Silicones versatile additives to formulations

ABSTRACT

Today's formulations contain a large number of silicone compounds. These versatile polymers are found in almost every market segment and in almost every formulation type within a category. This is due to the unique properties silicones confer on formulations. These attributes include surface tension reduction, emulsification, wetting, film formation, foaming, and surface modification.

Silicone polymers are a diverse class of compound that encompass traditional silicone fluids, water soluble polymers, oil soluble polymers, fluoro soluble polymers and polymers that have a range of solubility. They encompass a variety of forms from low viscosity fluids, to rubbery elastomers to resins. The choice of silicone is truly staggering. Despite the diversity, the reason to select silicone based chemistry is the fact that silicone products can be engineered to give properties unachievable using less expensive alternatives. These include: surface tension reduction, emulsification, wetting, film formation, and foaming.

Figure 1. Silicone Compounds are ultimately derived from Quartz (upper left), which is converted into silicon metal (lower right). Picture© 2005 Thomas O'Lenick, used with permission

Silicone compounds are made from silicon metal by a process developed by Rochow and his associates in the 1940's. The precursors to these versatile materials is quartz (SiO_2) a mineral making up 25 percent of the earth's crust. This common mineral is convertd into Silicone metal (Si), which is then converted via the Rochow process into chlorosilanes. Chlorosilanes are hydrolysed then converted into silicone deravitives. The transformation of quartz to silicone metal is visually one of the most dramatic steps in the process.

SURFACE TENSION

The surface tension that one sees at the interface is related to what functional groups dominate the structure. Water has a surface tension of around 72 dymes/cm^2. Fatty surfactants and in fact fatty compounds have a surface tension in the area of 30 - 35 dynes/cm^2. This is due to the abundance of methylene groups ($-CH_2-$) in the molecule. Silicone materials bristle with methyl groups ($-CH_3$), and as a result have a surface tension in the range of 20 -25 dynes/cm^2. If an even lower surface tension is required one must consider fluoro compounds. They have $-CF_2-$ groups and have a surface tension in the teens.

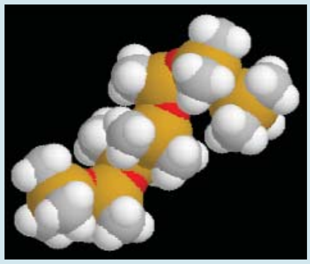


Figure 2. Silicone compounds bristle with methyl (CH_3)groups (shown below in white). This accounts for their surface tension

When surface tension is measured using pure materials, it is clear that depending upon the material examined surface tension is quite variable. Table 1 shows a typical range of surface tension values. If you want to cause the pure liquid to foam, wet, emulsify, you must lower the surface tension. Materials with a surface tension below 35 dynes/cm^2 will typically use a silicone surfactant. To perform these functions in liquids with surface tension values below 20 dynes/cm^2 a fluoro surfactant will be required. Table 1 shows surface tension values for pure materials.

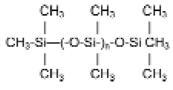
Product	Surface Tension (dynes/cm)
Mercury	**472.0**
Water	**72.6**
Isoparaffin (C12-C14)	**53.0**
Squalane	**46.2**
Soap Solution (1%)	**38.8**
Mineral oil	**33.1**
Dimethicone (20cs)	**26.6**
Acetone	**23.7**
Ethyl Alcohol	**22.2**
Cyclomethicone (D4)	**20.6**
Diethyl ether	**17.0**

Source: De Polo, K.F., *A Short Textbook of Cosmetology*, Verlag fur Chemische Indusrtie, 1998

Table 1. Surface Tension (Pure Materials)

Silicone homopolymers - dimethicone

Dimethicone compounds conform to the following structure:



Silicone fluids, also called silicone oils, or simple silicone are sold by their viscosity and range from 0.65 cst to 1,000,000 cst. If the product is not made by blending two different viscosity fluids the viscosity is related to molecular weight. The viscosity allows for an approximate calculation of the value of "n". The data is shown below in Table 2. The differences in viscosity, feel and cushion going from a low viscosity to a high viscosity silicone fluid is an important effect. Silicone homopolymers has a surface tension of between 20 and 25 dynes/cm^2.

Viscosity 25 C (Centistokes)	Approximate Molecular Weight	Approximate "n" Value	Average Construction
5	800	9	MD_9M
50	3,780	53	$MD_{53}M$
100	6,000	85	$MD_{85}M$
200	9,430	127	$MD_{127}M$
350	13,650	185	$MD_{185}M$
500	17,350	230	$MD_{230}M$
1,000	28,000	375	$MD_{375}M$
10,000	67,700	910	$MD_{910}M$
60,000	116,500	1,570	$MD_{1570}M$
100,000	139,050	1,875	$MD_{1875}M$

Table 2. Silicone Fluids

Mixed System Surface Tension

Most systems encountered by formulation chemists are not pure liquids. They are compositions (mixtures of materials). Consequently, to foam, emulsify or wet formulations that are composed of various components, the ability to lower surface tension with minimal concentration of surfactant is critical.

Surface tension reduction requires molecules that are surface active. Solutions of molecules that exhibit surface activity are fundamentally different than solutions of non-surface active agents. NaCl (salt) is an example of a non-surface active agent and Sodium Lauryl Sulfate (SLS) an example of a surface active agent. Both are water soluble, but what they do in solution is significantly different. The term solution relates to the clarity of a liquid and consequently the size of any particle present. Consider a 0.5 percent 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 amphillic). 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 which 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 material are the various oil phases (including mineral oil, squalene, esters, and many others). These oil phases have surface tensions values of around 32 dynes/cm2. This means if we can find a material soluble in the oil, amphillic 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 amphillic 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. Amphillic molecules because they are active at surfaces are in motion in the dynamic system created by spreading out. Figure 3 shows the complicated process.

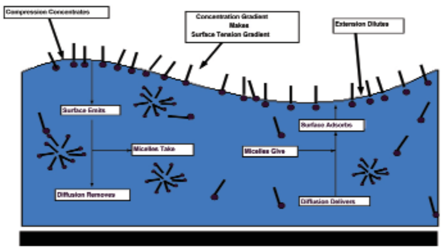


Figure 3. DynamicSurfaceTenison - Amphilic Silicone Molecules

ALTERED SOLUBILITY OF SILICONES - ORGANOFUNCTIONAL SILICONES

Silicone compounds are not soluble in oil or in water. As such they are a third phase. In order to capitalize upon the ability of silicone containing polymers to be surface active, the silicone molecule is modified to become soluble in a variety of different materials. This modification is made possible by a process called hydrosilylation (Figure 4). This process allows for the reaction of a vinyl compound (normally alpha), with silanic hydrogen containing silicone compounds (Si-H). The resulting compounds, depending upon the nature of the "R" group have improved solubility in many solvents. The nature of the reactant determines solubility (Figure 5).

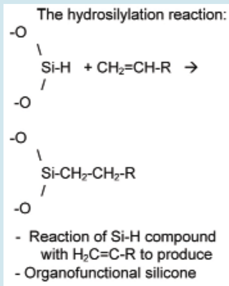


Figure 4. Hydrosilylation Reaction

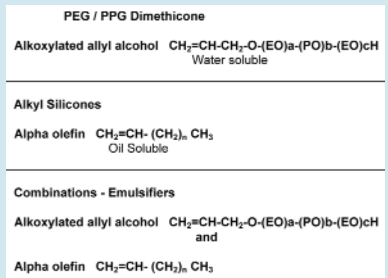


Figure 5. Hydrosilylation Reagents

Water Wetting - PEG-8 Dimethicone Water Soluble Silicone

While there is little difference in the surface tesnsion of the 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 moleculae weights, the CMC and surface tension at CMC are almost identical (Table 4).

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

Table 3. PEG-8 Dimethicone

Product	CMCmg/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

Table 4. PEG-8 Dimethicone Properties

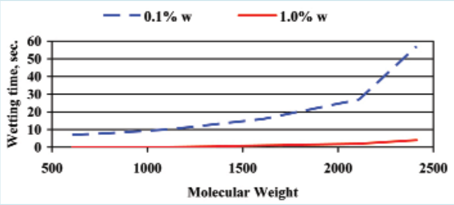


Figure 6. Draves wetting time

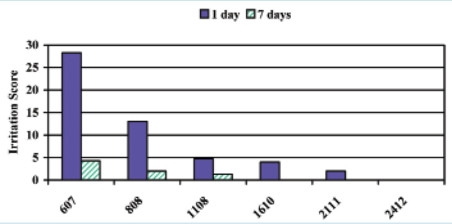


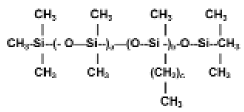
Figure 7. Eye Irritation

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 percent by weight) needs to be added to make the product function correctly. Figure 6 details the Draves wetting time as a function of concentration. Draves wetting time is the time it takes to sink a cotton skein.

Eye Irritation is also quite different (Figure 7). Despite many similarities in basic properties (CMC and Surface tension at CMC) there are very different functionality in terms of wetting, and irritation. These properties are critical to efficient formulation.

Oil Wetting -Alkyl Dimethicone

Alkyl dimethicone compounds conform to the following structure:



They have an oil soluble group on a silicone backbone. As such they are amphillic and surface active.
They lower the surface tension of oils to around 22 dynes/cm^2. Surface tensions reduction has number of important effects. The lowering of surface tension allows for improved spreadability of the oil. The aesthetics of the oil on the skin and in an emulsion can be dramatically altered by using different alkyl silicone compounds.

Surface Tension Reduction

A number of solvents can have their surface tension altered by addition of the proper silicones.
Table 5 shows the effect. The ability to lower surface tension of many materials that we commonly find in cosmetic products, allows for the improvement of spredability, 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 percent of a silicone amphyllic 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.

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 5. Reduction of Surface Tension of Oils with Silicone Derivatives

The above table shows that it is perfectly legimate to consider the question, what is the CMC of an cetyl dimethicone in toluene, or the CMC of PEG-8 dimethicone in isopropanol.

Emulsification

Alkyl Dimethicone Copolyol as Emulsifiers

Illustrative of the importance of structure is a series of emulsifiers that are designed to be effective in preparing both water continuous and water discontinuous types of emulsions. Specifically, alkyl dimethicone copolyol polymers conforming to the structure in figure 8.

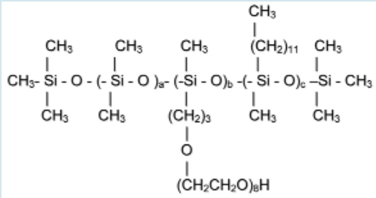


Figure 8. Alkyl Dimethicone Copolyol

The compounds all have the same construction, but differ in the number of alkyl and water soluble groups. That is the value of "b" and "c" is different but b + c is constant. This allows for a study of the effects of functionalization on a standard construction.
The series of products have been designed to have different solubility in a variety of solvents (see Table 4). Additionally, the amount of alkyl in the molecule is reported using the 3D HLB (1, 2)[1,2] system, since it is much more descriptive that the standard HLB. The composition of the products is disclosed in Table 5.
An important concept to understand is that silicone polymers, like all polymers, are made up of oligomers. That is there is not one molecular structure, but a range of structures. Unlike simple compounds like NaCl that have a very clear molecular weight arrives at by simply adding the molecular weight of the Na and Cl, polymers have a range of molecular weights. The values of "a", "b" and "c" are ranges. Typical values aree shown in figure 9.

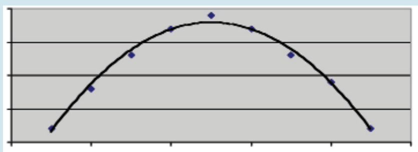


Figure 9. Oligomer Distribution a=5

The classical bell shaped curve for distribution reveals that the range of a value is from 1 to 9 with a maximum at 5. One must be very careful when using materials with very low values. The lowest value obtainable for a subscript is zero, since there simply is no physical relality to a negative subscript. The distribution is shown in figure 10. The difficulty with this type of distribution is there is a considerable amount of material in which "a" is 0. This can cause major problems with separation of the product, since those materials with zero subscript may well not be soluble in the rest of the composition and form a distinct layer upon exposure to cold. Care must be exercised not to use emusifiers that are not homogeneous.

Emulsifier Composition Table 4	%		3D HLB	
Product	EO	Alkyl	x	y
J208-212	48	6	9.6	1.2
J208-412	39	13	7.8	2.6
J208-612	28	22	5.6	4.4
J208-812	16	32	3.2	6.4

Figure 10a. Oligomer Distribution a=2

Solubility Table 5	Water		IPA		Mineral spirits		Mineral oil		Aromatic Solvent		Cyclic Silicone		Silicone Fluid	
Product	1 %	10 %	1 %	10 %	1 %	10 %	1 %	10 %	1 %	10 %	1 %	10 %	1 %	10 %
J208-212	S	S	S	S	I	I	D	D	S	S	D	D	D	D
J208-412	D	D	S	S	D	D	D	D	S	S	D	D	D	D
J208-612	I	I	S	S	S	S	S	D	S	S	D	D	D	D
J208-812	I	I	S	S	S	S	S	S	S	S	S	S	D	D

S is soluble I is insoluble D is dispersible

Figure 10b.

Petrolatum Emulsions (3)

Petrolatum emulsions are of interest in many areas. They have outstanding feel on the skin.

Effects of Varying Ratios of Petrolatum to Oil

The most effective emulsifier in the series studied for petrolatum was J208-612. It appears that it can handle a wide range of petrolatum / water ratios. By varying the ratio of petrolatum to water products with very different properties emerge.

Material	PET 905-A	PET 0905-B	PET 905-C
	% wt	% wt	% wt
Polysurf 67 CS	0.50	0.75	0.25
Tetrasodium EDTA Versene 100	0.40	0.40	0.40
Water	48.90	70.65	25.00
Propylene Glycol	2.00	2.00	
Silsurf J208-612	4.00	4.00	4.00
Petrolatum	44.00	22.00	70.15
Propylparaben	0.20	0.20	0.20
	100.00	100.00	100.00

RESULTS

A is a very heavy lotion, with an outstanding skin feel.
B is a thin lotion with a cooling effect on the skin.
C is a heavy cream with the texture and feel of petrolatum.

The technology can be expanded to cover many other oils including the iso-alkanes and esters.

Effects of Varying Emulsifier

Formula A repeated, only this time to investigate the effect of the other Silsurf surfactants.

Material	PET 905-A	PET 905-D	PET 905-E	PET 905-F
Polysurf 67 CS	0.50	0.50	0.50	0.50
Tetrasodium EDTA Versene 100	0.40	0.40	0.40	0.40
Water	48.90	48.90	48.90	48.90
Propylene Glycol	2.00	2.00	2.00	2.00
Silsurf J208-612	4.00			
Silsurf J208-412		4.00		
Silsurf J208-212			4.00	
Silsurf J208-812				4.00
Petrolatum	44.00	44.00	44.00	44.00
Propylparaben	0.20	0.20	0.20	0.20
	100.00	100.00	100.00	100.00

The emulsions made with Silsurf J208-612, Silsurf J208-412 and Silsurf J208-212 all gave good emulsions. The Silsurf J208-812 formed a very grainy looking product with visible flecks of petrolatum. Consequently, it appears that the higher HLB material is not suitable to forming good emulsions with petrolatum. Since the water and petrolatum ration are close to equal the nature of the emulsion (invert or regular) is effected by choice of emulsifier.

Clearly, the product made with J208-612 is an invert emulsion, and the product made with J208-212 is a regular emulsion. The product made with the J208-412 has some properties of both.

CONCLUSION

Silicone compounds that are organofunctional are amphillic surface active materials that offer the formulator opportunities to provide improved properties to formulations. The proper selection will include such variables as solubility, surface tension reduction and desired effect. The formulator is encouraged to look at the physical chemistry of the silicone compound being added to insure that the proper material is chosen to get the desired effect.

REFERENCES AND NOTES

1. O'Lenick, Anthony J, Parkinson, Jeff K., Cosmetics and Toiletries, Vol. 111 No. 10, October 1996 p. 37.
2. O'Lenick, Anthony J, Parkinson, Jeff K., Cosmetics and Toiletries, Vol. 112 No. 11, October 1997 p. 59.
3. www.siltechpersonalcare.com/pdfs/brochures/Petrolatum%20Emulsions.pdf

ANTHONY J. O'LENICK[1]*, KEVIN A. O'LENICK[2]

*Corresponding author

1. Siltech LLC
Dacula, Ga 30019, USA

2. SurfaTech Corporation
Dacula, Ga 30019, USA