Shampoos

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The term "shampoo" comes from the Hindi cāpna, to press or knead. By extension it has come to mean the action of washing the hair and scalp.

Shampoos today are the mainstay of the hair-care and cleansing market. They represent 50% of the total units sold in the hair products sector, which demonstrates their considerable importance in terms of the market and of social and individual habits.

Shampooing is undeniably the most common hair treatment. But what is expected of a shampoo? It may seem obvious to say that shampoos are products aimed at cleansing the hair and scalp. This is, however, too narrow a definition if one considers the diversity of qualities demanded of a good shampoo. If the prime function is indeed to fulfill an elementary hygienic need, the expectations of today's consumer go far beyond this commonplace function, which even tends to be disregarded. First of all, a cosmetic benefit is expected—that is, restoration of the hair's appearance, which must be not only clean but also beautiful: glossy, soft, airy, "free" without "flyaway," easy to comb and dress, with body, bounce, and volume. The consumer's expectations are numerous regardless of hair type and condition. But the formulator has to take into account all the possible variations associated with hair (dry, greasy, limpid, permed, dyed, short or long, crisp, relaxed, Caucasian, Negroid, Oriental); specific problems relating to the physiologic and superficial condition of the scalp, such as seborrhea and dandruff; and season, age, lifestyle, care habits (frequency of shampooing, use of a conditioner), new hairstyle techniques and dressings, and the whims of consumers.

In addition to these different states of hair, individual preferences for a certain texture, fragrance, foaming, and use characteristics come into play, as do the ease of rinsing and wet combing, the rapidity of drying, and so forth.

The huge amount of variables to be covered, some of them contradictory and hard to reconcile, makes adequate product formulation a difficult task and entails continuous investment in research, as is reflected by the large number of patents appearing in this field.

A vast range of products must be available to consumers to meet their diverse needs and circumstances—which, on an individual level, change over time and favor frequent product switching, experimenting, and the search for original performance.

Cleansing the Hair, or Detergency

The substrate to be cleansed amounts to a large surface area—100,000 to 150,000 individual hairs—which adds up to 4 to 8 sq m for an average female head of hair, representing 50 to 100 times the surface area of the scalp underneath. Cleansing is no small endeavor: think of the mass of water employed in rinsing to realize what a huge task is performed by a dose of shampoo.

The substrate to be cleansed is a hard hydrophobic protein that would not easily retain dust were it not for the presence of sebum, which is the sticking point. Secreted by the sebaceous appendage and flowing into the hair follicle, sebum is a natural lubricating oil. It contributes to luster but has one major drawback: it entraps and glues all that comes near it—environmental dust, pollutants, smoke, grease, keratinous debris off the scalp, organic or inorganic compounds carried by sweat, or cosmetics, such as hair sprays, styling aids, and tonics. What is more, the sebum's chemical composition evolves over time as a result of incubation and microbial enzymatic activity, leading to partial transformation of entrapped material.

The soil varies a great deal from one individual to another. The mixture depends on hairdressing habits, lifestyle, nutrition, environmental and systemic factors, and scalp and hair shaft condition. Moreover, cleansing may be hindered by the condition of the substrate—an uneven hair cuticle, a porous fiber, or a scalp with varying degrees of scaling. Whatever the soil and the conditions, the main point is to get the grease, in which soil is trapped, free from the hair. Detergency consists of weakening the physicochemical adhesive force that binds it to hair, taking it up and transferring it into aqueous rinses, and dispersing it while avoiding redeposition on the fiber. This physicochemically complex operation entails a number of interactions—water/air, lipids/water, solids (including hair)/water—is carried out by surfactant (Fig 1).

Surfactants Used in Shampoos

Surfactants are compounds that have a dual affinity. They are both lipophilic and hydrophilic. They are lipophilic by their hydrocarbon (mostly 12-14 carbon)
Arrangement of surfactants in water (Micellization)

**MICELLIZATION**

The hydrophilic polar head of anionics is negatively charged. The first anionic detergent used was soap, which is a salt of a fatty acid obtained by alkali treatment of vegetable or animal fats or oils. Soaps have two main drawbacks: first, they tend to hydrolyze in water, releasing alkali that is detrimental to both skin and hair shaft; second, in hard water they precipitate into calcium salts that attach to the hair, leading to a dull appearance, brittle feel, and poor disentangling ability. This is why soaps are virtually no longer used and have been replaced by synthetic surfactants; these compounds have a much stronger polarity and are thus free from the shortcomings inherent in soaps.

The anionic surfactants best known and most commonly used are the alkyl sulfates and alkyl ether sulfates, respectively derived from the sulfation of fatty alcohols and polyoxyethylene analogs. They are available as sodium, ammonium, monoethanolamine, or triethanolamine salts (Fig 3). They exhibit remarkable cleaning and foaming properties. Highly water soluble, they enable the formulation of clear shampoos. They have relatively poor cosmetic properties, which can be enhanced or compensated for by appropriate softening additives.

A large variety of other types of anionics may also be used, such as olefin sulfonates and paraffin sulfonates or more expensive, more sophisticated, fine surfactants whose foaming and cleaning properties are a little less efficient but which are milder and more suitable for sensitive hair and scalp: alkyl sulfosuccinates, alkyl ether carboxylates, alkyl isethionates, alkyl sarcosinates, acyl methyltaurates, and acyl peptides (Fig 3).

Combinations are used according to the qualities and cosmetic effect sought, their compatibility with the other additives, and their price.

Cationics

The polar head of cationics has a positive charge (Fig 4). Cationics show high affinity for hair fiber, to which they impart softness and ease of combing while reducing flyaway. The cosmetic characteristics of cationic surfactants and their beneficial effect on hair surface condition make them appropriate for the care of damaged hair.

Cationics are, however, poor cleansing and lathering surfactants, and they may give rise to some redeposition of soil onto the hair shaft. A lack of compatibility with anionic surfactants further limits their potential in shampoo formulations.

Cationics are combined with nonionic surfactants for specific shampoos designed for dyed, bleached, or very dry hair. Their use is widespread in conditioners, of which they are the basic components.

Amphoterics

Amphoterics bear both an anionic and a cationic group. They behave as cationics at lower pH values and as anionics at higher pH values. Therefore, they exhibit properties between those of anionics and cationics.
Figure 3.

Amphoteric complex with anion&, reducing the latter’s tendency to adsorb onto proteins. Having moderate foaming and cleaning properties, amphotericics are generally combined with other surfactants in the formulation of mild shampoos to modulate cleaning efficiency, enhance lathering qualities, and value polymer contribution to hair condition.

The most often used amphotericics are betaines, sulfobetaines, imidazolinium derivatives (eg, Miranol C2M), and alkylaminoacids (eg, Deriphats) (Fig. 5).

Nonionics

In contrast to the above mentioned surfactants, nonionics have no polar head and no electric charge and are therefore compatible with all other categories of surfactant. They are generally considered the mildest of all surfactants. They have good dispersing, emulsifying, and detergent properties, but their use has been restricted because of poor foaming capacity. They serve more as auxiliary cleaning agents. Their high level of tolerance by the skin has found application in their combination with alkyl ether sulfates or amphotericics in the development of very mild shampoos.

The most commonly used nonionics are polyoxyethylene fatty alcohols and polyglycerolated fatty alcohols, polyoxyethylene sorbitol esters (eg, Tweens), and alkyl polyglucosides (ie, sugar derivatives with grafted fatty chains) (Fig 6).

Natural Surfactants

Natural surfactants consist mainly of saponins, which are found in various plant species—for example, soap bark, soapwort, sarsaparilla, and ivy.

The hydrophilic component is a sugar, which makes them similar to nonionics, but their lipophilic moiety, either a steroid or a triterpene, often bears an acidic or basic group. Such is the case with soap bark, whose lipophilic moiety is quillaic acid.

These saponins make a very good lather but have less than average cleansing properties. High concentrations are therefore needed to yield sufficient detergency. At these concentrations, saponins are somewhat
harsh and may even exhibit unfavorable cosmetic characteristics.

As a consequence, natural surfactants are generally combined with or supplemented by synthetic surfactants to ensure good cleansing and satisfactory cosmetic qualities.

**Formulating a Shampoo**

Developing a cleansing system that is not selective, not too detergente, and well suited to scalp and hair while favoring or at least not negatively affecting the cosmetic benefits sought is a delicate challenge requiring compromise.

The variability of the substrate and the duality of the aim need to be addressed. Thus, many problems of compatibility, dosage, and equilibrium have to be solved—to cleanse without causing dryness, to lubricate dry hair while cleansing, to ensure that beauty treatment or other specific treatment also cleans the hair, and to achieve the delicate sequential removal of soil and its replacement by conditioner. This also means, inevitably, that if it is to beautify, cleanse, or specifically treat the hair, even the simplest shampoo formulation has to be composed of a variety of ingredients.

**Basic Shampoo Formulation**

A shampoo comprises a mixture of several surfactants, as a single surfactant can seldom adequately ensure all the aspects of the process and prerequisites of the task.
assigned; cosmetic (conditioning) additives; special care ingredient(s); foam stabilizer(s) or softener(s) or both; texture and pH modulator(s); opacifier(s) or pearlescent(s); chelating agent(s); preservative(s); and perfume and colorant(s).

**CONDITIONING ADDITIVES** These are intended to impart softness and gloss, to reduce flyaway, and to enhance disentangling facility. They are particularly useful in shampoos for dry and damaged hair. Their role in a shampoo is not as effective as that of a separate conditioner or a rinse, because of the many functions a shampoo has to fulfill, the likelihood of incompatibility, or even conflicts resulting in a compromise. They do, however, have a major effect on the feel, appearance, manageability, and esthetic and cosmetic qualities of hair after shampooing.

A great number of ingredients may be introduced, depending on the type of cleansing base and formulation and the objectives. They are mostly fatty ingredients—fatty alcohols, lanolin derivatives, vegetable or mineral oils or waxes, lecithins, essential fatty acid and derivatives, hydrolyzed proteins (keratin, collagen, silk, wheat, soya), and quaternized (cationic) derivatives, silicones, and cationic polymers. Antioxidants, sunscreens, vitamins, and panthenol are also used.

Special mention should be made here of cationic polymers and silicones, both of which have brought about a breakthrough in the approach to conditioning hair. As explained above, cationic surfactants are the preferred agents for smoothing and softening the hair shaft, for reducing friction when combing hair, and for neutralizing static electricity. But they are not compatible with anionic surfactants, which are the major cleansing agents used in shampoos.

Cationic polymers differ from cationic surfactants in that the substantive cationic ends are not attached to a fatty (hydrocarbon) chain but are part of a macromolecular structure either grafted onto the bone of the

Figure 7.
need for combing force and less damage during grooming. Each hair becomes lighter, freer, and more elastic.

Silicones are adaptable polymers: their polysiloxane backbone (Fig 8) may be varied by modification of the molecular weight or attachment of a myriad of different functional groups to yield anything from a fluid to a very viscous oil or wax, to confer various properties, and to meet the various needs of different hair types.

Other Components

FOAM STABILIZERS  Foam is an attribute highly prized by consumers. Psychologically it is associated with the cleaning effect, but it is also an indicator that the cleansing job has been achieved and a significant pleasurable component.

Foaming properties include the onset of the lather; its volume; its softness, texture, and stability; and its removal by rinsing. These properties are brought about mostly by the addition of copra alkanolamides or some amphoteric and polymers.

THICKENERS  Texture and richness are provided by natural gums (karaya, tragacanth), cellulose hydrocolloids (hydroxyethyl, hydroxyethyl, or carboxymethyl celluloses), and carboxyvinlyc polymers (eg, Carbopol). Viscosity is controlled by salts such as sodium or ammonium chloride and hexylene glycol.

PEARLESCENTS OR OPACIFIERS  These are added to change the appearance of shampoos, but they also play a softening role. Long-chain fatty alcohols, sulfates, or ethylene glycol and magnesium distearates are used primarily.

CHELATING AGENTS  These are intended to trap traces of metal salts in order to prevent the formation of insoluble complexes or salts as well as the catalytic degradation of fragrance or colorants. EDTA salts are used mostly.

Figure 8.

Polydimethylsiloxanes

\[ \text{Polydimethylsiloxanes} \]

\[ \text{Cationic silicone} \]

\[ R = (\text{CH}_3)_2\text{-NH-CH}_2\text{-CH}_2\text{-NH}_2 \]

PRESERVATIVES  These are intended to inhibit bacteriologic contamination on storage and until the end of use.

FRAGRANCES AND COLORANTS  These give each shampoo an individual identity and add to its attractiveness.

SPECIAL CARE INGREDIENTS  These are aimed at modifying unesthetic events, such as dandruff or greasy hair, and are most often based on pyridinethione salts, piroctone olamine, sulfur-containing compounds, tars, and essential oils.

Main Types of Shampoo

Shampoos may be marketed as clear or opaque liquids, liquid creams, gels, mousses, or powders (dry shampoos).

Most shampoos are offered in liquid form, which enables easy spreading on a wet scalp while they rapidly generate a generous foam over the whole head of hair.

Cream shampoos are an enriched form of liquid shampoos, thicker and pearlescent, intended to convey the concept of the more intensive conditioning they are designed to provide. They are often packaged in jars or tubes. Mousse shampoos are a sophisticated presentation of liquid shampoo as an aerosol that has the advantage of delivering shampoo as an unctuous mousse, with a very soft feeling when applied.

Dry shampoos are very different. They do not contain surfactants and do not require the use of water. They perform rapid cleaning to “refresh” the look, lightness, and volume of hair between washings. The action takes less time than that of a wet shampoo because it does not necessitate rinsing, drying, and styling—an important consideration for a dense head of hair. Dry shampoos usually are powders available in aerosol form and containing absorbent materials (rice or corn starch) to take up sebum and abrasive materials to shift soil and alkaline agents (borax, sodium carbonate). They are removed by brushing. Of course, this is a superficial transient cleaning, used as an interim measure before the next “water” shampoo.

It is easy to illustrate the various physical aspects that shampoo formulations can take. It is less so to identify the principal categories in terms of composition and performance, as the options vary so greatly. Nevertheless, an attempt to draw up a classification by objectives and cosmetic positioning is given below.

Ordinary Shampoo

This type of shampoo is commonly used by families and is economically priced.

Their goal is to obtain good lather and to cleanse the hair well without excessive detergent action, leaving the hair easy to comb and glossy without fluffiness, at a relatively low cost. These shampoos are generally based
on anionic surfactants such as alkyl sulfates and alkyl ether sulfates. Their distinctive image is usually a natural, plant, or biologic ingredient. Fragrance is important. They have no specific features; they should be versatile, but it is possible to adapt them for different types of hair (dry or greasy) by varying the nature of the surfactant mixture, the amount of surfactants, or the additives. Rather simple shampoos, they have to be agreeable to use with an image of mildness.

**Mild Shampoos**

In most countries, changes in hygiene habits, increased participation in sports, and the use of various styling aids have all resulted in the increasingly frequent use of shampoos. Yet whether frequent use is because of greasy hair, air pollution, sweat generated by physical activity, or cosmetic coating, it is important to avoid excessive detergency. An adequate combination of anionic and amphoteric surfactants is selected to ensure mildness to hair and scalp while the shampoo retains the ability to cleanse hair that may be exposed to soil. Such shampoos are also carefully fine-tuned in their conditioning features to contribute beauty and manageability of hair and at the same time to avoid build-up due to repeated deposits of conditioning agents that would weigh down the hair.

Baby shampoos are the ultimate development of mild shampoos. Their prime requisite is complete tolerance by the tender scalp and eye mucosa of infants. A three-component blend of very mild anionic, amphoteric, and nonionic surfactants is used as a cleansing base to prevent any stinging when it comes into contact with eye.

**Beauty Shampoos**

Beauty shampoos are created to provide excellent qualities in use, mild cleansing, and light and shining hair. The formulation approach is close to that for the mild shampoos, using a mixture of amphoteric and various anionic surfactants (alkyl ether sulfates, sulfosuccinates, alkyl ether carboxylates) and a limited quantity of conditioning additives to enhance hair beauty.

**Conditioning Shampoos**

In addition to good and pleasant foaming and cleansing properties, shampoos in this category should impart marked cosmetic benefits to the hair and alleviate the defects related to certain types of hair. To dry hair they should give softness, easier grooming, and luster. To greasy hair they should impart volume and lightness and reduce weighing down from regreasing. To fine hair they should provide bounce, body, and hold. To damaged hair they should give back smoothness, gloss, and manageability.

Formulating these shampoos demands a more elaborate process than for the other types. The cleaning property must be monitored together with the conditioning effect, ensuring efficient uplift and dispersal of soil, followed by microdeposition of suitable condition enhancers throughout the hair. This can be obtained by a combination of anionics (alkyl sulfates and alkyl ether sulfates) and amphoteric (betaines and imidazolinium derivatives). Cosmetic qualities are contributed, for the most part, by cationic polymers or silicones.

A significant introduction on the market in the 1990s was the “2 in 1” shampoo, combining two operations in one: shampoo and conditioning for all types of hair. The proposal was attractive to the consumer, saving time and money in getting hair clean and replenished and easy to style in one single step. Besides their practical aspects, such shampoos provide protection to hair during further grooming and brushing, and some offer intensive conditioning with vitamin complex/compound adjuncts. Despite their success on the market, however, they represent a compromise: they cannot attain the efficacy and benefits of a conditioner applied after shampooing and devoted entirely to hair care; they also cannot meet the particular needs of various types of hair. They are intended to meet nonspecific requirements.

“Lighter” versions of “2 in 1” shampoos have lately come on the market in the form of transparent products with a lower amount of silicone or none at all for those who feel, or fear, that it may leave the hair heavy or greasy. Also, “3 in 1” formulas are proposed, adding a third function addressing styling aid.

**Special Care Shampoos**

**SPECIFIC TO HAIR TYPE** Shampoos for dyed or permed hair are illustrative of this category. They should not negatively affect color or perm. They are designed to bring back shine to the hair shade and spring to hair waves or curls, as well as to provide softness, suppleness, and easy combing and untangling. Detergency should be well balanced, and the surfactant system should produce the desired quality of foam texture and volume. For that purpose, either an anionic/amphoteric combination or a cationic surfactant base is used. A polymer (cationic, amphoteric, mixed) specific to the hair type is added to provide the conditioning properties.

**SPECIFIC TO SCALP CONDITION** These shampoos are mainly for use on the scalp affected with dandruff or excess greasiness and are designed to alleviate esthetic consequences on hair. They are generally formulated around one or more specific ingredients selected for their effectiveness on these conditions.

The fight against dandruff is aimed at *Pityrosporum ovale*, whose proliferation induces a quasi-inflammatory process reflected by a scaling condition and itching. Specific inhibitors of this yeast must therefore form part...
of the formulation: piroctone olamine, zinc pyrithione, selenium disulfide, and plant or coal tars are the most common active ingredients found in antidandruff shampoos on the market. Regular use of these products, based on a mild cleansing surfactant system, clinically and significantly alleviates the dandruff condition.

For the greasy hair type, anionic shampoos with mild but efficient action are generally preferred because they come in contact with a scalp that is often in poor condition and in need of restoral. Even massage should be kept to a minimum, to prevent abrasive action by the hair on the scalp. Significant results have been obtained with a very mild fluid surfactant mixture based on non-ionic polyglycerol derivatives. Regular use of this type of formulation has been shown to delay the onset of regreasing after shampooing and to progressively improve the scalp condition.

Active topical ingredients able to efficiently control the production of sebum have yet to be identified. Attempts have been made with astringents and hydrophobic ingredients to hinder sebum excretion, spreading, and uptake by hair.

Recent Trends and Changes in Shampoo Formulation

As pointed out earlier, the true role of a shampoo is not merely to cleanse. It has evolved into a product designed to succor and beautify the hair. As such, it should continuously adapt to changing hairstyle trends, habits, needs, and highly versatile consumer demands. In recent years, an increased frequency in shampooing has been noted, along with a trend toward a one-step, single-dose procedure instead of two steps and a double dose to complete the cleaning process. Hairstyle techniques have evolved—for instance, drying naturally, scrunching by hand, and so on. In the early 1990s, a natural, unkempt grunge look was in vogue; in the mid-1990s, a more sophisticated, well-groomed, conditioned look seems to be back. New effects are desired from shampoo: a natural feel, exceptional lightness of styling.

After the success story of “2 in 1,” there is now a growing interest in increased conditioning benefits, individually tailored products that inevitably pose the question of how best to achieve the desired result: choosing between a multifunctional shampoo and a two- (or three-) step program in which the shampoo is closely allied to the subsequent conditioner(s) to gain maximum benefit. Still, multifunctional products—such as those that clean, foam, condition, and protect from sun damage or combat dandruff—have maintained their popularity. Other inclinations are toward mildness, “upscale” professional products for home use, and cost-effectiveness (added value).

These changes in consumer attitudes also reflect the variety of choices with which they are faced and the dramatic improvements brought about in recent years in the formulation and performance of shampoo from several important aspects: properties in use (enhanced foaming, soft and voluptuous lather, pleasantness of use); wet hair after shampooing (easily untangled, hair is soft but not limp, with a freestyle, lightweight impression); and hair after drying (has a pleasant, more natural feel without static, is smooth, and is voluminous yet lightweight).

Such improvements have been accomplished through the increased sophistication of surfactant blends (eg, the introduction of acyl glutamate or glucamine derivatives) and through the availability of new polymers and silicone oils and the skill of their incorporation in new formulations.

Multifunctionalism has also benefited from the availability of novel ingredients. When these are amalgamated into a surfactant blend, however, the issue at stake is to profit from their intrinsic qualities by optimal management and modulation of the interactions that occur. For instance, during the cleansing step, the conditioning agents should remain in suspension in the lather—only subsequently being released during rinsing in microfine droplets onto the hair to smooth it or individualize it or eliminate untoward interactions without interfering with soil dispersal. Such development programs need heavy investment in basic research.

Constant research to find new formulas is at the root of the progress achieved in the composition of cleansing agents and conditioning agents. For example, the recent identification of an essential sphingolipid of the hair’s cuticle cell cement, the synthesis of model ceramides, and the development of a synergic environment by the formulator have enabled the assembly of an innovative shampoo capable of strengthening weakened hair.

Development of a Shampoo

Developing a shampoo is a lengthy, arduous task, punctuated by a series of tests and checkpoints. A battery of tests is used to evaluate the foaming potential, detergency, ease of combing and disentangling, flyaway, springiness, hold, and so on, mostly on calibrated swatches. The ultimate appraisal of a shampoo can be achieved only by on-head trials. The best way to judge the qualities of a shampoo is to compare it with a selected reference shampoo and to apply them both on the same head. Both shampoos are applied simultaneously, using the massaging gesture on each side of the head. Numerous observations are made throughout the operation. Conditioning properties are assessed on wet hair after rinsing and on dried hair after setting. The evolution of hair condition is observed during a period of days after shampooing. The effects of repeated application must also be studied.

When development is completed, the performance of
the new shampoo is further monitored in consumer or salon testing.

Conclusions

There is a very great variety of shampoos from which to choose. This abundance may seem excessive, but in fact no two heads of hair are identical: the type of hair, its history, its treatment and care, and the manner in which it may suffer over the course of a lifetime mean that the needs of each person’s hair are hugely variable.

What is more, users are advised to change and alternate shampoos to avoid a decline in efficacy through habituation. They must be in a position to vary their choice of product.

Today’s shampoo is thus an assembled product, developed with care to meet a precise objective, supported by and benefiting from a permanent state of progress whose end result is to offer everyone the possibility of finding the formulation best suited to hair type, care needs, styling, and the most up-to-date beauty treatment.