Technical Bulletin:
Hair Shampoos
The science & art of formulation

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Before going to the bench to develop a shampoo formula, it is helpful to know what is already available in the marketplace and what the current market trends are. Several brand name products dominate the U.S. hair shampoo market. Without disclosing the actual product or manufacturer names, we will take a look at the major ingredients particularly surfactants used to formulate hair shampoo products currently on the market. Tables A and B below illustrate that most shampoo formulators are using a combination of alkyl sulfates and alkyl ether sulfates as the primary surfactants. The ether sulfates generally used in shampoo formulations can have 1 to 3 moles of ethylene oxide. Ether sulfates tend to be slightly milder than the corresponding lauryl sulfates. Ethoxylation may also improve the flash foaming characteristics, solubility and the cloud/freeze points. Lauryl sulfates, on the other hand may give denser foam and build comparatively higher viscosities with salt. A combination and balance of lauryl sulfate and lauryl ether sulfate will provide more desirable properties than either the lauryl or the lauryl ether sulfate alone.

Typically, betaines and amides are the secondary surfactants in shampoo base formulas. Incorporating other surfactants like amphoterics, sulfosuccinates, and ethoxylated sorbitan esters into a shampoo formula can further improve special properties such as mildness and low eye irritation. Cocamidopropyl betaine is a commonly used secondary surfactant in shampoo formulas. It improves a formula's mildness, viscosity, and enhances the foam properties. Cocamide MEA is the amide of choice because it is a foam stabilizer and viscosity builder. Most products in today's market no longer use the DEA version of cocamide. A plain and simple formula for a shampoo is a combination of lauryl sulfate, lauryl ether sulfate, cocamidopropyl betaine and cocamide MEA. A desirable pH of 5–6 is achievable with the addition of citric acid. An optimum viscosity is usually obtainable by incorporating sodium chloride into the formula. A formulator will typically add preservatives, perfumes and dyes to complete the formula. To realize all end use properties and marketing claims, some modifications with other additives may be necessary.

Table A: Surfactants used in commercial hair shampoos currently on the U.S market

Company-brand	Primary surfactants	Secondary surfactants
A-1	ALES, ALS	C-MEA, Betaine
A-2	ALES, ALS	C-MEA, Betaine
A-3	ALES, ALS	C-MEA
A-4	SLES, SLS,	C-MEA
A-5	SLES, SLS,	C-MEA
B-1	ALES, ALS	C-MEA, Betaine
B-2	ALES, ALS	C-MEA, Betaine
B-3	ALES, ALS	C-MEA
B-4	SLES	Sulfosuccinate, Betaine

C-1	SLES	Disodium Cocoamphodiacetate, Sulfosuccinate, C-MIPA
D-1	SLES	C-MIPA, Betaine
E-2	ALES, ALS	
E-1	SLS	Betaine
F-1	SLES, SLS	
G-1	SLES, SLS	L-DEA, Betaine

Table B: Surfactants used in professional or salon hair shampoos currently on the U.S market

Company-brand	**Primary surfactants**	**Secondary surfactants**
A-1	SLES	C-MEA, Betaine
B-1	SLES	C-MIPA Betaine
C-1	SLES	C-DEA, Betaine
D-1	SLES	C-MEA, Betaine
E-1	SLES	Betaine

ALES = Ammonium laureth sulfate, such as Calfoam EA-302
ALS = Ammonium lauryl sulfate, such as Calfoam ALS-30
Betaine = Cocamidopropyl betaine, such as Caltaine C-35
C-MEA = Cocamide MEA, such as Calamide MC
C-MIPA = Cocamide mixed isopropylamine
L-DEA = Lauramide DEA, such as Calamide L
SLES = Sodium laureth sulfate, such as Calfoam ES-302
SLS = Sodium lauryl sulfate, such as Calfoam SLS-30
Sulfosuccinate = Disodium laureth sulfosuccinate, such as Calinate LE

The science and art of formulating hair shampoo:

Hair shampoo formulations need to provide some or many of the following benefits to the consumer.

- Aesthetics
- Cleansing of hair
- Conditioning & antistatic effects
- Moisturizing effects
- Hydrating effects
- Aroma
- Shine and luster
- Body
- Wet and dry combing ease
- Nutrients for hair and scalp
- Split end repair
- Sunscreen / UV absorption
- Color protection
- Antidandruff effects

Before starting the actual formulating work, one should write a detailed product description outlying which of the following three main categories the new product will belong to.

- Economy shampoo
- Premium shampoo
- Specialty shampoo

A sub category can be picked from the following among others:

- Plain shampoo
- Clarifying shampoo
- Neutralizing shampoo
- Conditioning shampoo

- Antidandruff Shampoo
- Baby shampoo
- Shampoo for dyed hair
- Shampoo for dry hair
- Shampoo for oily hair
- Shampoo and body wash in one

Establishing a product's main and sub-categories helps one to write a detailed product description. For example, a premium, plain shampoo's description may look like:

Color	Green
Appearance	Clear, transparent
Odor	Herbal / Floral
Ammonia odor	Product must not give ammonia odor even at high pH
pH	5-6
Viscosity	15,000 – 25,000 cp. Brookfield DV-1 +, spindle # 3
% Solids	20 – 25 %
Special additives	None
Foam height	40 – 50 mm. cylinder shake test. 1 % sol. 10 shakes
Foam stability	Less than 10% loss of foam after 5 minute in cylinder
Flash foaming	High
Product application	Easy to mix and apply to the wet hair
Lather quality	Soft, rich, creamy lather
Feel	Creamy, silky
Cleaning performance	Excellent, must clean grease and dirt
Rinse	Easily rinsable
Wet combing	Easy, no tangling
Dry combing	Easy, smooth
After feel	Silky, soft with volume
Biodegradability	Readily biodegradable
Toxicity	None to low
Flash Point	High (Non Flammable or combustible)
Skin and scalp irritation	None to low
Raw material cost	Not more than 25 C/lb.
Benchmark market	ABC / XYZ shampoo

Below are some of important aspects to consider before a formulator goes to the bench to develop a shampoo product.

Cost: It is important for a formulator to have an idea of the raw material cost of the ingredients that a formula will use as well as the finished product's target cost. High foaming anionic surfactants like alkyl sulfates and alkyl ether sulfates are some of the lowest cost surfactants used in shampoo formulas.

Lather quality and quantity: An experienced formulator knows how to balance the quality and quantity of the lather produced by surfactants. Generally, common shampoo formulas will use a combination of anionic surfactants like alkyl sulfates and alkyl ether sulfates. The ratio of alkyl sulfate to alkyl ether sulfate is important for flash foaming, foam stability, lather quality and flow properties. For higher flash foaming use more alkyl ether sulfates whereas higher ratios of alkyl sulfates will produce creamier foam. Formulators commonly use alkanolamides and betaines for foam enhancement and foam stabilization.

Skin & eye irritation: Today's shampoo formulations use several low irritation surfactants. Formulators frequently use betaines because of their lower cost and their high foam and viscosity building properties. Shampoo formulas often incorporate other amphoterics like sodium

cocoamphoacetate as low irritation additives. Shampoo and body wash formulas can sometimes use sulfosuccinates, alkyl polyglucosides, ethoxylated sorbitan esters, and amino acid based surfactants like sodium cocoyl glycinate to achieve mildness and low irritation characteristics. Highly ethoxylated esters like PEG-120 methyl glucose dioleate are also suggested for lowering the skin and eye irritation of the formula.

Viscosity and flow characteristics: A wide variety of viscosity builders can increase a shampoo formula's viscosity; these include alkanolamides, betaines, amine oxides, polymers, PEG esters, salt etc. Shampoos must have easy, short flow properties out of the bottle, and a consistency that is not stringy. Use of propylene glycol or ethoxylated nonionic surfactants can reduce stringiness of the formula. Another important criterion for viscosity builders is that they should give relatively flat temperature – viscosity and pH – viscosity curves. In other words, reasonable changes in temperature and/or pH must not change the viscosity drastically.

A shampoo formula may contain the following ingredients:

Primary surfactants: Generally speaking, the primary surfactants make the bulk of the shampoo formula. For example, if a shampoo contains 20% total solids, the primary surfactants can contribute up to 10-15% of the total solids of the formula. The rest of the solids come from secondary surfactants, salt and minor ingredients such as preservatives, perfume, dye, and special additives (vitamins, proteins, herbal extracts, etc.). Primary surfactants are high foaming anionic surfactants like sodium lauryl sulfate, ammonium lauryl sulfate, sodium lauryl ether sulfate and ammonium lauryl ether sulfates. Ammonium salts may give somewhat better quality and quantity of lather, slightly better solubility, and better cloud points. On the other hand the ammonium salts may release ammonia at a higher pH. In some cases if one is using high pH soap and it mixes with a shampoo that has ammonium salt, it can release ammonia. Lauryl ether sulfates can have 1, 2, or 3 moles of ethylene oxide. Lower ethylene oxide, ether sulfates tend to build higher viscosity with salt. Table C below illustrates Pilot Chemical Co.'s lauryl sulfates and lauryl ether sulfate products.

Table C: Pilot Chemical Co.'s lauryl sulfates and lauryl ether sulfate products.

Product Name	# of ethylene oxide moles	Sodium or Ammonium	% Active	Contains alcohol
Calfoam ES-301	1	Sodium	26	No
Calfoam ES-302	2	Sodium	27	No
Calfoam ES-303	3	Sodium	28	No
Calfoam ES-603	3	Sodium	59	Yes
Calfoam ES-702	2	Sodium	70	No
Calfoam ES-703	3	Sodium	70	No
Calfoam EA-303	3	Ammonium	26	No
Calfoam EA-603	3	Ammonium	59	Yes
Calfoam EA-703	3	Ammonium	70	No
Calfoam SLS-30	None	Sodium	30	No
Calfoam ALS-30	None	Ammonium	30	No

The two lauryl sulfates, Calfoam SLS-30 (sodium lauryl sulfate) and Calfoam ALS-30 (ammonium lauryl sulfate) are both 30% active. The lauryl ether sulfates come in three different activity levels namely 25-28%, 58-60% and 70%. The 25-28% active materials, both ammonium and the sodium salts (EA are ammonium and ES are sodium salts) are the easiest to work with. They disperse in water very quickly due to their lower activity. However, they contain higher amounts of water than the 58-60, and 70% products, therefore they have higher shipping cost on active basis. The 58-60% active materials contain alcohol and therefore are flammable. The key to working with 58-60% and particularly 70% active material is to warm up the water to 100–120 F, and have the other primary anionic or secondary

amphoteric, sulfosuccinate, APG's etc. in the batch before slowly adding the 58-60% or 70% active ether sulfates.

Secondary surfactants: Betaines and amides are the most commonly used secondary surfactants for economy shampoo formulas. Betaines provide mildness, creamy foam, and good after-feel whereas amides are good foam boosters, foam stabilizers, and viscosity builders. The most common betaine is cocamidopropyl betaine, like Caltaine C-35. Lauramidopropyl betaines and oleamidopropyl betaines may be necessary to achieve special performance properties in a formula. lauramidopropyl may give slightly better foaming than the corresponding Coco version and oleamidopropyl group may build comparatively higher viscosity.

Coco amides are very common in today's shampoo formulas. Cocamide DEA is not the amide of choice in shampoos, Cocamide MEA is more common and in some formulas Cocamide MIPA is used. Cocamide MEA performance properties are similar to DEA amide with the exception that MEA amide is in the form of solid flakes or beads. Cocamide MEA requires heat (65–75 C) to ensure proper melting and batch mixing. Shampoo formulations sometimes use lauric and oleic amides. The lauric amides have somewhat better foam boosting and foam stabilizing properties than their coco counterparts. The oleic version seems to have comparatively better viscosity building properties.

Two broad categories typically classify amides, namely 1:1 and 2:1 amides. Personal care products like shampoos, shower gels, and hand soaps commonly use 1:1 amides. Formulators frequently reference 1:1 amides as super amides. Their primary function is viscosity building and foam stabilization. The 2:1 amides have a considerable amount of free amine in the product. The presence of free amine (diethanolamine, monoethanolamine or mixed isopropanolamine) increases the water solubility and detergency of the product. That is why detergents/industrial cleaners primarily use 2:1 amides. Neutralization of the free amine with a fatty acid in some products can form soap. These products can be a mixture of amide, soap, and free amine and can work as industrial cleaners. A formulator will use this type of amide and dilute it with water to make a ready to use industrial cleaner/degreaser. Table D below list Pilot Chemical Company's amides.

Table D: Pilot Chemical Co.'s amide products.

Product name	**Fatty group**	**Amine**	**1:1 or 2:1 / soap?**
Calamide C	Coco	DEA	1:1
Calamide CW-100	Coco	DEA	2:1
Calamide CWT	Coco	DEA	2:1 with soap
Calamide MC	Coco	MEA	1:1
Calamide O	Coco & Oleic	DEA	1:1
Calamide F	Oleic	DEA	1:1 modified
Calamide L (Developmental)	Lauric	DEA	1:1

Other secondary surfactants:
Shampoo formulations use a wide variety of other secondary surfactants. More common are sodium cocoamphoacetate, Sodium lauroamphoaceate, disodium cocoamphodiacetate, sulfosuccinates, alkyl polyglucosides, and nonionics like PEG-80 sorbitan laurate. One of the major performance benefits of these secondary surfactants is they reduce irritation potential of the formula.

Viscosity builders

Aesthetics are an important part of the marketing plan for a personal care product like shampoo. Most consumers buy products, at least the first time because of its appearance, smell, color and packaging. A nice thick viscosity not only looks appealing, but it also provides the perception of being "concentrated" and more value for the money as compared to a thin, runny product.

We have mentioned the use of amides and betaines as secondary surfactants. Both of these surfactants have viscosity building properties.

Common salt, sodium chloride, in conjunction with betaines and amides serves as an excellent viscosity builder. A formulator should avoid going over the maxima for the salt-viscosity curve. After the maxima, a further increase of salt will decrease the formula's viscosity, in some cases quite sharply.

Polymers both natural and synthetic, can serve as viscosity builders. Shampoo formulas can use cellulose derivatives like hydroxyethyl cellulose to increase viscosity. Other natural gums such as xanthan gum and guar gum are also viscosity builders. High molecular weight acrylate polymers such as carbomers also build viscosity in a formula. Some PEG esters can also function as a viscosity enhancer.

As mentioned before, an important criterion for viscosity builders is that they should give relatively flat temperature – Viscosity and pH – Viscosity curves. In other words, reasonable changes in temperature and/or pH should not drastically change the viscosity.

Conditioning agents

Conditioning shampoo formulas also referred to as 2 in 1 formulas, use conditioning agents such as fatty amines, fatty quats, polydimethyl siloxanes, organo modified siloxanes (amino functional, quaternized silicones), and quaternized polymers (cellulose and guar). Conditioning shampoos using quats and amines must be compatible with anionic surfactants, if the anionics are present in the formula. A formulator must carefully choose the quality and quantity of fatty quat and fatty amine to avoid heavy build up, dulling, and flattening effects in the final product. Silicones are good for shine and luster. Small amounts of silicones will do a good job of light conditioning without heavy build-up. Quaternized polymers like quaternized cellulose also provide a light conditioning effect and impart static control and easy combing, if used in proper amounts.

Special effect additives

Shampoo formulas may also include special additives. A list of some of these products is as follows.

- **Proteins:** Hydrolyzed vegetable protein, hydrolyzed wheat protein, hydrolyzed milk protein, hydrolyzed silk, hydrolyzed collagen, etc.
- **Vitamins:** Panthenol, biotin, vitamin E acetate, vitamin A & D palmitate
- **Moisturizers / Humectants:** Glycerin, propylene glycol, sodium PCA, amino acid based surfactants, hylauronic acid etc.
- **Emollients:** Esters like isopropyl myristate, decyl oleate, $C_{12\text{-}15}$ alkyl benzoate
- **Natural Oils:** Jojoba oil, aloe vera oil, safflower oil, almond oil, etc.
- **Botanicals:** Chamomile, aloe vera, rosemary, hops, etc.
- **Aromatherapy:** Lavender, ylang ylang, patchouli, and other essential oils.

Minor ingredients:
Almost all shampoo formulas include minor ingredients such as preservatives, dyes and perfumes. Common preservatives for shampoo formula include methylchloroisothiazolinone, methylisothiazolinone, DMDM hydantoin, quaternium-15 etc. It is important to run preservative challenge tests to ensure that the product has proper protection against any micro organism attack. Various FD&C dyes such as FD&C Blue #1, FD&C Yellow #5, FD&C yellow #6, FD&C Red #40 are commonly used. There is a wide variety of perfume compounds available on the market. A perfume must be compatible and soluble with the shampoo formula. Some perfumes may need additional solubilizer like polysorbate 20 added to the formula to achieve proper solubility.

Suggested starting formulas:

Economy shampoos

Economy or low ingredient cost shampoos generally use high foaming anionic surfactants that are relatively low cost. These formulas commonly use alkyl sulfates and alkyl ether sulfates as primary surfactants. Either ammonium or sodium salts of the surfactants are fine. The ratio of lauryl sulfate to laureth sulfate does affect the foam and lather profile, viscosity response to the salt, and the stringiness of the final product. A good place to start is a 50:50 blend. From there, one can fine tune to achieve the desirable properties of the final product.

Some surfactant suppliers offer surfactant blends for formulating shampoos. Blends have the advantage of simplicity, less processing time, less chances of blending errors, lower inventories, less warehouse space for storing the raw materials, and so on. For example Pilot Chemical offers a blend, CalBlend ECO-1, which is DEA free, readily biodegradable, and made with surfactants derived from natural renewable vegetable source. Twenty-five percent of this blend when diluted with water and thickened with 2.0% sodium chloride will give a product with a viscosity of 20,000 cp. (Brookfield DV-1 + viscometer, spindle # 3 @ 3 RPM). The addition of preservatives, dye and perfume will complete this economy shampoo that has high viscosity, copious foam and good after feel.

Formulas 1-4 below represent simple & plain shampoo formulations. sodium lauryl sulfate (Calfoam SLS-30) and sodium lauryl ether (2 mole) sulfate (Calfoam ES-2) are the primary, high foaming anionic surfactants. The addition of cocamidopropyl betaine (Caltaine C-35) improves the mildness, creaminess of the foam, and helps build the viscosity of the system. Coconut monoethanolamide acts as a foam booster, foam stabilizer and viscosity builder. The addition of salt and citric acid provides viscosity building and pH balancing, respectively. Modifications to these basic formulas may be necessary in order to achieve desirable specifications and properties of the finished product.

These formulas can incorporate ammonium salts of alkyl sulfates and/or alkyl ether sulfates if the product will not have exposure to high pHs. At higher pH, ammonium salts have the possibility of releasing ammonia.

Formulas 1 and 2 are low cost, low solid formulas whereas formulas 3 and 4 are comparatively higher cost, higher foam and higher viscosity products.

Formula #1: Economy shampoo

D.I. water		Q.S to 100%
Calfoam® ES-302[1]	(Sodium laureth sulfate)	10.0

Calfoam® SLS-30[1]	(Sodium lauryl sulfate)	10.0
Caltaine® C-35[1]	(Cocamidopropyl betaine)	3.0
Calamide® MC[1]	(Cocamide MEA)	1.0
Sodium chloride		3.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.

Procedure: Add water, then Calfoams and the Caltaine in the mixing tank and start mixing and heating. At 70^0 C add Calamide and mix until the batch is uniform, smooth, and homogenous without any lumps or particles. Add sodium chloride, continue mixing. Cool the batch down to 30^0 C. Add the rest of the ingredients in the order listed with continuous mixing.

Appearance	Clear liquid
Viscosity @ 70^0 F	15,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #2: Economy shampoo

D.I. water	Q.S to 100%
CalBlend® ECO-1[1]	25.0
Sodium chloride	2.0
Preservative, perfume, dye	Q.S
Citric acid	to pH 5.5

1 Pilot Chemical Co.

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	20,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #3: High foaming economy shampoo

D.I. water		Q.S to 100%
Calfoam® ES-302[1]	(Sodium Laureth Sulfate)	25.0
Calfoam® SLS-30[1]	(Sodium Lauryl Sulfate)	25.0
Caltaine® C-35[1]	(Cocamidopropyl Betaine)	10.0
Calamide® MC[1]	(Cocamide MEA)	2.0
Sodium chloride		1.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.

Procedure: Add water, then Calfoams and the Caltaine in the mixing tank and start mixing and heating. At 70^0 C add Calamide and mix until the batch is uniform, smooth, and homogenous without any lumps or particles. Add sodium chloride, continue mixing. Cool the batch down to 30^0 C. Add the rest of the ingredients in the order listed with continuous mixing.

Appearance	Clear liquid
Viscosity @ 70^0 F	40,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #4: High foaming economy shampoo

D.I. water		Q.S to 100%
CalBlend® ECO-1[1]		35.0
Calfoam® ES-302[1]	(Sodium Laureth Sulfate)	15.0
Sodium chloride		2.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	50,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Premium shampoos

While economy shampoos tend to have lower solids and thus less raw material cost, premium shampoos have relatively higher solid and active levels. Premium shampoo formulas may contain relatively milder surfactants such as sulfosuccinates (disodium laureth sulfosuccinate, disodium oleamido MIPA sulfosuccinate); amphoterics (sodium cocoamphoacetate, Sodium lauroamphoaceate, disodium cocoamphodiacetate, etc.) and nonionic (PEG 80 sorbitan laurate, polysorbate 20, alkyl polyglucosides), in addition to high foaming anionic surfactants. Premium shampoos may also contain special additives like glycerin, emollient esters, natural oils, proteins, vitamins, herbal extracts, etc.

Amphoteric surfactants like sodium cocoamphoacetate or disodium cocoamphodiacetate can reduce the irritation potential of the formula while increasing the viscosity when used in conjunction with high foaming anionic surfactants. Amide free formulas are possible by using a combination of anionic and amphoteric surfactants. Formulas 5-8 use amphoterics as the secondary surfactants.

Premium shampoos can also use sulfosuccinates like disodium laureth sulfosuccinate. Sulfosuccinates are mild, good foaming surfactants that produce creamy lather. Baby Shampoo formulas can also use sulfosuccinates in combination with other low irritation surfactants like ethoxylated sorbitan esters. Formula # 9 uses disodium laureth sulfosuccinate as part of the surfactant system for mildness. This formula also provides a light conditioning due to Polyquaternium-10.

Formula #5: Premium shampoo, amide free

D.I water		Q.S to 100%
Calfoam® TLS[1]	(TEA lauryl sulfate)	25.0
Caltaine® C-35[1]	(Cocamidopropyl betaine)	10.0
Mackam 2C[2]	(Diodium cocoamphodiacetate)	15.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.
2 McIntyre Group Ltd.

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	30,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #6: Premium shampoo, amide Free

D.I water		Q.S to 100%
Calfoam® TLS[1]	(TEA Lauryl Sulfate)	30.0
Mackam 2C[2]	(Diodium Cocoamphodiacetate)	20.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.
2 McIntyre Group Ltd.

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	24,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #7: Premium shampoo, amide free

D.I water		Q.S to 100%
Calfoam® ES-302[1]	(Sodium laureth sulfate)	25.0
Caltaine® C-35[1]	(Cocamidopropyl betaine)	5.0
Mackam HPC-32[2]	(Sodium cocoamphoacetate)	15.0
Plantaren 2000 [3]	(Decyl glucoside)	5.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.
2 McIntyre Group Ltd.
3. Cognis Corporation

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	16,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #8: Premium shampoo, DEA free

D.I water	Q.S to 100%

CalBlend® ECO-1[1]		30.0
Mackam HPC-32[2]	(Sodium cocoamphoacetate)	15.0
Sodium Chloride		2.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.
2 McIntyre Group Ltd.

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	15,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #9: Premium light conditioning shampoo

D.I water		Q.S to 100%
Glycerin		5.0
Mirapol PQ-10[2]	(Polyquaternium-10)	0.50
Calfoam® ES-302[1]	(Sodium laureth sulfate)	20.0
Caltaine® C-35[1]	(Cocamidopropyl betaine)	10.0
Calinate® LE[1]	(Disodium laureth sulfosuccinate)	20.0
Glycerox HE[3]	(PEG-7 glyceryl cocoate)	2.0
Sodium chloride		2.5
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.
2 Rhodia
3. Croda

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	33,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Specialty shampoos

The North American market offers a wide variety of hair shampoos to provide some special effect or they fill a niche consumer need. These can include the followings.

- Conditioning shampoos
- Shampoos for various hair type (dry, oily, damaged, etc.)
- Shampoo for chemically treated hair
- Hair & scalp shampoos
- Antidandruff shampoo
- Baby shampoo
- Pearlized shampoo
- Clarifying shampoo

- Neutralizing shampoo

Conditioning shampoo formulas can use a number of different hair conditioning agents. These conditioning agents can be divided into three major categories

- Cationic polymers.
- Fatty amines and quats
- Silicone and Silicone derivatives

Conditioning shampoo formulas may use cationic polymers such as quaternized cellulose (polyquaternium-10) and quaternized guar (guar hydroxylpropyltrimonium chloride). Conditioning shampoos can also utilize water dispersible quats (such as hydroxyethyl behenamidopropyl dimonium chloride), fatty amines, dimethicone, cyclopentasiloxanes, dimethiconol, and amino functional siloxanes. Silicones provide excellent wet and dry combing benefits as well shine to the hair. Formulas 10-13 are examples of conditioning shampoo formulations.

Formula #10: Light conditioning shampoo

D.I water		Q.S to 100%
Mirapol PQ-10[2]	(Polyquaternium-10)	0.50
CalBlend® ECO-1[1]		30.0
Glycerox HE[3]	(PEG-7 glyceryl cocoate)	2.0
Sodium Chloride		2.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.
2 Rhodia
3. Croda

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	10,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #11: Conditioning shampoo

D.I. water		Q.S to 100%
CalBlend® ECO-1[1]		35.0
Calfoam® ES-302[1]	(Sodium laureth sulfate)	15.0
Dow Corning 8500[2]	(Amodimethicone)	2.0
Crothix liquid[3]	(PEG-150 Pentaerythrityl tetrastearate (and) PEG-6 caprylic / capric glycerides (and) water)	2.0
Sodium chloride		2.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.
2. Dow Corning
3. Croda

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or

particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	3,000 cp. Brookfield DV-1 +, spindle # 2
pH	5.5

Formula #12: Conditioning shampoo

D.I. water		Q.S to 100%
CalBlend® ECO-1[1]		35.0
Calfoam® ES-302[1]	(Sodium laureth sulfate)	15.0
Dow Corning 1784[2]	(Dimethiconol (and) TEA dodecylbenzene sulfonate)	4.0
Tween 20[3]	Polysorbate 20	0.4
Sodium chloride		2.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.
2. Dow Corning
3. Uniqema

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	15,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #13: Conditioning shampoo

D.I. water		Q.S to 100%
CalBlend® ECO-1[1]		35.0
Calfoam® ES-302[1]	(Sodium laureth sulfate)	15.0
Lusterplex[2]	(Polyquaternium-70 (and) Dipropylene glycol)	2.0
Crothix liquid[2]	(PEG-150 Pentaerythrityl tetrastearate (and) PEG-6 caprylic / capric glycerides (and) water)	2.0
Sodium chloride		2.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.
2. Croda

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	2000 cp. Brookfield DV-1 +, spindle # 2
pH	5.5

Special hair type shampoo, for example shampoos for dry hair utilize moisturizers such as fatty esters, glycerin, panthenol, vitamins and proteins. Formula #14 illustrates a shampoo which uses Isopropyl Myristate and Panthenol for moisturizing benefits. Formula #15 uses a combination of polyquaternium-10, amino acid based surfactant and panthenol to help mend the split ends, and help repair the damaged hair. Formula #16 is a nourishing shampoo made with various proteins for that purpose.

Formula #14: Shampoo with emollient ester for dry hair

D.I. water		Q.S to 100%
Calfoam® ES-302[1]	(Sodium laureth sulfate)	25.0
Calfoam® TLS[1]	(TEA lauryl sulfate)	25.0
Caltaine® C-35[1]	(Cocamidopropyl betaine)	10.0
Isopropyl myristate		2.0
Tween 20[2]	(Polysorbate 20	4.0
Calamide® MC[1]	(Cocamide MEA)	2.0
Panthenol		1.0
Sodium chloride		3.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.
2 Uniqema

Procedure: Add water, then Calfoams, Isopropyl Myristate and the Caltaine in the mixing tank and start mixing and heating to 70^0 C. Add Calamide and mix until the batch is uniform, smooth, and homogenous without any lumps or particles. Add sodium chloride, continue mixing. Cool the batch down to 30^0 C. Add the rest of the ingredients in the order listed with continuous mixing.

Appearance	Clear liquid
Viscosity @ 70^0 F	1,000 cp. Brookfield DV-1 +, spindle # 2
pH	5.5

Formula #15: Amide free shampoo for damaged hair with amino acid based surfactant

D.I. water		Q.S to 100%
Mirapol PQ-10[2]	(Polyquaternium-10)	0.50
Calfoam® ES-302[1]	(Sodium laureth sulfate)	40.0
Caltaine® C-35[1]	(Cocamidopropyl betaine)	10.0
Amilite GCS-12[3]	(Sodium cocoyl glycinate)	10.0
Potassium chloride		1.0
Panthenol		0.2
Preservative, Perfume, Dye		Q.S
Citric Acid		to pH 5.5

1. Pilot Chemical Co.
2. Rhodia
3. Ajinomoto

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	18,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #16: Hair and scalp protein shampoo

D.I. water		Q.S to 100%
Calfoam® TLS-40[1]	(TEA lauryl sulfate)	20.0
Mackam HPC-32[2]	(Sodium cocoamphoacetate)	10.0
Calinate® LE[1]	(Disodium laureth sulfosuccinate)	10.0
Amisoft CS-22[3]	(Sodium cocoyl glutamate)	10.0
Caltaine® C-35[1]	(Cocamidopropyl betaine)	10.0
Calamide® MC[1]	(Cocamide MEA)	2.0
Sodium chloride		2.0
Hydrolyzed vegetable protein		0.5
Hydrolyzed wheat protein		0.5
Collagen amino acids		0.5
Hydrolyzed silk		0.5
Panthenol		4.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 ***Pilot Chemical Co.***
2 ***McIntyre Group Ltd.***
3. ***Ajinomoto***

Procedure: Add water, the Calfoam, Mackam, Calinate, Amisoft and the Caltaine in the mixing tank and start mixing and heating to 70^0 C. Add Calamide and mix until the batch is uniform, smooth, and homogenous without any lumps or particles. Add sodium chloride, continue mixing. Cool the batch down to 30^0 C. Add the rest of the ingredients in the order listed with continuous mixing.

Appearance	Clear liquid
Viscosity @ 70^0 F	7,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Antidandruff Shampoos may come under FDA jurisdiction. Before marketing and formulating an antidandruff shampoo, one must comply with the appropriate regulations. Formula #17 uses Zinc Omadine as antidandruff agent. It is important to add a suspending agent that will stabilize the formula.

Formula #17: Anti-dandruff shampoo

D.I. water		Q.S to 100%
Carbopol Aqua SF-1[2]	(Acrylates copolymer)	6.0
Sodium hydroxide 10%		1.5
Calfoam® ES-302[1]	(Sodium laureth sulfate)	25.0
Calfoam® SLS-30[1]	(Sodium lauryl sulfate)	25.0
Caltaine® C-35[1]	(Cocamidopropyl betaine)	10.0
Calamide® MC[1]	(Cocamide MEA)	2.0
Zinc omadine 48% FPS[3]		2.5
Sodium chloride		0.5
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1. ***Pilot Chemical Co.***
2. ***Noveon***
3. ***Arch Personal Care***

Procedure: Add water, Carbopol Aqua SF-1 (Liquid) mix well. Add sodium hydroxide slowly. Add Calfoams and the Caltaine and start mixing and heating to 70^0 C. Add Calamide and mix

until the batch is uniform, smooth, and homogenous without any lumps or particles. Add sodium chloride, continue mixing. Cool the batch down to 30^0 C. Add the rest of the ingredients in the order listed with continuous mixing.

Appearance	Opaque liquid
Viscosity @ 70^0 F	15,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #18 uses glycerin and Sodium PCA for hydrating effects. This formula is a good starting point for developing shampoos for oily hair. Glycerin and Sodium PCA help moisturize without adding the oil to the hair. No oil or other fatty moisturizers are in this formula.

Formula #18: Hydrating shampoo

D.I water		Q.S to 100%
Calfoam® ES-302[1]	(Sodium laureth sulfate)	30.0
Mackam HPC-32[2]	(Sodium cocoamphoacetate)	20.0
Glycerin		5.0
Sodium PCA		0.5
Sodium chloride		2.5
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.
2. McIntyre

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	12,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formulas 19 and 20 provide a pearly looking shampoo product, and formula #21 exploits the moisturizing benefits of jojoba beads. These formulas are starting points for various other special ingredients like vitamins, natural oils etc. that are in the form as microencapsulated beads.

Formula #19: Pearlized shampoo

D.I. water		Q.S to 100%
Calfoam® ES-302[1]	(Sodium laureth sulfate)	20.0
Calfoam® SLS-30[1]	(Sodium lauryl sulfate)	20.0
CalBlend® Pearl[1]		10.0
Caltaine® C-35[1]	(Cocamidopropyl betaine)	10.0
Calamide® MC[1]	(Cocamide MEA)	2.0
Sodium chloride		2.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1. Pilot Chemical Co.

Procedure: Add water, Calfoams, CalBlend and the Caltaine in the mixing tank and start mixing and heating to 70^0 C. Add Calamide and mix until the batch is uniform, smooth, and

homogenous without any lumps or particles. Add sodium chloride, continue mixing. Cool the batch down to 30^0 C. Add the rest of the ingredients in the order listed with continuous mixing.

Appearance	Pearlized opaque liquid
Viscosity @ 70^0 F	25,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #20: Pearlized shampoo

D.I. water	Q.S to 100%
CalBlend ECO-1[1]	30.0
CalBlend® Pearl[1]	10.0
Sodium chloride	2.0
Preservative, perfume, dye	Q.S
Citric acid	to pH 5.5

1. ***Pilot Chemical Co.***

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	22,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #21: Shampoo with colored Jojoba beads suspension

D.I. water		Q.S to 100%
Carbopol Aqua SF-1[2]	(Acrylates copolymer)	6.0
Sodium hydroxide 10%		1.5
Calfoam® ES-302[1]	(Sodium laureth sulfate)	20.0
Calfoam® SLS-30[1]	(Sodium lauryl sulfate)	20.0
Caltaine®C-35[1]	(Cocamidopropyl betaine)	10.0
Calamide® MC[1]	(Cocamide MEA)	2.0
Sodium chloride		2.0
Jojoba ester beads		1.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1. ***Pilot Chemical Co.***
2. ***Noveon***

Procedure: Add water, Carbopol Aqua SF-1 (liquid) mix well. Add sodium hydroxide slowly. Add Calfoams and the Caltaine and start mixing and heating to 70^0 C. Add Calamide and mix until the batch is uniform, smooth, and homogenous without any lumps or particles. Add sodium chloride, continue mixing. Cool the batch down to 30^0 C. Add the rest of the ingredients in the order listed with continuous mixing.

Appearance	Clear liquid
Viscosity @ 70^0 F	27,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Baby shampoo formulations combine high foaming anionic surfactants like alkyl ether sulfates and some mild amphoteric and / or nonionic surfactants. Mild surfactants commonly used in baby shampoos include.

- **Sulfosuccinates:** Disodium laureth sulfosuccinate or Disodium Oleamido MIPA Sulfosuccinate
- **Amphoterics:** Sodium Cocoamphoacetate, Disodium Cocoamphodiacetate or the Lauric versions and Cocamidopropyl Betaine
- **Alkyl Polyglucosides:** Decyl Glucoside or Coco Glucoside
- **Ethoxylated sorbitan esters:** PEG-80 Sorbitan Laurate and Polysorbate 20

Formulas 22, 23 & 24 provide a starting guideline for developing a baby shampoo.

Formula #22: Baby shampoo

D.I water		Q.S to 100%
Calfoam® ES-302[1]	(Sodium laureth sulfate)	23.5
Caltaine® C-35[1]	(Cocamidopropyl betaine)	15.7
Mackam 2C[2]	(Disodium cocoamphodiacetate)	3.9
Mackanate OPSV[2]	(Disodium oleamido--MIPA sulfosuccinate)	3.9
AtlasG-4280[3]	(PEG-80 sorbitan laurate)	11.8
Plantaren 818[4]	(Coco-glucoside)	5.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.
2 McIntyre Group Ltd.
3 Uniqema
4 Cognis Corporation

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	3,000 cp. Brookfield DV-1 +, spindle # 2
pH	5.5

Formula #23: Baby shampoo

D.I Water		Q.S to 100%
Glycerin		10.0
Calfoam® ES-302[1]	(Sodium laureth sulfate)	25.0
Caltaine® C-35[1]	(Cocamidopropyl betaine)	15.0
Mackam 2C[2]	(Disodium cocoamphodiacetate)	10.0
AtlasG-4280[3]	(PEG-80 sorbitan laurate)	15.0
Preservative, perfume, dye		Q.S
Citric acid		to pH 5.5

1 Pilot Chemical Co.
2 McIntyre Group Ltd.
3 Uniqema

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or

particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	11,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Formula #24: Economy baby shampoo

D.I water	Q.S to 100%
CalBlend® BSC[1]	32.5
Preservative, perfume, dye	Q.S
Citric acid	to pH 5.5

1 Pilot Chemical Co.

Procedure: Add all ingredients in the order listed with constant mixing. Mix well after each ingredient's addition until the batch is uniform, smooth, homogenous, and free of any lumps or particles. Mix well after the addition of all ingredients until the batch is clear, uniform, and homogenous.

Appearance	Clear liquid
Viscosity @ 70^0 F	7,000 cp. Brookfield DV-1 +, spindle # 3
pH	5.5

Any formulation work is not complete without proper safety, physical, chemical, performance, stability and consumer panel testing. It is a good idea to have more than one or two final prototype formulas. Subject the formulas through these tests and then choose the final formula. And have a few back up formulas. Another important aspect of product development is "product scale up". A formula is not good enough unless a manufacturing facility can produce it, no matter how good it looks in the lab.

The art of formulating a shampoo is the art of balancing the desirable properties in the formula and keeping the undesirables to a minimum, while achieving a specified raw material cost. In many formulas for example, an increase in viscosity can be associated with increase in stringiness. The formulator's job is to reach a high desirable viscosity without having the undesirable property of stringiness. The addition of glycerin, propylene glycol and/or ethoxylated nonionic surfactants like ethoxylated alcohols or ethoxylated sorbitan esters may improve the formula's short flow characteristics (reduce stringiness), but it is likely to reduce the viscosity. Finding the appropriate balance between viscosity and stringiness is the key.
A formulator is not only a scientist but an artist as well and the art comes from experience and time spent on the bench to learn the small tricks of formulation techniques.

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