graying hair affects all to a greater or lesser extent as part of the aging process. It seems to appear earlier in dark- than in light-haired people, and is less common in black people. Graying of the hair is usually a gradual process and irreversible.

The reason for going gray is not the production of a new "gray" pigment, but the visual result of a mixture of dark and non-pigmented, colorless hair. Due to the dispersion of light, hair which no longer contains any melanin appears to be white. The precise causes of graying hair are still under discussion. Hereditary factors seem to be predominant, meaning that genes regulate the exhaustion of the pigmentary potential of each individual hair follicle leading to reduced melanogenic activity with age. Recent research specifically traced the loss of hair color to the gradual dying off of melanocyte stem cells. Not only do they become exhausted with age, they also progressively make errors, turning into fully committed pigment cells in the wrong place within the hair follicle, where they are ineffective for providing color to hair [8].

For products designed to change the natural color of hair it is important to consider that the melanin granules are distributed throughout the cortex of the hair shaft, showing the greatest concentration towards the outer edge (Figure 30.4). As a general rule, the cuticle layer of hair carries no natural pigments and is therefore transparent. It is therefore imperative for any effective hair dye product to penetrate past the cuticle layer into the cortex of the hair fiber.

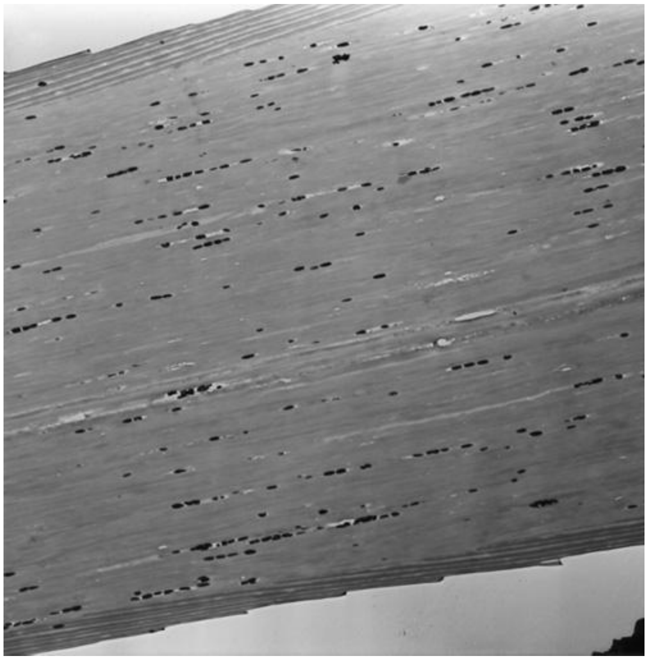


Figure 30.4 Longitudinal section of hair fiber showing melanin distribution across the cortex.

Permanent hair dyes

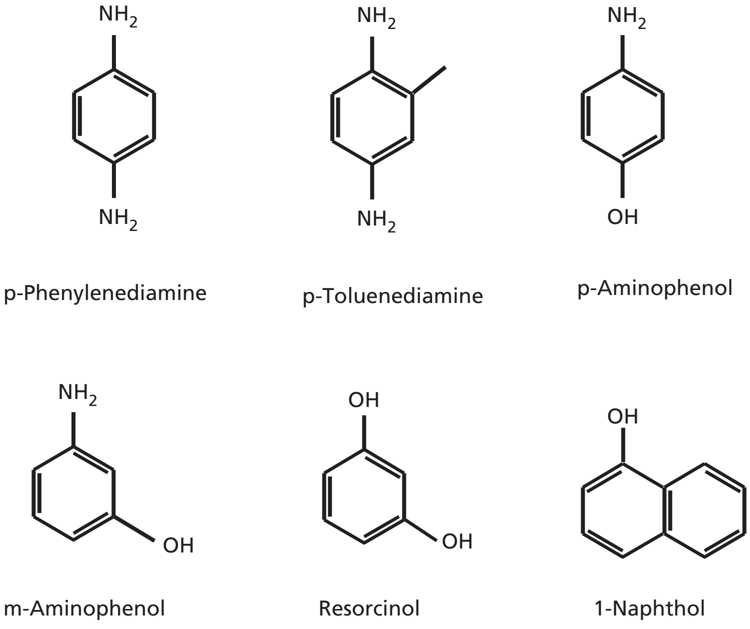
There are two chemical processes that take place during the permanent dyeing process, both of which contribute to the final color. The first is the oxidation of the melanin pigments and previously deposited dyes that lightens the underlying color. The second is the oxidation of the dye precursors to form color giving chromophores [9].

Melanin bleaching

Permanent hair dyes and hair bleach products have the capability to lighten the natural color of hair by removing some of the existing pigment. The melanin granules are partly dissolved and broken down. During a complete bleaching procedure the melanin granules are dissolved completely, leaving behind a tiny hole in the cortex of the hair. The process can be described as oxidative degradation of the melanins, leading to a variety of smaller degradation products. The reaction is diffusion-controlled and therefore time dependent [4]. It has been reported that pheomelanins is more resistant to photobleaching, and probably also chemical bleaching, than eumelanins [10].

Oxidative dye formation

Permanent hair dyes are based on the oxidation by hydrogen peroxide of so-called dye precursors or primary intermediates which typically belong to the chemical groups of p-diamines and p-aminophenols, in the presence of various couplers (for examples see Figure 30.5). To start the process, the highly alkaline pH of the dye formulations swells the hair fiber and allows the small active molecules to penetrate into the cortex where the dye formation takes place in three



p-Phenylenediamine p-Toluenediamine p-Aminophenol

m-Aminophenol Resorcinol 1-Naphthol

Figure 30.5 Some typical oxidative dye precursors (top) and couplers (bottom).

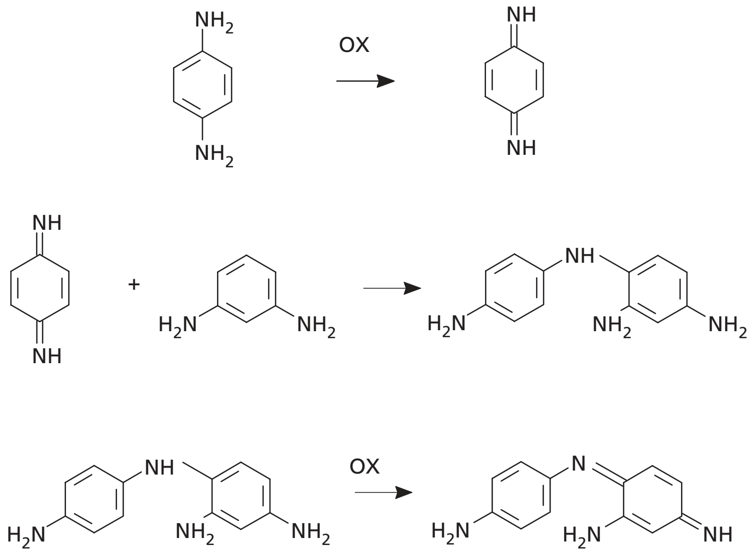


Figure 30.6 The three main steps in oxidative dye formation (here with p-phenylenediamine and m-phenylenediamine).

Table 30.2 Variety in color results given by different couplers in the presence of p-diamines and p-aminophenols.

Coupler	Color on hair with p-diamines	Color on hair with p-aminophenols
m-Phenylenediamine	Bluish brown–black	Reddish brown
1-Napthol	Blue–violet	Red
Resorcinol	Greenish brown	Light brown
3-Aminophenol	Warm brown/magenta	Red–brown
o-Aminophenol	Warm brown	Warm brown

main steps. The first step of the dye formation process is the oxidation of the primary intermediates to highly active imines, which are capable of reacting with their unoxidized counterparts to form polynuclear brown or black colored complexes. In the presence of couplers or color modifiers the imines then react preferentially with the coupler molecules at the most nucleophilic carbon atom on the structure. In step 3 this coupled reaction product is oxidized to form wash-resistant indo dyes (for an overview of the dye formation process see Figure 30.6).

Couplers do not themselves produce color but modify the color produced by the oxidation of the primary intermediates (Table 30.2). The final color is a function of the amounts and nature of the individual primary intermediates and couplers in the composition and consists of a variety of large color molecules. Their size makes them particularly resistant to removal by washing the hair, and means they undergo little fading [5].

Formulation

All permanent hair dyes are generally marketed as two component kits. One component (tint) contains the dye precursors and an alkalizer (typically ammonia or monoethanolamine) in a surfactant base, and the other is a stabilized solution of hydrogen peroxide (developer). The two components are mixed immediately prior to use and then applied to the hair. With the developer component being a liquid, the tint is usually a cream or a liquid. Which one to use is mainly a matter of individual preference, the liquids might be easier to mix while the creams might be applied with less dripping.

Table 30.3 summarizes common hair dye components and their functions, while also naming some specific examples as they would appear in the ingredients list of a marketed product.

Advantages and disadvantages

If all goes well, coloring hair can be life-transforming but there are a couple of considerations when it comes to weighing advantages and disadvantages of this category.

Advantages

The key strength of the hair dye category lies in its transformational potential. Changing one's hair color can have a dramatic physical effect but, more importantly, it can also have an impact on a psychologic level. Patients may not only feel more attractive and younger looking, they also report increased confidence both in their private and work environments which should not be discounted or belittled [2].

Table 30.3 Overview of common hair dye ingredients.

Component	Function	Sample ingredients
Peroxide	Oxidant, bleaching	Hydrogen peroxide
Alkalizer	Swell hair, bleaching	Ammonia, monoethanolamine (MEA), aminomethylpropanol (AMP)
Dye precursors	Impart color	p-Aminophenol, 1-naphtol, p-phenylenediamine, 4-amino-2-hydroxytoluene
Solvent	Dye vehicle	Water, propylene glycol, ethanol, glycerin
Surfactant	Foaming, thickening	Sodium lauryl sulfate, ceteareth-25, cocoamide MEA, oleth-5
Buffer	Stabilizing	Disodium phosphate, citric acid
Fatty alcohols	Emollients	Glyceryl stearate, cetearyl alcohol
Quaternary compounds	Conditioning	Polyquaternium, cetrimonium chloride

In our youth-obsessed society coloring gray hair can be seen as a simple yet powerful tool in the arsenal of "antiaging" procedures and products.

Another advantage of modern hair dyes is the variety of technologies and benefits that it offers. Virtually everyone can find a product that suits them and their personal requirements, and the range of offered shades is ever-expanding.

Disadvantages

Most hair dyes (with the exception of pure bleaching products) have the potential to cause allergic reactions, even if only a small fraction of the population is affected (see section on 'Safety and regulatory considerations' for more detail).

All oxidative hair dyes, including demi-permanent, permanent, and bleaching products, contain ingredients such as hydrogen peroxide and ammonia, which may cause irritation. It is imperative that usage instructions are followed carefully, and that all products are kept well out of the reach of children.

It should also be mentioned that permanent hair dyes require a certain amount of upkeep and maintenance from the user. Visible root regrowth, especially if the natural color has been significantly changed, necessitates the regular reapplication of product. This is one of the main reasons why a large group of consumers who color their hair choose to do so themselves, at home, rather than visiting a professional hairdresser every single time they feel the need to recolor.

Lastly, one drawback of hair dyes, again mainly relevant to oxidative products, lies in the fact that hydrogen peroxide at alkaline pH conditions can alter the hair structure, leading to undesirable sensorial attributes described by consumers as poor shine, poor feel, and reduced strength [11]. It should be noted that these problems mostly occur with frequent use and that they can be reduced with the right application techniques. We return to this in more detail in the section "Physiological changes to hair during coloring".

Product application

The most important step in hair dyeing is the right choice of product, including both the type of hair dye and the color shade.

Individuals with no previous experience in dyeing their hair who want to blend away some first grays, or a subtle enhancement of their natural color, are perhaps best advised to choose a semi-permanent colorant. If the person has a higher percentage of gray (up to 30%) and wants to stay close to their natural hair color, a demi-permanent product could be the best solution. Covering larger percentages of gray and/or achieving significant changes in the natural hair color will require the application of a permanent hair dye product.

Once the right type of hair dye has been identified, it is all about finding the right shade. The final color result is a combination of the existing hair color and the shade produced by the colorant – shade guides on the packaging are usually very helpful in exploring which result should be expected based on those two parameters. For home hair dyes a useful guideline is to stay within two shades of one's natural color, and if in doubt chose a lighter over a darker shade. To be sure about the outcome of the coloring process, which will also be affected by the condition of the hair and previous treatments, a strand test can be helpful. For this test a small strand of hair (0.25 inch) is cut from the darkest or grayest part of the head and covered with the product for the advised time. Checking after different time points allows finding the optimum processing time to accomplish the desired end result.

Another check that should always be completed before coloring hair is a skin sensitivity test. The test should be carried out 48 hours prior to product use and involves applying a small amount of the product to the skin (typically recommended is the inside of the elbow). If a rash or redness, burning, or itching occurs the patient may be allergic to certain product ingredients and must not use the tested product.

Lastly, it is very important, especially for first time colorers, to read the (admittedly often lengthy) product usage directions carefully. Oxidative colorants require the mixing of several components before application and each product might be slightly different in terms of how it should be mixed and used. It is therefore imperative for a successful coloring experience to follow the recommended procedure step by step.

Impact of hair dyes on hair structure

Oxidative coloring and bleaching have been shown to cause several changes to the hair structure, especially with frequent use (Figure 30.7). Alkaline peroxide partially removes the outer hydrophobic surface barrier of hair, called the f-layer, made of 18-methyl eicosanoic acid. This layer can be considered a natural protection or conditioning system of hair and its destruction leads to significant changes in how hair feels and behaves [12]. At the protein level, peroxide at alkaline pH conditions attacks certain amino acids which are part of the hair fiber structure, especially cystine, leading to oxidative degradation products. The resulting physicochemical changes of the hair surface are irreversible and can lead to hair that feels coarse, is more difficult to comb, lacks shine, and is weakened [11,13]. Importantly, hair that has been treated and thus changed by oxidative treatments is more prone to physical and environmental stress and subsequent damage [14].

Recent formulation strategies to minimize fiber damage

While the above described hair fiber changes can be mainly attributed to hydrogen peroxide itself, it is also well known that hydrogen peroxide at high pH is likely to form reactive radical species which have been shown to be an additional source of fiber damage. The reaction is catalyzed by the presence of redox metal ions such as copper and iron which are prevalent in tap water. It has been reported that the addition of metal chelating agents to oxidative colorants can reduce the surface damage caused in the presence of copper in tap water [15]. Key is to find a chelant that selectively binds to transition metal ions such as copper in the presence of high concentration of water hardness ions, especially calcium. N,N′-ethylenediamine disuccinic acid (EDDS) has been found to fulfill this requirement [15].

Caring for colored hair

Based on the described changes to the hair surface structure, it is important that consumers take the right steps to care for their hair after coloring. This will help in keeping the color vibrant for as long as possible, and in protecting the already weakened hair from further damage from daily wear and tear.

The first step in treating colored hair correctly is to use the most appropriate application technique when recoloring. Covering visible regrowth only requires the hair dye to be used on the hair sections affected – the hair roots. This

Figure 30.7 Change in surface hydrophobicity before (a) and after (b) bleaching.

will protect the bulk of the hair from unnecessary exposure and overprocessing.

The basis for a suitable hair care routine after dyeing should be the use of a shampoo and conditioner specifically developed for colored hair. They contain ingredients that are tailored to the altered hydrophilic surface conditions of the hair and help to smoothen the cuticle surface, protecting it against mechanical damage. Secondly, sun exposure should be minimized because UV radiation not only contributes to hair damage but also has a direct impact on color fading. Lastly, it should be pointed out that water exposure is the biggest contributor to color fading (also called wash fading). It can therefore be beneficial not to wash freshly colored hair too frequently.

Safety and regulatory considerations

As part of cosmetics, hair dyes are thoroughly safety regulated by global regulatory authorities such as the US Food and Drug Administration (FDA) or EU Cosmetic Directive, and their scientific advisory board, the Scientific Committee on Consumer Safety (SCCS, formerly SCCP, SCCNFP) [16,17]. Hair dyes are one of the most thoroughly studied cosmetics and consumer products and there is an overwhelming amount of safety data on hair dyes [18]. Despite the extensive safety testing and close safety regulation regimen, two safety concerns are typically associated with hair dyes: skin allergy and allegations regarding a slightly increased cancer risk.

Allergy

Like other products such as certain foods or drugs, hair dyes can cause allergic reactions in a few individuals. Allergic reactions to hair dyes are well known but still relatively rare when compared to the daily global use of millions of hair colorants. The majority of allergic reactions to hair dyes are classified as delayed hypersensitivity or type IV reactions. Type IV reactions are normally localized to the area where the product is applied. Only in very rare exceptional cases more severe and spreading symptoms like facial oedema can occur. Type IV reactions are triggered by a different immune-response mechanism than the systemic type I allergies, which are more typically reactions to food or drugs and in severe cases may be life-threatening. Type IV reactions typically are not life-threatening.

Key hair dye ingredients such as para-phenylenediamine (pPD), but also para-toluenediamine (pTD), are known skin sensitizers. pPD is part of the standard patch test series in certain countries; pTD is part of the hairdresser patch test series [19]. Used for many decades as key hair dyes, no superior technology emerged to date, despite intensive research efforts.

Among consumers and clients, allergy incidence against pPD has been more or less stable over the past years [20]. While a few authors have concluded that pPD allergy incidence among patch-tested individuals has slightly increased over the years [21], most authors conclude that pPD allergy incidence is stable or even slightly decreasing [22–24].

Nonetheless, hair dye allergy remains an issue for a small number of consumers and therefore following safety measures can help to minimize the allergy risk [25]:

- Consumers should read and follow the usage instructions of hair colorants carefully. All concerned hair dyes carry clear allergy warning labels, making aware of the potential allergy risk.
- For permanent and most semi-permanent hair colorants, consumers are advised to conduct a product tolerance test (also called skin sensitivity or consumer self test) with the shade of interest 48 hours before each hair coloring, by following the recommendations of each product. However, the absence of a reaction at the test site is no guarantee that a reaction will not occur during hair coloring. In case of a skin reaction at the test site, consumers should not color their hair and seek dermatologic advice. When consumers experience initial signs of an adverse reaction at the scalp during the hair coloring session, the hair dye should be rinsed off immediately.
- Temporary black henna tattoos are an important contributor to pPD allergy in humans [26,27]. Consumers may develop an allergy to hair dyes over time as a result of other products than hair dyes. This emphasizes the importance of conducting a skin sensitivity test.
- Professional hairdressers should follow key occupational safety measures, such as wearing protective gloves during preparation, application, and rinsing of hair colorants [28].
- In the case of consumers who are positively patch-tested against a specific hair dye ingredient, special caution should be applied to using a hair dye lacking the respective allergen. Some hair dyes are known to cross-react (e.g. pPD and pTD).

Overall, it should be emphasized that vast majority of consumers can safely use hair colorants and that following the use instructions plus the above guidance can help to minimize the allergy risk for the small number of individuals who may be allergic to hair dyes.

Cancer

Cancer concerns were raised early in the context of oxidative hair dyes, because of their chemical nature. Numerous epidemiologic studies into hair dye safety have been conducted, the vast majority concluding that there is no association of hair dye use and an increased cancer risk. Occasional, single epidemiologic studies reporting a slightly increased risk for certain cancer types have not been confirmed by multiple epidemiologic studies. Early 2008, leading cancer experts of the International Agency of Cancer Research

(IARC, a subsidiary of the WHO) reviewed all relevant studies and scientific papers published to date and concluded that there is no evidence that personal hair dye use is associated with any increased cancer risk [29]. The US Cosmetic Ingredient Review (CIR) panel came to the same conclusion.

Conclusions

Modern hair dyes are an effective tool in altering the natural color of hair. Different product types offer a wide range of results, from subtly enhancing color to dramatic color changes and complete gray coverage. While the potentially huge beneficial effect on peoples' perceived attractiveness is undisputed, a thorough understanding of the different available technologies and their benefits and drawbacks is essential to advise consumers on the most suitable products to use.

The main future challenge in hair color lies in preventing or even reversing hair graying via stimulating melanocyte activity at the molecular or even genetic level. The recently reported modulation of hair follicle melanocyte behavior with corticotropin-releasing hormone peptides could be a first step into an exciting new world of changing hair color [30].

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Chapter 31: Permanent hair waving

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BASIC CONCEPTS

- Permanent hair waving is a two-step chemical treatment modifying hair protein to achieve and retain a curly shape.
- The chemical treatment involves a thioglycolate reduction reaction that plasticizes hair while being wound on a rod. The following oxidation step with hydrogen peroxide reforms the hair in a new curly shape.
- Curl retention depends on hair thickness, rod diameter, and hair quality.
- Undesirable hair damage can occur with the wrong choice of perm and neutralizer, too much heat, incorrect processing time, or improper perm solution amount.

Introduction

Since ancient cultures curly hair represented femininity and beauty. Women with straight hair purchased expensive wigs or spent hours for hair ondulation with water and heat, which was temporary. A ground breaking invention occurred in 1906 when Carl Nessler offered irreversible hair shaping to clients by means of heat and borax.

Improvements followed during the 20th century by creation of "cold waves," using sulfite or thioglycolate as actives, which still are the most popular waving agents in home and salon perms.

Hair physiology

Hairs are composed of cells packed in tight cell bundles that grow out from up to 3 mm skin depth. About 5 million hairs cover the human body and scalp classified as vellus hairs (5–10 µm in diameter) or terminal hairs (5–120 µm in diameter). The human head contains 100 000–150 000 fibers, which grow 1 cm per month through rapid cell division in the living, lowest part of their hair follicle, known as the hair bulb.

The hair surface contains flattened cells, known as the cuticle, which forms an imbricated structure resembling shingles on a roof. The cuticle provides protection and support for the inner spindle-shaped "cortical cells," which makeup 80% of the hair mass. During hair growth, the interdigitated cells are organized into a three-dimensional network resembling a jigsaw puzzle. This construction contributes to cell cohesion and hair fiber strength (Figure 31.1).

While all hair fibers contain a cuticle, only thicker hair fibers with a diameter greater than 75 µm contain a central line of hollow cells, known as the medulla (Figure 31.2). The medulla functions in animal hair to provide enhanced thermal insulation.

The active growth period of scalp hair is known as the anagen phase and is limited to 3–6 years. Then the hair disconnects from the papilla, a period known as the catagen phase, and enters a 2-month resting phase, known as the telogen phase, and subsequently sheds. Hair shedding and renewal results in an average loss of up to 100–125 scalp hairs per day. With constant hair growth and no cutting, bulk hair may reach up to 1 m in length (for more hair growth details, the reader is referred to more detailed references [1,2]).

Permanent wave hair relevant properties

Hair geometry

Usually, scalp hair is visualized as a circular fiber but cross-sections of individual hairs reveal variation in hair shape. The typical appearance of a person's hair is determined by its special mixture of thick, thin, elliptical, kidney-shaped, and triangular cross-sectional shapes [3]. Unmanageable hair is often because of a high percentage of irregular hair shapes. Irregular hair geometry, small diameter, and large hair diameter all create permanent waving challenges. Hair thickness has a large influence on the shape and hold of permanent wave curls [4]. Naturally curly hair [5] can also be challenging as it is sometimes desirable to use a permanent for straightening purposes.

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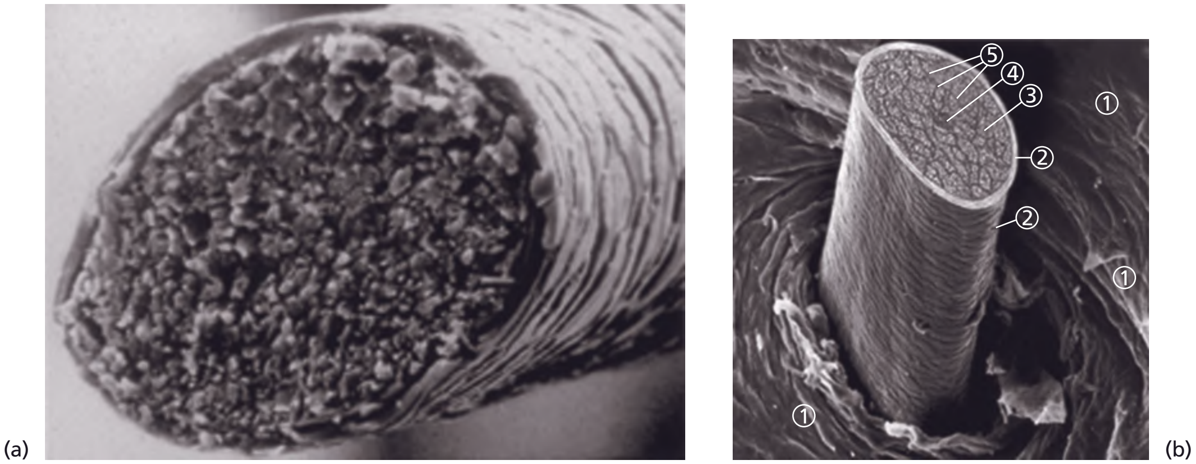

Figure 31.1 (a) The fracture plane of a hair fiber clearly shows the composite of a fibrillar core with flattened cuticle cell coating (SEM ×1420). (b) Just emerging hair: 1, scalp surface; 2, cuticle pattern of hair fiber surface; 3, interior of the hair with cortical cells; 4, medullary cells; 5, cell membrane.

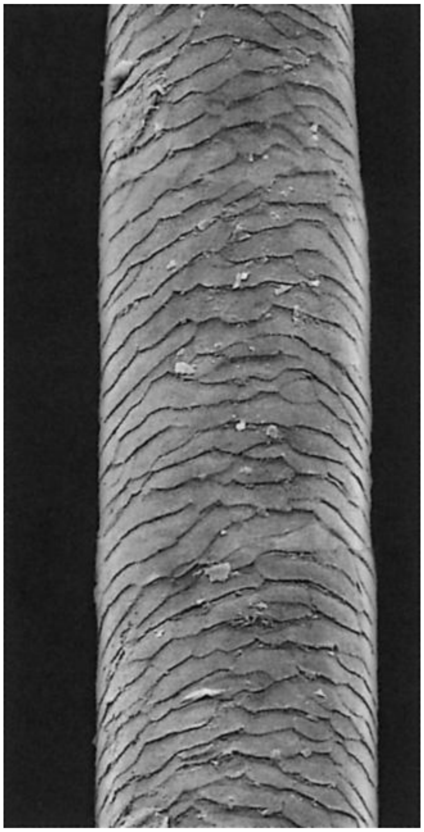

Figure 31.2 The intact cuticle pattern of the hair fiber near the scalp (SEM ×800).

Hair and water interaction

Although hair is not soluble in water, its interaction with water is of particular importance [2,6]. Hair surface is hydrophobic and water repellent. Permanent waving lotions contain surfactants for enhanced wetting, which is the first step in the curling process. Under certain climatic conditions, hair adsorbs atmospheric water up to 30% of its weight.

Although feeling dry at ambient temperature, hair still contains 15% water. Excess water can be bound by capillary forces. The hair water content dictates its chemical reactivity because water widens the hydrogen-bond network of protein side chains and acts as the vehicle for all permanent waving ingredients. Proper water balance is important for a successful permanent waving. Moreover, water functions as the plasticizer for hair; permed hair loses curls more rapidly after washing or exposing it to humid conditions, which can be measured by a curl retention test [7].

In presence of water, hair displays its amphoteric character. A hair “isoionic point” exists where the positive and negative charges of hair proteins are at equilibrium. The natural “intrinsic point of neutrality” of hair is pH 6, slightly more acidic than water at pH 7. This is the point of greatest stability. This intrinsic point of neutrality must be restored after permanent waving to maintain the structural integrity of the hair.

Closely related to hair fiber water hydrophilicity is its thermal behavior. Dry hair can withstand a temperature of 240 °C for a short time but wet hair suffers damage at 140 °C.

Hair aging

Hair fibers undergo aging when exposed to grooming trauma and the environment [2,6,8]. The hair emerges in a virgin state but suffers heat damage during blow-drying, physical trauma from daily brushing with constant stretching, and photodamage. Oxygen radicals further cause chemical oxidation of the hair surface.

The final effect is chemical and mechanical wear of the hair. Hair proteins are cleaved, amino acids are converted, cystine is oxidized to cysteic acid, and histidine is decomposed. As a consequence, stability and elasticity of hair ends decrease, flexibility is reduced, and hair fibers get more rigid and brittle, a process termed "weathering" of hair. Unsightly split ends occur and the hair feels dry (Figure 31.3).

The structural differences between hair roots and hair ends require special attention in hair permanent waving because hair ends react faster and break more easily.

Hair chemical structure

The protein content of a normal hair at ambient conditions is approximately 80 wt% [2,9]. Further components are approximately 5 wt% internal lipids; <1 wt% trace elements and metals; 14 wt% water. Of the 22 amino acid types found in hair, the most important is "L-cystine" (56-89-3), a sulfur-containing amino acid (Figure 31.5), which facilitates covalent cross-linking between two different protein chains. Up to the high amount of 9 mol% (750 µmol/g hair) [10] is typical for cornified tissues, such as hair, nail, hooves, horn, or cornea. Covalently cross-linked by this interproteinacous amino acid, hair demonstrates high mechanical strength and shear resistance, insolubility in water, but is prone to swelling.

Figure 31.3 The worn cuticle-free split end of hair (SEM ×800).

Two types of proteins constitute the hair content: low and high sulfurous proteins. It is their typical arrangement that differentiates hair proteins from proteins in the rest of the body:

- About 50% of the proteins are present in an unorganized, amorphous form, called matrix proteins, with frequent disulfide bridges.
- The rest coil up to form a helical configuration in certain sections, constitute microfibrils, which are embedded in and anchored to the matrix proteins.

Figure 31.4 shows the network of hair proteins, with the "disulfide bonds" marked in yellow, which gives hair properties similar to a fiber-reinforced plastic [11] or the elastic rubber of a tire. This special architecture is the source of hair's elasticity.

Perming agents cleave disulfide bonds in these matrix proteins, causing the plastification or softening that is necessary for shaping hair.

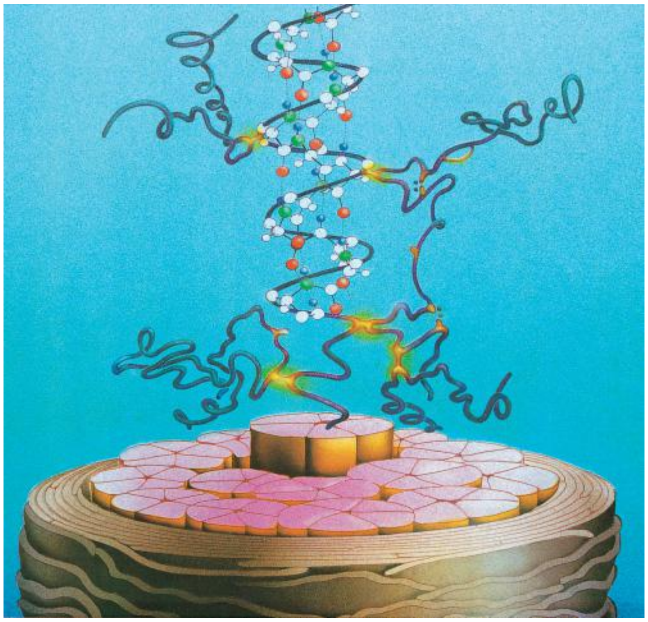

Figure 31.4 Coiled (alfa-helical) and amorphous molecules of hair proteins are cross-linked by disulfide bonds inside the cortical cells. Helical proteins are stabilized by hydrogen bonds.

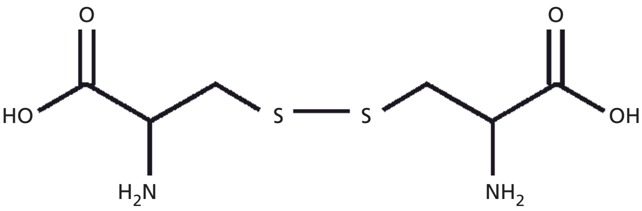

Figure 31.5 Chemical formula of the amino acid "cystine".

However, an excess of a reducing agent is necessary, as cross-linked sulfur proteins in the cuticle make the hair mantle hard to dissolve and penetrate.

Additional support of the chemical network is provided by the acid and basic amino acids in hair protein. As these make up more than 40%, low energy bridges, salt linkages, and hydrogen bonds are formed, which are also cleaved and reformed in the perming process.

Chemophysical principles of hair waving

Because of hair's great elasticity and strong resilient forces, it quickly resumes its original straight shape. Therefore it has to be softened and subsequently rehardened chemically to maintain a conformation change. Especially with permanent waving, it is important to select a reversible reaction to allow repeated treatments without hair destruction. The sulfur bridges of the amino acid cystine, linking the proteins, are best suited [6,12,13].

The conditions for permanent waving to be well tolerated are:

- Low temperature (20–50 °C), convection or contact heat;
- Short process time (5–30 minutes); and
- Mildness to the skin.

A permanent wave occurs with two solutions:

1 *Solution 1:* the perming lotion, which contains a reducing agent, a "thiol" compound, designed to split off about 20–40% of hair cystine bonds.

2 *Solution 2:* a fixing lotion, which contains an oxidizing agent, usually hydrogen peroxide, designed to rebuild cystine bridges between proteins at new sites in the curled hair shape (Figure 31.6).

It must be emphasized that permanent waving is a two-step procedure where the chemical reaction and physical effects run in parallel (Figures 31.7 and 31.8) [14–16]: reduction of disulfide-bonds, softening of hair, lateral swelling and length contraction, stress development and protein flow, then reoxidation of cystin bonds and deswelling, fixation of a new curly shape. Table 31.1 summarizes how hair reacts chemically and physically during each of the permanent waving steps.

Usually only 85% of the cleaved disulfide is reformed during neutralization. Some hair cysteine oxidizes to give cysteic acid (Figure 31.6, formula 2), which renders hair more hydrophilic, incompletely cross-linked, and more vulnerable to subsequent treatments. Therefore, permed hair gradually loses its curl and relaxes to a straight hair conformation again (for additional details, the reader is referred to Robbins [2] and Wickett and Savaides [17]).

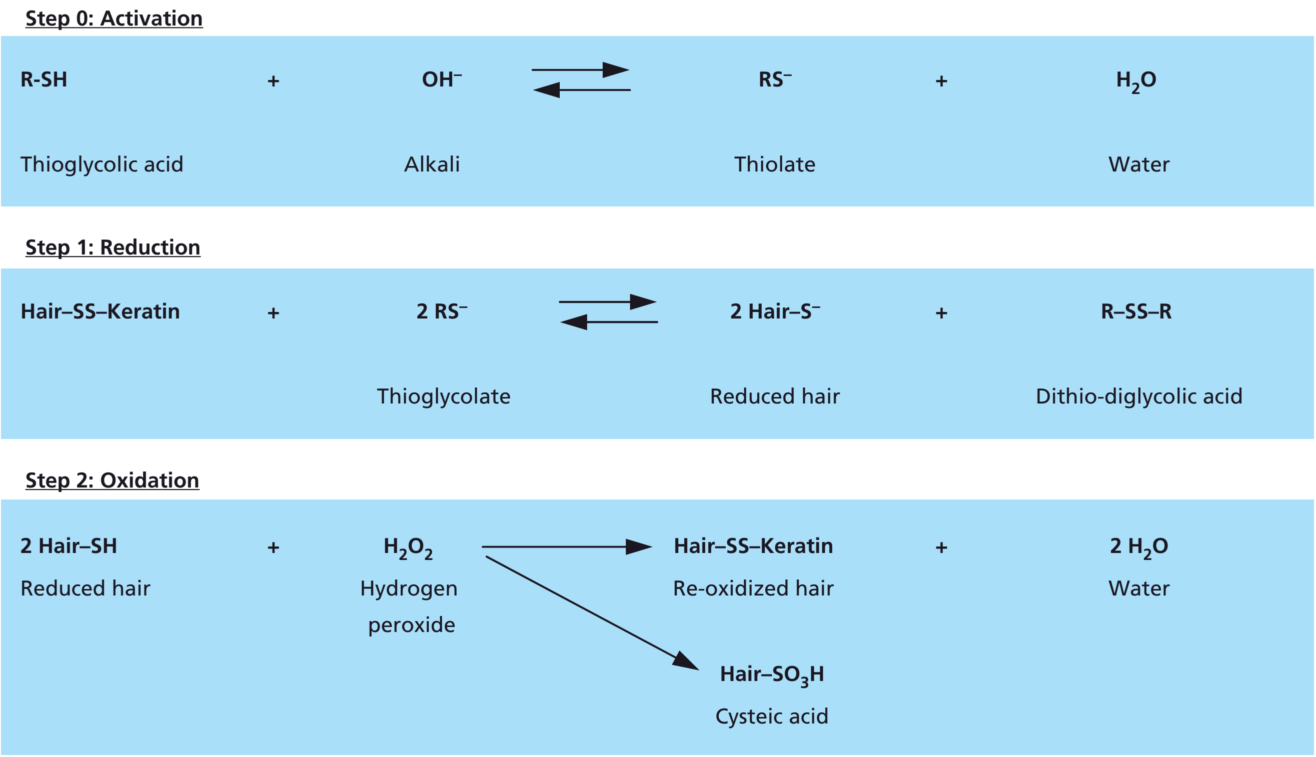

Figure 31.6 Chemical reaction formulas 0–2.

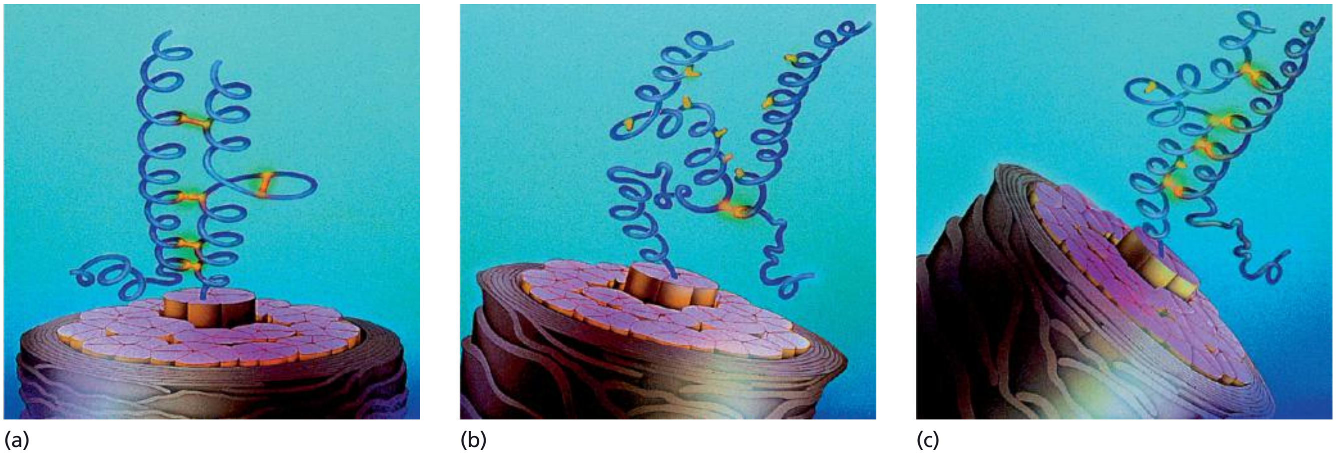

Figure 31.7 (a) Sulfur bridges between the proteins are closed. (b) Part of the sulfur bridges are being cleaved, proteins shift, take on the form. (c) Sulfur bridges are being rebuilt at a different site, neutralizer fixes the new shape.

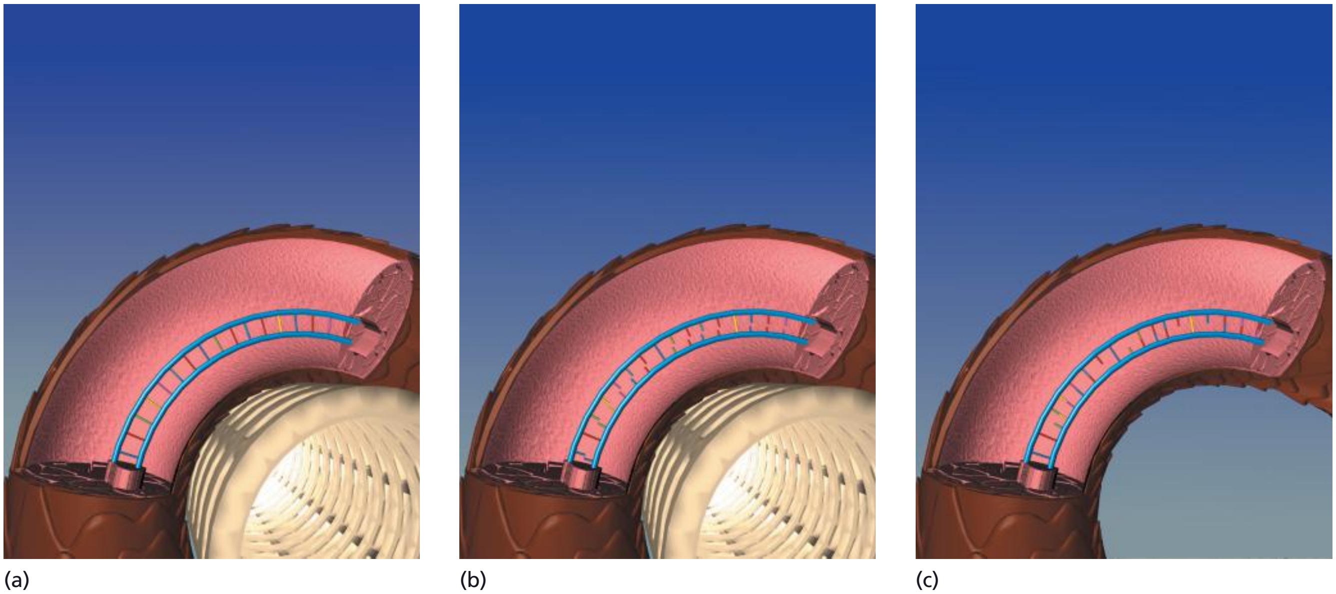

Figure 31.8 (a) Shampooed hair is wound on curlers while still moist. Bending strain is applied to the protein chains. (b) Perm-wave lotion 1 is applied to the hair and cleaves part of the sulfur bridges by the reducing (thioglycolic acid) and the alkalizing agent. Hair is softened, proteins creep and adjust to the shape of the curler. (c) Neutralizing process: an acid neutralizer (peroxide) rebuilds the sulfur bridges at different sites and the new shape is permanent.

Perm products and types

Permanent waving products contain an elaborate mixture of ingredients to make the reactions controllable and appropriate for different hair types, such as normal hair (N-type), sensitive hair (S-type), coarse/difficult hair (F-type), and colored/bleached hair (C- or G-type).

Typical formulations for a one-component perm lotion and a fixing lotion are shown in Table 31.2. Each ingredient is listed by its International Nomenclature of Chemical Ingredients (INCI) name as is on the package; each ingredient has its own distinct role in making the solution active, pleasant to the hair, and odor free (for different formulations see [18,19]).

Role of permanent waving product ingredients

This section reviews the individual ingredients important in achieving a successful permanent waving solution [20].

Reducing agents

Reducing agents, most commonly ammonia or sodium salts of thioglycolic acid (TGA), have been used since the late 1950s to avoid skin and hair irritation while producing a

Table 31.1 The usual steps of perming.

Steps in practical perming	Hair reacts chemically/physically
1. Ask and consult the client concerning the desired hairstyle (curly head or gentle waves)	–
2. Assess the hair quality regarding the hair thickness, hair and scalp health, split ends	–
3. Shampoo the hair with a mild shampoo to remove fat and residual cosmetics	Water swells hair by 15% in diameter, about 2% in length and softens it at the same time
4. Apply a conditioning pre-product, aqueous or oily	Hair surface, root to tip differences in hair structure are equalized, lowers chemical reactivity of hair tips
5. Divide hair into sections with comb to get flat and small hair tresses	–
6. Take/use endpapers, wrap them around the weathered hair tips, wind the hair tightly on curlers, up to 60 on one head of hair	Paper helps to align tip end hair fiber, protects and delays instant reaction. Moistened hair is usually wound on a rigid rod. Bending hair around the curler produces a slight tension on hair
7. Take on gloves, protect clients face by cotton plugs	Protection for hands and face/neck skin against dripping solution
8. Apply the perming lotion (about 75 mL), avoid dripping	Fluid penetrates into the hair, starts chemically reducing it from outside in, softens hair
9. Apply heat by means of a hairdryer, heat processor or use ambient temperature	Heat accelerates: (a) penetration; (b) the reduction step; (c) moveability of hair proteins
10. Develop process time of perming lotion with heat for 5–20 minutes	Reductive cleavage of the hair cystine-network proceeds, hair swells up to 50%, contracts approx. 2% generates internal stress, which relaxes by creeping and flowing of the protein mass The hair substance is transferred from an elastic into a "plastic" state adopting the shape of the curler
11. Monitor curl development unwinding a test curler	Although wet, unwound test lock shows degree of wave/hair deformation (measurable by an electronic test curler), proteins cysteine side chains changed their position relative to each other
12. Rinse thoroughly off the perming lotion with water (up to 3 minutes)	Chemicals are diluted, removed from hair, reaction stops, but physical swelling and shrinking onto the curler peaks by osmotic forces
13. Apply a neutralizing liquid or foam. Process the neutralizer for up to 10 minutes followed by rinsing and unwinding the hair	Reoxidation of cysteine to cystine by hydrogen peroxide restores hair's protein network again, fixing new cystine cross-links at different positions. Residual cysteine oxidizes to cysteic acid Deswelling and hardening occurs Unwinding the hair results in curl relaxation
14. Apply an acid conditioning product as an after treatment	Restores hairs neutrality, also neutralizes residual perm molecules. The deformation process is now complete
15. Dry and style the hair by means of a brush or setting curlers and a hairdryer	Curl relaxation starts in wet hair, brushing, combing diminishes curl retention. Best: air drying

Table 31.2 Ingredients in a typical perm solution 1 and neutralizer solution 2.

Ingredient	Content % w/w	Action
Ammonium thioglycolate 70%	14	Waving agent
Ammonium hydrogen carbonate	5	Buffer
Ammonia 25%	1	Alkalizing agent
1,2 Propylene glycol	2	Carrier
Styrene/PVP copolymer	0.1	Opacifier
Polyquaternium-6 [poly(dimethyl diallyl ammonium chloride)]	0.2	Conditioning agent
Perfume	0.4	Fragrance
Coceth-10 (alkyl polyglycol ether)	0.4	Solubilizing agent
Water	76.9	Basis
pH	8.2–8.5	
Neutralizer		
Hydrogen peroxide 50%	5	Oxidizing/fixing agent
Ammonium hydrogen phosphate	0.3	Stabilizing agent
Phosphoric acid	0.1	Stabilizing agent
EDTA	0.2	Complexing agent
Perfume, conditioning agent, surfactant, water		As in perm solution
pH	2.5–3.5	

lasting hair curl. Other alternatives are glycerol monothioglycolate (GMT), active at neutral pH. Cysteine [21] and cysteamine (2-mercaptoethylamine) are used for perming Asian hair. Thiolactic acid, with less reducing power, can be used as co-reducing agent. Many home permanent waves contain sulfite.

Alkalizing additives

Alkalizing additives, such as ammonia or monoethanol amine, are included in the formulation to achieve the appropriate pH at which the reducing agent as well as the hair disulfide is activated, which is normally at pH 7–9.5 (Figure 31.6, step 0). Glycerol monothioglycolate, the active component of an “acid wave”, works at pH 7; however, TGA requires a pH of 8.5–9. Hair damage is often related to a higher product pH.

Buffer salts

Buffer salts, such as ammonium (hydrogen) carbonate, affect the alkalinity. These ingredients buffer the working pH as hair, a natural ion exchanger, lowers the pH when it comes into contact with the perm solution.

Carriers

Carriers (e.g. urea, ethanol, or 2-propanol) enhance penetration of actives into hair and thus the effectiveness of the perm product.

Surfactants

Surfactants are included to ensure wettability of the originally hydrophobic hair surface. They also facilitate foaming of perm solutions or neutralizers to be applied without dripping. In permanent wave foams, the type and concentration of surfactants are especially critical for skin compatibility [13].

Conditioning polymers

Conditioning polymers are included to allow an easy manageability of the new shape and mask the somewhat harsh handle of hair after perming.

Complexing agents

Complexing agents in thioglycolate-based perm lotions prevent intensive red–violet coloring with iron contamination. In the neutralizer lotion, complexing agents avoid decomposition and boosting of hydrogen peroxide.

Opacifiers

Opacifiers, such as styrene-vinyl-pyrrolidone-copolymers, and coloring agents (e.g. azulene) give a pleasant appearance to the product, but also serve as an identifying feature.

Thickeners

Thickeners (e.g. cellulose derivatives or polyacrylate salts) are used to convert fluid preparations to gels, which prevent dripping off from the hair or enable a more intensive perm treatment of the hair root portion.

Solubilizing agents

Oily fragrances afford a solubilizing agent for better miscibility.

Neutralizers

Neutralizer ingredients are in principle oxidizing agents, mostly hydrogen peroxide at concentrations of roughly 0.5–3% and acid at pH 2–4.5. Advantages are:
- Low solution concentrations;
- Excellent environmental compatibility; and
- Physiologic safety.

Moreover, at acid pH hydrogen peroxide has no bleaching power for the natural hair color, but specifically reoxidizes hair cystein to cystin and truly neutralizes the alkaline hair. However, metal salts catalyze the explosion of hydrogen peroxide, which contains as stabilizer inorganic phosphates, phenacetin, or 4-acetaminophenol.

As alternatives, bromate salts are used. The concentration is roughly 6–12 wt% at pH 6–8.5. Bromate-based neutralizers are preferentially used in Asia, because they do not lighten dark hair. Less widely used are sodium perborate and percarbamid.

Different product types

The majority of commercial waving and neutralizing lotions are aqeuous solutions, but a few are designed as gels, creams, or aerosol permanent waves [17,18].

Preparations chiefly differ in:
- Mixture of reducing agent;
- Concentration of reducing agent;
- pH value;
- Form of application.

Alkaline perms

Alkaline perms are alkalinized by ammonia to a pH 9–9.5. Because of their frequent association with skin inflammation, these products were largely replaced by mildly alkaline preparations at pH 7.5–9.

Acidic and neutral permanent wave

Acidic and neutral permanent wave preparations mostly contain glycerol monothioglycolate (GMTG) as reducing agent. It allows easy control of the processing behavior, leaves hair with a pleasant feel, and the danger of overwaving is slight. Often it is highly retained in hair, imparts an unpleasant smell, and causes sensitization of hairdressers' hands even by touching hair that was processed weeks ago. Therefore, although it is not legally forbidden, esters must not be used according to the technical directives for dangerous substances in hair salons [22].

Thermal waves

Thermal waves produce heat during the perming procedure. Hydrogen peroxide reacts with excess thioglycolic acid to release heat. Such warming is meant to generate a pleasant feeling on the client's head and to render the addition of external heat unnecessary.

Sulfite perms

Perming lotions containing ammonium sulfite are used in home waving. At neutral pH 7 and without thiols, they act best on healthy, undamaged hair. However, stable "Bunte" salts are formed during their chemical reaction with hair. This leads to poor fixation, rough feel, and hair damage on tinted or fine hair.

An overview of product types is summarized in Lee *et al.* [23].

Regulatory aspects

Formulation is limited by some legal regulations [20]. First, the cosmetic chemist selects the ingredients from a pool of chemicals, which are compatible with the cosmetic legislation in the countries where the product is introduced. The *EC Cosmetics Directive*, Annex III, Part 1 [24], restricts the pH of permanent wave preparations with thioglycolic acid, its salts, and esters to pH 7–9.5 for the acid and salts, pH 6–9.5 for esters. The maximum concentration calculated as thioglycolic acid is 8 wt% ready for use for retail and 11 wt% for professional use. A special warning label is required.

In the USA, the Cosmetic Ingredient Review (CIR) expert panel considers 15.4 wt% maximum of thioglycolic acid as safe in permanent wave products. The CIR recommendations are respected by the manufacturers.

In Japan, permanent wave products are classified as quasi-drugs. Thioglycolic acid and its salts are permitted, as is cysteine, but restrictions on concentration and pH are given. Thioglycolic esters are not allowed.

Hydrogen peroxide concentrations are limited to 12% in the EU [24].

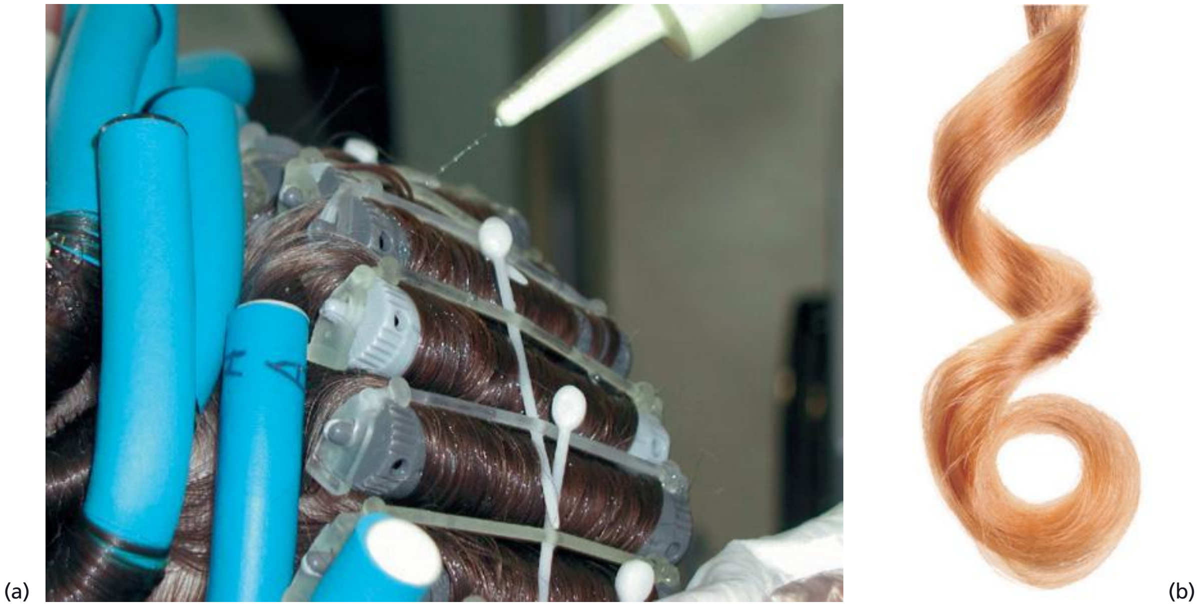

Figure 31.9 Hair, properly wound, fixed on rollers, and wetted by the perming lotion (a) delivers perfect locks (b).

Perming practise – how to achieve a perfect curl

The question of perming safety is not only a function of product composition, but also depends on the use conditions [6,25]. Therefore, each package of perms on the market contains a list of instructions for the hairdresser or consumer. Table 31.2 summarizes the recommended steps and how hair answers (i.e. reacts), chemically and physically.

Any deviations from this course of action will be specified in the instructions for use. The correct execution of each step should produce the desired result, a curl lasting up to 3 months, a well-preserved hair structure, and an easy styling of the hair assembly (Figure 31.9).

In salons, where hairdressers use long-lasting perms, an appropriate permanent wave must be selected to achieve the best result. The hair thickness and quality must be assessed to determine if the hair is healthy or damaged. If the hair feels rough, is of a lighter color, or possesses split ends, it may have a porous structure produced by previous weathering, bleaching, coloring, or perming. This increased porosity allows the perming lotion to react faster. Damaged hair requires bigger curlers, a reduced perm strength, and shortened processing time.

Heat from a drying hood (45 °C) accelerates the chemical reaction, but should not be used in persons with sensitive scalp skin.

To ensure that the proper amount of curling has been achieved, a test curl should be performed. A test curl is loosely unwound from a curler after several minutes to determine the degree of curl achieved and whether to extend the processing time.

After thoroughly rinsing off the perming lotion, complete hair neutralization is strongly advised as the second fundamental step in perming. Three to ten minutes are recommended to obtain a lasting perm, to reoxidize the hair, and to neutralize the alkalinity of the reducing step. Physically, hair only gains its strength and integrity with thorough neutralization.

Application of an acidic conditioning lotion as an after-treatment, removes residual peroxide, restores the hair internal pH to neutrality, helps to stabilize the hold of the curl, and makes it less prone to future damage.

Safety and adverse reactions to perm products

Safety requirements from consumer expectations are adequately summarized by the corresponding text within the EU Cosmetics Directive: “A cosmetic product put on the market within the Community must not cause damage to human health when applied under normal or reasonably foreseeable conditions of use” [24].

Therefore, as permanent wave preparations contain reactive chemicals, these have to pass a complete toxicologic characterization. Essentially, the potential for:

- Acute systemic toxicity;
- Local compatibility and irritation;
- Sensitizing potential, allergenicity;
- Mutagenicity;
- Tumorigenicity;
- Teratogenicity; and
- Percutaneous absorption.

From past experience with the safety of waving products, and regularly updated statistics published by intoxication advisory centeres, manufacturers obey the rules. Statistics of adverse reactions from cosmetic products sold between 1976 and 2004 revealed only 1.1 undesired effects per 1 million packages sold [26]. This confirms cosmetic products are very safe (for more detailed information about toxicologic test methods and safety assessment processes see references [20,27,28]).

Even though a perm product has been approved as safe by legal authorities, occasional hair or skin damage can occur from incorrect usage:

- Consumers apply a home wave without reading/understanding instructions; or
- New hairdressers in salons are untrained and less skilful.

The first signs of a failure in perming are lack or excess of curliness. This is not only because of the wrong choice of product, excessive development time, and temperature, but may also result from incomplete rinsing of the active substances and shampoo components. Surfactant residues, residual reducing, and oxidizing agents in the hair encourage irreversible side reactions, such as incomplete reoxidation and cysteic acid formation.

Moreover, the stylist or the client may try to "repair" the unexpected result by repetition of the permanent waving process. Multiple treatments, as well as the combination of perming and bleaching or coloring in the same session, lead to heavily damaged hair. Electron microscopy reveals residual softening, even complete peeling of hair surfaces (Figures 31.10 and 31.11).

Instrumental methods can further detect the degree of damage. These include hair tensile testing, elasticity, curl hold, swelling behavior, and static charging [2,20]. Chemical damage of hair may also be assessed by analyzing dissolved hair proteins [29,30] and hair lipids [30]. Residual cysteine and cysteic acid are signs of weak hair structure [30]. Table 31.3 lists examples for hair and skin symptoms indicating mistakes during a perm treatment [25,31–34]).

Although ammonium thioglycolate has been reported to have a low sensitization potential, occasionally sensitization, skin irritation, contact dermatitis [33,34], or seborrhea occur [32]. Itching, burning, and redness are normally confined to the neck and scalp margins after prolonged contact with perm solution [31]; however, high levels of alkalinity and heat [33,34] may also precipitate irritation. Scalp skin damage seldom occurs. Scalp skin, which contains keratin proteins like hair, is less reactive to reduction by thioglycolate. This contributes to a lower swelling response of the skin than hair (22% vs. 38%) and the lower cystine content and hydrophobic nature of skin vs. more cystine and hydrophilicity in hair [35]. The skin is more susceptible to surfactants, however, causing hairdresser's hands to be affected by an allergy to perms. When the hands are softened by routinely shampooing of clients' hair, monothioglycolate esters found in acid waves may be problematic [31].

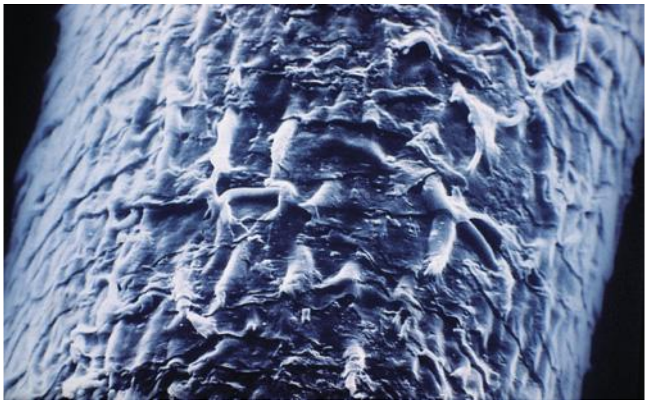

Figure 31.10 The curtain-like structure of a hair surface indicates heavy perming damage.

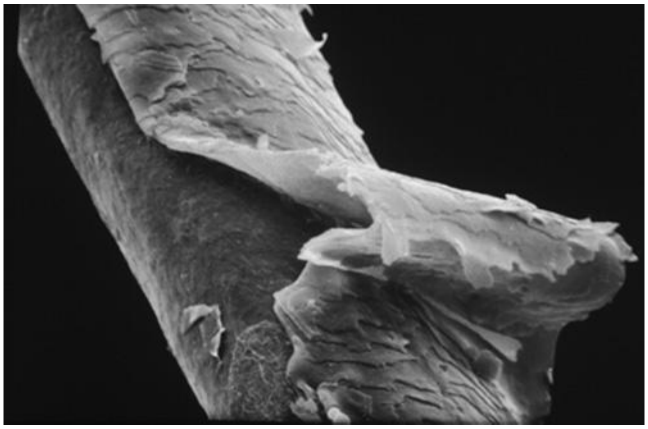

Figure 31.11 A bleach applied immediately after a perming treatment chips off the cuticle as a whole (SEM ×700).

Table 31.3 Symptoms of hair/skin damage by perm products.

Symptom	How it happened
Hair loss (rarely)	Telogen hair effluvium Temporary contact allergic reaction
Hair breakage	False hair quality diagnosis
Near root	Perm choice too strong for fine or predamaged/ bleached hair Stress on root hair by tight winding or rubber band Winding against hair growth direction
In hair length	Hair growth with thinning diameters Winding on curlers with " fish hooks" Incomplete neutralization
Near tip ends	Forgot pretreatment with equalizer Processing without wrap end paper protection Excess perm solution stored by hair tips
Hair modification (consumer complaints)	
Unwanted kinky curls	Perming power of product too high Curler thickness too thin Processing time with heat too long
Limp hair/curls without springiness	Loose winding, impaired protein creep False time and fluid saving as well as excess time, heat, fluid
Wet hair feels plastified, spongy, extensible	Overprocessed by extended application Loss of keratin elasticity Increased hydrophilicity Neutralization too short
Dry hair feels rough, brittle, uncombable, "matting", is dull, ready to break	Intermediate rinsing too short Increased hair surface friction by shrunken cuticle cells Loss of hair lipids and proteins
Highlighted natural color or tint	Dissolution of natural pigment/tint Excess perm conditions
Skin damage	
Redness	Too much heat (heat rollers, hood defect)
Pustules	Skin swelling during extensive prewash
Irritant skin	Soaked cotton pads for face protection not removed

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Chapter 32: Hair straightening

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BASIC CONCEPTS

- Hair is straightened to improve manageability and provide style versatility.
- To straighten hair, an alteration of the cortex must occur.
- To achieve temporary straightening – a lower energy process – hydrogen bonds and salt linkages are altered while permanent straightening is achieved through the modification of covalent bonds, which requires more energy.
- Permanent hair straightening can be accomplished with ammonium thioglycolate, sulfites, and hydroxide.

Introduction

The desire for straight hair was once attributed to a "universal" vision of beauty and social status associated with straight hair; however, recent information links this style preference to improved manageability and style versatility. In order to achieve the straight look, it is necessary to transform the natural hair configuration, which has been linked to the shape of the follicle. Bernard *et al.* [1,2] found that the asymmetric protein expression in curved follicles was associated with the formation of curly hair. At this time, it is not possible to straighten hair by changing the shape of the follicle. However, it is possible to straighten hair based on its chemical composition. For mature hair, the composition is generally the same and consists of roughly 90% protein with smaller quantities of water, lipids, and minerals but does not vary by degree of curl, despite differences that exist in the early stages of hair production. To understand how hair can be transformed, it is important to know the different components of hair. Hair is made-up of three macro structures including the cuticle, cortex, and medulla, the latter being of little significance. The major morphologic part of the hair is the cortex, which is made up of highly organized α-helical proteins packed in a cystine-rich matrix. To straighten hair, an alteration of the cortex must occur.

There are three types of bonds in hair: hydrogen, electrostatic salt linkages, and covalent, each consecutively requiring more energy to break. Based on the bonds that can be affected, there are two categories of straightening: temporary and permanent. To achieve temporary straightening, a lower energy process is required involving alteration of hydrogen bonds and salt linkages while permanent straightening is achieved through the modification of covalent bonds, which requires more energy. Thermal appliances can be used to disrupt and rearrange the weaker hydrogen bonds and salt linkages required for temporary straightening. Depending on the approach, the results can last from a few days to several months. However, permanent straightening is obtained through a chemical process that alters the protein structure by cleaving and reforming covalent bonds, preventing the hair from returning to its natural curly state until it grows out from the scalp.

The following are usually considered when choosing the type of hair straightening process or treatment: degree of curl, degree of desired straightness, point of service, convenience, environmental conditions, and the desired frequency of straightening. All of these are important; however, the degree of curl in hair may be the most influential because it impacts other desired attributes. It is often subjectively described and ranges from various degrees of wavy to tightly curled. These descriptors are relative and can be confusing because they often overlap. Thus, the L'Oréal Curl Classification was recently developed to quantitatively describe the degree of curl in hair (Figure 32.1) [3]. This classification used hair from around the world and identified eight distinct curl types, where the degree of curl increases directly with number. People with curl types I–IV often have concerns about hair frizz and volume while higher curl types are more concerned about manageability. Thermal techniques can be used to achieve straight hair for all curl types but, typically, curl types V and above are difficult to straighten permanently without the use of hydroxide-based systems.

Hair straightening appliances and chemicals are centuries old; however, instrument designs and formulations have evolved to improve effectiveness while limiting the negative attributes. New materials are used for the heated surface of flat irons and product formulas have been modified and

Cosmetic Dermatology: Products and Procedures. Edited by Z.D. Draelos.

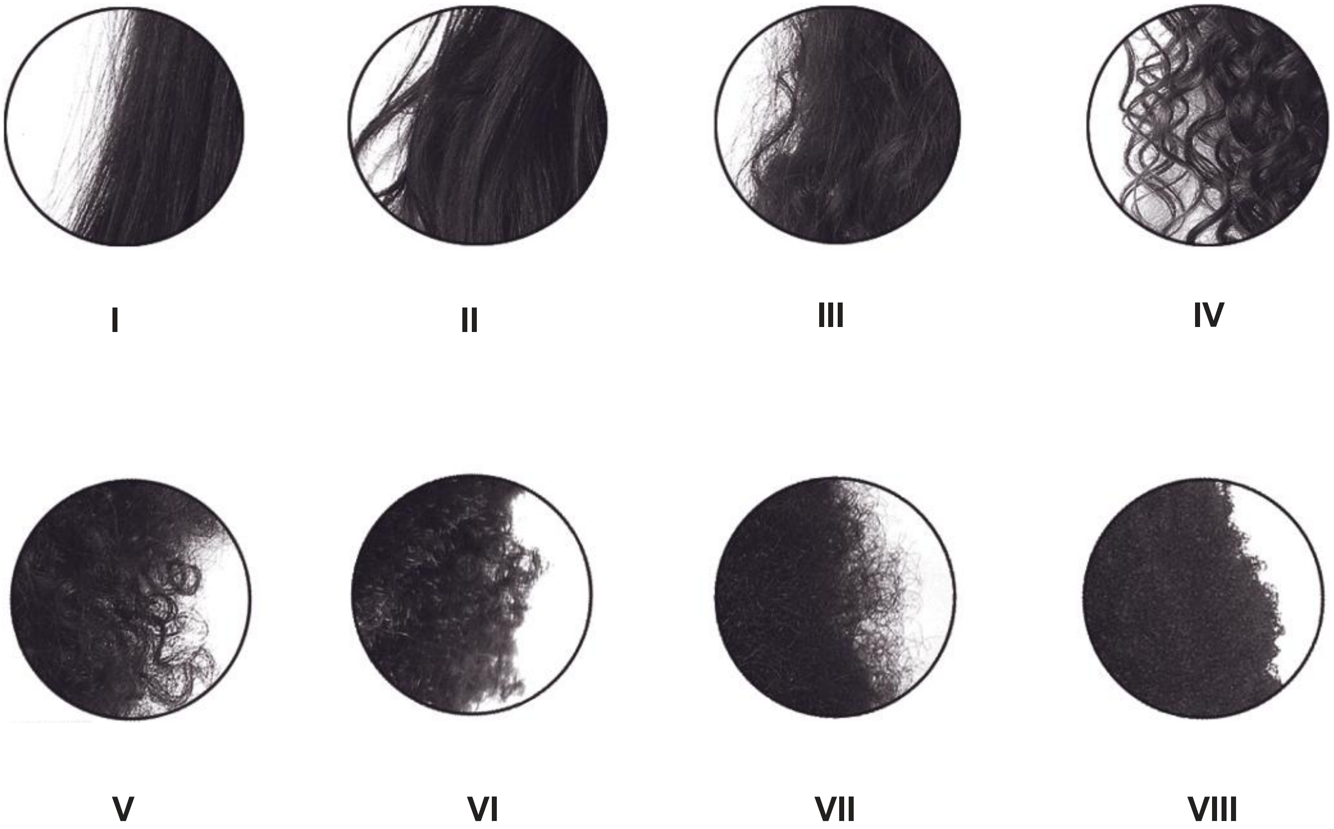


Figure 32.1 Hair classification types to differentiate the degree of curl in hair.

developed to protect hair and scalp and aid in the ease of application. In some markets, the combination of heat and chemicals is often used. This chapter briefly reviews the most common straightening practices, including a description of the procedures and perceived advantages and disadvantages.

Thermal processing

The use of thermal appliances dates back to the Egyptian period and is still considered to be a necessity to most women in today's world. In the Egyptian period, hot metal was used to straighten hair. A less aggressive method was popularized in the late 1800s with the invention of the blow-dryer; the handheld version for home use became available in the 1920s. This increased the ability for women with curl types I–IV to have a variety of temporary and permanent styles (hot waving).

Because curl types V–VIII were inherently more resistant to reconfiguration, there was a specific need to straighten these hair types. This was achieved with the popularization of the hot comb combined with pressing oil, attributed to Madame C.J. Walker in the early 1900s. The hot comb, still in use today, is a metal comb heated to temperatures reaching 450 °F. Whether utilizing a hot comb, professional tongs heated in a Marcel oven, or one of the electronic devices such as a blow-dryer, curling iron, or flat iron, the process involves using heat and mechanical stress. These common thermal appliances represent an alternative way for people with naturally curly hair to achieve manageability and straight hair styles.

The combination of heat and mechanical stress, in the form of combing or brushing while blow-drying and smoothing with the other devices, straightens hair by rearranging hydrogen bonds. Once straightened, the new configuration of the hair is only temporary and will revert back to its natural state after exposure to moisture from any source such as environmental conditions and perspiration. Temperatures of thermal appliances typically range from 150–232 °C (302–450 °F). While thermal processing is considered temporary in terms of styling, it can have a permanent effect on hair. For example, the proteins in hair can start to denature at high temperatures. Protein denaturation is a process by which proteins are irreversibly altered by an external stimulus, and for hair can result in decreased fiber integrity. The denaturation temperature is 235–250 °C (455–482 °F) and 155–160 °C (311–320 °F) for dry and wet hair, respectively [4–6]. The upper temperature limits for some of the appliances exceeds the denaturation temperature for wet and dry hair so care must be taken to avoid repeated applications and overheating.

Of all heat appliances currently available to straighten hair, the flat iron is rapidly becoming the most popular; therefore, it is the focus of technologic advancements. Important attributes of a good flat iron are the ability to provide even heat and maintain a consistent temperature. Recent improvements in temperature control promote thermal stability and coatings, including ceramic and titanium, provide durability and reduced friction. Reduced friction is critical to maintaining a smooth cuticle surface and reducing breakage during thermal processing. Other advances in materials include the incorporation of pure ceramic heating elements and minerals (tourmaline) that allow manufacturers to make claims about the positive effects of ions and far infrared radiation on the final state of the hair.

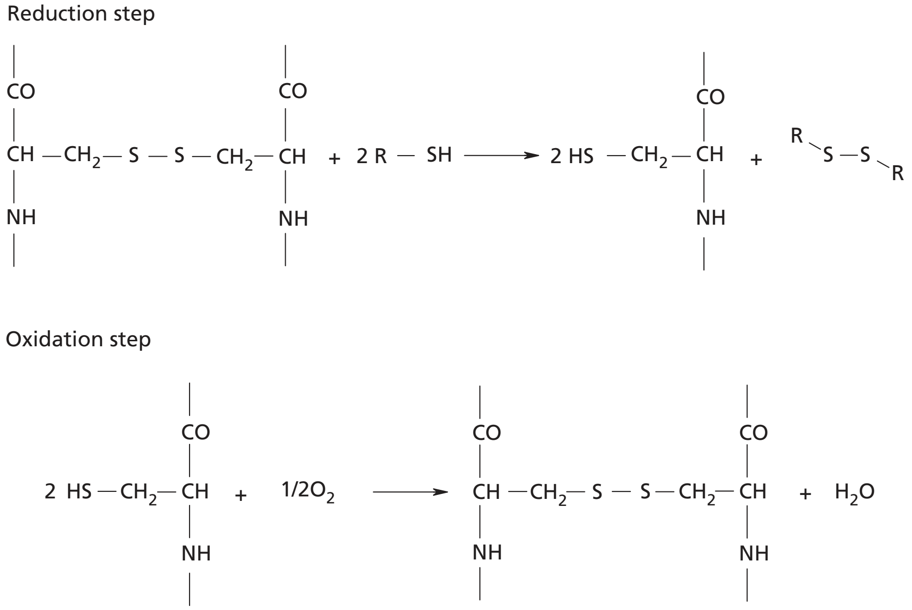
The product offerings associated with the use of thermal appliances typically contain hydrocarbon-based ingredients (e.g. petrolatum and mineral oil) and polymers (e.g. silicone-derived, cationic, and non-ionic) to condition, protect, and accommodate styling preferences. Because blow-drying typically starts in the wet state when hair is vulnerable to damage, conditioning polymers (e.g. polyquaternium 10) that improve wet combing by reducing frictional forces are typically used. Prior to heat application, products that contain ingredients such as sugars and silicones can be applied. Sugars help to increase thermal integrity while silicones protect the hair by acting as a thermal barrier. Silicones also can function as lightweight films whereas hydrocarbons are often used when a heavier coating is desired for style preferences.

Reducing agents

Reducing treatments are traditionally known to curl hair (hot and cold permanent waving); however, they can also be used to straighten hair. The chemistry involves a two-step process where the disulfide bonds in hair keratin are cleaved in the first (reducing) step followed by oxidization in the second step to form new disulfide bonds (Scheme 32.1). The difference between straightening and waving using reducing agents is the configuration of hair prior to oxidation and the form of the product during the reducing step. The reducing product for waving the hair is usually a liquid and the hair is curled using rollers before oxidizing. For straightening, the product is usually in the form of a thick cream so that the viscosity of the product can assist in holding hair fibers in a straightened configuration during manipulation. The most commonly used reducing agents in this process are ammonium thioglycolate (thiols) and sulfite.

Ammonium thioglycolate

Thioglycolate straighteners come in several product strengths. Treatment procedures and strength should be based on the hair attributes according to product recommendations. For curl types V–VIII, these products usually leave the hair with residual curl so the result can be disappointing if a straight style is desired. In addition, the hair can feel dry as a result of the treatment; thus, products that contain glycerin are used to provide moisture. Thioglycolate straighteners can be used on hair that has been previously colored or permed; however, it is not recommended for bleached or relaxed hair.



Scheme 32.1

In addition to traditional thiol straighteners, a new technique is becoming popular that includes the incorporation of heat with thiol-based cream products. These treatments are used to permanently straighten and/or reduce volume in curl types I–V. They are commonly used on Asian and Brazilian hair and go by several names that are listed in Table 32.1. Even though there are several names, they all use similar processes to achieve hair characteristics that consumers describe as straight, soft, and shiny. The main point of differentiation between this new treatment and the traditional straightening method is the application of heat prior to the oxidation step for the Asian and Brazilian treatments. Details about the specific procedure can be found in the appendix. This straightening technique is not recommended for natural hair that is higher than curl type V, particularly hair from people of African descent because it is inherently more fragile than other hair [7].

After a period of time, the processes described above will need to be repeated to the new hair growth because of its natural configuration. The treatment should only be performed on the new growth, referred to as a "touch-up," to minimize overlapping of treatments which may result in overprocessed hair. It is recommended that the time between treatments is maximized, with a minimum of 6 weeks, depending on the rate of hair growth.

Table 32.1 Common names for thiol-based straighteners that use heat.

Culture that introduced the technique	Popular thiol-based treatments
Japanese/Filipino	Hair rebonding Thermal reconditioning and restructuring Ion retexturizing Bio ionic system Japanese hair restructuring Straightening and reconditioning Japanese straightening perm
Brazilian	Chocolate, strawberry, kelp, milk, sugar, passion, mint, gold, orchid, French, gumbo, etc. treatment (or brushing) Brazilian keratin treatments (may contain up to 2% formaldehyde)

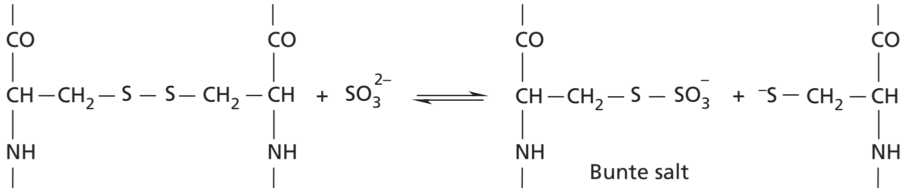
Note: To be comprehensive, it is cautiously noted that products containing or that are altered with formaldehyde (formol) at higher than approved levels (0.2% as an antimicrobial) are sometimes used to straighten hair. However, formaldehyde is classified as a probable human carcinogen by the Environmental Protection Agency and should not be used to straighten hair.

Sulfite

Sulfites are an additional class of reducing agents that can be used for hot waving or straightening depending on the procedure. Even though sulfite straighteners have been around for decades, they are less common than hydroxide relaxers because they tend to result in less effective straightening of highly curled hair (types VI–VIII). However, they are believed to be less irritating to the scalp. The decrease in straightening efficacy may be related back to the reactivity of the disulfide bonds, which depends on the pH of the active solution. The maximum reactivity is reached at pH 4–6, but sulfites are not stable at such low pH conditions [8,9]. Because of this, commercial products generally range in pH from 6.5 to 7.5. At pH 7, only about 15% of the cystine residues can be reduced [10]. The first step of the reaction mechanism involves a reduction of the cystine via a nucleophilic reaction similar to thioglycolate, with the exception of the formation of Bunte salt (Scheme 32.2). To lock the hair into the desired conformation, a neutralizing solution is used which typically contains sodium carbonate or bicarbonate. The application procedure is similar to that of a thioglycolate straightener except no oxidant is used, resulting in poor or modest straightening.

Hydroxide straighteners

According to legend, Garrett A. Morgan was the first person to stumble upon a chemical to permanently straighten hair in the early 1900s [11]. While experimenting with substances to reduce the heat of friction during sewing, he wiped his hands on a cloth that was made of curly pony fur. Later, he found that the fur had been straightened. Following trials on different types of hair, including his own, he started selling the G.A. Morgan Hair Refining Cream. To this day, the identity of this substance is a mystery, but the first known composition for chemically straightening hair was formulated in household kitchens in the 1930s. This contained a chemical mixture of potato starch, lard, egg, and sodium or potassium hydroxide. Because of its corrosive



$$\mathrm{CH{-}CH_2{-}S{-}S{-}CH_2{-}CH} + SO_3^{2-} \rightleftharpoons \mathrm{CH{-}CH_2{-}S{-}SO_3^{-}} + {}^{-}\mathrm{S{-}CH_2{-}CH}$$

Scheme 32.2

nature, it was advised to protect or base the scalp with petrolatum before treatment. The use of this concoction led to the development of relaxers.

The first commercially available relaxer, based on sodium hydroxide (lye), was introduced in the 1950s by Johnson Products. Even though the relaxer formula included petrolatum, basing the scalp was still a requirement to minimize scalp irritation. The relaxer technology continued to improve in the early to mid 1960s with the invention of the no-base relaxer. This version incorporated higher percentages of petrolatum and mineral oil in the formula and decreased the amount of sodium hydroxide to make it less irritating, thus it claimed to eliminate the need to base the scalp.

In the late 1970s, the first no-lye relaxer was marketed that significantly reduced the amount of irritation during treatment [12]. The technology uses a two-part system where a calcium hydroxide cream is mixed with a guanidine carbonate liquid activator to produce guanidine hydroxide.

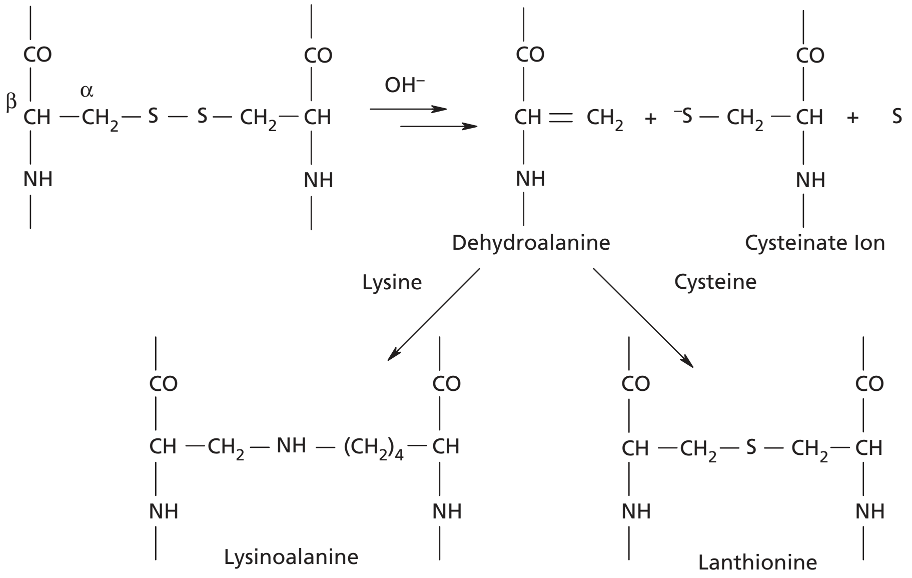
Several other relaxer versions were introduced over time that improved the product attributes, the cosmetic properties, and integrity of the hair. This was achieved through the addition of conditioning agents such as cationic polymers and by incorporating various alkali metal hydroxides in both product forms, mix or no-mix [13,14]. The most commonly used hydroxides are sodium, guanidine, lithium, and potassium (see Table 32.2 for definitions of key terms).

Chemistry of relaxing

Amino acid analysis of relaxed hair hydrolysates indicates lanthionine is the primary product of the reaction. The formation of lanthionine can occur via two pathways. The first is through a binuclear nucleophilic substitution reaction [10]. The second is beta-elimination that is initiated by abstraction of the hydrogen beta to the disulfide (Scheme 32.3) [15]. This results in the formation of dehydroalanine, cysteinate ion, and sulfur. Dehydroalanine is a highly reactive intermediate that continues to react with cysteine and lysine moieties in hair to form lanthionine and lysinoalanine, respectively. It can also react with ammonia to form beta-aminoalanine. The new thioether bonds (lanthionine) are stable in the presence of reducing agents, such as thioglyco-

Table 32.2 Vocabulary list of select terms related to straightening curly hair.

Relaxer	Hydroxide technology used to permanently straighten curly hair. It is sometimes mistakenly referred to as a "perm"
Lye relaxer	Technology that commonly utilizes sodium hydroxide as the active ingredient
No-lye relaxer	Non-sodium hydroxide-based system that includes but is not limited to guanidine and lithium hydroxides. Some of these products require mixing prior to use; those that do not are sometimes referred to as no-lye no-mix
No-base relaxer	A relaxer that may not require basing the scalp with a petrolatum product prior to relaxer application
Texturizer	A lower concentration version of relaxer used to permanently reduce or loosen curl in hair
Perm	Thiol-based products used to permanently curl hair according to a sequential reduction–oxidation process



Scheme 32.3

late or sulfite, compared to cystine. This is evidenced by the decrease in solubility of hair protein and the inability to permanently curl relaxed hair.

While lanthionization is popularly believed to be the cause of permanent straightening of curly hair, Wong *et al.* [16] believe that it is not the critical step in hair straightening. They propose that the permanent straightening depends on supercontraction of the fiber. They report that fiber supercontraction is what "locks" the fiber into the straight configuration and the formation of lanthionine is a by-product rather than a requirement.

Application

The relaxer process involves a chemical reaction in addition to mechanical manipulation, which involves the action of smoothing the hair into the desired configuration during application. This can be accomplished with the back of a comb, an application brush, or the fingers. However, the most recommended tool is a comb. Applicator brushes can increase the chance of scalp irritation and the use of fingers is not suggested because of the caustic nature of the relaxer ingredients. The initial relaxer is applied to the full length of the fiber. Subsequent treatments are only applied to new growth, which typically occurs within 6–8 weeks. The exact period of time should be determined based on the amount of new hair growth, which varies with the individual. For example, hair growth rates can range from approximately 4 mm/month to 18 mm/month [17].

Several key factors are used to determine the relaxer type, such as hair diameter, degree of curl, porosity, and type of prior chemical treatments. To help maintain the integrity of hair, it is important to follow the directions on the package carefully. Overprocessing and improper neutralization are problems that are commonly associated with relaxer misuse. Similar to thermal processing, repeat application on the same section of hair and treating the hair longer than the recommended time can result in overprocessing and may result in hair breakage. Determination of proper application time can be achieved by performing the recommended strand test. To insure proper removal of the relaxer, hair should be rinsed thoroughly followed by the application of a neutralizing shampoo, sometimes referred to as chelating or decalcifying. These shampoos are acidic with a pH typically ranging from 4.5 to 5.5. The neutralizing step is an important part of the relaxer process because it helps return the hair to a neutral pH. This is necessary because, at high pH, hair swells up to 70–80% during relaxing making the hair susceptible to damage [18].

Effect of relaxers on hair

In 2006, Yang and Barbosa [19] performed a national study to obtain consumer perceptions of relaxers. From this study, consumer responses on the effects from relaxer use were grouped into three categories including scalp irritation, hair quality, and relaxer efficiency. Users of lye technology reported a higher incidence of scalp irritation while no-lye users experienced more hair quality issues. The same study showed that consumers were more likely to take action for hair quality issues and more often seek advice from a stylist as opposed to consulting a dermatologist or physician. In a separate study, it was noted that those who frequently obtain services at a salon, more than 50% of them were unaware of the specific relaxer type being used [20].

All hydroxide-based relaxers follow the same chemistry and are designed to straighten hair but to varying degrees. Due to the high pH, relaxers cause swelling of the fiber, cuticle abrasion, loss of the hydrophobic lipid layer, an increase in porosity, a loss in tensile strength, and an increase in plasticity.[1] All of these affects weaken the hair compared with its natural state. The swelling and deswelling of the hair during the process may in part, be responsible for loss in fiber strength as it can result in cracks proposed to be related to the change in osmotic pressure also associated with permanent waving [18]. In addition to cracks, cuticle swelling may cause cuticle erosion. Figure 32.2 shows the progression of the cuticle surface during the relaxer process. After the relaxer has been rinsed from the hair before neutralizing, the image shows the presence of cuticle scales that have been abstracted from the hair fiber but still remain on the hair. After neutralizing, the loose cuticle scales are removed. The images representing neutralized and conditioned fiber surfaces show that while relaxers erode cuticle layers from the hair, some amount of the protective layer is still present.

In addition to the cuticle, the cortex, which is mainly responsible for the hair's strength, is also affected during relaxing. The original protein linkages in hair are altered, and when this occurs the hair becomes more fragile. The decrease in break stress and increase in break extension indicates that the hair becomes weaker and is more prone to deformation after relaxing. Even though hair quality is compromised, the straightened configuration of hair increases combability as shown in Figure 32.3. This in turn helps to decrease breakage that is known to be associated with combing curly hair and mitigates further decreases in mechanical properties [21].

It is important to follow relaxer services with post-relaxer treatments such as conditioners to further enhance manageability and improve the quality of hair. A good conditioner should exhibit the following qualities: improved wet and dry combing, flyaway reduction, and surface protection of the hair. These qualities can be achieved by adding conditioning agents that will reduce the frictional force during combing. Key ingredients commonly used are conditioning agents

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[1] Plasticity: a material property whereby it undergoes irreversible deformation when a high enough force is applied.

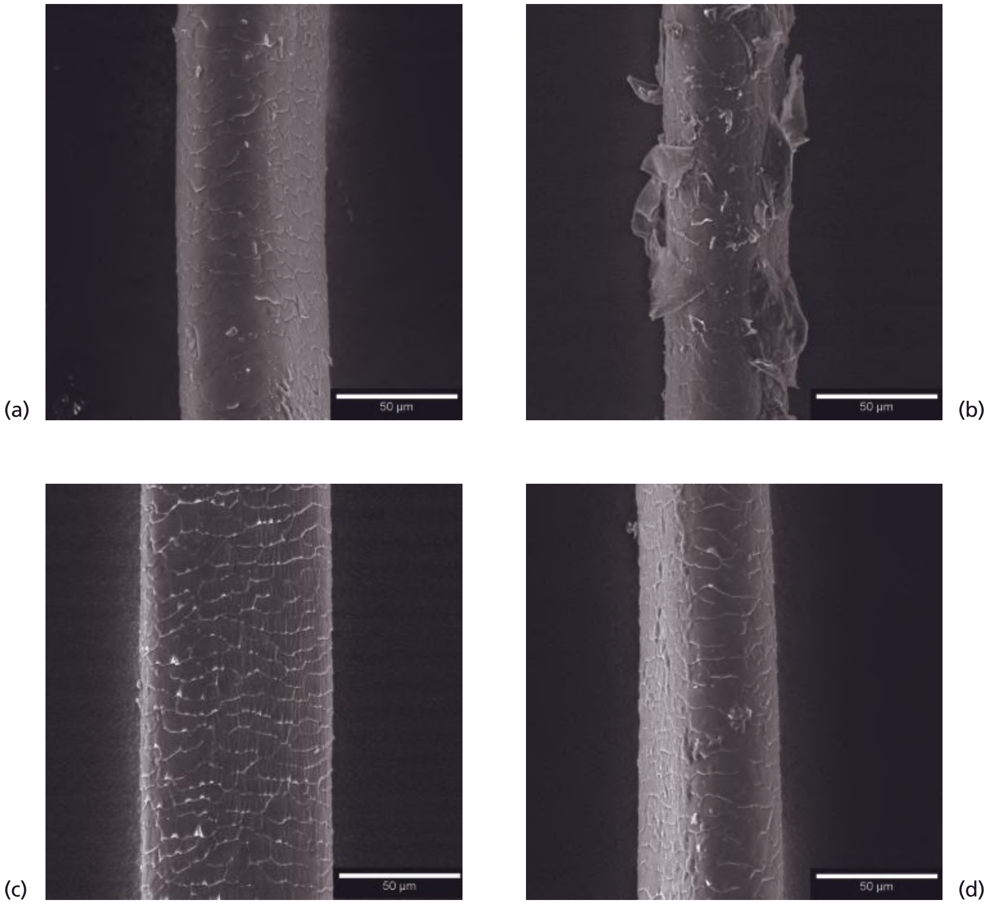

Figure 32.2 Scanning electron micrograph images of hair fibers under different treatment conditions, (a) virgin; (b) after relaxer rinse only; (c) after neutralization; (d) after conditioning.

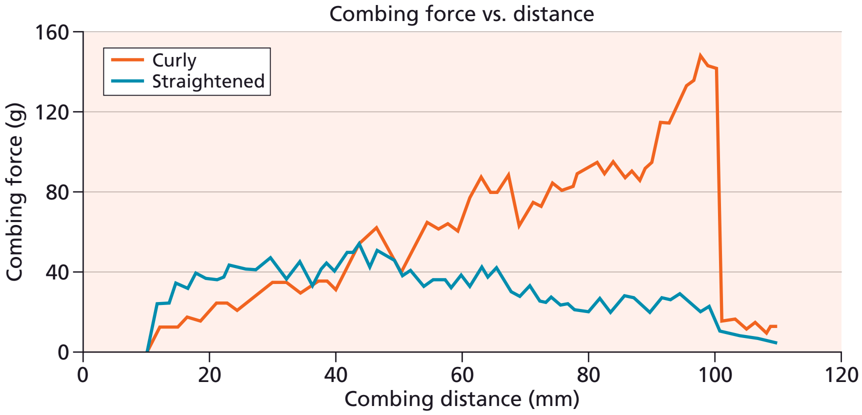

Figure 32.3 Combing profiles of curly and straightened hair.

such as polyquaternium-6, behentrimonium chloride, and hexadimethrine chloride. In addition, ceramides and panthenol are linked to increasing the cuticle integrity and relative strength of hair [22].

Although sodium hydroxide (lye) and guanidine (no-lye) relaxers straighten the hair via the same chemical pathway, some important differences exist between the two technologies. It is well established through published and unpublished studies that the guanidine systems are milder to the scalp causing less incidence of irritation [23]. In addition, unpublished laboratory studies indicate that guanidine systems create more lanthionine (7.4% vs 5.2% lanthionine) in the same time than the sodium hydroxide systems. The majority of sodium hydroxide relaxer users visit the salon while home users tend to use the guanidine system. These differences should be considered by professionals, home users, and dermatologists involved in deciding which relaxer system is most appropriate for individual use.

Conclusions

Hair straightening treatments are popular and can be used to achieve individually desired styles. However, care must be taken to decrease the chances of overprocessing that may occur when processes and chemical treatments are performed improperly. The future of straightening processes and treatments is only limited by science and technology. History shows that even though there have been major scientific advancements, the technology to straighten hair either temporarily or permanently still involves the use of heat with mechanical stress or chemical products. Over time, incremental improvements in thermal appliances and formulations for chemical treatments will continue to occur. Despite the advances, it will remain important to understand the advantages and disadvantages and proper techniques of each method based on personal style preference, hair type, and quality to reduce adverse effects.

Appendix

Thiol procedure with heat

After the hair is washed and towel-dried, the reducing cream is applied to a small section of hair for the recommended time for a strand test. The minimum time that it takes to achieve the level of curl reduction in that section is noted and the section of hair is rinsed after that time. The hair is then saturated with the cream and gently smoothed into a straight configuration. The cream should be left on the hair for the minimum time that was noted during the strand test; however, the time should not exceed the recommended time. The hair is rinsed thoroughly with water then the hair is 80% dried. A protecting smoothener is applied to the hair and then a brush in conjunction with a blow-dryer or a flat iron is used to straighten the hair in small sections. The hair should be neutralized using an oxidizing solution which should be left on the hair for the recommended time during that step. To keep from drying out, the neutralizing solution is usually reapplied (for 5 minutes) and then the hair is rinsed abundantly with warm water followed by towel drying. The hair should be conditioned with a rinse-out conditioner and styled as desired. The time for the procedure can be up to 6 hours.

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Chapter 33: Hair styling – technology and formulations

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BASIC CONCEPTS

- Hair styling aids arrange and maintain hair in a groomed position and impart conditioning, shine, body, and increased manageability.
- There are a wide variety of styling aids including hairsprays, gels, mousses, creams, waxes, lotions, and brilliantines. Heated styling implements such as blow-dryers and curling or straightening irons are also used to achieve style.
- Polymers, emollients and waxes are the main functional ingredients in styling aids. Polymers bond hair strands together to provide hold. Emollients and waxes – amongst other ingredients – increase single hair fiber intercation and smooth cuticles, imparting shine and reduced hair frizz.
- Styling aids are in general safe for skin and hair; however, misuse can result in hair damage.
- Styling aids may be useful in improving the appearance of hair dermatologic conditions that result in thinning hair, hair dullness, or unruliness.

Introduction

The appearance of person's hair, its length, shine, and smoothness, is a strong indicator of general age, health, and attractiveness [1]. Additionally, hair style or conformation may be used to express personality traits or may make a social statement. Marie Antoinette was said to have changed her iconic hairstyle to promote her French identity [2], and who can forget the long flowing hair of the rebellious 1960s flower child? However, today as in the days of Marie Antoinette, hair does not grow naturally into the wide variety of hair styles desired by men and women – manipulation through brushing, setting, and the use of styling aids is necessary to smooth and arrange the hair into a pleasing style. The use of hair styling agents to help achieve hair styles is also not new – Ancient Egyptians were know to use castor and other oils as hair dressings and bees wax to help style and plait wigs [3].

Styling aids not only correct the hair, but can also help transform hair for those with hair loss or hair damage resulting from medical concerns – hairsprays give lift to thinning hair, smoothing creams help tame unruly frizz, and gloss serums can help restore a more youthful shine. This chapter describes the wide variety of hair styling aids – their basic chemistry, utility, and potential issues that clinicians need to be aware of in their everyday practice.

Cosmetic Dermatology: Products and Procedures. Edited by Z.D. Draelos.

Definitions

Hair styling is the act of reshaping the hair mass to an arrangement or style that can be maintained over time. Hair, by its nature, is easily reshaped when wet and dried or through the application of heat; however, because of hair's susceptibility to atmospheric humidity these changes require the assistance of chemical styling aids to maintain the shape over time. Styling aids with polymers can help improve hair volume and height by increasing hair strand stiffness and hair fiber interactions. Styling aids with emollients and waxes can help smooth out frizz and increase hair shine by aligning fibers and reducing friction and can also have a conditioning effect on the hair fibre (Figure 33.1). Styling products, such as sprays, gels, and waxes, modify only the surface of hair – not the structure itself. These products are not meant to be permanent, unlike permanent waves and chemical straighteners, and the majority of these products are designed for easy removal by shampooing.

Physiology

Hair strands are made up of lengths of bundles of keratin polymer chains [4]. These chains are linked by two main types of bonds: strong and weak (Figure 33.2). Strong bonds are made of cystein amino acids and can only be broken chemically (e.g. by permanent wave solutions). Weak bonds include van der Waals, salt bonds, and hydrogen bonds which can be affected by changes in water concentration alone [5,6].

Figure 33.1 Styling aids can provide improved appearance of hair volume and smoothness. (a) Frizzy unruly hair dried without styling aids. (b) Frizzy unruly hair smoothed with application of styling aids. (c) Fine/thin hair dried without styling aids. (d) Fine/thin hair volumized through the application of styling aids.

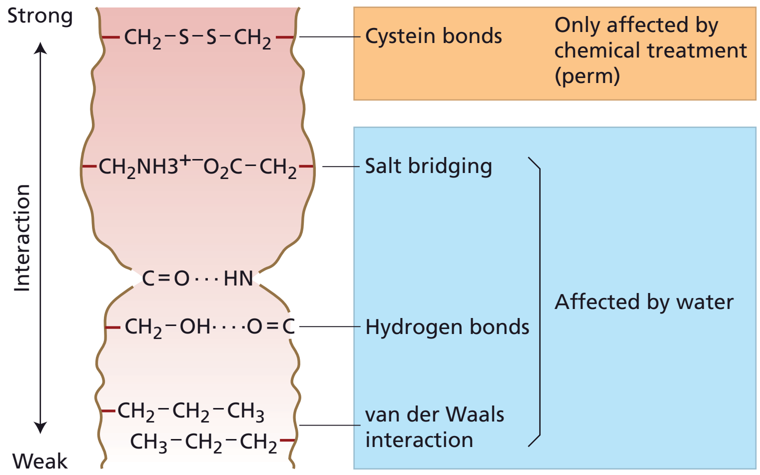

Figure 33.2 Mechanisms to stabilize hair structure and shape via keratin chain interactions [7].

Wet setting is the mechanism of shaping hair strands through controlled wetting and drying conditions. Hydrogen bonds can be easily opened by humidity or water accessing the hair from the environment. Rearrangement of the hydrogen bonds will occur by removing water while drying and reformation of new bridges into a different shape by holding the hair strand in the desired shape while drying. Unfortunately, these new bonds are also susceptible to humidity from the environment and may revert back to their natural state of frizzy, curly or weak, straight hair over time.

Styling aids help make the styling process and finished style to be more independent of the molecular interactions inside the hair and more robust against environmental influences because the polymers are less affected by humidity. With the correct polymers, adequate deposition, and sufficient distribution of styling product significant style holding power can be achieved. Figure 33.3 shows hair treated with styling aids in a high humidity environment will keep the shape much longer than wet set hair alone.

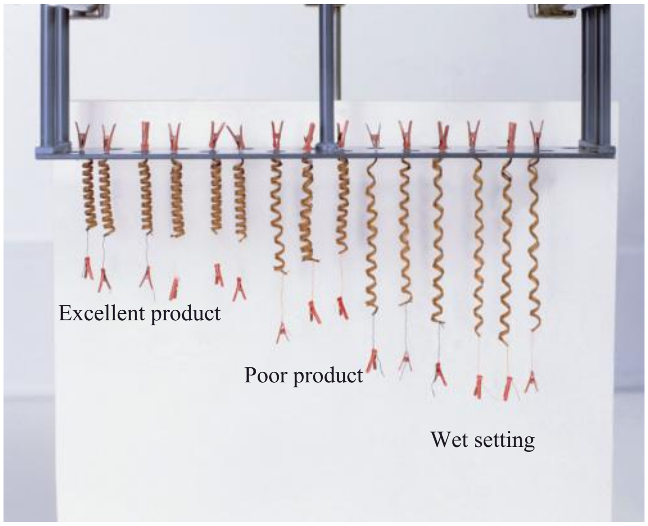

Figure 33.3 Curl retention with and without addition of spray in high humidity (85% relative humidity [8].)

Formulation

Because of very different hair structures, needs, and fashion trends a very broad range of styling products covers today's consumer needs and demands (Figure 33.4). In general, there are two technologies to differentiate:

- Polymer-based formulations that cover hair with a film and form dry welds between hair strands:
  - Advantage: high mechanical strength, dry touch, gloss
  - Disadvantage: will break with mechanical stress, cannot be reformed once broken except by rewetting
- Wax and emollient-based formulations that deposit hydrophobic material on hair. These hydrophobic materials do not dry over time and create fluid bonds that can be broken and reformed.
  - Advantage: no spot welds will break, interaction of single hair fibers can be opened and closed again, styling is remoldable
  - Disadvantage: limited mechanical strength, in high concentrations can feel waxy/oily, potentially look negative on thin hair

Polymer formulations

Hairsprays, gels, mousses, and liquid settings work on the principle of film-forming polymers. The active ingredients can be divided into three groups:

1 *Film-forming polymers:* main ingredient in application such as hairsprays and gels but also as minors in waxes.

2 *Conditioning and film-forming polymers:* usually in wet applications such as mousses to improve wet combability.

3 *Rheology modifier:* usually does not contribute to fixation but controls consistency of the product.

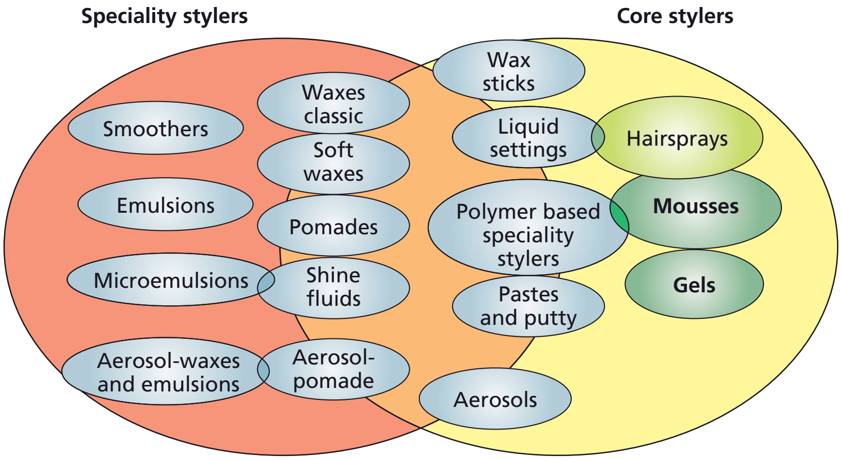

Figure 33.4 The broad range of modern styling aid forms and chemistries.

Table 33.1 Typical ingredients for polymer-based styling aids.

Ingredient (INCI)	Function	Hairspray	Gel	Mousse
PVP (Polyvinylpyrrolidone)	Film former		x	x
Octylacrylamide/Acrylates/Butylamino-ethylmethacrylate Copolymer	Film former	x		
PVP/VA Copolymer (PVP/Vinylacetate)	Film former	x	x	
PQ-11	Film former			x
PQ-16	Film former			x
PQ-4	Film former			x
Chitosan (derived from Chitin)	Film former			x
Carbomer (cross-linked Acrylic Acid)	Rheology modifier		x	
Acrylates/Ceteth-20-itaconate Copolymer	Rheology modifier		x	
Hydroxyethylcellulose	Rheology modifier		x	
Alcohol	Solvent	x	(x)	(x)
Water	Solvent	(x)	x	x
Dimethicone	Plasticizer	x		
Panthenol	Moisturizer	x	x	x
Propane/butane	Propellant	x		x
DME (Dimethylether)	Propellant	x		x
Ethylhexymethoxycinnamate	UV-absorber	x	x	x
PEG-40-hydrogenated Castor oil	Emulsifier		x	x
Laureth-4	Emulsifier			x
Aminomethylpropanol	Neutralizer	x	x	
Phenoxyethanol	Preservative		x	x
Methylparaben	Preservative		x	x
Fragrance	Scent	x	x	x

These film-forming active ingredients are modified to optimized performance by additional ingredients such as emollients (including silicone), solvents, plasticizers, fragrance, and preservatives. Table 33.1 provides a list of typical ingredients found in polymer-based styling aids.

Wax and emollient formulations

The area of waxes and emollients covers a broad range of products:

- *Pure waxes:* water-free formulations often without preservatives. Mostly compact appearance and provide high control. Matte (i.e. low shine) derivatives are also called clay, paste, or putty.
- *Cream emulsions:* contain three main types of ingredients: water, emulsifiers, and oil/wax components. Consistency from soft lotion to rich cream.

Table 33.2 provides a list of typical ingredients found in wax and emollient-based styling aids.

Product forms, application, and uses

Hairsprays and liquid settings

Aerosol hairspray is one of the most widely used styling products. The ease of use and broad application areas make it a versatile tool for stylists and consumers. These products

Table 33.2 Typical ingredients in wax and emollient-based styling aids.

Ingredient (INCI)	Function	Wax	Cream
Carnauba wax	Hard wax	x	x
Paraffin liquid	Oil	x	x
PEG-60 (Polyethylene glycol)	Wax	x	x
Cetyl alcohol	Wax	x	x
PEG-90M (Polyethylene glycol high molecular)	Creates thread-like consistency		x
PVP (Polyvinylpyrrolidone)	Film former		x
PVP/VA Copolymer (PVP/Vinylacetate)	Film former		x
Carbomer	Stabilizer		x
Hydroxyethylcellulose	Stabilizer		x
Triceteareth-4-phosphate	Emulsifier	x	x
PEG-24 hydrogenated Castor oil	Emulsifier	x	x
PEG-40-hydrogenated Castor oil	Emulsifier		x
Dimethicone	Care/combability	(x)	x
Panthenol	Moisturizer		x
Ethylhexylmethoxycinnamate	UV-absorber	x	x
Aminomethylpropanol	Neutralizer		x
Phenoxyethanol	Preservative		x
Benzyl alcohol	Preservative		x
Fragrance	Scent	x	x

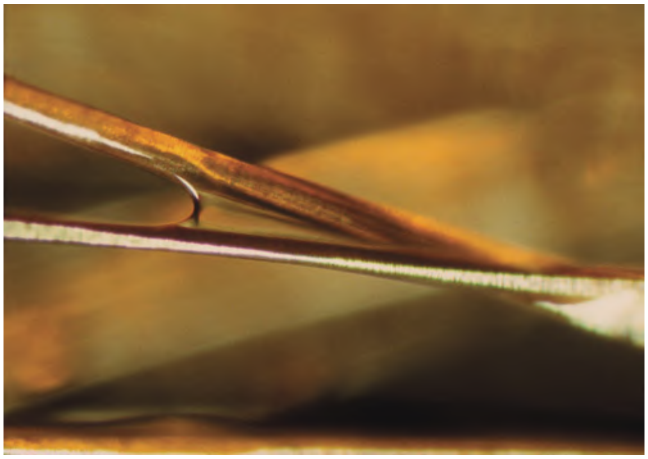

Figure 33.5 Hairspray bond – spot weld.

are usually finishing products and are applied in the very last step of styling on dry hair. Aerosol hairsprays contain a solution of polymer ingredients, alcohol, water, and liquefied propellants under pressure. The release of propellant pressure during dispensing results in a fine mist of polymer-containing liquid that deposit on the hair fibers, spreads, covers hair, and forms spot welds between the fibers (Figure 33.5).

Besides the aerosol version, hairsprays are also sold in non-aerosol sprays where distribution of the liquid to droplets is done mechanically by a pump. These sprays are perceived by consumers to be wetter than aerosol hairsprays on application because of the bigger droplet size resulting from the pump spray mechanism.

The main ingredients of hairsprays in general are:

- *Polymer:* film-forming polymer;
- *Solvents:* ethanol, water;
- *Propellant:* e.g. Dimethylether (DME), Propane/butane, Fuorinated Hydrocarbons (HF-152 A) for VOC-formulations in USA;
- *Additives:* e.g. silicones, UV-absorber, vitamins;
- *Fragrance*;
- Non-aerosols have similar ingredients only without any propellant.

Hairsprays have been the target of regulatory restrictions ever since the banning of CFHC-based propellant compounds in the 1970s because of concerns about the ozone layer. A more recent development has been the restriction of volatile organic compounds (VOCs) to 80/55% of hairspray formulas in the USA. Formulas have now been developed that substitute propellants judged to have a lower risk of impacting the ozone layer water (such as Hydrofluorocarbon 152A or HFC 152A) and an increased proportion of water in the formulas. While initially this negatively impacted hairspray performance, more recently new polymer systems have been developed to work at these lower alcohol and higher water contents [9].

Hairsprays are safe when used as directed; however, there are some potential issues surrounding misuse. First, aerosols can create a fine mist of droplets which may be inhaled. Hairspray manufacturers carefully check the droplet size and proportion of the formulas and dispensers in order to avoid significant inhalable quantities of droplets to insure consumer safety during typical use at home or in a hair salon [10]. Additionally, hairsprays need to be removed periodically by shampooing. Hairspray polymers have been formulated to breakdown in the presence of shampoo surfactants. However, if hair is not shampooed frequently, hairspray and other styling aids can build up on the hair causing dullness, potential hair breakage, and polymer flaking reminiscent of dandruff.

Setting lotions are a special application form of hairspray and pump-spray. The formulation is similar but the usage is different. Typically, the damp hair is prepared with rollers and the product is applied from a small bottle with a nozzle. After blow-drying the rollers are removed and the hair is brushed. The deposition of polymer increases surface friction and creates volume, the main benefit of this product type. One significant consumer segment has gray hair and uses lotions containing blue dyes to make their hair color brighter and less yellowish. Overdosing and build up resulting from low shampoo frequency may cause a bluish appearance of the hair that can be removed by washing.

Mousse

Mousses belong also to the widely used products such as hairsprays. Typically, they are wet application products for volume in combination with a blow-dryer. As combing and/or brushing are important parts of the styling procedure, good wet combability is a base requirement. Mousses in general consist of:

- *Polymer:* mostly quaternized, single or in combination with other cationic on non-ionic polymers ("film former");
- *Surfactants*
- *Solvents:* water, ethanol
- *Additives:* e.g. silicones, UV-absorber, vitamins;
- *Propellant:* e.g. propane/butane, DME;
- *Fragrance;*
- Non-aerosol mousses have similar composition without propellants but a mechanical actuator to create the mousse.

As mousses contain cationic charged polymers they may interact in special conditions (hair structure) with anionic polymers from hairsprays. The resulting complex could be hard to remove because of its poor solubility. Repeated shampooing in combination with a conditioner will remove depositions. Overdosing may create a weighted down effect, residues, reduction of shine, or appearance of white flakes similar in appearance to dandruff.

Gels and spray gels

In the last 25 years gels became more popular for a more visible styling effect. Today, gels are designed to create every style from smooth hold to extreme looks with spikes to express personality or fashion. The use depends strongly on habits; different looks result if applied to wet hair or dry hair or when the hair is blow-dried or air-dried.

Spray gels start at the lower end of the hold scale and provide a well-groomed look. Spray gels are easy to apply evenly throughout the hair. The consistency is usually from water-thin to low viscous. Tube gels have a medium to high viscosity and represent the upper end of a hold scale. The amount of film-forming polymer usually determines the hold level. Typical ingredients for gels include:

- *Thickener:* e.g. polyacrylates (carbomer), polysaccharides;
- *Polymer:* "film former";
- *Moisturizer:* e.g. glycerin for wet look;
- *Solvents:* water, ethanol;
- *Additives:* e.g. silicones, UV-absorber, vitamins;
- *Preservatives:* e.g. paraben types, phenoxyethanol;
- *Fragrance.*

Removal of a gel requires shampooing – in some cases a second lathering is recommended. Dry, brittle gels with high hold levels may tend to generate flakes when touched, similar to hairsprays. Build up is not usually observed with regular shampooing. Some gels may also be sold as creams as their appearance is not clear but turbid to white and texture is more rich and soft than a typical gel.

Creams, pomades, and emulsions

Creams, pomades, and emulsions are a growing segment which contains very specialized niches for texture and styling results. The common base of cream-like products is always:

- Hydrophobic base such as wax, oil, or related chemistry;
- Water, mainly as the continuous phase (oil-in-water emulsions);
- Emulsifier combination.

The composition and structure of the emulsion control the application properties. By adding polymers the level of hold can be modified, the texture might be changed by adding polymeric thickeners or particles such as bentonite or diathomaceous earth to provide a rough, clay-like feel with a matte effect to take away shine. The following list shows typical components:

- Wax compound:
  - Synthetic: e.g. paraffin type, polyethylene glycol
  - Natural: e.g. carnauba wax, bees wax
- *Surfactants/emulsifiers:* Trideceteareth-4-phosphate
- *Solvent:* water;
- *Polymers:* if required for hold or texture;
- *Additives:* e.g. silicones, UV-filter, vitamins;
- *Particles* (optional)*:* e.g. bentonite, silica for special texture;
- *Preservatives:* e.g. paraben types;
- *Fragrance*.

Application is related to desired effect or style in dry or damp hair for finger styling. Usually, this procedure is part of the finishing touches to a hairstyle. The advantage over polymer-based formulations is the softer nature of hair and the remoldability of the style without reapplication of new product. A special type of emulsion is the clear jelly-like microemulsion. One attribute is the so-called ringing effect that will be recognized when the jar is held with two fingers and another finger hits the container.

These formulations contain a high amount of surfactants so formulators must keep in mind irritation, especially eye irritation, in their selection of ingredients. In combination with sweat there is a risk of running into the eye. Good formulations contain a combination of emulsifiers and surfactant that are not irritating in *in vitro* and patch testing.

Waxes and clays

Water-free waxes are a special group that provides strong control and bigger effects than cream-like products. Their consistency is harder and application needs more education or skills by the consumer – especially to prevent overusage and build up.

- *Wax compound:*
  - Synthetic: e.g. Polyethylene glycol
  - Natural: e.g. Carnauba wax, Bees wax
- *Surfactants/emulsifiers:* only for washability;
- *Additives:* e.g. silicones, UV-filter, vitamins;
- *Particles:* e.g. bentonite, silica for special texture;
- *Preservatives:* usually *not* required;
- *Fragrance:* if desired.

Application is on damp or dry hair similar to creams. The stiff consistency requires warming in the hands before application. Shampooing and use of conditioning agents remove waxes, but in some cases may require repeated application to ensure no build up is formed after repeated usage.

Silicone serums and sprays

Silicones – mostly used as oils – are a part of many of the formulations described above to add care properties, improve combability, shine, or modify polymer-based formulations as plasticizer. Apart from this use of silicones, some formulations are mainly based on silicones. The main benefit of these products is to provide pure shine or highlight strands to finish the styling process (Table 33.3).

Formulations differ from application form and heaviness of the effect:

1 *Serums:*
- Oily liquids that provide long-lasting, high gloss effects;
- Contain low volatile silicones and low amounts of solvents such as alcohol;
- Designed to highlight strands, no fill head application;
- Have to be carefully applied by hands – need expertise in use.

2 *Pump sprays:*
- Are lighter in effect than serums;
- Effect is less durable as the silicones are more volatile;
- Contain solvents such as alcohol;
- Easier to apply for consumers;
- Also for full head application.

Table 33.3 Typical ingredients in silicone products.

Ingredient (INCI)	Function	Serum	Spray/Aerosol
Dimethicone	Shine enhancer	x	x
Dimethiconol	Shine enhancer	x	x
Cyclopentasiloxane	Shine enhancer	x	x
Alcohol	Solvent		x
Propane/butane	Propellant		x
Panthenol	Moisturizer	x	x
Ethylhexymethoxycinnamate	UV-absorber	x	x
Fragrance	Scent	x	x

3 *Aerosol sprays:*

- Are comparable to pump sprays in performance;
- Designed to intensify gloss of styling for finish;
- Also suitable to refresh shine.

Table 33.4 shows hair products according to categories, physical description, typical applications, and desired result.

Products designed for African hair types

Hair of people of African descent has always been treated very differently from Caucasian or Asian hair. The structure of African hair is different from other hair types, as its extreme curvature is thought to be caused by the different profile of the hair shaft, which may be caused by differences in the morphology of the upper hair follicle. African hair has a distinctively more oval profile than Caucasian or Asian hair (Figure 33.6).

These structural characteristics go hand in hand with further challenges when styling African hair, especially as the time and effort spent on styling African hair tend to be higher than Caucasian hair for example: heightened brittleness of the hair shaft, regular use of relaxing chemistry, knotting, braiding, use of extensions. Excessive braiding and the use of extensions can often cause strain on the hair shaft in the follicle and therefore can lead to temporary hair loss, which is often seen especially along the hairline of the forehead and the partings.

The majority of the African specialty styling products are targeted at helping to relax and smooth the curly African hair. Therefore, most products (such as brilliantines and pomades) contain high levels of waxes and oils and/or polymers. These ingredients deliver the hold African hair needs and are typically applied with the fingers and whole hand to achieve good coverage and maximum hold benefits. Another advantage of the high levels of oils and waxes in these products, but also in other products like oil sheens, is that they enhance the light reflected from the hair surface, which gives especially dark hair a more healthy appearance.

Lotions are often used to protect the hair shaft and are useful for African hair as it tends to be more brittle and more prone to breakage. Lotions are mainly emulsions that offer combinations of conditioning ingredients and styling ingredients. The conditioning ingredients (such as silicones and fatty alcohols) protect the hair and enhance its appearance. Lotions are highly beneficial for African hair as they have a good efficacy as leave-in products and as they can help to counteract the negative effects of the variety of damaging styling techniques used.

Table 33.4 Hair products (categories, physical description, typical applications, desired result).

Category	Physical description	Typical applications	Desired result	Typical packaging
Hairspray (aerosol)	Liquid, clear, low viscous	Spray with propellant on dry hair after styling	Hold of finished styling, invisible net	Aerosol can, aluminum or tinplate with actuator
Hairspray (non-aerosol pump spray)	Liquid, clear, low viscous	Spray without propellant on dry hair or on damp hair for blow-drying	Hold of finished styling	Bottle with mechanical actuator
Gel/Gel spray	Medium to viscous, clear jelly-like consistency	Dry hair for air drying or wet hair for blow-drying	Visible styling effects, shaping of hair bundles, creating spikes, etc.	Tube or dispenser
Mousses	Soft, creamy mousse, semi-stable that breaks under mechanical stress	Wet hair with blow-drying, rollers might be used, typically brushed	Volume and hold	Aerosol can
Emulsions	Creamy consistency, typically white appearance, soft feel, and slightly fatty touch	Mostly wet hair, but also dry hair as finish product	Weight down effect, antifrizz properties, alignment, and control of shape, moldability	Jar, tube, or dispenser
Waxes	Tough to hard consistency that melts under mechanical stress	Dry hair	Visible styling effects, bundling of hair, textured looks, also matte effects desired	Jar
Silicones	Clear, oily liquids	On dry hair for styling purpose with fingers or as spray	Pure shine in addition to hold provided by styling products applied before	Small bottles

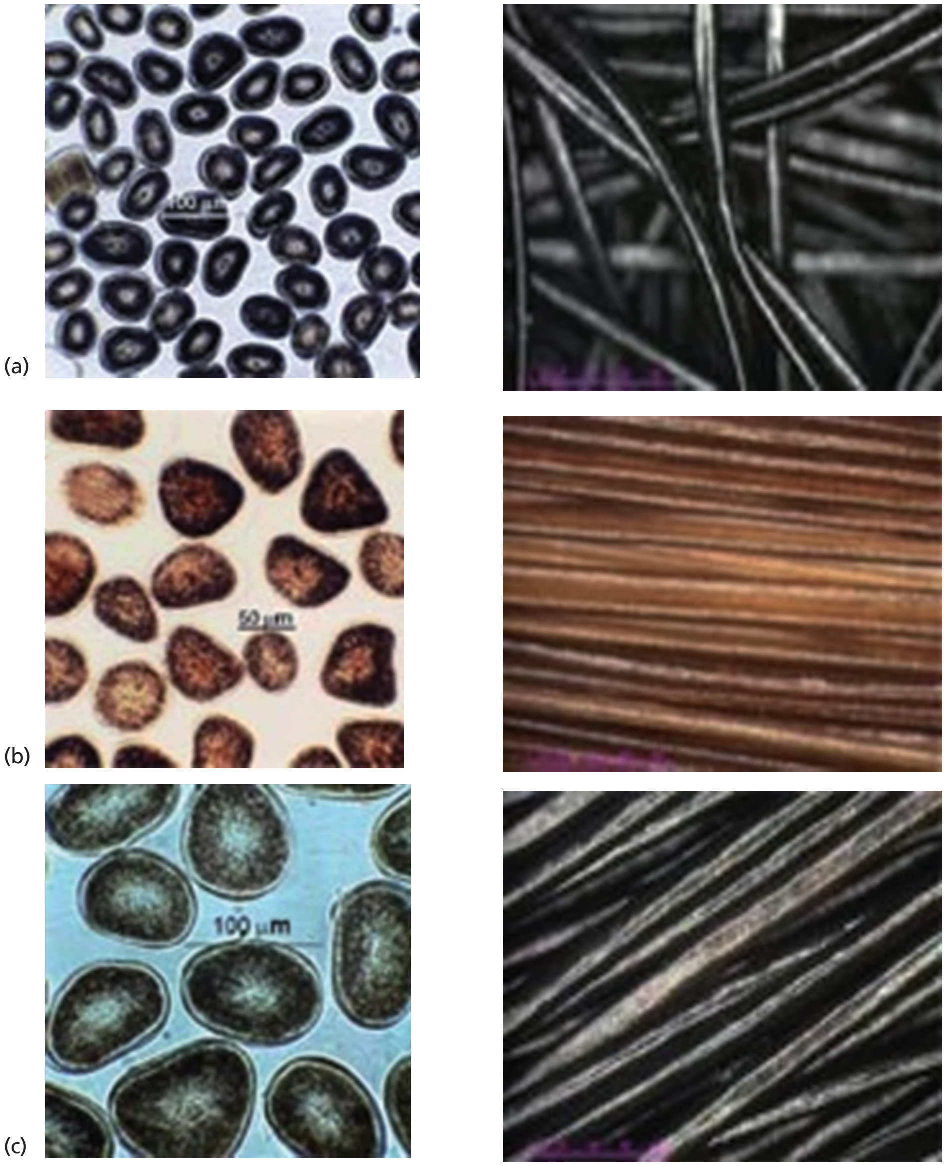

Figure 33.6 Comparison of African (a), Caucasian (b), and Asian (c) hair structure.

As the vast majority of African specialty products tend to have higher levels of styling polymers and/or waxes/oils, it is crucial to wash the hair regularly to prevent excessive build up and associated hair negatives.

Considerations for consultations with patients about hair styling

Despite the many advantages and fundamental benefits for appearance – and consequently confidence – misuse of styling products can have an adverse effect on the hair quality and appearance [11,12]. Often, patients overuse or misuse styling products, and especially styling appliances, in their quest for a better appearance. For example, the misuse of heat styling appliances has wide consequences for the hair quality, as studies have shown [13]. Some modern heat styling appliances operate with temperatures of well over 200 °C, which is beyond the temperature that the hair's molecules, especially keratin and its amino acids, can withstand without major structural damage. Patients with high heat styling needs and habits should be advised to use tailored products that have a reduced heat output and/or tailored technology to minimize hair damage and overheating. Furthermore, modern ion technology in heat styling appliances can help to reduce some adverse effects from excessive heat styling. Mechanical stress whilst heat styling is one factor that can cause damage to the hair fiber. Therefore, the use of appliances especially designed to reduce hair damage during the heat styling process is recommended. Design features of these include low friction styling surfaces such as ceramics, flexible plates, etc.

Other potential issues with styling products include overuse or mix of the wrong styling product technologies. Overuse of styling products without removal through proper hair hygiene can lead to negative effects on the appearance and tactile properties of hair. The polymers used as main actives can – when overused and not removed – accumulate on the hair surface and can lead to dullness, adhesion of dust and dirt, and to hair being less easy to manage and prone to tangling – the opposite effect to what users are trying to achieve.

Because of the character of the ingredients used, styling products are generally safe to use. However, as with other cosmetic products, in rare cases the use of some styling products may be associated with allergies or irritations if there is a history of contact allergic reactions to selected ingredients. These may stem from single ingredients in the product formulations such as fragrance ingredients. Even though the risk of this is low because of limited prolonged contact of the products with skin, in case of irritations or adverse reactions that could be associated with styling products, it is advisable to investigate the type of product used, and the ingredients contained, and to identify known allergies of the patient. In case of an identified allergic reaction, dermatologists are advised to patch test the patient and/or to contact the manufacturer of the product to find out about the nature of the ingredients used in the product.

In consultations with patients concerning styling-related issues, it is imperative to assess the specific hair-related issues of the patients first and then to understand what styling and haircare products were used. This should enable a good understanding of what caused the issues and the psychologic impact on the patient. The advice to patients with hair styling-related issues should be focused on the right selection, and the right amount of styling products targeted at their hair needs and used in combination with a good quality haircare regime. Often manufacturers of high quality haircare and styling products tailor their different product technologies to match and provide maximum styling benefits with minimum negative effects. A recommendation to patients who overuse or misuse styling products should include a recommendation to reduce the amount and to select the right products.

Future of hair styling aids – trends and technologic development

As there are continuous research efforts dedicated to hair, the knowledge of hair (hair biology, hair structure, and hair biochemistry) is growing and will continue to grow in the future. Styling aides are a prime example that trends and science and technology advancements are closely interwoven. Over the course of the last 50 years or so, emerging trends demanded new technologies to be developed to enable the creation of new hair styles. Vice versa, the development of new styling technologies enabled the creation of new trends in fashion and beauty. One example is the trend of “big hair” in the 1980s which drove the development of maximum volume and hold products, which in turn allowed for the creation of even bigger hair styles. A key development over the years, which will continue into the future, is the focus on ease of use of the new styling products to enable everybody to create impressive styles.

Consequently, the current science and technology advancements will – no doubt – have a profound effect on future trends and will enable new hair styles that everybody can create and recreate, from the most advanced fashion stylists to consumers in their homes.

Conclusions

Styling aids come in a wide variety of types and are used by many to augment hair appearance. Familiarity with the range and use of hair styling aids will help a clinician not only diagnose potential problems arising from misuse or allergy, but can also help when counseling those with thinning, aging, or damaged hair. Styling products can impart the appearance of healthier hair by improving hair shine and smoothness, increasing the appearance of hair amount by building in body and volume.

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