

# Silicone Spectator

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## The Silicone Conundrum

Editors Note: The last edition of **The Silicone Spectator** began to address “**The Silicone Conundrum**”. The term conundrum is 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? This edition will address two key areas:

- (1) selecting the proper silicone for a specific application; and
- (2) silicone resins, and elastomers .

### Silicones in Formulation

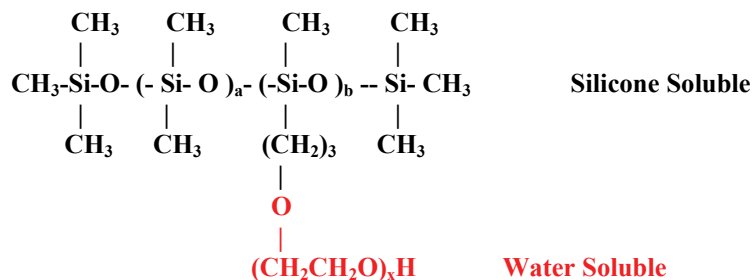
Silicone surfactants are amphiphilic nature and consequently lower surface tension of water<sup>1</sup>. The reduction of surface tension is a necessary first step in the providing foam, emulsification, wetting and other surfactant properties. Each of these surfactant properties require a material that lowers surface tension. Put another way, all materials that foam, emulsification, or wetting lower surface tension, but not all materials that lower surface tension provide these properties. The structure of the molecule at the surface that lower surface tension determines which molecule functions in a particular way.

The function of a silicone compound, in this case a dimethicone copolyol, alone in aqueous solution while of academic interest, is of limited interest to a formulator. This is due to the fact that formulations are never simply water and dimethicone copolyol, The key to formulation is the interactions between the surfactants and other ingredients that alter the performance of the surfactants at the surface. There are interactions between different formulation components and understanding them and optimizing them for a given effect is key to formulation success.

This article will begin to investigate some of the interactions between selected dimethicone copolyol compounds. The materials chosen for evaluation are shown in Table 1. Sodium lauryl sulfate (SLS), sodium laureth 2 sulfate (SLES-2) were chosen because they are important materials for use in personal care products.

### Raw Materials

#### Dimethicone Copolyol



#### Sodium Lauryl Sulfate



## Sodium Laureth 2 Sulfate



Table 1 outlines the molecular weight information, the INCI name and the short hand used to designate the compounds in this article.

Table 1 Compounds Evaluated		
Material	Aprox MW	INCI
SLS	320	Sodium Lauryl Sulfate
SLES-2	410	Sodium Laureth 2 sulfate
DMC-1	700	PEG-8 dimethicone
DMC-2	5800	PEG-8 dimethicone
DMC-3	2500	PEG-8 dimethicone
DMC-4	1620	Bis-PEG-8 dimethicone

## Surface Tension ( 1% Weight Aqueous Solutions)

The surface tension of the various materials was first evaluated. Table 2 lists the results. The table clearly shows that the sulfated fatty alcohol surfactants have a surface tension in the range of 30 – 32 dynes/cm<sup>2</sup>. The silicone surfactants have lower surface tension, in the range of 21- 28 dynes /cm<sup>2</sup>. The variation of surface tension within the class of silicone compounds is noteworthy. There has been a tendency to make generalizations that all silicone surfactants have essentially identical surface tension values. Clearly, this is not the case. As the silicone molecule contains less and less silicone in it the surface tension becomes more fatty surfactant like. The orientation on the surface and the groups that one sees at the interface determines the surface tension.

The silicone portion of the molecule has an abundance of methyl groups, (which make the surface tension lower) and the standard surfactant groups have an abundance of methylene groups (-CH<sub>2</sub>-), which makes the surface tension higher. What is seen at the interface is the group, which predominates at the surface when the molecule is in the lowest free energy conformation. Table 2 shows a graphic representation of a silicone molecule. The presence of the methyl groups predominate the surface of the polymer.

Table 2  
Model Silicone Molecule

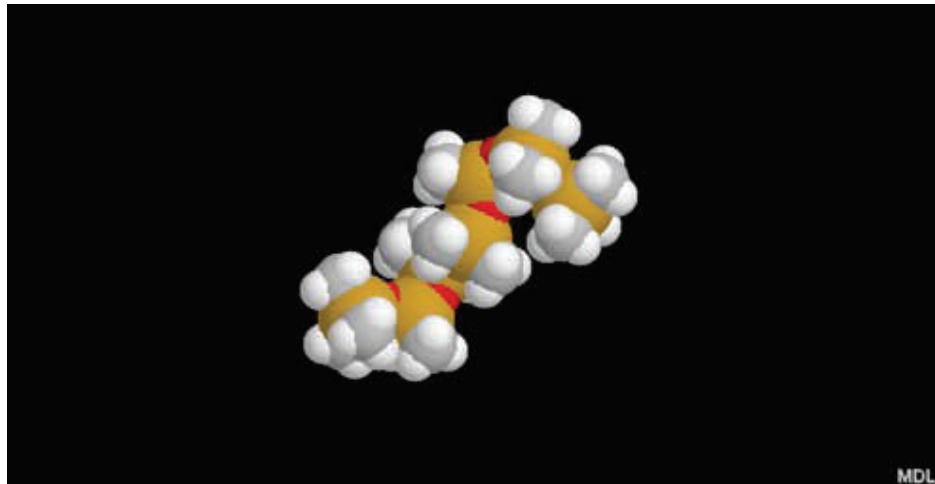
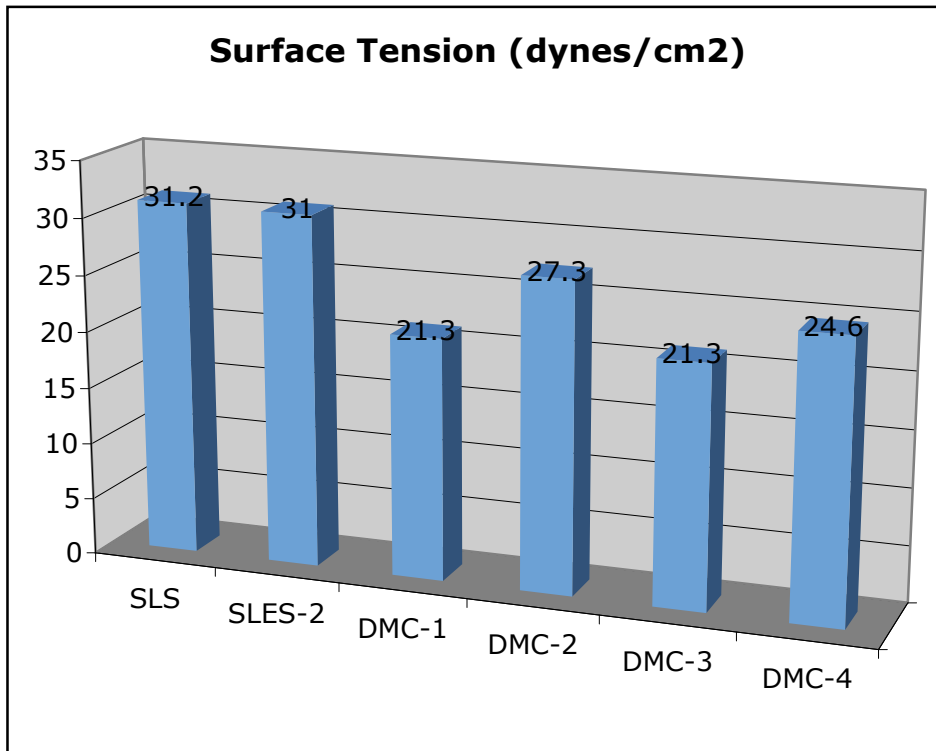


Table 3 shows the surface tension of the pure compounds studied at 1% active in water..

Table 3 1% Aqueous Surface Tension	
	Dynes/cm <sup>2</sup>
SLS	31.2
SLES-2	31.0
DMC-1	21.3
DMC-2	27.3
DMC-3	21.3
DMC-4	24.6

Table 4 shows graphically the data in table 3. The surface tension of the silicone is determined by how it orientates at the surface. It is very important to note that all silicone surfactants do not have the same low surface tension. The desire to place all silicone compounds into one group in terms of surface tension while simplistic, is simply incorrect. Molecules that have long EO/PO chains have surface tensions like fatty surfactants, not silicone surfactants. As we will discuss, the performance in formulations is complex depending upon the other components present.

Table 4



### Surface Tension – Binary Mixed Systems

As one looks at the combination of sodium lauryl sulfate or sodium laureth-2-sulfate with the various dimethicone copolyols, one can envision a number of interactions. Firstly the interactions that occur because of the incompatibilities of the silicone, fatty and water-soluble groups. Secondly, interactions related to hydrogen bonding and thirdly interactions between polyoxyalkylene groups on those materials that contain such groups. It is the nature of those interactions that will determine the surface tensions on the various blends.

### DMC SLES 2 Interactions

1% solutions of SLES-2 and different ratios of DMC compounds were made and evaluated for surface tension. Table 5 shows the results. Only one DMC had an impact on the surface tension of the solution. That DMC-1 which is the lowest molecular material we evaluated. DMC-2 through 4 did not alter surface tension. The interaction between the various functional groups in a formulation and the stability of the resulting complexes is critical to functionality of a formulation. If lowering surface tension is the goal of the addition, DMC-1 is the only one of the group to effectively accomplish the goal.

<b>Table 5 Blend (@ 1% active)</b>	<b>Surface Tension (dynes/cm)</b>
95% SLES-2/5% DMC-1	30.3
90% SLES-2/10% DMC-1	29.9
50% SLES-2/50% DMC-1	26.7
95% SLES-2/5% DMC-2	30.9
90% SLES-2/10% DMC-2	30.9
50% SLES-2/50% DMC-2	30.9
95% SLES-2/5% DMC-3	30.6
90% SLES-2/10% DMC-3	30.6
50% SLES-2/50% DMC-3	30.6
95% SLES-2/5% DMC-4	30.3
90% SLES-2/10% DMC-4	30.3
50% SLES-2/50% DMC-4	30.3

1% solutions of SLS and different ratios of DMC compounds were made and evaluated for surface tension. Table 6 shows the results. As in the case of SLES-2 only one DMC had an impact, albeit slight on the surface tension of the solution. That DMC-1 which is the lowest molecular material we evaluated. DMC-2 through 4 did not alter surface tension.

<b>Table 6 Blend (@ 1% active)</b>	<b>Surface Tension (dynes/ cm)</b>
95% SLS/5% DMC-1	30.3
90% SLS/10% DMC-1	30.0
50% SLS/50% DMC-1	28.1
95% SLS/5% DMC-2	30.9
90% SLS/10% DMC-2	31.0
50% SLS/50% DMC-2	31.0
95% SLS/5% DMC-3	31.0
90% SLS/10% DMC-3	30.9
50% SLS/50% DMC-3	31.0
95% SLS/5% DMC-4	30.4
90% SLS/10% DMC-4	30.5
50% SLS/50% DMC-4	30.5

## Foam and Wetting

### A. Pure compounds 1% Aqueous

Table 7 shows the Draves Wetting times for the neat surfactants at 1% in water. SLS and SLES-2 are both good wetting materials and good foaming compounds. DMC-1 is a good wetter and a fair foaming agent. DMC-2 and DMC-3 are neither good wetting agents nor good foaming compounds.

Table 7	SLES-2	SLS	DMC-1	DMC-2	DMC-3	DMC-4
Draves (sec)	4.8	3.8	8.4	82.7	28.3	13.4
Ross Miles (mm)						
Immediate	170	180	115	105	100	120
1 Min	155	165	110	95	80	115
5 Min	150	150	110	85	65	105

### B. Blended Systems

#### SLES-2 Systems –

Since SLES-2 is a high foaming surfactant, it was not expected that addition of DMC to SLES-2 would improve foam. This in fact was observed. At concentrations of up to 10% added DMC, there was no negative effect upon foam or wetting with all blends of SLES-2. The foam was adversely effected with 50% added DMC. Table 8 shows the results.

Table 8

Blend	95% SLES	90% SLES-2	50% SLES-2
<b>DMC-1</b>			
Draves (sec)	4.0	4.4	5.3
Ross Miles (mm)			
Immediate	175	170	150
1 Min	165	160	135
5 Min	160	150	130
<b>DMC-2</b>			
Draves (sec)	3.7	4.9	7.7
Ross Miles (mm)			
Immediate	185	180	150
1 Min	170	170	140
5 Min	160	160	135
<b>DMC-3</b>			
Draves (sec)	4.5	4.6	12.9
Ross Miles (mm)			
Immediate	180	170	155
1 Min	165	160	145
5 Min	160	150	140
<b>DMC-4</b>			
Draves (sec)	3.6	3.7	7.0
Ross Miles (mm)			
Immediate	170	170	145
1 Min	150	155	120
5 Min	140	150	40

## SLS Systems

At all concentrations of added DMC, there was no negative effect upon foam or wetting with all blends of SLS. DMC-4 however improved wetting in SLS systems. Table 9 shows the result.

Table 9

Blend	95% SLS/5% DMC	90% SLS/10% DMC	50% SLS/50% DMC
<b>DMC-1 (Middle MW)</b>			
Draves (sec)	3.5	3.0	7.7
<b>Ross Miles (mm)</b>			
Immediate	175	165	155
1 Min	160	150	140
5 Min	155	145	135
<b>DMC-2 (Low MW)</b>			
Draves (sec)	3.53	3.84	9.78
<b>Ross Miles (mm)</b>			
Immediate	170	170	160
1 Min	150	150	140
5 Min	145	150	135
<b>DMC-3 (High MW)</b>			
Draves (sec)	3.7	4.8	14.3
<b>Ross Miles (mm)</b>			
Immediate	185	180	165
1 Min	160	160	145
5 Min	150	155	135
<b>DMC-4</b>			
Draves (sec)	2.4	3.0	6.6
<b>Ross Miles (mm)</b>			
Immediate	180	180	150
1 Min	155	160	135
5 Min	145	155	130



### 3. Simple Shampoo System

The effect of DMC compounds on simple shampoos was studied using the formulation in Table 10. The results are shown in Table 11. Conditioning was evaluated in on hair swatches on a scale of 1 to 5 – five being best, one being worst.

<b>Formulation Table 10</b>	
<b>Compound</b>	<b>wt%</b>
Water	47.0
SLES-2	40.0
Cocamidobetaine	10.0
Cocamid DEA	2.0
DMC	1.0

**Performance of DMC in SLES Shampoo  
Table 11**

Shampoo	DMC-1	DMC-2	DMC-3	DMC-4
Draves (sec)	8.4	82.7	28.3	13.3
Ross Miles (mm)				
Immediate	115	105	100	120
1 Min	110	95	80	115
5 Min	110	85	65	105
Conditioning	1	4	3	2

### Results

The selection of a silicone to add to a formulation depends upon why one chooses to add it.

Referring to Table 11 the following becomes clear:

For wetting effects DMC-1 provides the best results.

For foaming effects DMC-4 provides the best results

For conditioning effects DMC-2 provides the best results.

## Conclusion

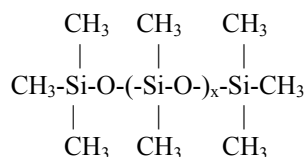
The selection of dimethicone copolyol for inclusion in hair care products is a complex process. The use of INCI names alone will be fruitless for picking the proper dimethicone copolyol for use in formulations. Likewise, the use of properties of dimethicone copolyol themselves in water to predict the functionality in formulation can be misleading. This is because there are a variety of interactions between the dimethicone copolyol and the other surface active agents in the formulation. The formulation itself needs to be tested to determine if the formulation performs as desired. The best test will be in the salon, because in the final analysis, consumer perception is the key to formulation performance. Dimethicone copolyols can be engineered to be formulator friendly and provide the desired effect(s) in formulations.

It also needs to be noted that the compounds studied in this project are nonionic silicone compounds, an important but albeit limited class of materials. Improved conditioning can be obtained by working complexes of anionic and cationic silicones, designed specifically for that application.

## Silicone Polymers - Terminology

### Silicone Fluids and Silicone Gums

One class of silicone polymers of interest to this discussion can be shown by the following structure:



The first important concept to introduce here is degree of polymerization or “dp”. This term relates to how many monomeric silicon units are contained in the polymer backbone, it is defined by

$$dp = x$$

As the dp increases, so does the viscosity. If “x” is zero, the material is the volatile product often called “0.65 viscosity fluid”. As the “x” value increases, the viscosity increases, but the product remains liquid. Silicone fluids have an ability to rotate around the Si-O-Si bond resulting in liquidity as the value of “x” increases tremendously.

<b>Volatile</b>	<b>Low viscosity</b>	<b>Regular Viscosity</b>	<b>High Viscosity</b>	<b>Ultra High Viscosity</b>	<b>Gum</b>
0.65 visc	1 – 20	50-1,000	10,000 – 100,000	200,000 1,000,000	1,000,000+

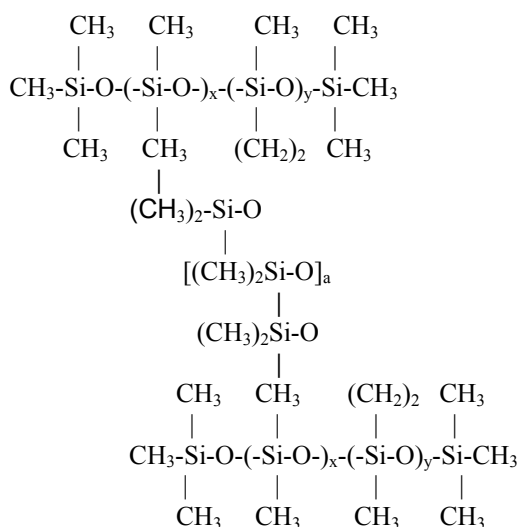
As one goes from left to right ( that is increasing viscosity) the “dp” increases but there is no crosslinking in these systems. This is the salient property of fluids and gums. Gums are extremely viscous, but have no crosslinking and like glass will flow with time.

There are a number of organofunctional fluids and gums having alkyl groups, vinyl groups and many others.

Silicone fluids are used for their ability to lower surface tensions in formulations. If they have a low degree “dp” they have a dry feel. This dry feel can be augmented by volatility, but there are many dry feeling materials that do not evaporate under ambient conditions.

## Silicone Elastomers and Resins

In order to address the concept of resins and elastomers one needs to address the concept of crosslink density. Consider the following very simple molecule (INCI dimethicone / vinyl dimethicone cross-polymer):

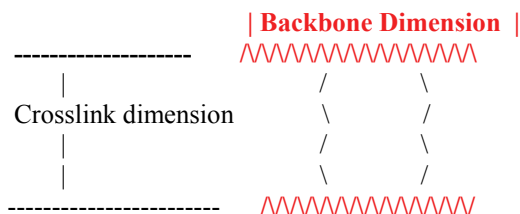


The crosslink density (“cd”) is defined by the value of y times two (one for each silanic hydrogen being crosslinked).

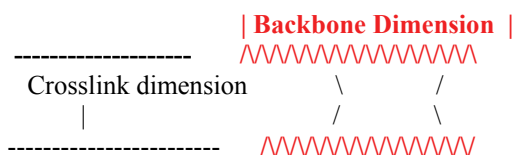
What of the “dp”? This becomes more complicated. There are two groups that have a “dp”, the silanic hydrogen compound which has a “dp” defined by the equation “dp”= x+y for each group in the polymer. There is also a “dp” contribution for each crosslinker which is defined by the equation “dp”= a

The following graphics are offered to provoke thought about the structure function relationship in silicone polymers. The first set demonstrates the relationship between the crosslink length and backbone length. When the two are roughly equal a “square polymer” results. This polymer is resin like while a polymer with a “disproportionate resin” one which tends to be more elastomeric.

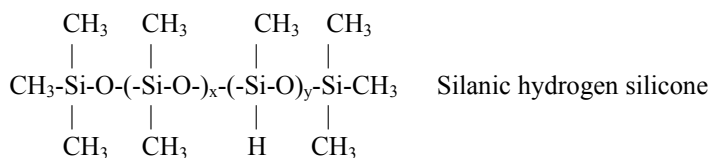
Example 1 "Square Resin" Backbone and Crosslink about equal



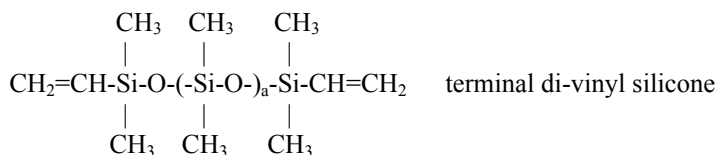
Example 2 "Disproportionate Resin" Backbone and Crosslink not equal



This molecule crosslinks the silanic hydrogen polymer using a vinyl silicone, made by the following reaction:



and



The INCI name is confusing, there are no vinyl groups in the molecule, only two methylene groups. Methylene groups  $\text{-(CH}_2\text{)}_2\text{-}$  are not vinyl  $\text{-CH=CH-}$ . If one then says vinyl dimethicone is a reactant and the concept is to register the product as a product by process, the name still is confusing. If this were the intent then dimethicone should be the other reactant, which clearly it is not.

Assuming we ignore the name and concentrate on if the product is a fluid, an elastomer or a resin?

We can eliminate fluid since there is crosslinking. Recalling that the salient property of fluids and gums is lack of crosslinking, elastomers and resins by contrast have crosslinking. This crosslinking determines the physical properties of the product. The term resin and elastomer define crosslinked systems but they are very specific systems. Elastomers and resins are solid systems. The elastomer is rubbery (like an elastic band) and resins being more highly crosslinked will crumble when pressed. The very simple test is to press the material between the fingers, if it does not crumble, and rebounds it is an elastomer. If it crumbles it is a resin.

We are completely without clue beyond this without specific values of “x”, “y”, and “a”. The y value determines crosslink density. As it goes up the product goes from a liquid ( a so-called crosslinked fluid) to an elastomer to a resin, however the value of “x” and the value of a and the ration one to the other will also determine the physical state. If “x” and “a” are both low a resin will result. As “a” and “x” are increased holding “y” constant the resin will first become elastomeric then fluid. It helps to consider the polymer like a spring, the higher the “x” value the more flexible the silanic hydrogen polymer. There are simply more groups between crosslink points. If “x” is zero all groups will be crosslinked with no spacers in between. The “a” value is also important for as it goes up the distance between the silanic hydrogen groups becomes greater. If “a” were made infinite, the product would have almost no effect of the crosslinking.

## Conclusion

This more accurate view of the world of silicone polymers results in some interesting though complicating concepts:

All elastomers and resins are crosslinked, but not all crosslinked products are elastomers or resins. There are in fact a class of liquid products that have crosslinking that are liquid and flow they are the so-called crosslinked fluids . They have interesting properties vis-à-vis silicone fluids, but are neither fluids (no crosslinking) nor elastomers nor resins (solids).

The fact that the terms elastomer and resin describe physical rather than chemical terms, the exact structures that meet these criteria are dependant upon the crosslinker structure and the backbone crosslink density. A single generic structure cannot adequately predict if the product will be an elastomer or a resin unless all the structural factors are described together.

The terms elastomer and resin and the implications as to waterproofing, film formation and transfer resistance properties cannot be clearly established unless one fully defines the system and all the values.

A full disclosure as to structure and all the values rarely happens either between silicone manufacturer and customer or patentee and patent office. Yet adequate disclosure is required to enable a patent and to ensure functionality in a formulation.



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