Silicone Spectator

P.O. Box 715
Dacula, GA 30019
www.SiliconeSpectator.com

Silicone Spectator™ is electronic newsletters in the field of Silicone Chemistry, placed on the web four times a year. We welcome comments, articles and information on the content of this newsletter.

Supplemental Edition

Editors Note: This supplement to the **Silicone Spectator** is provided to allow our readers to be familiar with the terminology used for making silicone materials. The three steps,

Construction

Functionalization

and

Derivitization

are the key unit operations that make silicones function. They are a well guarded mystery in most commercial materials, but nonetheless are vital for understanding. We encourage the reader to become familiar with these and to ask about them when working with silicone polymers. Knowledge and understanding will make formulation more fruitful and less frustrating.

The following article is entitled:

Silicone Chemistry

and was contributed by:

Anthony J. O'Lenick, Jr.
Siltech LLC

Kevin A. O'Lenick
SurfaTech Corporation

Silicone Chemistry

In order to understand silicone polymers, and apply them effectively in personal care products the chemistry must be first understood. There is clearly a structure / function relationship[1,2].

Silicone compounds do not occur in nature, despite the fact that 25% of the earth's crust is composed of silicone dioxide. Silicone compounds have been known since the 1860, 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.

The first step is the transformation of quartz into silicon metal. This strange metamorphis takes a crystalline material to a shiny metallic material. A picture of this appears on page one of the Silicone Spectator ™ in the left column.

The next step is the now famous "Rochow process", based upon the reaction of silicon metal and methyl chloride to make a series of products called chlorosilanes. The reaction is as follows;

Rochow Process

$Si + CH_3Cl \rightarrow (CH_3)_4\text{-}Si$
$(CH_3)_3\text{-}Si\text{-}Cl$
$(CH_3)_2\text{-}Si\text{-}(Cl)_2$
$CH_3\text{-}Si\text{-}(Cl)_3$
$Si\text{-}(Cl)_4$
$CH_3\text{-}SiH(Cl)_2$
$(CH_3)_2\text{-}SiHCl$

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

From chlorosilanes, silicone materials are derived. The formulator must keep in mind that the performance of a given silicone is dictated by three equally important factors; (a) construction, (b) functionalization and (c) derivitization.

A. Construction

Highly specialized activities often create a jargon or language that makes facilitates improved more rapid communication to its practitioners, and keeps people outside the filed from feeling comfortable in these specialized 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, it's branching and the positions it contains for insertion of organic groups is determined.

Nomenclature

The shorthand for the construction is as follows;

M for mono functional with regard to oxygen

CH_3
|
$CH_3\text{-}Si\text{-}O_{1/2}$
|
CH_3

D for di functional with regard to oxygen

$$\begin{array}{c} CH_3 \\ | \\ O_{1/2}\text{-}Si\text{-}O_{1/2} \\ | \\ CH_3 \end{array}$$

T for tri functional with regard to oxygen

$$\begin{array}{c} O_{1/2} \\ | \\ O_{1/2}\text{-}Si\text{-}O_{1/2} \\ | \\ CH_3 \end{array}$$

Q for quad functional with regard to oxygen

$$\begin{array}{c} O_{1/2} \\ | \\ O_{1/2}\text{-}Si\text{-}O_{1/2} \\ | \\ CH_3 \end{array}$$

Clearly, there are no real ½ O. This nomenclature is used so that when two or more groups are linked together a single oxygen exists between them. For example MM is often referred to as 0.65 viscosity silicone fluid or hexamethyl disiloxane. Its structure is:

MM (0.65 Visc Silicone)

$$\begin{array}{ccc} & CH_3 & & CH_3 & \\ & | & & | & \\ CH_3\text{-} & Si & \text{---O-} & Si & \text{- }CH_3 \\ & | & & | & \\ & CH_3 & & CH_3 & \end{array}$$

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

Silicone fluids, elastomer and resins are the result of Construction and are devoid of Functionalization or Derivitization

Organo-functional Silicones

B. Functionalization

Up to now we have only considered silicone homo-polymers. This class is best understood and an important class of compounds, but only a small portion of the total products available to make products useful in the personal care market. 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 functionalization 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 analogs depending upon which functional group is placed onto the backbone in the functionalization reaction.

In order to make these products more easily formulated, organo-functional dimethicone compounds have been developed. These include dimethicone compounds with improved oil soluble called alkyl dimethicone compounds; dimethicone compounds with improved water solubility, called PEG/PPG dimethicone. There are 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 whom have not been given the necessary structure / function relationships to make intelligent choices in picking products. Often the formulator is left to use products recommended by suppliers, rather than to be a participant in choosing the optimized 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. This article will review those important relationships and propose compounds for the formulator to consider.

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.

$$\begin{array}{l} \backslash \\ -Si-H\ +\ CH_2=CH-(CH_2)_7CH_3 \rightarrow -Si-(CH_2)_9CH_3 \\ / \end{array}$$

The shorthand for the construction of reactive compound is as follows;

M* for mono functional with regard to oxygen and a reactive H.

$$\begin{array}{c} CH_3 \\ | \\ CH_3-Si-O_{1/2} \\ | \\ H \end{array}$$

D* for di functional with regard to oxygen and a reactive H.

$$\begin{array}{c} CH_3 \\ | \\ O_{1/2}-Si-O_{1/2} \\ | \\ H \end{array}$$

T* for tri functional with regard to oxygen and a reactive H.

$$\begin{array}{c} O_{1/2} \\ | \\ O_{1/2}-Si-O_{1/2} \\ | \\ H \end{array}$$

These materials are reacted within the equilibration reaction to make reactive intermediates, which are hydrosilylated in the functionalization reaction. The vinyl containing groups that are reacted include;

a. Alpha olefin

$$CH_2=CH-(CH_2)_7CH_3$$

b. Ally alcohol alkoxylates

$$CH_2=CH-CH_2-O(CH_2CH_2O)_8H$$

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

Dimethicone with improved water solubility

The preparation of an amphilic silicone having both a water soluble and silicone soluble group can be demonstrate using PEG-8 dimethicone as a model. The molecular weight of a PEG 8 dimethicone has a dramatic effect upon performance of the compound as far as both wetting and irritation. Molecular weight is a measure of construction. The graph below shows the molecular weight of molecules studied. Essentially, in the construction the compounds have the same ratio of D to D*, only higher numbers of both. As can be seen there are a number of very good wetting compounds using the Draves Wetting Test, which measures the time it takes to wet a cotton skein.

Dimethicone with improved oil solubility - Alkyl Dimethicone

Just as allyl alcohol alkoxylates can be reacted with silanic hydrogen polymers to giving products with improved water solubility, they can also be reacted with alpha olefin to produce a series of oil soluble silicone polymers with very interesting properties. Silanic hydrogen compounds can be reacted with alpha olefin, to give mineral oil soluble materials. The compounds conform to the following structure;

Alkyl Dimethicone

```
         CH3       CH3          CH3       CH3
          |         |            |         |
CH3-Si--(- O—Si--)a—(O--Si -)b-O--Si--CH3
          |         |            |         |
         CH3       CH3         (CH2)c    CH3
                                 |
                                CH3
```

The inclusion of a very small amount of alkyl group into the molecule results in a product that is amphilic and soluble in mineral oil. Alkyl silicones are insoluble in water, isopropanol, and propylene glycol.

C. Derivitization

The final unit operation to consider is Derivitization. In this step, reactive groups added in the functionalization step are reacted further to give new compounds. An example is the reaction of a hydroxyl group on a dimethicone copolyol. A variety of reactions have been carried out on dimethicone copolyol to make numerous derivatives. In fact a series of surface active silicones that parallel the world of standard surfactants has been created and sold commercially. They are outlined in below.

COMPARISON OF HYDROCARBON AND SILICONE DERIVATIVES

Traditional Products	Silicone Products
ANIONICS	
Phosphate Esters	Silicone Phosphate Esters[3]
Sulfates	Silicone Sulfates[4]
Carboxylates	Silicone Carboxylates[5]
Sulfosuccinates	Silicone Sulfosuccinate[6,7]
CATIONICS	
Alkyl Quats	Silicone Alkyl Quats[8]
Amido Quats	Silicone Amido Quats[9]
Imidazoline Quats	Silicone Imidazoline Quat[10]
AMPHOTERICS	
Aminopropionates	Silicone Amphoterics[11]
Betaines	Silicone Betaines[12]
NONIONICS	
Alcohol Alkoxylates	Dimethicone Copolyol
Alkanolamides	Silicone Alkanolamides[13]
Esters	Silicone Esters[14]
Taurine Derivatives	Silicone Taurines[15]
Isethionates	Silicone Isethionates[16]
Alkyl Glycosides	Silicone Glycosides[17]

Silicone Esters

Silicone esters are a good example of the effect of Derivitization upon silicone performance. They are prepared by the esterification reaction of a dimethicone copolyol with a fatty acid have been introduced. Incorporation of the fatty group by the esterification reaction results in a product that has a water-soluble, a silicone soluble and a fatty soluble group present in the same molecule.

Reaction

```
       CH3  CH3   CH3  CH3
        |    |     |    |
CH3-Si-O-Si-O-Si-O-Si- CH3    + CH3-(CH2)10CO-OH  →
        |    |     |    |
       CH3 CH3  (CH2)3 CH3
                   |
                  O-(CH2CH2O)7H


              CH3  CH3   CH3  CH3
               |    |     |    |
       CH3-Si-O-Si-O-Si-O-Si- CH3
               |    |     |    |
              CH3  CH3 (CH2)3 CH3
                          |
                         O-(CH2CH2O)7-OC(O)-(CH2)10-CH3
```

Properties

Dimethicone copolyol esters have the following general properties;

1. Compounds with less than twelve carbon atoms in the fatty group are liquids at room temperature.
2. Saturated linear compounds with more than fourteen carbon atoms in the fatty group are solids at room temperature.
3. Compounds in which the fatty group is unsaturated or branched are liquids at room temperature.
4. The most hydrophobic products have more than sixteen carbon atoms in their fatty group.
5. The greatest spreadability and lubrication is obtained from the liquid iso-stearic esters.
6. Selection of the fatty group is extremely important in determining the solubility of the compound in many organic solvents.
7. All products are soluble in lower molecular weight alcohols, such as isopropanol.

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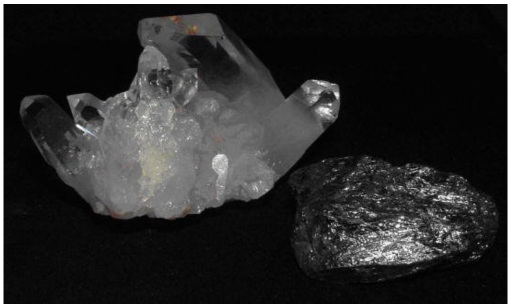

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