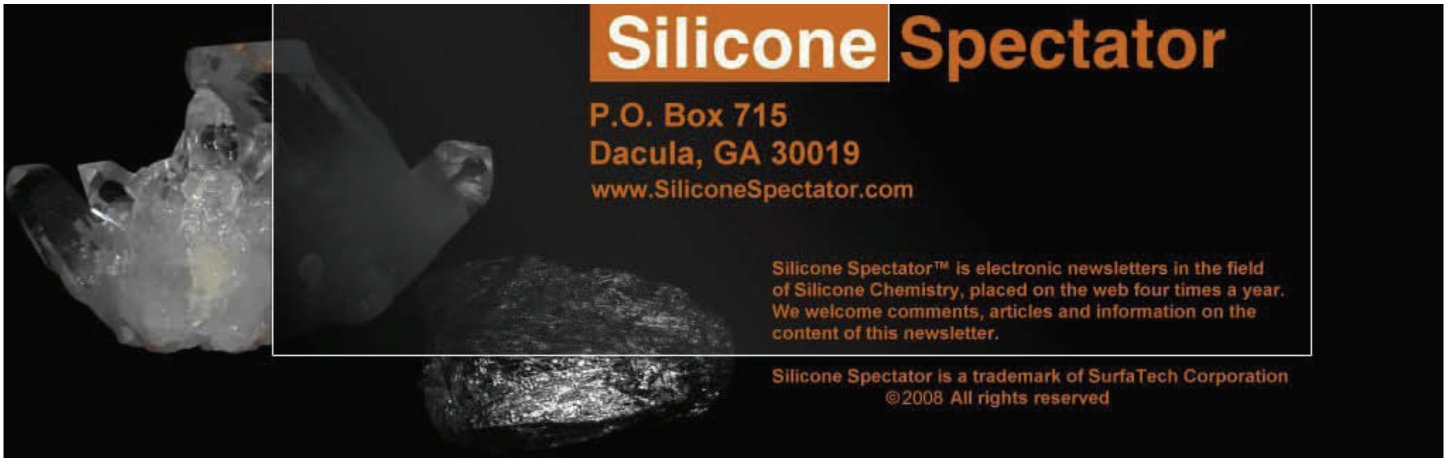

The Silicone Conundrum

Editors Note: This edition of **The Silicone Spectator** will begin to address **"The Silicone Conundrum".** The term conundrum defines as an intricate and difficult problem. The problem is how do I get the highly desirable properties of silicone in my formulation, when formulating with silicone can provide its owe set of problems?

Every formulator that works with silicone initially needs to face the silicone conundrum. Silicone provides great functional properties to me formulation, BUT can offer problems if formulation. Specifically, formulators ask:

- **Why do silicone compounds fail to act in a predictable way in my formulation?**
- **Why is there so much trial and error in using silicone compounds?**
- **Why are compounds purporting to have the same INCI name act so differently?**

The answer is that silicone compounds are not as simple as INCI names and need to be understood in order to allow for proper formulating. This issue will address the three structural properties that dictate performance.

- Construction
- Functionalization
- Derivitization

Silicone Polymers

The functionality of silicone compounds is directly related to the structure. Unlike traditional fatty compounds, the "structure" is more complex. It requires an understanding of three components of structure. These are (1) Construction, (2) Functionalization and (3)

Derivitization. Each is critical to functionality.

- **Construction relates to the make up of the silicone backbone.**
- **Functionalization relates to the groups that are on the silicone backbone.**
- **Derivitization relates to chemistry conducted on the groups added by Functionalization.**

1. Construction – Polymer Backbone Preparation

The "Construction" relates to the polymer backbone. It is prepared by reacting various silicone precursors to make the "silicone backbone". The "M", "D", "T" are part of the construction.

A shorthand has been developed to describe construction. It is based upon the number of oxygen atoms connected to the Si. It is as follows:

"M unit" is monosubstituted	CH_3 | $-O_{1/2}$-Si-CH_3 | CH_3
"D unit" is disubstituted	CH_3 | - $O_{1/2}$ -Si- $O_{1/2}$ - | CH_3
"T unit" is trisubstituted	$-O_{1/2}$ | - $O_{1/2}$ -Si- $O_{1/2}$ - | CH_3
"Q unit" is Quadsubstituted	$-O_{1/2}$ | - $O_{1/2}$ -Si-$O_{1/2}$- | $-O_{1/2}$

If the Si atom has anything other than CH_3 on it, it is referred to as a "*" compound

"M* unit" is monosubstituted

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

"D* unit" is disubstituted

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

"T* unit" is trisubstituted

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

Examples

There are three classes of compounds based upon their construction:

Comb

```
         CH3        CH3         CH3         CH3
          |          |           |           |
 CH3 --Si-O----(-----Si---O-)50--( -Si----O-)10----Si--- CH3
          |          |           |           |
         CH3        CH3          R          CH3
```

This type of construction is referred to as M D50 D*10 M.

Terminal

```
      CH3     CH3        CH3
       |       |          |
 R--Si-O----( -Si----O-)10----Si--- R
       |       |          |
      CH3     CH3        CH3
```

This type of construction is referred to as M* D10 M*.

Multifunctional

```
        CH3          CH3         CH3          CH3
         |            |           |            |
R --Si-O----(-----Si---O-)50--( -Si----O-)10----Si---R
         |            |           |            |
        CH3          CH3          R           CH3
```

This type of construction is referred to as M* D50 D*10 M*.

It should be clear that each class of compound will have different properties based upon its construction.

2. Functionalization – The hydrosilylation reaction

The "Functionalization" relates to the functional groups that are present. They are generally a direct consequence of Si-H groups reacted with unsaturated groups in a process called "Hydrosilylation".

```
     CH3       CH3          CH3
      |         |            |
H--Si-O----( -Si----O-)10----Si---H  +  2 CH2=CH-(CH2)9CH3  ------à
      |         |            |
     CH3       CH3          CH3
```

```
                   CH3       CH3          CH3
                    |         |            |
CH3(CH2)11--Si-O----( -Si----O-)10----Si-(CH2)11CH3
                    |         |            |
                   CH3       CH3          CH3
```

Vinyl Compound	Example	Produces
Alkoxylated allyl alcohol	CH_2=CH-CH_2-O-$(EO)_a$H	PEG-dimethicone
Alpha olefin	CH_2=CH- $(CH_2)_n$ CH_3	Alkyl dimethicone
Fluoro alpha olefin	CH_2=CH-CH_2- (CF_2)n CF_3	Fluoro dimethicone
Combinations	Mixtures	Multifunctional

- The "construction" is the molecular knitting machine that makes the silicone backbone.

- The "Functionalization" is the "Lego Set" of appendages that provide functionality.
- "Construction" without "Functionalization" results in silicone homopolymers (fluids).
- "Functionalization" is not possible without "Construction".

The question then becomes is PRG-8-Dimethicone water-soluble? The answer is it depends upon functionalization. There is no derivitization on PEG-8-dimethicone since is a product of construction (back bone preparation) and functionalization (hydrosilylation) only.

Product	**Old INCI Name**	**New INCI Name**
MD10D*5M	**Dimethicone Copolyol**	**PEG 8 Dimethicone**
MD10D2*M	**Dimethicone Copolyol**	**PEG 8 Dimethicone**
MD40D22*M	**Dimethicone Copolyol**	**PEG 8 Dimethicone**

Solubility (1%/10% Weight)

	Water	**Mineral Oil**	**Propylene Glycol**	**Cyclo Methicone**	**Silicone Fluid**	**IPA**
MD10D*5M	**I/I**	**I/I**	**S/S**	**I/I**	**D/I**	**S/S**
MD10D*5M	**S/**	**I/I**	**S/S**	**I/I**	**D/D**	**S/S**
MD10D2*M	**I/I**	**I/I**	**I/I**	**I/I**	**D/I**	**S/S**
MD40D22*M	**I/I**	**I/I**	**D/D**	**D/I**	**D/D**	**S/S**

Legend I = Insoluble D = Dispersible S = Soluble

3. Derivitization – Subsequent Chemistry

In instances where the functionalization results in a molecule that has a reactive group present, subsequent chemistries can be applied to that group.

An illustrative group is the PEG-8-dimethicone

```
       CH3     CH3        CH3       CH3
        |       |          |         |
CH3-Si-O- (- Si- O )a- (-Si-O )b -- Si- CH
        |       |          |         |
       CH3     CH3       (CH2)3     CH3
                           |
                         O-(CH2CH2O)8H
```

Since the OH group is a carbanol, it can be reacted in many of the same ways the hydroxyl group in lauryl alcohol ethoxylates can be reacted. These reactions are called derivitization. Many reactions have been conducted using products of construction and functionalization as reactants. These are the derivative silicones. The attached table is an example of products made using this powerful technique.

COMPARISON OF HYDROCARBON COMPOUNDS WITH SILICONE-MODIFIED COMPOUNDS

ANIONIC COMPOUNDS

Hydrocarbon Products	**Silicone Products**
Phosphate Esters	Silicone Phosphate Esters [1,2]
Sulfates	Silicone Sulfates [3]
Carboxylates	Silicone Carboxylates [4,5]
Sulfosuccinates	Silicone Sulfosuccinates [6,7]

CATIONIC COMPOUNDS

Hydrocarbon Products	**Silicone Products**
Alkyl Quats	Silicone Alkyl Quats [8]
Amido Quats	Silicone Amido Quats [9]
Imidazoline Quats	Silicone Imidazoline Quats[10]

AMPHOTERIC COMPOUNDS

Hydrocarbon Products	Silicone Products
Amino Proprionates	Silicone Amphoterics [11]
Betaines	Silicone Betaines [12]
Phosphobetaines	Silicone Phosphobetaines [13]

NONIONIC COMPOUNDS

Hydrocarbon Products	Silicone Products
Alcohol Alkoxylates	Dimethicone Copolyol
Alkanolamids	Silicone Alkanolamids[14]
Esters	Silicone Esters [15,16,17]
Taurine Derivatives	Silicone Taurine[18]
Isethionates	Silicone Isethionates[19]
Alkyl Glycosides	Silicone Glycosides[20]

References

1. U.S. Patent 5,149,765, September 1992 to O'Lenick.
2. U.S. Patent 4,724,248, February 1988 to Dexter et al.
3. U.S. Patent 4,960,845, October 1990 to O'Lenick.
4. U.S. Patent 3,560,544, February 1971 to Haluska.
5. U.S. Patent 5,296,625, March 1994 to O'Lenick.
6. U.S. Patent 4,717,498, January 1988 to Maxon.
7. U.S. Patent 4,777,277, November 1998 to Colas.
8. U.S. Patent 5,098,979, March 1992 to O'Lenick.

9. U.S. Patent 5,153,294, October 1992 to O'Lenick.
10. U.S. Patent 5,196,499, February 1993 to O'Lenick.
11. U.S. Patent 5,073,619, December 1991 to O'Lenick.
12. U.S. Patent 4,654,161, March 1987 to Kollmeier.
13. U.S. Patent 5,237,035, August 1993 to O'Lenick.
14. U.S. Patent 5,070,171, December 1991 to O'Lenick.
15. U.S. Patent 5,070,168, December 1994 to O'Lenick.
16. U.S. Patent 4,724,258, issued February 1988 to Dexter.
17. U.S. Patent 6,338,042, December 2002 to O'Lenick.
18. U.S. Patent 5,280,099, January 1994 to O'Lenick.
19. U.S. Patent 5,300,666, April 1994 to O'Lenick.
20. U.S. Patent 5,120,812, June 1992 to O'Lenick

Silicones in Paint and Coatings Manufacturing

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Silicones have been used in the Paints and Coatings industry for many years, but have come a long way from their initial use as defoamers. Formulators of coatings used to think of silicones as an ingredient that could be detrimental to their system and cause defects such as fish eyes etc. This is no longer the case. By using organically modified silicones, they can be used as defoamers that will not cause surface defects, but can also be used as additives to increase flow, leveling, mar and stain resistance, slip, gloss and act as dispersing and wetting aids.

Due to more recent advances, silicones can also be used as co-reactants or monomers to actually react into the coating system to help improve the flexibility, heat. and UV resistance and scuff resistance of the coating in a more permanent manner.

Some of silicone's properties include low surface tension, high lubricity, enhanced softness, low toxicity and non-stick properties. The Si-O backbone provides flexibility and freedom of rotation which enables the molecules to adopt the lowest energy configuration at interfaces, providing a surface tension that is substantially lower than most organic based products.

The strength of the Si-O bond not only provides thermal stability, but also chemical inertia, making it highly resistant to oxidizing and to ultraviolet, radiation, ozone and electrical discharges.

The structure of a silicone polymer can be summarizes as follows:

$$
\begin{array}{ccccccccccccccccc}
 & & CH_3 & & & & CH_3 & & & & CH_3 & & & & CH_3 & & \\
 & & | & & & & | & & & & | & & & & | & & \\
R & - & Si & - & (O & - & Si)_x & - & (O & - & Si)_y & - & O & - & Si & - & R \\
 & & | & & & & | & & & & | & & & & | & & \\
 & & CH_3 & & & & CH_3 & & & & R & & & & CH_3 & &
\end{array}
$$

Where R = CH

or R is polyether group = $-(CH_2)_3-O-(CH_2CH_2O)_a-(\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_2O)_b-OH$

Or R can be a long chain alkyl, aryl, fluoro, acrylate, carbinol or other functional groups.

From the diagram above it can be seen that the silicone copolymer can be either a branched or "multi functional" with R groups hanging off the backbone, or it can be linear or "difunctional" with the R groups at the terminal end or it can be both, having functional groups at terminal ends and hanging off the backbone.

Silicones can also be thought of as Lego blocks, so one can attach a combination of organic groups on the backbone to give the silicone better compatibility to specific formulations. For instance, one can make an alkyl polyether, alkyl fluoro, or fluoro polyether silicone etc.

The applications where silicones can be used can be broken down into three categories, Defoamers, Additives and Reactants

Defoamers:

This is probably the best known application for silicones. Silicones are advantageous since they have low surface tension for effective foam control, are long lasting, and can act as both defoamers and antifoams.
Standard silicone fluids, where the R groups in figure 1 are all methyl, usually incorporated with silica, are the standard products used for defoaming. They are very hydrophobic and can be emulsified for use in water based systems. The problem with these types of defoamers is that in certain applications they can cause surface defects such as fish eyes, orange peel etc. due to the incompatibility of the silicone fluid.

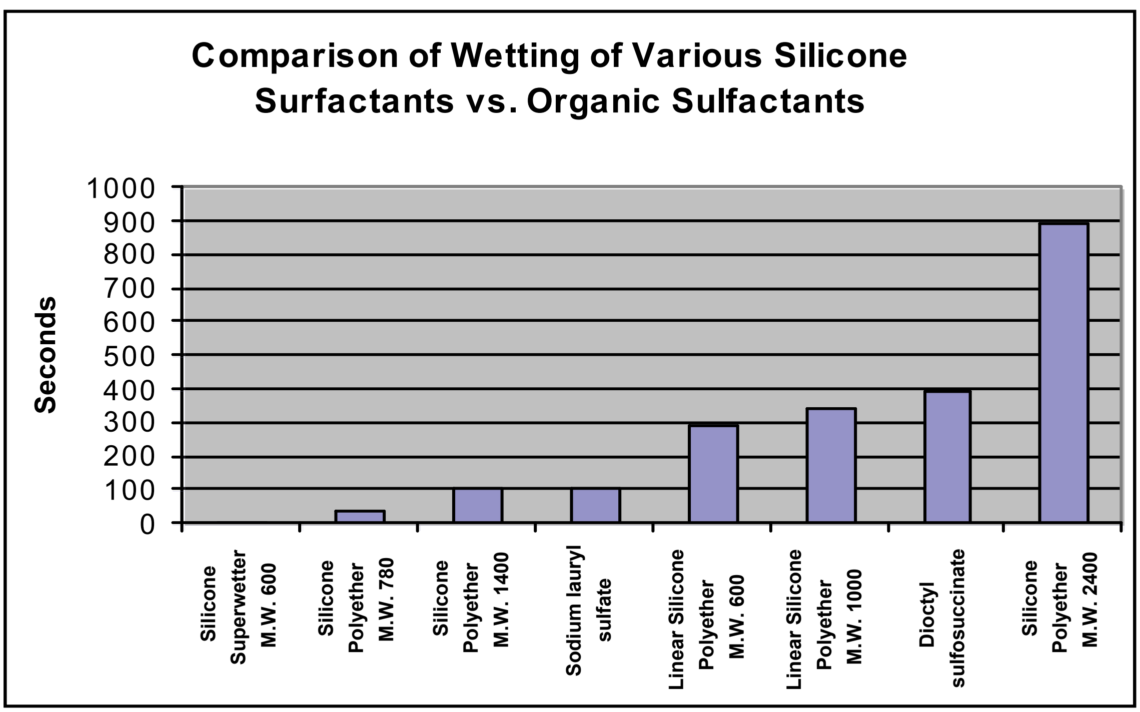
Silicone polyethers have been used more recently as defoaming agents. Their advantage is that they are 100% active for lower use levels, and do not contain any silica that can separate and cause defects.. They are also self-emulsifying for easier incorporation into aqueous or polar coatings.

By varying the ratio of the hydrophobic silicone and the hydrophilic polyether, one can alter the compatibility of the silicone to help increase the defoaming for the specific formulation without making it so incompatible that it will cause surface defects. Increasing the x portion in figure 1 will make the product more hydrophobic while increasing the y or polyether portion will make the silicone more hydrophilic. The ratio of a and b can also be changed. The higher the ratio of a:b, (ie EO:PO) the more hydrophilic the polyether portion will be. Usually there is more PO than EO when these product are used as defoamers.

Fluoro and alkyl aryl silicones are also used as defoamers in solvent and non – solvent based coatings and more recent advances have used acrylate based silicones as defoamers.

Additives:

Silicones are used in paints and coatings as additives to help increase slip, mar and stain resistance, flow, leveling, act as pigment dispersants and can also improve gloss. They are used in waterborne, solvent and solventless based systems. Because of low intermolecular forces, the silicone is able to migrate to the air/surface interface and provide slip, mar resistance, leveling and wetting. These performance attributes are related to the surface tension of the silicone surfactant. The lower the surface tension, the better the wetting capabilities. In silicones, because one can alter the ratio of x and y in Figure 1, the best wetting can be achieved when the value of x, y, a and b are small. Silicone superwetters are silicone polyethers where x = 0 and y = 1 and a and b are anywhere from 2-10 units long. The molecular weight of the polyether portion can be varied to make the molecule more hydrophobic or hydrophilic. Silicone superwetters can have a surface tension as low as 21 dynes/cm. Chart 1 gives a brief comparison of the wetting of various silicone polyethers compared to standard surfactants.



Because of their low surface tension, the use of silicone surfactants can help replace solvents for use as flow and leveling agents.

In coatings, surface defects are usually the result of little or too much flow which is directly related to wetting. Too much flow or wetting can result in sagging, running or curtailing and too little flow can result in fish eyes, craters and uneven leveling. By adding a silicone with the proper ratio of silicone to organic groups and as well having the proper molecular weight one can provide a silicone additive that will give optimal wetting characteristics to prevent any defects.

Usually the larger % silicone in the molecule (ie greater amount of x in figure 1), the better slip, mar resistance and anti-blocking. The greater the amount of organic moiety, the better the recoatability and compatibility of the silicone in the formulation. It is a matter of finding the delicate balance between all of these to get the best performance from the silicone. Usually linear silicone polymers will provide better slip and mar resistance due to the uninterrupted silicone chain that can orient itself to the air/interface surface. Alkyl, aryl, and fluoro silicones and any of the combinations of those groups are also used to increase organic compatibility and help with recoatability.

Recent advances in silicone additives include the use of silicone quats to improve slip and mar and water resistance and also improve anti-stat and anti-bacterial properties.

Silicones as Reactants in Coatings:

Perhaps the most interesting use of silicones is the incorporation of silicone into the polymer matrix in UV, electron beam and other types of coatings to help increase slip, mar resistance, UV resistance, water resistance and also to help increase water permeability. In this case the silicone is not just an additive, but reacted right into the polymer so it becomes a permanent part of the coating.

The linear silicones when incorporated into the polymer matrix will act as chain extenders and usually result in a more flexible coating system whereas the branched silicones will provide more crosslinking.

For electron beam and UV curing systems, acrylate functional silicone and epoxy silicones are normally employed. Urethane systems can co-react with silicone carbinols and amines.

A summary of the reactions that can take place are as follows:

Silicone Acrylates

Reaction With Vinyl Monomers

```
                       O                                     O
   |                   ||                             |      ||
--Si-CH2CH2CH2OCCH=CH2 + R-C=CH2 à ----Si-CH2CH2CH2OCCH2CH2 –( CH2CH)x
   |                                          |                     |
                                                                    R
```

Reaction With Acrylic Monomers

```
                       O          O                          O
   |                   ||         ||                  |      ||
--Si-CH2CH2CH2OCCH=CH2 + R-CCH=CH2 à ----Si-CH2CH2CH2OCCH2CH2 –( CHCH2)x
   |                                          |                    |
                                                                  C=O
                                                                   |
                                                                   R
```

Silicone Epoxides

Reaction With Organic Epoxides

```
                          O                   O                            OH
   |                     /  \                / \         |                 |
--Si-CH2CH2CH2O CH2CH---CH – R  +      R2-CH-CH2  à  -----Si- CH2CH2CH2 O CH2CHCH2-O-CH2CH2R2
   |                                                     |
```

Reaction With Alcohols

```
                             O                                          OH
   |                        /  \                        |               |
--Si-CH2CH2CH2O CH2CH---CH – R      +      R-OH à   -----Si- CH2CH2CH2 O CH2CHCH2-O-R
   |                                                    |
```

Reaction With Amines

```
                             O                                     OH
   |                        /  \                   |               |
--Si-CH2CH2CH2O CH2CH---CH – R  +  R1R2-NH   à -----  Si- CH2CH2CH2OCH2CHCH2-N-R1R2
   |                                               |
```

Silicone Carbinols

Reaction With Isocyanates

$$--Si\text{-}CH_2CH_2CH_2\text{-}R\text{-}OH \quad + \quad R\text{-}NCO \quad à \quad ----Si\ CH_2CH_2CH_2OC(=O)NH\text{-}R$$

Where R can be a polyether or R can = 0

Reaction With Carboxylic Acids

$$--Si\text{-}CH_2CH_2CH_2\text{-}R\text{-}OH \quad + \quad R_1COOH \ à \quad ----Si\ CH_2CH_2CH_2OC(=O)R_1 \ + H2O$$

Reaction With Epoxides

$$--Si\text{-}CH_2CH_2CH_2\text{-}R\text{-}OH \quad + \quad CH_2\text{---}CH - R^1 \ (\text{epoxide, O bridging}) \quad à \quad ------Si\text{-}\ CH_2CH_2CH_2OCH_2CH(OH)\text{-}R^1$$

Silicone Amines

Reaction With Isocyanates

$$--Si\text{-}CH_2CH_2CH_2NH_2 \quad + \quad R\text{-}NCO \ à \ ----Si\ CH_2CH_2CH_2NHC(=O)NH\text{-}R$$

Reaction With Carboxylic Acids

$$--Si\text{-}CH_2CH_2CH_2NH_2 \quad + \quad R_1COOH \quad à \quad ----Si\ CH_2CH_2CH_2NHC(=O)R_1 \quad + \quad H2O$$

Reaction With Epoxides

$$--Si\text{-}CH_2CH_2CH_2NH_2 \quad + \quad CH_2\text{---}CH - R \ (\text{epoxide, O bridging}) \quad \text{->} \quad ------Si\text{-}\ CH_2CH_2CH_2NHCH_2CH(OH)\text{-}R$$

Vinyl Silicones

Reaction With Vinyl Monomers

```
   |                                   |
--Si-CH=CH2 + R-C=CH2 à          ----Si-CH2CH2 –( CH2CH)x
   |                                   |                  |
                                                          R
```

Reaction With SiH

```
   |                 |              |             |
--Si-CH=CH2 +   ---- SiH à        --Si-CH2CH2 –Si ------
   |                 |              |             |
```

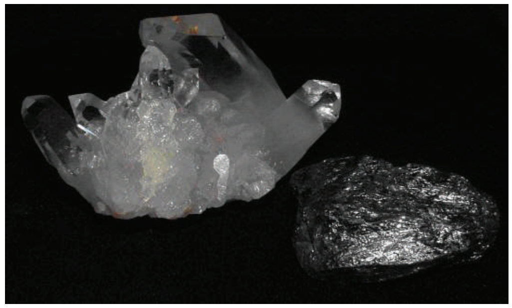
The reactive silicones can also be modified with polyether groups, alkyl groups, fluoro etc. to make them more compatible, or to increase chemical and stain resistance.

Because of the unique attributes of the silicone backbone, they can provide water repellency and water permeability, as well as UV and chemical resistance which can be very useful in architectural coatings, such as masonry and wood coatings.

Summary:

Silicones have come a long way in their use in paints and coatings. Because of the versatility of the silicone molecule, it can be modified with various organic groups and the molecular weight can be modified to make a molecule that can be tailor made for specific formulations for use as defoamers, slip, flow, mar resistance, pigment dispersants and as reactants into the polymer system to help improve heat stability, flexibility, water repellence and water permeability. They can be used in basically all types of coatings including automotive, wood, anti-fouling, architectural, inks and paints etc. As more formulators discover the uniqueness and adaptability of silicones, the future for coatings will look very bright.

Posted September 1, 2008



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