

Kevin O'Lenick – SurfaTech Corporation, United States
 Tony O'Lenick – Siltech LLC, United States

SILICONES

Organo-functional silicones – choices for formulations

A question asked by every formulator is: "How do I get the highly desirable properties of silicone in my formulation when formulating with silicone can provide its own set of problems?"

In short this is what we define as "The Silicone Conundrum", an intricate and difficult problem. The selection of the proper silicone for a formulation requires the formulator to understand why the silicone is in the formula (for wetting, conditioning, emulsification, skin feel, film formation...) and which silicone provides that property most efficiently in the formula (with all the other ingredients). First and foremost, one must understand the chemistry of silicone polymers and the effect of structure on function.

Silicone compounds have been known since the 1860s, but it was not until the pioneering of Rochow in the 1940s that this important class of compounds achieved commercial viability. This was due in large part to the development of a process which was called the direct process, and now bears Rochow's name. Silicone chemistry provides the polymer chemist with the ability to construct precise

molecules having desirable nanotechnology properties.

Silicone polymers are derived from SiO_2 , a naturally occurring mineral that makes up 25% of the earth's crust. SiO_2 is converted to Si at high temperature in the presence of a carbon source. Figure 1 shows the two materials.

The resulting Si metal is then crushed and reacted in a fluidised bed reactor to produce chlorosilanes, using the Rochow process. The reaction is shown in Figure 2.

The preparation of chlorosilanes is practised by a small number of manufacturers who grind up silicon metal and react it in a tubular reactor with methyl chloride. The manufacturers of chlorosilanes are affectionately referred to as "crushers".

Chlorosilanes are hydrolysed in water to make intermediates used to make silicone derivatives. The reaction product of water and chlorosilanes is referred to as hydrolysate.

The chlorosilanes are placed into water, HCl stripped off and after distillation and a variety of clean-up processes, a series of silicone building blocks emerge.



Figure 1: The transformation of quartz to silicon metal is the first step in making silicone compounds. Quartz is on the upper left, silicon on the bottom right.

Chlorosilane synthesis

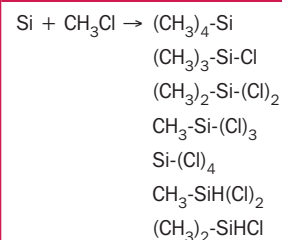


Figure 2.

Unit operations to make silicones

- Construction
- Functionalisation
- Derivatisation

Figure 3.

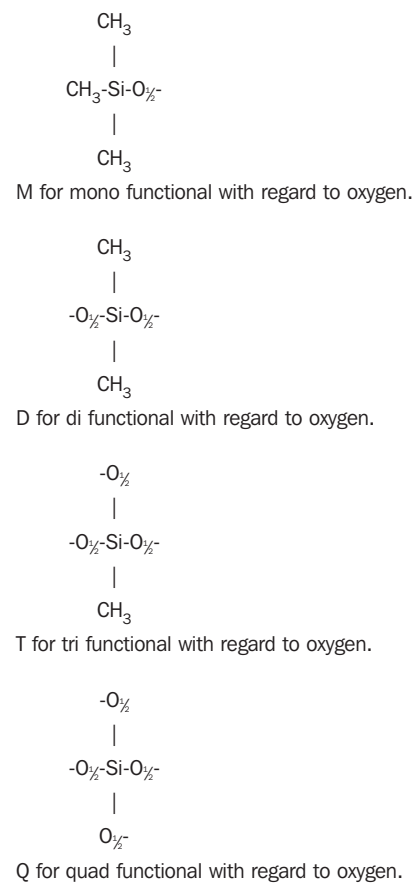


Figure 4.

SILICONES

Figure 5.

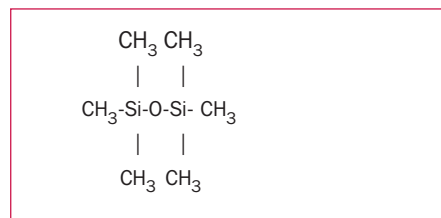
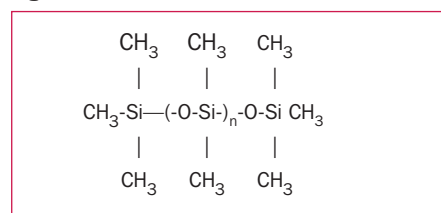


Figure 6.



The most important of these include hexamethyldisiloxane (MM), cyclomethicone (D4) and silanic hydrogen compound. That is just the start of the story.

These materials are combined in a variety of ways to make silicone polymers of interest. The unit operations are shown in Figure 3.

Construction

Highly specialised activities often create a jargon or language that facilitates improved communication among practitioners, and keeps people outside the field from feeling comfortable in these specialised activities. Chemistry, law and government are but a few examples. Silicone chemistry is also an example. The language makes use of the letters M, D, T and Q to specify structural groups placed into a molecule by its construction. The construction step is the process in which the length of the polymer chain, its branching and its positions for insertion of organic groups is determined. The shorthand for construction is shown in Figure 4.

Clearly, there is no real $\frac{1}{2}\text{O}$. This nomenclature is used so that when two or more groups are linked together a single oxygen exists between them. For example MM (hexamethyldisiloxane) a key material is often referred to as 0.65 viscosity silicone fluid or hexamethyl disiloxane. Its structure is shown in Figure 5.

M units are chain terminators since they are mono-functional.

Silicone fluids – dimethicone

To show the importance of construction, one needs only look at silicone fluids (dimethicone). Reaction of M and D will result in silicone fluids – an example is shown in Figure 6.

D units are linear chain extenders. They provide larger and larger molecules having higher and higher viscosity. The correct name for this molecule is MD80M

Silicone fluids, also called silicone oils,

Figure 7.

Silicone fluids.			
Viscosity 25 °C (Centistokes)	Approximate molecular weight	Approximate "n" value	Average construction
5	800	9	MD ₉ M
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

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 in Figure 7. The differences in viscosity, feel and cushion going from a low viscosity to a high viscosity silicone fluid is an important effect. This effect is strictly a function of construction. Silicone fluids are insoluble in oil and water.

Figure 8.

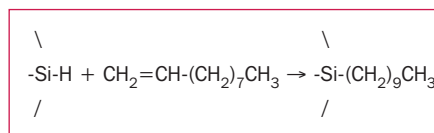
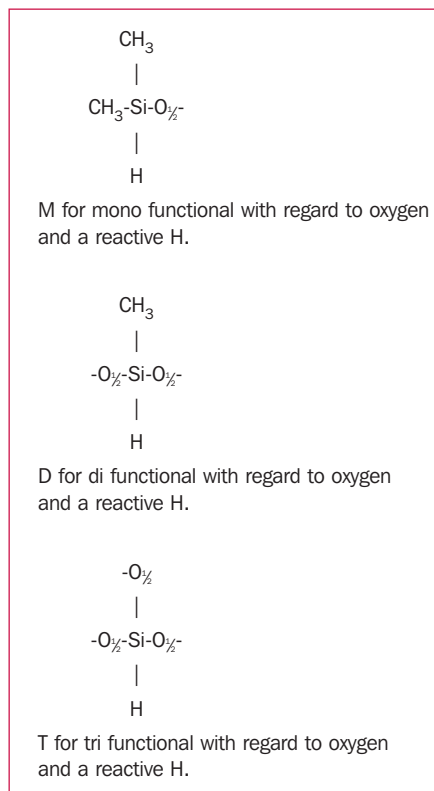


Figure 9.



Blending silicone of different viscosity results in products with very different cosmetic aesthetics. The high viscosity fluid (generally 60,000 or above) is generally sticky when applied to skin. Addition of low viscosity silicone (generally 100 cps of below), provides wetting and spreading on the skin.

Functionalisation

Up to now we have only considered silicone homo-polymers. This class is best understood and an important class of compounds.

It would indeed be a sad situation if the organo-functional materials were not available, or if the formulation chemist was not made aware of the advantageous of such materials.

The preparation of a silanic hydrogen containing polymer by the construction process does not alter solubility. The silanic hydrogen pre-polymer assumes its altered solubility only after the functionalisation reaction is run. For this reason silanic hydrogen containing polymers are considered precursors to organo-functional products. A single silanic hydrogen polymer can give rise to an entire family of analogues depending on which functional group is placed onto the backbone in the functionalisation reaction.

In order to make these products more easily formulated, organo-functional dimethicone compounds have been developed. These include dimethicone compounds with improved oil solubility called alkyl dimethicone compounds; and dimethicone compounds with improved water solubility, called PEG/PPG dimethicone. There is also a series of compounds in which surfactant groups are grafted onto the backbone to improve virtually all surfactant properties including detergency, conditioning, wetting, and emulsification. This ability to provide silicone products with improved applicability in personal care products not only opens

the possibility of many high performance products, but also can be a source of frustration to many formulators who have not been given the necessary structure/function relationships to make intelligent choices in picking products. We refer to properly selected silicone compounds as "formulator friendly™". Often the formulator is left to use products recommended by suppliers, rather than to be a participant in choosing the optimised product for an application. The key to avoid this situation is to learn the rules of structure/function related to silicones and apply them to new products, resulting in the most cost-effective products possible. The reaction used to place organo-functionality into silicone compounds is called hydrosilylation. This process is used in the construction part of silicone preparation. The key reaction is one in which a silanic hydrogen (Si-H) is reacted with a terminal double bond. This results in a stable Si-C bond (Fig. 8).

These materials are reacted with in the equilibration reaction to make reactive intermediates which are hydrosilylated in the functionalisation reaction. The vinyl containing groups that are reacted include

- Alpha olefin
 $\text{CH}_2=\text{CH}-(\text{CH}_2)_7\text{CH}_3$
- Ally alcohol alkoxyates
 $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}(\text{CH}_2\text{CH}_2\text{O})_8\text{H}$
- Fluoro vinyl compounds
 $\text{CH}_2=\text{CH}-\text{CH}_2(\text{CF}_2)\text{CF}_3$

The comparison of products within a class shows the importance of the construction.

Dimethicone copolyol compounds – improved water solubility

By adding water-loving portions of the molecule to silicone polymers at the proper ratio, one can produce products that are water soluble but still provide low surface tension. PEG-8 dimethicone is an example. The molecular weight of a PEG 8 dimethicone has a dramatic effect on performance of the compound as far as both wetting and irritation. Molecular weight is a measure of construction. A graph (Fig. 10) shows the molecular weight of molecules studied. Essentially, in the construction the compounds have the

Figure 12.

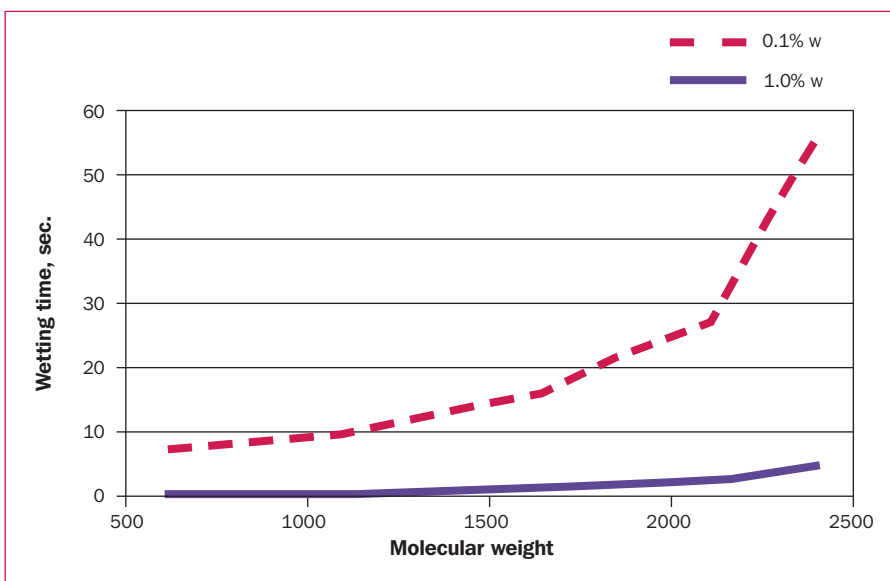
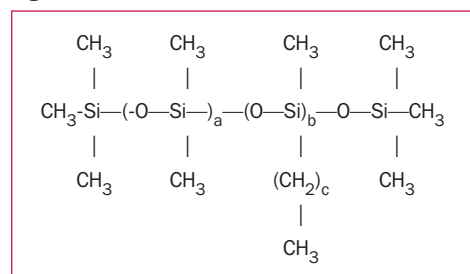


Figure 10: Draves wetting time.

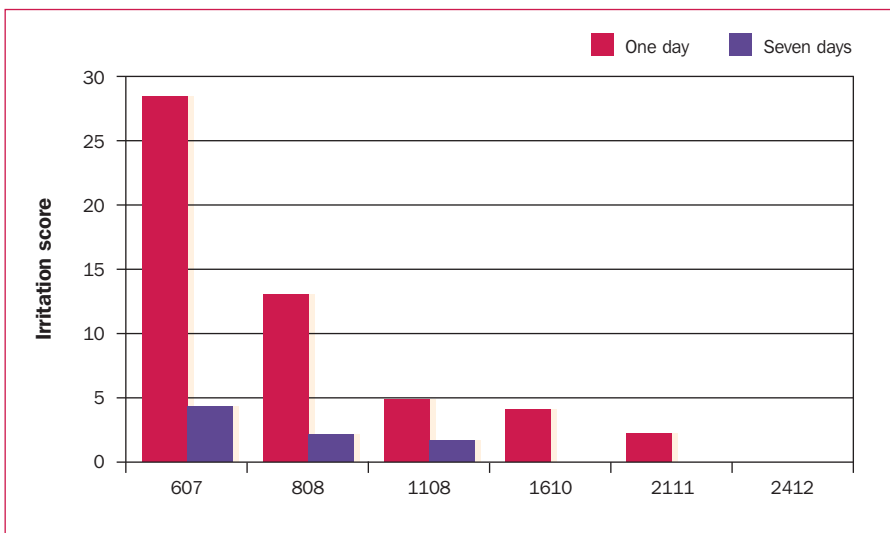


Figure 11: Eye irritation.

same ratio of D to D*, only higher numbers of both.

Wetting is a critical and 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 10 details the Draves wetting time as a function of concentration. Draves wetting time is the time it takes to sink a cotton skein or hair.

Construction also has a profound effect on eye irritation, essentially disappearing at a molecular weight of 2412, as seen in Figure 11.

As the molecular weight increases, silicone compounds with the identical amount of PEG, and exact same ratio of D to D*, transform from wetting

agents to emulsifiers, to conditioners to waterproofing agents. This transformation is a direct consequence of the lowest free energy conformation the molecule assumed in water. This is in turn related to the ease at which rotation occurs around the molecule backbone.

As the molecular weight increases, the wetting properties are lost and emulsification properties develop. As the molecular weight is increased further conditioning properties are seen. Formulators commonly use PEG-8 dimethicone of several different molecular weights to provide these different functions to formulations.

Alkyl dimethicone – improved oil solubility

The inclusion of alkyl groups in a silicone backbone increases the solubility in oil. Alkyl dimethicone compounds conform to the structure shown in Figure 12.

SILICONES

Figure 13: Solubility of alkyl dimethicone (10% weight).

Product	Water	Mineral oil	PG	D5	Silicone fluid	IPA
C-26 dimethicone	I	S	I	D	D	I
C-18 dimethicone	I	S	I	D	I	I

Legend I = insoluble D = dispersible S = soluble

Figure 14: Effect of cetyl dimethicone on soybean oil.

	Soybean oil (% weight)	Cetyl dimethicone (% weight)	Surface tension (Dynes/cm ²)
Example 1	100	0	31.4
Example 2	75	25	25.5
Example 3	50	50	24.8
Example 4	25	75	24.1
Example 5	0	100	23.6

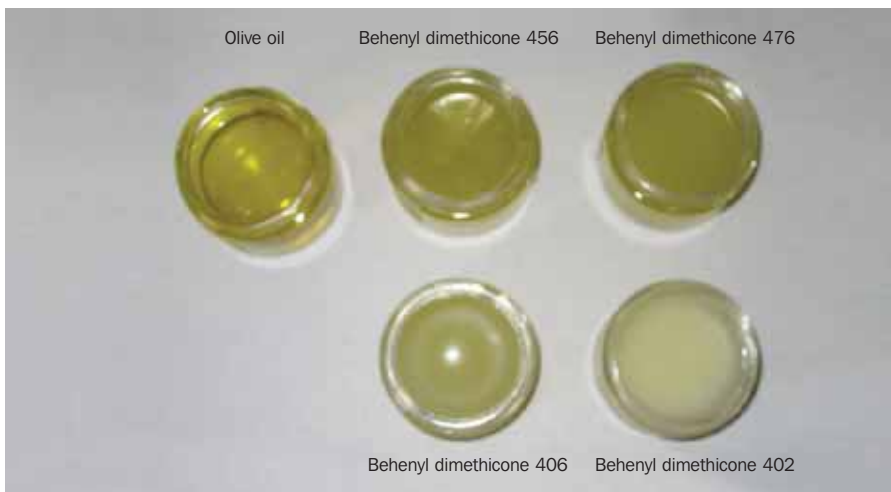


Figure 15: Olive oil thickened with 10% behenyl dimethicone.

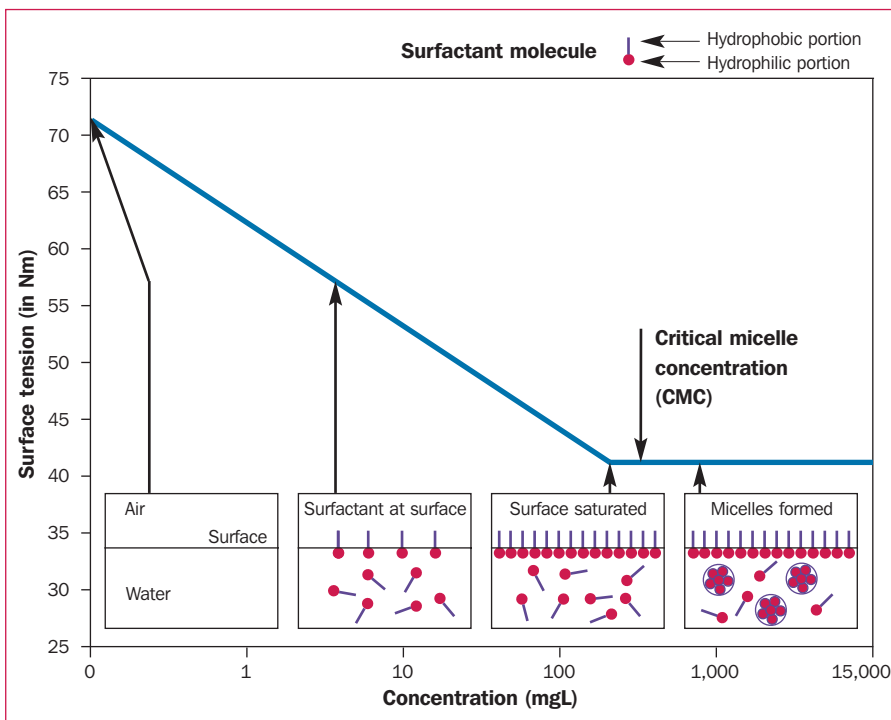


Figure 16: Surface chemistry of alkyl dimethicone in soybean oil (surfactant in water at 20 °C).

The type and size of alkyl group as well as the size of the siloxane group present in the molecule determines the functional properties such as solubility and melting point.

As seen in Figure 13, these organo-functional silicones have a very different solubility than that of either silicone fluids or dimethicone copolyol.

These materials are insoluble in alcohol and water. They are soluble in mineral oil and cosmetic esters.

The inclusion of an alkyl silicone into a formulation results in a silicone-like feel and by varying the alkyl group one can alter the cushion, play time and skin feel both in anhydrous and emulsion products.

Another very interesting use of alkyl silicones is to lower the surface tension of many oils. Typical is the effect of cetyl dimethicone (a liquid product) on soybean oil seen in Figure 14.

Finally, as the concentration of alkyl dimethicone increases, micelles form and the oil is gelled. In this case behenyl dimethicone is added to olive oil.

If the amount of silicone present in the molecule is low, the gel will be essentially clear (as seen in Figure 15 for 456 and 476). As the concentration of silicone is increased the clarity is lost (406 and 402), but the silicone feel increases.

The optimisation of the gel structure is the topic of several pending patent applications. The effect is seen in Figure 15. The formation of micelles that drives the gellation is seen in Figure 16.

Conclusions

Using two classes, dimethicone copolyol and alkyl dimethicone, we have shown an approach to optimise silicones to improve formulations. This approach works with, and is being used with, virtually all classes of silicone polymers. The ability to successfully solve "The Silicone Conundrum" is a challenge the formulator faces with every formulation. The ability to provide cost-effective, fully optimised silicones to help the formulator meet the challenge is something that the enlightened silicone producer can do. Together, formulators and silicone chemists can make silicones formulator-friendly by proper selection of polymers used in formulation. PC

References

- O'Lenick, Anthony J.; Parkinson, Jeff K. *Cosmetics and Toiletries*, Vol. 111 No. 10, October 1996 p. 37.
- O'Lenick, Anthony J.; Parkinson, Jeff K. *Cosmetics and Toiletries*, Vol. 112 No. 11, October 1997 p. 59.