Surfactants:

Strategic Personal Care Ingredients

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Prologue

The original version of *Surfactants : Strategic Personal Care Ingredients* was published in 2005 by allured Publishing. It went out of print in 2014, whereupon the copyright reverted to the author. Sine the book was still being used by students in several cosmetic science programs, it was decided to make the book available to them in electronic form.

Shortly thereafter, there was an interest developed in providing additional information on topics of interest to Cosmetic chemists was expressed. This supplement was then added to include an additional eight chapters to the original book.

The author makes this additional information available to all as a free electronic book.

Acknowledgements

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Supplemental Chapter 1

Surfactants – Amphilic Materials

The foundation of surfactant science is the physical chemistry of surfactants at surfaces. The ability of a molecule to remain clear in a solvent, but at the same time go to and alter the air-liquid interfacial surface tension is the key to surfactant efficiency. In order to get foam, emulsification, wetting, or conditioning, one must have as a prerequisite a lowering of surface tension. In other words, all surfactants lower surface tension but the structure of the surfactant determines if it will provide foam, emulsification, wetting, or conditioning.

Surface tension of a liquid is a result of internal attractive forces. These forces cause the liquid's surface to act as if it were a stretched elastic membrane, thus causing it to form spherical droplets.

Amphilic materials have two or more groups in the same molecule that in pure form are insoluble in each other. The groups that are mutually insoluble are:

1. Water
2. Oil Phases
3. Silicone Phases
4. Fluoro Phases

Each group in pure form has a surface tension associated with the predominant moiety present. The surface tension is determined by the surface tension of the group that is found at the interface.

Group	**Surface Tension**	**Dominant group**
Water	**72 dynes/cm^2**	**H_2O**
Oil	**30- 35 dynes/cm^2**	**$-CH_2-$**
Silicone	**20-25 dynes/cm^2**	**$-CH_3$**
Fluoro	**below 20 dynes/cm^2**	**$-CF_2-$**

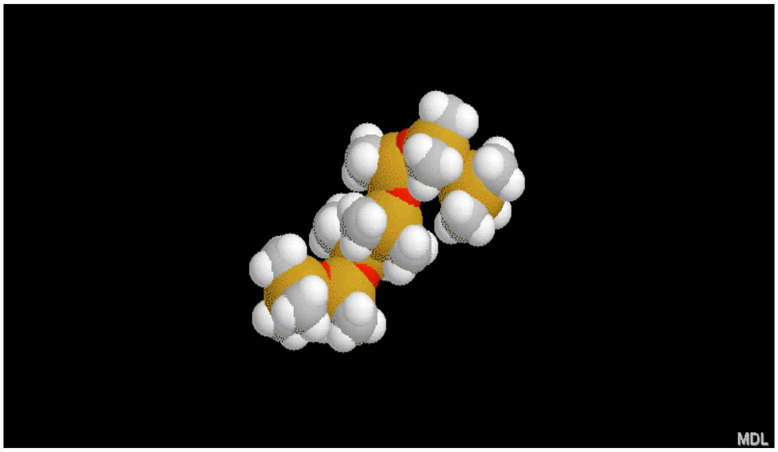


Figure 1-1
Polydimethylsiloxane model
White groups are methyl

Surfactants

Surface-active agents (also called surfactants) possess at least two of these groups on the same molecule. Consequently, they orientate themselves in solution to obtain the lowest free energy. Initially this is at the air /solvent interface. As the concentration of surfactant is raised above the so-called *critical micelle concentration*, aggregations called micelles form. It is very interesting to note that these organized structures are soluble. This is because the structures are below the size that effects clarity. Solubility and homogeneity of concentration cannot be confused.

Surfactant Structure

The most common and best understood surfactant is one that possesses of a hydrophilic portion and a hydrophobic portion as shown.

The hydrophilic end is water-soluble and is a polar or ionic group. The hydrophobic end is water-insoluble and can be either hydrocarbon chain or silicone. This dual functionality, hydrophobic and hydrophilic, is the source of the surface activity. The activity is due in large part to the unique structure of water. The water molecule has a great deal of inter-molecular hydrogen bonding. This accounts for the surface tension of water. Anything that disrupts the hydrogen bonding in water does so at a high energetic cost. Put another-way oil floating on water, which appears to be an ordered system, is at the lowest free energy since the oil molecules disrupt the fewest number hydrogen bonds in the water. This concept of lowest free energy of the system drives all of the surfactant properties.

Many years ago, hydrophobes were almost exclusively hydrocarbon based. In recent years, silicone, a material that is insoluble in both water and hydrocarbon has been introduced. This hydrophobic (water hating) material is also oleophobic (oil hating). The result is the need to expand the definition of Group opposites[1].

Hydrophilic (water loving) **Oleophilic** (oil loving) **Siliphilic** (silicone loving)	**Hydrophobic** (water hating) **Oleophobic** (oil hating) **Siliphobic** (silicone hating)
Hydrophobic (water hating) materials can be either oleophilic or siliphilic. **Oleophobic** (oil hating) materials may be either hydrophilic or siliphilic. **Siliphobic** (silicone hating) materials may be either oleophilic or hydrophilic.	

In instances where there are different types of groups other than oil and water soluble the model is essentially the same but the surface tensions of each group changes.

The Physical Chemistry of Surfaces

In simple terms, surfactants are compounds that are both hydrophilic (“water-loving”) and lipophilic (“oil-loving”). The water-soluble portion may be a salt group, which ionizes in solution to yield a charged, anionic or cationic group. It can also be a polar moiety, such as a hydroxyl group (OH), which can easily hydrogen-bond to enhance water solubility of the entire molecule. The oil-soluble portion is generally a hydrocarbon, usually a relatively long, branched or straight, carbon chain. Based on the simple chemical principle of “like dissolves like,” the long, non-polar chain associates itself with oily materials, while the polar head group is attracted to water.

Molecules that possess at least two groups, which in pure form would be insoluble in each other, are referred to as amphilic materials. These molecules are of major importance because of the way in which they organize in solution. Water, the most commonly encountered solvent used in the personal care industry is an amazing material. The unique physical properties of water make it a material that is necessary for life, as we know it. Table 10.1 outlines the unique properties of water.[2]

Table 1.1
Salient Properties of Water

1. Water is a tasteless, odorless liquid at ambient temperature and pressure.
2. Water is a polar molecule. Since oxygen has a higher electronegativity than hydrogen, the charge difference is called a dipole. The interactions between the different dipoles of each molecule cause a net attraction force.
3. Another very important force that causes the water molecules to stick to one another, and have a high surface tension, is the presence of hydrogen bonding.
4. Water has a high surface tension caused by the strong cohesion between water molecules because it is polar. The apparent elasticity caused by surface tension drives the capillary waves.
5. Water also has high adhesion properties because of its polar nature.
6. Capillary action refers to the tendency of water to move up a narrow tube against the force of gravity.
7. Water is a very strong solvent, referred to as the universal solvent, dissolving many types of substances.
8. All the major components in cells (proteins, DNA and polysaccharides) are also dissolved in water.
9. Water has the second highest specific heat capacity of any known chemical compound, after ammonia, as well as a high heat of vaporization (40.65 kJ mol^{-1}), both of which are a result of the extensive hydrogen bonding between its molecules.
10. Water is miscible with many liquids, for example ethanol, in all proportions, forming a single homogeneous liquid. On the other hand water and most oils are immiscible usually forming layers according to increasing density from the top. As a gas, water vapor is completely miscible with air.

Perhaps the most important factor to consider in working with surfactants is how they impact on the hydrogen bond is found between water molecules. In a discrete water molecule, water has two hydrogen atoms and one oxygen atom. Two molecules of water can form a hydrogen bond between them; the simplest case, when only two molecules are present, is called the water dimer and is often used as a model system. When more molecules are present, as is the case in liquid water, more bonds are possible because the oxygen of one water molecule has two lone pairs of electrons, each of which can form a hydrogen bond with hydrogen atoms on two other water molecules. This can repeat so that every water molecule is H-bonded with up to four other molecules (two through its two lone pairs, and two through its two hydrogen atoms.)

Liquid water's high boiling point is due to the high number of hydrogen bonds each molecule can have relative to its low molecular mass, not to mention the great strength of these hydrogen bonds. Realistically the water molecule has a very high boiling point, melting point and viscosity compared to other similar substances not conjoined by hydrogen bonds.

Surfactants, having an oil soluble portion and a water soluble portion, even if soluble in water, do not partition themselves uniformly in solution. The reason for this is that oil mixed with water disrupts the hydrogen bonding network that exists between water molecules. The expression oil and water do not mix is a well-known adage. Surfactant molecules like oil molecules likewise disrupt hydrogen bonding, a situation that is energetically unfavorable.

Definitions

As technical people we want to our formulations to be governed by clear technical rules and to use simple concepts to organize our world. If we organize our world according to simple definitions, we would observe:

1. A **solution** is a homogeneous mixture composed of one or more substances, known as solutes, dissolved in another substance, known as a solvent.

2. A **suspension** is a colloidal dispersion in which a finely-divided species is combined with another species, with the former being so finely divided and mixed that it doesn't

rapidly settle out. In everyday life, the most common suspensions are those of solids in liquid water.

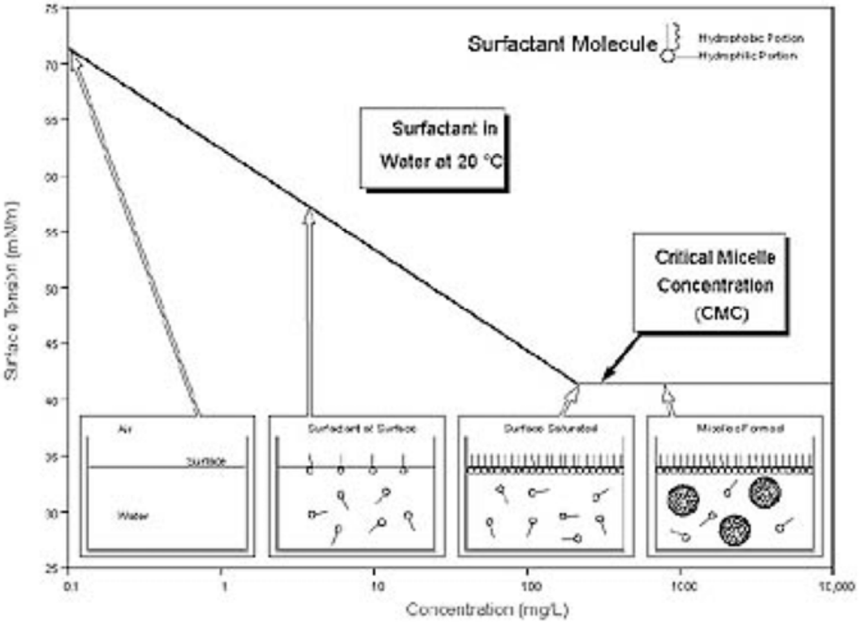
3. An **emulsion** is a mixture of two immiscible substances. One substance (the discontinuous phase) is dispersed in the other (the continuous phase).

Solutions

However the simplisity we desire is often simplistic and elusive. Consider the term solution. Now consider a fully dissolved 1% solution of sodium chloride in water. This simple system has sodium ion (Na^+), chloride ion (Cl^-) and water, roughly equally distributed over the entire mass of the system. The solution is clear and homogeneous.

Now consider a 1% solution of a surfactant. Surfactant, or surface active agent has a water soluble head and a water insoluble tail. A very well known surfactant is sodium lauryl sulfate (CAS 151-21-3). Like NaCl, Sodium lauryl sulfate has two ions with opposite charge, but sodium lauryl sulfate in water is very different. The presence of a large fatty portion makes the product surface active. The structure of sodium lauryl sulfate is shown in figure 1. Please note the oil soluble fatty group and the water soluble sulfate group. Not only is sodium lauryl sulfate a very important anionic surfactant, it demonstrates effects when added to water that are typical for surfactants.

Figure 1

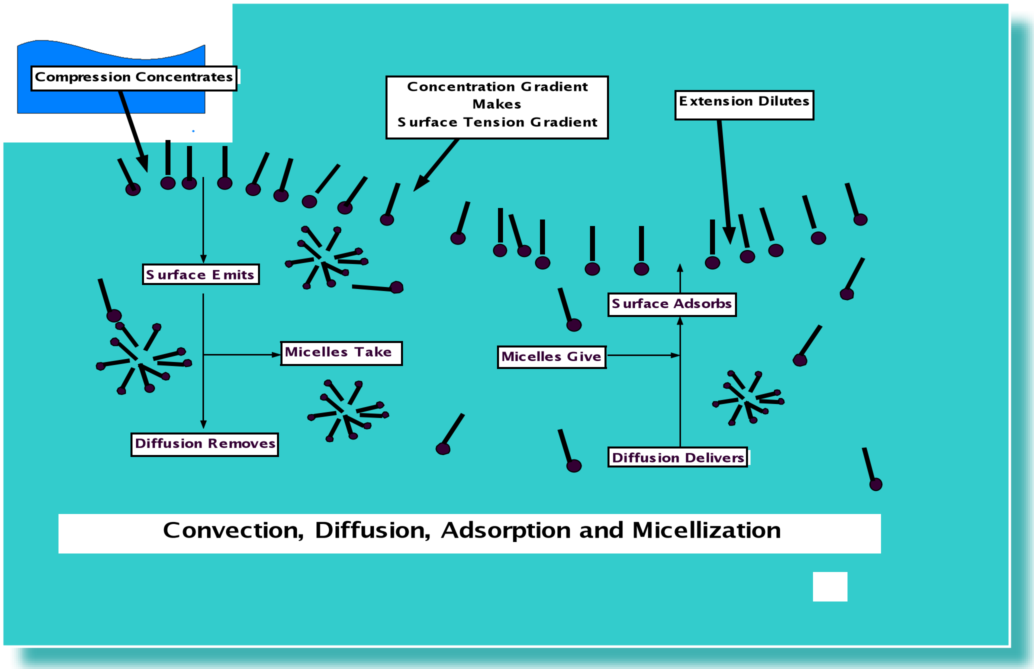


A 1% solution of sodium lauryl sulfate, like that of sodium chloride, is clear but not homogeneous. As one adds sodium lauryl sulfate to water, achieving the lowest overall free energy drives the orientation of the material in the water. In this case minimize disrupting hydrogen bonding in water. The sodium lauryl sulfate organizes itself at the air water interface and then begins to self assembly into micelles. Figure 1 shows this[2] . The first box shows pure water, having a surface tension is around 72 dynes/cm^2. As surfactant is added, demonstrated by the second box, surface tension is falling as dilute surfactant organizing at the surface. As the surface reaches saturation a very significant situation develops. The surface tension no longer drops even with additional surfactant. It is at this concentration called critical micelle concentration that micelles become the dominant form of surfactant. (The third box in Figure 1 shows this situation.)

In aqueous solutions, surfactants cause a reduction in surface tension, usually expressed in mN/cm (or dynes/cm). By reducing surface tension, surfactants are able to disperse oil in water. The surface tension is generally reduced from 72 dynes/cm^2 to 32 dynes/cm^2 for fatty surfactants and 22 dynes/cm^2 for silicone surfactants. Surface tension created by a formulation is of great importance to cosmetic products.

Surfactants are used as wetting agents, foaming agents, emulsification agents, conditioning agents, and detergents. While each of these applications require a specific class of compounds to maximize efficiency, all surfactants regardless of function in a formulation must lower surface tension in order to provide the other properties listed above

The importance of surface tension reduction cannot be overstated when making personal care products. The application to hair and skin always is based upon the formation of new surface area, lipsticks are spread on the skin, shampoos spread on the hair, and so on. The through and efficient spreading requires a lowering of surface tension.

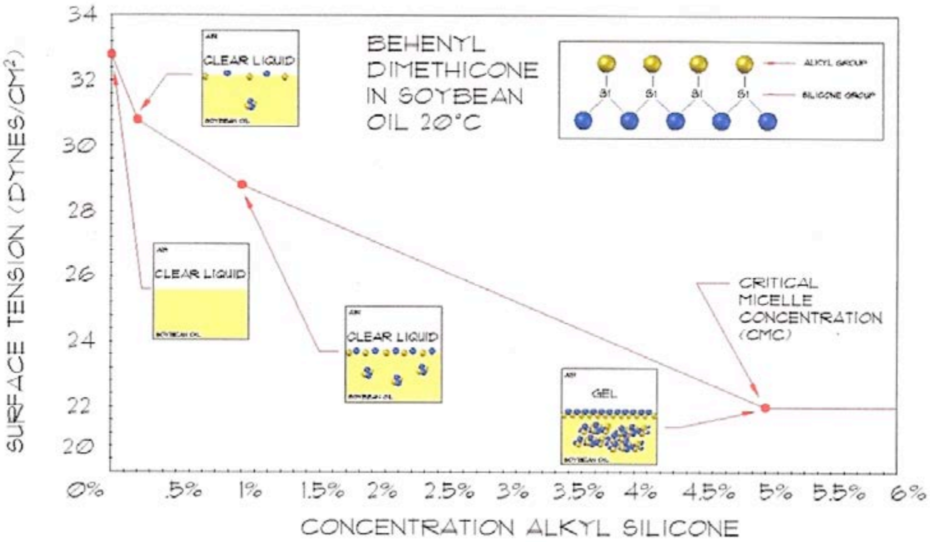


The Complex Surface Chemistry of Spreading

Non-Traditional Surfactant Systems

The traditional view of surfactants is to evaluate them in water for their key properties. While of academic interest, the formulator cannot work in such a simple world. There are numerous interactions between ingredients in formulations. In fact there interactions are critical to the performance of the formulation. The reader is encouraged to reads the chapter added in this edition related to interactions.

Alkyl silicones perform exactly the same way then added to soybean oil.



The interactions of surfactants in non-aqueous solution and the interaction between the different types of surfactants is an important and needs to be considered.

The choice of non-traditional surfactants to lower surface tension is important. Silicone surfactants can be used to lower surface tension to 25 dynes/cm^2 or lower, using solvents including toluene, 2 butoxy ethanol, methanol and water.

Reduction of Surface Tension of Oils with Silicone Derivatives

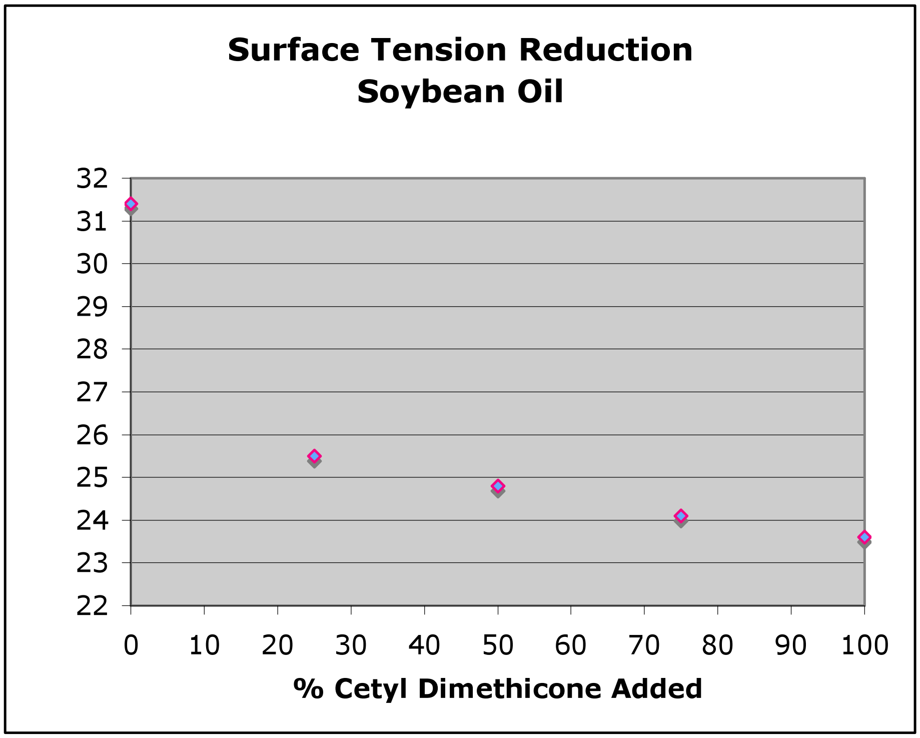
Solvent	Surface Tension (as is) Dynes/cm^2	Silicone Added (0.5% weight)	Surface Tension Dynes/cm^2
Toluene	28.9	C-26 alkyl dimethicone	25.0
2-butoxy ethanol	29.1	Stearyl dimethicone	22.0
Methanol	23.4	Octyl PEG-8 dimethicone	22.2
Water	72.3	PEG-8 dimethicone	20.1

Traditional surfactants like cocamidobetaine can be made more silicone like by adding the proper amounts of silicone surfactants.

	Cocamidobetaine (% Weight)	PEG-8 Dimethicone (% Weight)	Surface Tension (Dynes/cm^2)
Example 1.1	100%	0%	31.3
Example 1.2	75%	25%	26.0
Example 1.3	50%	50%	23.1
Example 1.4	25%	25%	21.6
Example 1.5	0%	100%	20.1

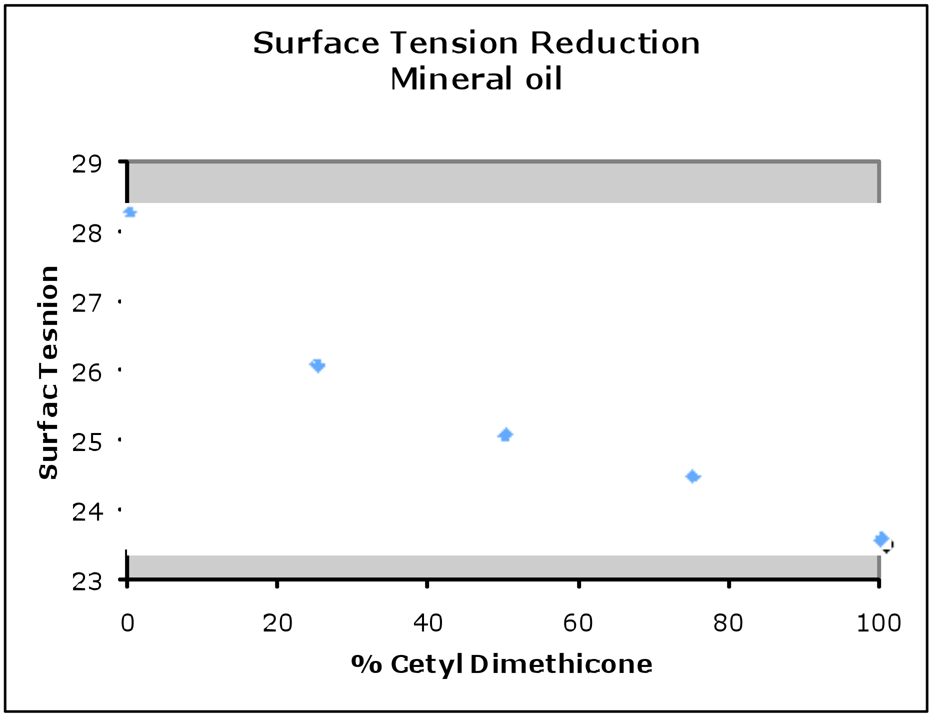
Natural oils can also be made more silicone like by adding silicones to reduce surface tension.

	Soybean oil (% Weight)	Cetyl Dimethicone (% Weight)	Surface Tension (Dynes/cm^2)
Example 2.1	100%	0%	31.4
Example 2.2	75%	25%	25.5
Example 2.3	50%	50%	24.8
Example 2.4	25%	75%	24.1
Example 2.5	0%	100 %	23.6



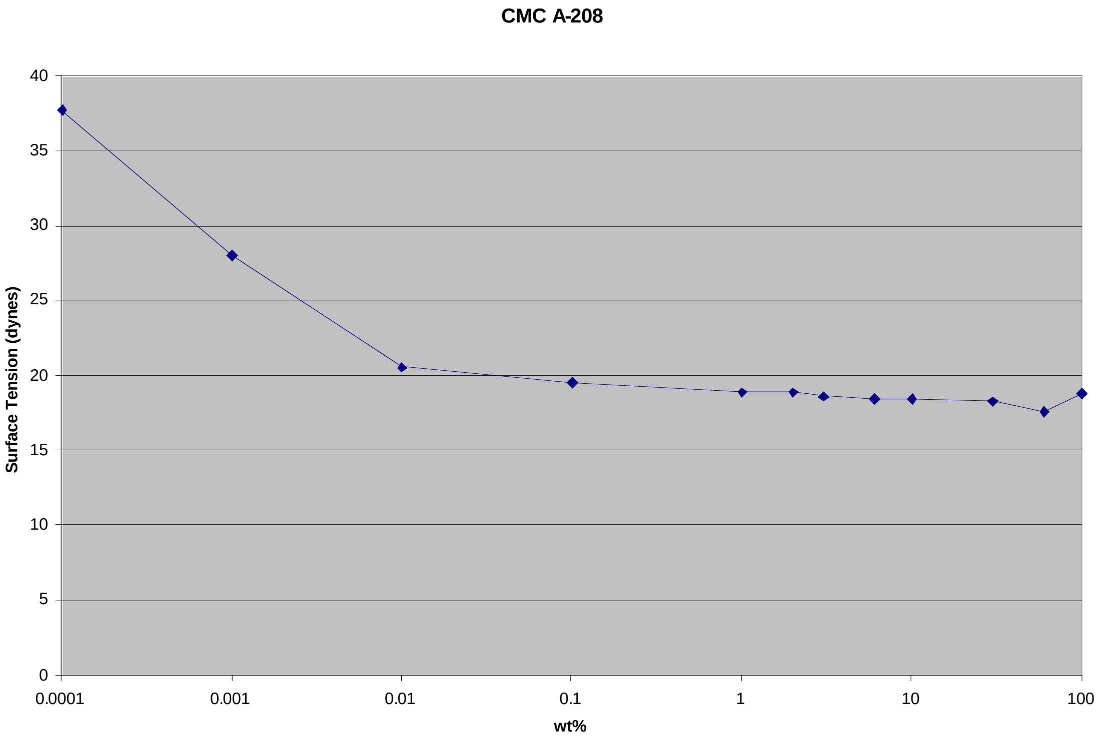
Mineral oils can also be made more silicone like by adding silicones to reduce surface tension.

	Mineral oil (% Weight)	Cetyl Dimethicone (% Weight)	Surface Tension (Dynes/cm^2)
Example 3.1	100%	0%	28.3
Example 3.2	75%	25%	26.1
Example 3.3	50%	50%	25.1
Example 3.4	25%	75%	24.5
Example 3.5	0%	100 %	23.6

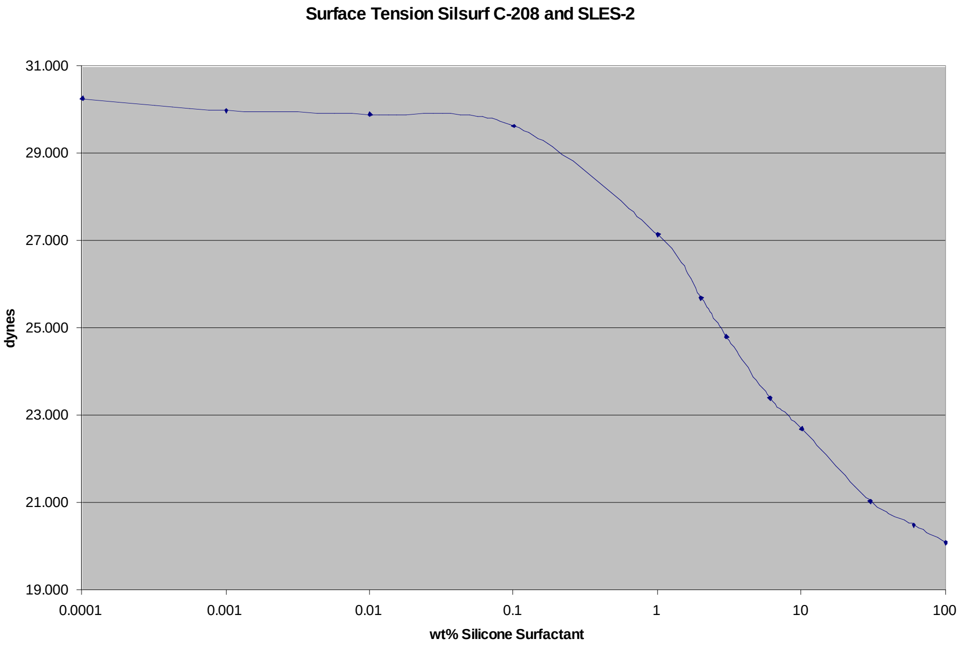


Efficiency of Surface Tension Reduction in Mixed Systems

CMC of PEG 8 Dimethicone



Surface Tension of SLS solution with added PEG 8Dimethicone



RF_{50} = the concentration of silicone surfactant added to reduce the surface tension half of the difference between the fatty surfactant's surface tension and the silicone surfactant's surface tension.

Silicone Surfactant	**Fatty Surfactant**	**RF_{50}**
A-208	SLS	1.2
A-208	SLES-2	1.2
C-208	SLS	1.5
C-208	SLES-2	3.5

Surfactant Properties

Detergency

One of the most common functional characteristics of surfactants is cleansing. Cleansing surfactants, or detergents, are key components of such personal-care products as soaps, facial washes and shampoos. The cleansing power or detergency of these products can be described as their ability to remove grease and dirt from a surface. In cosmetic products, the surfaces typically dealt with are hair and skin.

To understand the mechanism of detergency, consider how a shampoo works. When shampoo is applied to wet hair, surfactant molecules are in solution and are free to orient themselves around oily particles on the hair.

In this first stage of detergency, the surfactant molecules position themselves along the oil-and-water interface, with their hydrophilic ends pointed toward the aqueous solution and their hydrophobic ends associated with the oil droplet. As described in The Principles and Practice of Modern Cosmetics,[4] the detergent molecule wets the hair shaft by "dragging" water along the surface of the hair, underneath the oil, thus separating the oil from the hair shaft.

The next stage of detergency involves the suspension and removal of the oily "dirt." Using the shampoo example, the surfactant separates the oil from the hair, while simultaneously surrounding and penetrating the rest of the droplet. When enough surfactant is available, the oil droplet will be completely surrounded and suspended in the water. This combination of oil and surfactant forms a spherical particle known as a micelle. This micelle stays suspended until more water can rinse it away.

The ability of the formulation to remove soil can be evaluated using hair soiled with sebum at 0.5%concentration, water hardness 50 ppm and 350ppm at room temperature.

Foaming Properties

It is important to note that detergency is only one of the physical properties by which a cleansing surfactant is chosen for personal-care product usage. Foaming properties, for example, are also very important. Although the amount of foam produced by a surfactant has little to do with its inherent cleaning ability, most consumers are convinced it has everything to do with this benefit. In fact, it has been suggested that the single most important factor of a shampoo to a consumer is its foaming ability[5]. In addition to foam characteristics, other important surfactant properties include: wetting ability, risibility and safety (i.e., irritation potential/toxicology). A surfactant chosen for use in a personal-care product formulation must excel at both cleansing and foaming.

Ken Klein offers a rather detailed review of evaluating foam in an article appearing in Cosmetics and Toiletries[6].

Solubilization

The same mechanism, which enables a surfactant to remove grease and dirt from a surface, allows it to solubilize oil in a water-based formulation. This is important. While water is the major component in many cosmetic formulations, other important ingredients are not water soluble, such as emollients or fragrances. A surfactant can be used to disperse these oil-soluble components. In this process, known as solubilization, the surfactant once again forms a micelle with the oil. But, instead of assisting in the removal or rinse-away process, as in the case of detergency, the function of the micelles is to keep the oil dispersed in the water phase. Through this, relatively small amounts of hydrophobic materials (e.g., fragrances) can be carried by water systems without loss of clarity. Typically, nonionic surfactants are used for this purpose, due to their ability to couple oil and water without negatively affecting other characteristics of personal-care formulations.

Two types of nonionic surfactants commonly used for solubilization are ethoxylates and propoxylates. These compounds are ethers formed by reacting ethylene oxide or propylene oxide with a fatty compound. The degree of ethoxylation or propoxylation will affect the solubility of these compounds in water, alcohol and oil. Generally, the more ethylene or propylene oxide present, the more hydrophilic the surfactant will be. Commonly used ethoxylates are polysorbate 80 or sorbitan oleate. An example of a propoxylate is PPG-10 cetyl ether.

Emulsification

As we know, surfactant molecules can disperse oil in water by virtue of their ability to reduce surface tension. This ability allows certain types of surface-active agents to form relatively stable mixtures of oil and water. These mixtures, known as emulsions, provide the basis for a variety of products ranging from cosmetic milks, lotions and creams to pharmaceutical ointments. As defined by Paul Becher, emulsions are two-phase systems “consisting of a fairly coarse dispersion of one liquid in another, in which it (the first liquid) is not miscible.”[6] Becher admits that this, although accurate, is a rather incomplete definition. He goes on to state that specific properties must be considered in order to define a given emulsion completely. Such defining properties include the character of the two phases, the physical properties of the dispersion (e.g., the size of the dispersed particles) and how stable the emulsion is over time. A “stable” emulsion can be defined as one that has no separation during the useful lifetime (shelf life) of the final (finished) product. A good theoretical discussion of factors that influence emulsion stability can be found in the Encyclopedia of Emulsion Technology.[8]

Cosmetic emulsions typically consist of mixtures of hydrocarbon oils and water. The importance of combining these two immiscible materials is obvious. Water is a good carrier for many materials; it is innocuous and inexpensive. It also evaporates without leaving a residue. On the other hand, oily materials, such as those typically employed in hair conditioners and skin lotions, can be good moisturizing and conditioning agents. However, they may be esthetically unacceptable if used in concentrated form. By employing emulsifying surfactants, formulators can combine the benefits of both oils and water in one product.

We can demonstrate how the structure and properties of an emulsifying surfactant (i.e., an emulsifier) differ from those of a detergent, using sodium lauryl sulfate (SLS) as in the previous example. As we described, SLS is very water-soluble, by virtue of the salt-like nature of its polar, sulfate group and its relatively short carbon chain. But imagine that, instead of it having a 12-carbon, lauryl backbone, the chain was lengthened to 18 carbons. And, instead of the molecule being capped with a sulfate anion, it is closed with a carboxylic acid group (COOH). We now have stearic acid.

This material has a substantially higher melting rate, and is significantly less water-soluble than SLS. But, it is still surface active, since it contains both a lipophile (long-carbon chain) and a hydrophile (COOH group). Furthermore, its properties are significantly different than SLS. Instead of imparting high-foaming detergency when added to water, stearic acid can help form emulsions. The exact configuration of the emulsion depends on the composition of the materials in the internal and external phases, and the specific emulsifiers employed.

As with detergents, emulsifiers can be anionic, cationic, nonionic, or amphoteric by nature. McCutcheon’s Detergents and Emulsifiers[9] lists numerous examples of these materials.

Nonionic surfactants are commonly used in cream and lotion products. Unlike anionic surfactants and cationic surfactants, nonionic surfactants have no electric charge; therefore, they are compatible with a variety of materials. Furthermore, they are generally unaffected by pH and salt concentration. This allows formulators more latitude. Those nonionics containing ethylene oxide linkages have “adjustable” water solubility. The exact balance of water and oil solubility can be varied by changing the nature of the carbon chain and the number of moles of ethylene oxide.[10]

A system of indexing the ratio of hydrophile to lipophile is commonly used to categorize nonionic emulsifying materials. This system, known as hydrophile-lipophile balance (HLB), is used to characterize the surfactant requirements of a given water-and-oil mixture.

Conditioning

Surfactants have other properties not directly related to their ability to disperse oil; “conditioning” is one such property. Conditioning can be defined as “putting a material into a workable state.”[11] In the case of hair, this usually means leaving the hair smooth, soft and not prone to static flyaway. For skin, it may mean leaving the surface of the skin feeling smooth and “moisturized.”

Cationic surfactants are used to condition because of their dual ability to be substantive to hair and skin, and to impart lubricity and emolliency. In the case of cationic surfactants, this substantivity—or ability to resist being rinsed away—is due to the interaction of the positive charge on the polar portion of the surfactant molecule with the negative charges, which occur as a result of damage to the protein structure of hair or skin.

Wetting

Wetting is one of the most important, and overlooked attribute of a personal care product. When we wash hair, condition hair, apply pigments to skin or almost any other process used in personal care, we are spreading a formulation on hair or skin. This requires proper reduction in surface tension of the formulation so the product spreads easily and in a cosmetically acceptable manner. Generally nonionic surfactants and dialkyl sulfosuccinates function to provide wetting.

Draves Wetting is a commonly used method to determine the wetting properties of a surfactant or a formulation. (ASTM test method D 2281). The Draves Wetting test involves determining the time required for a cotton skein, a truss of hair or sample of skin to sink in a solution of surfactant or formulated product.

Special Effects

We have demonstrated that surfactants (as detergents, conditioning agents and emulsifiers) play a critical role in the primary form and function of many personal-care products. Surfactants may also have secondary effects. For example, auxiliary surfactants can be used to alter the performance or properties of detergent systems. Specifically, amides may be used to enhance the foam of a shampoo while sulfosuccinates or amphoterics can be used to improve mildness. Many anionic surfactants are also excellent viscosity builders in detergent systems.

In emulsion systems, surfactants, such as cetyl alcohol, help provide thickness and body to creams and lotions. Other surfactants aid in the rinsing of emulsion products. Still other surface-active agents provide the slip and emolliency desired in certain skin- and hair-care formulations. Surfactants like glycol stearate provide pearlizing or opacity to cosmetic products. In hair conditioners, cationic surfactants also help control static electrical charge. Some cationic surfactants may possess antimicrobial properties that are useful in cosmetic products.[11]

There are individual chapters covering each of these topics.

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Supplemental Chapter 2

Compounds or Compositions

Surfactants as explained Chapter Supplemental 1 are amphilic materials that are active at the surface of many different types of interfaces. It is the ability of these materials to alter surface tension that is the reason for the surface activity.

This chapter will address additional properties of the materials that we call surfactants and hopefully provide an understanding why the full characterization of these materials, even when the INCI name is known. The duplication of a formulation using merely the ingredient list on the bottle is one of the most difficult and frustrating undertakings that can be undertaken by a formulator due to the differences in raw materials that are commercially available.

Compounds are single chemical entities. Examples include NaCl and glucose. These materials cannot be separated into components using analytical techniques. The preparation of a 1 percent solution of these materials using pure water and pure compound is not a challenge. The preparation of more complex formulations based upon raw materials is far more complicated and challenging, especially if the formulator wants to match viscosity, color, odor and esthetics.

Compositions on the other hand are mixtures of materials rather than one single compound. Formulations are always *compositions,* raw materials are commonly *compositions*. Formulations that are made from raw materials that are in turn compositions are complex and can be difficult to analyse. Raw materials can be mixtures for a variety of reasons including;

(1) the fact that the raw materials used in the preparation of the compositions are themselves compositions, like coconut oil (which is a mixture of a variety of carbon chain lengths ranging from C12 to C20);

(2) the fact that the process under which the raw materials were made provides an oligomer distribution of compounds rather than a single compound (like ethoxylation);

(3) the fact that the raw materials are not used in stiochiometric ratios leaving an excess of one raw material present after the reaction is complete (like alkanolamides, which are run with an excess of amine);

(4) the fact that some by-products are produced during the reaction (like chlorosulfonic sulfation);

(5) the fact that additives are placed in the product as processing aides to alter viscosity, or change salt response in a formulation;

(6) the fact that bleaches, anti-oxidants or related materials are added.

The ability to use one material as a replacement for another in a formulation requires an understanding of all these issues, making substitution difficult under many conditions. Certainly one cannot rely upon INCI names for anything other than their intended use, namely providing label names.

1. Raw Material Compositions

A. Natural oil based surfactants

As an example consider coconut oil a very common raw material**.**

Coconut Oil (Cocos nucifera)

Coconut oil is the most abundant natural oil processed. Coconut oil comes from the seeds of the *Cocos nucifera* plant. It is the most common oil raw material used in the cosmetics industry. Geographically, coconut oil is cultivated principally in Southeast Asia and the Philippines. It is the major source of lauric acid (C12).

Coconut Oil (Cocos nucifera)

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Coconut oil has 8 different alkyl chains present in the triglyceride. The composition is as

follows;

Component	**Typical Concentration**
C8	**8**
C10	**7**
C12	**48**
C14	**19**
C16	**8**
C18	**3**
C18:1	**5**
C18:2	**2**

B. Derivatives

If one simply makes a diethanolamine using DEA and coconut oil, there will be at least 12 compounds in the composition. These include;

8 different alkyl chain compounds
Glycerin
Unreacted oil
Free DEA
Catalyst

Clearly, this is a composition not a compound. INCI name cocamid DEA.

1. Oligomer Distributions

Many unit operations used in the preparation of surfactants result in oligomer distributions. The most common is ethoxylation. The reaction of ethylene oxide with the hydroxyl group shows very little group specificity. The new molecule of ethylene oxide is unable to differientate the hydroxyl group on the molecule mixture resulting in a wide distribution.

A 3 mole ethoxylate of lauryl alcohol will have between 0 and 10 moles of ethylene oxide on the molecule, with the single most common species being the unethoxylated material making up 17 percent by weight. There are eleven different species present in the ethoxylate by virtue of the ethoxylation. If the alcohol chosen is not pure lauryl alcohol, but is rather a coco alcohol, there are eight different alkyl species with ten each of the ethoxylate species, or eighty different molecules present. Despite this there is a single INCI name applied to this material.

2. Unreacted Raw Materials

Many reactions are carried out with non-stiochiometric ratios. This is done to minimize the residual level of one reactant over another. An example is a chlorosulfonic acid based sulfate. Since the chlorosulfonic acid highly reactive any left in the reaction after the completion would be highly undesirable.

Take the sulfation of the lauteth-3 described above, there would be eighty different species coming into the reaction, some eighty additional species genereated during the reaction making a minimum of 160 compounds present.

3. Process Aides

Now consider the additives placed into the process to control viscosity and processability. The example given above Sodium laureth-3 sulfate having 180 compounds present can have ethanol, water, propylene glycol, PEG 400 or other materials or mixtures thereof added to control viscosity. This adds to the number of compounds present.

4. By-products

Now consider the potential by-products formed. Continuing with the sodium laureth 3 sulfate, there are at least two by-products in chlorosulfation, namley NaCl, Na_2SO_4 others are possible.

5. Bleaches and Antioxidants

It is not common for sodium laureth 3 sulfate to be bleached with hydrogen peroxide or sodium borohydride depending upon the color. It is also not uncommon for antioxidants to be added or pH adjustments to be made with acids like citric or lactic acid.

The reason for providing this information is to show the formulator that many of the raw materials used commonly in our products are complex compositions. In fact we use very few raw materials that are compounds. This information should not be a source of concern, just a cautionary tale on the reason why many materials are difficult to replace just using the INCI name. The only way to successfully replace one raw material with another is to place it in formulation. The formulator is also encouraged to use more sophisticated testing methodologies including computerized FTIR to fingerprint raw materials.

Supplemental Chapter 3

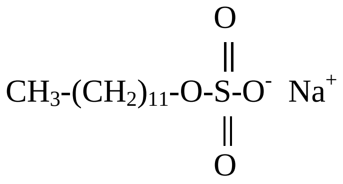
Surfactant Interactions

The interaction that occurs when combining the raw materials used in the formulation of personal care products is more than the sum of the properties of each of the raw materials. There are a number of interactions, which include formation of self assembling complexes. These complexes can either enhance or detract from the functional attributes of the formulation. Since most of today's high performance formulations are very complex containing a plethora of ingredients, it is difficult to predict the effect of changes in those formulations. In an attempt to understand these interactions we have gone back to simple systems. The results of these interactions can then be used to help formulate more effective products.

Surfactants

Surface active agents, commonly called surfactants, can be divided into groups depending upon the charge on the organic portion of the molecule[1]. According to such a scheme surfactants are classified as:

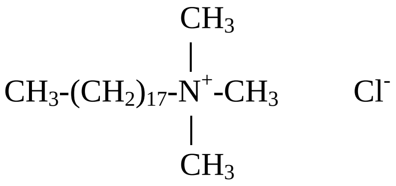
Anionic (- charge)



$$CH_3\text{-}(CH_2)_{11}\text{-O-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}\text{-}O^-\ Na^+$$

Sodium lauryl sulfate

Cationic (+ charge)



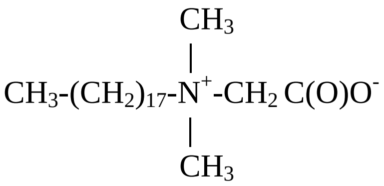
$$CH_3\text{-}(CH_2)_{17}\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}\text{-}CH_3 \quad Cl^-$$

Stearyl trimethyl ammonium chloride

Non-ionic (no charge)

$CH_3\text{-}(CH_2)_{11}\text{-}(CH_2\,CH_2O)_8\text{-}H$ Lauteth-8

Amphoteric (+/ - charge)



$$CH_3\text{-}(CH_2)_{17}\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}\text{-}CH_2\,C(O)O^-$$

These materials are used in a variety of formulations and rarely are used alone. A look at a typical shampoo bottle will show numerous materials together which all interact, in many instances producing viscosity altering nanostructures. It is the nature of these interactions that make our formulations work or fail. Consequently, it is helpful to understand the interactions between the groups. Ken Klein has suggested the possibility of maximizing the effect of the interaction as far back as the late 1970s. This paper is a result of our attempt to understand these interactions.

Most commonly understood is the interaction between anionic and cationic materials. Most formulators put stearalkonium chloride and sodium lauryl sulfate together and observed the white, pasty gunk that results. The nature of such interactions and maximizing the effect in formulation is an important aspect of formulation science. In a previous study[2] we investigated the interaction of cationic and anionic surfactants. In that work we defined two types of quats, one hard and the other soft. Hard quats were those products which were incompatible with anionic surfactants. Soft quats on the other hand, were defined as those quats that formed thick, clear, high foaming complexes with anionic surfactants. There were differences in the hardness of the anionic surfactants, with SLES-2 (Sodium laureth-2-sulfate) being more compatible with quats than SLS (sodium lauryl sulfate).

The nature of water and the hydrogen bonding that occurs between molecules of water makes water a unique material that is essential to life as we know it. The interaction of ionic surfactants in dilute aqueous solution is important in formulation and utilization of personal car products.

Surfactants that possess charges can be selected and combined to form self assembling units. These units are important to the functionality of these materials forming useful nanostructures. The first step is to engineer the polymer, using well known techniques. The driving force for assembly is obtaining the lowest free energy in the system. Many times the lowest free energy state is not the least ordered, but rather the most ordered system. This is particularly true in aqueous systems, where oil floats on water.

Since anionic and cationic materials have an opposite charge they will attract each other and form a salt complex. It is the nature of this complex rather than the properties of the surfactants themselves that determines how the formulations function. As ionic materials are added to water, opposite charges attract and the same charges repel. As the concentration of point charges are increased, the solution becomes so ordered that either (a) the solubility product of the salt is exceeded and a precipitate occurs, (b) The viscosity of the solution increases or (c) the complex becomes insoluble. It is the nature of this interaction that is of interest to the present study. We have dubbed complexes that are made of anionic and cationic surfactants in aqueous solution that thicken and remain clear soft complexes, while insoluble complexes are referred to as hard complexes. The chemical structure of each determines the hardness or softness of the complex. As a 10% active cationic surfactant is titrated into a 10% active solution of an anionic, like sodium lauryl sulfate, more and more of the cationic surfactant complexes with the anionic. As the number of anionic and cationic species becomes equal, the number of interaction complexes will be greatest and at the same point, the concentration of uncomplexed surfactant becomes lowest. It is for this reason that the highest viscosity of the blends of anionic and cationic surfactant occurs at roughly equal amounts.

Rehology of Complex

While the peak viscosity is a measure of the interaction of the anionic and amphoteric surfactants, the resistance to shear is a measure of the stability of the complex.

The term "Newtonian" describes a material in which a linear relationship exists between shear stress and shear rate. In Newtonian fluids (typically water and solutions containing only low molecular weight material) the viscosity is independent of shear strain rate.

The term pseudoplastic is used to describe a material that experiences a decrease in viscosity with increasing shear rate (shear-thinning). Pseudoplastic materials instantaneously decrease in viscosity with increase in shear strain rate (*e.g.* flow) and are therefore easier to pump and mix. They are shear-thinning. This is often a consequence of high molecular weight molecules being untangled and oriented by the flow. Generally this behavior increases with concentration.

A specific type of pseudoplastic material is a thixotropic liquid. It exhibit a time-dependent response to shear strain rate over a longer period than that associated with changes in the shear strain rate. They may liquefy on being shaken and may or may not solidify when the shaking has stopped

The term dilatant is used in common practice to refer to material that increases in viscosity as shear rate increases, that is they are shear-thickening.

The objective of this paper is to expand the study of interactions to include several amphoteric surfactants including, betaines, amido betaines and aminopropinate surfactants. Since amphoteric surfactants have both a positive and negative charge on the structure, the interactions were thought to be somewhat different than the interactions between quats which have only a positive charge on them.

1. Anioinc Cationic Interactions

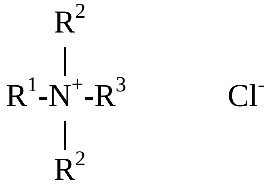
Fatty quaternaries have been known for many years. Because of their fatty nature and positive charge, these compounds find application in a variety of areas including as conditioners for hair and skin. Despite the fact these materials have been recognized as key cosmetic additives, there is little published on the structure function relationship on basic properties. For example, some quats are very insoluble when added to anionic surfactant, others have improved compatibility. The ability to select quats that have optimum compatibility with anionic systems offers the formulator flexibility in formulating heretofore unavailable. There is also much confusion related to deposition of cationic material onto hair as measured by a number of red dye uptake tests. These tests merely measure cationic on the surface of the hair. Since deposition on hair made from a solution containing cationic and anionic, contains no free cationic, no red color is observed with these tests. This does not mean however there was no deposition, it simply means the deposited material does not have an overall positive charge and consequently does not bind dye.

Anyone that has added stearylalkonium chloride to sodium lauryl sulfate and observed the white sticky solid that results knows anionic and cationic surfactants can be incompatible. We have begun to call anionic and cationic materials that produce a white gunky solid when mixed together *hard complexes.* As the expression implies the cationic and anionic compound possess properties which when added together form insoluble complexes (salts). We set out to determine if there are cationic materials having different structures which could be more soluble in the presence of anionic surfactants. The terms used here for quats and anionic materials are an adaptation of the work of Pearson used to describe acids and bases. Pearson proposed that "hard acids bind strongly to hard bases and soft acids bind softly to soft bases"[1]

The structural changes that can be made to cationic molecules can "soften" them, making them more compatible with anionic systems. Alternatively, there should also be the possibility of developing an anionic material that has increased compatibility with cationic surfactants, perhaps a more highly ethoxylated sulfate or a sulfosuccinate. However, this concept of modifying the anionic, is a topic for another investigation.

A study was undertaken to determine (1) compatibility of specific quats with SLS and SLES, (2) foam properties of the combinations with SLS and SLES (3) substantivity of these combinations with SLS and SLES and (4).

The quats studied conform to the following structure:



$$R^1\text{-}\overset{\overset{\textstyle R^2}{|}}{\underset{\underset{\textstyle R^2}{|}}{N^+}}\text{-}R^3 \qquad Cl^-$$

The preferred definitions for the study groups are:

R^1
1. Alkyl (C12)
2. Ricinoleylamidopropyl
3. Dilinoleylamidopropyl
4. Cocamidopropyl

R^2
1. Methyl -CH_3
2. 2-hydroxy ethyl - CH_2CH_2OH

R^3
1. Methyl -CH_3
2. Benzyl -CH_2-C_6H_5
3. Glyceryl -CH_2-CH(OH)-CH_2-OH

Table 1 Compounds Studied

Name	R^1	R^2	R^3	Description
AMB	Alkyl (C12)	CH_3	Benzyl	Coco dimethyl benzyl ammonium chloride
AME	Alkyl (C12)	CH_2CH_2OH	CH_3	Coco di-2 hydroxyethyl methyl ammonium chloride
AMG	Alkyl (C12)	CH_3	Glyceryl	Coco dimethyl glyceryl ammonium chloride
AMM	Alkyl (C12)	CH_3	CH_3	Coco tri-methyl ammonium chloride
AEB	Alkyl (C12)	CH_2CH_2OH	Benzyl	Coco di-2 hydroxyethyl benzyl ammonium chloride
AEG	Alkyl (C12)	CH_2CH_2OH	Glyceryl	Coco di-2 hydroxyethyl glyceryl ammonium chloride
CaMB	Castor Amido	CH_3	Benzyl	Ricinoleylamidopropyl dimethyl benzyl ammonium chloride
CaMG	Castor Amido	CH_3	Glyceryl	Ricinoleylamidopropyl dimethyl glyceryl ammonium chloride
DMB	Dimer Amido	CH_3	Benzyl	Dilinoleylamidopropyl dimethyl benzyl ammonium chloride
DMG	Dimer Amido	CH_3	Glyceryl	Dilinoleylamidopropyl dimethyl glyceryl ammonium chloride
DMM	Dimer Amido	CH_3	CH_3	Dilinoleylamidopropyl trimethyl ammonium chloride
MMB	Cocamido	CH_3	Benzyl	Cocamidopropyl dimethyl benzyl ammonium chloride
MMG	Cocamido	CH_3	Glyceryl	Cocamidopropyl dimethyl glyceryl ammonium chloride
MMM	Cocamido	CH_3	CH_3	Cocamidopropyl trimethyl ammonium chloride

(A) Compatibility with anionic

A determination of compatibility of a variety of quats with two anionic surfactants, sodium lauryl sulfate and sodium laureth-3-sulfate was made. The compatibility was determined by titration. The point at which an anionic solution containing 10% anionic either became hazy formed a precipitate was determined.

PROCEDURE- Solution preparation

1. Prepare 50g of a 10% active test solution of surfactant. Record pH.

SURFACTANTS-

Sodium Lauryl Sulfate

Sodium Laureth Sulfate

Ingredient	**W/W**
Surfactant	34.00%
Distilled Water	65.50%

Combine ingredients listed with slow to medium agitation. Mix until uniform at 20-25^{o}C. Prepare test solutions for both SLS and SLES.

10% active SLS

10% active SLES

2. Prepare 100g of a 10% active test solution for each quat sample.

Preparation of 10% Active Quat

Ingredient	**W/W**
Stock Quat Solution (35% w/w)	28.50%
Distilled Water	71.50%

Combine ingredients listed with slow to medium agitation. Mix at 20-25°C until uniform.

3. Using a hot plate and stir bar set on medium agitation, slowly titrate surfactant test solution with quat solution using a 5mL disposable pipette, at a rate of one drop per second. Continue adding quat solution until a precipitate is observed. (Subjective evaluation). Solution will appear cloudy and translucent at this point. Record the amount (grams) of quat solution added at the cloud point, final pH, and the viscosity. Repeat for remaining quat solutions. Store at 20-25°C for use in part II. Observe Solutions after 24 hours. If solution remains cloudy, then titration is complete. If solution is clear, then repeat step 3. Perform titration for each quat using SLS and SLES individually.

CALCULATIONS

$$\text{\% QUAT ADDED} = \frac{\text{GRAMS OF QUAT ADDED}}{(50 + \text{GRAMS OF QUAT ADDED})} \times 100$$

RESULTS

Table 2: Titration Data (SLS)

Quat Sample	**Amount of quat solution added to achieve haze point in SLS (g)**	**Final pH**	**Viscosity (cps)**	**Notes**
AMB	9.75	7.6	4,400	Formed an opaque, pearlescent gel beyond the haze point
AME	6.28	7.1	<10	Did not form a gel
AMG	30.49	8.1	<10	Did not form a gel
AMM	17.63	7.8	<10	Did not form a gel
AEB	14.58	7.9	<10	Did not form a gel
AEG	29.53	7.7	<10	Did not form a gel
CaMB	25.72	7.6	1,000	Formed a gel
CaMG	44.47	7.1	1,000	Formed a gel
DMB	18.33	7.6	<10	Did not form a gel
DMG	40.25	7.6	12,000	Formed a gel
DMM	23.85	7.6	6,000	Formed a gel
MMB	15.28	7.4	14,000	Formed a
MMG	31.02	8.0	13,000	Formed a gel
MMM	21.25	8.0	13,400	Formed a gel

TABLE: 3 Titration Data (SLS)

Hard Quats – No Gel in Sodium Lauryl Sulfate

Quat Sample	**Amount of quat solution added to achieve haze point in SLS (g)**	**Viscosity (cps)**	**Notes**
AMB	9.75	<10	Did not form a gel
AME	6.28	<10	Did not form a gel
AEB	14.58	<10	Did not form a gel
AMM	17.63	<10	Did not form a gel
DMB	18.33	<10	Did not form a gel
AEG	29.53	<10	Did not form a gel
AMG	30.49	<10	Did not form a gel

Soft Quats – Gel Formers in Sodium Lauryl Sulfate

Quat Sample	**Amount of quat solution added to achieve haze point in SLS (g)**	**Viscosity (cps)**	**Notes**
MMB	15.28	14,000	Formed a gel
MMM	21.25	13,400	Formed a gel
DMM	23.85	6,000	Formed a gel
CaMB	25.72	1,000	Formed a gel
MMG	31.02	19,200	Formed a gel
DMG	40.25	12,000	Formed a gel

The quats that showed the best compatibility and gellation properties with sodium lauryl sulfate were the amido quats. The only exception was the amido quat that contained an aromatic group (DMB).

Table : 4 Titration Data (SLES)

Quat Sample	**Amount of quat solution added to achieve haze point in SLS (g)**	**Final pH**	**Viscosity (cps)**	**Notes**
AMB	18.67	6.6	<10	Did not form a gel
AME	4.47	7.0	<10	Formed a gel
AMG	25.04	7.2	1,000	Formed a gel
AMM	17.44	7.2	<10	Did not form a gel
AEB	18.35	7.2	<10	Did not form a gel
AEG	38.72	7.1	1,000	Formed a gel
CaMB	24.31	7.6	1,000	Formed a gel
CaMG	46.23	7.3	1,000	Formed a gel
DMB	11.09	7.3	<10	Did not form a gel
DMG	28.37	7.9	6,800	Formed a gel
DMM	20.00	7.0	6,200	Formed a gel
MMB	25.00	7.1	<10	Formed a gel.
MMG	26.68	7.1	40,000	Formed a gel
MMM	20.23	7.3	50,000	Formed a gel

TABLE: 5 Titration Data (SLS)

Hard Quats – No Gel in Sodium Laureth-3-Sulfate

-

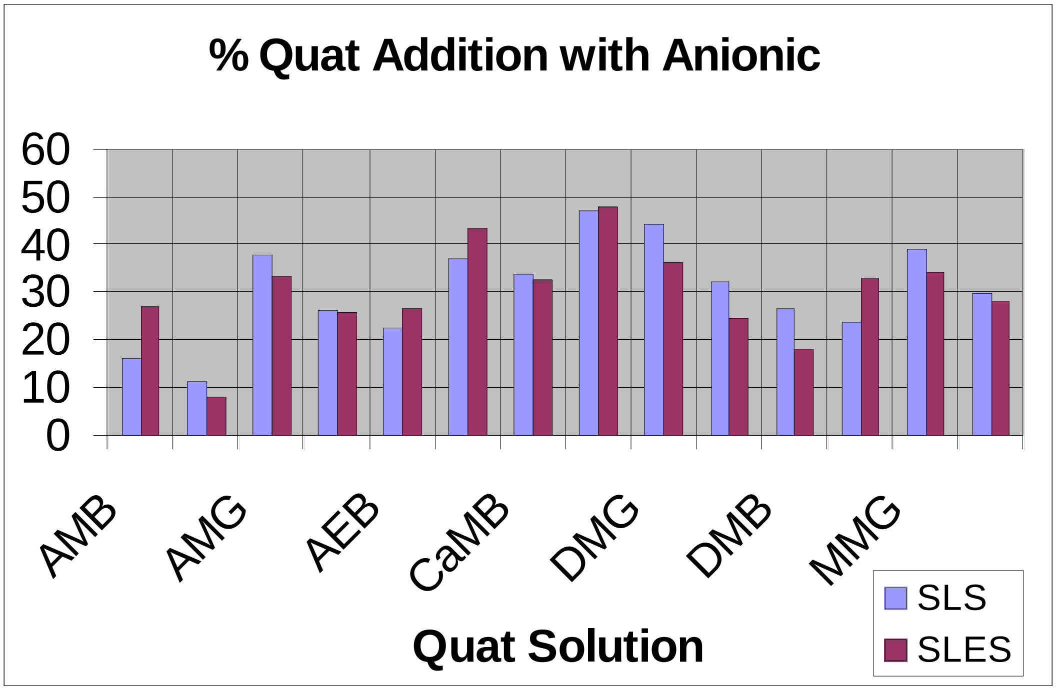
Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
AMB	18.67	<10	Did not form a gel
AMM	17.44	<10	Did not form a gel
AEB	18.35	<10	Did not form a gel
DMB	11.09	<10	Did not form a gel

Soft Quats – Gel in Sodium Laureth-3-Sulfate

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
AME	4.47	7,000	Formed a gel
DMM	20.00	6,200	Formed a gel
MMM	20.23	50,000	Formed a gel
CaMB	24.31	1,000	Formed a gel
AMG	25.04	1,000	Formed a gel
MMB	25.00	9,800	Formed a gel
MMG	26.68	40,000	Formed a gel
DMG	28.37	6,800	Formed a gel
AEG	38.72	1,000	Formed a gel
CaMG	46.23	1,000	Formed a gel

There was improved compatibility with sodium laureth-3-sulfate when compared to sodium lauryl sulfate. This leads to the conclusion that SLES is a softer anionic than SLES.

Graph 1



All quat compounds reached a cloud point when titrated into anionic. However the amount necessary to reach the haze point was different and the nature of the end point were different. The so-called hard quats have very little tolerance for anionic, forming insoluble precipitates with very little addition. Quaternary compounds having intermediate hardness show compatibility with anionic surfactants at near stoichiometric amounts, but do eventually haze. Soft quats do not exhibit a haze, but rather show a clear gel.

(B) FOAM HEIGHT AND STABILITY

It has been generally assumed that a gel made using an anionic and cationic combination would not foam. An evaluation of the gelled system was therefore undertaken to see if this is true.

PURPOSE

Determine the height and stability of foam produced from aqueous solutions of anionic surfactant containing quaternium compounds.

PROCEDURE

QUAT SOLUTIONS

TITRATED QUAT SOLUTIONS FROM PART I ABOVE

CONTROLS

INCI: Polyquaternium-10

Sodium Lauryl Sulfate

Sodium Laureth Sulfate

Name	ARL-4-84A	ARL-4-84B	ARL-4-84C	ARL-4-84D
Polyquaternium 10	1.00%	1.00%	-	-
Deionized Water	91.00%	91.00%	92.00%	92.00%
Sodium Lauryl Sulfate	8.00%	-	8.00%	-
Sodium Laureth Sulfate	-	8.00%		8.00%

1. Prepare ARL-4-84A and B by mixing polyquaternium 10 and deionized water with a prop mixer set on low speed until uniform. (1-5min, 20-25°C).
2. Add surfactant and mix with medium agitation until uniform. (1-2min 20-25°C).
3. Prepare ARL-4-84C and D by combining deionized water and surfactant. Mix with medium agitation until uniform. (1-2min 20-25°C).

RESULTS

Table : 6 Foam Heights of SLS Titrations

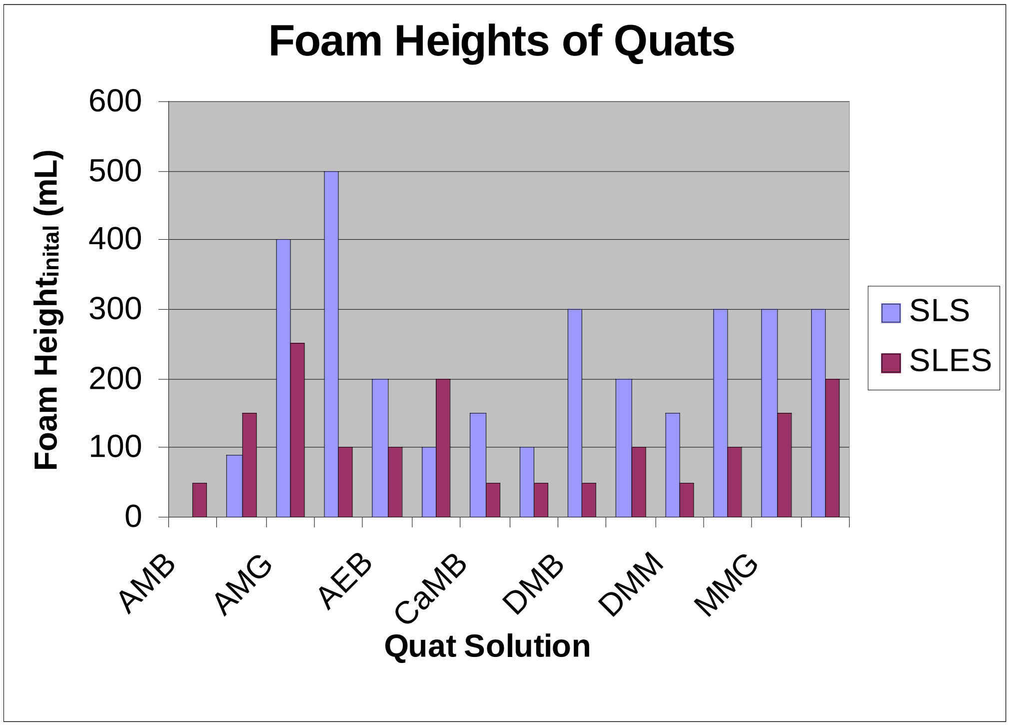
Quat Sample	**Foam Height$_{max}$ (mL)**	**Foam Height$_{inital}$ (mL)**	**Foam Height$_{final}$ (mL)**	**Foam Stability (min)**
AMB	-	-	-	Does not foam
AME	190	90	140	30.0
AMG	500	400	300	30.0
AMM	600	500	350	15.0
AEB	300	200	200	40.5
AEG	200	100	150	40.0
CaMB	250	150	175	95.0
CaMG	200	100	150	79.0
DMB	400	300	250	14.0
DMG	300	200	200	8.0
DMM	250	150	150	13.0
MMB	400	300	250	29.0
MMG	400	300	250	97.0
MMM	400	300	250	1440.0

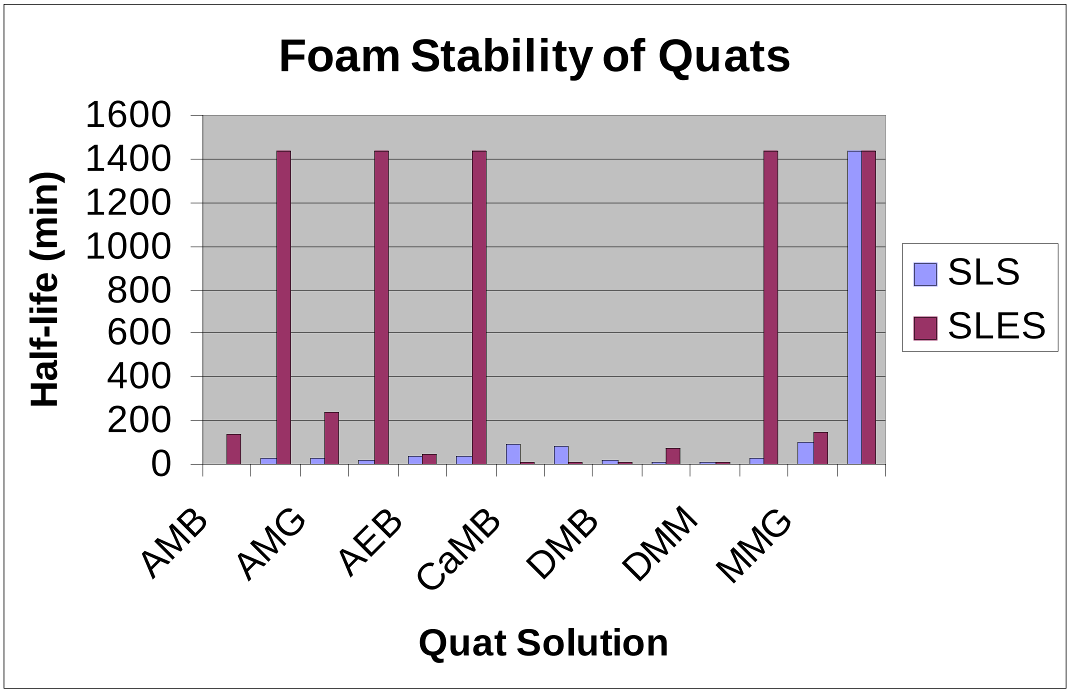
Table : 7 Foam Heights of SLES Titrations

Quat Sample	Foam Height$_{max}$ (mL)	Foam Height$_{inital}$ (mL)	Foam Height$_{final}$ (mL)	Foam Stability (min)
AMB	150	50	100	141.0
AME	250	150	175	1440.0
AMG	350	250	225	240.0
AMM	200	100	150	1440.0
AEB	200	100	150	47.0
AEG	300	200	200	1440.0
CaMB	150	50	125	8.50
CaMG	150	50	125	6.0
DMB	150	50	125	5.5
DMG	200	100	150	75.0
DMM	150	50	125	9.0
MMB	200	100	150	1440.0
MMG	250	150	175	146.5
MMM	300	200	200	1440.0

Table: 8 Foam Heights of Controls

Control	Foam Height$_{max}$ (mL)	Foam Height$_{inital}$ (mL)	Foam Height$_{final}$ (mL)	Foam Stability (min)
ARL-4-84A	200	100	100	31.0
ARL-4-84B	200	100	150	1440.0
ARL-4-84C	600	500	350	25.0
ARL-4-84D	450	350	275	180.0


Foam Heights of Quats
Foam Height$_{inital}$ (mL)
600
500
400
300
200
100
0
AMB
AMG
AEB
CaMB
DMB
DMM
MMG
Quat Solution
SLS
SLES


Foam Stability of Quats
Half-life (min)
1600
1400
1200
1000
800
600
400
200
0
AMB
AMG
AEB
CaMB
DMB
DMM
MMG
Quat Solution
SLS
SLES

Quat solutions titrated with sodium lauryl sulfate (SLS) produced higher levels of foam than those titrated with sodium laureth sulfate (SLES). However, the quat solutions that were titrated with SLES exhibited greater foam stability than those titrated with SLS. In some cases the quats titrated with SLES had a half-life greater than 24 hours (1440 minutes), including the control. After running all controls, it can be concluded that the addition of quaternium compound had a negative effect on the foaming capabilities of SLS and SLES. Stock SLS produced a foam height of 600mL, while the average foam height produced from quat/SLS was around 250mL.

Quat AMB (SLS) produced no foam. Unlike all the other quats that were titrated with SLS, which formed translucent, cloudy, gels at their respective cloud points, quat AMB produced a white, opaque paste. This is evidence that a complex is forming between this quat and SLS. This did not occur when quat AMB was titrated with SLES.

Controls for this experiment produced expected results. ARL-4-84A, which contained 1% polyquaternium 10, produced a higher foam height than ARL-4-84B, which also contained 1% polyquaternium 10, but in SLES. This also proved true for

ARL-4-84C and D as well, which produced the same results. Based on these test results, SLES produced greater foam stability than SLS, however SLS produced higher levels of foam.

Quat AMM and MMM performed superior in SLS and SLES compared to all the samples tested, including the controls. AMM showed superior foaming capabilities, by achieving the greatest foam height in SLS (500 mL), as well as having one of the best foam stabilities in SLES (over 1440 minutes). This stability was roughly ten times greater than all other quats and controls tested, with the exception of AEG, CaMB, MMG, and MMM, which all had foam stabilities of over 1440 minutes. It can be concluded that these quaternium compounds did not have a great effect on the expected foaming capabilities of SLS or SLES, with the exception of AMM and MMM. These two quat solutions increased foam stability by a factor of ten without suppressing foam height.

(C) SUBSTANTIVITY (AQUEOUS DELIVERY SYSTEM)

PURPOSE

Determine the substantivity of quaternium compounds in an aqueous delivery system. To human hair.

PROCEDURE

TEST SOLUTION	ARL-2-73A$_1$ LOT#: 020604
STOCK SOLUTION	ARL-2-73A LOT#: 020604
	DIRECT RED 80 (ALDRICH 365548-25G, LOT#: 04927) GLACIAL ACETIC ACID (ALDRICH 338826-25ML, LOT #: 12405LA)

TREATMENT SOLUTIONS

Name	**W/W**	**Formula #**
35% Active Quat Solution	0.5%	ARL-4-85A-N
Deionized Water	99.5%	

CONTROL Polyquaternium-10

RESULTS

Table: 9 Cationic Substantivity: 0.5% Quat Solutions

			RESULT	
Quat Solution	**Tress Sample**	**Treatment**	**Positive**	**Negative**
AMB	A	ARL-4-85A	Pink	-
AME	B	ARL-4-85B	Purple	-
AMG	C	ARL-4-85C	-	No Color Change
AMM	D	ARL-4-85D	Purple	-
AEB	E	ARL-4-85E	Purple	-
AEG	F	ARL-4-85F	-	No Color Change
CaMB	G	ARL-4-85G	Purple	-
CaMG	H	ARL-4-85H		No Color Change
DMB	I	ARL-4-85I	Purple	-
DMG	J	ARL-4-85J	Purple	-
DMM	K	ARL-4-85K	Purple	-
MMB	L	ARL-4-85L	Purple	-

			RESULT	
Quat Solution	**Tress Sample**	**Treatment**	**Positive**	**Negative**
MMG	M	ARL-4-85M	Purple	-
MMM	N	ARL-4-85N	Purple	-
-	O	PositiveControl	Pink	-
-	P	Negative Control	-	No Color Change

Hair Tresses exhibiting substantivity with 0.5% Quat Solution

Positive and Negative Controls for 0.5% Quat Solutions

Hair Tresses that Exhibit Substantivity with 0.5% Quat Solution

All quat solutions, with the exception of three, (AEG, AMG, CaMG) exhibited cationic substantivity when delivered to hair tresses in a 0.5% aqueous solution. It is likely that these quat solutions did not exhibit substantivity because of their glyceryl groups. However, quat DMG, which also contained a glyceryl group, did exhibit cationic substantivity. It is also possible that the quat group was damaged, or reacted out somewhere in the study, because they were no longer cationic.

(D)_SUBSTANTIVITY (ANIONIC SURFACTANT SYSTEM)

PURPOSE

Determine the substantivity of quaternium compounds in an anionic surfactant delivery system to human hair.

***PROCEDURE** – STM – PE#4*

QUAT SOLUTIONS

TITRATED QUAT SOLUTIONS FROM PART 1.

INCI: Polyquaternium-10

SURFACTANTS

Sodium Lauryl Sulfate

Sodium Laureth Sulfate

Lot #	**Name**	**ARL-4-86A**	**ARL-4-86B**	**ARL-4-86C**	**ARL-4-86D**
565720	Polyquaternium 10	0.5%	0.5%	-	-
0321605	Sodium Lauryl Sulfate	40.00%	-	40.00%	-
04107056	Sodium Laureth Sulfate	-	40.00%	-	40.00%
062906	Deionized Water	59.50%	59.50%	60.00%	60.00%

Table:10 Substantivity of Titrated Quat Solutions in SLS

		RESULT	
Tress Sample	**Treatment**	**Positive**	**Negative**
A	Test	-	No Color Change
B	Test	-	No Color Change
C	Test	-	No Color Change
D	Test	-	No Color Change
E	Test	-	No Color Change
F	Test	-	No Color Change
G	Test	-	No Color Change
H	Test	-	No Color Change
I	Test	-	No Color Change
J	Test	-	No Color Change
K	Test	-	No Color Change
L	Test	-	No Color Change
M	Test	-	No Color Change
N	Test	-	No Color Change
O	Positive Control	-	No Color Change
P	Negative Control	-	No Color Change

Table: 11 Substantivity of Titrated Quat Solutions in SLES

		RESULT	
Tress Sample	**Treatment**	**Positive**	**Negative**
A	Test	-	No Color Change
B	Test	-	No Color Change
C	Test	-	No Color Change
D	Test	-	No Color Change
E	Test	-	No Color Change
F	Test	-	No Color Change
G	Test	-	No Color Change
H	Test	-	No Color Change
I	Test	-	No Color Change
J	Test	-	No Color Change
K	Test	-	No Color Change
L	Test	-	No Color Change
M	Test	-	No Color Change
N	Test	-	No Color Change
O	Positive Control	-	No Color Change
P	Negative Control	-	No Color Change

No substantivity was observed when quat solutions were delivered from a 10% active, anionic solution of surfactant. (SLS and SLES). The test measures cationic deposition as opposed to deposition of a compound of any nature. Since the quat and anionic form a complex, the deposited material is not cationic and consequently does not provide a color when tested with the dye test. More representative of the deposition is combing force.

(E)_INSTRUMENTAL ANALYSIS OF COMBING FORCE

PURPOSE

Determine the force needed to comb wet and dry hair tresses treated with 0.5% active quaternium compound by instrumental analysis.

PROCEDURE

TREAT HAIR TRESSES

1. Treat hair tresses by soaking them in 10-15mL of 0.5% active quat solution for two minutes at 20-25^{o}C.
2. Rinse hair tresses under running tap water (2.0-2.5 gallons/min, 35-40^{o}C), for one minute. Allow hair tresses to air dry for 24 hours at 20-25oC and 40-50% relative humidity.

RESULTS

Table: 12 Measured Combing Force (grams)

Subject A	**1st Combing**	**2nd Combing**	**3rd Combing**	**Average**
Blue	10.0	15.0	13.0	12.6
Yellow	25.0	19.0	15.0	19.6
Red	30.0	13.0	13.0	18.6
Green	40.0	38.0	30.0	36.0
Black	12.0	13.0	15.0	13.3
Subject B	**1st Combing**	**2nd Combing**	**3rd Combing**	**Average**
Blue	25.0	13.0	15.0	17.6
Yellow	29.0	20.0	10.0	19.6
Red	30.0	28.0	20.0	26.0
Green	45.0	40.0	35.0	40.0
Black	25.0	15.0	10.0	16.6
Subject C	**1st Combing**	**2nd Combing**	**3rd Combing**	**Average**
Blue	10.0	12.0	10.0	10.6
Yellow	15.0	10.0	10.0	11.6
Red	15.0	25.0	20.0	20.0
Green	22.0	24.0	25.0	23.6
Black	30.0	23.0	30.0	27.6
Subject D	**1st Combing**	**2nd Combing**	**3rd Combing**	**Average**
Blue	10.0	10.0	12.0	10.6
Yellow	35.0	22.0	25.0	27.3
Red	15.0	15.0	10.0	13.3
Green	43.0	40.0	35.0	39.3
Black	20.0	10.0	13.0	14.3
Subject E	**1st Combing**	**2nd Combing**	**3rd Combing**	**Average**
Blue	27.0	16.0	10.0	15.0
Yellow	40.0	20.0	20.0	26.6
Subject E	**1st Combing**	**2nd Combing**	**3rd Combing**	**Average**
Red	20.0	20.0	12.0	17.3
Green	38.0	40.0	45.0	41.0
Black	23.0	20.0	15.0	19.3

Table:13 Average Values of Combing Force (grams)

Tress Color	**Total Score**
Blue	13.20
Yellow	17.02
Red	19.04
Green	35.98
Black	18.22

The instrumental analysis of 0.5% active quat compounds showed that Blue (MMM), performed the best followed by yellow (MMG), black (deionized water), and red (Polyquaternium 10).

Quaternium compounds can be classified as hard or soft by their ability to form gelled systems with anionic systems. Cationic systems that form a gel at near stoichiometric amounts are classified as “soft”, those that form precipitates of haze without appreciable viscosity build are classified as “hard” quats. “Soft quats” can produce foam in the systems they gel, albeit at levels below the volume of foam generated by the anionic per se.

Quaternium compounds titrated with sodium laureth sulfate (SLES) produced greater viscosities with amido quats. The exception was amido quats containing a benzyl group, which exhibited a low viscosity in SLES.

Compounds that contained a benzyl group, or were a alkyl rather than amido, (i.e. AMB, AME, AMG, AMM, AEB, AEG), precipitated at lower levels of titration and are consequently classified as “hard quats”.

Overall, all quat/anionic solutions tested had less foam than when the anionic itself was tested. This was true for both SLS and SLES.

With the exception of quats AEG, AMG, and CaMG, and the negative control, all 0.5% active, aqueous solutions of quaternium compounds produced positive results for cationic substantivity, when evaluated per se.

In aqueous solutions of anionic surfactants, all quat solutions, including the positive control (polyquaternium 10), produced negative results. This is thought to be due to the fact that there is no net positive charge of the hair, due to the fact that the anionic and cationic in combination have a new zero charge. This is not to be confused with no deposition. Instrumental dry combing analysis of human hair tresses treated with aqueous quat solutions confirmed conditioning, showing that quat MMM indeed performed the best, followed closely by MMG, polyquaternium 10, and the negative control. Again, quat DMG did not show any improvement in performance.

Quat AMB concluded to be the poorest performer yielding opaque surfactant mixtures in part one at low levels. Foam height and stability was dramatically suppressed in part two. Although AMB was substantive to human hair when delivered from an aqueous solution, no substantivity was observed from an anionic mixture.

Quat MMM concluded to be the best performer, yielding a thick, translucent gel with a viscosity well over 10,000 cps for both SLS and SLES titrations. MMM/Anionic Solutions produced an above average foam height without suppression and extended foam stability well over 24 hours or, ten times greater than SLS and SLES, controls, and positive controls (polyquaternium 10 and SLS/SLES). MMM performed equally as well in substantivity tests when delivered from an aqueous system. Like all other quat solutions, no substantivity was observed when delivered from an anionic mixture. Because of its performance, MMM was chosen for subjective and combing analysis. Like quats DMG and MMG, quat MMM performed poorly in the wet combing test of part V. However, it did perform slightly better in the dry combing test. Quat MMM turned out to perform the best in the instrumental analysis of combing force, part VI. The average performance of quat MMM was superior to all quats in this study, including the positive control, polyquaternium 10.

References

1. R.G. Pearson, *J Am Chem Soc*, **85**, 335 (1963).

2. Amphoteric Anionic Interactions

Surfactants Chosen

The surfactants chosen were the most traditional surfactants in the cosmetic industry.

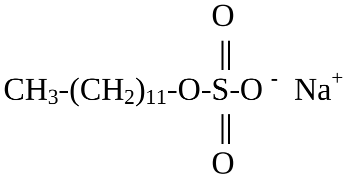
Anionic Surfactants

The anionic surfactants chosen for study in this paper were:

Designation	Description
S-1	SLS
S-2	SLES-2

Structures:

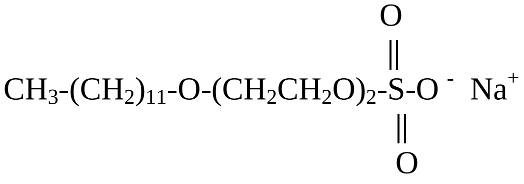
S-1 Sodium Lauryl Sulfate (SLS)



$$CH_3\text{-}(CH_2)_{11}\text{-O-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-O}^- \; Na^+$$

CAS 151-21-3

S-2 Sodium Laureth-2-Sulfate (SLES)



$$CH_3\text{-}(CH_2)_{11}\text{-O-}(CH_2CH_2O)_2\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-O}^- \; Na^+$$

CAS 3088-31-1

These products were obtained commercially from Colonial Chemical So. Pittsburg, Tn.

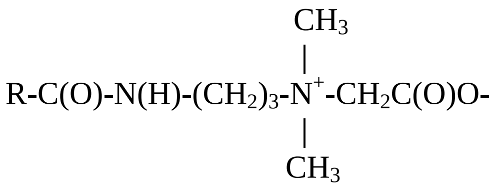
Amphoteric Surfactants

There are a large number of amphoteric surface active agents that could be evaluated in the study. For simplicity we chose to look at betaines and propionates, two important classes of compounds to the personal care market. Candidates were chosen in each class. The amphoteric surfactants used in this study were:

Designation	Description	Abbreviation
A-1	Cocamidopropyl betaine	(CAB)
A-2	Dimer amido propyl betaine	(DAB)
A-3	Cetyl Betaine	(PB)
A-4	Lauric Myristic Amido Betaine	(LMAB)
A-5	Lauramphopropionate	(LP)
A-6	Coco Betaine	(CB)

Amphoteric Structures:

A-1 Cocamidopropyl betaine (CAB)

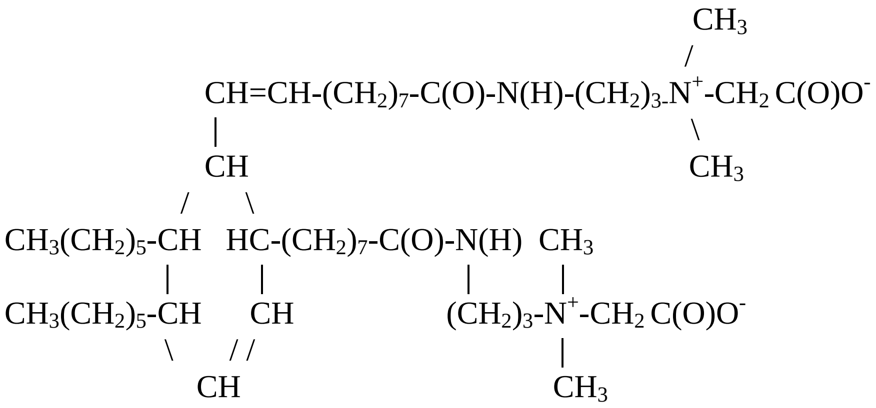


$$R\text{-}C(O)\text{-}N(H)\text{-}(CH_2)_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}\text{-}CH_2C(O)O\text{-}$$

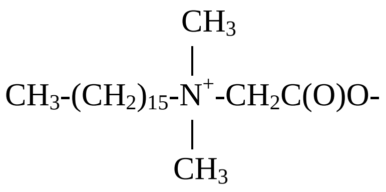
R is derived from coco.

CAS No. 61789-40-4

A-2 Dimer amido propyl betaine (DAB)



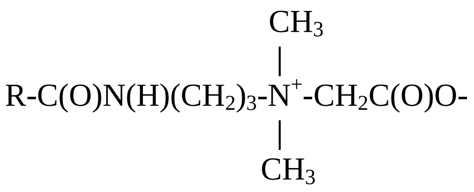
A-3 Cetyl Betaine (PB)



$$CH_3-(CH_2)_{15}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-CH_2C(O)O-$$

CAS 693-33-4

A-4   Lauric Myristic Amido Betaine (LMAB)



$$R-C(O)N(H)(CH_2)_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-CH_2C(O)O-$$

CAS 4292-10-8

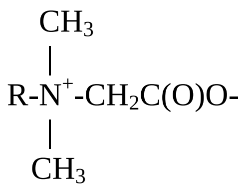
A-5 Lauramphopropionate (LP)

$R-N-(CH_2CH_2COOH)_2$

sodium-n-lauryl-β-iminodipropionic acid

CAS No. 14960-06-6

A-6 Coco Betaine (CB)



$$\mathrm{R\text{-}N^{+}(CH_3)_2\text{-}CH_2C(O)O\text{-}}$$

CAS 68424-94-2

These products were commercially obtained from Colonial Chemical So. Pittsburg, Tn.

I Anionic Interaction Study

The protocol used was on in which surfactants were diluted to 10% actives in order to evaluate the interactions.

Test Methodology:

1. A 10% solution of anionic was prepared.
2. A 10% solution of amphoteric was prepared
3. Blends at 25/75, 50/50 and 75/25 by weight were prepared.
4. Viscosity was run at 60 rpm, 30 rpm and 6 rpm using a Brookfield viscometer LV Spindle 4.

Results

A-1 CAB

CAB : SLS

Ratio	25/75	50/50	75/25
60 Rpm	5	5,850	3,950
30 RPM	4	12,000	7,900
6 RPM	4	31,500	39,500

COAB SLES

Ratio	25/75	50/50	75/25
60 Rpm	11	2,550	10
30 RPM	10	3,200	9
6 RPM	10	3,500	9

A-2 DAB

DAB:SLS

Ratio	25/75	50/50	75/25
60 Rpm	5	4,800	2,000
30 RPM	4	8,100	2,800
6 RPM	4	14,000	6,000

DAB SLES-2

Ratio	25/75	50/50	75/25
60 Rpm	6	1,700	3,000
30 RPM	4	3,800	5,100
6 RPM	4	14,500	18,500

A-3 Palmitic Betaine (PB)

PB:SLS

Ratio	25/75	50/50	75/25
60 Rpm	7		9,650
30 RPM	7	SPLIT	11,400
6 RPM	7		23,000

PB SLES-2

Ratio	25/75	50/50	75/25
60 Rpm	6.5	1,200	5,430
30 RPM	5	1,620	7,160
6 RPM	5	3,400	12,000

A-4 Lauramphoproprionate

LP SLS

Ratio	25/75	50/50	75/25
60 Rpm	4	4	4
30 RPM	4	4	4
6 RPM	4	4	4

LP SLES-2

Ratio	25/75	50/50	75/25
60 Rpm	10	10	10
30 RPM	10	10	10
6 RPM	10	10	10

No viscosity build was noted at any ratio using this amphoteric and either sodium lauryl sulfate or sodium lauryl ether sulfate.

A-5 Lauric Myristic Amido betaine

LMAB
SLS

Ratio	25/75	50/50	75/25
60 Rpm	6	4,100	57
30 RPM	6	6,900	57
6 RPM	6	14,500	55

LMAB SLES-2

Ratio	25/75	50/50	75/25
60 Rpm	9	4,100	120
30 RPM	7	6,700	120
6 RPM	5	13,500	100

A-6 Coco betaine

CB SLS

Ratio	25/75	50/50	75/25
60 Rpm	13	218	367
30 RPM	13	361	365
6 RPM	20	1,250	375

CB SLES-2

Ratio	25/75	50/50	75/25
60 Rpm	367	3,700	7
30 RPM	7,200	7,200	7
6 RPM	28,800	28,800	2

Conclusions

There are significant differences in the degree if interactions which occur between anionic surfactants and amphoteric surfactants depending upon the nature of the amphoteric surfactant studied. Amino propionates exhibit no interaction. Alkyl betaines exhibit some interaction but can become insoluble as the concentration approaches stoichiometric, amidobetaines have strong interactions and better solubility producing gels.

There are likewise differences in the degree and direction of the interactions that occur between amphoteric surfactants and SLS or SLES-2. The effect of going from SLS to SLES-2 is variable and determined by the exact solubility of the amphoteric evaluated.

Complex Interaction

The nature of the interaction causes the observed differences in clarity, and viscosity. The interactions can be classified as follows:

Property	**Insoluble Complex**	**Marginally Soluble**	**Soft Complex**	**Soluble Complex**
Viscosity	Low	Some Viscosity	High	Low
Appearance	Solid Chunks	Milky	Clear	Clear
Example	PB SLS (50/50)	PB SLS (25/75)	DAB/SLES (50/50)	LP SLS (50/50)

B. Foam Data

Since in all instances the 50/50 had the highest viscosity a 1% active solution of the 50/50 blend was subjected to the Ross miles test

Product	50/50 COAB/SLS	50/50 COAB/SLES-2	50/50 DAB/SLS	50/50 DAB/SLES-2
Immed (mm)	200	200	175	160
1 min (mm)	170	170	155	145
5 min (mm)	160	160	150	135
Draves (sec.)	3.03	3.34	39.50	42.1

Product	50/50 SLES-2/LMAB	50/50 SLS/LMAB	50/50 SLES-2/PB	50/50 SLES/PB
Immed (mm)	180	195	190	Insoluble
1 min (mm)	155	170	165	Insoluble
5 min (mm)	150	160	155	Insoluble
Draves (sec.)	12.41	2.90	3.10	Insoluble

Product	50/50 SLES-2/CB	50/50 SLS/CB	100 SLES-2	100 SLS
Immed (mm)	200	250	175	180
1 min (mm)	175	225	160	165
5 min (mm)	165	185	155	155
Draves (sec.)	4.0	8.8	12.4	4.8

Initial Foam (From highest to lowest)

Material	**Foam**
CB-SLES-2	250
COAB-SLS	200
COAB-SLES	200
CB-SLS	200
LMAB-SLS	195
LMAB-SLES	180
PB-SLES-2	190
SLES-2	180
SLS	175
DAB-SLS	175
DAB-SLES-2	160

It was a surprise that SLS and SLES-2 appear near the bottom of the list, meaning there is a synergistic effect of including betaine upon the foam. Even the combination with lowest foam was comparable to SLS. This result means there is a wide possibility to formulate products that have outstanding foam using blends of anionic and amphoteric. It also implies that the complex so formed has different foam properties than the SLSD or SLES alone. This explains why betaines are so commonly used in personal care formulation. They improve foam an attribute that is very important to the consumer.

Wetting (From fastest to slowest)

We evaluated Draves wetting. The test measures the amount of time it takes for a 1% solution of surfactant to cause a cotton skein to sink. Consequently, the lower the time required to sink, the better the wetting.

Material	**Wetting**
LMAB-SLS	2.9 sec
COAB-SLS	3.0 sec
PB-SLES-2	3.1 sec
COAB-SLES	3.3 sec
CB-SLS	4.0 sec
SLS	4.8 sec
CB-SLES-2	8.8 sec
LMAB-SLES	12.4 sec
SLES-2	12.4 sec
DAB-SLS	39.5 sec
DAB-SLES-2	42.1 sec

The wetting times of the blends vary quite a bit depending upon the betaine used. The addition of all but the DAB material improved the wetting time of both SLS and SLES-2. The DAB products are much slower in terms of wetting time. This is not unexpected, since they are the most substantive products evaluated and provide outstanding conditioning not seen in combinations of anionic and other betaines.

Salt Addition

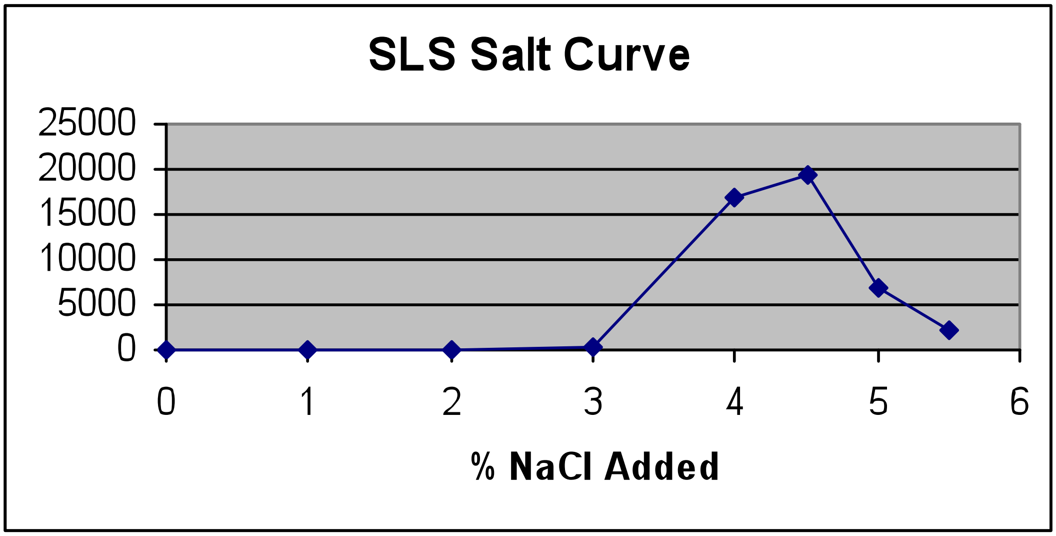
A standard method employed in formulation of cosmetic product is a so called salt curve. Salt is added in increments and the viscosity is tracked with each add. There will be an increase, but at a certain point the maximum viscosity will be reached, then the viscosity will drop. This is why the addition of water to a shampoo formulation might actually increase viscosity. Two salient attribute of the salt curve are important, the maximum viscosity and the amount of salt needed to reach it.

Salt additions were made to the 10% solids blends consisting of 75% anionic and 25% betaine to determine peak viscosity. This ratio was chosen for two reasons, first the viscosity of the 50 / 50 was already high in mot instances, and second the 25% amphoteric 75% anionic was more commercially interesting in terms of formulation cost.

Increments of 0.5% salt were added at a time to a 10% active solution of the specified blend. The viscosity was measured after every addition @ 22.0 ±0.3º C using a Brookfield Synchro-lectric^R Viscometer.

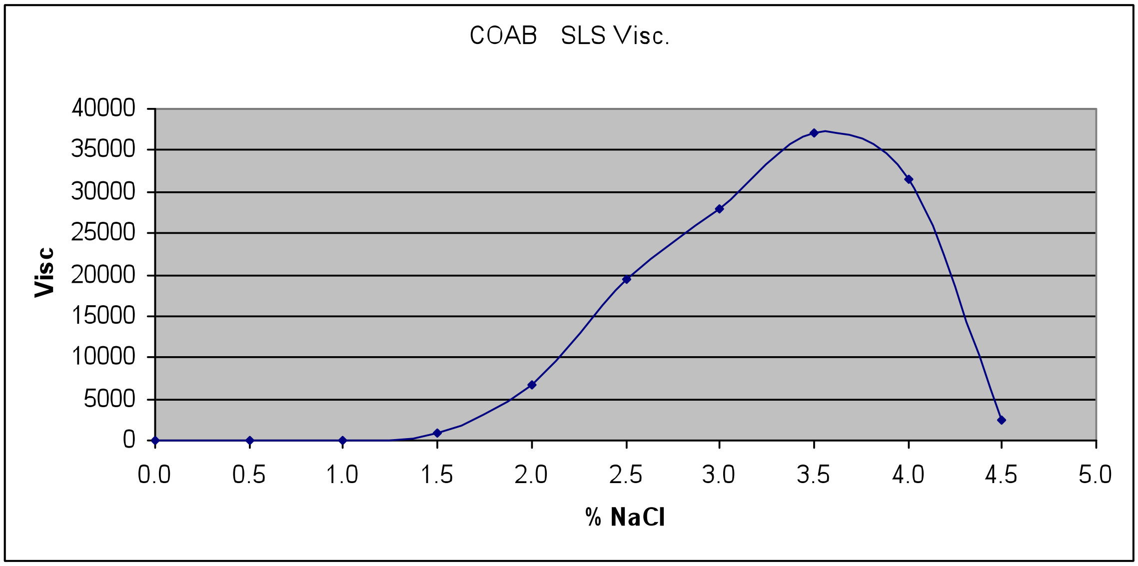
Control Salt Curve Data for SLS (100%)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	4
0.5	LV 1	60	4
1.0	LV 1	60	4
1.5	LV 1	60	5
2.0	LV 1	60	12
2.4	LV 1	60	50
3.0	LV 2	60	362
3.5	LV 3	30	2,120
4.0	LV 4	12	17,000
4.5	LV 4	12	19,500
5.0	LV 4	12	7,000
5.5	LV 3	30	2,060



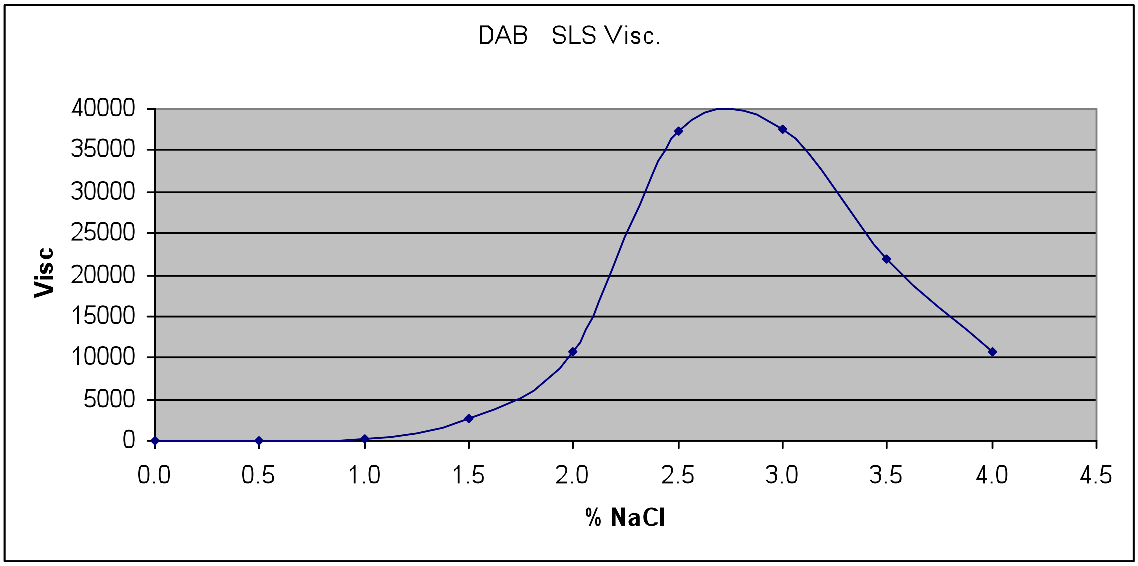
A-1 Salt Curve Data for SLS (75)/COAB (25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	4
0.5	LV 1	60	8.5
1.0	LV 2	60	67.5
1.5	LV 3	30	880
2.0	LV 3	12	6,800
2.5	LV 4	12	19,500
3.0	LV 4	12	28,000
3.5	LV 4	12	37,000
4.0	LV 4	12	31,500
4.5	LV 4	12	23,250



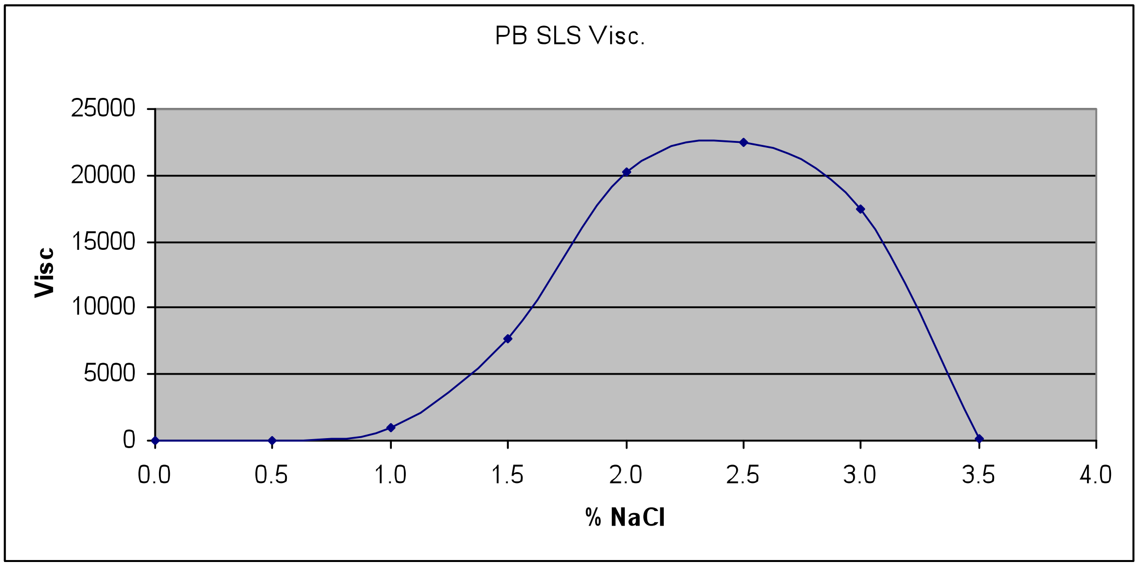
A-2 Salt Curve Data for SLS (75)/ DAB (25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	5
0.5	LV 1	60	13
1.0	LV 2	30	165
1.5	LV 3	30	2,680
2.0	LV 4	12	10,800
2.5	LV 4	12	37,250
3.0	LV 4	12	37,500
3.5	LV 4	12	22,000
4.0	LV 4	12	10,750



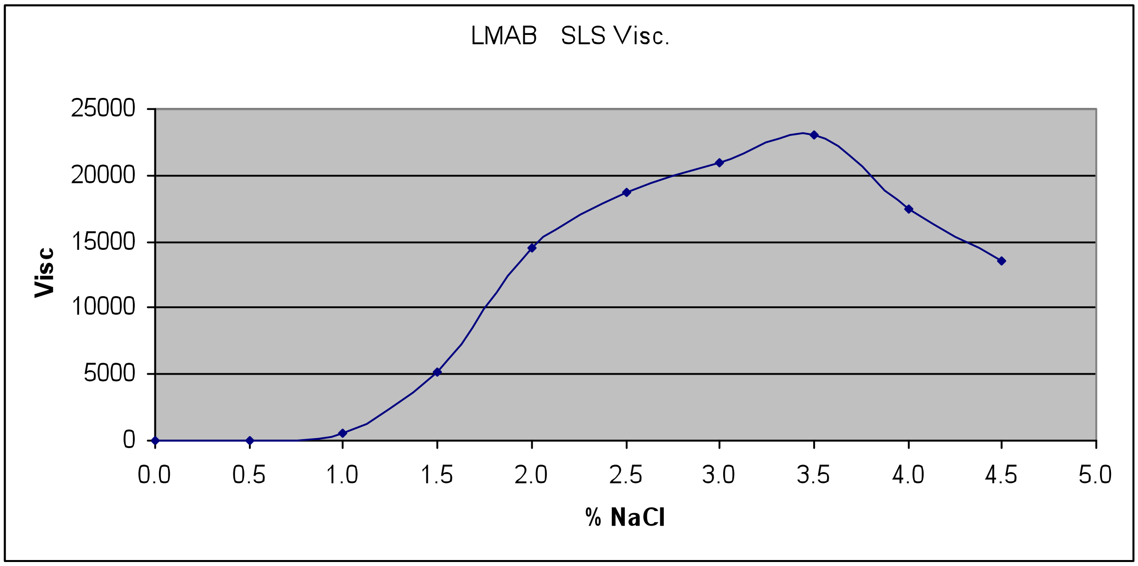
A-3 Salt Curve Data for SLS (75)/PB (25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	6
0.5	LV 1	60	37
1.0	LV 2	12	1,012
1.5	LV 3	12	7,650
2.0	LV 3	12	20,250
2.5	LV 4	12	22,500
3.0	LV 4	12	17,500
3.5	LV 2	12	162



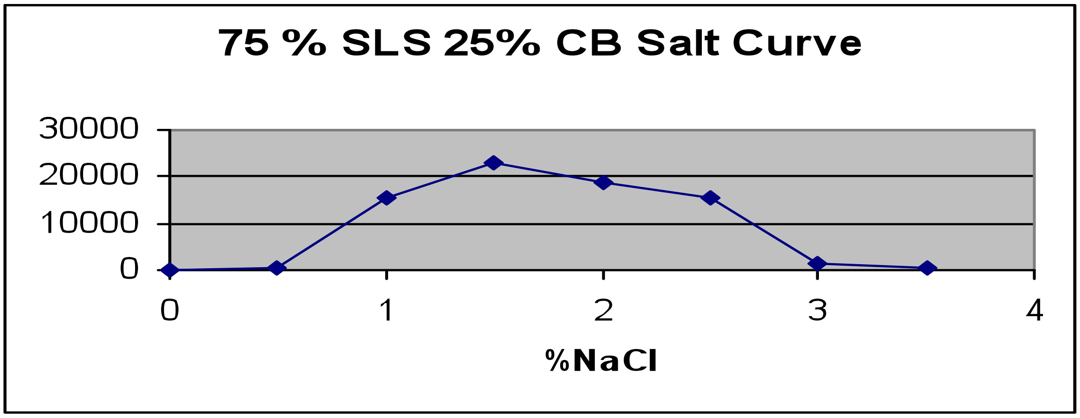
A-4 Salt Curve Data for SLS (75) / LMAB(25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	7
0.5	LV 1	60	34
1.0	LV 2	30	562
1.5	LV 3	30	5,150
2.0	LV 4	12	14,500
2.5	LV 4	12	18,750
3.0	LV 4	12	21,000
3.5	LV 4	12	23,000
4.0	LV 4	12	17,500
4.5	LV 4	12	13,500



A-5 Salt Curve Data for SLS (75) / CB(25)

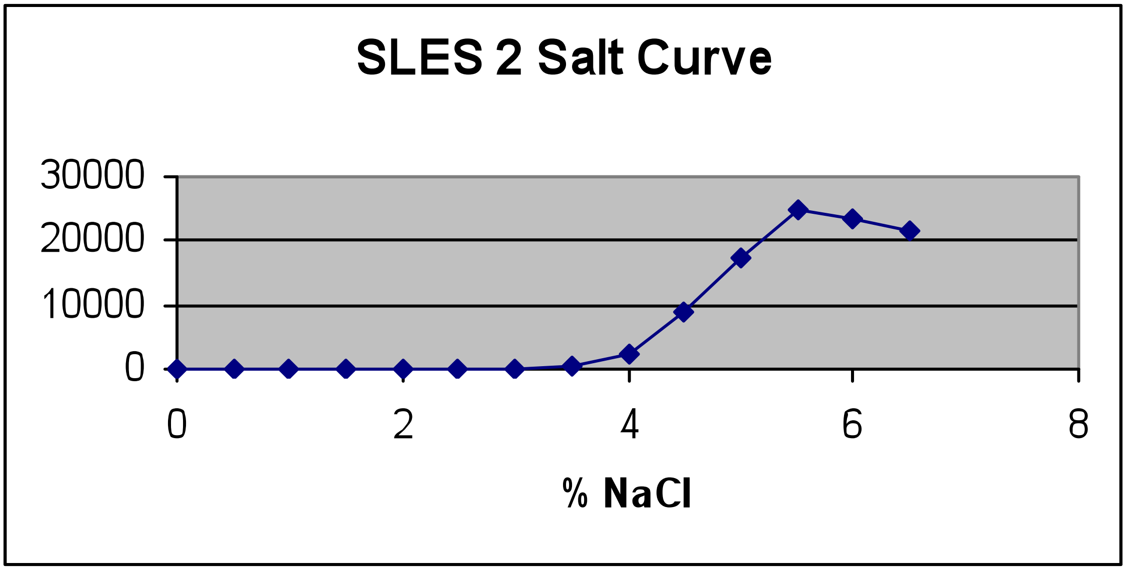
% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	20
0.5	LV 2	60	428
1.0	LV 4	12	15,500
1.5	LV 4	12	23,000
2.0	LV 4	12	18,600
2.5	LV 4	12	15,500
3.0	LV 3	30	1,620
3.5	LV 2	30	580



SLES-2 Salt Curves

Control Salt Curve Data for SLES-2 (100%)

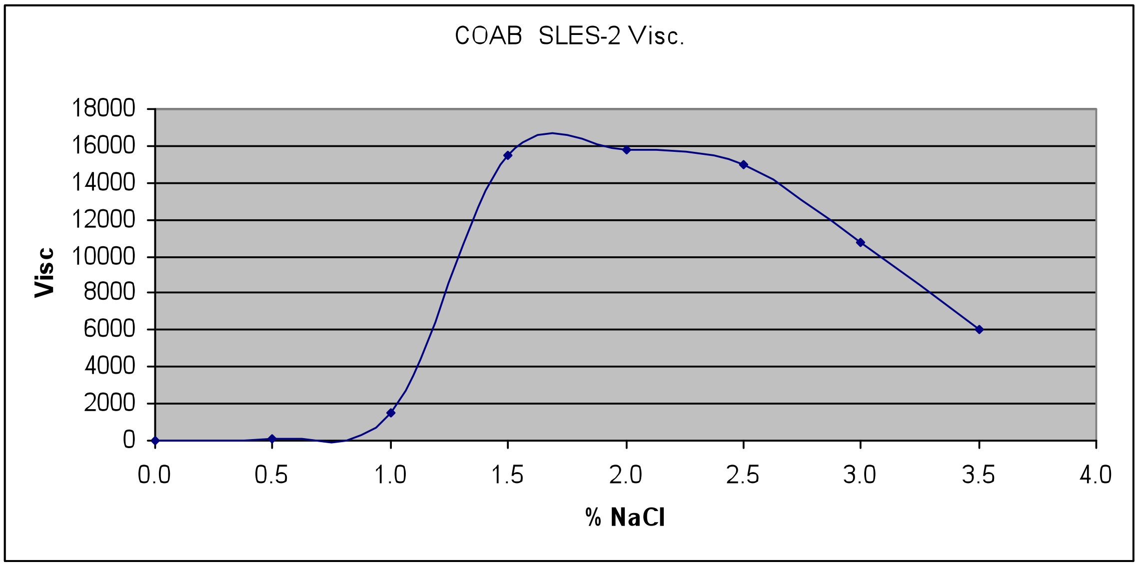
% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	4
0.5	LV 1	60	6
1.0	LV 1	60	6
1.5	LV 1	60	6
2.0	LV 1	60	7
2.5	LV 1	60	15
3.0	LV 1	60	67
3.5	LV 3	30	540
4.0	LV 3	12	2,204
4.5	LV 4	12	8,750
5.0	LV 4	12	17,250
5.5	LV 4	12	25,000
6.0	LV 4	12	23,250
6.5	LV 4	12	21,500



A large concentration of salt is needed to get to the peak viscosity.

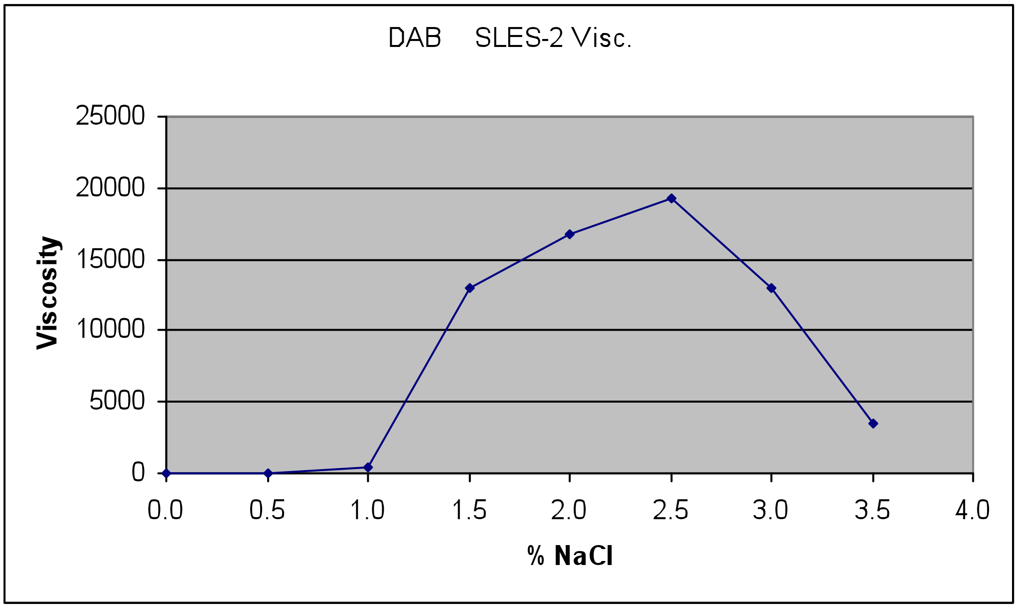
A-1 Salt Curve Data for SLES2 (75)/COAB (25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	10
0.5	LV 2	60	95
1.0	LV 2	12	1,475
1.5	LV 4	12	15,500
2.0	LV 4	12	15,750
2.5	LV 4	12	15,000
3.0	LV 4	12	15,000
3.5	LV 4	12	10,750
4.0	LV 4	12	6,000



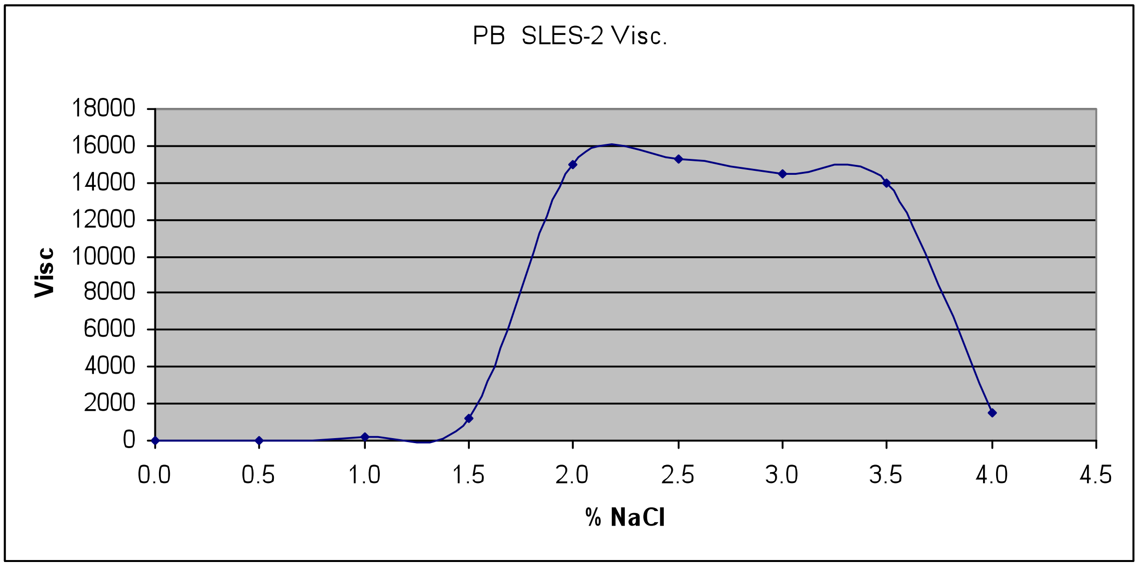
A-2 Salt Curve Data for SLES2 (75)/ DAB (25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	6
0.5	LV 2	60	30
1.0	LV 2	12	425
1.5	LV 4	12	13,000
2.0	LV 4	12	16,750
2.5	LV 4	12	19,250
3.0	LV 4	12	13,000
3.5	LV 4	12	3,500



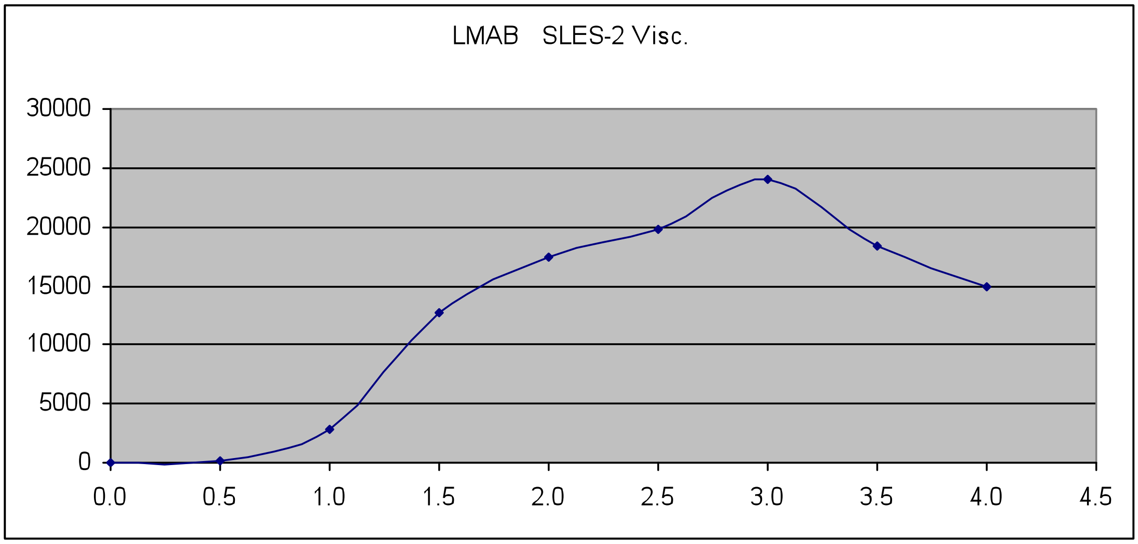
A-3 Salt Curve Data for SLES2 (75)/PB (25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	6
0.5	LV 2	60	25
1.0	LV 2	30	175
1.5	LV 2	12	1,225
2.0	LV 4	12	15,000
2.5	LV 4	12	15,250
3.0	LV 4	12	14,500
3.5	LV 4	12	14,500
4.0	LV 4	12	1,500



A-4 Salt Curve Data for SLES2 (75) / LMAB(25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	9
0.5	LV 2	60	95
1.0	LV 4	12	2,750
1.5	LV 4	12	12,750
2.0	LV 4	12	17,500
2.5	LV 4	12	19,800
3.0	LV 4	12	24,000
3.5	LV 4	12	18,350
4.0	LV 4	12	15,000



A-5 Salt Curve Data for SLES2 (75) / CB(25)

% Salt	Spindle #	RPMs	Viscosity (cps)
0	LV 1	60	6
0.5	LV 1	60	24
1.0	LV 3	60	300
1.5	LV 4	12	4,500
2.0	LV 4	12	15,750
2.5	LV 4	12	18,500
3.0	LV 4	12	15,000
3.5	LV 4	12	6,000
4.0	LV 4	30	1,700

Conclusions

Peak Viscosity / Salt

SLS Materials

Material	Peak Viscosity	% NaCl Added
DAB-SLS	37,500	3.0
COAB-SLS	37,000	3.5
LMAB-SLS	23,000	3.5
PB SLS	22,500	2.5
SLS	19,500	4.5
CB-SLS	18,600	2.0

The addition of betaine and salt to the SLS resulted in improved peak viscosity in all cases but the CB betaine. Additionally, in all instances addition of betaine shifted the salt curve to the left. That is the amount of salt needed to reach peak viscosity dropped when betaine is present. In many instances the curve was also broadened The presence of the conditioning betaine DAB actually increased peak viscosity and lowered the amount of salt needed to reach it in SLS systems and did so without adverse effect upon foam.

SLES-2

Material	Peak Viscosity	% NaCl Added
SLES-2	25,000	5.5
LMAB-SLES-2	24,000	3.0
DAB-SLES-2	19,250	2.5
CB-SLES-2	18,500	2.5
COAB-SLES-2	15,750	2.0
PB-SLES-2	15,200	2.5

The addition of betaine and salt to the SLES-2 resulted in lowering of the peak viscosity in all cases. LMAB decreased peak viscosity least. In all instances the addition of betaine shifted the salt curve to the left. That is the amount of salt needed to reach peak viscosity dropped when betaine is present. The inclusion of the conditioning betaine DAB provided good viscosity along with conditioning.

The combination of betaines and anionic surfactants provides a powerful tool to the formulator to provide value added formulations. We looked at only a few of such attributes. In addition to those we studied, foam thickness and bubble structure, feel on the skin and conditioning are all properties that will benefit by proper selection of a betaine. We encourage the formulator to investigate such interactions and maximize them for the specific formulation goals desired.

References

1. O'Lenick, Anthony, *Surfactants Strategic Raw Materials*, Allured publishing 2004 p. 1.

2. O'Lenick, Anthony, *Surfactants Strategic Raw Materials*, Allured publishing 2004 p. 112.

Supplemental Chapter 4

Detergency

At first blush the concept of detergency as applied to hair and skin should be well developed and rather simple. As like most things in life, that which appears simple often becomes the most complex. That which appears to be most clear is often most obscure.

The definition of the words in the American Heritage dictionary[1] does little to clear up the confusion. They are;

de·ter·gent (d¹-tûr“j…nt) *n.* **1.** A cleansing substance that acts similarly to soap but is made from chemical compounds rather than fats and lye. **--de·ter·gent** *adj.* Having cleansing power.

cleanse (klµnz) *tr.v.* **cleansed**, **cleans·ing**, **cleans·es**. To free from dirt, defilement, or guilt; purge or clean.

The cleansing and detergency is supplied to the formulation by seletion of surfactants. Almost every paper written about surfactants includes something about HLB. The groundbreaking work of Griffin some fifty years ago remains a cornerstone of surfactant technology. The system is limited to non-ionic surfactants and unfortunately most detergents used in the personal care market are anionic. That not withstanding, the HLB system is very helpful in determining what makes a detergent. Detergents in laundry and many industrial applications is in fact based upon ethoxylates.

The use of alkoxyated non-ionic as surface active agents is well known. The ethoxylation of fatty alcohols results in compounds that have both water soluble and oil soluble groups. The result is a so called “surfactant”, a contraction for surface active agent. The addition of ethylene oxide to fatty alcohol results in increasing water solubility.

The term "HLB" was first employed by the lab staff of the Atlas Powder Co. in America. This means the balance between the oil soluble and water soluble moieties in a surface active molecule, and is expressed as the "Hydrophile - Liphophile Balance". A more oil-soluble emulsifier shows a lower HLB and a more water-soluble emulsifier shows the reverse. HLB is a very useful method in selecting an emulsifier, but it still has several limitations to application for every surfactant.

The HLB system was developed by Griffin some 50 years ago. The system depends upon the observation that the solubility of the surfactant is related to the percentage by weight of polyoxyalkylene portion of the molecule and is relatively independent of the nature of the fatty group.

HLB Value= % EO/5

[009]

Water Dispersibility	**HLB**	**% EO .**
Not dispersible	1-4	up to 20%
Poorly dispersible	4-6	20%- 30%
Milky dispersion	6-8	30%- 40%
Stable milky dispersion	8-10	40%- 50%
Translucent to clear	10-13	50%- 65%
Clear Solution	13+	Over 65%

HLB	Application .
4-6	W/O Emulsifier
7-9	Wetting Agent
8-18	O/W Emulsifier
13-15	Detergents
15-18	Solubilizers

It is therefore clear that non-ionic detergents are materials that are very water soluble, having between 65 and75 % by weight EO. But this requirement does little to predict the efficiency of detergency of a specific compound.

My first experiences with detergency relate to the laundry detergent business, which uses non-ionic compounds extensively. In the laundry business there are a series of well defined tests that are used under laboratory conditions to clean a series of standardized fabrics of standardized stains. All these are outlined in test methodology sanctioned by the American Association of Textile Colorists and Chemists (AATCC). The ingredients used in the formulation of a laundry detergent are very different than those used in a shampoo. Nonionic surfactants namely fatty alcohol ethoxylates are used in the laundry products, while fatty alcohol sulfates and ether sulfates are commonly used in cosmetic products. The nature of the soil, the substrate and the cleansing process are also quite different. Also and very importantly, consumer perception of what constitutes an acceptable product is very different for a laundry detergent than for a shampoo designed for the hair. Consumers of shampoos demand high levels of copious foam. Consumers of laundry detergents demand no foam in the rinse to allow for a perception of clean. Substitution of one detergent for another can clearly result in consumer dissatification. It would be reasonable to assume that a methodology should be available to the cosmetic chemist that allows for the determination of cleansing efficiency of products used in shampoos.

Perhaps such tests exist but they are not readily available. In fact there was not a lot of information available. Firstly, a working definition of “clean hair” is difficult to ascertain. Hair which is exposed to harsh detergents often has straw like raspy feel. This type of clean hair is not cosmetically appealing. Somewhere between a non-washed state and a state in which hair I denuded from oils should be designated as clean. It should be therefore possible to create a scale of cleansing efficiency with a water wash being a zero and a denuded hair being 100. Somewhere between the two lies the proper level of detergency to provide the consumer a clean hair that is aesthetically appealing. Knowing what is stripped off the hair in cleansing should allow for development of optimized detergents that provide consumer acceptable cleansing and the proper consumer feel.

Soil Types

A determination of what is removed during cleaning of hair is critical to the understanding of detergency and any potential scale of detergency. The ability to pick a detergent from the virtual cornucopia of compounds available should be determined by the efficiency of the detergent to remove the specific oils found commonly on hair.

Hair in its native state is made up of protein. Protein in turn is composed of amino acids which are assembled into what is referred to as primary structure. The peptide bond as it is referred to by biochemists is referred to as polyamides by organic chemists. The amino acid structure has a secondary structure which relates to hydrogen bonding, giving each protein a three dimensional structure. There are also disulfide bonds between sulfur bearing amino acids. For the most part, unless you are relaxing or perming hair you do not want to do anything to alter the protein structure.

The hair also contains oils that come from the scalp. The build up of which constitutes the major portion of what is commonly called “soils”. Some of these materials are superficial on the hair and can be easily removed while others soils are located deeply within the hair and this cannot be easily removed. An understanding of these materials and how they function is critical to understanding what is removed in cleaning hair.

A key article related to this analysis is entitled *Hair Lipids and their contribution to perception of hair oiliness*[2]. The Koch article defines two types of oils, the first referred to as “external oiliness” and the second as “internal oiliness”. The article points out that some of the oil that designated external oil is superfacial and is removed by shampooing. The remainder of the oil remains strongly absorbed onto the hair and in the cuticle and can only be removed by strong extraction[3]. It has been shown by consumer testing that the internal oil does not contribute to the consumer perception of oiliness. It does however function as what Koch calls a “storage capacity” for oil. This is important because the internal oil works its way to the hair’s surface. This replenishing mechanism explains why hair becomes oily quite regularly even with regular washing. It likewise explains why some hair types require application of more oil, while others require more oil removal.

Koch also points out that the nature of the oil and not only its concentration has a major effect upon the consumer perception of oiliness both on hair and on skin. Others point out that the chemistry of the oil on the hair has effects upon such variables as the velocity of oil spreading from the internal oil storage, the feel of the oil as it is received by the consumer. The oil’s physical properties including it’s melt point, stickiness, and viscosity all contribute to the consumer’s perception of oiliness [4].

The oils observed on the hair vary considerably in terms of polarity. If the extraction of oils is not the same based upon this difference in polarity, the extracted oils will not be the same as those removed by shampooing. Koch developed extraction methodologies that both showed the composition of internal and external oils and related directly to those extracted by shampooing. This outstanding analytical work has allowed for both structure elucidation and quantification of the components of both internal and external oils. The methodology finds both non-polar oils like triglycerides, and far more polar components like mono acyl glycerides commonly found on the hair and skin. Since these classes of compounds differ appreciably in polarity, an extraction of external oils must pick the polar and non-polar oils from the hair and leave the internal oils in tact. It was determined in the Koch reference that the best extraction solvent for the polar and non-polar oils on the hair as external oils is a mixture of water and chloroform. The presence of water has a profound effect upon cleaning hair. Water swells the hair during shampooing, which is thought to have an impact on the availability of the internal oiliness especially just under the cuticle. The object of the experiment of Koch et al was to identify the external oils extracted from the hair during shampooing. The fact that shampooing almost always used water, an extraction with a partial water containing system seems appropriate.

It was determined that the "average commercial shampoo" removes only 40-60% of the total oils in the hair[5]. This quantity matches up well with the extraction method of Koch. The internal oils are extracted using extreme methods. Specifically, the extraction s conducted by Soxhlet extractions with boiling ether and water for 16 hours.

Table 1 details the composition of the so- called "external oils". These are the oils removed by shampooing. A good detergent will remove these materials efficiently.

Table 1
Composition of External Oils (Hair)[1]

External	mg extracted	% Comp
Squalene	0.26	9.4
Cholesterol Esters	0.56	20.3
Triglycerides	0.51	18.5
Free Fatty Acid	1.27	46.0
Cholesterol	0.05	1.8
Monoglycerides	0.11	4.0
Total	2.76	100.0

Table 2 details the composition of the so called "Internal oils". These are the oils are not removed by shampooing. A good detergent will not remove these materials efficiently.

Table 2
Composition of Internal Oils (Hair)[1]

Internal	mg extracted	% Comp
Squalene	0.31	30.4
Cholesterol Esters	0.11	10.8
Triglycerides	0.12	11.8
Free Fatty Acid	0.15	14.7
Cholesterol	0.21	20.6
Monoglycerides	0.12	11.8
Total	1.02	100.0

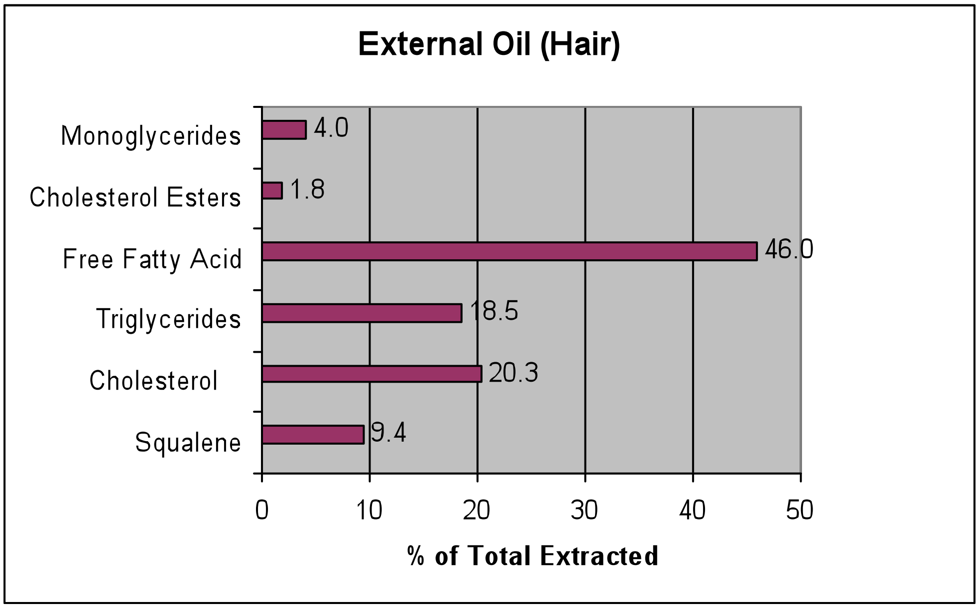
Table 3 details the difference in each compound in the composition of "internal oils" and "external oils". The fact that the composition of internal oil and external oil is not identical indicates there is some preferential absorption of compounds rich in internal oil but lean in the external oil.

Table 3
Comparison of External Oils v. Internal Oil Location (Hair)[1]

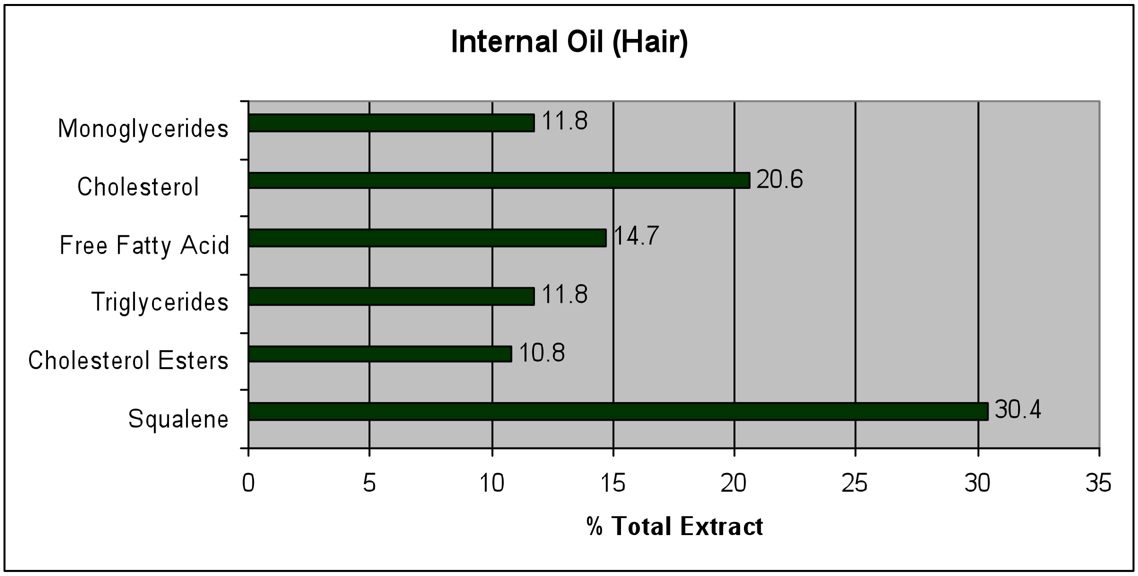
	External	Internal	Total	% Internal	% External
Squalene	0.26	0.31	0.57	54.4	45.6
Cholesterol Esters	0.56	0.11	0.67	16.4	83.6
Triglycerides	0.51	0.12	0.63	19.0	81.0
Free Fatty Acid	1.27	0.15	1.42	10.6	89.4
Cholesterol	0.05	0.21	0.26	80.8	19.2
Monoglycerides	0.11	0.12	0.23	52.2	47.8
	2.76	1.02	3.78	-	-

Graphs 1-3 show the same data as Table 1-3 only in graphic form.

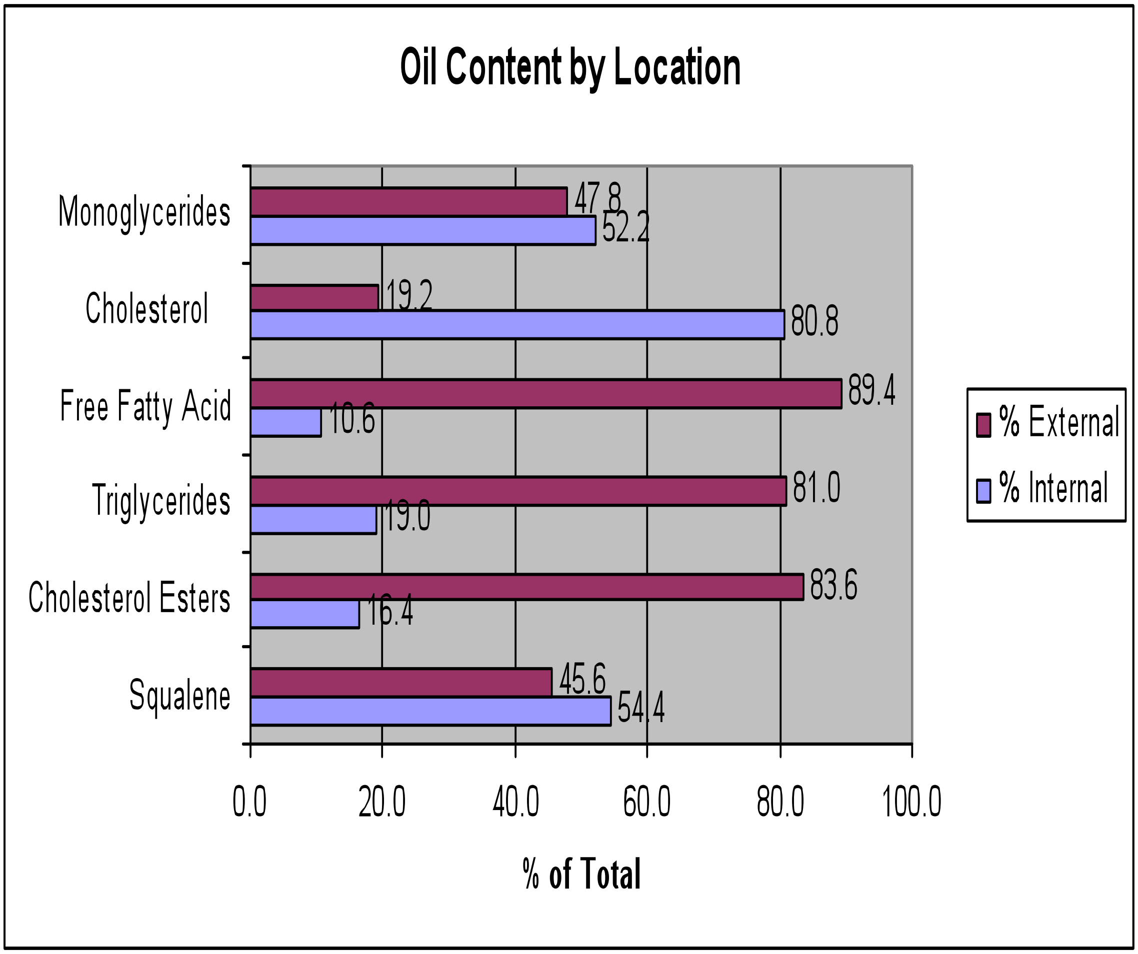
Graph 1



Graph 2


Internal Oil (Hair)
Monoglycerides
11.8
Cholesterol
20.6
Free Fatty Acid
14.7
Triglycerides
11.8
Cholesterol Esters
10.8
Squalene
30.4
0
5
10
15
20
25
30
35
% Total Extract

Graph 3



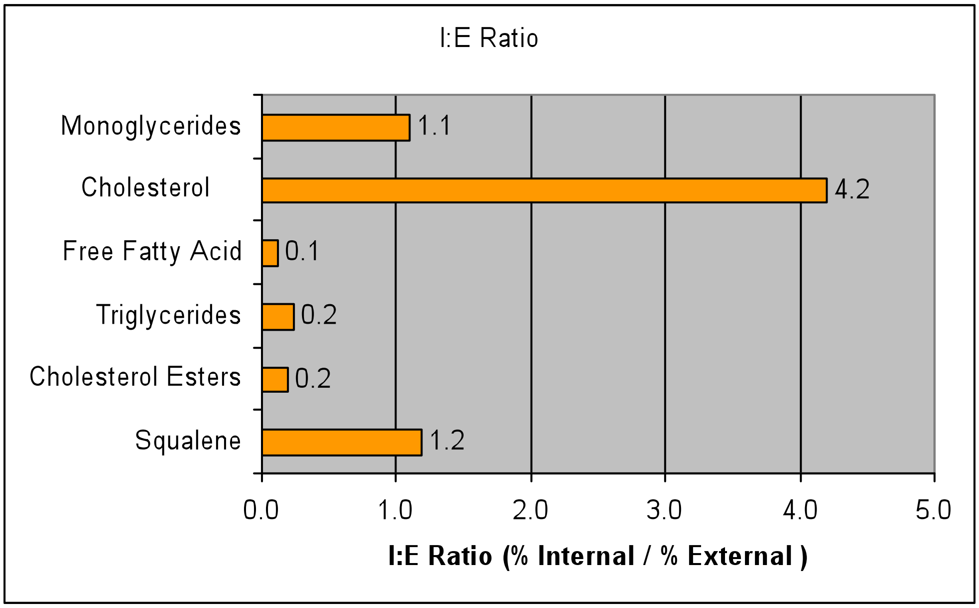
Oil Content by Location
Monoglycerides
Cholesterol
Free Fatty Acid
Triglycerides
Cholesterol Esters
Squalene
47.8
52.2
19.2
80.8
89.4
10.6
81.0
19.0
83.6
16.4
45.6
54.4
0.0
20.0
40.0
60.0
80.0
100.0
% of Total
% External
% Internal

Internal to External Ratio

Table 4

	% Internal	% External	I:E Ratio
Squalene	54.4	45.6	1.2
Cholesterol Esters	16.4	83.6	0.2
Triglycerides	19.0	81.0	0.2
Free Fatty Acid	10.6	89.4	0.1
Cholesterol	80.8	19.2	4.2
Monoglycerides	52.2	47.8	1.1

Graph 4



High I:E ratios indicate a component that is held within the hair and does not readily pass to the outside. Cholesterol Esters are strongly retained on the inside by a 4.2:1 ratio. Monoglycerides and Squalene are roughly equal showing little preference for internal or external. Free fatty acids, triglycerides and cholesterol esters favor the external phase.

Substrate

In the standardization of any process, the substrate upon which the process is measured needs to be clearly defined. This allows for a reproducibility of results and the ability for investigators to repeat the work done by others. Hair is structurally very different from grope to group and from person to person. Various factors like the mount of bleaching, straighten, perming and the like as well as environmental exposure and even cosmetic products used all effect the hair and make standardization very difficult. For this reason a preliminary test methodology was sought that was not dependant upon substrate. That methodology is shown in the detergency section below.

Detergency Testing

In order to evaluate the detergency of given surfactants a test methodology was developed. It was assumed that since squalene is a component of both internal and external oiliness, it would be a good starting material to evaluate. The method developed called Squalene Titer (SQ), measures the minimal quantity of detergent to emulsify a standard quantity of squalene. The SQ test is carried out in a testube with increasing amounts of surfactant, until upon shaking the oil globules are no longer present at the surface.

Test Methodology:

A. Preparation of Test Solution

1.5 grams of squalene is added to a testube.
1.5 grams of water is then added.

The result is squalene is the top phase, water the bottom phase. There is no interfacial emulsification and a clearly discernable separation between the phases.

B. Preparation of Detergent Solution

The detergent is prepared at 10% active and standardized by Epton titration.

C. Titer Evaluation

The 10% solution of detergent is added drop wise and the testube is shaken. The oil will be observed on the testube surface as globular and irregular. As the detergent is added the oil globules will disappear and a uniform white liquid results. At this point foam, which was previously lacking, is also noted in the testube. The Titer Point is described as the point in the titration in which the globular oil droplets disappear on the glass testube, and that foam is noted.

Calculation:

Squalene Titer Point =

1.5 grams of squalene/ grams of detergent solution added * (activity of detergent solution)

Results:

1. SLS

Squalene Titer = 1.5 grams /(0.95 grams) * (0.10) = 15.8

Upon overnight settling a white upper thick liquid phase and clear water white lower phase were observed.

2. SLES-2

Squalene Titer = 1.5 grams /(0.75 grams) * (0.10) = 20.0

Upon overnight settling a white upper thick liquid phase and clear water white lwer phase were observed.

3. Cocamidopropyl betaine

Squalene Titer = 1.5 grams /(2.0 grams) * (0.10) = 7.5

Upon overnight settling a white upper thick liquid phase and clear water white lower phase were observed.

4. Nonyl phenol 9 mole ethoxylate

Squalene Titer = 1.5 grams /(0.8 grams) * (0.10) = 37.5

Upon overnight settling a white upper thick liquid phase and clear water white lower phase were observed.

5. Disodium laureth -3-sulfosuccinate Sodium Salt

Squalene Titer = 1.5 grams /(1.3 grams) * (0.10) = 11.5

Upon overnight settling a white upper thick liquid phase and clear water white lower phase were observed.

6. Sodium Laurylglucosides Hydroxypropyl Sulfonate

Squalene Titer = 1.5 grams /(0.8 grams) * (0.10) = 18.75

Upon overnight settling a white upper thick liquid phase and clear water white lower phase were observed.

Table 5

Material	**Squalene Value**
Nonyl phenol 9 mole ethoxylate	37.5
SLES-2	10.0
Sodium Laurylglucosides Hydroxypropyl Sulfonate	18.7
SLS	15.8
Disodium laureth -3-sulfosuccinate Sodium Salt	11.5
Cocamidopropyl betaine	7.5

Conclusions

Since SLS and SLES-2 are commonly used detergents in hair care, their performance is not unexpected. NP-9 while not used in our industry, is known to be a good laundry detergent. What is unexpected is the magnitude of the Squalene Titer for the sulfates. Specifically, the high Squalene Titer Value observed. The magnitude of the number would lead to a conclusion that the amount of detergent present in shampoos is far beyond the level that one would need simply to cleanse the hair.

If the detergent is in fact present at levels far beyond the level needed for cleansing, it must then be concluded it s present for other reasons, namely foam, ability to provide viscosity to the formulation and other consumer perceptible reasons. Since detergency requires lower concentrations of surfactant than foaming and other attributes, detergency is not what drives the level of surfactant chosen. This may well be the reason that there is so little published on detergency for hair.

References

1. American Heritage Dictionary 3rd Edition (1993).

2. Koch, J. et al, *Hair Lipids and their contribution to perception of hair oiliness,* J. Soc. Cosmet. Chem. 33, 317-326, Nov 1982.

3. Shaw, D.A., Hair Lipids and Surfactants, Int. J. Cosmet. Sci. 1, 317 (1979)

4. Eberhardt, H. The regulation of sebum excretion in man, Arch. Dermatol. Forsch. 251, 155 (1974)

5. Koch, J. et al, Hair lipids and their contribution to the perception of hair oiliness, J. Soc. Cosmet. Chem. 33, 330-342, Nov 1982

Acknowledgement

The studies in this paper on titer point were conducted by Thomas O’Lenick, a summer student at SurfaTech Corporation. Thomas is pursuing a doctorate in chemistry at the University of Tennessee.

Side Bar

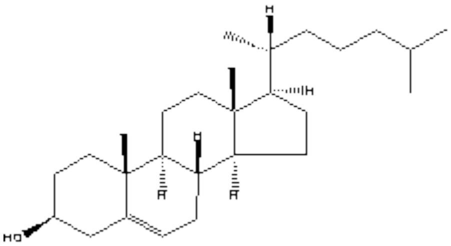
Oils found on Hair

The following are compounds are found on hair.

1. Cholesterol

Formula: $C_{27}H_{46}O$
Molecular Weight: 386.6
Melt Point 148.5°C
CAS No. 57-88-5

Structure:

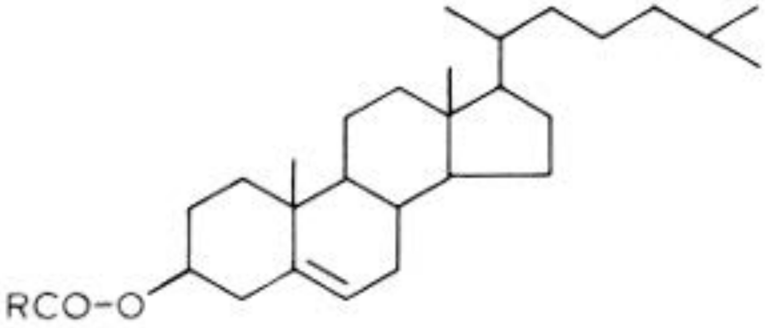


2. Cholesterol Esters

Cholesterol esters are largely found in body fluids and may be also found in vessel walls as fatty streaks in atherosclerosis. The esterification of free cholesterol with fatty acids increases the lipid solubility of the cholesterol. This reaction occurs within intestinal cells (by acyl CoA:cholesterol acyltransferase, ACAT) allows the cholesterol to be stored as a neutral lipid in cytosolic droplets and in the packing of cholesterol into lipoprotein particles for export via the plasma to liver cells.

The compounds conform to the following structure;

cholesteryl esters



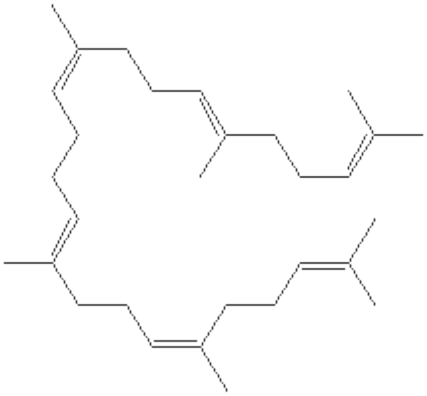
3-*O*-acyl-cholest-5-en-3β-ol

3. Squalene

Squalene is a colorless unsaturated aliphatic hydrocarbon, $C_{30}H_{50}$, found especially in human sebum and in the liver oil of sharks, that is an intermediate in the biosynthesis of cholesterol and is used in biochemical research. Squalene is produced in the body when cholesterol is converted to fat. Squalene is a key material in the biosynthesis and degradation of cholesterol. Squalene has 6 isoprene units and contains 6 trans double bonds.

Molecular Weight:	422.8
Melt Point	- 38^{o}C
CAS No.	111-02-4

Structure:



4. Monoglycerides and Triglycerides

Monoglycerides and triglycerides are members of a class of materials found on hair. They are all derived from triglycerides (neutral fats). Monoglycerides have had two acyl groups removed leaving only one and two hydroxyl groups. Because of the two hydroxyl groups the compound is much more polar than the triglyceride.

CH_2-O-C(O)-R	CH_2-O-C(O)-R
|	|
CH_2-O-C(O)-R	CH-OH
|	|
CH_2-O-C(O)-R	CH_2-OH
Triglyceride	**Monoglyceride**

Triglycerides are composed of one molecule of glycerol and three long-chain fatty-acid molecules, which may be the same or different. In contrast to the short-chain or volatile fatty acids produced by bacterial fermentation of ingested carbohydrates, which contain only two to five carbon atoms, most long-chain fatty acids in fat contain 16 to 20 carbon atoms. The more unsaturated the long-chain fatty acids (i.e., the greater the number of double bonds between its carbon atoms) and the shorter their chain length (i.e., the fewer carbon atoms they consist of), the lower the melting point of the triglyceride. When the melting point is less than room temperature, the triglyceride is referred to as an oil; when it is greater than room temperature, it is referred to as a fat

5. Free Fatty Acid

Free Fatty Acids are the groups removed from the triglyceride to give the monoglyceride and free fatty acid. These materials readily form soaps when present at pH above 3. Fatty acids conform to the following structure:

$$\mathbf{R\text{-}C(O)\text{-}OH}$$

Saturated

R Formula	Common Name	Molecular Weight
C_7H_5	caprylic	144
C_9H_{19}	capric	172
$C_{11}H_{23}$	lauric	200
$C_{13}H_{27}$	myristic	228
$C_{14}H_{29}$	pentadecanoic	242
$C_{15}H_{31}$	palmitic	256
$C_{17}H_{35}$	stearic	284
$C_{19}H_{39}$	arachidinic	312
$C_{21}H_{43}$	behenic	340

Unsaturated

R Formula	Common Name	Molecular Weight
$C_{17}H_{33}$	oleic	282
$C_{17}H_{31}$	linoleic	280
$C_{17}H_{29}$	linolenic	278
$C_{15}H_{29}$	palmitoleic	254
$C_{13}H_{25}$	myristicoleic	226
$C_{21}H_{41}$	erucic	338

Supplemental Chapter 5

Wetting

Water Wetting

Wetting, specifically wetting from aqueous systems is the type of wetting that occurs on hair and skin when washing as opposed to the type of wetting that occurs when an oil is applied to a pigment. When cosmetic chemists look at surfactants for water based formulations, they can easily neglect wetting as an important attribute and concentrate on detergency for cleansing systems and conditioning for systems designed to condition the hair. However, both systems need to possess the requisite wetting to achieve a product with the proper aesthetics. If a shampoo does not wet the hair satisfactorily, it will not apply easily and will not spread onto the hair. Recalling that most consumers want thick shampoos when applied to their hands from a bottle, but rapid spreadability onto the hair, wetting is an important attribute. The same is true of a conditioner, only here there is an added benefit of a good wetting formula. Many cationic systems are rather hydrophobic and consequently need help in spreading out on the hair. A conditioner that lacks spreadability is often referred do as leaving gunky deposits on the hair.

Wetting phenomena are complex and depend upon several processes and factors such as diffusion, surface tension, concentration and also the surface being wet.[1] This article will describe some of the features of surfactants that alter wetting properties. Many types of surfactants including specific compounds from the anionic, cationic, non-ionic and amphoteric class can have wetting properties. The choice of the best wetting agent in each class depends upon chemical structure.

Surfactant Structure

There is a commonality in the structure of a surfactant is the presence of a hydrophilic portion and a hydrophobic portion as shown.

The hydrophilic end is water-soluble and is a polar or ionic group. The hydrophobic end is water-insoluble either hydrocarbon chain, an aromatic group or silicone. This dual functionality, hydrophobic and hydrophilic is the source of the surface activity. The activity is due in large part to the unique structure of water. The water molecule has a great deal of inter-molecular hydrogen bonding. This accounts for the surface tension of water. Anything that disrupts the hydrogen bonding in water does so at a high energetic cost. Put another way oil floating on water, which appears to be an ordered system, is at the lowest free energy since the oil molecules disrupt the fewest number hydrogen bonds in the water. This concept of lowest free energy of the system drives all of the surfactant properties.

An understanding of how surfactants behave in aqueous systems is key to understanding the functionality of these materials. When a surfactant is added to water, the surface tension of the water drops. If the surfactant is titrated in small increments and the surface tension measured, the drop in surface tension as a function of surfactant concentration can be plotted. Fatty surfactants will lower the surface tension from the 70 dynes/cm^2 to the mid 30's dynes/cm^2 depending upon the exact product chosen. At some concentration, adding more surfactant will not lower the surface tension any more. Instead, micelles form. This is refereed to as the *Critical Micelle Concentration* or CMC.

Before dealing with wetting, a good working definition is required.
The BASF website states[1]:

Wetting is the displacement of one fluid on a surface by another. Thus, wetting always involves three immiscible phases. Traditionally, we think of the three phases as consisting of a solid, a liquid and a gas. Theoretically, only two fluid phases are required for wetting to occur.

A wetting agent is any substance that increases the ability of water to displace air from a liquid or solid surface. Wetting agents can cause three different kinds of wetting: spreading, adhesion and immersion.

The Draves wetting test measures the time required for a skein of weighted, waxed cotton yarn to completely sink in a cylinder of surfactant solution. When the surfactant displaces sufficient air from the skein (by spreading wetting), the skein suddenly sinks to the bottom of the cylinder. The faster the skein sinks, the greater the wetting ability of the surfactant solution. (The Draves Wetting Test is ASTM D2281-68(1997) and is officially entitled "*Standard Test Method for Evaluation of Wetting Agents by the Skein Test*")

We will describe two different measurements of wetting. The first is the Draves Wetting and is a measure of how long it takes to sink a skein of fiber in a solution of surfactant at the critical micelle concentration. The units of *Draves Wetting* is seconds. The second is wetting power. This latter test is the number of grams per liter which is needed to cause a sink time of the fiber in 25 seconds. The units of *Wetting Power* is concentration expressed in grams/liter.

General Considerations

Some of the attributes of wetting agents are specific to the type of compound being evaluated. Others attributes are required properties independent of the chemistry of the surfactant. The following are required attributes of wetting agents independent of the type of compound.

A. Surface Tension Reduction

Wetting agents must reduce surface tension. They must provide a surface tension of below 30 dymes/cm^2. This is one key requirement for a wetting agent.

B. HLB

No discussion of surfactants is complete without a discussion of HLB. The concept of HLB was developed some 50 years ago by Griffin, and remains a very useful concept to this day. HLB theory tells us that wetting is also related to HLB. HLB is a measure of the % of ethylene oxide in a non-ionic molecule. Generally non-ionic surfactant water solubility is achieved at an HLB of around 10. Since HLB is defined as:

$$\text{HLB} = \underline{\text{ \% Ethylene Oxide in a molecule}}$$

5

The molecule will be 50% ethylene oxide. Wetting agents contain more ethylene oxide.

Table 1[3]

Solubility in Water	HLB Value	Description
Insoluble	4 - 5	water in oil emulsifier
Dispersible	9 - 14	wetting agent
Translucent to clear	12 -15	detergent
Very soluble	14 - 18	oil in water emulsifier

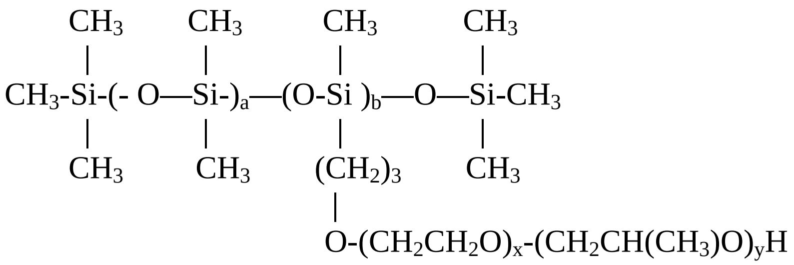
Therefore, we can expect a wetting agent to have between 45% (9 times 5) and 70% (14 times 5) water soluble portion on it to be a wetter. It is interesting that there is overlap between the properties and the composition. Between 12 and 14 a surfactant will have both wetting and detergency properties. It is quite common to see both wetting and detergency properties in a single molecule, but it is far more common to see formulations containing multiple surfactants to cleanse and wet.

Structure Function

While many of the attributes of surfactants that make them wetting agents are of a general nature, specific compounds have attributes that relate to that class of surfactants that effect wetting.

1. Effects of Molecular Weight

The effect of molecular weight upon wetting is easily demonstrated by considering a homologous series of dimethicone copolyol compounds. These materials now called PEG/PPG dimethicone compounds are a class of silicone / polyoxyalkylene derivatives. DMC surfactants are a class of compounds that conform to the following general structure:



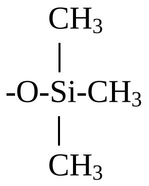
$$CH_3\text{-}Si(CH_3)_2\text{-}(\text{-}O\text{—}Si(CH_3)_2\text{-})_a\text{—}(O\text{-}Si(CH_3)[(CH_2)_3\text{-}O\text{-}(CH_2CH_2O)_x\text{-}(CH_2CH(CH_3)O)_yH])_b\text{—}O\text{—}Si(CH_3)_2\text{-}CH_3$$

The compounds are surface active agents because they have a water soluble polyoxyalkylene group and a water insoluble silicone portion.

Nomenclature

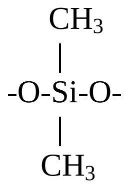
A shorthand has been developed to describe there molecules that is based upon the type of groups present in the molecule.

“M unit” is monosubstituted (one oxygen atom shared by the silicon)



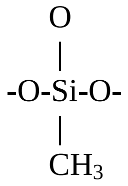
$$-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_3}$$

“D unit” is disubstituted (two oxygen atoms shared by the silicon)



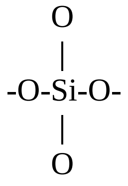
$$-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-$$

“T unit” is trisubstituted (three oxygen atoms shared by the silicon)



$$-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{O}}{\mathrm{Si}}}-\mathrm{O}-$$

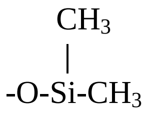
“Q unit” is tetrasubstituted (four oxygen atoms shared by the silicon)



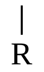
$$-\mathrm{O}-\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{Si}}}-\mathrm{O}-$$

If organofunctional groups other than carbon are introduced, the group is given an asterisk ”*“, which is added to its designation.

“M* unit” is monosubstituted (one oxygen atom shared by the silicon)

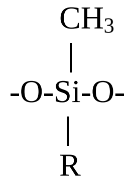


$$-\mathrm{O}-\overset{\mathrm{CH_3}}{\mathrm{Si}}-\mathrm{CH_3}$$



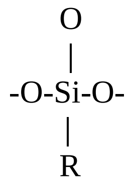
$$\begin{array}{c} | \\ R \end{array}$$

"D* unit" is disubstituted (two oxygen atoms shared by the silicon) with organofunctionality



$$\begin{array}{c} CH_3 \\ | \\ -O-Si-O- \\ | \\ R \end{array}$$

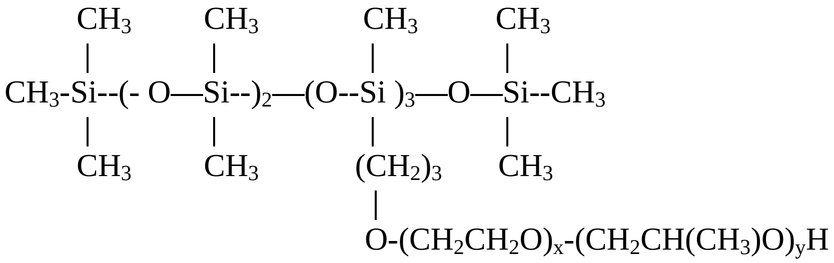
"T* unit" is trisubstituted (three oxygen atoms shared by the silicon) with organofunctionality



$$\begin{array}{c} O \\ | \\ -O-Si-O- \\ | \\ R \end{array}$$

There is no "Q* unit" since there is no possibility of functional groups.

Thus, for example, the structure for MD_2D_3*M is:



$$\begin{array}{ccccc} & CH_3 & CH_3 & CH_3 & CH_3 \\ & | & | & | & | \\ CH_3- & Si--(-\,O— & Si--)_2—(O-- & Si\,)_3—O— & Si--CH_3 \\ & | & | & | & | \\ & CH_3 & CH_3 & (CH_2)_3 & CH_3 \\ & & & | & \\ & & & O-(CH_2CH_2O)_x-(CH_2CH(CH_3)O)_yH & \end{array}$$

Table 2

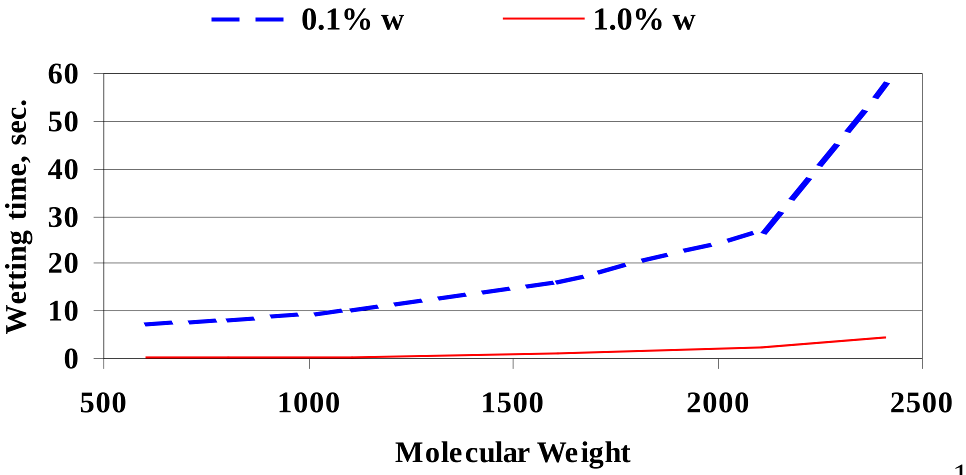
Surface Tension and CMC
Homologous Series of DMC Compounds

Designation	CMC, mg/L	δ at CMC, dynes/cm^2
MD*DM	3	20
MD_2*D_2M	4	19
MD_3*D_5M	6	23
MD_3*D_7M	5	21
MD_4*D_8M	14	21

The above information is helpful in understanding several key aspects of surfactants. Firstly, it is not too surprising that a series of homologous silicone surfactants has almost identical surface tensions at the CMC. Secondly, it is also not too surprising to see that the CMC is somewhat higher as one increases the molecular weight. This can be contributed to the observation that smaller molecules can better pack the surface of the water and be more effective at lowering surface tension.

Wetting

The most interesting property that varies as the molecular weight is increased is wetting.



Draves Wetting of DMC

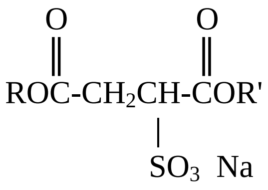
The data shows that there is a strong relationship between molecular weight (and structure) and wetting for DMC. The lower molecular weight materials have faster wetting times. Again, the smaller molecule allows for more efficient packing efficiency and dynamics. The materials with lower molecular weight were extremely effective at the higher concentration of 1.0% w. Their wetting speeds were almost instantaneous.

The data shows the slope of the curve does not changes much until the molecular weight of the DMC reaches approximately over 1200. The non-linearity of the graph of wetting time vs. molecular weight of the DMC predicts that molecules having a molecular weight between 600 and about 1200 should be effective wetting agents.

2. Effects of Branching

The effects of branching on wetting are seen with sulfosuccinate diesters. These materials are an anionic class surface-active agents. They are sulfonated diester derivatives of maleate esters. Because they are sulfonates, they have a stable C-S bond. However, they also have ester linkages in the molecule, so unlike alpha olefin sulfonates, sulfosuccinates are not stable in acid or base.

Sulfosuccinate diesters conform to the following formula:



$$\overset{\overset{\mathrm{O}}{\|}}{\mathrm{ROC}}\text{-}\mathrm{CH_2}\underset{\underset{\mathrm{SO_3\ Na}}{|}}{\mathrm{CH}}\text{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{COR'}}$$

Table 3[4]

Sulfosuccinate Wetting Power

R Group	Molecular Weight	Solubility in water @ 30°C g/l	Wetting Power g/l
2,methyl, butyl sulfosuccinate	360	530	10.0
n-pentyl sulfosuccinate	360	460	4.4
2,2 dimethyl butyl sulfosuccinate	388	310	1.1
n-hexyl sulfosuccinate	388	270	1.1
1, methyl hexyl sulfosuccinate	416	142	0.53
n-heptyl sulfosuccinate	416	65	0.25
2 ethyl hexyl sulfosuccinate	443	15	0.20

n octyl sulfosuccinate	444	14	0.32
n-butyl, pentyl sulfosuccinate	472	4.7	1.1
n-decyl sulfosuccinate	500	1.5	--

General Structural Properties of Sulfosuccinates

The following general structure / function relationships for sulfosuccinates have been established:

- Sulfosuccinate diesters having a total of eight carbon atoms or less in the two hydrophobic groups are too water-soluble to be of interest as surfactants. For example, dibutyl sulfosuccinate has eight carbon atoms in the two hydrophobic groups, four in each.

- Sulfosuccinate diesters having a total of twenty or more carbon atoms in the two hydrophobic groups, like didecyl sulfosuccinate, are generally too water-insoluble to be of interest as surfactants.

- As the number of carbon atoms in the surfactant increases, the solubility in water decreases and the wetting power increases until about eighteen carbon atoms are present in the non-polar hydrophobe.

-The best wetting agents in the diester class are those products that have a total of between fourteen and eighteen carbon atoms in the two hydrophobic groups.

- When branched alcohols are used in synthesis of diester sulfosuccinates, the resultant products are more water soluble than the homologous diester sulfosuccinates based upon linear alcohols.

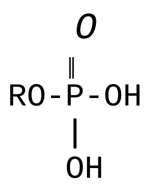
-Symmetrical sulfosuccinate diesters (*i.e.,* those made from the same alcohol, R = R') generally have the best wetting properties.

The wetting properties of sulfosuccinates are maximized at or near their critical micelle concentration

3. Combination Effects

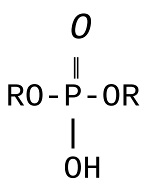
A somewhat more complicated structure function relationship for wetting properties is observed with phosphate esters. Phosphate esters are a well known class of surfactants that have been used historically as emulsifiers. More recently, however, there has been a trend to use mono-alkyl phosphate esters in a variety of personal care formulations. The proper selection of a phosphate ester for use in personal care applications is likely to result in wider usage of this class of compounds as emulsifiers and detergents.

Phosphate esters are part of a class of anionic surface-active agents. The commercial products are complex mixtures of the following components;



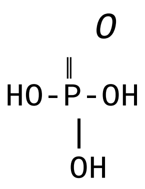
$\mathrm{RO{-}}\underset{\underset{\mathrm{OH}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}\mathrm{{-}OH}$

Mono Ester



$\mathrm{RO{-}}\underset{\underset{\mathrm{OH}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}\mathrm{{-}OR}$

Diester



$\mathrm{HO{-}}\underset{\underset{\mathrm{OH}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}\mathrm{{-}OH}$

Phosphoric Acid

ROH

Nonionic

General Properties

The monoester component of a phosphated product is most commonly the fastest wetter in the series. When using higher molecular weight nonionic surfactants or process modification increases its concentration, the best wetting agent is obtained. It is highly desirable to keep the free phosphoric acid content as low as possible in most applications. Most phosphate esters used in personal care are so called MAP products (Mono-alkyl phosphate esters).

Wetting Speeds

Phosphate Type	Hydrophobe C Atoms	Wetting Time (sec.)
Hexyl 0 EO Phosphate	6	15

Octyl 0 EO Phosphate	8	17
Decyl 0 EO Phosphate	10	28
Decyl 2.5 EO Phosphate	10	8
Decyl 6.0 EO Phosphate	10	23
Decyl 8.0 EO Phosphate	10	33
Tridecyl 0 EO Phosphate	13	34
Tridecyl 6.5 EO Phosphate	13	29
Myristyl 0 EO Phosphate	*14*	*34*
Myristyl 3.0 EO Phosphate	14	30
Myristyl 7.0 EO Phosphate	14	39
Myristyl 9.0 EO Phosphate	14	49
Myristyl 12.0 EO Phosphate	14	42

Alkyl Group

As the molecular weight of the hydrophobe increases, the wetting time likewise increases. The lowest molecular weight hydrophobe (hexyl phosphate) with no ethylene oxide was the best wetter in the series of non-ethoxylated species. In fact, as the molecular weight of the hydrophobe containing no ethylene oxide increases the phosphate produced will have a longer wetting time. This is true for hydrophobes having 6 to 14 carbon atoms.

Ethoxylation Degree

Within each set of hydrophobes, the ethoxylated materials all reached the fastest wetting times with between 2 and 3 moles of ethylene oxide added.

Summary and Conclusions

Wetting is an important function of surfactants. It is related to (1) molecular weight, (2) branching, (3) ethylene oxide content and many other attributes. Wetting is a also important in formulation of cosmetic products. Products which effectively wet hair and skin are more aesthetically appealing. When formulating cosmetic products not only should the more often considered surfactant properties like foam, and detergency be considered, but one also needs to consider the effect surfactants have upon wetting as well as the ultimate effect wetting has on the product performance.

References

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2. BASF website www.basf.com

3. O'Lenick, Anthony J. Surfactants: *Chemistry and Properties,* Allured Publishing 1999.

4. Linfield, Warner, M., Anionic Surfactants, Surfactant Series Volume 7, Marcel Dekker 1976, p. 433

Supplemental Chapter 6

Emulsions

Emulsification is a process that allows for the preparation of a **metastable single phase** of **two insoluble materials**. The preparation of cosmetically appealing emulsions is a very challenging and often frustrating undertaking. The metastable nature of the two insoluble materials is critical to understanding the nature and performance of emulsions. The metastable nature of the emulsion, and the requirement that the emulsion be cosmetically appealing, offer unique challenges to the formulator. This article will deal with the nature of the emulsion and what factors affect the emulsion.

Ken Klein, an expert on emulsions, defines an emulsion as “a system of two (or more) immiscible materials (usually liquids) in which one material (the dispersed/internal phase) is suspended or dispersed throughout another material (the continuous/external phase) in separate droplets”. After having said this, Ken points out the admonition offered by Graham Barker which warns: “All emulsions are inherently unstable (with the exception of spontaneously forming micro emulsions). All we can do is delay the day when the instability will arrive.”

a. Group Opposites

The first requirement for making an emulsion is that it must be made up f two insoluble materials. If the two materials are soluble in each other, a solution is the result. Solutions are clear and can be prepared in any ratio of the two or more soluble liquids. The most commonly understood insoluble phases are oil and water. It is a standard phrase used commonly in ordinary speech that two people are like oil and water, they simply do not mix. We are all familiar with the separation of oil on top of water in salad dressing. The lowest free energy of the system is with the two phases separated from each other.

Silicone is a third phase which like oil is insoluble in water, but at the same time is insoluble in oil. This third phase complicates our simple system of water and oil soluble. This model is even further complicated when one considers fluoro compounds which are insoluble in other three. When one talks of oil phase, a full description of the nature of the oil needs to be provided.

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Hydrophobic Materials

Hydrophobic literally means water hating. By calling a materials hydrophobic, we simply define a material by what it is not (water loving) not by what is. Hydrophobic materials can be soluble in silicone, oil, or fluoro phases which are all insoluble in water and each other. To really define the material an expanded vocabulary is needed. We have proposed the following[5];

Class	**Definitions**
Water insoluble	Lipophilic – Oil loving
	Siliphilic – Silicone loving
	Fluorophilic – Fluoro loving
Silicone insoluble	Lipophilic – Oil loving
	Hydrophilic – Water loving
	Fluorophilic – Fluoro loving
Fluoro insoluble	Lipophilic – Oil loving

Siliphilic – Silicone loving
Hydrophilic – Fluoro loving

Why are these terms important? There are a number of very practical reasons. A key concept we need to keep in mind is the old adage that likes dissolve likes. This leads us to the understanding that the most stable emulsions will be the ones in which there is compatibility between the different phases obtained by selecting a surfactant that has some affinity for each phase present. In today's world of personal care products water, silicone, oil and fluoro compounds are quite common.

An example of the importance of the proper selection of hydrophobic materials is seen in the carpet industry. Carpets have hydrophobic agents added to make the repel water. The choice of the material uses to make the carpet hydrophobic has a dramatic impact upon the usefulness of the carpet. If an oil soluble material is used to provide the coating, the carpet will have the desired water repellency that is it will be hydrophobic, but it will have an affinity for oil. Since cooking oil is quite common homes, any spilled on the carpet so treated will be rapidly absorbed and very difficult t remove. Fortunately, most homes do not have silicone oil in them and consequently a silicone coating to provide hydrophobicity is preferred. This also explains the popularity of fluoro coatings for carpet and fabric.

This can be important in pigmented products. Almost all pigments are "coated" today. This coating process provides products that range from simple non-bonder coatings to chemically resistant permanent bonding to the pigment. In preparing an emulsion containing a coated pigment the emulsifier should have an affinity for the coating on the pigment. Silicone coated pigments should be used with silicone emulsifiers, fluoro coated pigments should be used with fluoro emulsifiers. However, if the coating is merely chem-absorbed on the pigment it will end up in the phase n which it has its lowest free energy and might well migrate from the pigment on storage. This can easily manifest itself in poor oven stability. The instability is causes by pigment coating, not by improper choice of emulsifiers. The nature of the coating is critical to formulation.

b. Hydrogen Bonding and Free Energy

Chemists all recall from physical chemistry that systems left alone will tend to the lowest free energy or most random state. The laws of thermodynamics win out with time, which is why we define emulsions s metastable. Even the best products given enough time will break and revert to the lowest free energy. The trick for the emulsion chemist is to minimize the difference between the emulsion’s free energy and the lowest free energy and to maximize the time it takes for the emulsion to break.

We could at first glance consider oil floating on water as a more ordered state than if oil is in the water. This observation is an indication of the important often overlooked property of water, namely hydrogen bonding. Water is very different from many other compounds. It has a very high boiling point when one considers its molecular weight (100^{o}C for water with a molecular weight of 18, and 30^{o}C for methanol with a molecular weight of 32. Water also has a very high surface tension, 76 dyne/cm^{2}. Water unlike most other compounds increases in volume as it freezes. We are all familiar with the broken bottle of water that occurs when we put a full bottle of room temperature water in the freezer. These properties are all related to the ability of water to for intermolecular hydrogen bonds. In fact, life as we know it requires water related to these unique properties.

Anything that disrupts hydrogen bonding will require a lot of energy. In order to get even a temporary uniform mixture of oil and water, a vigorous shake or agitation is required. This energy is used to break up hydrogen bonding. Stable emulsions are those that minimize the disruption of hydrogen bonding. As should become clear this can be achieved in several ways.

c. Emulsion Types

Traditional Non-ionic Surfactants

The selection of a surface-active agent for a specific emulsification application has been made simpler and more systematic by the development of the HLB System. The system proposed by Griffin[6] some 50 years ago and widely promoted by ICI[7], is a very valuable aide to the formulator.

HLB SYSTEM

HLB, the so-called Hydrophile - Lipophile Balance, is the ratio of oil soluble and water-soluble portions of a molecule. The system was originally developed for ethoxylated products. Listed in Table 1 are some approximations for the HLB value for surfactants as a function of their solubility in water. Values are assigned based upon that table to form a one-dimensional scale, ranging from 0 to 20.

We are using the generic term "hydrocarbon" to designate the oil soluble portion of the molecule. This generic term includes the more specific terms fatty, lipid, and alkyl.

Table 1

Solubility in Water	HLB Value	Description
Insoluble	4 - 5	water in oil emulsifier
Poorly dispersible (milky appearance)	6 - 9	wetting agent
Translucent to clear	10 - 12	detergent
Very soluble	13 - 18	oil in water emulsifier

There are two basic types of emulsions envisioned by the current HLB system. They are the oil in water (O/W) and the water in oil (W/O). The phase listed first is the discontinuous phase. That is it is the phase that is emulsified into the other. Bancroft[3] postulated that upon mixing of the two phases with a surfactant present, the emulsifier forms a third phase as a film at the interface between the two phases being mixed together. He also predicted that the phase in which the emulsifier is most soluble will become the continuous phase. The continuous phase need not be the predominant quantity of material present. There are emulsions where the discontinuous phase makes up a greater weight percent than the continuous phase. A simple test is if the emulsion is readily diluted with water, water is the continuous phase.

It has been stated "The HLB system has made it possible to organize a great deal of rather messy information and to plan fairly efficient systematic approaches to optimize emulsion preparation. If one pursues the concept too far however the system tends to lose itself to complexities.[8]" We have in the HLB system an approach and a direction in the selection of an emulsifier.

CALCULATION OF HLB

The HLB system, in its most basic form, allows for the calculation of HLB using the following formulation:

$$\text{HLB} = \frac{\text{\% Hydrophile by weight of molecule}}{5}$$

Example Oleyl alcohol 5 E.O.

$$\frac{\text{M.W. Hydrophile (5) (44) = 220}}{\text{Total M.W of molecule}} = 45.0\ \%$$

HLB= 45% / 5 = 9.0 HLB = 9.0

APPLICATION OF HLB

One can predict the approximate HLB needed to emulsify a given material and make more intelligent estimates of which surfactant or combinations of surfactants are appropriate to a given application. When blends are used the HLB can be estimated by using a weighted average of the surfactants used in the blend.

HLB NEEDED TO EMULSIFY

Acetophenone	14
Acid, Lauric	16
Acid, Oleic	17
Beeswax	9
Benzene	15
Butyl Stearate	11
Carbon Tetrachloride	16
Castor oil	14
Chlorobenzene	13
Cottonseed oil	6
Petrolatum	7
Lanolin	12
Lauryl amine	12
Mineral spirits	10
Nonylphenol	14
Orthodichlorobenzene	13
Pine oil	16
Toluene	15
Xylene	14
Kerosene	14
Cyclohexane	15
Chloronated paraffin	8

For those materials that are not listed above, it is recommended that the oil be tested using specific blends of known emulsifiers. This allows the formulator to calculate the HLB needed to emulsify the non-listed oil.

The appearance of the emulsion is dependant upon the particle size of the discontinuous phase.

Particle size
(in nanometer)

Size	Appearance
> 1	White
0.1 -1.0	Blue White
0.05 - 0.1	Translucent
< 0.05	Transparent

3D HLB[9,10]

Since the HLB system described above relates to nonionic surfactants that have water soluble and oil soluble groups only it is applicable only to surfactants having only water and oil soluble groups present. Surfactants containing water soluble, oil soluble and silicone soluble groups cannot be accommodated using standard HLB A system has been proposed to cover these surfactants. The system incorporates a third dimension to HLB making it effective in systems that have al three components present.

Emulsion Terminology[11]

Dispersed Phase	Continuous Phase	O/W (Oil-in-Water) Emulsion	W/O (Water-in-Oil) Emulsion
The phase which is disrupted or finely divided within the emulsion.	The phase or medium in which the dispersed phase is suspended.	An emulsion in which the oil phase is dispersed into a water phase, e.g., mayonnaise, whipped toppings, infant formulas, salad dressings, lotions.	An emulsion in which the water phase is dispersed into the oil phase, e.g., margarine, icings, some hand creams.

The graphic, below illustrates the O/W (A) and W/O (B) emulsions:

I. Continuous phase

The continuous phase is the phase that is also called the external phase. While it is true in many emulsions that the continuous phase is the larger of the two phases as far as weight percentage is concerned it des not have to be the larger. The general rule is that if you can dilute an emulsion with water without splitting it is a water continues emulsion, or an O/W emulsion.

II. Discontinuous phase

The discontinuous phase is the phase that is dispersed into the continuous phase. Again it may be the predominant percentage by weight material, but does not have to be so.

III. Dispersion or Emulsion

There has been much confusion generated in the difference between an emulsion and a dispersion. The former is metastable and can be diluted and remain stable, while the later is only stable in a thickened state. The high viscosity is required to keep the product from splitting. Antifoam compounds are dispersions. They stay together by virtue of their viscosity. If diluted they split into two phases, but can be made into one phase again only by adding thickener. Care must be exercised to make sure the so called emulsion is indeed not a dispersion, since use of a dispersion will almost always result in an unstable product. High viscosity materials may in fact fail to split t high viscosity, but are not stable upon dilution. True emulsions can be diluted to low viscosity with addition of continuous phase, while dispersions will spilt into two phases.

IV. Triple Emulsions

Recently, there has been developed a series of emulsions that are the so-called W/O/W emulsions. This is only one type of multiple emulsion. These emulsions are water in oil emulsions that re emulsified n water. They have unique properties including outstanding skin feel, but can present problems in preparation, being the most technically sophisticated emulsions made. The technology has been around since the late 1970's and is now gaining acceptance as more sophisticated technology becomes available. Stability is still a difficulty.

V. Emulsion Equipment

Generally the making of emulsions includes not only the proper selection of a discontinuous phase, the proper selection of a continuous phase and an emulsifier, it will also include a number of additives like salt and processing aides, <u>and</u> includes high energy processing to provide small particle size. As previously stated the smaller the particle size the more stable the emulsion. There are a number of high energy pieces of equipment which include;

Homogenizer

Homogenization is a mechanical treatment to lower particle size of the discontinuous phase brought about by passing the emulsion under high pressure through a tiny orifice, which results in a decrease in the average diameter and an increase in number and surface area, of the oil globules. The net result, from a practical view, is a much reduced tendency for separation. Three factors contribute to this enhanced stability: a decrease in the mean diameter of the globules (a factor in Stokes Law), a decrease in the size distribution of the globules (causing the speed of rise to be similar for the majority of globules such that they don't tend to cluster during creaming), and an increase in density of the globules (bringing them closer to the continuous phase).

Auguste Gaulin's patent in 1899 consisted of a 3 piston pump in which product was forced through one or more hair like tubes under pressure. It was discovered that the size of fat globules produced were 500 to 600 times smaller than tubes. The homogenizer consists of a 3 cylinder positive piston pump (operates similar to car engine) and homogenizing valve. The pump is turned by electric motor through connecting rods and crankshaft.

Colloid Mill

A colloid mill does its work by hydraulic shear, bringing to bear a tremendous amount of energy on a small portion of material in the form of a thin film. This action overcomes the strong polar forces which bind together small clumps of solids or which hold together drops of liquid. A colloid mill will not break down hard crystalline particles by fracturing them across the crystal planes as an impact type mill would do. It will, however, reduce these particles down to their ultimate crystal size by breaking up the agglomerates into which they form.

In the case of emulsions, the same principle holds. As the particles of the dispersed phase of the emulsion get smaller and smaller it requires progressively more energy to overcome the surface tension holding them together. Enormous hydraulic shear is needed to do the job and a colloid mill is an ideal means of accomplishing it.

VI. Emulsion Stability

The following factors contribute to improved emulsion stability[12]:

1. Interfacial Tension - As indicated above, most emulsifying agents are amphiphilic compounds. They will concentrate at the oil-water interface, producing a significant reduction of the interfacial tension and will need less energy to form emulsions. Despite a lowering of interfacial tension when surface-active agents are added, the free energy of the interface remains positive, leaving a persisting state of thermodynamic instability.

2. Repulsion by Electric Charge - Emulsion stability is often explained by the presence of repulsive electrical charges on the surfaces of emulsion droplets. According to the DLVO theory, the dispersed particles are subject to two independent forces: the van der Waals force of attraction and the electrostatic force of repulsion arising from the presence of electrical double-layers at the particle surfaces. The net interaction between the particles is obtained by summing these two terms. If the repulsion potential exceeds the attraction potential, an energy barrier opposing collision results. If the magnitude of this energy barrier exceeds the kinetic energy of the particles, the suspension is stable. The van der

Waals negative potential becomes significant only when the distance between the particles is quite small.

At intermediate distances, the repulsive potential is larger than the attractive potential. Attention should be taken on application of the DLVO theory, which was originally developed for inorganic sols (in which the dispersed phase consists of submicroscopic spherical solid particles), to emulsions (where the dispersed phase consists of oil droplets stabilized by adsorbed emulsifying agents). For example, in emulsions, coalescence involves disruption of an adsorbed film around the droplets, and calculations of the potential energy barrier opposing the collision of oil globules must take into account such factors as the distortion or flattening of the oil droplets upon close approach. However, the DLVO theory still provides a good approximation of the electrostatic contribution to emulsion stability.

Ionic surfactants contribute significantly to the stability of O/W emulsions by contributing to the establishment of electric double layers in the aqueous phase adjacent to each oil droplet. Reversibly, this mechanism is of little importance in the stabilization of W/O emulsions, since the oil phase does not generally supply counter ions in sufficient amounts to establish a strong potential gradient.

3. Stabilization by Finely Divided Solids - Solid particles of very small size, as compared with the size of the dispersed oil droplet, can stabilize an emulsion by adsorbing at the interface to form a physical barrier around the droplets. In addition, energy is required to dislodge solid particles from the interface, since the oil/water interface must be increased to do so. Powdered silica, various clays, basic salts and plant cell fragments are examples of such agents.

The emulsion type produced and its stability depend largely on the relative abilities of the two phases to wet the solid particles. The phase that preferentially wets the solid particle tends to become the continuous phase. If the interfacial tension between solid and oil (γ_{SO}) is greater than that between solid and water (γ_{SW}), the contact angle (θ) of the solid with the aqueous phase is less than 90º, and the major portion of the solid particle resides in the water phase, thus favoring an O/W emulsion. The converse takes place if $\gamma_{SW} > \gamma_{SO}$. Nevertheless, if solid particles remain exclusively in either phase, they have no stabilizing effect. On the other hand, the most stable emulsion is formed when the angle of contact between the two liquids and the solid surface is close to 90º. The surface of the solid and its contact angle may be modified by adjusting pH and by adsorbing various amphiphilic compounds to its surface. Concentration and chain length of the amphiphile’s hydrophobic group are important in this regard.

Based on these considerations, it has been recommended that, for the preparation of emulsions stabilized by solid particles, a surface-active substance should be added that is soluble in the least- wetting (discontinuous) phase, and that the concentration of the surface-active agent should be adjusted to give a contact angle in the vicinity of 90º between the powder and the two liquids.

Several methods have been introduced to aid in the selection of an appropriate emulsifier, or blend of emulsifiers, for a given purpose. The most prominent of these is the one based on the relative importance of the hydrophobic and hydrophilic properties of the molecules (HLB system).

d. Polarizing Microscope Evaluation of emulsion Stability

An extensive amount of work has been done by John Carson[13]. This work shows not only the structure of emulsions, but also provides some predictions on emulsion stability.

Two polarizing filters are needed in the microscope one in the incident light path, and the other one after the light passes through the sample.

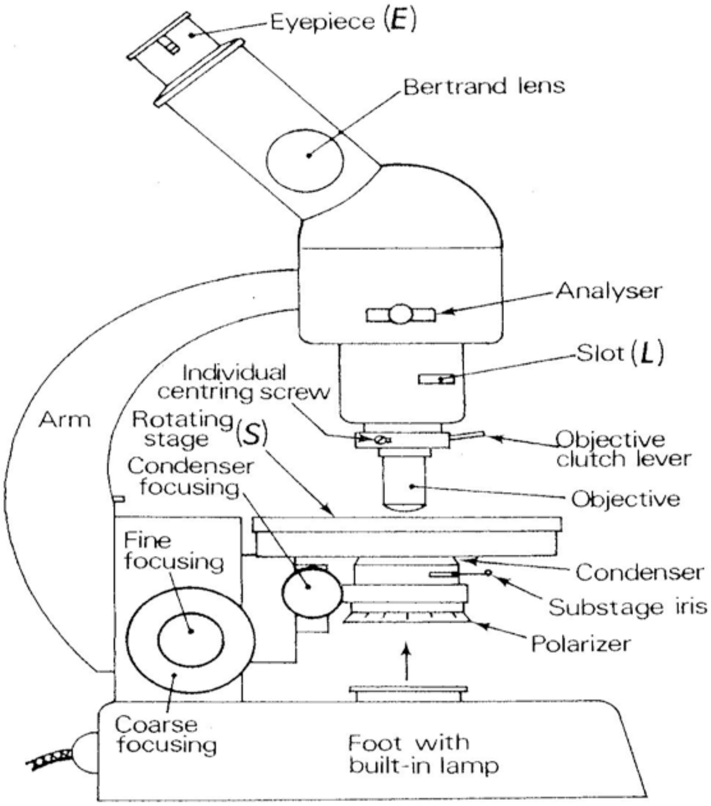


FIG. 2.5. The polarizing microscope.

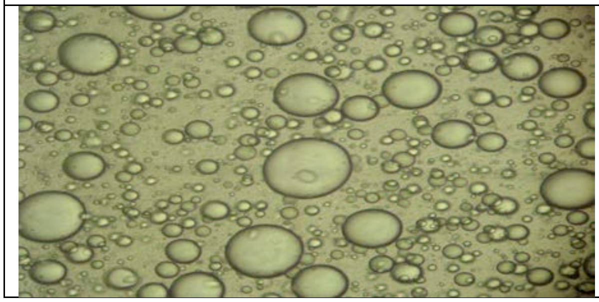
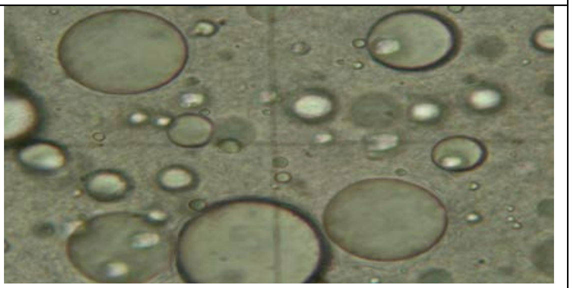
Emulsion Formulas

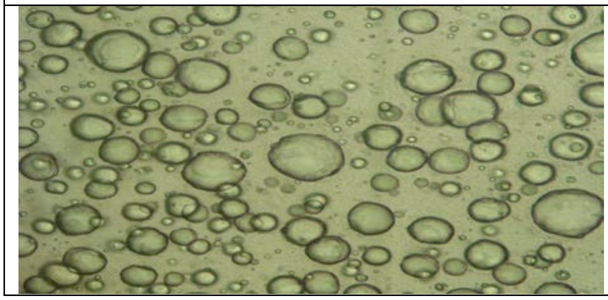
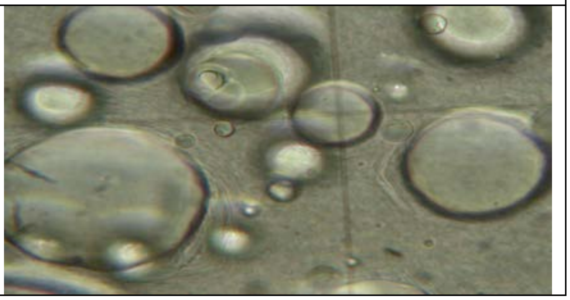
The emulsion formulations were divided into several types depending upon the nature of the emulsifier used. The equipment used for preparation of the emulsion is a

Anionic (Formulas 206-1 & 209-1)

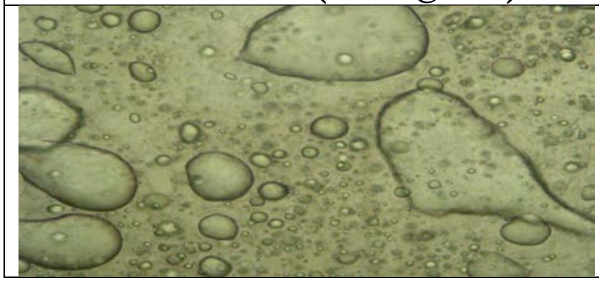
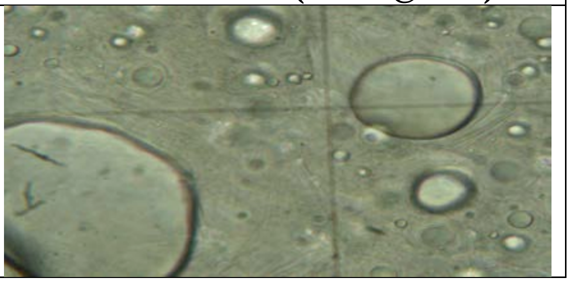
Ingredients	% #1	% #2
1. Water	79.94	79.44
2. Stearic Acid (TP)	0.65	1.00
3. Mineral Oil (50 sus)	15.00	15.00
4. Cetyl Alcohol	2.00	2.00
5. Stearyl Alcohol	2.00	2.00
6. Triethanolamine	0.35	0.50
7. Methylchloroisothiazolinone (and) Methylisothiazolinone	0.06	0.06
Moles of TEA Stearate = 0.0024 #1 (formula 206-1) Moles of TEA Stearate = 0.0036 #2 (formula 209-1)		

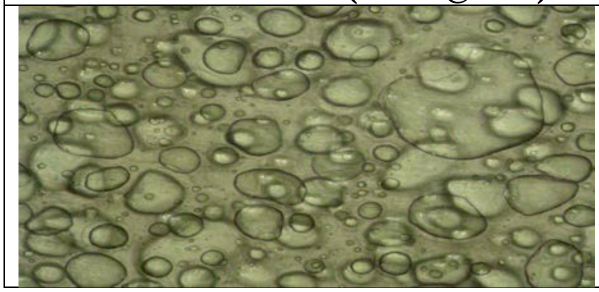
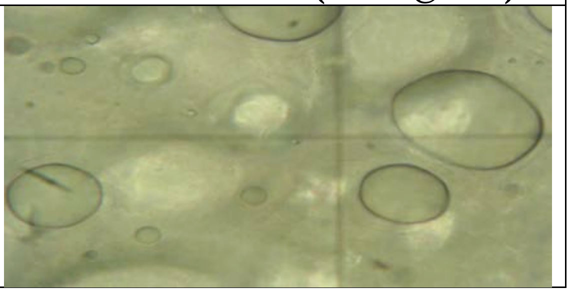
Initial photomicrographs

Anionic # 1 – 100X	**Anionic # 1 – 400X**
	

Anionic #2 – 100X	**Anionic #2 – 400X**
	

Aged photomicrographs

Anionic # 1 – 100X (1 Mo @ 50C)	**Anionic # 1 – 400X (1 Mo @ 50C)**
	

Anionic #2 – 100X (1 Mo @ 50C)	**Anionic #2 – 400X (1 Mo @ 50C)**
	

Comparisons

As can be seen the two emulsions have similar particle size and distribution. It will also be noted that the higher the concentration of High HLB surfactant (i.e. the TEA Stearate), then more Surfactant Hydrate Structure forms.

As far as stability is concerned, it can be stated that;

1. Emulsions made with the lower concentration of anionic surfactant are less stable, exhibiting creaming @ 50°C.

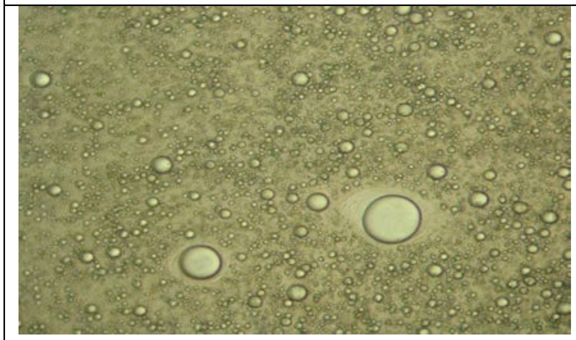
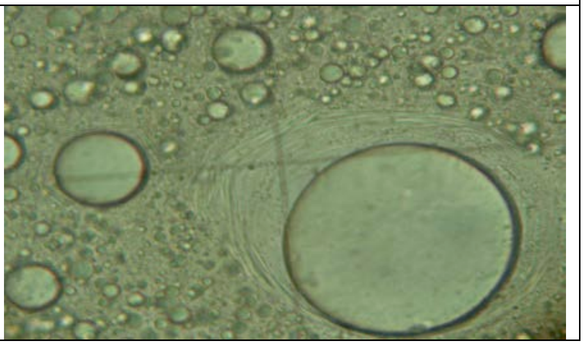
2. Emulsions made with higher concentration of anionic surfactants produce more emulsions that have a uniform structure and generally have smaller particle sizes.

3. Emulsions made with higher anionic surfactant concentration produces more surfactant hydrate structure.

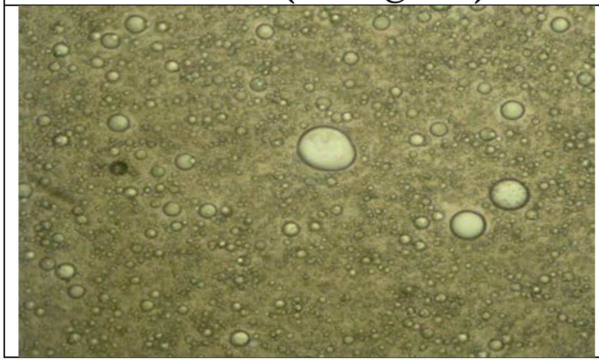
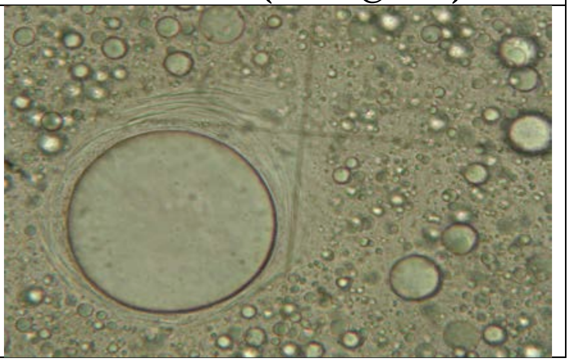
Nonionic (Formula 206-2)

Ingredients	%
Water	78.29
Steareth-20	2.65
Mineral Oil (50 sus)	15.00
Cetyl Alcohol	2.00
Stearyl Alcohol	2.00
Methylchloroisothiazolinone (and) Methylisothiazolinone	0.06
Moles of Steareth-20 = 0.00231	

Initial photomicrographs

Nonionic – 100X	**Nonionic – 400X**
	

Aged photomicrographs (1 month at 50 C.)

Nonionic – 100X (1 Mo @ 50C)	**Nonionic – 400X (1 Mo @ 50C)**
	

Stability

Emulsions made with nonionic surfactants make a finer particle size emulsion with the addition of 4% cetearyl alcohol than those made with anionic surfactants alone.

Emulsions made with nonionic surfactants change very little both in structure and in surfactant hydrate formation with storage for 1 month @ 50°C, consequently, nonionic surfactants are commonly used in the preparation of emulsions.

Polymeric surfactants

Polymeric # 1 (Formula 209-2)

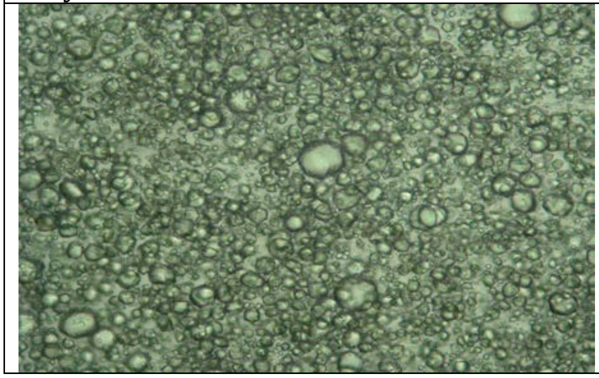
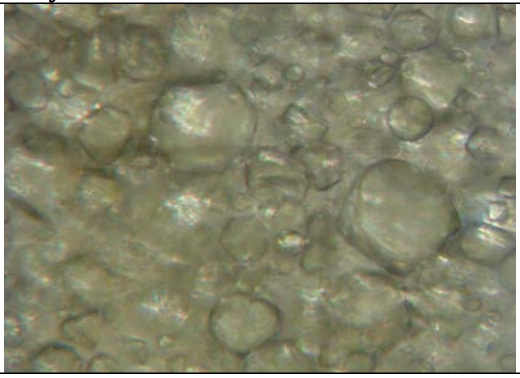
Ingredients	%
Water	79.94
Acrylates/C10-30 Alkyl Acrylate Crosspolymer	0.50
Mineral Oil (50 sus)	15.00
Cetyl Alcohol	2.00
Stearyl Alcohol	2.00
Triethanolamine	0.50
Methylchloroisothiazolinone (and) Methylisothiazolinone	0.06

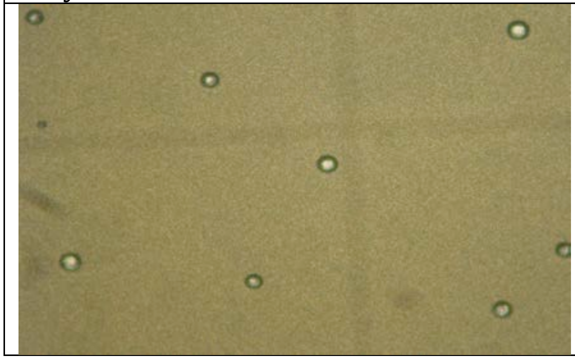
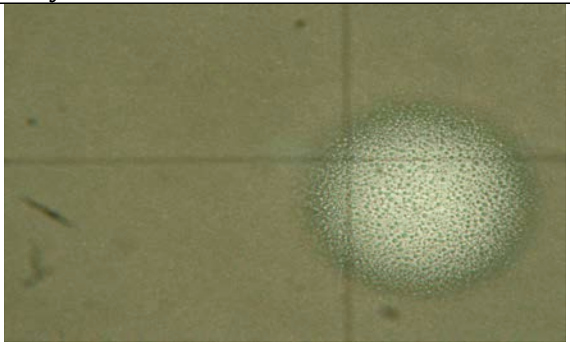
Moles of Acrylates/C10-30 Alkyl Acrylate Crosspolymer = 0.00XXX

Polymeric # 2 (Formula 209-3)

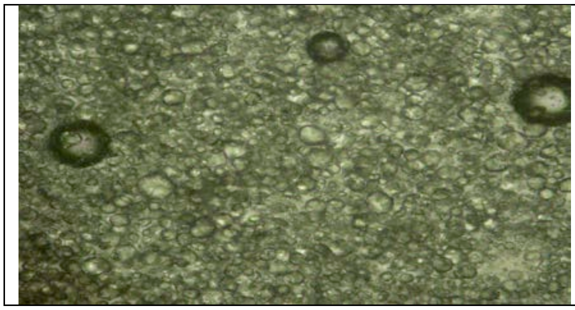
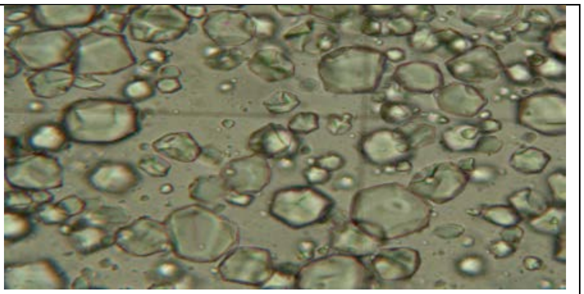
Ingredients	%
Water	70.94
Distdeareth-100 IPDI	10.00
Mineral Oil (50 sus)	15.00
Cetyl Alcohol	2.00
Stearyl Alcohol	2.00
Methylchloroisothiazolinone (and) Methylisothiazolinone	0.06

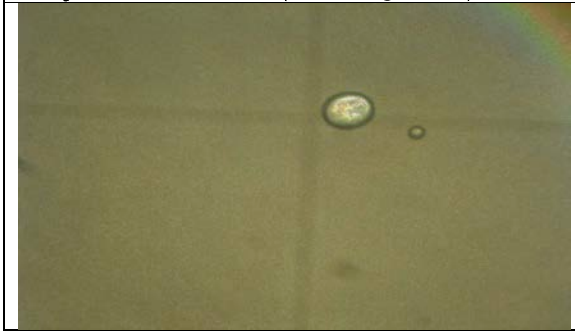
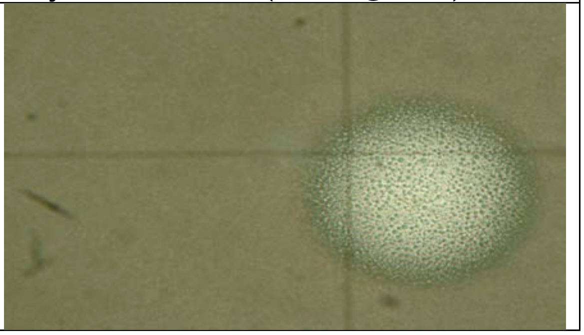
Moles of Steareth-100 IPDI = 0.00105

Polymer 1 – 100X	**Polymer 1 – 400X**
	

Polymer 2 – 100X	**Polymer 2 – 400X**
	

Polymer 1 – 100X (1 Mo @ 50C)	**Polymer 1 – 400X (1 Mo @ 50C)**

Polymer 2 – 100X (1 Mo @ 50C)	**Polymer 2 – 400X (1 Mo @ 50C)**
	

Stability

1. Emulsions made with polymer surfactant 1 have liquid crystal/gel phase stabilized emulsion with 4% Cetearyl Alcohol

2. Emulsions made with polymer surfactant 1 do not show significant surfactant hydrate structure changes when aged for 1month @ 50°C

3. Emulsions made with polymer surfactant 2 have a very fine particle size emulsion with 4% Cetearyl Alcohol, providing a uniform gel structure.

4. Emulsions made with polymer surfactant 2 do not show significant surfactant hydrate structure changes when aged for 1month @ 50°C.

e. Patent Literature

Over the years there have been many patents covering different aspects of emulsion technology. We tend to want to believe that emulsions represent a new technology. Despite the fact that there is more and more acceptance of emulsions in personal care products, they have been known for many years.

U.S. Patent 1,500,670 issued July 8, 1924 to Melvin Degroote is entitled "*Making Dilute Permanent Turbid Emulsions*". It deals with emulsions made to keep flavoring oils from forming scum on the top of beverages. The emulsion uses sodium oleate as a soap to make the emulsion.

U.S. Patent 2,052,025 issued August 25, 1936 to Benjamin Harris entitled "*Emulsion*" is an important old patent. This patent is an early water in oil emulsion (invert emulsion). It uses potassium stearate soap and diethylene glycol mono-stearate as emulsifiers. It is surprising how much information is given in this patent. It discusses mayonnaise as an invert emulsion and describes a series of non-ionic emulsifier. U.S. Patent 2,109,842 issued March 1, 1938 also to Harris includes additional emulsifiers in the preparation of the invert emulsion described in the '025 patent.

U.S. Patent 2,129,836 issued September 13, 1938 to Herman Goodman entitled "Cosmetic Cream Base". It is assigned to Cosmetic Research Inc. on N.Y.. This is one of the early cream base patents made up of beeswax, soap, liquid petrolatum.

U.S. Patent 2,173,203 issued September 19, 1939 again to Benjamin Harris entitled “Cosmetic Preparation” This patent describes cosmetic water in oil emulsions, specifically cold cream compositions.

U.S. Patent 2,223,558 issued December 3, 1940 to Albert Epstein entitled “Emulsion” describes invert emulsions as cream bases using soybean oil and non-ionic emulsifiers.

U.S. Patent 2,269,529 issued January 13, 1942 to Henry Goldsmith entitled “Emulsifier and Emulsions” describes invert emulsions using ester based non-ionic emulsifiers.

U.S. Patent 2,702,276 issued February 15, 1955 to Larry Green entitled “Water Dispersible Emulsions of Polysiloxanes” describes silicone emulsions of he oil in water type using cationic emulsifiers.

U.S. Patent 2,223,558 issued December 3, 1940 to Albert Epstein entitled “Emulsion” describes invert emulsions as cream bases using soybean oil and non-ionic emulsifiers.

While these patents are not the most recent, they represent technology used historically to prepare emulsions. They offer an interesting perspective on the age of emulsion technology.

f. Conclusions

Emulsions will continue to grow in importance in the personal care industry. As the consumer becomes more and more sophisticated in the demands that they make, the formulations will become ever more complex. This is true for standard emulsions, but is even more important in the preparation of invert emulsion.

There are a number of tool and rules that can be used to make the selection of ingredients for the preparation of emulsions easier for the formulator. However, the preparation of cosmetically elegant emulsions will always require an element of art. Consequently, the formulator not the computer will always have the final say as to what consumers will accept.

A new innovative kit of emulsifiers that will take some of the stress out of formulating. These molecules are composed of three parts; (1) an alkyl soluble part; (2) a water-soluble part and (3) a silicone soluble part. Choosing the right ratio of the three parts is critical in creating a stable emulsion. As the required HLB of your formulation changes with selection of oil or oils, the HLB of your emulsifier will change along with it.

Emulsion Formulation

The first set of experiments are conducted using all four emulsifiers, and allow the formulator not only the ability to evaluate emulsion stability, but also cosmetic aesthetics. The formulation is shown in Table 7.

Table 7 Emulsifier Formula

Material	**%**
Water	47.25
Oil	47.25
Emulsifier	5.00
Salt	0.5

Procedure:

1. Place emulsifier or emulsifier blend into the oil phase.
2. Mix well, noting clarity.
3. Add salt to water phase.
4. Heat both phases to 50°C
5. Add water phase to oil phase and using mixer mix for 120 seconds.
6. Note appearance.

The above process is repeated with emulsifier blends depending upon the results of the first emulsion

Sheer Mixer – Laboratory Evaluation

Sheer Mixer	
	
	Sheer apparatus for lab evaluation Picture by Kevin O'Lenick

Product Evaluation

Typical results are shown below. Two of the formulations are emulsions, and the others are not. This means the HLB needed for the emulsion is between that of Silube -208-212 and Silube J208-412.

The process is repeated using blends of Silube J208-212 and Silube J208-412 until optimized. The material is then homogenized using commercial equipment.

Mineral Oil

Time = 0

J-208-212 J-208-412 J-208-612 J-208-812

Time = 3 hours

J-208-412 J-208-612 J-208-812

Time = 24 Hours

J-208-212 J-208-412 J-208-612 J

Regular Emulsion Invert Emulsion

Soybean oil

Time =0

J-208-212 J-208-412 J-208-612 J-208-812

Time = 3 hours

J-208-212 J-208-412 J-208-612 J-208-812

Time = 24 hours

J-208-212 J-208-412 J-208-612

Regular Emulsion Invert Emulsion

Cetyl Dimethicone

Time = 0

J-208-212 J-208-412 J-208-612 J-208-812

Time = 3 hours

J-208-212 J-208-412 J-208-612 J-208-812

Time = 24 hours

J-208-412 J-208-612 J-208-812

Regular Emulsion Invert Emulsion

Emulsion Equipment

The examples given above do not make use of any high energy emulsification equipment. The making of emulsions includes not only the proper selection of a discontinuous phase, the proper selection of a continuous phase and an emulsifier, it will also include a number of additives like salt and processing aides, <u>and</u> includes high energy processing to provide small particle size. As previously stated, the smaller the particle size the more stable the emulsion. There are a number of high energy pieces of equipment that include;

Homogenizer

Homogenization is a mechanical treatment to lower particle size of the discontinuous phase brought about by passing the emulsion under high pressure through a tiny orifice, which results in a decrease in the average diameter and an increase in number and surface area, of the oil globules. The net result, from a practical view, is a much reduced tendency for separation. Three factors contribute to this enhanced stability: a decrease in the mean diameter of the globules (a factor in Stokes Law), a decrease in the size distribution of the globules (causing the speed of rise to be similar for the majority of globules such that they don't tend to cluster during creaming), and an increase in density of the globules (bringing them closer to the continuous phase).

Auguste Gaulin's patent in 1899 consisted of a 3 piston pump in which product was forced through one or more hair like tubes under pressure. It was discovered that the size of fat globules produced were 500 to 600 times smaller than tubes. The homogenizer consists of a 3 cylinder positive piston pump (operates similar to car engine) and homogenizing valve. The pump is turned by an electric motor through connecting rods and a crankshaft.

Colloid Mill

A colloid mill does its work by hydraulic shear, bringing to bear a tremendous amount of energy on a small portion of material in the form of a thin film. This action overcomes the strong polar forces which bind together small clumps of solids or which hold together drops of liquid. A colloid mill will not break down hard crystalline particles by fracturing them across the crystal planes as an impact type mill would do. It will, however, reduce these particles down to their ultimate crystal size by breaking up the agglomerates into which they form.

In the case of emulsions, the same principle holds. As the particles of the dispersed phase of the emulsion get smaller and smaller it requires progressively more energy to overcome the surface tension holding them together. Enormous hydraulic shear is needed to do the job and a colloid mill is an ideal means of accomplishing it.

Supplemental Chapter 7

Foam

One of the most important attributes of personal care products is foam. Foam is a metastable material the formation of which is governed by some complicated physical chemistry.

Foam has both quantitive and qualaitative properties that make it of interest to personal care formulators. Not only is it important how much foam is generated, but also the nature of the foam. Bubbles can be large or small, can be rich or dry. It is for this reason that the definitative foam evaluation are conducted in salons, matching consumer expectations with the product type. For example, shaving cream foam has very different foam attributes than does a body wash or tooth paste. Consumer expectations determine market success and cannot be avoided. Laboratory methods are important in screening and there is much debate as to which methods are most appropriate.

Foam

Foam is a complicated physical phenomenon which is made up of aty least two distinct phases, a liquid continuous phase in which there is a surfactant anf other formulation ingredients, and a gas phase, commonly air. In some instances a third phase can be present that phase is a oil phase. The formulation ingredients all interact with each other and the soil present and taken together with the physical methods used for agitation determine the foam properties. Another variable that affects foam structure is the container in which the foam is held. Many factors are responsible for foam quality, including some over which the formulator has no control (for example both qualitative and quantitive aspects of the soil present on the hair will affect foam properties delivered by a shampoo). In recent years a number of analytical techniques have been developed to look at foam structure and stability, including different types of light microscoposy and electron microscosopy.

The bulk properties of foam are very important to formulation success. Cosmetic elegance is determined by the size, shape and longevity of foam provided by formulations. Foam instability is even a factor as the consumer expects the foam to be easily and effectively removed by rinsing once the action of the foam is complete. For these reasons, the ultimate determination of suitability of a particular type of foam for a particular formulation will be determined by the consumer and therefore salon testing is the best measure of foam quality.

The cosmetic industry has embraced several different terms to describe foam. The following is an alphabetical list of commonly used terms.

Billowing - This expression refers to quality of foam, describing large bubbles that are fluid and flexible.

Copious – This expression applies the quantity of foam, describing a great deal of foam but does not describe the nature of the foam.

Dense (tight) – This expression describes a quality of the foam, that is small bubble foam.

Firm – This expression describes a quality of the foam, that is a bubble that lacks flexibility and resists deformation

Lacy - This expression describes the quality of a foam and is used to describe a foam that is neither dense nor rich, rather is has a dryness and is easily disrupted.

Rich- This expression is used to describe a foam that has a cosmetically appealing feel. It describes a highly desirable skin or hair feel encountered by the consumer in the use of the product. A rich foam is desirable in a shampoo, but not in a toothpaste.

Evaluation of Foam in Cosmetic Products

The following is a review article written by industry expert Ken Klein on evaluating foam in cosmetic products. It is a good review of the state of the art in foam evaluation found in the appendix.

Foam Methodology

Not with-standing the desirability of using one type of foam test or another, expressed by industry expert Ken Klein, the Ross Miles test remains the best accepted throughout the detergent industry and the type of testing that has the most comparative data. Dr. Milton Rosen, the highly respected authority on surfactant chemistry and professor at Brooklyn College of the City of New York did a study in August 1969 looking at the Ross Miles Test and concluded “the data obtained indicate that, at least for the systems studied, the initial foam produced in the Ross Miles test is remarkably constant in character with variation in the nature or concentration of the surface active solute.” (Journal of American Oil Chemists’ Society (vol. 46 p. 399 -402).

This lack of standardized foam testing in our industry is an area that need to be addressed. Until a full study is done, the use of foam data to provide laboratory evaluation will likely be done on a comparative basis. The reality is that salon testing and ultimately consumer testing will decide the viability of new products and foam will be one of many criteria for selection of formulations.

Supplemental **Chapter 8**

Conditioning

Conditioning is a very important aspect of hair care. As the consumer becomes more sophisticated, the benefits a conditioner provides becomes more encompassing.

Hair in its normal state has certain oils, sebum and other components present on it's the surface. When a detergent is used on the hair, these materials can be removed, leaving the hair stripped of its natural conditioning oils. Stripped hair is generally dry, raspy, dull and has problems with static electricity which results in a condition called, "fly away". The ability to treat the hair to remove these undesirable properties is the most basic aspect of conditioning. There are several others. One additional aspect of conditioning is wet comb, which is the ability to effortlessly comb the hair in a wet state. Wet comb relates to wetting of the hair with a surfactant to make combing easier. Another aspect of conditioning relates to providing the hair with a treatment that the consumer perceives as soft and conditioned many hours after the hair has been treated. The advent of two in one systems that provide this type of advanced conditioning as been made possible by inclusion of polymers, often silicone polymers into hair care products[2,3]. In recent years this type of conditioning has been achieved by inclusion of oil soluble esters[4] and making complexes of anionic and cationic surfactants that contain silicone[5]. It is expected that this area will be a growth area as the structure / function rules related to this type of long term conditioning are better understood. Yet another desirable affect of a conditioner is "dry comb", which is the ability to comb the hair effortlessly and without entanglement after the hair is dry. Materials which function in wet comb are not necessarily the same as those that function as dry comb agents.

Quats

The isoelectric point of untreated hair is 3.7. Using the Henderson Hasselbasch equation, it is clear that when the pH is below this 3.7 the hair is cationic, and when the pH is above 3.7, the hair is anionic. Therefore it is safe to assume that when using products having a pH above 3.7 we can consider the hair coated with aqueous product as anionic. This means that cationic materials will have an attraction to the hair and by virtue of ionic charge be substantive to the hair.

Fatty quaternaries (quats) have been known for many years. Because of their fatty nature and positive charge, these compounds find application in a variety of areas including as conditioners for hair. The proper selection of quat can result in a conditioner that addresses the most basic aspects of conditioning, dryness, raspiness, dullness and static build up.

The use of quats in hair care products can be problematic, since many of these materials are not compatible with anionic materials. This incompatibility can be manifested as a precipitate, or as cloudiness in formulation. Some quats are very insoluble when added to anionic surfactant, others have improved compatibility. The ability to select quats that have optimum compatibility with anionic systems offers the formulator flexibility in formulating heretofore unavailable. The nature of the anionic / cationic interaction is key to the functionality, or lack of functionality of conditioners.

The situation is further complicated by our testing methodology. Historically, deposition of cationic material onto hair was measured by a number of dye uptake tests. These tests merely measure the presence of cationic material on the surface of the hair.

Since deposition on hair made from a solution containing cationic and anionic molecule, contains no free cationic, no red color is observed with these tests. This does not mean there is no deposition and no conditioning. Correctly interpreted, it simply means the deposited material does not have an overall positive charge and consequently does not bind dye.

Anyone that has added stearylalkonium chloride to sodium lauryl sulfate and observed the white sticky solid that results knows anionic and cationic surfactants can be incompatible. Anionic and cationic materials that produce a white gunky solid when mixed together are referred to as *hard complexes*[6]. As the expression implies the cationic and anionic compound possess properties which when added together form insoluble complexes (salts). We set out to determine if there are cationic materials having different structures which could be more soluble in the presence of anionic surfactants. The terms used here for quats and anionic materials are an adaptation of the work of Pearson used to describe acids and bases. Pearson proposed that "hard acids bind strongly to hard bases and soft acids bind softly to soft bases"[7] , the anionic and cationic interactions are exactly analogous.

Supplemental Chapter 9

Green Star Rating for Cosmetic Compounds and Formulations[1]

Today's consumer and formulator have become increasingly aware of the consumption of resources that are not renewable. Products derived from fossil fuels are nonrenewable. This includes products like gasoline, coal, natural gas, diesel, and other commodities. Green resources are defined as renewable resources, replenished by natural processes. Green products are renewable resources include oxygen, fresh water, timber, and biomass. Green products also include commodities such as wood, paper, and leather. Furthermore, alcohol, oils from plants and seeds are considered green products.

These green raw materials are the most environmentally friendly and their use are the most conservative in minimizing negative impact on the earth. However, these basic green products cannot be combined it a way that provides consumer products that meet the demands of the consumer. For example soap can be a green detergent, but it does not possess all the desirable properties that give the consumer a laundry detergent. In order to make high performance formulations, some materials that are not strictly speaking green are required.

While the concept of green products is straightforward, the ability for the formulator and the consumer to quantify the greenness of a given shampoo or other consumer product is elusive. Given a proper understanding, the consumer and formulator can make better informed better educated decisions as to making products with the best combination of green properties and formulation attributes. In other words, the need of the consumer and the need of the environment can be intelligently determined.

All too often, the determination of the greenness of a raw material or formulation was more an emotional rather than a scientific decision and required either an all or noting approach to environmental stewardship. Simply put materials are green or they are not. Unfortunately, the formulation of consumer products that are commercially acceptable require a trade off in optimizing the performance and greenness. Consumers demand many formulation benefits that cannot be achieved with all green ingredients. Some "non-green" products are required. The consumer then needs a systematic approach to develop a measurable metric for the level of greenness in a formulation and trade off some greenness for performance. This quest has resulted in the development of "Green Star Rating" system or simply "GSR".

The Green Star Rating provides a process by which a formulator can easily ascertain the "greenness" of a raw material and as importantly a consumer can determine and compare the "greenness" of a formulation to similar types of products. This process allows the formulation chemist a way to break a molecule down into green portion and a non-renewable resource portion. The evaluation of this data allows for the generation of a Green Star Value, which is the percentage of the molecule that is based upon green chemistry divided by 10. Once this number is known, the effect of replacing one ingredient in a formulation with a "greener" compound can be ascertained. Specifically, if a raw material used in a formulation at 20% by weight has a Green Star Rating of 1 is replaced with a product with a Green Star Rating of 7, the impact on the formulation is (7-1) times 0.20 or 1.2. This means that much more renewable resources are being used in the formulation and its consumption will impact less negatively on the environment. This approach allows the formulator to make greener product and the consumer to choose greener products. By greener products is meant products based upon a greater percentage of renewable resources. Greener products are those with a higher Green Star Rating.

The Green Star Rating is determined using the following steps::

(1) determining the empirical formula for chemical compounds used to make formulated products;

(2) determining which portions of the molecule are green;

(3) determining the percentage by weight of the green portion of the molecule

(4) determining the green star value

and optionally

(5) optimizing the formulation by selecting components with the greatest green star value.

Raw Materials

Example 1 - Sodium Coco Alcohol Derived From Natural Alcohol

Step one - determining the empirical formula for chemical compounds used to make formulated product:

Example – Sodium Coco sulfate

$C_{12}H_{23}SO_4Na$

Step two – determining which portions of the molecule are green;

Example – Sodium coco sulfate

Renewable Material	Natural Alcohol	$C_{12}H_{23}$
Non-Renewable	Synthetic Sulfation	SO_4Na

Step three – determining the percentage by weight of the green portion of the molecule. This is done by multiplying the weight of each atom by the number of atoms of in each portion

Renewable - Natural Alcohol $C_{12}H_{23}$

Carbon has a molecular weight of 12 there are 12 present in the renewable portion so the molecular weight contribution of the carbon is 12 times 12 or 144.

Hydrogen has a molecular weight of 1 there are 23 hydrogen atoms present in the renewable portion so the molecular weight contribution of the hydrogen is 1 times 23 or 23.

The sum of all the elements in the renewable portion is 144+23 or 167.

The Non-renewable portion is SO_4Na.

Sulfur has a molecular weight of 32 there is 1 sulfur atom present in the non-renewable portion so the molecular weight contribution of the sulfur is 1 times 32 or 32.

Oxygen has a molecular weight of 16 there are 4 oxygen atoms present in the non-renewable portion so the molecular weight contribution of the hydrogen is 4 times 16 or 64.

Sodium has a molecular weight of 23 there is 1 sodium atom present in the non-renewable portion so the molecular weight contribution of the sulfur is 1 times 23 or 23.

The sum of all the elements in the non-renewable portion is 32+64+23= 119

Total Molecular Weight = Renewable Portion + Non-Renewable portion

Total Molecular Weight = 167+ 119= 289

Renewable Portion/ Total = 167/289 = 57.7%

Step 4 determining the Green Star Value

Green Star Value (GSV)= % Renewable rounded to unit = 58

Raw Material Example 2 Sodium laureth 3 Sulfate

$C_{12}H_{23}\,O(CH_2CH_2O)_3SO_3Na$

Empirical Formula: $C_{18}H_{35}O_7SNa$

Renewable	$C_{12}H_{23}$ Natural Alcohol	Synthetic	$-(CH_2CH_2O)_3SO_4Na$ EO-Sulfate

Calculations

Renewable Portion

	C	H	N	O	P	S	Na	K
Number	12	23	0	0	0	0	0	0
MW	144	23	0	0	0	0	0	0
Total	167							

Non-Renewable

	C	H	N	O	P	S	Na	K
Number	6	12	0	7	0	0	1	0
MW	72	12	0	112	0	0	23	0
Total	219							

Total	386
% Renewable	43
Green Star Rating	43

Raw Material Example 3 Sodium Lauryl Sulfate (Ziegler Alcohol derived)

Example – Sodium lauryl sulfate

$C_{12}H_{23}SO_4Na$

Step two – determine which parts of the molecule are natural (derived from green natural raw materials) and which are synthetic.

Example – Sodium lauryl sulfate

Synthetic $C_{12}H_{23}$ SO_4Na

Step three –

Renewable Portion

	C	H	N	O	P	S	Na
Number	0	0	0	0	0	0	0
MW	0	0	0	0	0	0	0
Total	0						

Non-renewable

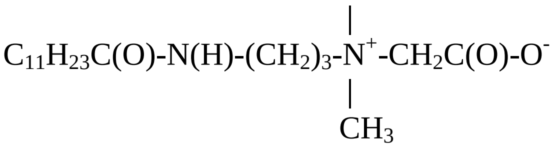
	C	H	N	O	P	S	Na
Number	12	23	0	4	0	1	1
MW	144	23	0	64	0	31	23
Total	285						

Total	285
% Renewable	0
Green Star Rating	0

Raw Material Example 4 Cocamidopropyl Betaine

Structure

CH_3



$$C_{11}H_{23}C(O)\text{-}N(H)\text{-}(CH_2)_3\text{-}\overset{|}{\underset{\underset{CH_3}{|}}{N^+}}\text{-}CH_2C(O)\text{-}O^-$$

Formula $C_{18}H_{38}O_3N_2$

Step two – determine which parts of the molecule are natural (derived from green natural raw materials) and which are synthetic.

Renewable $C_{12}H_{23}O$ Nonrenewable $C_6H_{14}O_2N_2$

Step three –

Renewable Portion

	C	H	N	O	P	S	Na	K
Number	12	23	0	1	0	0	0	0
MW	144	23	0	16	0	0	0	0
Total	183							

Non-Renewable

	C	H	N	O	P	S	Na	K
Number	6	14	2	2	0	0	0	0
MW	72	14	28	32	0	0	0	0
Total	146							

Total		329
% Renewable		55.6
Green Star Rating		56

Raw Material Example 5 – Cocamid DEA

Structure $C_{11}H_{23}\text{-}C(O)\text{-}N\text{-}(CH_2CH_2OH)_2$

$C_{16}H_{30}O_3N$

Step two – determine which parts of the molecule are natural (derived from green natural raw materials) and which are synthetic.

$C_{11}H_{23}\text{-}C(O)\text{-}N\text{-}(CH_2CH_2OH)_2$

Renewable $C_{12}H_{23}O$ Non-renewable $C_4H_{10}O_2N$

Step three –

	C	H	N	O	P	S	Na	K
Number	12	23	0	1	0	0	0	0
MW	144	23	0	16	0	0	0	0
Total	183							

Synthetic

	C	H	N	O	P	S	Na	K
Number	4	10	1	2	0	0	0	0
MW	48	10	14	32	0	0	0	0
Total	104							

Total	287
% renewable	63
Green Star Rating	63

Raw Material Example 6 – Cocamid MEA

Structure $C_{11}H_{23}\text{-}C(O)\text{-}NH\text{-}CH_2CH_2OH$

$C_{14}H_{29}O_2N$

Step two – determine which parts of the molecule are natural (derived from green natural raw materials) and which are synthetic.

$C_{11}H_{23}\text{-}C(O)\text{-}NHCH_2CH_2OH$

Renewable $C_{12}H_{23}O$ Non-renewable C_2H_6ON

Step three –

Renewable Portion

	C	H	N	O	P	S	Na	K
Number	12	23	0	1	0	0	0	0
MW	144	23	0	16	0	0	0	0
Total	183							

Non-Renewable

	C	H	N	O	P	S	Na	K
Number	2	6	1	2	0	0	0	0
MW	24	6	14	32	0	0	0	0
Total	76							

Total	259
% Renewable	70.6
Green Star Rating	71

Formulations

The Green Star Process can also be used on any formulation .

Conditioning Shampoo

%weight

Water	55.0
Sodium Lauryl Sulfate	18.0
Sodium Laureth 3 Sulfate	16.0
Cocamidopropyl Betaine	8.0
Cocamid DEA	3.0

Example 7 Conditioning Shampoo

This product is based on sodium lauryl sulfate (synthetic alcohol)

	%weight	% Solids	Example	GRS	Contribution	
Water	55.0	-	-	-	-	
Sodium lauryl Sulfate	34.0	9.5	Example 3	0	0	(.095 times 0)
Cocamidopropyl Betaine	8.0	2.8	Example 4	56	1.6	(.028 times 56)
Cocamid MEA	3.0	3.0	Example 6	71	2.1	(.03 times 71)
				Total	3.7	

Example 8 Conditioning Shampoo (Version 1)

This product is based on sodium lauryl sulfate (synthetic alcohol) and SLES-3

	%weight	% Solids	Example	GRS	Contribution	
Water	55.0	-	-		-	
Sodium Lauryl Sulfate	17.0	4.5	Example 3	0	0	(.045 times 0)
Sodium Laureth 3 Sulfate	17.0	4.5	Example 2	43	2.0	(.045 times 43)
Cocamidopropyl Betaine	8.0	2.8	Example 4	56	1.6	(.028 times 56)
Cocamid DEA	3.0	3.0	Example 5	63	1.9	(.03 times 63)

				Total	5.5

Example 9 **Conditioning Shampoo**

This product is based on sodium coco sulfate (renewable alcohol)

	%weight	**% Solids**	**Example**	**GRS**	**Contribution**
Water	55.0	-	-	-	-
Sodium Coco Sulfate	17.0	4.5	Example 1	58	2.6 (.045 times 58)
Sodium Laureth 3 Sulfate	17.0	4.5	Example 2	43	1.9 (.045 times 43)
Cocamidopropyl Betaine	8.0	2.8	Example 4	56	1.6 (.028 times 56)
Cocamid DEA	3.0	3.0	Example 5	63	1.9 (.03 times 63)
				Total	8.0

Example 10 **Conditioning Shampoo**

This product is based on sodium coco sulfate (renewable alcohol)

	%weight	**% Solids**	**Example**	**GRS**	**Contribution**
Water	55.0	-	-	-	-
Sodium Coco Sulfate	17.0	4.5	Example 1	58	2.6 (.045 times 58)
Sodium Laureth 3 Sulfate	17.0	4.5	Example 2	43	1.9 (.045 times 43)
Cocamidopropyl Betaine	8.0	2.8	Example 4	56	1.6 (.028 times 56)
Cocamid MEA	3.0	3.0	Example 6	71	2.1 (.03 times 71)
				Total	8.2

The simple formulations above show the power of the new system. Minor changes in the formulation made be properly selecting raw materials result in a 2.2 times improvement in the green star rating. This process allows the formulator to fine tune formulations to maximize greenness and to inform the consumer about the degree amount of a given formulation that is renewable. The same approach works not only on shampoos but all formulations.

Example	Green Star Rating
7	3.7
8	5.5
9	8.0
10	8.2

Conclusion

The **Green Star Rating System** provides the formulator and consumer with a metric by which both formulations and raw materials can be evaluated. The determination allows for the consumer to pick the product with the *highest Green Star Rating that provides the consumer attributes that customer demands.* Inherent in this system is the belief that consumers can make educated selections of cosmetic formulations that balance the desire for green products and at the same time answer all the consumer's demands vis-à-vis performance.

Reference

1. O'Lenick, Anthony J., U.S. Patent application **20090259409, entitled** *Process for determining the green star rating of compounds and formulations,* Filed 4/12/2008as provisional patent 61/123,879.

Surface Active Phospholipids for Personal Care

Abstract

Phospholipids are an important class of compounds. They perform many functions in the cell including being constituents of cell membranes. A series of products based upon this chemistry has been developed and recently expanded. These materials offer many desirable surfactant properties including foaming, detergency, and conditioning.

Introduction

Over the last quarter century, a great deal of work has been done to develop surface-active agents that contain phosphorous. This is due in part to the natural occurrence of phospholipids, a necessary chemical for life, as we know it. Synthetic phosphorous-based surface-active agents can provide a number of properties to formulations including;

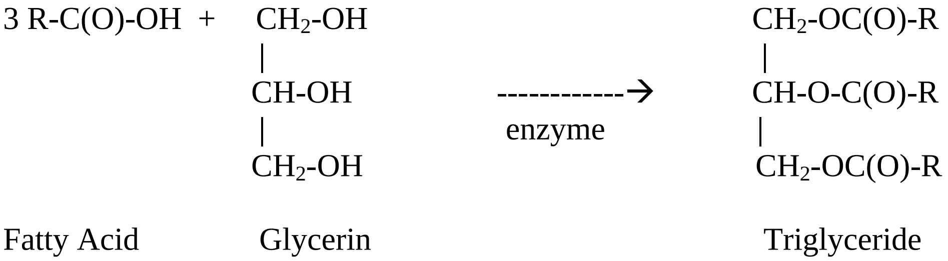
1. wetting
2. emulsification
3. foam
4. conditioning
5. anti-microbial propertied

While there is no single compound with all of these various properties, the properties are a direct consequence of the structure of the compounds. There are three very different classes of phosphorus-based compounds with different properties. These include the mild high foaming, detergent molecules called phosphobetaines, the emollient conditioning compounds, which have become known as phospholipids and the antimicrobial super conditioning agents called phospho-quats.

This article offers a review of the chemistry of natural phospholipids, synthetic phospholipids, phosphobetaines and phospho-quats.

Natural Lipids

Naturally occurring lipids are actually triglycerides made by the reaction of a fatty acid and glycerin. These materials can be made in the laboratory with catalyst at high temperature ($180\text{-}200^{o}$ C). However, the reaction occurs in living cells at low temperatures using specific enzyme systems.



$$3\ R\text{-}C(O)\text{-}OH\ +\ \begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{array} \xrightarrow[\text{enzyme}]{} \begin{array}{l} CH_2\text{-}OC(O)\text{-}R \\ | \\ CH\text{-}O\text{-}C(O)\text{-}R \\ | \\ CH_2\text{-}OC(O)\text{-}R \end{array}$$

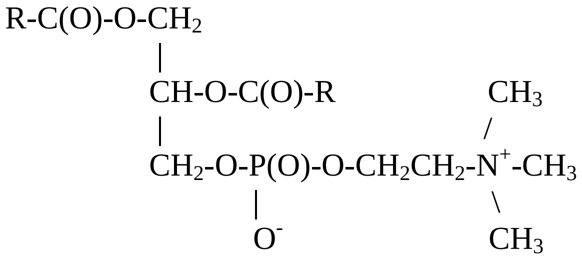
Triglycerides are the storehouse of energy in the cell. They exist in a wide variety of plants, and animals. Related terms are oils, and butters. These terms are often confused.

Lipids are water insoluble, oil soluble compounds that dissolve only very sparingly in water. This property is a direct consequence of the energetics of the hydrogen bond in water. Water is a very unique material and is essential to life as we know it. The polarity of water results in the formation of hydrogen bonding between molecules of water. This bonding results in the variety of unusual properties of water. The high surface tension, the ability to dissolve polar molecules and the relatively high boiling point in relation to molecular weight, are all a direct result of the hydrogen bonding of water.

The lowest free energy state of water is the state in which oil floats on top and the water is in the lower phase. This is why separated oil on water is common. It takes energy to disrupt the hydrogen bonding in water to allow for mixing in oil.

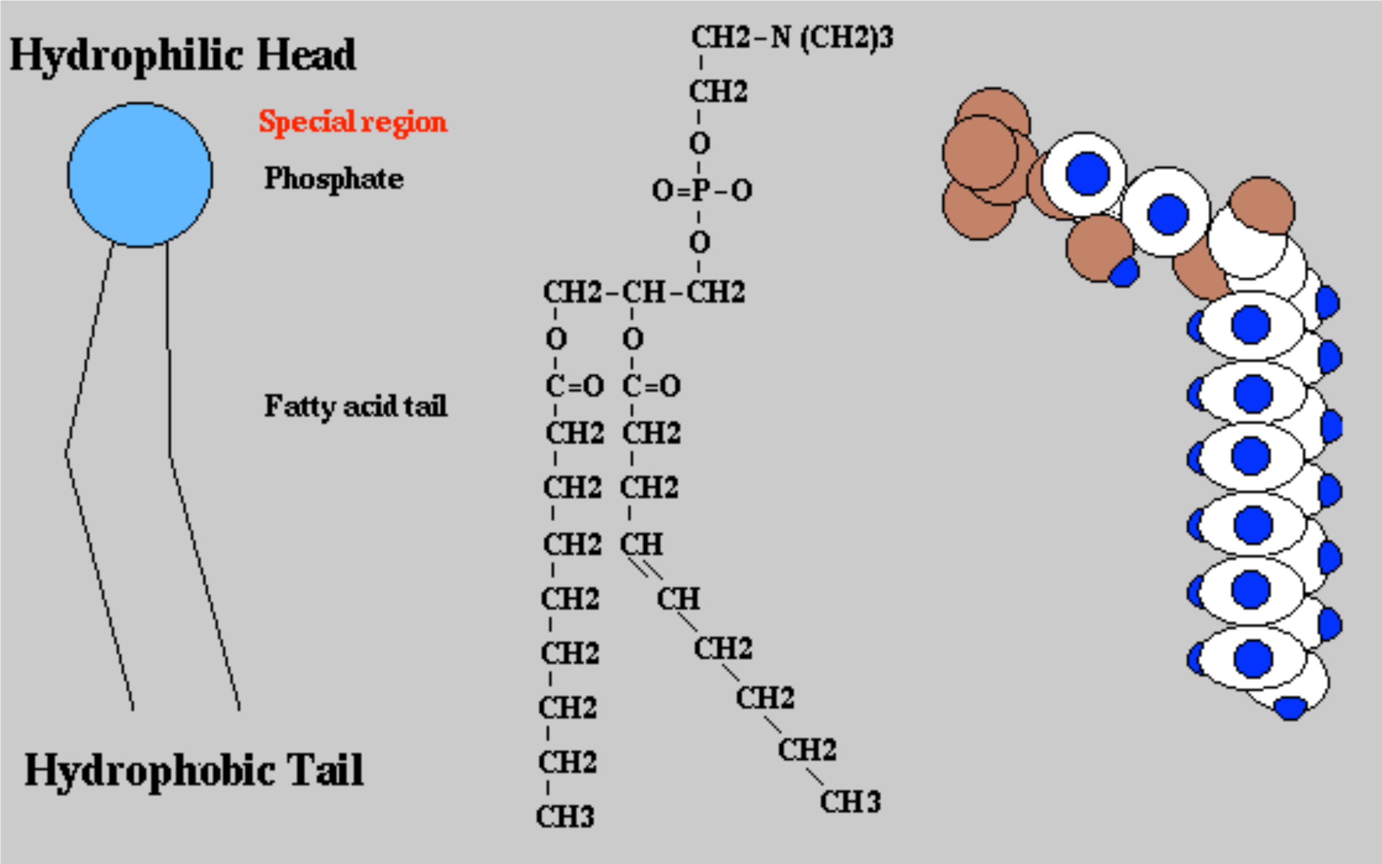
Phospholipids

Natural Phospholipids are a vital class of compounds found in cell membranes. These compounds are related to lipids, but have a polar phosphate group and a polar quaternized nitrogen molecule present.



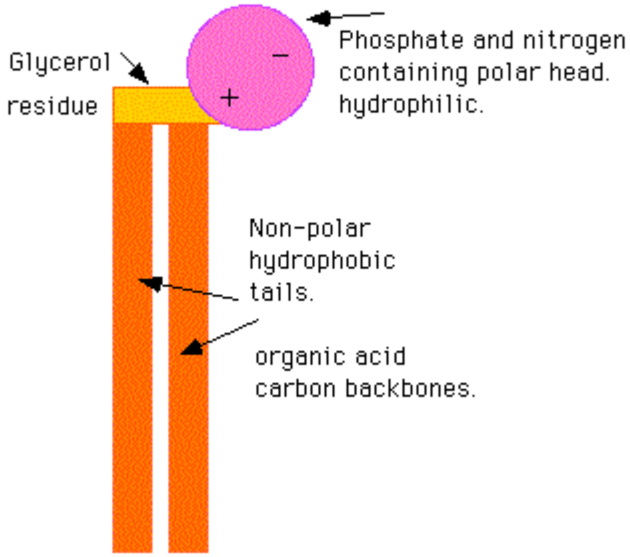
$$\begin{array}{lll}
R\text{-}C(O)\text{-}O\text{-}CH_2 & & \\
\qquad\qquad | & & \\
\qquad\qquad CH\text{-}O\text{-}C(O)\text{-}R & & CH_3 \\
\qquad\qquad | & & / \\
\qquad\qquad CH_2\text{-}O\text{-}P(O)\text{-}O\text{-}CH_2CH_2\text{-}N^+\text{-}CH_3 & & \\
\qquad\qquad\qquad\quad | & & \backslash \\
\qquad\qquad\qquad\quad O^- & & CH_3
\end{array}$$

Phosphatidyl Choline



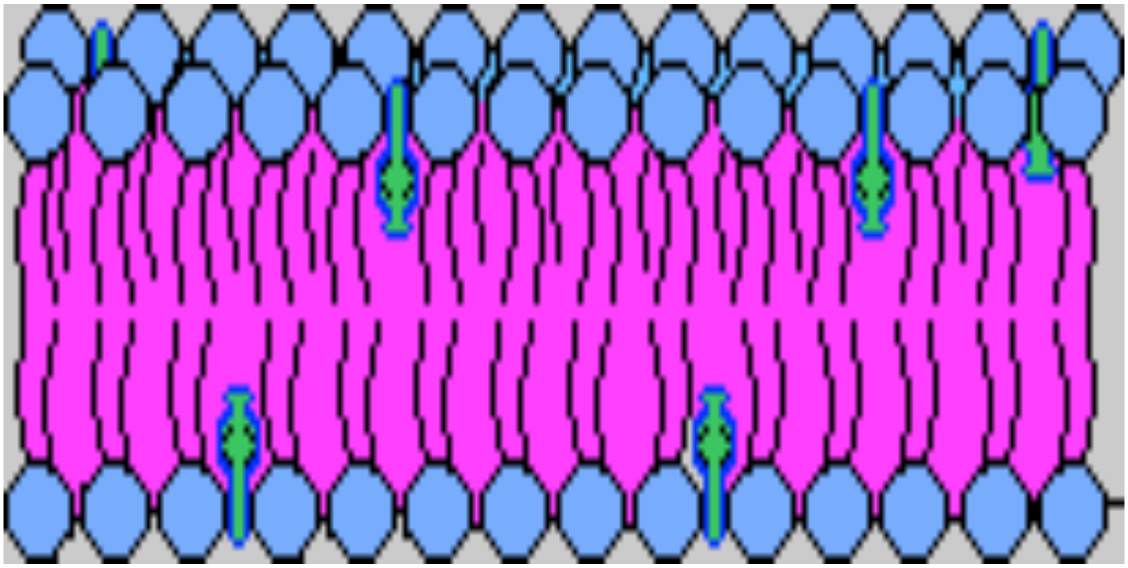
As can easily be seen, the compound is far more polar than lipids.

Graphically the compounds are:



Unlike the lipid compounds, the phospholipids shown above have both water loving polar groups and oil loving groups. This allows the compounds to be much more water-soluble. It is both interesting and important to functionality that the two groups on the compound are different, one saturated and the other unsaturated. This results in the proper combination of properties to make the necessary cell membrane.

The phospholipid bilayer, which the cell membrane is an example of, is composed of various cholesterol, phospholipids, glycolipids and proteins. Below is an example of a simple phospholipid bilayer:

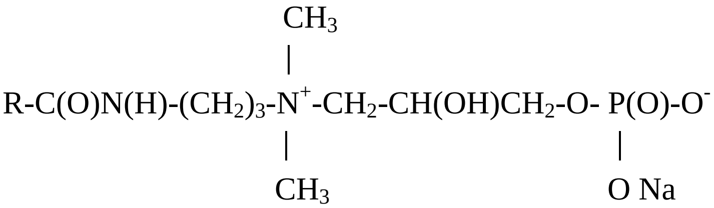


Surfactant Products

Phosphobetaines

The first set of materials that are of interest in this class of materials is the so-called phosphobetaines. These compounds were first described in 1981 in U.S. Patent 4,283,542. The patent, now expired, deals with compounds that have the following structure;

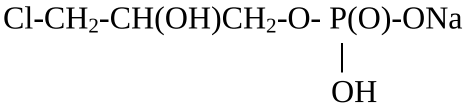
Alkylamido Phosphobetaine Structure



$$R\text{-}C(O)N(H)\text{-}(CH_2)_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}\text{-}CH_2\text{-}CH(OH)CH_2\text{-}O\text{-}\underset{\underset{O\,Na}{|}}{P}(O)\text{-}O^-$$

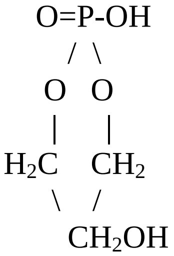
The products from this class differ in the “R” composition. The common attribute is that the products are all mono substituted and are amphoteric products since they bear one and only one + and one and only one – charge in the same molecule.

The process patent describes the effect of ring closure upon foam and solubility. The intermediate used to make the product is prepared by reacting sodium phosphate and Epichlorohydrin. The intermediate that forms exists in a linear and two cyclic forms depending upon the pH at which the reaction is conducted.

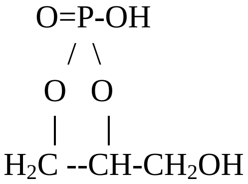


$Cl\text{-}CH_2\text{-}CH(OH)CH_2\text{-}O\text{-}P(O)(OH)\text{-}ONa$

Linear Structure



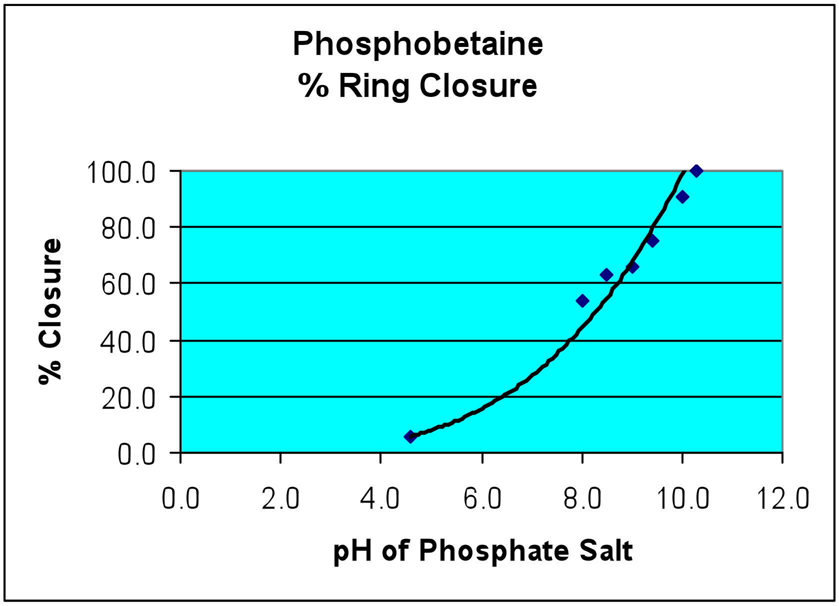
6 member cyclic compound



5 member cyclic compound

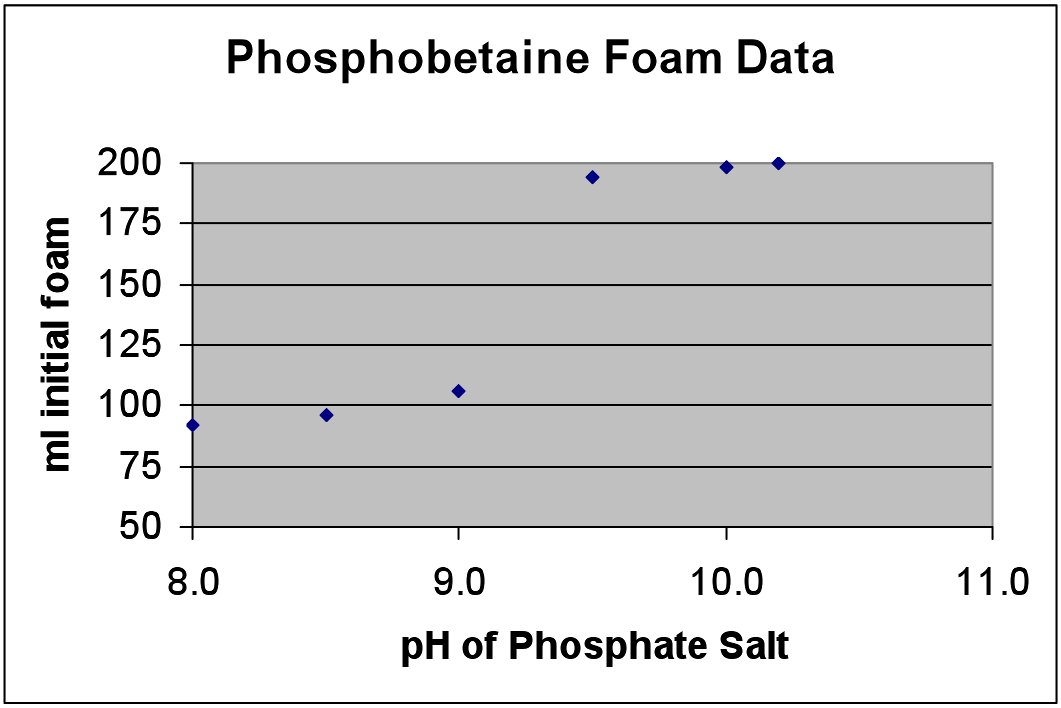
The % ring closure can be monitored by chromatographic analysis, but it has been found that the % NaCl generated during the reaction is a good indication of the degree of cyclization. The difference is the location of ring closure. As the pH of the reaction increases, the amount of cyclic product likewise increases.

pH	**Ring Closure via % NaCl**
4.6	5.5
8.0	54.0
8.5	63.0
9.0	66.2
9.4	75.0
10.0	91.0
10.3	100.0



The foam properties of the product prepared by the reaction of the intermediates made at different pH values also varies as a function of pH. The foam value is initial foam for a cylinder shake foam test using 0.4% active product in deionized water.

pH Phosphate Salt	Foam
8.0	92 ml
8.5	96 ml
9.0	106 ml
9.5	194 ml
10.0	198 ml
10.2	200 ml



The phosphobetaines are detergent systems that are mild and have good foam. They form anionic cationic complexes with sulfates and ether sulfates. These complexes are more substantive to hair, are very mild and are good for personal care products where mildness is of interest, like baby products.

Other patents, now expired, which name Mayhew, and O’Lenick as inventors are as follows:

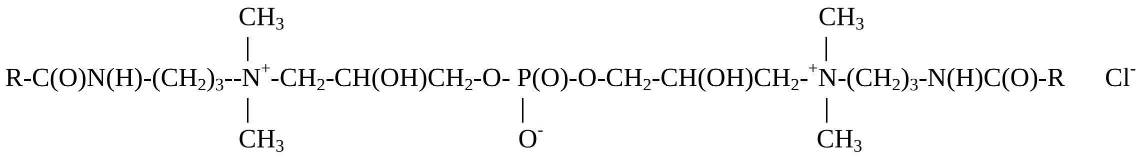
Phospholipid Patents

	Number	Date of Issue	Topic
#1	**4,209,449**	**24-Jun-80**	**Phosphate Quats**
#2	**4,215,064**	**29-Jul-80**	**Phosphobetaines**
#3	**4,243,602**	**06-Jan-81**	**Phosphate Quat**
#4	**4,261,911**	**14-Apr-81**	**Phosphitaines**
#5	**4,283,542**	**11-Aug-81**	**Phosphobetaine Process**
#6	**4,336,385**	**22-Jun-82**	**Phosphate Quats from Imidazolines**
#7	**4,336,386**	**22-Jun-82**	**Phosphite Quaternaries**
#8	**4,380,637**	**19-Apr-83**	**Imidazoline Phosphobetaines**
#9	**4,503,002**	**05-Mar-85**	**Phosphate Quat Compounds**

Phospholipids

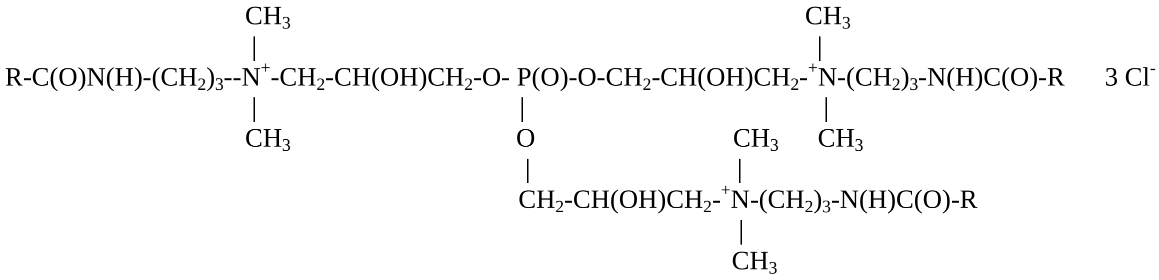
The term phospholipid is properly reserved to compounds in which there is more than one functional group. While at first this sounds unimportant, looking at the structure, one becomes aware of the differences.

Alkylamido Phospholipid StructuresDifunctional



$$R\text{-}C(O)N(H)\text{-}(CH_2)_3\text{--}\overset{CH_3}{\underset{CH_3}{N^+}}\text{-}CH_2\text{-}CH(OH)CH_2\text{-}O\text{-}\underset{O^-}{P}(O)\text{-}O\text{-}CH_2\text{-}CH(OH)CH_2\text{-}\overset{CH_3}{\underset{CH_3}{{}^+N}}\text{-}(CH_2)_3\text{-}N(H)C(O)\text{-}R \quad Cl^-$$

Phosphate quaternary



$$R\text{-}C(O)N(H)\text{-}(CH_2)_3\text{--}N^+(CH_3)_2\text{-}CH_2\text{-}CH(OH)CH_2\text{-}O\text{-}P(O)[O\text{-}CH_2\text{-}CH(OH)CH_2\text{-}{}^+N(CH_3)_2\text{-}(CH_2)_3\text{-}N(H)C(O)\text{-}R]\text{-}O\text{-}CH_2\text{-}CH(OH)CH_2\text{-}{}^+N(CH_3)_2\text{-}(CH_2)_3\text{-}N(H)C(O)\text{-}R \quad 3\ Cl^-$$

The phospholipid structures listed above show that as the degree of substitution around the phosphate group increases the product is no longer an amphoteric and becomes more and more cationic. The difunctional material has two + charges and one – charge, leaving a net charge of +1. The phosphate quaternary has three positive charges and no negative charges, having a net charge of +3.

This change in charge has profound affect upon the properties of the material. As the product becomes more functionalized;

1. the molecular weight increases;
2. the skin penetration decreases;
3. the cationic nature increases;
4. the skin and hair substantivity increases;
5. the amount of fatty in the molecule increases;
6. the skin feel improves.

This explains why the phospholipids are used in skin care as emollients and conditioners and not as detergents.

Emollients work in one of two ways (1) prevent transepidermal water loss, or (2) provide hydration to the skin. Oily materials function in the first way, and to a great extent phospholipids function in the latter way. A good way to show that the compounds provide hydration is the fact that they provide self-preserving properties to aqueous solutions.

Complexation with Anionic Surfactants

One of the critical functionalities observed with phosphobetaine and phospholipid technology is the interaction between the products and sodium laureth sulfate. When the two are combined, a complex forms. The more cationic the phosphobetaine, the less soluble the complex with ether sulfate.

Cocamidobetaine

The first material to consider is an ampholyte, namely a cocamidobetaine. Sodium Trideceth sulfate and cocamidobetaine were combined at differing ratios. All Solutions were prepared at 10% active in water

STDES / Cocamidobetaine	Result
90 / 10	Clear, high foam, low viscosity
80 / 20	Clear, high foam, low viscosity
70 / 30	Clear, high foam, low viscosity
60 / 40	Clear, high foam, low viscosity
50 / 50	Clear, high foam, low viscosity
40 / 60	Clear, high foam, low viscosity
30 / 70	Clear, high foam, low viscosity
20 / 80	Clear, high foam, low viscosity

Over all ranges, the mixture was clear and homogeneous.

Phosphobetaine (Mono Product)

The mono-substituted product functions like the cocamidobetaine.

STDES / Cocamido phosphobetaine	Result
90 / 10	Clear, high foam, low viscosity
80 / 20	Clear, high foam, low viscosity
70 / 30	Clear, high foam, low viscosity
60 / 40	Clear, high foam, low viscosity
50 / 50	Clear, high foam, low viscosity
40 / 60	Clear, high foam, low viscosity
30 / 70	Clear, high foam, low viscosity

Over all ranges, the mixture was clear and homogeneous.

Phospholipid (Di-Product)

A distinct difference is noted with the di-product, due to the greater amount of cationic charge.

STDES / Cocamidophospholipid	Remarks
90 / 10	Clear, high foam, low viscosity
80 / 20	Cloudy, moderate foam, low viscosity
70 / 30	Clear, high foam, low viscosity
60 / 40	Cloudy, moderate foam, low viscosity
50 / 50	Cloudy, moderate foam, low viscosity
40 / 60	Cloudy, moderate foam, low viscosity
30 / 70	Clear, moderate foam, low viscosity
20 / 80	Clear, moderate foam, low viscosity

Phospholipid (Tri-Product)

The increasing amount of cationic charge is noted in the product that is predominately tri-ester, and the compatibility with anionic is even lower. The product called tri-product is actually a mixture of di and tri functional product.

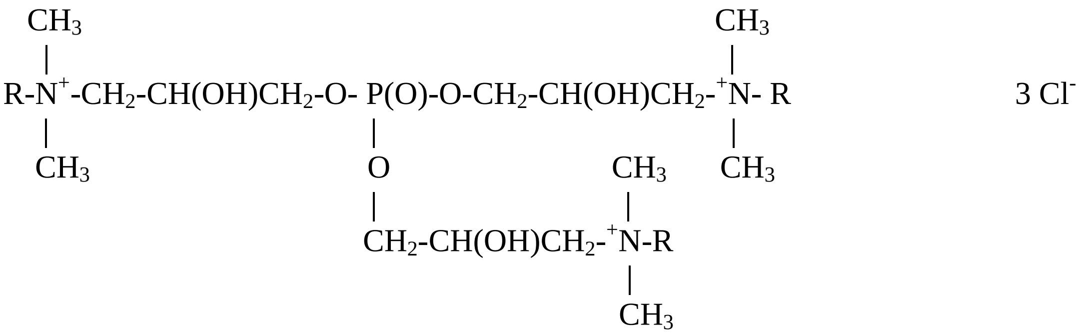
STDES / Cocamidophospholipid	Remarks
100 / 0	High dense lasting foam, solution is clear and thin
90 / 10	High dense lasting foam, solution is clear and thin
80 / 20	High dense lasting foam, solution is clear and thin
70 / 30	High very dense lasting foam, solution is viscous
60 / 40	Low thin foam, solution is clear and viscous
50 / 50	Low thin foam, solution phase separates into two distinct layers
20 / 80	High moderately dense less durable foam, solution is opaque and thin
10 / 90	High moderately dense less durable foam, solution is clear and thin
100 / 0	High moderately dense foam, solution is clear and thin

Antimicrobial properties

Recently, there have been several patents, naming Fost and Perella as inventors, directed to specific alkyl functional phosphate quaternary compounds that have spermicidal, or antimicrobial activity. Recalling the structure of the alkylamido given above, the alkyl products have the following structure;

Alkyl Phosphate Quaternary Compounds

In these products, the “R” group is alkyl. Commonly C_{12} to C_{14}. This is the same distribution as found in germicidal quats.



$$R\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}\text{-}CH_2\text{-}CH(OH)CH_2\text{-}O\text{-}\underset{\displaystyle O\text{-}CH_2\text{-}CH(OH)CH_2\text{-}{}^+\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{N}}\text{-}R}{P(O)}\text{-}O\text{-}CH_2\text{-}CH(OH)CH_2\text{-}{}^+\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}\text{-}R \qquad 3\,Cl^-$$

R is $C_{12}H_{25}$.

The patents of interest assigned to Mona Industries, now Uniquema are as follows;:

Patent #	Topic	Issued
5,215,976	Phospholipids as Spermicidal Agents	6/1/93
5,286,719	Phospholipids as Viricidal Compositions	2/15/94
5,648,348	Phospholipids as Antimicrobial Agents	7/15/97
5,650,402	Phospholipids as Antimicrobial Agents	7/22/97

While these alkyl substituted materials are not registered antimicrobial compounds, and consequently cannot be used as the sole antimicrobial in formulations, they do enhance performance of the antimicrobial and are self-preserving. It is very interesting that the antimicrobial activity is limited strictly to prokaryotic life, with complete selectivity towards eukariotic life. The explanation appears to be that the mode of action is that these materials increase the permeability of the cell wall to water, thereby causing lyses. Since eukarotic life has no cell wall, the cells are not affected. This phenomenon is of interest, since it shows that these compounds do in fact provide emmoliency by hydration, rather than decreasing trans epidermal water loss.

The most interesting class of products for personal care is the amido functional products. These products are multifunctional, natural oil derived phospholipids composed predominantly of diester and triester phosphates. Through the careful selection of specific natural oils as raw materials, the products deliver a broad range of functional properties which include gentle cleansing, anti-irritation effects, unusually high substantivity, long lasting conditioning, emulsification attributes, and exceptional mildness to skin and eyes.

Natural Oils

The specific natural oils will have a dramatic effect upon the properties of the phospholipid prepared. This relates to properties like foam, conditioning, substantivity and skin feel. Below are the carbon distributions of specific oils. The oil compositions are taken from a book entitled *Primary Ingredients.*

A. Coconut Oil *(Cocos Nucifera)*

1. Source

Coconut oil is the most abundant oil processed. Coconut oil comes from the seeds of Cocos Nucifera. It is the most common oil raw material used in the cosmetic industry. Geographically, is cultivated principally from Southeast Asia and the Philippines and is the major source of lauric acid (C-12).

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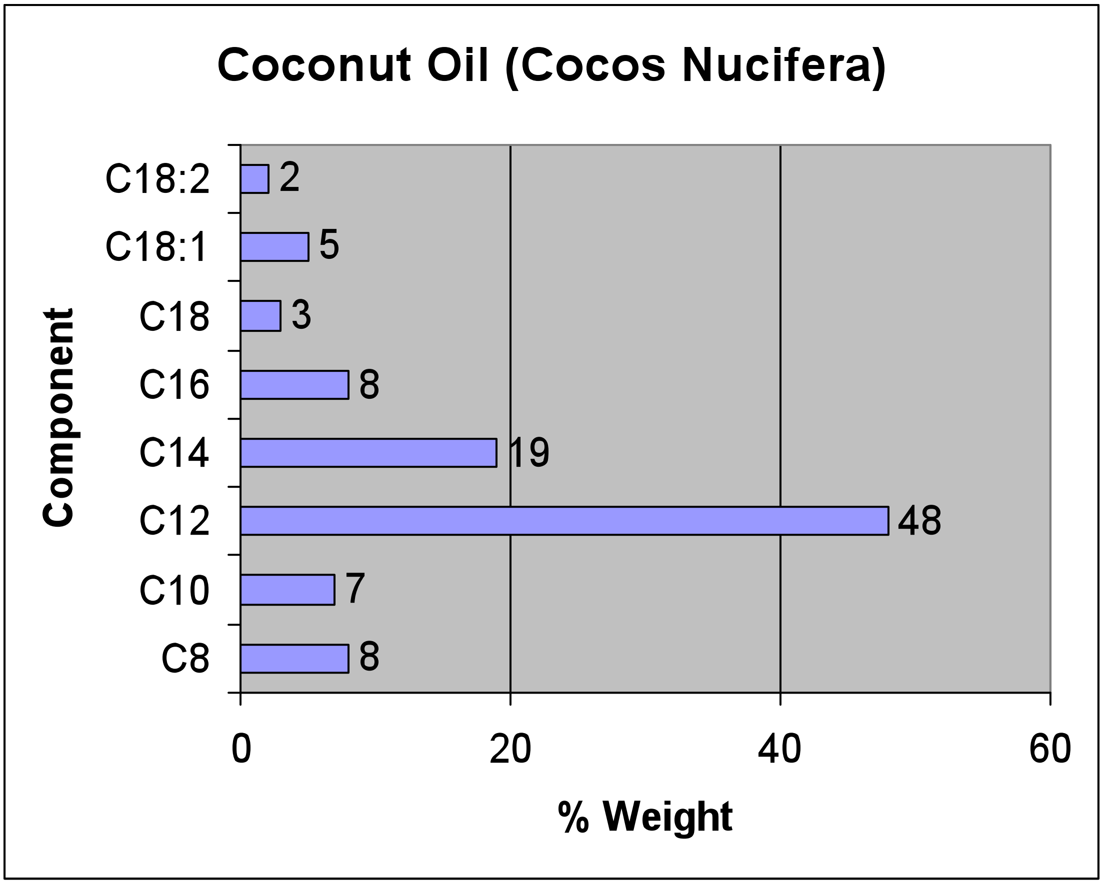
2. Fatty Components



3. Properties

<u>CAS Number: 8001-31-8 EINECS Number: 232-282-8</u>

Iodine Value: 8	Titer Point: 22° C (free fatty acid)
Carbon Number 12.84	

4. Commercial Availability

Coconut oil is a commodity, the price fluctuates depending upon market conditions.

5. INCI Status

Coconut oil is listed in the CTFA dictionary, both per se and in 162 derivatives.

6. Status in Japan

Name: Coconut Oil
Ingredient Code: 500543
Categories: All categories with no limits

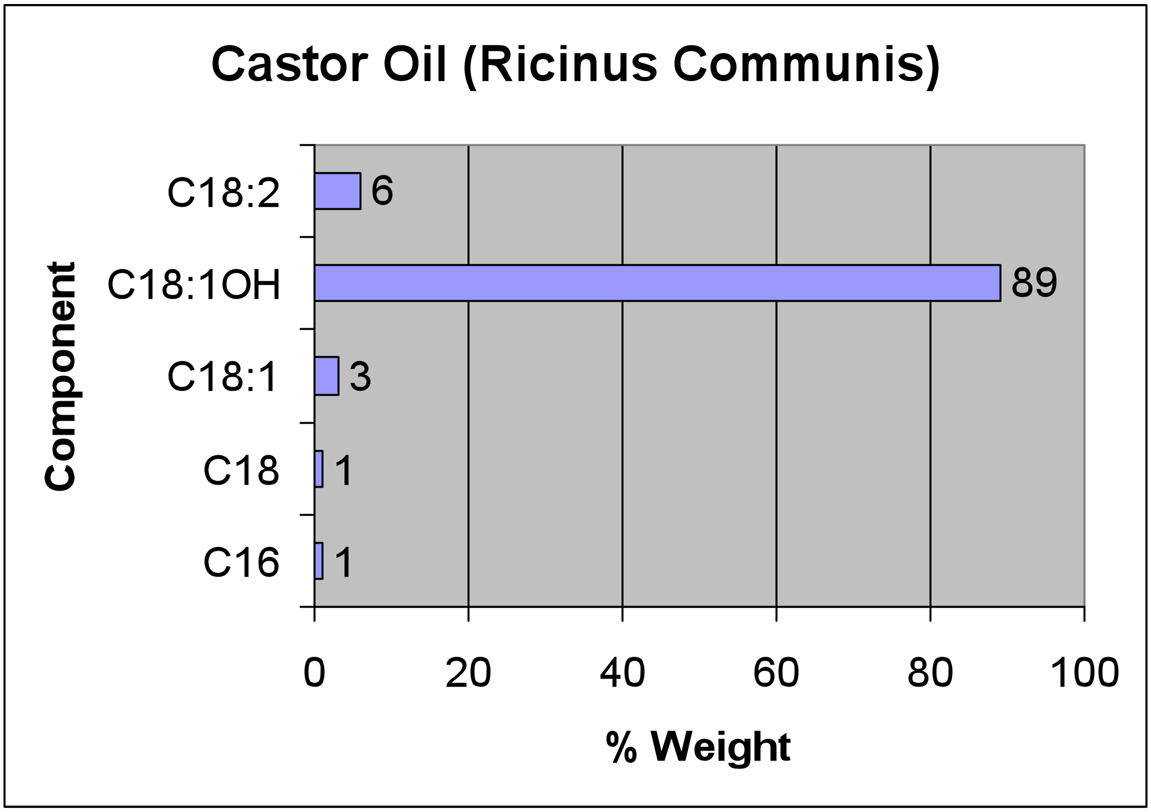
B. Castor Oil *(Ricinus communis)*

1. Source

Castor oil is a unique triglyceride. It is derived from Ricinus communis L. The castor plant grows wild in many subtropical and tropical areas. Today Brazil, China and India provide over 90% of the oil. Castor oil contains a large content of hydroxy containing compounds that are unsaturated.

Castor Oil is a clear, viscous, light colored fluid that is nondrying and quite stable. The Purity of Castor Oil occurs with remarkable uniformity. Regardless of country of origin, or season it is grown, the composition and chemical properties remain within a very narrow range. Castor Oil has broad compatibility with oils, waxes, natural resins, and gums.

2. Fatty Components



3. Properties

CAS Number: 8001-79-4
Titer Point 2 ° C
Carbon Number: 18.0

EINECS Number: 232-293-8
Iodine Value: 85

4. Commercial Availability

Castor oil is an item of commerce, available in a variety of grades.

5. INCI Status

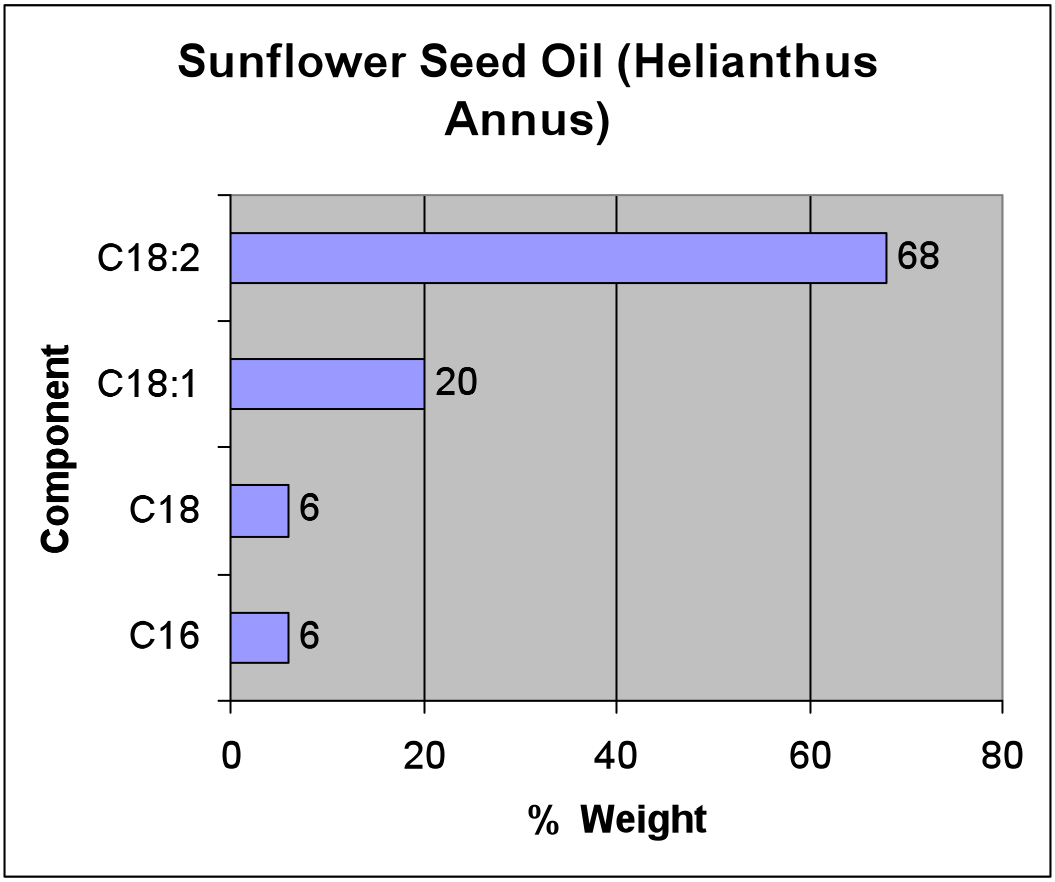
Castor oil is listed in the CTFA dictionary, both per se and in 69 derivatives. Silicone derivatives as well as surfactant derivatives are available.

C. Sunflower Seed Oil *(Helianthus annuus)*

1. Source

Sunflower seed oil is a triglyceride derived from the seeds of the sunflower (Helianthus annus L.). It was originally cultivated in North America by native Indians. It is now cultivated in North America, Russia, Europe South America, India and China. It is a rather common plant.

2. Fatty Components



3. Properties

CAS Number: 8001-21-6 EINECS Number: 232-273-9
Titer Point: 18 ° C (free fatty acid) Iodine Value: 130
Carbon Number: 16.0

4. Commercial Availability

Sunflower seed oil is an item of commerce. It is used principally in food.

5. INCI Status

Sunflower oil is listed in the CTFA dictionary and is in 6 derivatives.

6. Status in Japan

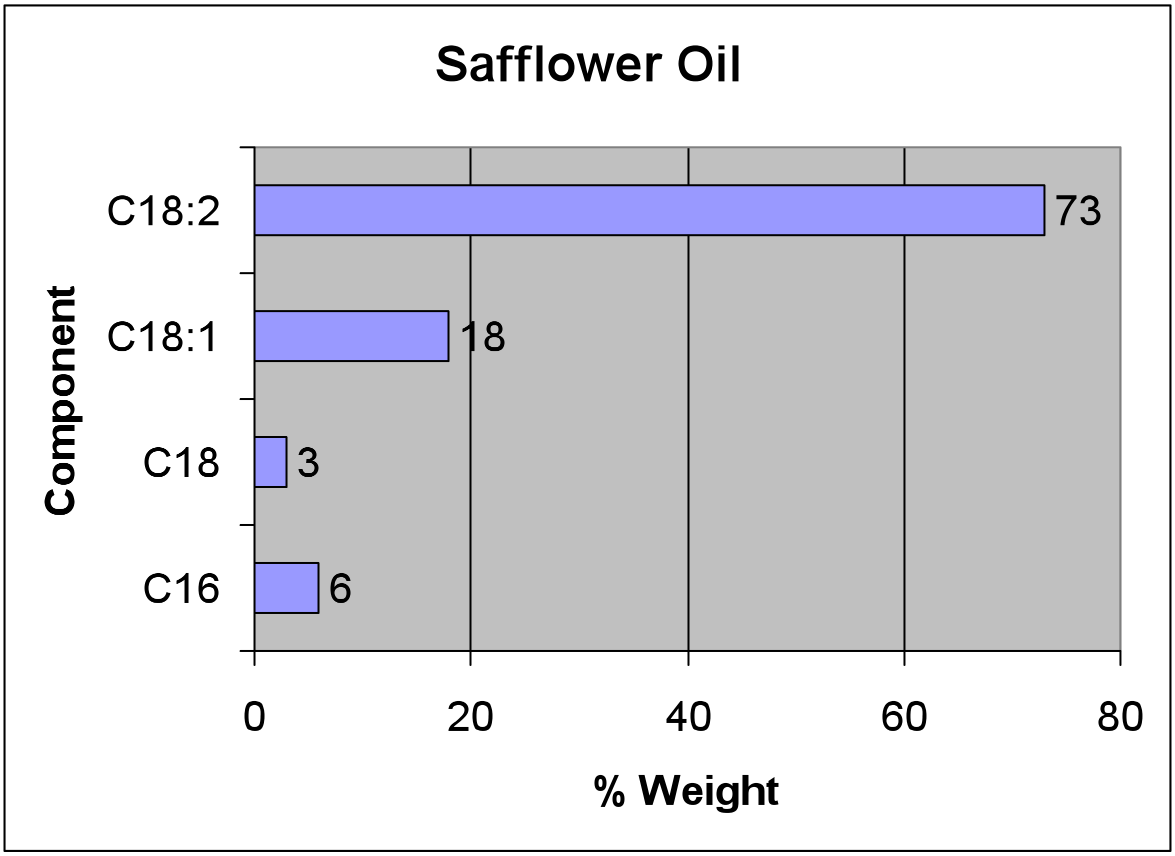
Name: Sunflower Seed Oil
Ingredient Code: 520923
Categories: All categories with no limits, except eyeliners (category 8).

D. Safflower Oil

1. Source

Safflower oil is a triglyceride derived from the species Carthamus Tinctorius. It originates in the Orient, but the U.S. production has been selected to maximize the polyunsaturate content.

2. Fatty Components



3. Properties

CAS Number: 8001-23-9 EINECS Number: 232-276-6
Titer Point: 16 ° C (free fatty acids) Iodine Value: 145
Carbon Number: 17.9

4. Commercial Availability

Safflower oil is an item of commerce.

5. INCI Status

Safflower oil is listed in the CTFA dictionary, both per se and in derivatives.

6. Status in Japan

Name: Safflower Oil
Ingredient Code: 500186
Categories: All categories with no limits

E. Hydrogenated Palm Oil *(Elaesis guineensis)*

A. Source

Palm oil is a triglyceride extracted from the fruit of Elaeis guineensis Jacq, which is among the most efficient oil producing plants per acre in the world. Palm oil is the principal source of palmitic acid for isopropyl palmitate.

B. Carbon Distribution

Component	Typical % Weight
C-14	1
C-16	42
C-18	57

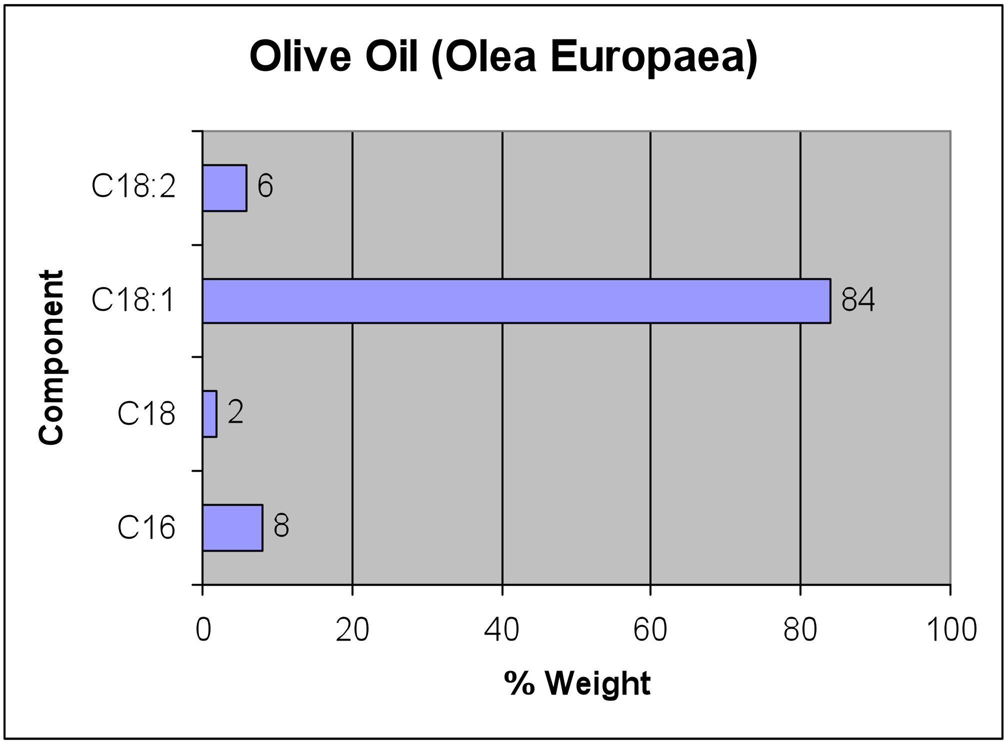
CAS Number: 8002-75-3
EINECS Number: 232-316-1

F. Olive Oil *(Olea europaea)*

1. Source

Olive oil is a triglyceride, which has occupied a unique position in civilization. It is the oldest oil known to man. It is produced throughout the area that was once the Roman Empire.

2. Fatty Component



3. Properties

CAS Number: 8001-25-0 EINECS Number: 232-277-0
Titer Point: 20 °C (free fatty acid) Iodine Value: 84
Carbon Number: 17.8

4. Commercial Availability

Olive oil is available as an item of commerce.

5. INCI Status

Olive oil is listed in the CTFA dictionary, both per se and in 21 derivatives. Silicone derivatives are available.

6. Status in Japan

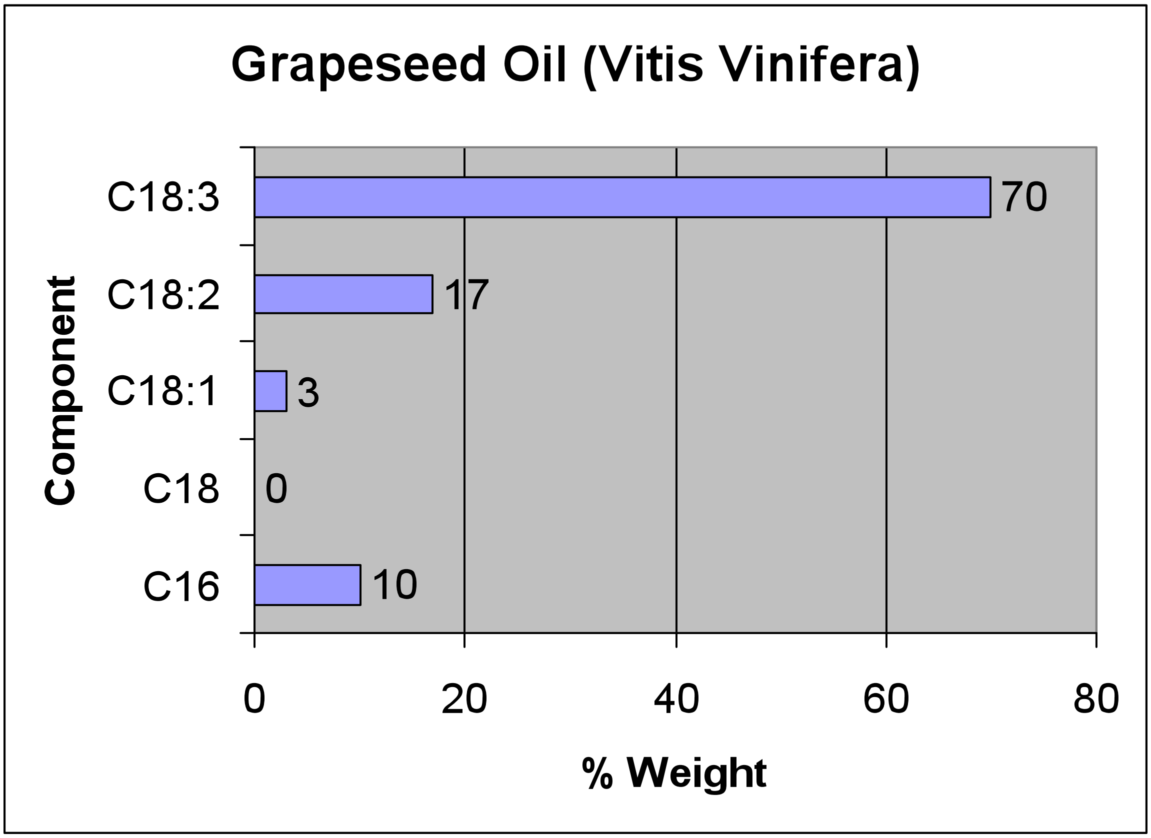
Name: Olive Oil
Ingredient Code: 001191
Categories: All categories with no limits

G. Grape Seed Oil *(Vitis vinifera)*

1. Source

Grapeseed oil is a triglyceride derived from grape (Vitis Vinifera). It is cultivated in many areas of the world, but originated in the Mediterranean coast (Italy, France, Turkey, Greece and Yugoslavia).

2. Fatty Components



3. Properties

CAS Number:	8024-22-4	EINECS	287-896-9
Iodine Value:	135	Titer:	-3° C (free fatty acid)
Carbon Value:	17.8		

4. Commercial Availability

Grapeseed oil is an item of commerce.

5. INCI Status

Grape seed oil is listed in the CTFA dictionary.

6. Status in Japan

Name: Grape Seed Oil
Ingredient Code: 520938
Categories: All categories with no limits, except eyeliners.

Properties of Products

Due to the ampholytic character of the products, they are compatible with virtually all other types of ingredients including anionic surfactants. The products have multiple hydrophobic groups, as well as, multiple cationic binding sites, which provide unusually high degrees of substantivity. Typical are the products are as follows;

Product	**Chemical Description**	**Oil Source**	**Primary R-Group**
1	Cocamidopropyl Phosphatidyl PG-Dimonium Chloride	Coconut	Coco
2	Di-Linoleamidopropyl Phosphatidyl PG-Dimonium Chloride	Safflower	Di-Linoleyl
3	Linoleamidopropyl Phosphatidyl PG-Dimonium Chloride	Safflower	Linoleyl
4	Sunfloweramidopropyl Phosphatidyl PG-Dimonium Chloride	Sunflower	Linoleyl
5	Stearamidopropyl Phosphatidyl PG-Dimonium Chloride	Palm	Stearyl
6	Grapeseedamidopropyl Phosphatidyl PG dimouium Chloride	Grapeseed	Linoleyl

PRODUCT	FORMULATION BENEFITS / APPLICATIONS
Cocamido propyl dimethyl phospholipid	• **Gentle cleansing, highly substantive skin conditioning, good wetting properties.** • Baby care products, sensitive skin cleansers, bio-deodorants.
***Stearyl amido* propyl dimethyl phospholipid**	• **Emulsification, long-lasting skin smoothing properties, eliminates the tacky / greasy feel of other ingredients, such as glycerin.**
Ricinoleamido propyl dimethyl phospholipid	• Beneficial properties of castor oil without a greasy feel. • Substantive toward skin and hair with long-term aesthetics. • Useful for tanning products, compromised skin care, and post-relaxer conditioners.
Dimer amidopropyl dimethyl phospholipid	• **Exceptional barrier properties due to dimerized hydrophobic groups.** • Barrier crèmes, lotions, emollient tissue and diaper liner treatments.
Safflower amido propyl dimethyl phospholipid and PEG 8 dimethicone	• The benefits of Colalipid SAFL complexed with silicone technology. • Enhanced conditioning for skin and hair.

These products exhibit moderate to low foaming properties, depending upon the specific structure chosen.

Formulations

Formulations are provided by Colonial Chemical South Pittsburg, Tn.

Sunscreen Crème

	Compounds	Wt.%
Phase A.	Stearamidopropyl PG-dimonium Chloride Phosphate	3.0
	Cetyl Phosphate	1.0
	Triethanolamine	0.5
	Titanium dioxide	0.5
	Glycerin	2.0
	Water	70.5
Phase B.	Steareth-2	1.0
	Cetyl alcohol	1.5
	Hexyl laurate	1.5
	Diisopropyl adipate	2.0
	Menthyl anthranilate	5.0
	Octylmethoxy cinnamate	7.5
	Benzophenone-3	3.0
	Dimethicone, 350 cs.	1.0

After Shave Lotion

	Compounds	Wt.%
Phase A.	Water	66.0
	Phenyl dimethicone	1.5
	Carbopol 940	0.3
	Triethanolamine	0.6
Phase B.	Water	30.0
	Stearamidopropyl PG-dimonium chloride Phosphate	1.0
	Menthol	0.1

Foaming Facial Cleanser

Compound	Wt.%
Water	58.0
Disodium Laureth-3 Sulfosuccinate	22.0
Lauramidopropyl betaine	8.0
Lauramine Oxide	5.0
Cocamidopropyl PG-dimonium Chloride Phosphate	4.0
Glycerin	2.0
PEG-18 glyceryl oleate/cocoate	1.0

Frequent Use Hand Soap

Compound	Wt.%
Water	53.0
Sodium laureth 2 sulfate	25.0
Disodium laureth-3 sulfosuccinate	10.0
Cocoamphoproprionate	6.0
Lauramine Oxide	4.0
Cocamidopropyl PG-dimonium chloride phosphate	2.0

Leave-on Scalp and Hair Conditioner

Compound	Wt.%
Water	91.5
Hydroxyethyl cellulose	0.5
Glycol distearate	1.5
Cetyl alcohol	2.0
Lauramidopropyl PG-dimonium chloride phosphate	2.5
Dilinoleamidopropyl Phosphatidyl PG-dimonium Chloride	2.0

Skin Care Lotion

	Compound	Wt.%
Phase A.	Water	83.8
	Dilinoleamidopropyl Phosphatidyl PG-dimonium Chloride	3.0
	Cocoamphodiacetate	1.0
	Glycerin	5.0
	Titanium dioxide	0.5
	Triethanolamine	0.7
Phase B.	Cetyl Phosphate	1.0
	Isopropyl palmitate	3.0
	Cetyl alcohol	2.0
	Dimethicone, 350 cs.	1.0

Finishing Hair Spray

Compound	Wt.%
SD Alcohol 40	93.50
Vinyl acetate / Crotonic acid copolymer	3.75
Water	1.20
Aminomethyl propanol	0.35
Sunfloweramidopropyl Phosphatidyl PG-dimonium	1.20

Shower Gel

Compound	Wt.%
Water	55.5
Sunfloweramidopropyl Phosphatidyl PG-dimonium	2.0
Lauramidopropyl betaine	5.0
Sodium laureth-2 sulfate	35.0
Cocamide MEA	2.0
Sodium chloride	0.5

Facial Scrub for Acne Control

Compound	Wt.%
Water	44.0
Sodium C14-C18 Olefin Sulfonate	40.0
Lauramidopropyl betaine	10.0
Linoleamidopropyl PG-dimonium Chloride Phosphate	2.0
Sodium chloride	2.0
Salicylic acid	2.0

Conditioning Hair Rinse

Compound	Wt.%
Water	87.8
Hydroxyethyl cellulose	0.7
Glycol distearate	2.0
Cetearyl alcohol	2.5
Linoleamidopropyl PG-dimonium Chloride Phosphate	5.7
Linoleamidopropyl PG-dimonium Chloride Phosphate	1.3

Conditioning Shampoo

Compound	Wt.%
Water	31.0
Sodium laureth-2 sulfate	57.7
Lauramidopropyl betaine	9.4
Ricinoleylpropyl PG-dimonium Chloride Phosphate	1.4
Sodium chloride	0.5

Skin Therapy Crème

	Compound	Wt.%
Phase A.	Water	80.4
	Ricinoleylpropyl PG-dimonium Chloride Phosphate	3.7
	Cetyl Phosphate	1.0
	Glycerin	2.0
	Titanium dioxide	0.5
	Aminomethyl propanol	0.4
Phase B.	Cetyl alcohol	2.0
	Steareth-2	2.0
	Squalane	0.8
	Octyl stearate	4.0
	Isopropyl palmitate	2.4
	Dimethicone, 350 cs.	0.8

Conditioning Body Cleanser

Compound	Wt.%
Water	17.5
Sodium laureth-2 sulfate	50.0
Disodium Laureth Sulfosuccinate	15.0
Cocoamphodiacetate	10.0
PEG-8 dimethicone and linoleamidopropyl PG-dimonium chloride phosphate	4.0
Lauramid DEA	3.0
Sodium chloride	0.5

Moisturizing Make-Up Foundation

	Compound	Wt.%
Phase A.	0.5% Xanthan gum in 1% NaCl	65.0
	PEG-8 dimethicone and linoleamidopropyl PG-dimonium chloride phosphate	3.0
	Glycerin	8.0
	Pigment	15.0
	Steareth-20	1.6
Phase B.	Isopropyl palmitate	2.0
	Hexyl laurate	2.0
	Steareth-2	2.4
	Dimethicone, 350 cs.	1.0

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