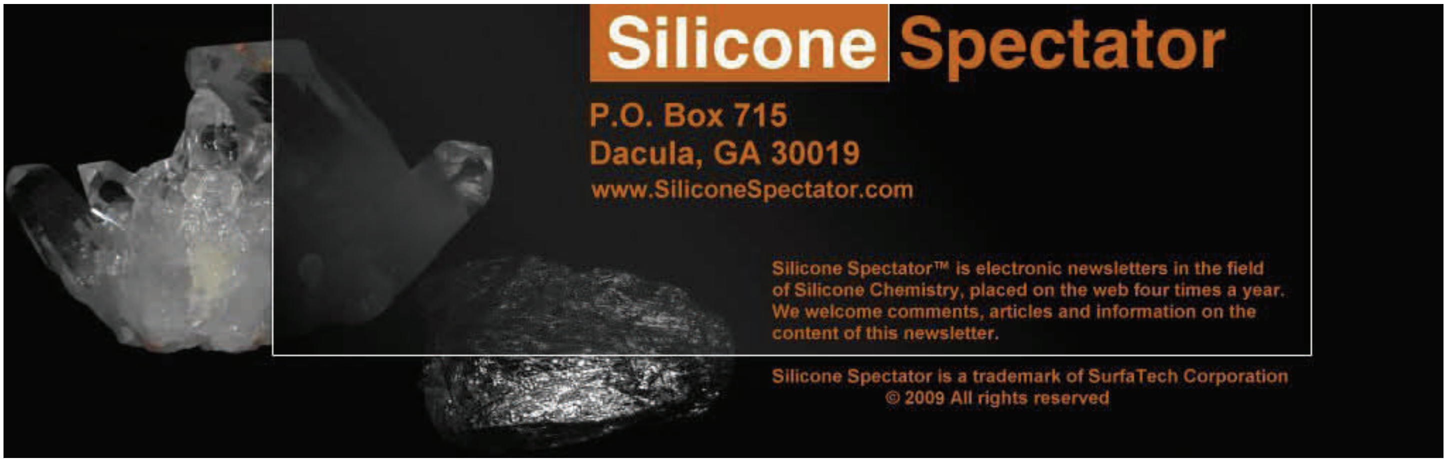

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Editors Note: This edition of the Silicone Spectator will present a new concept: Greening with Silicone$^{(SM)}$, a research and consultation offered by Siltech LLC, aimed at developing cosmetic silicone compounds that allow for the production of greener formulations. The question to address is if silicones are not generally thought of as green materials, how can one use them to make a product having greater environmental acceptability? The answer is that when a properly chosen silicone is added into a formulation at a low concentration to provide an effect the consumer demands and one that cannot be obtained by the use of a non silicone, a greener formulation is created. We have previously presented the Green Star Rating® system, which we will refer to in this article. See

http://www.siliconespectator.com/articles/August_15_2008_Supplement.pdf.

Products have developed both the products and the techniques used to work with formulators to choose a silicone that

(1) lowers surface tension of aqueous and oil systems to levels unattainable using fatty components alone,

(2) provides a more siliphilic (silicone like) feel to either aqueous solution or to oil phases or to both, making the amount of silicone added to the formula dramatically less,

and

(3) replaces D4 and D5 with materials that have the same dry feel without the ability to re-form cyclomethicone when used alone, or better yet provide a dry skin feel when used in certain organic esters at very low concentrations.

Happy Reading!

Greening With Silicones
An Overview

Tony O'Lenick
Siltech LLC
March 1, 2009

Abstract

Compounds that have two or more groups in the same molecule that in pure form are insoluble in each other are said to be amphilic. These materials while soluble in different solvents do not form uniform solutions. Because they are surface active, these materials are found at the interface where they modify the surface tension. The ability to modify either oil or water to have the surface tension of silicone compounds offers tremendous advantages to the formulator, providing desirable silicone aesthetics at very low concentrations. This allows for the formulator to make the products with both the consumer demanded aesthetics, and a more environmentally friendly Green Star Rating®

Amphilic Compounds

Compounds that have two or more groups in the same molecule that in pure form are insoluble in each other are said to be amphilic. Amphilic Compounds, also called surfactants have at least two of the following groups:

- ♦Oil Soluble Groups
- ♦Water Soluble Groups

- ♦Silicone Soluble Groups
- ♦Fluoro Soluble Groups

The amphilic compounds of interest in this article are those that contain silicone soluble group and another group. These compounds by virtue of their structure have very interesting physical chemical properties and formulation attributes. These attributes allow the formulator to provide foam, emulsification or wetting to consumer products which are directly related to the activity of the amphile at the surface and in particular the ability to lower surface tension.

Solubility

We can organize our world based upon solubility according to the following simple definitions[1]:

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 collodial 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).

However, the world of chemistry is rearly so easy to organize. 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 opposite ions, but sodium lauryl sulfate in water is very different. The presence of a large fatty portion makes the product surface active.

Most systems encountered by formulation chemists are not pure liquids; they are compositions (i.e. mixtures of materials). The ability to obtain wetting, foaming, and emulsification requires that the compound added lower surface tension. Not all materials that lower surface tension are effective for all of the above surfactant properties, but lowering surface tension is a prerequisite for all of these.

Surface tension reduction requires molecules that are have a particular function in solution. Solutions of amphilic molecules are fundamentally different than solutions other type of solutions. Consider NaCl (salt). It is an example of an ionic, non-surface active agent and Sodium Lauryl Sulfate (SLS) an example of a surface active agent. Both are water soluble (i.e. clear in water), but what they do in solution is significantly different and key to their properties.

The term solution relates to the clarity of a liquid and consequently the size of any particle present. Consider a 0.5% solution of salt. NaCl is not a surface-active agent, since it does not have a hydrophobic portion. Consequently, upon dissolution in water at low concentrations, it is present at the same concentration at the top of the beaker as at the bottom, at the left and at the right of the beaker. At this concentration salt can be considered sodium ion and chloride ion.

This is a key concept. If sodium chloride and potassium sulfate are mixed in dilute solution, the solution contains all four ions rather than two compounds. As the concentration of ionic material in solution is increased nearing saturation structured systems form due to repulsion of the ions.

Surfactant systems are much different. They contain hydrophobic and hydrophilic portions. SLS has a C12 fatty portion and a water-soluble sulfate portion covalently bonded in one molecule (such molecules are referred to as amphilic). When such molecules are added under dilute solution a clear "solution" results, but the distribution of molecules in solution is not the same. As one adds SLS to water the molecules go to the surface, lowering surface tension. At the air / water interface the water-soluble groups align in the water and the water insoluble material C12 groups point into the air. This is the lowest free energy for the system. As one continues to add more SLS, the ability to pack the surface stops. This is the Critical Micelle Concentration (CMC). At concentrations below the CMC, surfactants are found at the surface. At the CMC point the surfactants assemble to form micelles. Water soluble groups into the water, oil soluble groups in the center associating with each other.

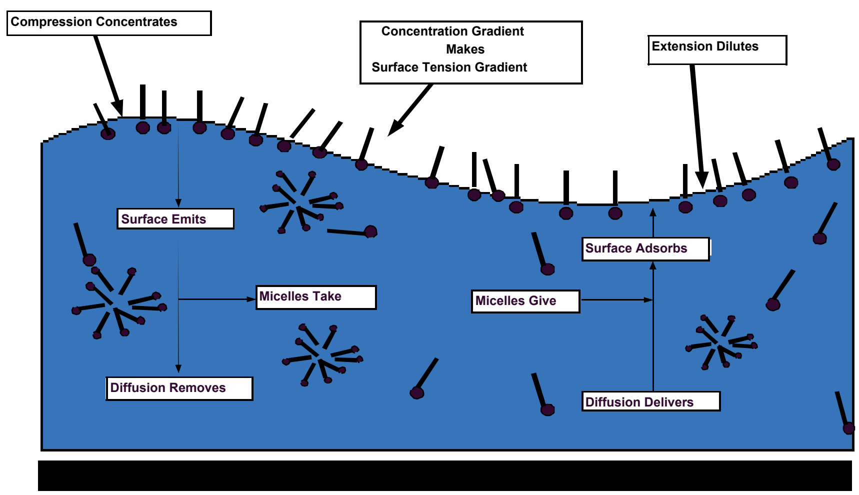
While both beakers contain solutions, the organization of the molecules in the respective liquids is far different. Likewise, the surfactant properties, (surface tension, ability to wet, foam, cleanse or emulsify) are very different.

The ability for surface-active materials to provide desirable properties by lowering surface tension is an important reason to use surfactants. The SLS discussed above is added to water, a solvent that not only has a high surface tension, but also one in which the surfactant is soluble. SLS provides wetting, foam and detergency to the water, by virtue of lowering its surface tension.

Cosmetic formulators work with materials other than water. One major group of materials is the various oil phases (including mineral oil, squalene, esters, and many others). These oil phases have surface tensions values of around 32 dynes/cm^2. This means if we can find a material soluble in the oil, amphilic in nature and having a lower surface tension, the surface tension of the oil can be reduced exactly analogously to the water example with SLS. SLS is not of interest in oil phases because it is not soluble. Alkyl silicones are the amphilic materials of choice for oil phases.

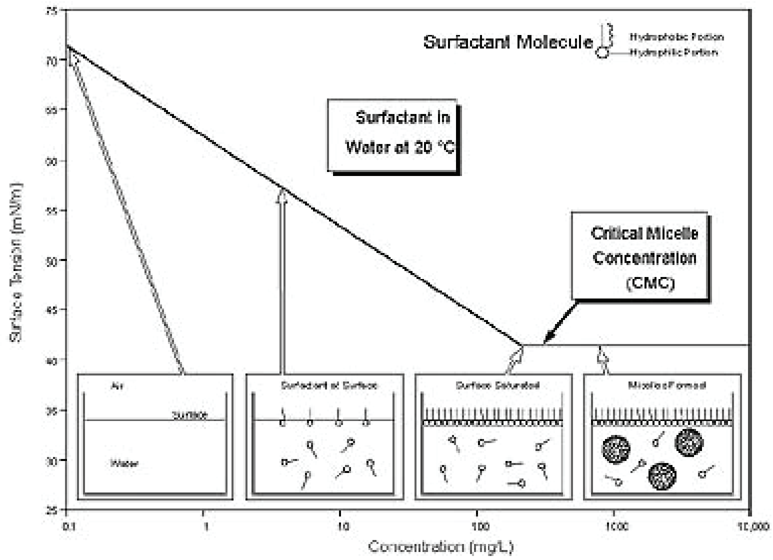
The importance of surface tension reduction cannot be overstated when making personal care products. The application to hair and skin always is based upon the formation of new surface area; lipsticks are spread on the skin, shampoos spread on the hair, and so on. The through and efficient spreading requires a lowering of surface tension. Amphilic molecules because they are active at surfaces are in motion in the dynamic system created by spreading out. Figure 1 shows the complicated process.

Dynamic Surface Tension
Amphilic Silicone Molecules
Figure 1



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 tensions no longer drops, even with additional surfactant, this concentration called critical micelle concentration that micelles become the dominant form of surfactant. This situation is shown in the third box, Figure 2.

Figure 2 Surfactant Orientation[2]



Siliphilic / Hydrophilic Amphilic Compounds

The first class of compounds to consider is dimethicone copolyols. These compounds feature a silicone loving group and a water-loving group. There are truly a large number of terms used to refer to these materials, including silicone surfactant, silicone glycols, dimethicone copolyol, and more recently PEG dimethicone. Regardless of the preference for a name chosen by a particular industry the materials are the same. The structure is shown in

Figure 3
PEG-8 Dimethicone

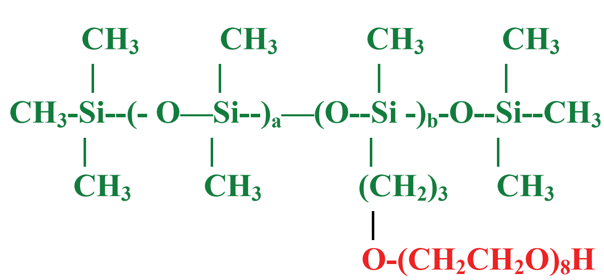
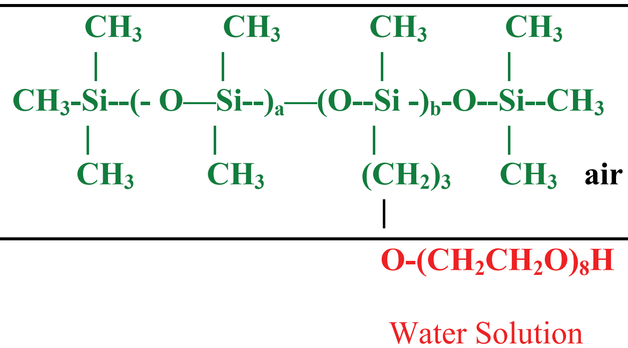


Figure 3. The key structural attribute is the presence of the siliphilic group (green) and of the hydrophilic group (red).

Figure 4
Orientation of PEG-8 Dimethicone



At the surface of water, the PEG-8 dimethicone will orientate itself at the lowest energy as Figure 4.

The surface tension will be between 23 and 20 dynes/cm^2 (dropping the water from 72 dynes/cm^2). While there are minor differences in the surface tension of various PEG-8 dimethicone compounds, the structure has a profound effect upon wetting and eye irritation, two critical parameters for personal care. Consider the products in Table 3; despite the major differences in molecular weights, the CMC and surface tension at CMC are almost identical (Table 4).

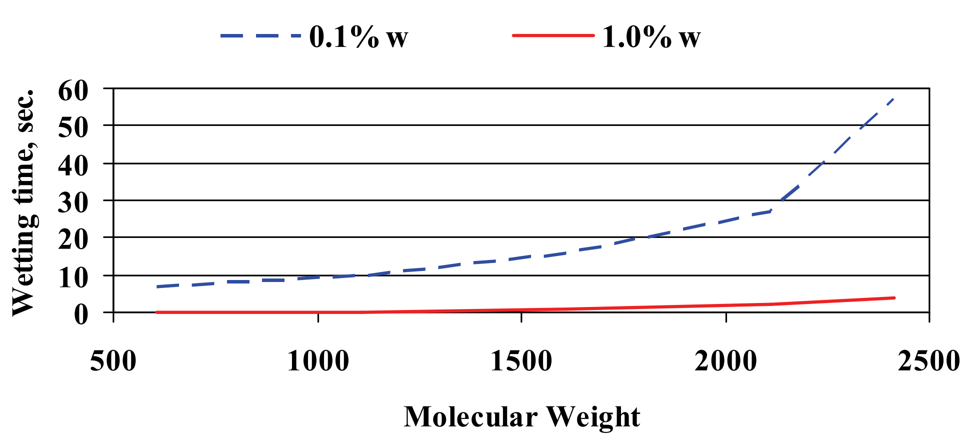
Table 3
PEG-8 Dimethicone

Product	Molecular Weight
A-008	633
A-208	855
B-208	1398
C-208	2105
D-208	2706
J-208	6334

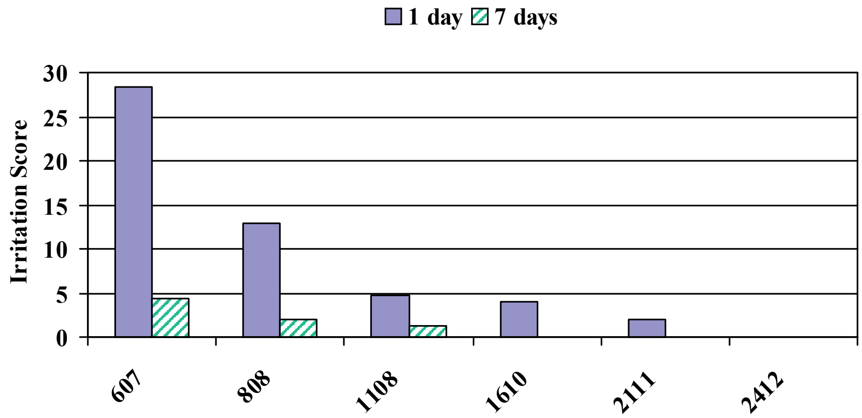
Table 4
PEG-8 Dimethicone Properties

Product	CMC mg/l	SurfaceTension@ CMC
A-008	20	20
A-208	20	20
B-208	20	20
C-208	23	22
D-208	23	22
J-208	23	23

Despite almost identical surface tensions, there are significant differences in wetting. Wetting is a critical often overlooked aspect of cosmetic formulation. If you are applying something to the hair, skin, a pigment or any other surface how that surface wets is critical to the usefulness of the formulation. Low concentration of silicone wetting agent (0.1 to 1.0 % by weight) needs to be added to make the product function correctly. Figure 5 details the Draves wetting time as a function of concentration. Draves wetting time is the time it takes to sink a cotton skein[3].



Eye Irritation is also quite different (Figure 6)[3]. Despite many similarities in basic properties (CMC and Surface tension at CMC) there exists very different functionality in terms of wetting, and irritation. These properties are critical to efficient formulation.



The effect of concentration on surface tension was also studied, with several different systems. Table 5 shows the results.

Concentration Effects on Reduction of Surface Tension of Oils with Silicone

Blends of several ratios of different materials were evaluated for surface tension reduction. The results are shown in tables 5 and 6.

Table 5	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

Table 6	Isopropanol (% Weight)	PEG-8 Dimethicone (% Weight)	Surface Tension (Dynes/cm^2)
Example 4.1	100%	0%	21.7
Example 4.2	75%	25%	20.8
Example 4.3	50%	50%	20.5
Example 4.4	25%	75%	20.5
Example 4.5	0%	100 %	20.5

Why is the cosmetic formulator interested in surface tension? Surface tension effects spreadbility and cushion. The addition of the proper silicone to a high viscosity ester can improve spreadbility without effecting the play time (i.e. the time it takes to spread out). A different silicone can improve spreadbility and reduce playtime. The result is an ability to alter aesthetics in personal care products by adding low concentrations of silicones. This allows one to significantly alter the cosmetic feel of a product without dramatic alteration in the formulation!

The addition of the proper silicone can also improve wetting time and alter bubble structure.

Table 7

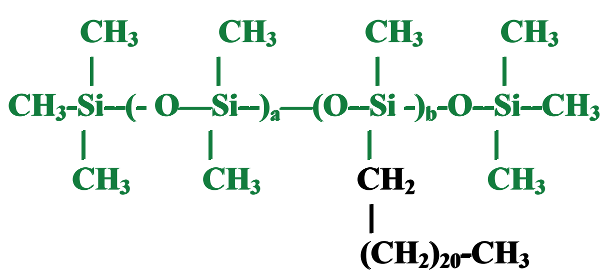
Effects of Added PEG-8 dimethicone upon Cocamido betaine

Table 7	Draves Wetting (seconds)	Ross Miles Foam (Initial)	Ross Miles Foam (5 minutes)
Example 7.1	9.6	175	150
Example 7.2	7.5	170	145
Example 7.3	4.8	155	135
Example 7.4	3.6	145	115
Example 7.5	2.0	135	110

Siliphilic / Oleophilic Amphilic Compounds

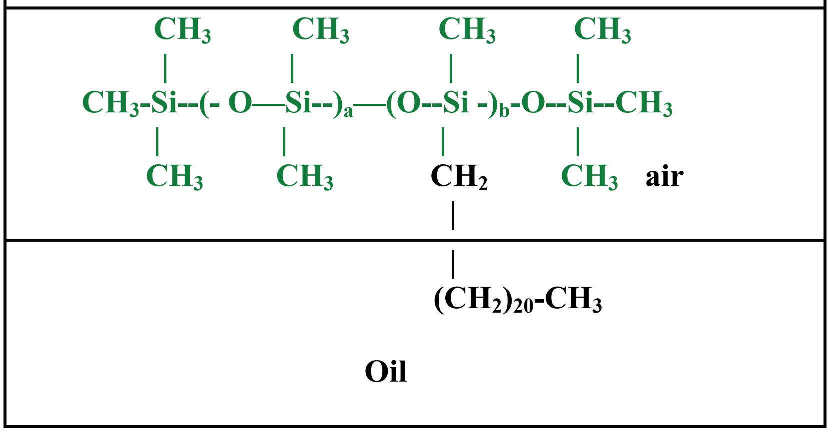
The second class of compounds to consider is alkyl dimethicones. These compounds feature a silicone loving group and an oil loving group. The addition of an oil soluble silicone to an oil results in exactly the same situation shown above, namely reduction of surface tension and micelle formation. Most oils have a surface tension around 32 dnes/cm^2 addition of alkyl silicone can drop them into the 20-25 dyne/cm^2 range. The structure is shown in Figure 7. The key structural attribute is the presence of the siliphilic group (green) and of the oleophilic group (black).

Figure 7
Behenyl Dimethicone



At the surface of an oil like sweet almond oil, the behenyl dimethicone will orientate itself at the lowest energy. This is shown in Figure 8.

Figure 8
Orientation of Behenyl Dimethicone in Oil



Surface tensions reduction has number of important effects. The lowering of surface tension allows for improved spreadbility of the oil. Using different alkyl silicone compounds can dramatically alter the aesthetics of the oil on the skin and in an emulsion.

Surface Tension Reduction

A number of solvents can have their surface tension altered by addition of the proper silicones. Table 8 shows the effect[4]. The ability to lower surface tension of many materials that we commonly find in cosmetic products, allows for the improvement of spreadbility, alters skin feel and provides new cosmetic properties to existing formulations. This approach is useful for both oil phases and polar phases. In fact the addition of 0.5% of a silicone amphilic polymer to a formulation can result in very different consumer perceptions. This approach allows the formulator to make small modifications to existing formulations to meet new product profiles.

Table 8
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

Table 8 shows that it is perfectly proper to consider the question, what is the CMC of behenyl dimethicone in toluene?

Table 9 shows the effect of adding cetyl dimethicone to soybean oil.

Table 9	Soybean oil (% Weight)	Cetyl Dimethicone (% Weight)	Surface Tension (Dynes/cm^2)
Example 9.1	100%	0%	31.4
Example 9.2	75%	25%	25.5
Example 9.3	50%	50%	24.8
Example 9.4	25%	75%	24.1
Example 9.5	0%	100 %	23.6

Table 10 shows the effect of adding cetyl dimethicone to mineral oil.

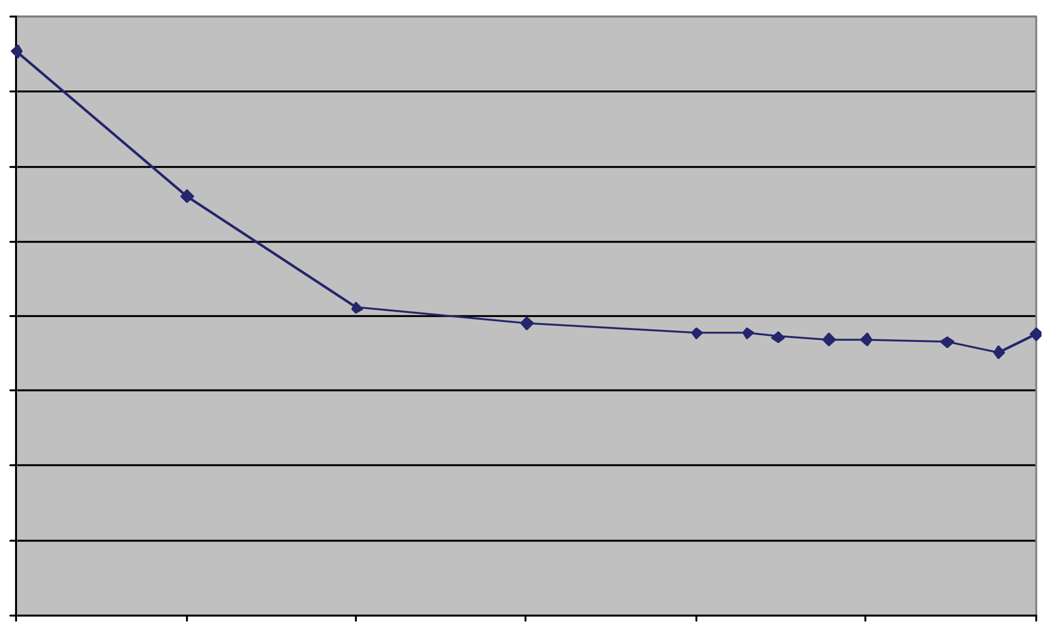
Table 10	Mineral oil (% Weight)	Cetyl Dimethicone (% Weight)	Surface Tension (Dynes/cm^2)
Example 10.1	100%	0%	28.3
Example 10.2	75%	25%	26.1
Example 10.3	50%	50%	25.1
Example 10.4	25%	75%	24.5
Example 3.5	0%	100 %	23.6

Quantifying Surface Tension Reduction

Graph 1 presented below is a plot of surface tension vs. concentration. What is observed is that at low concentrations, addition of more surfactant lowers surface tension by increasing the concentration of surfactant. As the concentration reaches a critical level, the ability to lower surface tension further is impossible. Addition of the more surfactant does not lower surface tension. This concentration is the critical micelle concentration.

Graph 1

CMC graph for higher molecular weight PEG-8-dimethicone



Mixed Systems

Evaluating the effect of concentration of surfactant upon surface tension when more than one type of surfactant is present is important to the formulator since these so-called mixed systems are what is present in a formulation.

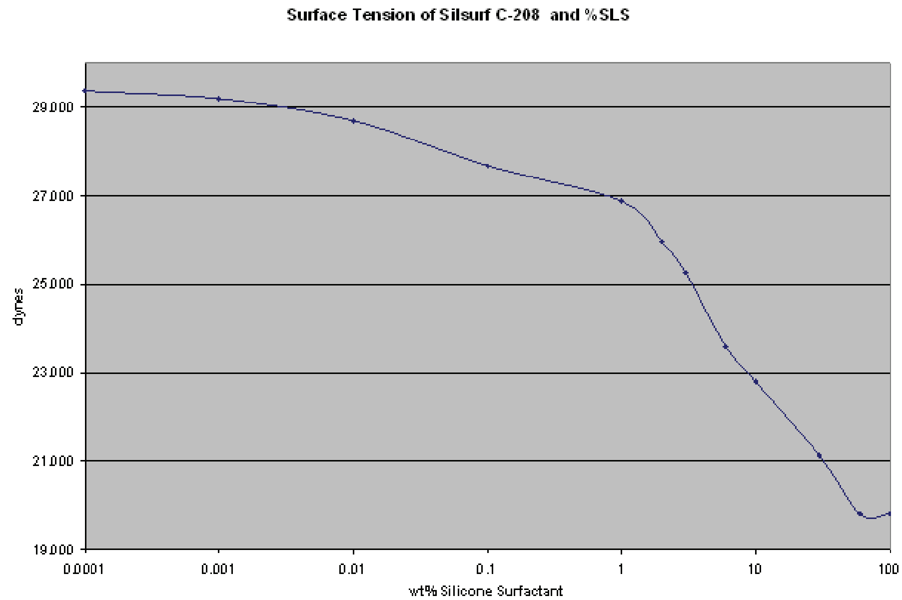
In order to quantify the effect of adding silicone surfactant to fatty surfactant to fatty surfactant the following procedure was followed:

To a 1% solution of the fatty surfactant was added different amounts of silicone surfactant and the surface tension was measured and plotted. This approach allows one to study the effect of adding silicone surfactant to fatty surfactant to observe interactions and synergies. Since all cosmetic formulations contain more than water and silicone surfactant, the interaction of the silicone with the formulation is critical to formulation.

A typical graph of surface tension of a 1% solution of SLS (sodium lauryl sulfate) with differing amounts of silicone surfactant added is seen in Graph 2.

Graph 2

Graph 2



While not having the clear break point observed with a pure surfactant at the critical micelle concentration, the above graph does resemble a plot of surface tension for a surfactant.

Since a clear critical micelle concentration cannot be determined by the above graph, we suggest that for mixed systems the RF_{50} be evaluated in order to compare effectiveness of surface tension reduction. The RF_{50} is the ***R**eduction **F**actor 50%* for each silicone surfactant in each system. The definition is as follows:

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.

The lower the RF50 the better able is the silicone surfactant to compete with the fatty surfactant for surface and the more efficient the silicone surfactant will be. This technique allows one to design molecules that will be optimized for a particular formulation. Not only can surfactant systems be evaluated but also complex formulations can be evaluated, by simply defining the Fatty Surfactant's Surface tension as the formulation's initial surface tension. Not only surface tension, but also foam and the like can be tested and optimized by evaluating foam as the property rather than surface tension.

Table 11 shows the RF_{50} values for specific combinations.

Table 11

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

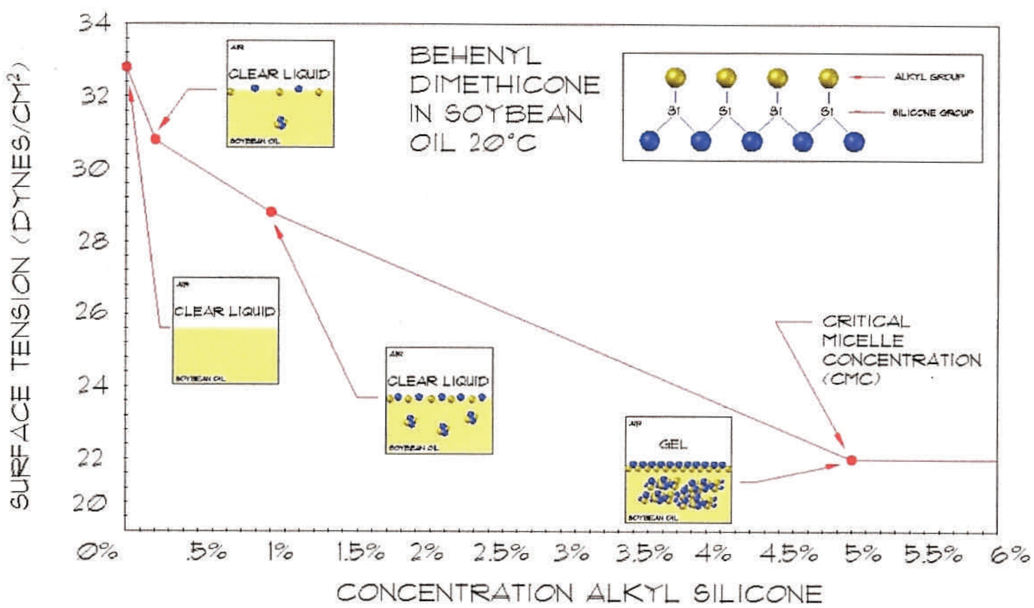
The so-called RF_{50} value is a measure of the effectiveness in lowering surface tension in mixed systems. The lower the RF50 value the lower the concentration needed to reach a 50% reduction in surface tension between the two surfactants in a mixed system.

Gellification and Siliphilication

Because amphilic materials go to the surface then for micelles as shown below, if properly selected, they can make oils feel like silicone (siliphilication) and / or make oils gel (gellification). Both properties are of interest to the formulator.

Behenyl Dimethicone in Soybean Oil

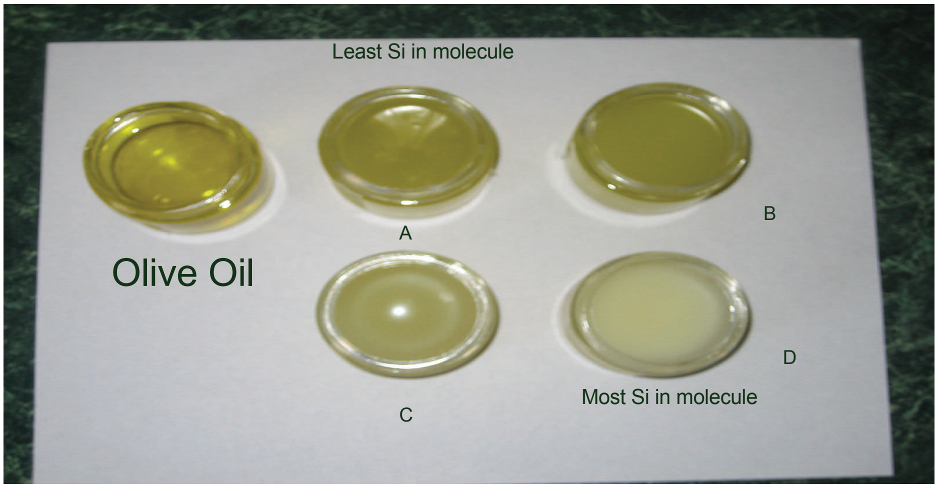
Figure 9



The ability to gel oils and lower surface tension to allow oils to feel like silicone allows for the formulator to both make their products more green, lower costs and maintain the desired aesthetics. Figure 10 shows the effect of adding different Behenyl dimethicone compounds having differing compositions. Each of the compounds provide gels, but those silicone compounds that have the highest concentration of alkyl groups are the most clear, while those with the highest concentration are the most opaque. This patent pending technology allows the formulator tremendous latitude in feel, rheology and aesthetics.

Behenyl Dimethicone

Gellation of Olive Oil (5% Additive)



Conclusions

1. Many of the most interesting properties that are founding silicone compounds are found in those molecules that are amphilic.

2. The salient property is surface tension lowering and can include wetting, emulsification, foaming, and gellation, depending upon the specific structure.

3. The specific structure of the compound determines the properties a silicone amphile will have.

4. Since silicone polymers are almost never the sole ingredients in the formulation, it is critically important to consider the interaction of the various components in formulations.

5.The effect of a silicone surfactant in formulation is structure dependant and since INCI names do nothing to relate structure, far more details are needed to construct meaningful models.

6.**Silicone compounds while not generally thought of as green materials by themselves, when a properly chosen silicone and used at a low concentration in a formulation provide the consumer WOW effect and simultaneously a greener formulation is created.**

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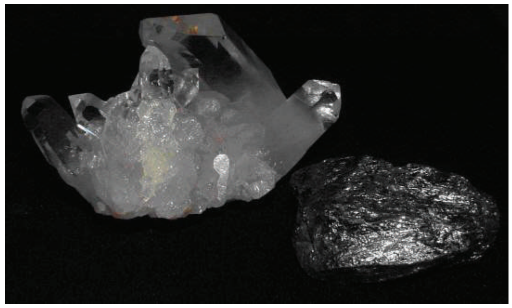

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