



Editors Note: This edition of the Silicone Spectator is presenting a second general article on Silicone Chemistry. This one was written in 2000. While the paper was written a long while ago the contents are still topical today. We hope you enjoy.

Silicone Emulsions and Surfactants – A Review

Anthony J. O'Lenick, Jr.
Siltech Inc.
Dacula, Ga. 30019
Originally Published: May 2000

Silicone Spectator®
P.O. Box 715
Dacula, Ga 30019

Andrew O'Lenick
Editor

Siliconespectator.com

This review, written in two parts, has the objective of supplying a working knowledge of the chemistry of silicone compounds to the practicing chemist. It has been divided into two parts, the first dealing with basic chemistry of silicones, and the second dealing with silicone based surfactants. This is the second part of the review.

Despite the fact that silicone compounds have been around for over fifty years, the chemistry of these materials remains elusive to the average formulating chemist. This is indeed unfortunate, since the chemistry of silicon atom and resulting silicone compounds is every bit as wide in scope and rich in content as the chemistry of the carbon atom and the resulting surfactant chemistry upon which it is based.

Background

Since most silicone compounds are water insoluble, delivery these material in aqueous systems is from emulsions. The use of emulsions in many processes is acceptable, but emulsions complicate other process and are completely ineffective in other processes.

Emulsions

All emulsion products comprise (a) water typically at least 40%, (b) silicone (typically 55%) and the remainder surfactant to make an emulsion. The fact that the silicone is contained in an emulsion by necessity requires that the delivery be from a micelle. Since there is an equilibrium that exists between the silicone on the substrate, like fabric, fiber, metal, rubber, hair or skin, and the silicone in the emulsion, much of the silicone ends up in the wash water. Not only is this very costly and an inefficient use of expensive raw materials, but there are real environmental concerns since the wash water ends up in the sewer. Emulsions are susceptible to freeze thaw instability and if detergents are added the emulsion will split due to shifting on the HLB. These problems notwithstanding, silicone emulsions are used in many industrial applications. These include thread and textile lubricants, mold release agents for rubber and many others. The emulsions tend to be specialized in their formulation to be ready to use, or just cut with water. Minimizing the additives, other than water, will allow for the formulation of the most stable products.

Some more interesting applications areas for emulsions include:

Printer's Solution

Oil based inks in lithographic printing use oil based inks. These inks contain a resin, which undergoes polymerization. Since the inks are not instantly cured, during the curing process a semi-solid ink occurs. This period during which the ink cures is referred to as "setting". In ordinary oil-based inks, setting will usually require 15 to 30 minutes. Complete curing will usually require 3 to 10 hr. During the setting and drying of oil based inks the printed

matter is subjected to smearing and destruction of the printed good. In addition, the substrate upon which the printing is done needs to be moved during the set and cure time, several problems can be encountered, including (a) ink smudge; (b) static electricity build-up and (c) paper tearing by the process of moving the paper through the high speed processing.

Silicone emulsions or emulsions containing both silicone oil and mineral oil are oversprayed on the printed goods during the drying process right after printing¹. These materials, called printer's solution in the trade, allow for lubrication, anti-smudge and anti-static properties on printed goods.

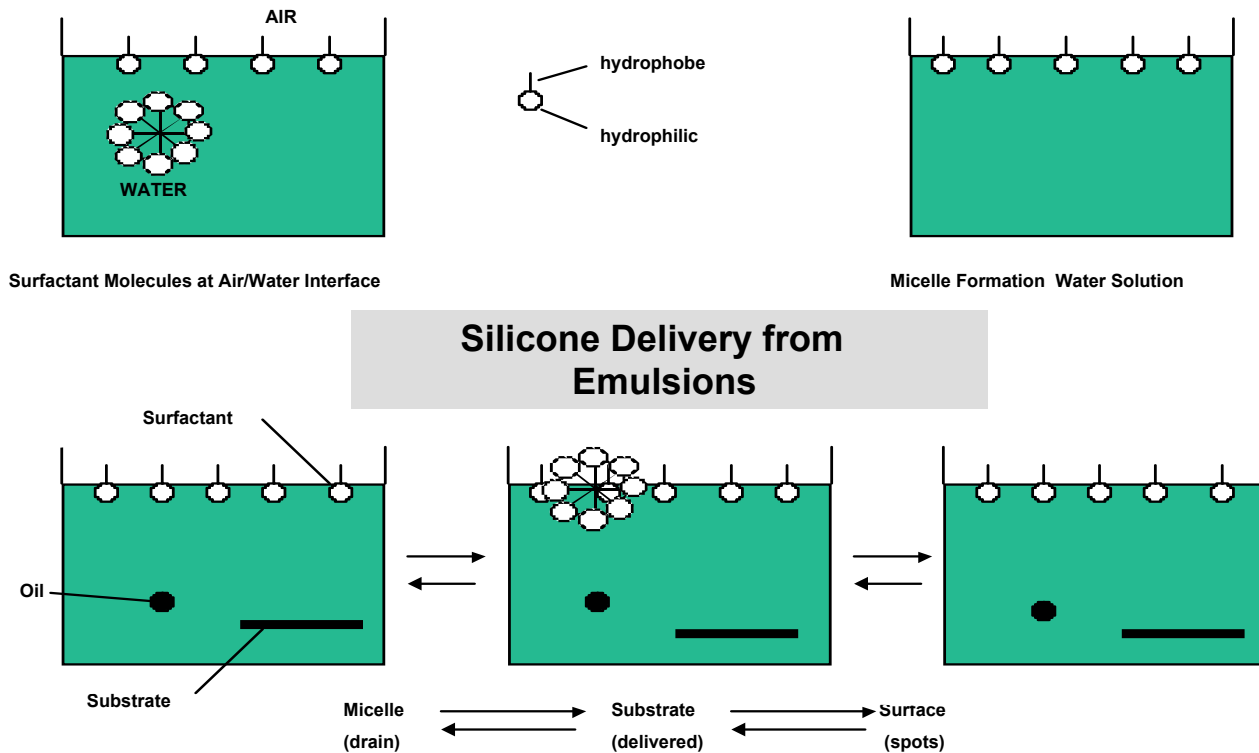
Tire Gloss

The use of silicone emulsions on automotive tires, as dressings is well known. These products make up a set of commercially important products for consumer application. The products are emulsions of an silicone fluid in water. Each product is then specialized for specific market niches. Many products contain additives. These include polyols, sugars like sorbitol, and other additives like diethylene glycol and glycerin. Newer products include cleaning agents and anti-oxidants.²

Typically, the preservative composition is first used to thoroughly wet the surface. After wetting the surface, sufficient time is then allowed for thorough penetration of the preservative into the surface layer of the material. It is believed that penetration occurs by capillary action whereby the molecules of the preservative composition, and especially the silicone fluid, are drawn into the surface. There, the molecules can hook or wrap around the molecules of the material to be protected to physically attach themselves thereto. At least one additional re-wetting of the surface should then be made, followed by a period of penetration. Some products suggest at least three applications of the preservative to the surface to be protected for best results³.

Silicone Delivery

Silicone delivered from emulsions are delivered from micelles as shown;



In order to overcome the limitation on the use of emulsions or silicone oils per se, silicone surfactants have been developed that provide non-micellar delivery to a variety of substrates.

Silicone Surfactants

A series of surfactants which are based upon silicone as a hydrophobe that contain other functional groups, similar to those seen in traditional surfactants have been and continue to be developed. In some instances, silicone is incorporated into a surface-active agent, with a polyoxyalkylene portion of the molecule and or a hydrocarbon portion of the molecule. As will become clear, this results in several unique properties of the surfactant.

Historically, silicone compounds have been available as water insoluble oily materials. This has limited the number of silicone compounds that the formulator could use in many

applications. Knowing some of the limitations in the use of silicone fluids, it is no surprise then that there is a desire to make more functional silicone compounds. Silicone compounds that not only provide the desired softening, conditioning and treatment affects but are self-emulsifying. The logical place to look for bridging technology is in the surfactant world. Surfactants are materials with an oil soluble group, generally fatty, and a water-soluble group. If one either includes a silicone group as the hydrophobe, or includes a silicone hydrophobe into the molecule a whole new world of formulator friendly compounds opens up.

In order to make silicone useful in aqueous systems, there are a variety of emulsions available. The use of an emulsion makes the silicone easier to handle, but there are issues related to emulsion stability that must be addressed. Specifically, the addition of surfactants to the emulsion may shift the HLB and split the emulsion. In addition, emulsions have a limited freeze thaw stability. Finally, there is an equilibrium between the silicone, the emulsifier and the substrate being treated. Often the emulsifier also has detergent properties and the majority of the silicone ends up in the wash water.

There are now a wide variety of silicone products, which differ both in structure and functional properties, available to the formulator. This allows for the greater formulation latitude and the creation of products that are optimized for some applications. The use of silicone, not merely as an oil phase requires the functionalization of the molecule to make it useful in application areas where a water insoluble product is not appropriate. Too often in the past the formulator has had to accept many of the drawbacks of the use of silicone oils in formulations, or leave them out altogether. Attempting to use silicone oils and compounds known prior to the 1990's in all applications would be like attempting to use fatty alcohol ethoxylates in all applications. The ability to make silicone formulator friendly has led to the synthesis of many new silicone based surfactants. Many of the newer products already in the market contain these materials, and more will in the future.

In order for one to make a surface-active molecule, one needs to have both a water-soluble and an oil soluble portion in the molecule. The traditional oil soluble portion of the molecule is fatty. The silicone surfactants substitute or add on silicone based hydrophobicity.

This results in materials that have the substantivity, lower irritation, skin feel and other attributes of silicone in addition to the properties one expects from the fatty surfactant. In molecules where silicone is predominate, the functional attributes of silicone will predominate. If the molecule has both a silicone and fatty hydrophobe present it will function with attributes of both of the materials. This allows for the formulation of a wide variety of products that have oil, water, silicone or variable solubility.

SILICONE MISCONCEPTIONS

1. SILICONES DEFOAM MINIMIZING THEIR USE IN FORMULATIONS.
2. ALL SILICONES ARE DIFFICULT TO FORMULATE.
3. ALL SILICONES ARE WATER INSOLUBLE.
4. ALL SILICONES ARE MINERAL OIL INSOLUBLE.
5. ALL SILICONES ARE GREASY.
6. SILICONES ARE AVAILABLE ONLY AT LOW HLB VALUES.
7. ALL SILICONES ARE LIQUIDS.
8. ALL SILICONES POLYMERIZE.
9. SILICONE PRODUCTS ARE NOT ANALOGOUS TO CARBON CHEMISTRY
MAKING COMPARISONS MEANINGLESS.
10. SILICONE COMPOUNDS ARE OF LIMITED USE IN FORMULATIONS.

There has been an explosion of new silicone compounds available that open a new world of applications possibilities. This process appears to be one of expanding scope covering both new applications and new molecules. Consequently, the review of all new technologies in the field of silicone surfactants is beyond the scope of this review. In order to

give the reader a flavor of the type of things that can be done with this technology, the dimethicone copolyol compounds and their related esters were chosen.

Dimethicone copolyol

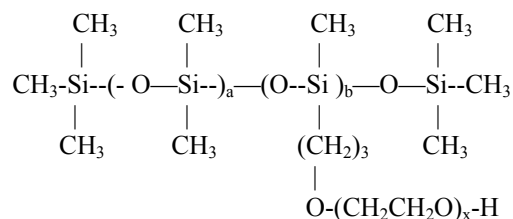
a. Structure

The dimethicone copolyol has been the workhorse of the personal care industry for many years. Since silicone fluids are difficult to formulate into aqueous products, many formulators have used dimethicone copolyol.

Since the molecule contains water-soluble groups, the resulting surfactant is easily added to aqueous products. The problem is that most of the products so derived are generally so water soluble as to become ineffective as conditioners and softeners.

Dimethicone Copolyol Chemistry

There are a number of descriptive names used to denote dimethicone copolyol. Silicone glycols, silicone surfactants, and many others have been used by differing industries. These materials are very important additives in the urethane field for foam applications, in agricultural applications as super wetters and in personal care as conditioners. The Cosmetics, Toiletry and Fragrance Association uses the term dimethicone copolyol to describe this class of silicone / polyoxyalkylene derivatives. Dimethicone copolyol surfactants are a class of compounds that conform to the following structure:



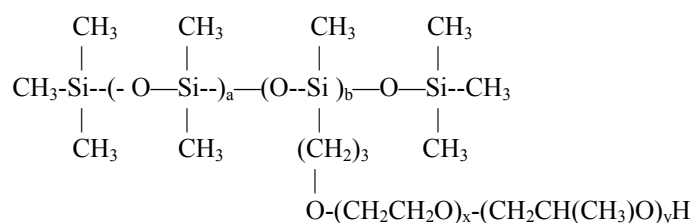
The nomenclature was developed to reflect the fact that the molecule is (a) a silicone polymer (dimethicone), (b) a copolymer (copolyol part), and (c) hydroxyl functional (ol ending).

The original concept while creative does not give the total information needed for defining the molecular structure. For example, the current practice is to call methoxy capped product dimethicone copolyol, even though they lack the hydroxyl group that originally justified the ol ending. Since the capping process is not totally efficient, there is residual hydroxyl groups found even in the dimethicone copolyol compounds that claim to be capped. Other names include silicone glycols, and silicone polyethers.

Terminal Group Functionality

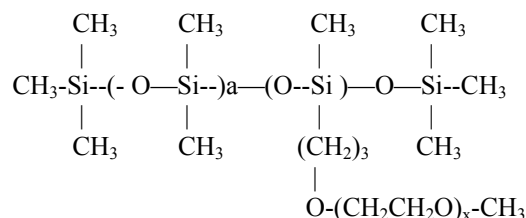
Hydroxyl Terminated Dimethicone Copolyol

The structure of the dimethicone copolyol having a hydroxyl-terminated group is as follows:



Methoxy Terminated Dimethicone Copolyol

The structure of the dimethicone copolyol having a methoxy-terminated group is as follows:

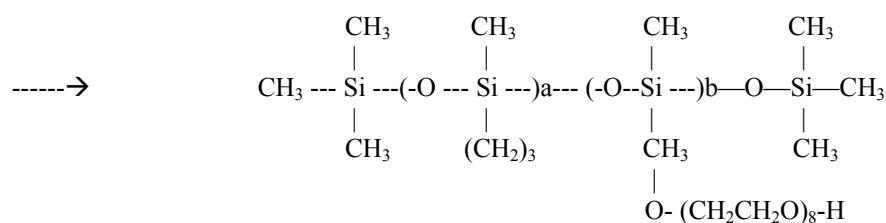
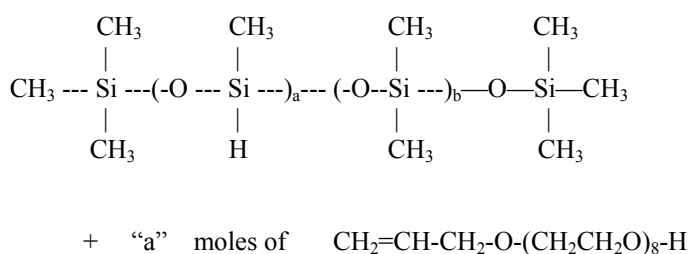


The molecular structure is complicated further by the fact that the values of a, b, and x and y vary quite considerably within the class and are generally not revealed by manufacturers.

Finally, the raw materials used to synthesize these polymers are themselves polydisperse polymers having an oligomeric distribution. The resulting polymer is an oligomeric distribution of an oligomeric distribution.

Despite the complications, which are not too unlike those found in ethoxylated fatty surfactants, silicone polymers can be analyzed and structure function properties determined. The process used for their synthesis is reproducible and gives products with little variation, albeit complex mixtures.

It must be clearly understood that the polymer structures given in the above table are equilibrium mixtures having a nominal or average structure as shown. This is not unlike ethoxylated alcohols that are also oligomeric mixtures of different ethoxylated species. The reaction is as follows²⁰;



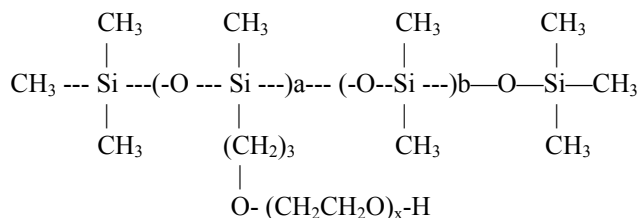
Dimethicone Copolyol Properties

One of the determining factors in the functional properties of dimethicone copolyol compounds is polymer's the molecular weight. Generally, the very low molecular weight polymers are

outstanding wetting agents. Because of their proclivity to wet surfaces, they penetrate tissue and are irritating. As one increases the molecular weight, the wetting properties decrease marginally. As the molecular weight increases, the dimethicone copolyol compound becomes a conditioner and emulsifier. Wetting properties are lost. This variability of function as a function of molecular weight needs to be understood by formulators using these materials.

Structure

Since dimethicone copolyol compounds are the produced by an equilibration reaction, the result is a complex series of homologous oligomeric products. Recalling the structure:



This means that there is not one product, but a range of products in which the value of “a” and “b” vary. If the value of “a” relative to “b” is too low, regardless of the number of moles of ethylene oxide (the “x” value), a soluble product will not result. This is because there will be a concentration of insoluble oligomer present. The number of D units to D* units necessary to make a product that forms a microemulsion in water, can be calculated using a formula;

$$D^* = (0.15)(D)+1$$

This product that forms a microemulsion is significant since if the number of D* units relative of D units in increased, a water-soluble product will result. The formula was determined making and evaluating a variety of dimethicone copolyol products having eight moles of ethylene oxide added.

The results are as follows⁴

Table 1
Solubility (10% Water)

D	D*	Predicted	Observed
---	----	-----	-----
5	1.0	Insoluble	Insoluble
5	2.0	Soluble	Soluble
10	2.0	Insoluble	Insoluble
10	2.5	Micro	Micro
10	3.0	Soluble	Soluble
20	3.5	Insoluble	Insoluble
20	4.0	Micro	Micro
20	4.5	Soluble	Soluble
24	4.0	Insoluble	Insoluble
24	4.5	Micro	Micro
24	5.0	Soluble	Soluble
40	6.0	Insoluble	Insoluble
40	7.0	Micro	Micro
40	8.0	Soluble	Soluble

The above observation explains why there is not an unlimited wide range of dimethicone copolyol compounds offered. Since most dimethicone copolyol compounds are sold into water-soluble applications, the compounds generally have a very low D/D* ratio.

Properties⁵

The functional attributes of dimethicone copolyol compounds are directly related to the structure. The molecular weight is one of the salient factors in determining functionality.

	<u>Designation</u>	<u>M.W.</u>	<u>E.M.W.</u> **
A	MD*M	632	632
B	MD*DM	701	701
C	MD ₂ *D ₂ M	1240	620
D	MD ₃ *D ₅ M	1917	639
E	MD ₄ *D ₇ M	2525	631
F	MD ₄ *D ₈ M	2594	649

D* is $-(\text{CH}_2)_3\text{-O-(CH}_2\text{CH}_2\text{O)}_8\text{-H}$

** - Molecular weight divided by number of D* units

Cloud Point

Dimethicone copolyol compounds, like many hydrocarbon based non-ionic surfactants exhibit high cloud points when an aqueous solution is heated. As a 1-% solution of the dimethicone copolyol is heated, a temperature is encountered at which the material is no longer soluble. This is referred to as the high cloud point.

The high cloud point phenomenon is related to how the polyoxyalkylene portion of the molecule hydrogen bonds with water molecules. At higher temperatures the hydrogen bonding with water is lost as the polyoxyalkylene groups in the tail of the molecule rotate, resulting in lower solubility. Upon cooling, the dimethicone copolyol again becomes soluble.

	<u>Designation</u>	<u>M.W.</u>	<u>Cloud Point (1 %DW)</u>
A	MD*M	632	58 °C
B	MD*DM	701	58 °C
C	MD ₂ *D ₂ M	1240	57 °C
D	MD ₃ *D ₅ M	1917	58 °C
E	MD ₄ *D ₇ M	2525	58 °C
F	MD ₄ *D ₈ M	2594	58 °C

The cloud point is related to the length of the polyoxyethylene group in the molecule and was rather independent from the silicone portion of the molecule. A statistical analysis of the cloud point data suggests that fully 98.7% of the data variability is accounted for by the length of the ethylene oxide chains.

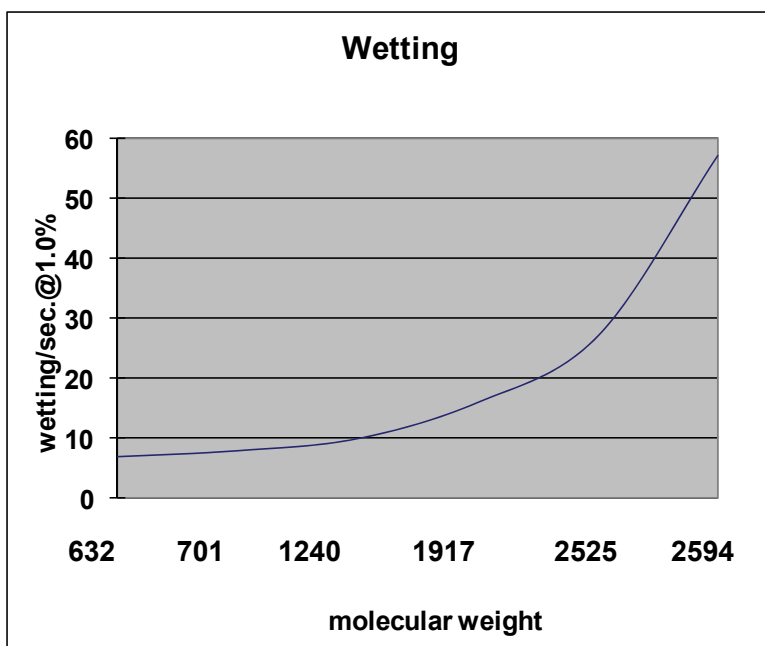
Wetting

Draves Wetting Test- In this test a 0.1% solution of dimethicone copolyol is used to sink a cotton skein.

	<u>Designation</u>	<u>M.W.</u>	<u>Wetting @ 0.1%</u>
A	MD*M	632	7 sec
B	MD*DM	701	8 sec
C	MD ₂ *D ₂ M	1240	10 sec
D	MD ₃ *D ₅ M	1917	16 sec
E	MD ₄ *D ₇ M	2525	27 sec
F	MD ₄ *D ₈ M	2594	57 sec

The above data shows that there is a strong relationship between molecular weight and wetting. The lower molecular weight materials have lower wetting times. The shape of the curve is also very important. Specifically, the fact that the curve does not become steep until the molecular weight of the dimethicone copolyol reaches over 1240 is a significant finding. The non-linearity of the graph of wetting time vs. molecular weight of the dimethicone copolyol

predicts that molecules having a molecular weight between 700 and 1250 should be effective wetting agents. This coupled with irritation data will allow for the selection of cost-effective materials that are both good wetting agents and possess low irritation.



CMC and Surface Tension at CMC

The CMC (critical micelle concentration) and the surface tension at CMC are major properties of surfactants. The data suggests that the lower limit for surface tension for compounds of this type is 20 dynes/cm², due to the abundance of methyl groups at the interface.

	<u>Designation</u>	<u>MW..</u>	<u>CMC</u>	<u>ST@CMC</u>
A	MD*M	632	20 mg/l	20 dynes/cm ²
B	MD*DM	701	20 mg/l	20 dynes/cm ²
C	MD ₂ *D ₂ M	1240	19 mg/l	19 dynes/cm ²
D	MD ₃ *D ₅ M	1917	23 mg/l	21 dynes/cm ²
E	MD ₄ *D ₇ M	2525	21 mg/l	23 dynes/cm ²
F	MD ₄ *D ₈ M	2594	21 mg/l	21 dynes/cm ²

Solubility and % polyoxyethylene group

	<u>Designation</u>	<u>MW</u>	<u>Water</u>	<u>Mineral Oil</u>	<u>Methanol</u>
A	MD*M	632	S/S	D/D	S/S
B	MD*DM	701	S/D	D/D	S/S
C	MD ₂ *D ₂ M	1240	S/S	D/D	S/S
E	MD ₄ *D ₇ M	2525	S/S	D/D	S/S
F	MD ₄ *D ₈ M	2594	S/S	D/D	S/S

The water solubility is directly related to the amount of ethylene oxide in the molecule.

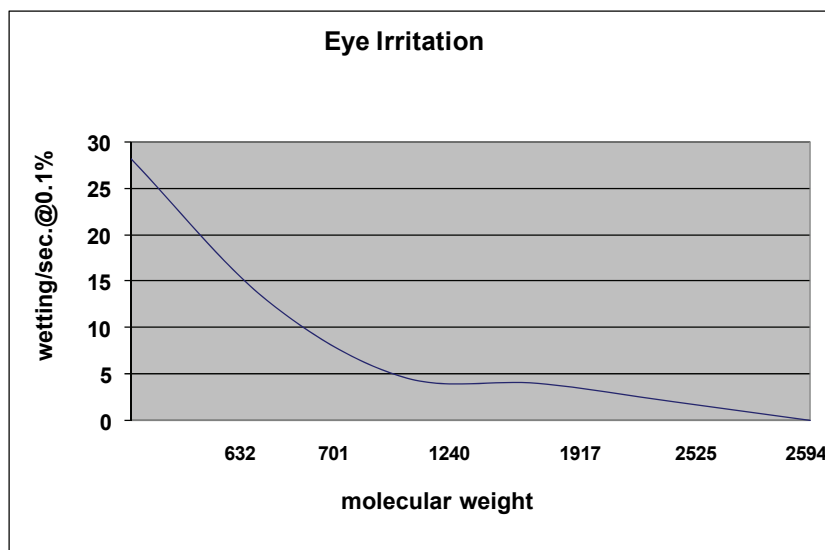
	<u>Designation</u>	<u>MW</u>	<u>%EO</u>
A	MD*M	632	74.4
B	MD*DM	701	67.0
C	MD ₂ *D ₂ M	1240	75.8
D	MD ₃ *D ₅ M	1917	73.5
E	MD ₄ *D ₇ M	2525	74.5
F	MD ₄ *D ₈ M	2594	74.7

Eye Irritation

Perhaps one of the most interesting properties evaluated in our study is the effect of molecular weight upon eye irritation. There have been many models proposed for the irritation properties of surfactants.

	<u>Designation</u>	<u>MW</u>	<u>1 day</u>	<u>3day</u>	<u>7 day</u>
A	MD*M	632	28.3	17.0	4.3
B	MD*DM	701	13.0	9.0	2.0
C	MD ₂ *D ₂ M	1240	4.7	9.3	2.0
D	MD ₃ *D ₅ M	1917	4.0	2.0	0.0
E	MD ₄ *D ₇ M	2525	2.0	0.7	0.0
F	MD ₄ *D ₈ M	2594	0.0	0.0	0.0

The above data does in fact indicate that the irritation potential is related to molecular weight. The data was also quite surprising in that there is a very sharp drop in irritation as the molecular weight is increased. The graph below shows the effect.



The proper selection of a dimethicone copolyol can result in a product that has a desirable combination of properties for personal care formulations. The molecule that exhibits the lowest wetting times are those that are low in molecular weight, which happen to be those materials that are the most irritating to the eye. The non-irritating compounds are poor wetting agents. There are molecules that are very efficient when one desires a low irritation wetting agent.

Future Trends

New markets will continue be developed based upon specialty applications of silicone materials. The technology used to make silicone compounds, although immense and very interesting, is still in its infancy relative to surfactant chemistry. The balance between the fatty-soluble, silicone-soluble and water-soluble groups in surfactant molecules determine the functional properties of the molecule. The utilization of new silicone compounds will be increasingly determined by three key factors. They are:

- a. the synthesis skills of the organo silicone chemist,
- b. the formulating and engineering skills of the chemists and engineers that design formulations and processes using these materials and
- c. the ability of both types of companies to modify molecules for specific applications and formulate the products to meet consumer expectations.

References

1. U.S. Patent 5,460,856 issued October 1995 assigned to Siltech Inc.
2. U.S. Patent 5,432,217 issued July 1995, assigned to Siltech Inc.
3. U.S. Patent 3,956,174 issued May 1976 assigned to VIP Products.
4. Vrckovnik, Richard, Unpublished work
5. Preito, Nelson and O'Lenick, Jr. Anthony, Structure Function Relationship of Dimethicone Copolyols, Journal of Surfactants and Detergents, Vol2., No. 3 (July 1999) p. 438. Presented as a paper 1999 AOCS Annual Meeting.



© 2005 Thomas O'Lenick

Siltech believes that the information in this supplement is an accurate description of the typical uses of the product. However, we disclaim any liability for incidental or consequential damages, which may result from the use of the product that are beyond its control. Therefore, it is the user's responsibility to thoroughly test the product in their particular application to determine its performance, efficacy and safety. Nothing contained herein is to be considered as permission or a recommendation to infringe any patent or any other intellectual property right.

© March, 2009 Siltech LLC

Silwax[®], Siltech[®], Silsurf[®] are registered trademarks of Siltech, all rights reserved

Silicone Spectator[®] is a registered trademark of SurfaTech Corporation.

All rights reserved.

About Silicone Spectator[™]

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.