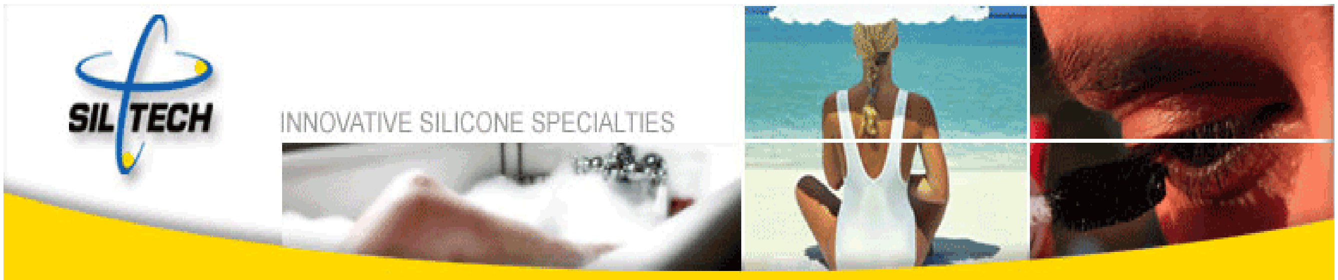
Products for Personal Care



Select-a-Sil™ silicone selection system

Silicone Polymers
New Possibilities in Nanotechnology

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Background

According to the National Science and Technology Council Committee on Technology Interagency Working Group on Nanoscience, Nanotechnology has been defined as the creation and utilization of materials, devices, and systems through the control of matter on the nanometer-length scale – that is, at the level of atoms, molecules, and supramolecular structures. Silicone technology offers the ability to make very specific molecules through the control of molecules. This makes them of great interest in the field of nanotechnology.

Silicone polymers and their ability to form self assembling units is the key to the functionality of these materials in making useful nanostructures. The first step is to engineer the polymer, using well known techniques. The next step is to look at the functionality of these materials in the solvent system of interest. Since very few formulations contain only silicone polymer, the most interesting nanostructures that develop using silicone technology are those based upon interactions of solvent, polymer and other species present in a product and not only those based upon the silicone polymer itself. The driving force for assembly is obtaining the lowest free energy in the system. Many times the lowest free energy state is not the ease, but rather the most ordered. This is particularly true in aqueous systems. The reason for this is that breaking up on hydrogen bonding in water is a very costly process energetically. Large molecules will assume many structures that are more energetically favorable than breaking up many intra-molecular hydrogen in water. The silicone polymer is interesting since internally substituted materials (the so-called comb materials) are free to rotate around the Si-O-Si backbone to obtain the lowest free energy system. The so-called terminal substituted silicones do not have free rotation available forming more complicated hair in and other larger structures.

Silicone Technology

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. Silicone chemistry provides the polymer chemist with the ability to construct precise molecules having desirable nanotechnology properties.

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

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

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".

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

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. The most important of which include; hexamethyldisloxane (MM), cyclomethicone (D4) and silanic hydrogen compound. That is just the start of the story. These materials are combined to make compounds of interest using three types of processes. These are:

- Construction
- Functionalization
- Derivatization

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, its branching and its positions for insertion of organic groups is determined.

Nomenclature

The shorthand for the construction is as follows;

CH_3
|
M   for mono functional with regard to oxygen CH_3-Si-$O_{1/2}$
|
CH_3

CH_3
|
D   for di functional with regard to oxygen $O_{1/2}$-Si-$O_{1/2}$
|
CH_3

$O_{1/2}$

T for tri functional with regard to oxygen

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

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 (hexamethyldisiloxane) a key material is often referred to as 0.65 viscosity silicone fluid or hexamethyl disiloxane. Its structure is:

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

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

Dimethicone

Reaction of M and D will result in silicone fluids, for example:

$$\begin{array}{ccccccc} & CH_3 & & CH_3 & & CH_3 & \\ & | & & | & & | & \\ CH_3\text{-} & Si & \text{—(-O-} & Si & \text{-)}_{80}\text{-O-} & Si & CH_3 \\ & | & & | & & | & \\ & CH_3 & & CH_3 & & CH_3 & \end{array}$$

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

MDM products are all called dimethicone. Historically, silicone fluids are the most understood and commonly used silicone product. These materials are homopolymers that are insoluble in water and in mineral oil. Dimethicone is also called by a number of less technically acceptable terms including silicone fluids, silicone oils, or merely silicones. They are sold by viscosity and vary from low molecular weight very thin materials to products that are very thick and sticky.

While commonly used, the inability to easily formulate personal care products based upon dimethicone has been limited.

Elastomeric Silicones

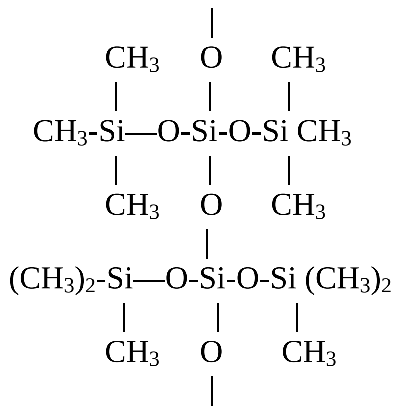
Reaction of T units with M units introduces a one dimensional branching, and is commonly used to make elastomeric products.

```
            CH3    CH3   CH3
             |      |     |
      CH3-Si—O-Si-O-Si CH3
             |      |     |
            CH3     O    CH3
                    |
  (CH3)2-Si—O-Si-O-Si (CH3)2
             |      |     |
            CH3    CH3   CH3
```

These products are used in skin care where they provide a dry powdery feel on the skin.

Silicone Q Resins

Reaction of Q units with M units introduces a multi dimensional branching, and is commonly used to make resinous products.



MD reaction products can rotate freely and thereby remain liquid. MT reaction products have some restriction of rotation and become elastomeric (rubber like), MQ reaction products have very little rotational freedom and become resins (plastic like).

Group Opposites

So far all compounds discussed are homo-polymers of silicone. They are water insoluble making them hydrophobic, but they are also oil insoluble. Normally, materials that are hydrophobic contain oil loving groups (referred to as oleophillic groups). However, in this case the water insoluble group is oil hating (oleophobic) and silicone loving (siliphillic).

This complexity has resulted in the introduction of the concept of group opposites.

Hydrophobic (Water Hating)	can be ether	Siliphillic (silicone loving)	or	oleophillic (oil loving)
Siliphillic (silicone loving)	is both	oleophobic (oil hating)	and	hydrophobic (water hating)
Oleophillic (oil loving)	is both	siliphobic (silicone hating)	and	hydrophobic (water hating)

The importance of this classification can be made using two examples, one from the carpet industry and the other from the personal care industry.

In the preparation of carpets, it is desirable to have a finish that rejects both oil and water. The ability to repel water is a result of making the surface hydrophobic. If that hydrophobicity is achieved by making the product oleophillic (that is putting on an oleophillic finish), the carpet will attract oil. Such a carpet is likely to soil permanently if cooking oil is spilled on it, due to the affinity of the carpet for oil. If the carpet on the other hand has been rendered hydrophobic (water repelling) by using a silicone coating, (a siliphillic material) both oil and water will be repelled.

One additional application relates to coated pigments. Almost all pigments have some sort of coating on them. An oil coating or a silicone coating. The ability to disperse the pigment efficiently is achieved using the phase in which the coating is most compatible. Consequently, a silicone coated pigment often gets used in a silicone phase. An oil coated pigment often gets used in an oil phase. One additional comment on pigments, some are chemically reacted forming covalent bonds between pigment and coating. Others are merely chemisorbed. Those pigments in which the coating is not chemically bonded can be metastable in emulsion systems. Keeping in mind that the materials in an emulsion will go to the phase in which the lowest free energy is achieved, the non-bonded pigment can over time migrate off the pigment into another phase. The result can appear as emulsion instability over time. The modification of the emulsifier package will not solve this problem. We recommend testing all pigments for the type of coating and its permanence.

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 advantages 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.

```
 \                                      \
-Si-H  +  CH2=CH-(CH2)7CH3  →  -Si-(CH2)9CH3
 /                                      /
```

$-Si-H + CH_2=CH-(CH_2)_7CH_3 \rightarrow -Si-(CH_2)_9CH_3$

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

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

```
        CH3
         |
  CH3-Si-O1/2
         |
         H
```

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

```
        CH3
         |
  O1/2-Si-O1/2
         |
         H
```

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

```
        O1/2
         |
  O1/2-Si-O1/2
         |
         H
```

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

$CH_2=CH-CH_2-O(CH2CH_2O)_8H$

c. Fluoro vinyl compounds

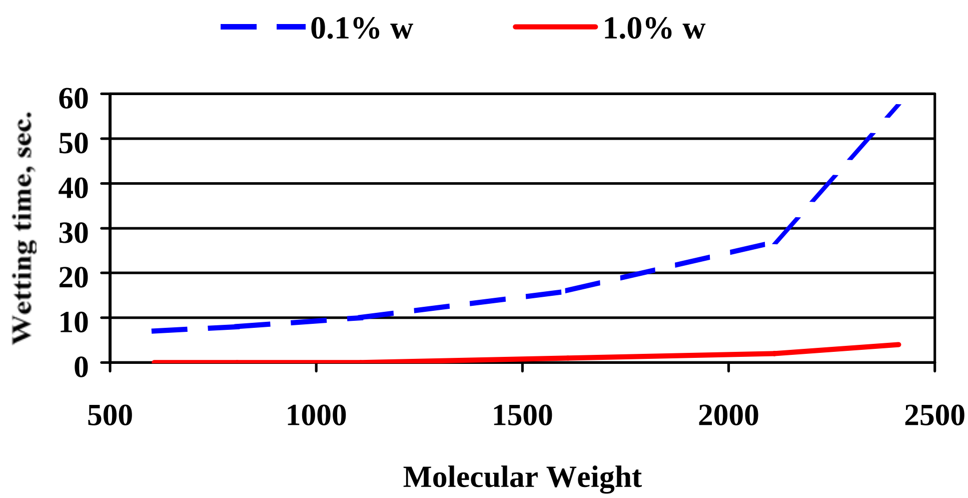
$CH_2=CH-CH_2 (CF_2)CF_3$

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

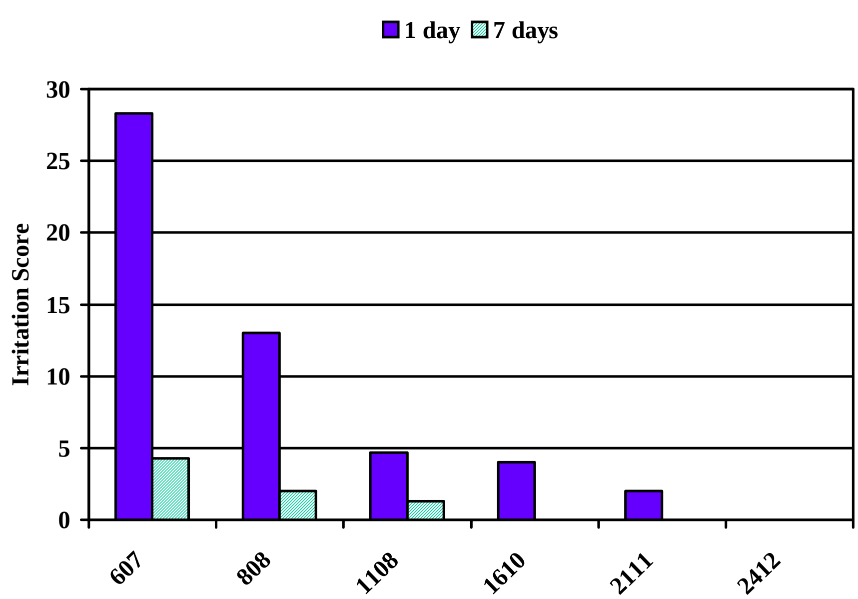
PEG-8 Dimethicone Water Soluble Silicone

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.

Wetting is a critical often overlooked aspect of cosmetic formulation. If you are applying something to the air, 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.



Construction also has a profound effect upon eye irritation, essentially disappearing at a molecular weight of 2412.



As the molecular weight increases, silicone compounds with the identical amount of PEG, exact same ratio of D to D*, the products transform from wetting agents to emulsifiers, to conditioners to water proofing 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.

Alkyl Dimethicone Oil Soluble Silicones

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;

```
       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 soluble in mineral oil. This solubility offers the ability to use these materials in a variety of clear systems based upon many oils, where the use of silicone fluids in these systems is not possible,

Solubility (10% Weight)

Product	***Water***	***Mineral oil***	***Mineral spirits***	***PG***	***D-5***	***Sil Fluid 350 Visc***	***Iso-propanol***	***Aromatic Hydrocarbon***
Silwax D-026 Cerotyl Dimethicone	I	S	D	I	D	D	I	D
Silwax J-226 Cerotyl Dimethicone	I	S	S	I	D	D	I	S
Silwax H-418 Stearyl Dimethicone	I	S	S	I	D	I	I	S
Silwax L-118 Stearyl Dimethicone	I	S	S	I	I	I	I	S

Legend I = insoluble d= dispersible s = soluble

Physical Properties of Silicone Waxes

Differing amounts of Alkyl Group on same Silicone Backbone

Silwax	Alkyl Group	State RT	% Silicone	% Alkyl	MP (^{o}C)
J1012	Lauryl	Liquid	82.0	18.0	Liquid (thin)
J1016	Cetyl	Liquid	77.0	23.0	Liquid (thin)
J1018	Stearyl	Liquid	75.0	25.0	Liquid (viscous)

J1022	Behenyl	Soft solid	72.0	28.0	20.0
J1026	Cerotyl	Solid	68.0	32.0	46.0
J1032		Hard solid	64.0	36.0	60.5

Differing amounts of Silicone using the same Alkyl Group

Silwax	Alkyl Group	State RT	% Silicone	% Alkyl	MP (^{o}C)
D1026	Cerotyl	Solid	69.0	31.0	42.0
D2026	Cerotyl	Solid	81.0	19.0	37.0
D3026	Cerotyl	Solid	86.0	14.0	36.0

Silwax	Alkyl Group	State RT	% Silicone	% Alkyl	MP (^{o}C)
H-418	Stearyl	Liquid	61.0	39.0	Liquid (Thin)
P-418	Stearyl	Soft Solid	58.0	42.0	Liquid (Viscous)
L-118	Stearyl	Soft Solid	38.0	62.0	30.0

There are several important trends that become apparent when one looks for a structure / property relationship. They include;

1. The length of the alkyl chain has a dramatic effect upon the melt point of the wax.
   - Waxes based upon alkyl groups having between 12 and 16 carbon units are liquids at room temperature.
   - At carbon lengths of 18 and above products become solid and the melt point increases as the carbon length goes up.

2. The amount of silicone in the molecule, for a given alkyl length, has a minimal impact on melting point.

3. The amount of silicone in the molecule, for a given alkyl length has a minimal, has an effect upon wax hardness.

- As the amount of alkyl group in a wax is increased in a wax having over 18 carbon atoms in the alkyl group, the wax becomes harder.

Understanding these trends allow for the selection of a wax for the specific application chosen. All silicone waxes offer improved oil solubility over silicone fluids. Waxes added to oil phases offer an ability to alter the viscosity and skin feel of a formulation. Mineral oil can be gelled by addition of the proper wax. Petrolatum can be thinned out and made less grainy by adding liquid waxes. The play time at a given melt point can be altered by (a) selecting the specific alkyl chain (melt point) and adding differing amounts of silicone to the molecule (hardness).

In addition, silicone waxes are great at minimizing syneresis in pigmented products. The alteration of the amount of alkyl group relative to silicone group determines which wax is best at lowering syneresis in a given formula.

Alkyl Dimethicone Copolyol Silicone Emulsifiers

Alkyl dimethicone copolyol polymers conforming to the following structure;

```
                                              CH3
                                               |
         CH3       CH3        CH3           (CH2)x    CH3
          |         |          |              |        |
   CH3- Si - O - (- Si - O )a- (-Si - O)b -(- Si - O)c –Si - CH3
          |         |          |              |        |
         CH3       CH3       (CH2)3          CH3      CH3
                               |
```

O

|

$(CH_2CH_2O)_dH$

A series of products have been designed to have different solubility in a variety of solvents and act as emulsifier pairs.

Composition

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

The differing concentration of both alkyl and water soluble materials are used to make emulsions either alone (J-208-812 for water in oil emulsions) in combination. The products are clear stable liquids and are used in sun care and pigmented products.

Solubility

Table 2	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 %
Silube J208-212	S	S	S	S	I	I	D	D	S	S	D	D	D	D
Silube J208-412	D	D	S	S	D	D	D	D	S	S	D	D	D	D
Silube J208-612	I	I	S	S	S	S	S	D	S	S	D	D	D	D
Silube 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

Typical Emulsion

The following example is offered showing the functionality of these emulsifiers. Typically we would recommend using a blend of two emulsifiers, the so called "emulsifier pair".

Sunscreen Stick / Lip Pot Sunscreen

SIL 022805-A

Material	% wt
Resin 12029	8.50
Microcrystalline Wax 190/195	3.25
Ozokerite 1070	16.50
Octyl Methoxycinnamate	7.50
Octocrylene	7.00
Benzophenone-3	6.00
Octyl Salicylate	5.00
Silube J-208-612	4.00
Silica spheres MSS-500	12.50
Siltech F-0.65 dimethicone	29.75
	100.00

1. Add all ingredients except Spheres and .65 dimethicone
2. Heat to 80^{o}C until all waxes are melted
3. Add silica Spheres and Dimethicone and maintain temp at 75oC for 5 min
4. Cool to 58^{o}C and pour.

Notes:

Resin 12029 adds water resistance and long wearing properties

Silube 208-612 helps to solubilize the silicones and Sunscreen esters

Anhydrous Makeup

Sil 022805-M

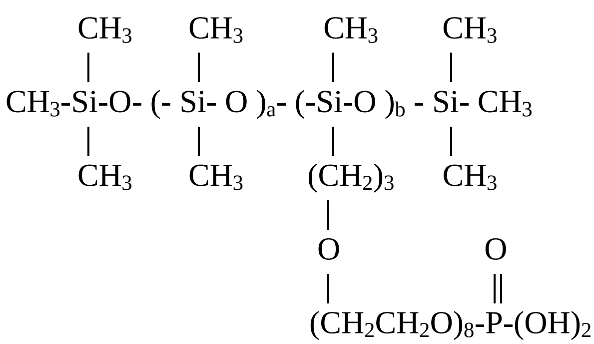
Material	% wt
Resin 12029	4.25
Ozokerite 1020P	10.00
Silube J-208-612	2.50
Siltech F 0.65	23.75
Siltech CS-9955	30.00
Mica 280	2.50
Titanium Dioxide	19.08
Yellow Iron Oxide	1.80
Red Iron Oxide	0.54
Black Iron Oxide	0.18
Excel Talc	5.40
	100.00

1. Mix Resin, Ozokerite, Silube J-208-612, Siltech F-0.65 and Siltech CS-9955.
2. Heat to 75-80^{o}C until wax is completely melted
3. Add Pigments, Maintain temperature at 75oC until Pigments are completely dispersed
4. Cool to 60^{o}C and Pour.

Notes:

A. The texture of this formula can be adjusted. It may be softened by lowering the Ozokerite as low as 6%.
B. The Resin Adds long wear properties.
C. The Silube J-208-612 is very effective in dispersing the pigments in the silicone base.

"**Derivatization**" relates to the chemistries practiced on the groups added to the silicone backbone by functionalization. An example of a compound that has construction, functionalization and derivatization is PEG-8-dimethicone phosphate.



United States Patent 5,859,161 to Imperante issued January 12, 1999 teaches that silicone phosphate esters of the type shown above mitigate eye and skin irritation when used in synergistic combinations with fatty alcohol sulfates and fatty alcohol ether sulfates. These materials form complexes which have surprisingly low irritation properties. These compounds are also used in sunscreens to improve the deposition of the film on the skin and improve SPF values.

Conclusion

Silicone compounds offer a wide range of possibilities to engineer molecules that offer nanostructures in a variety of applications. The understanding of the chemistry is key to effective use. The properties of these materials in various solutions vary as the structure does. The making of several types of compounds and the study of their properties is key to efficient use of these materials. It requires candor on the art of the silicone manufacturer and evaluation on the part of the formulator to be successful. The possibilities offered to the formulation chemist by silicone chemistry is endless and yours to explore.

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