Shampoo Formulation: The Basics

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To the uninitiated, formulation of shampoos seems easy! It's a one-phase, water-based surfactant blend that foams! Simple, isn't it? While that may indeed be the case when compared to inherently unstable systems, such as emulsions, many complications may arise that make it a more complex task than may first meet the eye.

Let's start with the basics. Table 1 presents an outline of a typical shampoo.

Getting Started

Now that we have a general overview of the raw materials that go into making a shampoo, let's discuss how to get started. The first thing we need to have is a discussion with our marketing friends, and yes they are (or should be) our friends. We need to determine who will be using the shampoo (men, babies, women, teenagers, etc.), hair type, the packaging, selling price/cost of raw material target and claims that will be made. Once we have this key information we can begin. Please recognize that this short article can only touch the surface of formulation intricacies.

Primary Surfactant

The primary surfactant is the key foaming/cleansing agent in the shampoo. When I first got started formulating shampoos the most popular primary surfactant was SLS (sodium lauryl sulfate). In more recent years it has been replaced by ALS (ammonium lauryl sulfate). I'm not really sure why this change was made, because they both foam and clean the same and their irritation potential is also the same. One possible reason is that ALS shampoos are formulated at a lower pH (to insure we don't get liberation of ammonia), and at this low pH (typically 4.5-6.0) we can add polyquaternium materials that are more substantive to hair at a low pH.

If the target users are babies, then the lauryl sulfates would not be used, but we would then find amphoteric surfactants such as propionates and highly ethoxylated sulfates and carboxylates being used.

Very often, cost plays a major role in the choice of a primary surfactant. Shampoos are, by far, the personal care

Table 1. Shampoo components

Ingredient	Chemistry Options	%(Active)	Function
Primary surfactant	Sulfates, sulfonates, etc.	8-12	Foaming, cleansing
Secondary surfactant	Betaine, sarcosinate, sulfosuccinate, taurate, ether sulfate, glucoside, glutamates, etc.	2-5	Foaming, cleansing, reduce irritation
Viscosity builder	Alkanolamide, "salt", amine oxide, PEG-distearate, etc.	2-3	Control viscosity
Foam booster	Amine oxide, sarcosinate, lactylate, etc.	1-2	Boost foam
Foam stability	Lactylate, "gum", etc.	0.1-1	Stabilize foam
Active (when appropriate)	Zinc pyrithione, salicylic acid, etc.	As per FDA	Antidandruff agent
Suspending agent	Xanthan gum, carbomer, guar, etc.	0.1-1.0	Suspend zinc pyrithione or other materials
Conditioner	Polyquat., silicone, etc.	0.1-1.0	Hair conditioning
Opacifier	EGMS, EGDS, etc.	1.0-2.0	Pearlizer
Preservative	Paraben, etc.	0.1-0.5	Preservation
Fragrance	Fragrance	0.2-1.0	Fragrance
Humectant	Propylene glycol, glycerin, etc.	0.25-1.0	Improve clarity, reduce cloud point, modify viscosity
Color	Approved colorants	As needed	Color
Marketing additives	Vitamins, aloe, antioxidants, UV absorbers, etc.	As "dictated"	Marketing claims
Chelating agent	EDTA salt	0.05-0.15	Color/odor stability, preservative enhancer

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category most sensitive to pricing. This must be kept in mind when choosing all ingredients and the percentages of those ingredients used.

Secondary Surfactant

Very often the secondary surfactant is used to reduce the drying effect of the primary surfactant and modify the aesthetic properties of the shampoo. The most popular secondary surfactant is the ether sulfate analogue of the primary surfactant (ALES). Most often we see the 1 and 2 mole (ethylene oxide) material being used. This is the case because if we chose a more highly ethoxylated version, viscosity building would be a problem. And who wants to buy a water-thin shampoo?

The second most popular secondary surfactant is the betaine. Betaines (most often cocamidopropyl) have a permanently quaternized nitrogen. Because of this they can be a good hair conditioning agent and also complex with the sulfate to build viscosity and improve clarity. While it was believed that they also reduce the irritation of anionics, more recent information (personal communication with Tom Schoenberg of McIntyre Chemical) disputes this and presents data to show quite the opposite is true. Other surfactants such as sulfosuccinates, glutamate and sarcosinates can also have a very beneficial effect but will substantially increase the raw material cost.

Viscosity Builder

Few things are more important to consumers than seeing/using a thick (rich) shampoo. They equate it with value and "concentration." Of course neither necessarily is true.

Alkanolamides have historically been used to increase the viscosity. Experienced shampoo formulators actually know that alkanolamides don't really boost viscosity but only change the position of the salt curve; in other words, less salt is required to build viscosity so it appears that they are boosting the viscosity. Alkanolamides have in recent years come under attack (particularly the DEA amides) and we now see the MEA amides being widely used.

Alkanolamides also improve shampoo clarity by acting as fragrance couplers while also improving foam stability (to a very limited extent when they are used at low use levels) and offering some hair conditioning (due most likely to their water insolubility).

Other more effective viscosity builders include betaines. They complex with the anionics to form an enlarged surfactant micelle that builds viscosity. Additionally, they contribute electrolyte (sodium chloride) that also builds viscosity. Electrolytes are almost always used to build viscosity of shampoos. They are inexpensive and effective. If too much is used, then a low cloud point will be the result.

While sodium chloride is most used, ammonium chloride is also widely used. Ammonium chloride is more efficient than sodium chloride and will also not raise the cloud point. When it is used, like ALS, the pH should be kept below 6.5 to insure that ammonia is not liberated.

Foam Booster/Stabilizer

Consumers equate foaming with cleansing and believe that unless copious amounts of foam are generated, their hair will not be cleaned. This, of course, is not true. All shampoos, even the low foaming baby shampoos, contain more than enough surfactant to clean the grimiest, dirtiest hair. Low levels of secondary surfactant (lactylates, glutamates, taurates, sulfosuccinates, sarcosinates, amine oxides, etc.) can effectively boost foam at low concentrations (1-2%).

It is also crucial to deal with foam stabilizers. Having a voluminous quick breaking foam doesn't make sense. We need to add materials that slow the breakage of the foam bubbles. This can be accomplished by stabilizing the wall of the foam bubble. We have several materials that can play this role for us: gums (cellulose, guar, xanthan, etc., at 0.05-0.15%) and surfactants that form a liquid crystal layer at the bubble wall and thus slow the break and stabilize the foam.

Suspending Agents

When we have the need, based on marketing input, to incorporate materials that must be suspended, we need to incorporate a suspending agent. Most often we will use one or more of the following materials: xanthan gum, carbomer, magnesium aluminum silicate, cellulose gum. The choice will depend on factors such as cost, electrolyte content, pH, the desire for clarity and the feel of foam.

Conditioner

Practically all shampoos sold today will contain a hair conditioner of some type. This is even true for those shampoos that make no conditioning claim whatsoever. Consumers expect and demand that their hair is smooth

and conditioned after shampooing. Conditioning agents are most often quaternary in nature because they possess a negative charge that makes them substantive to hair. They will also have at least one fatty group to improve wet comb and gloss. Most often polyquats are used in shampoos since they are (due to stearic hindrance) more compatible with the primary anionic surfactants. We also see wide usage of silicone and other "fatty" materials to provide conditioning and gloss to the hair. These materials plate out onto the hair during the rinsing process.

Opacifiers

To the consumer, a pearlescent shampoo connotes richness. Often it can be used to hide a cloudy shampoo, turning a negative into a positive. EGDS (glycol distearate) and EGMS (glycol stearate), or a combination of both, are effective in this endeavor. Both crystallize out and form a lovely pearlescense. Be careful to slowly cool the shampoo to maximize this visual effect. Also, the addition of electrolyte can help.

Preservative, Chelating Agent, Color

Every shampoo must be preserved. Very often the primary surfactant will contain some preservative but additional must be added to insure a well protected product. Since shampoos are rinse off products, we have a wide range of preservatives from which to choose. The addition of a salt of EDTA will also help preservation and color stability. Speaking of color stability, we should consider the addition of a UV absorber to insure color stability on the shelf.

Fragrance

No fragrance-free shampoo has ever been successfully marketed, and I doubt one ever will! The fragrance adds to the shampoo experience and is thus a crucial part of the shampoo. It should be presolubilized into some surfactant to insure good product clarity.

Marketing Additives

While it's easy to make fun of the myriad of ingredients that marketing asks (demands?) we incorporate (such as vitamins, minerals, aloe, fruit, nuts, bark, twigs – just kidding here), they are important to the overall picture/image of the shampoo and must be added even though science tells us that they have no function whatsoever.

Conclusion

So you can see that formulating a shampoo offers us lots of opportunity for individual creativity. Just let your minds wander — **but keep in mind the cost of goods!**

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