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Review Article

Shampoo, conditioner and hair washing

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ABSTRACT

Modern shampoos are much more than just cleansing agents. With rising demands for new milder and 'greener' products, the developments in the field of shampoo and conditioners are moving at a faster pace than ever before. Soaps were initially used to clean scalp but are not recommended for hair cleansing because they leave behind a soap scum when mixed with hard water that is difficult to rinse from the hair and scalp. There are different types of shampoos. Besides "normal" cleaning shampoo, there are "specific" shampoos that have additional ingredients targeting some hair problems. Dermatologists most frequently prescribe shampoos but little is taught in medical schools about the hair cosmetics. Most of the prescriptions are based only on the treatment of the scalp and usually disregards the hair fibre health. Hence it is imperative for dermatologists to known about the mechanism of shampoos, different surfactants and where to choose which shampoo.

Keywords: Shampoo, Conditioner, Hair, Sulfates, Hair treatment

INTRODUCTION

Shampoos are liquid cleansers and the word "shampoo" is derived from the Hindi word meaning "to massage". Shampoos are intended to rid the hair of sebum, sweat, desquamated cells, styling products, and environmental dirt. It is desirable that whatever may the disease or scalp condition be, the shampoo must preserve the softness, health and shine of the hair shaft. Shampoos are not only scalp cleaners, because they also act on the hair shaft.[1] Unfortunately, a thoroughly cleaned hair, which is harsh, rough, dull, and prone to get tangled, is not well accepted by the consumer.

CONTENTS

Shampoo usually contains a mix of primary and secondary surfactants for cleaning, viscosity builders, solvents, conditioning agents, pH adjusters and other components such as fragrance, colour for commercial appeal.[2] Sometimes they contain special additives like sunscreen (Table 1).

Table 1: Contents in a shampoo and their examples.

Category	Examples
Surfactants	Sodium lauryl sulfate, ammonium lauryl sulfate, ammonium laureth sulfate, alpha olefin sulfonate
Thickeners	Electrolytes, cellulose derivatives, natural gums
Sequestering agents	EDTA
Others (for product appeal)	Fragrance, dyes, menthol, perfume oils, liquid crystal concentrate

Continued.

Category	Examples
Additives	Viscosity control agents(polyacrylate), foam stabilizers, dispersing agents
Humectant	Propylene glycol, polyethylene glycol, glycerin, sorbitol
Moisturizers	Alkanolamides, natural oils
Preservatives	Parabens
UV absorbers	Benzophenones
Buffers	Sodium citrate
Anti-dandruff agents	Selenium disulfide, zinc pyrithione, ciclopirox olamine, ketoconazole, piroctone olamine

Surfactants

Surface-active ingredients, or surfactants, facilitate the removal of dirt by reducing surface tension between water and dirt. Various surfactants are used in shampoos. Depending upon the electric charge of the polar extremity, surfactants can be classified as anionic, cationic, amphoteric and non-ionic surfactants. The main cleansers are anionic.

Anionic: Anionic surfactants are the primary surfactant and are characterized by a negatively-charged hydrophilic polar group. Anionic surfactants are very good in removing sebum and dirt; however, they increase of the electrical negative charges on the hair surface, leading to frizz and friction. The soap, which is also an anionic detergent, in contact with water, leaves an alkaline residue that precipitates in the form of calcium salts, which accumulate in the hair strands. Such effects do not happen with the new anionic surfactants (alquil sulfates, alquil ether sulfates), which are smooth cleansers and cosmetically superior.

Lauryl sulfates: Examples of lauryl sulfate detergents include: sodium lauryl sulfate, triethanolamine lauryl sulfate, and ammonium lauryl sulfate. They work well in both hard and soft water, produce rich foam, and are easily rinsed but harsh on hair.

Laureth sulfates: They provide excellent cleansing, but leave the hair in good condition and produce abundant foam. Examples are sodium laureth sulfate (SLS), triethanolamine laureth sulfate, and ammonium laureth sulfate. SLS is readily biodegradable which can be derived from both synthetic and naturally occurring sources like palm kernel oil, petrolatum, and coconut oil.

Sarcosines: Do not remove sebum well from the hair. However, they are excellent conditioners. Sarcosines are used in conditioning shampoos and dry hair shampoos. They include lauryl sarcosine and sodium lauryl sarcosinate.

Sulfosuccinates: They are a class of strong detergents useful for oily hair. Examples are disodium oleamine sulfosuccinate and sodium dioctyl sulfosuccinate.

Cationic: Cationic surfactants are quaternary ammonium compounds with a positively charged hydrophilic end and are used mainly as conditioners. They balance hair negative charges after washing thereby reducing frizz. Due to their chemical nature, they also have bacteriostatic properties.[3] They are efficient softeners and substantive for hair because of the hair's low isoelectric point (pH-2.15). Due to its high level of cysteine, damaged hair contains a higher number of negatively-charged acid groups and thus absorbs more quaternary ammonium compounds than intact hair, making them an ideal conditioning agent for damaged hair.[4] Although they make hair easier to comb and manage, they are poor cleansers and do not lather well. They are also potentially strong irritants, and are thus only used with less irritating non-ionic surfactants in shampoos designed for chemically-treated or very dry hair. They cannot be combined with other anionic detergents and are primarily used in shampoos where minimal cleansing is desired, such as in daily shampoos designed for permanently dyed or chemically bleached hair. Here minimal sebum removal is desired e. g., trimethyl alkylammonium chlorides, benzalkonium chloride or bromide

Amphoteric (zwitterionic): They are anionic or cationic surfactants in alkaline or acid solutions respectively. At low pH values they behave as cationic agents and at higher pH values as anionic agents. They are very mild, with good foaming, wetting and detergent properties, making it ideal for chemically treated hair. Hence, they are used to reduce the electric effects of anionic surfactants. Amphoteric surfactants form complexes with anionic surfactants and reduce their tendency to attach to proteins. They are non-irritating to the eyes (as in baby shampoos). They include the betaines, sultaines, and imidazolinium derivatives e. g., alkyl iminodipropionate and (amido) betaines, cocamidopropyl betaine and sodium lauraminopropionate.

Cocamidopropyl betaine: It is an amphoteric surfactant which is frequently used in cosmetic products especially baby shampoos. Cases of contact allergy due to it are reported by Groot et al.[5]

Non-ionic: They are often plant derived- glucosides, citrates, sulfosuccinates and hydrolysates proteins and do not exhibit electric charge in aqueous solution. They can be formulated within a wide range of pH values and do not cause much irritation, and still have a cleansing effect but only with a small amount of foam. They do not possess a charged polar group and are hence compatible

with all other surfactants. They make good cleansers with dispersion and emulsification properties. They serve to enhance tolerability in very mild cleansers such as baby shampoos, in combining with amphoteric surfactants. Examples of nonionic surfactants are fatty alcohol ethoxylates, sorbitan ether esters, and alkanolamides. Many long chain alcohols like fatty alcohols, cetyl alcohol, stearyl alcohol, and cetostearyl alcohol, and oleyl alcohol exhibit some surfactant property. Some sugar esters that area biodegradable like lauryl glucoside, coco glucoside, decyl glucoside, and caprylyl/capryl glucoside are also found in many shampoos.

Natural detergents: Natural surfactants come from plants such as sarsaparilla, soapwort, soap bark, and ivy agave. These have excellent lathering capabilities, but are poor cleansers and hence combined with other synthetic detergents.

Sequestering agent: The function of sequestering agents is to chelate magnesium and calcium ions preventing the formation of insoluble soaps, known as 'scum' which forms a film on hair surface and scalp which can cause dull hair, seborrheic dermatitis and scalp pruritus, as and when bar soap is used for cleansing the hair.

Preservatives like organic acids and their derivatives, e.g., parahydroxybenzoic acid ester, salicylic and sorbic acid; methylparaben are used to avoid bacterial growth.

Foaming agents promote foaming of the shampoo.

pH adjusters and buffers: Damaged hair can swell with alkaline detergents. Hence, when formulating suitable shampoos for such hair, an acidic pH adjustment is done. The substances used include citric acid, lactic acid and phosphate buffers.

Additives: UV absorbers to protect oxidation-sensitive oils or dyes against light (benzophenone derivatives), anti-dandruff agents, antioxidants to protect oxidation-sensitive substances (ascorbic acid, tocopherols, butyl hydroxyanisole), fragrances, moisturizers and humectants (propylene glycol, polyethylene glycol, glycerine, sorbitol, natural oils, fatty acid esters, and alkanolamides.

MECHANISM OF ACTION

Scalp gets accumulated with residue that does not dissolve with water. To remove this, surfactant form micelle. They have a hydrophobic end which bind with the fat and a hydrophilic end that bind with water. This micelle can be rinsed with water easily. Hair fibres are negatively charged which will repel the negative charge of micelle. However, the result is an increase of the pre-existing negativity of the strands increasing the repulsion between the strands due to excessive static electricity. Cationic, amphoteric and non-ionic surfactants are added to some shampoos to reduce the effects caused by the anionic surfactants.[6] Although the cationic agents try to neutralize this effect, there is the interference of the shampoo pH, which can increase the static electricity.[7] Topically applied surfactant solutions can also swell corneocyte proteins, which results in the removal of natural moisturizing factors and enhances penetration of irritant chemicals into the viable epidermis.[8]

HAIR KERATIN AND pH OF SHAMPOO

The scalp pH is 5.5 and the hair shaft pH is 3.67. The pH at which a protein or particle does not migrate (moment of charge neutrality) in an electric field is the isoelectric point (3.67 pH). The pH of which a protein or particle has an equivalent number of total positive and negative charges is called the isoionic point (pH-5.6). A protein that is in a pH region below its isoelectric point will be positively charged, and vice versa. Any product applied on hair that has pH higher than 3.67 may increase the negative electrical net charge of the hair fibre surface and, therefore, increase the friction between the fibres increasing the damage to the A-layer and the epicuticle of the hair fibre.[6,9]

Rinsing hair with water (pH-7), increases negativity, creates frizz. Water penetrates the scales that open, hydrating the strand and breaking the hydrogen bonds of the keratin molecule. Keratin is a spiral molecule that keeps itself in that shape due to chemical bonds. To tackle the effects of shampoo with a high pH, it is necessary to choose a shampoo with a pH lower than 5.5 by using a 'pH balancing' shampoo with the addition of an acidic substance such as glycolic acid, adding cationic ingredients to shampoo or by using a conditioner after shampoo. A conditioner of low-pH neutralizes electric charge, reduce the frizz effect and close cuticular cells.[10] A high pH shampoo, will have a positive effect in oily and thin hair, as it can add volume to the hair post shampoo because of the increase in static electricity. However, a pH higher than 5.5 may cause irritation of the scalp.

TYPES

Shampoo with conditioner (2 in 1 shampoo)

'2-in-1' shampoos means that conditioning agents incorporated into shampoos (conditioning shampoos). Amphoteric detergents are commonly found in 2-in-1 cleansers.

Baby shampoo

Baby shampoos are mild cleansers and are non-irritating to the eyes. It usually contains ingredients that are harmless to the scalp, hair, as well as less irritating to the eyes. Most of the paediatric shampoos focus on "no tears" concept rather than conditioning the hair fibre. They mostly have a higher pH, a pH closer to the tear physiological pH. These shampoos use detergents from the amphoteric group, such as the betaines.[11] The

detergent prevent stinging, but can still cause eye damage if the baby shampoo is accidentally introduced into the eye, but the injury is not painful. Hence it is recommended that adults especially with dyed hairs should not use paediatric shampoos to cleanse their hair.[10]

Sulphate free shampoo

Sulfate-free shampoos are cleansers without anionic surfactants and switched with surfactants of less detergency. Their cleansing action is relatively milder and it focuses more on hair fibre health.

Dry shampoo

They are used without water. The alcohol or starch in the product soaks excess oil and grease on the hair. It is available as powder and aerosol spray.

Shampoo bars

It looks like regular soap but is usually infused with oils and lathers well. Because they eliminate water in the final product, the preservatives amount is relatively less.

All-natural shampoo

"Herbal", "botanical", "organic" are all labels used for natural shampoo. Herbal shampoos mainly use soapnut/reetha, amla, and dried pods of sheekakai, that have been traditionally used in India for centuries to wash hair. Due to high amount of saponins, reetha and sheekakai ingredients produce a rich lather when shaken with water.[12] Reetha is said to have antimicrobial properties. Furthermore, it makes hair shine, restoring the natural hair texture.[13] Sheekakai retain natural oils of hair, reduces hair loss, adds volume, gives hair strength, and is a powerful antidandruff and conditioning agent.[13] Other common herbal ingredients used for shampoo formulation are: *Azadirachta indica* (Neem), *Ocimum sanctum* (Tulsi), aloe vera (aloe), *Terminalia chebula* (harda, haritaki) and *Terminalia bellirica* (bahera). Though "natural"/ "herbal" shampoos claim themselves to be fully natural, most of them contain chemical surfactants in addition to the 'natural' products.

Everyday shampoo

They generally contain mild detergents. They typically do not incorporate the conditioners found in the dry or damaged hair shampoos, and an instant conditioner can be used in combination with these products.

Professional shampoo

There are shampoos those intended for hair washing prior to cutting and those intended to precede or follow a chemical process. Though most of the salon shampoos have similar formulation as that of over-the-counter-varieties, some of them serve specific function: anionic, acidic professional shampoos used after bleaching to neutralize residual alkalinity and prepare the hair for subsequent dyeing; cationic, acidic shampoos used after colouring e. g., 'colour revival shampoos'.

Colour protect shampoo

Cationic detergents, also known as quaternaries or quaternary ammonium compounds or quats, neutralize static electricity based on the negative (anionic) charge of processed or damaged hair thus improving manageability. These qualities make them an excellent cleanser of choice in patients with permanently dyed or permanently waved hair.

Medicated shampoos

They include shampoos that are intended for certain conditions like seborrheic dermatitis, scalp psoriasis etc.

Shampoos for different types of hair

For normal hair/chemically naive hair, shampoos containing SDS (named also sodium lauryl sulfate) as the main detergent, provides a good cleaning of the scalp. For dry hair/chemically treated hair, amphoteric and anionic detergents are preferred. Anionic surfactants may have a positive effect in extremely greasy and thin straight hair, of adding volume to the hair. Medicated shampoo use should be limited to scalp especially in those with dry damaged hair.

NEWER CONCEPTS AND TRENDS

Lo-poo shampoo

Low poo shampoos are sulfate-free shampoos. This trend is becoming highly popular and is of use in those with dry, damaged and chemically treated hair.

No-poo method

It refers to the avoidance of commercial shampoos and use other methods of cleansing the hair, such as baking soda, apple cider vinegar [ACV] or treating the scalp with tea tree oil, or simply rinsing the hair with water. They claim to have healthier hair, retain natural oils, and less exposure to chemicals in shampoo.

"Co-washing" or "conditioner washing" is a method of cleansing the hair with only conditioner.[14] Here, a nonionic surfactant, such as cetyl alcohol, is used as the main surfactant or may also contain cationic surfactants and oils.[15] They claim to prevent hair breakage and reduce the overproduction of sebum and dryness that follow the deep cleansing. But there are no scientific data to prove it. Silicones, mineral oil or petrolatum products are not preferred as it may cause a build-up. However, co-washing doesn't provide any cleansing to scalp.

Hair-care market is developing with new formulations coming in every day. Specific shampoos for each indication are in market. Shampoos are also currently being developed that are enriched with amino acids.

SIDE EFFECTS

A simple process like shampooing can be associated with many side effects. It is important for a clinician to know the possible adverse effects of shampoo and adopt measures to take care of those.

Hair damage

Surface lipids within the 18-methyl eicosanoic acid (18-MEA) lipid layers of hair are removed during shampooing.[16] Though internal lipids stay unaffected initially, repeated shampooing can affect them.

Acute felting

Damaged hair or hair that has undergone certain chemical treatments is particularly prone to sudden entanglement. The raised cuticle cells and electric charge of the damaged hair can lead the hair become tangled. Certain methods like use of a conditioner, hair serum, smooth combing and detangling of hair and use of the prescribed shampoo can reduce the above-mentioned effect.

Environmental safety

Certain chemicals like silicones are not biodegradable and hence found to accumulate in environment and water bodies and adversely affect the ecosystem.

Skin allergies

Given that shampoos are diluted by water, have a short contact time, and are rinsed off, the risk of sensitization is highly unlikely.[7] Nevertheless, in patients who are already sensitized, exposure could trigger eczema. Common allergens in shampoos are: Cocamidopropyl betaine, methyl chloroisothiazolinone, formaldehyde-releasing preservatives, propylene glycol, vitamin E (tocopherol), parabens and benzophenones.[18,19]

CONDITIONERS

Conditioners prevent static electricity, improve shine and increase hair protection. Conditioning agents mainly belong to four categories: film formers (polymers), protein containing (hydrolysed proteins), cationic detergents (quarternary ammonium compounds), silicone (dimethicone, ciclomethicone). Conditioners seal the cuticular gap which gets lifted after the shampoo wash. This prevents exposure of cortex to environmental damage.

The film-forming conditioners are used as coating fibres with a thin polymer layer. Protein-derived substances are popular conditioners for damaged hair, as they can temporarily mend split ends (trichoptilosis). Protein is attracted to the keratin, and holds the cortex fragments together until the next shampooing occurs. Protein that penetrates the hair shaft during conditioning will exit the hair shaft during the next shampoo, requiring reapplication. Proteins can also coat the hair shaft, temporarily increasing its thickness ("hair- thickening" conditioners).[20] Silicones add lubricity, reduce friction, aid detangling and combing, add shine and act as anti-frizz agents. Silicones are classified as water-soluble and non-soluble. Dimethicone, the most widely used silicone and the main ingredient of the two-in-one shampoos.

Types of conditioners

Rinses or instant conditioners: They are applied to washed hair especially post shampoo, left on for few minutes, and rinsed off. They improve the combability of the hair.

Leave on conditioner: They are applied to towel-dried hair. They basically contain cationic surfactants like polyquaternarium-10, cetrimonium chloride and stearalkonium chloride; long- chain fatty alcohol, lipid components (cetyl alcohol, stearyl alcohol), silicones such as dimethicone etc. applied to washed and dried hair, and remain on till the next shampoo. They smoothen down the cuticle and protect the hair from weathering.

Leave in conditioner: These are products used for curly or unmanageable hair prior to styling or blow drying and on hair that has been damaged by chemical processes. They are designed to stay on the hair shaft until removal by the next shampooing. These film-forming conditioners apply a thin layer of polymer, such as polyvinylpyrrolidone (PVP), over the hair shaft which fills hair-shaft defects, creating a smooth surface while eliminating static electricity. This coating gives a false 'thickening' of hair shaft.

Deep conditioner: It is popular as parlour procedure which is applied and left on for 20-30 minutes, with or without a steamer and then rinsed off. This contains conditioning agents and proteins. The extended application time and heat causes hair-shaft swelling and allows increased conditioner penetration.

OILS

Use of oil on scalp is highly prevalent among certain areas of the country. Most of the times, dermatologist forbid the use of oils on scalp in view of conditions like seborrheic dermatitis and folliculitis. However, oils play a role in protecting hair shaft from damage. Certain oils can penetrate the hair and reduce the amount of water absorbed in the hair, leading to a lowering of swelling.[21]

The oil can fill the gap between the cuticle cells and prevent the penetration of the aggressive substances such as surfactants into the follicle. Among coconut, sunflower and mineral oil, coconut oil was the only oil found to reduce the protein loss for both undamaged and damaged hair when used as a pre-wash and post-wash grooming product.[22] Coconut oil, because of its low molecular weight and straight linear chain, is able to penetrate inside the hair shaft. The mineral oil and the sunflower oil may have a film effect and adsorb to the surface of the cuticle enhancing shine and diminishing friction. Mineral oil has no affinity to hair's proteins and is not able to diffuse in the fibre.[23]

Morrocan argan oil (Argania spinosa kernel oil) has become very popular as an ingredient in hair cosmetics. The oil is rich in tocopherols and polyphenols which are powerful antioxidants. The two main fatty acids found in Argania spinosa kernel oil are oleic acid (46-48%) and linoleic acid (31-35%), a monounsaturated and di-unsaturated fatty acid, respectively.[24] It was also found that Argania spinosa kernel oil in hair care formulation statistically reduced the protein loss when compared to basic conditioner components in coloured hair.[25]

CONCLUSION

Shampoos form an inevitable part of everyone's hair care routine whether they have a scalp or hair disease. This article aims to enlighten dermatologists about hair washing, shampoos and conditioners, their basic action and effects on hair and scalp thereby helping them to choose the ideal shampoo for patients depending on their scalp/hair disease without compromising their hair shaft health.

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