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REVIEW ARTICLE: SLS AND PARABEN FREE HAIR CLEANSER

Gaikwad Renuka*, Harode Prajakta, Bhajikhaye Pratiksha, Dubey Yash, Wankhede Yogita and Dr. Mitali Bodhankar

Gurunanak College of Pharmacy Nagpur Maharashtra.

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***Corresponding Author**
Gaikwad Renuka
Gurunanak College of Pharmacy Nagpur Maharashtra.

ABSTRACT

Sulfate free shampoos are the cosmetic preparations that with the use of Traditional ayurvedic herbs are meant for Cleansing the hair and scalp just like the Regular shampoo. They are used for removal of oils, dandruff, dirt, environmental pollution etc. Shampoo occupies a prominent and very important place among the Products available today. Due to the increasing awareness and importance of Cleanliness and healthiness of hair, the use of "sulphate free shampoo" is increasing Every day. Earlier the Use of herbal shampoo was confined to the upper and upper Middle classes of urban society, but with increasing awareness the Use of herbal shampoos has become well established in even rural households. Sulphate free Shampoos can keep the hair clean, nurtured and meet the need of stronger, softer And shinier hair. They are also Perceived as helping to maintain the colour of dyed Hair. We offer an array of sulphate alternatives to meet the increasing Consumer Demand for sulphate-free option.[8]

INTRODUCTION

The hair care sector is probably one of the largest sales units amongst the cosmetics. Shampoos are used to cleanse the hair and the scalp. Today the cosmetic market has become extremely competitive, producing various brands in order to catch the customer's attention, each claiming to be better than others. Synthetic detergents used in shampoos available in the market are harmful and toxic; affecting the health as well as the environment. They destroy the environment by releasing non-biodegradable chemicals affecting the aquatic life and algae. These detergents leave chemical residues on clothes, which enter our bodies, either through the skin or lungs, leading to several health problems, including allergies and skin

infections. The fragrances used in detergents can also prove allergic and be irritating to the lungs, causing health effects on people with asthma or chronic heart problems.[9]

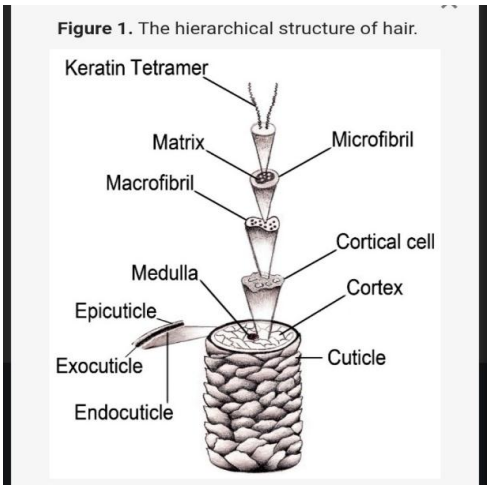


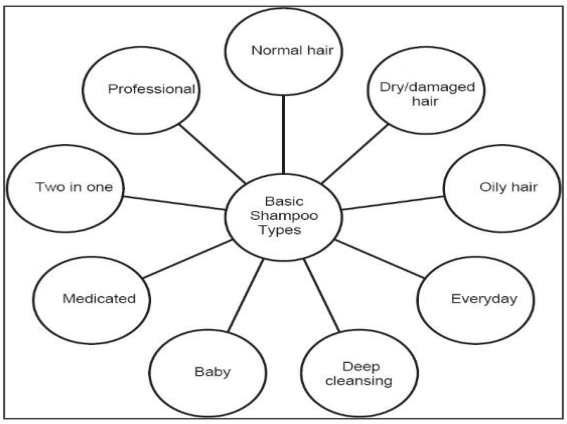
Fig.1: The hierarchical structure of hair.[10]

Note –

The scalp pH is 5.5, and the hair shaft pH is 3.67. An alkaline pH may increase the negative electrical net charge of the hair fiber surface and, therefore, increase the friction between the fibers.[12]

Shampoo

Shampoos are probably the most widely used cosmetic products for cleansing hairs and scalp in our daily life.[11] Shampoos are not only scalp cleaners, because they also act on the hair shaft. The It is desirable that whatever may the disease or scalp condition be (dermatitis, seborrhea, alopecia, psoriasis), the shampoo must preserve the softness, comparability and shine of the hair shaft.[12]



TYPES[13]

Composition:[14] The basic shampoo recipe is listed in [Table 1]

Detergents	Functions to remove environment dirt, styling products, sebum, and skin scales from the hair and scalp
Foaming agents	This agent allows the shampoo to form suds, as consumers equate cleansing with foaming even though the two are unrelated
Conditioners	Leave the hair soft and smooth after sebum removal by the detergent
Thickeners	Thicken the shampoo, as consumers feel that a thick shampoo works better than a thin shampoo
Opacifiers	Added to make a shampoo opaque as opposed to translucent for aesthetic purposes, unrelated to cleansing
Sequestering agents	Functions to prevent soap scum from forming on the hair and scalp in the presence of hard water; The basic difference between a liquid shampoo and a bar cleanser
Fragrances	Added to give the shampoo a consumer-acceptable smell
Preservatives	Prevent microbial and fungal contamination of the shampoo before and after opening
Specialty additives	Treatment ingredients or marketing aids added to impart other benefits to the shampoo, besides hair and scalp cleansing

SURFACTANTS

- Surfactants are cleaning agents that substituted soap. They act through the weakening of the physicochemical adherence forces that bind impurities and residues to the hair. Surfactants dissolve these impurities, preventing them from binding to the shaft or the scalp. The cleansing ability of a shampoo depends on how well it removes grease as well as the type and amount of surfactants used.[15]
- Residues are nonsoluble fats (sebum) that do not dissolve with water. In order to be removed from the hair shaft, surfactants present a hydrophobic molecular portion, and another hydrophilic. The former will chemically bond with the fat, while the latter will bond with the water. The surfactants are generally composed of a chain of fatty hydrocarbons (tail) and a polar head. The polar extremity is capable of giving this portion of the molecule hydrophilic traits that allow it to dissolve in water and wash away the residues. The surfactants in contact with the water attain the structural formation of a micelle. Their structure becomes spherical with a hydrophilic exterior, which can be rinsed with water, and a hydrophobic interior where the fats and residues are binded. When enough shampoo molecules have embedded their hydrocarbon ends in the particle,

the surrounding water molecules attract the ionic ends of the surfactant. The particle then becomes emulsified, or suspended in water. In this form, it can be rinsed away.[15]

- Depending upon the electric charge of the polar extremity, the surfactants are classified in four groups: Anionic, cationic, amphoteric and nonionic. The main cleansing agents are anionic. The soap, which is also an anionic detergent, in contact with water, leaves an alkaline residue that is very harmful to the hair and skin and that precipitates in the form of calcium salts which accumulate in the hair strands, leaving them opaque and tangled. Such effects do not happen with the new anionic surfactants that are derived from the sulfation of fatty acids and analogue polioxiethilenes (alquil sulfates, alquil ether sulfates) which are smooth cleansers and cosmetically superior. The current expression "sulfateless shampoo" refers to a preparation without the anionic surfactant. Theoretically the sulfatless shampoo creates a minimum electrical net, but there are no published analysis about effectiveness of these products regarding either cleansing power or hair shaft aggression.[15]

Shampoo surfactants		
Class	Example	Characteristics
Anionic	Ammonium lauryl sulfate, sodium laureth sulfate, sodium lauryl sarcosinate, sodium myreth sulfate, sodium pareth sulfate, sodium stearte, sodium lauryl sulphate, alpha-olefin sulfonate, ammonium laureth sulphate	Deep cleansing
Cationic	Trimethylalkylammonium chlorides, and the chlorides or bromides of benzalkonium and alkylpyridinium ions	Hair softener. Mild cleansing
Nonionic	Fatty alcohols, cetyl alcohol, stearyl alcohol, and cetostearyl alcohol (consisting predominantly of cetyl and stearyl alcohols), and oleyl alcohol	Mild cleansing Some considerations about the eco-system
Amphotheric	Alkyl iminopropionates and (amido) betaines	Do not irritate the eyes. Moderate cleansing

Anionic surfactants

Anionic surfactants are characterized by a negatively-charged hydrophilic polar group. Examples of anionic surfactants are ammonium lauryl sulfate, sodium laureth sulfate, sodium lauryl sarcosinate, sodium myreth sulfate, sodium pareth sulfate, sodium stearte, sodium lauryl sulfate, alpha-olefin sulfonate, ammonium laureth sulfate. Although very good in removing sebum and dirt, anionic surfactants are strong cleaners and may cause an increase

on electrical negative charges on the hair surface and increase frizz and friction. In order to minimize damage, other surfactants called secondary surfactants such as nonionic and amphoteric surfactants are added to the formulation.[15]

Cationic surfactants

Cationic surfactants have a positively charged hydrophilic end. Typical examples are trimethylalkylammonium chlorides, and the chlorides or bromides of benzalkonium and alkylpyridinium ions. All are examples of quats, so named because they all contain a quaternary ammonium ion. They tend to neutralize the negatively charged net of the hair surface and minimize frizz. They are often used as shampoo's softeners.[15]

Amphoteric surfactants

For the amphoteric surfactants, the charge of the hydrophilic part is controlled by the pH of the solution. This means that they can act as anionic surfactant in an alkalic solution or as a cationic surfactant in an acidic solution. They are very mild and have excellent dermatological properties. There are two types of amphoteric compounds: Alkyl iminopropionates and (amido) betaines.[15]

Nonionic surfactants

Nonionic surfactants have no electric charge. They do not ionize iaqueous solutions because their hydrophilic group is of a nondissociable. Many long chain alcohols exhibit some surfactant properties. Prominent among these are the fatty alcohols, cetyl alcohol, stearyl alcohol, and cetostearyl alcohol (consisting predominantly of cetyl and stearyl alcohols), and oleyl alcohol.[15]

Side effect of Sulfate

- Sulfates are potent surfactants, they can remove dirt and debris as well as naturally produced healthy oils from the hair and scalp.
- As a result, sulfates can leave the hair feeling dry and stripped of moisture.

Alternatively, sulfate-free shampoos are cleansers compounded by the removal of the anionic group and switched for surfactants with less detergency.[2]

Natural Surfactant are

- Saponin -saponins are group of water soluble glucosides.

It occurs in plants as a mixture of structurally forms with similar polarity comprising of large numbers of Surfactants.[7]

- Shikakai - pods of shikakai have traditionally being used for washing hair.[7]
- Seto Siris - it's leaves are used as a natural detergent.[7]

PARABEN

- The parabens are the most frequently used antimicrobials preservative found in Commercial shampoo.[16]
- The preservative effects of parabens are at least in part due to disturbances of membrane transport and mitochondrial function in microorganisms.[2]

Parabens refer to a group of esters of 4-hydroxybenzoic acid presence of parabens in shampoos And other cosmetics have been raised by patients for their Reputed estrogenic and antiandrogenic effects and suspected involvement in carcinogenesis via endocrine modulation.

Mehylparaben, ethylparaben, propylparaben, and butylparaben Are safe as cosmetic ingredients in the present practices of

- Use." [Parabens continue to be the most widely used preservatives in personal care products, usually in conjunction With other preservatives][2]

Parabens are good biocides

Short-chain esters (eg, methylparabens, ethylparabens) Are effective against gram-positive bacteria and are weakly Effective against gram-negative bacteria.

Long-chain paraben esters (eg, propylparabens, butylparabens) are effective Against mold and yeast.

The addition of other preservatives creates a broad spectrum of antimicrobial defense in consumer products.[2]

Side effects of Paraben

- ❖ Parabens can enter the systemic circulation via oral intake or by transdermal penetration, which was confirmed by the detection of systemic paraben concentrations upon exposure to these compounds
- ❖ Parabens have been associated with disturbances of estrogen hormone action and potential estrogenic activities of parabens have been extensively investigated in the past decades.

- In 2004, Darbre et al. reported the detection of unconjugated parabens in breast cancer tissue, triggering further investigations into estrogenic activities of parabens.[17]

PRESERVATIVES

Defination

The term Preservative is defined as natural or synthetic chemical agent that prevents decomposition by microbial growth or any undesirable chemical change in finished products. Preservatives are used in pharmaceutical industry to prevent the growth of bacteria, mold, fungi and other microbes. They are used in the manufacture of pharmaceutical drugs and cosmetics, for their individual antibacterial (destroying and inhibiting the growth of bacteria), antifungal (destroying and inhibiting the growth of fungus) and antioxidant (to prevent oxidation) properties.[5]

CLASSIFICATION OF PRESERVATIVES

Preservatives are classified into two main classes: Artificial Preservatives and Natural Preservatives.

Artificial Preservatives

These are chemical substances of synthetic origin used to prevent spoilage and contamination of finished product by micro-organisms e.g. Sodium benzoate, propyl gallate, potassium sorbate etc.

Natural Preservatives

These are the chemical substances obtained from natural sources that offer intrinsic ability to protect products against microbial growth. These include essential oil constituents, flavonoids, phenolic compounds, etc.

The natural preservatives are further classified into four types:

- Plant derived products as preservatives
- Animal derived products as preservatives
- Certain microbes and/or their metabolites

Based on mode of action, Natural preservatives are also classified into two groups: Antimicrobial preservatives and Antioxidants. Antimicrobial preservatives are included in the preparations to kill or to inhibit the growth of micro-organisms during manufacture or use. Antimicrobial preservatives are further classified into two main subclasses: Anti-fungal

preservatives and Anti-bacterial preservatives. Anti-fungal preservatives include compounds such as benzoic and ascorbic acids and their salts etc. where as Antibacterial preservatives include compounds such as quaternary ammonium salts, alcohols, phenols etc.

Antioxidants are included in the pharmaceutical products to prevent decomposition from oxidation. Antioxidants are classified into three sub-groups. The first one is known as true antioxidants, or anti-oxygen, probably inhibit oxidation by reacting with free radicals blocking the chain reaction. The second one consists of reducing agents; these substances have lower redox potentials than the drug or adjuvant which they are to be protected, and are therefore, more readily oxidized. Reducing agents may act also by reacting with free radicals. The third one consists of antioxidant synergists which usually have little antioxidant effect themselves but probably enhance the action of antioxidants in the first group by reacting with heavy metal ions which catalyze oxidation.[5]

Preservative Mechanisms of Action

Unlike antibiotics, which act on specific sites of biosynthetic processes of microorganisms, preservatives act on multiple targets

However, at sub-inhibitory concentrations, preservatives may act on a single target, what can lead to the development of resistance in microorganisms

Preservatives can penetrate the cell envelope of Gram-negative bacteria by three routes:

(1) The hydrophilic pathway, through porins;

(2) The hydrophobic pathway by the lipid bilayers; and

(3) Self-promoting, which involves the displacement of divalent cations that bind adjacent lipopolysaccharide (LPS) molecules, thereby disrupting the structure of the outer membrane and exposing the phospholipid bilayer area.[6]

Preservatives are incompatible with some chemicals are listed below in [Table no. 3][3]

Chemicals	Incompatibility
Ethyl alcohol	In acidic conditions, ethanol solutions may react vigorously with oxidizing materials. Mixtures with alkali may darken in color owing to a reaction with residual amounts of aldehyde.
Ascorbic acid	Incompatible with alkalis, heavy metal ions, especially copper andiron, oxidizing materials, methenamine, phenylephrine hydrochloride, pyrilamine maleate, salicylamide, sodium nitrite, sodiumsalicylate, theobromine salicylate, and picotamide. Additionally, ascorbic acid has been found to interfere with certain colorimetric assays by reducing the intensity of the color produced.
Sodium benzoate	Incompatibilities Incompatible with quaternary compounds, gelatin, ferric salts, calcium salts, and salts of heavy metals, including silver, lead, and mercury.

	Preservative activity may be reduced by interactions with kaolin or nonionic surfactants. Method of Manufacture Prepared by the treatment of benzoic acid with either sodium carbonate or sodium bicarbonate.
Sodium chloride	Incompatibilities Aqueous sodium chloride solutions are corrosive to iron. They also react to form precipitates with silver, lead, and mercury salts. Strong oxidizing agents liberate chlorine from acidified solutions of sodium chloride. The solubility of the antimicrobial preservative methyl parabenis decreased in aqueous sodium chloride solutions and the viscosity of carbomer gels and solutions of hydroxylethylcellulose or hydroxypropyl cellulose is reduced by the addition of sodium chloride.
Methyl paraben	The antimicrobial activity of methylparaben and other parabens is considerably reduced in the presence of nonionic surfactants, suchas polysorbate 80, as a result of micellization. However, propylene glycol (10%) has been shown to potentiate the antimicrobial activity of the parabens in the presence of nonionic surfactants and prevents the interaction between methyl paraben and polysorbate 80. Incompatibilities with other substances, such as bentonite, magnesium trisilicate, talc, tragacanth, sodium alginate, essential oils, sorbitol, and atropine, have been reported. It also reacts with various sugars and related sugar alcohols.

Compatibility

A suitable preservative must be compatible with the chemical compounds of a cosmetic formulation such as surfactants, solvents, dyes, perfumes, and other promotional additives .In this regard, several preservatives will be inactivated by the antagonistic effect of certain cosmetic ingredients. Formaldehyde is influenced by many types of organic compounds, such as surfactants and nonionic proteins, and can lead to undesired side reactions in the formulation.

The antimicrobial activity of certain preservatives, such as parabens, may be altered, in particular, by non-ionic surfactants. On the other hand, the presence of high concentrations of solid minerals (carbonates and silicates, among others) or organic solids (cellulose and starch) causes absorption of preservatives. Talc, for example, decreases the antimicrobial activity of more than 90% of methylparaben.

EDTA is known for its synergy with several chemical preservatives; it disrupts the external lipid layer of bacteria and increases the penetration of other antimicrobial compounds into the cell. Physical compatibility is also important. The addition of a preservative can influencethe appearance of the cosmetic product and, for this reason, must be tasteless, odorless, and colorless. The type of container used to package a cosmetic product will influence the concentration and activity of preservatives. Generally, lipophilic preservatives are associated with a greater risk of absorption by containers. Some containers are not compatible with

certain preservatives, such as nylon with parabens or polyethylene with certain phenolic compounds, mercurial, and benzoates.[6]

Stability

Several factors may influence the stability of preservatives such as solubility and partition in oil/water (O/W) or water/oil (W/O) emulsions, formulation pH, and temperature during use, and the volatility of the preservative. A good preservative must have a good O/W partition coefficient, since this will allow enhancing its activity in the aqueous phase of the formula. In O/W emulsions, lipophilic preservatives, such as parabens, may be distributed in the lipid phase, and the product actually becomes unpreserved. Additionally, the distribution of preservatives in stacked products can compromise in situ efficiencies.

Thus, pH is an important parameter that can influence the stability of preservatives, either by provoking their decomposition or by modifying their conservative activity.[6]

Selection of Appropriate Preservatives

Successful preservation depends on several factors that affect the antimicrobial efficacy and physicochemical stability of antimicrobial agents. Overall, an ideal preservative should be stable, compatible, effective at low levels, non-toxic, consistent with cosmetic legislation, and non-expensive.[6]

Component		Influence	Effects	Example	References
Solvent	Water	Negative	Main source of contamination		
	Ethanol	Positive	Antimicrobial agent	Ethanol (more than 30%)	[20]
Thickener and emulsifiers based on lipids				Fats, oils, waxes	
	Cationic		Perturbation of cell membranes	Alkylamines, quaternary ammonium compounds	
Surfactants	Anionic	Positive	Or increase in membrane porosity which	Sulfates, sulfonates and carboxylates	[20]
	Amphoteric		Also facilitates penetration of	Alkylamidobetain and alkylamidoglyconate	[20]
	Non ionic		Other antimicrobial agents	Fatty acids monoethanolamides, ethoxylated fatty alcohols and alkyl	

				polyglucosides	
Humectants		Positive	At concentrations of 5 to 10% effectively reduce biologically available water	Sugars (sorbitol), glycerol and glycol	[20]
Gelling agents		Positive	Antimicrobial agent and reduction of biologically available water	Polyacrylic acids and hydroxypropyl methyl cellulose	[20,172]
Emollients		Negative	Promote the growth of microorganisms	Silicon derivatives, proteins (milk proteins and albumin hydrozylate)	[20]
Plant extracts and mineral raw materials		Positive or negative	Positive: polyphenols can exert antibacterial effect, Negative: source of contamination especially for spores, mycotoxins and Clostridium	Melissa officinalis extract, rosmarinic acid and phenylethyl alcohol	[20,100]

Safety

- A great part of preservatives have a low molecular weight, and thus can cause reactions of intolerance during the use of cosmetics. In general, the cosmetic industry has a major concern in finding effective and non-toxic substances. Additionally, the safety factors and risks associated with the handling of antibacterial agents during manufacture must be considered. However, sometimes the manufacturers do not respect the allowed concentrations of preservatives. Examples of these situations include the recovery of 24 cosmetic products because they contained methylisothiazolinone (0.025–0.36%), methyldibromo glutaronitrile, triclosan (0.4%), and benzalkonium chloride (1%), these concentrations being above the limits authorized by European Regulation 1223/2009. In another situation, 15 cosmetic products were recalled due to the presence of methyldibromo glutaronitrile, a preservative forbidden in cosmetics. Another product contained benzalkonium chloride at a concentration 10-fold higher than the maximum allowed. Moreover, 32 cosmetic products were recalled because they contained formaldehyde (0.3–25%) in concentrations above the established limits.[6]
- Surfactants in low concentrations potentiate the activity of such preservatives by lowering the interfacial tension at microbial surface and hence facilitate the adsorption of preservative molecules on the surface of the cells. At high concentrations, they solubilize the preservatives resulting in reduction in the concentration of free preservatives available to react with microorganisms. However, nonionic surfactants form micelles at very low concentrations. For this reason, being used either as emulsifiers or solubilizers, nonionic

surfactants are always present at concentrations above their critical micelle concentration. Loss of preservative activity, particularly the phenolic preservatives such as the parabens due to solubilization may be anticipated. It has been reported that the macromolecules without surface active properties also reduce the efficacy of preservatives. For instance, polyvinylpyrroridone used antimicrobials found in commercial polyethylene glycols, methyl. cellulose, carboxymethyl cellulose or tragacanth. This degree of binding, although of a far lesser order than that which occurs with non-ionic surfactants, might lower some condition which necessitate the addition of a supplementary amount of preservative. Natural products are difficult to preserve because they provide such a good nutrient media for the growth of microorganisms. Some common sequestering agents including EDTA and its salts, citric acid, and tripolyphosphates, which form soluble complexes with metal ions, are introduced to improve the activity of antimicrobial agents and to avoid discoloration of the product.[1]

- Typically, contact dermatitis (CD) is an eczematous reaction, usually to a substance applied to the surface of the skin. CD affects approximately 20% of the population in the United States. Pathophysiologically, CD can be divided into allergic contact dermatitis reactions (affects 6% of the general population) and irritant contact dermatitis reactions. The Scientific Committee on Consumer Safety recommended new lower concentration limits for propylparaben and butylparaben, which it found to have "a low endocrine-modifying potential". The European authorities have continuously updated the use of preservatives. The French National Agency of Medicine and Health Products Safety, has banned the manufacture, import, export, and marketing of cosmetic products containing chloroacetamide. The use of preservatives can induce undesirable effects for consumers, which can appear either after first contact or after years of cosmetic use. These effects range from mild irritation of the skin to estrogenic activity and, in the latest, it can be related with the mammary tumors inducing.[6]
- Parabens refer to a group of esters of 4-hydroxybenzoic acid commonly used as preservatives in foods, pharmaceuticals, and cosmetics whose widespread use dates back to 1923.Other preservatives include formaldehyde releasers or phenoxyethanol, as well as chelating agents such as EDTA, which improve the stability of these cosmetic products when exposed to air. In 2005, the Scientific Committee on Consumer Products (now known as the Scientific Committee for Consumer Safety) in Europe stated that methylparaben and ethylparaben can be used at levels up to 0.4% in products.[2]

CONCLUSION

The awareness and need for cosmetics with herbs in on the rise, as it is strongly believed that these products are safe and free from side effects. It is seen that many products making natural claims are still based extensively on synthetic functional ingredients to which natural raw materials or extracts are added.

It is suggested that shampoo manufacturers / formulators must refer and follow the specifications given by Bureau of Indian Standards in SI 4011:1997 "Methods of test for safety evaluation of cosmetic,'' second revision and also refer the "General Guidelines for Herbal Cosmetics'' by Bureau of Indian Standards.[18]

Shampoo surfactant technology is changing rapidly at present, as the result of consumer needs for more environmentally sustainable products, for 'sulphate-free' products and for products with much more interesting rheological profiles.[19]

It helps to researcher to seek out area of problems where easy to solution concerning hairs and also provides selection best polymers utilized for treating the hairs problems with cost effectiveness and its better stability with selecting proper preservatives.[20]

Indeed, the challenge of cosmetic technology is to develop new strategies and techniques for the formulation of cosmetic products consisting mainly of natural origin ingredients, lowering the associate costs, and meeting the consumer requests.[10]

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