Silicones for Personal Care,

2nd Edition

Anthony J. O'Lenick Jr.

Silicones for Personal Care, 2^{nd} Edition

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Table of Contents

Preface

First Edition

The intention of this book is to provide a source of information to the cosmetic chemist on the basic chemistry and properties of silicone polymers used in the cosmetics industry. Over the years, these silicone polymers have become more and more important in advanced cosmetic formulations. As these materials have a tendency to be more expensive compared to traditional fatty materials, the benefit that silicones provide to formulations needs to be either more effective at lower concentrations or must provide benefits not attainable with other traditional products. While silicone compounds can do both, it is critically important to properly select the right silicone compound, and therefore, understanding the structure of these materials is crucial to successful selection.

The book stresses the various steps on the synthesis of silicone compounds: construction, functionalization and derivitization. As you will see, each has a profound impact on the performance and each needs to be understood. Many suppliers of these materials do not provide such critical information, which makes using their products in cosmetic formulations much like throwing darts in the dark—you may hit the bull's-eye, but the odds are highly unlikely.

The topic of silicone polymers for personal care is broad in scope and cannot be contained within a single work. It is also a topic in which many new developments are being made, any of which could revolutionize the industry. Each new invention builds upon the work of the previous inventor and the science as a whole advances. It is incredible that, in 1946, the silicone pioneer Rochow, looking at the very impressive body of work that he had done, wondered if there was any commercial utility to these products. The commercial reality of silicone technology requires a different skill set—that of the chemist and the engineer. It is the combination of the two contributions that keeps product development moving forward.

Second Edition

The years have passed rapidly since the first edition. I am most grateful to update this work for a second edition. What is most interesting to me is the rate of growth of the use of silicone compounds in our industry and the collective creativity of the raw material manufacturer, finished product formulator and the consumer product marketer. The raw materials, finished products and substantiated claims that have been developed in the last five years have been truly magnificent. **Table P.1** shows the dramatic growth in patents that include the terms "silicone" and "cosmetic." One US patent was issued in the five-year period 1976–1980. In the last two years, there have been an incredible 6,034 US patents located by the same search.

Both the number of patents and products based upon silicone have grown immensely. It is the goal of this book to provide information that will allow the researcher to develop and commercialize new products that meet consumer needs.

Table P.1. US Patents Containing Words "Silicone" and "Cosmetic"

Period	Patents	% Issued
1976–1980	1	0.01
1981–1985	11	0.1
1986–1990	28	0.3
1991–1995	69	0.9
1995–1999	131	1.3
2000–2004	3,282	34.3
2004–2006	6,034	63.1
Total	9,556	100.0

The Author

Anthony J. O'Lenick Jr.

Anthony J. O'Lenick Jr. is president of Siltech LLC, a company he founded in 1989, specializing in organo-functional silicones and specialty chemicals. He has more than 250 patents and 30 years of experience in innovative personal care ingredients. He has held technical and executive positions at Alkaril Chemicals, Henkel Corp. and Mona Industries.

Tony has four published books: *Patent Peace of Mind* (Allured Publishing Corp., 2008); *Surfactants—Strategic Personal Care Ingredients* (Allured Publishing Corp., 2005); *Silicones for Personal Care* (Allured Publishing Corp., 2003) and *Primary Ingredients* (Zenitech, 1998). He has written more than 40 technical articles in scientific and industry journals, including *Cosmetics & Toiletries magazine* and *HAPPI*. Additionally, he has authored two book chapters and co-edited *Chemistry of Colored Cosmetics* (Marcel Dekker). His next books, being published by Allured Publishing Corp., include *Oils of Nature* and *Silicones for Personal Care, 2nd Edition*. Tony also writes the *Comparatively Speaking* column for *Cosmetics & Toiletries magazine*.

Tony is the recipient of numerous awards for his research on silicone-based surfactants, including awards from the Soap and Detergents Association and the American Oil Chemists' Society. His work in developing a three-dimensional HLB system (oil-water-silicone) and its use in formulating emulsions was recognized by the Advanced Technology Group. In 2006, Tony was elected as a fellow of the Society of Cosmetic Chemists (SCC), having served the society as a member of its Committee on Scientific Affairs and Education. He teaches a course for the SCC on silicones and on patents. Additionally, Tony has been an invited speaker at a symposia organized by the Cosmetics Toiletry and Fragrance Association (CTFA), Allured Publishing and HBA. Tony and his wife reside outside of Atlanta. They have three sons (Kevin, Thomas and Andrew), two daughters-in-law (Nicole and Courtney) and two grandsons (Ty and Jackson).

Acknowledgements

The author gratefully acknowledges his wife, Alice, who has provided him with encouragement during the various phases of his work and throughout the last 30 years. He also acknowledges the contribution of Kevin O'Lenick, for reading the manuscript and making helpful suggestions.

Chapter 1

Introduction

Since the publication of the first edition of this book, the importance of silicone compounds in a variety of personal care products has continued to grow. New materials have been introduced and the technology has been expanded. Since its original military use to make grease to coat aircraft spark plugs during World War II, the use of silicones has virtually exploded.

The ultimate raw material for the preparation of silicone compounds is SiO_2. **Table 1.1** shows the properties of SiO_2.

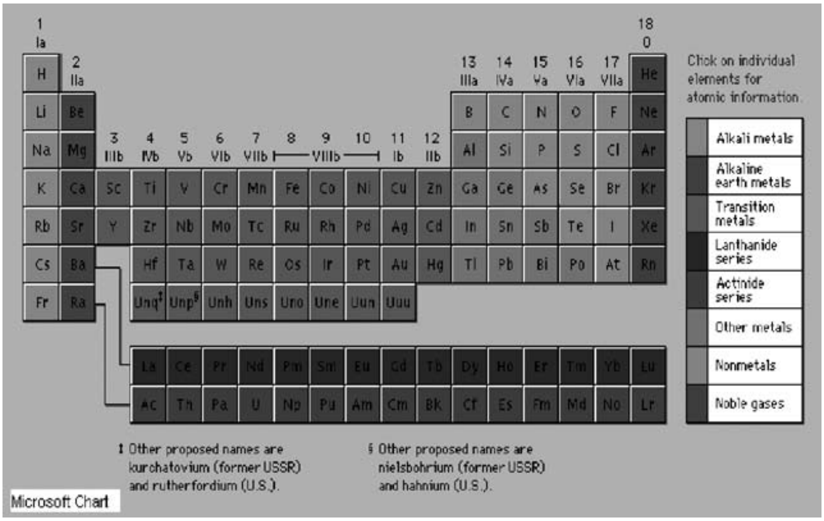
Table 1.1. Properties of SiO_2

Molecular Formula	**SiO_2**
Molecular Weight	60.1 Grams/ mole
CAS Number	14808-60-7
Melting Point	1650°C
Boiling Point	2230°C
Other Names	Silica Silicone dioxide Sand Quartz Glass Amethyst Flint Jasper Opal

Silicon

Silicon is the 14th element in the periodic table. It rarely occurs naturally in its free state, but it accounts for about 25% of the earth's crust in its combined form. Pure silicon crystals are only occasionally found in nature as inclusions with gold and in volcanic material. Silicone compounds are unique materials both in terms of the chemistry and in the wide range of useful applications. In combination with organic moieties, silicon provides unique properties that function in a wide temperature range, making the silicone-based products less temperature sensitive than most organic surfactants. These properties can be attributed to the strength and flexibility of the Si-O (silicon-oxygen) bond, its partial ionic character and the low interactive forces between the nonpolar methyl groups, characteristics that are directly related to the comparatively long Si-O and Si-C (silicon-carbon) bonds. The length of the Si-O and Si-C bonds also allows an unusual freedom of rotation, which enables the molecules to adopt the lowest energy configuration at interfaces, leading to surface tension values substantially lower than those of organic polymers. A review of the periodic chart reveals that silicon and carbon are one over the other (see **Figure 1.1**)[1]. This allows one to predict a great number of similar properties between the two elements.

Figure 1.1. Periodic Chart



1 Ia	2 IIa	3 IIIb	4 IVb	5 Vb	6 VIb	7 VIIb	8	9 VIIIb	10	11 Ib	12 IIb	13 IIIa	14 IVa	15 Va	16 VIa	17 VIIa	18 0
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Unq†	Unp§	Unh	Uns	Uno	Une	Uun	Uuu							
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Click on individual elements for atomic information.

- Alkali metals
- Alkaline earth metals
- Transition metals
- Lanthanide series
- Actinide series
- Other metals
- Nonmetals
- Noble gases

† Other proposed names are kurchatovium (former USSR) and rutherfordium (U.S.).

§ Other proposed names are nielsbohrium (former USSR) and hahnium (U.S.).

Microsoft Chart

Comparing Silicon with Carbon

There has been a lot of science fiction interest in the similarity between silicon and carbon. In an episode of Star Trek a life form referred to as a "Horta" was said to have its chemistry based upon silicon. While interesting as science fiction, this is not a scientific possibility in a world where our chemistry applies. **Table 1.2** shows the comparison of silicon with carbon. One of the major similarities is the affinity for oxygen exhibited by the two elements, but there are also fundamental differences. The fundamental differences include:

- The oxides of the two elements are vastly and fundamentally different. CO_2 is a gas at room temperature and atmospheric pressure. It consists of simple CO_2 molecules, O=C=O. The oxide of silicon SiO_2 is a crystalline polymer with a very high melting point. It is difficult to envision a life cycle that replaces CO_2 with SiO_2, since the latter is a crystal.
- The hydrides of silicon are called silanes. These analogous compounds in the carbon world are referred to as alkanes. Silanes are very reactive compounds. They react violently with oxygen, and ignite or explode spontaneously in contact with air. Fortunately, alkanes do not react the same way. It would be equally difficult to envision a world based upon silanes rather than alkanes.
- Silicon compounds do not form multiple bonds between atoms while carbon compounds do.

It's clear we are not likely to encounter silicon-based life forms in the near future, but the chemistry is interesting and important to the cosmetic chemist. **Table 1.2**[2] shows a comparison of the elements silicon and carbon.

Table 1.2. Comparison of Silicon and Carbon

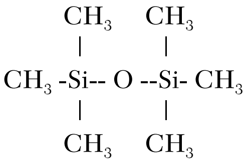
Property	Silicon	Carbon
Atomic Weight	28.0855	12.000
Phase	Solid	Solid
Melt Point	1414°C	4427°C
Boiling Point	3583°C	Sublimes
Electronegativity	1.90	2.55
Isotopes	^{28}Si (92.2%) ^{29}Si (4.67%) ^{30}Si (3.1%) Provides ^{29}Si NMR	^{12}C 98.8% ^{13}C 1.2% Provides ^{13}C NMR

Terminology

One of the most basic technical errors made by chemists is confusing silicon with silicone. Silicon is used to refer to the elemental material, (Si); silicone to refer to materials in which silicon is bonded to oxygen. Silicon is the most elemental raw material from which all silicone chemistry finds its roots. Since it is not common in the metallic form in nature, the first step is to produce silicon from quartz. The term silicone is actually a misnomer. It was incorrectly thought that the early silicone polymers were silicon-based ketones, hence the contraction silicone. Despite this error, the term is still widely used and accepted.

Another important nomenclature issue is the difference between silicone and silane. A silicone compound has a Si-O-Si bond while the silane has only one Si atom. Hence, $(CH_3O)_3$-Si-CH_3 is methyl trimethoxysilane.

The difference between a volatile and a cyclic is also an important distinction. The most commonly understood cyclic compound is the D4 and D5. These cyclic compounds are ring structures with alternating Si and O having four and five Si and O atoms, respectively. These compounds are also volatile, meaning they evaporate. Cyclic structures that have a higher number of silicon and oxygen atoms, like 20 Si and 20 O, are referred to as D20 and, despite being cyclic, are nonvolatile. For example, hexamethyl disiloxane (MM) is volatile but not cyclic. The structure of hexamethyl disiloxane is:



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

Silicone Compounds

The commercial process for making silicone compounds is a multistep transformation that converts inorganic quartz, a common mineral, into the multifunctional silicone compounds used in many formulations. This transformation process is shown in **Figure 1.2**.

Silicon from Quartz

Silicon is obtained by the thermal reduction of quartz (SiO2) with carbon. The reaction is conducted at a very high temperature and therefore is commonly carried out where there is abundant inexpensive power. The reaction is as follows:

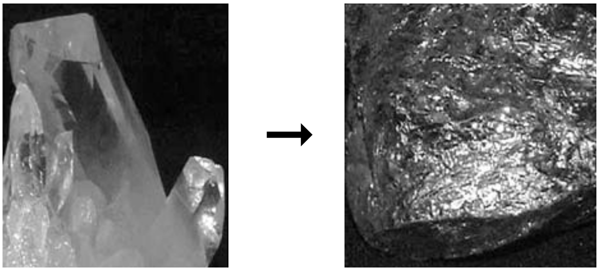
$$SiO_2 + C \xrightarrow{1700°C} Si + CO_2$$

The resulting silicon is generally at least 99% pure. In addition, certain trace contaminants must also be controlled to obtain a material that is suitable for the preparation of silicone compounds. Since the silicon produced is a solid metallic material, it must be crushed into powder with a particle size of between 100 and 350 nanometers (nm) for use in the next reaction—the Rochow process (a process named after Eugene G. Rochow, the father of silicone chemistry[1]).

Rochow Process[2]–Chlorosilanes from Silicon

The Rochow process technology is complicated and requires high capital for the

Figure 1.2. Silicone Transformation



Quartz → **Silicon**

Silicon →

Rochow Process

Si + CH_3Cl —> $(CH_3)_2$–Si–Cl_2
$(CH_3)_3$–Si–Cl
CH_3–Si–Cl
Si–Cl_4
CH_3HSiCl_2
CH_3HSiCl
Others

Chlorosilanes

Rochow Process

Si + CH_3Cl —> $(CH_3)_2$–Si–Cl_2
$(CH_3)_3$–Si–Cl
CH_3–Si–Cl
Si–Cl_4
CH_3HSiCl_2
CH_3HSiCl
Others

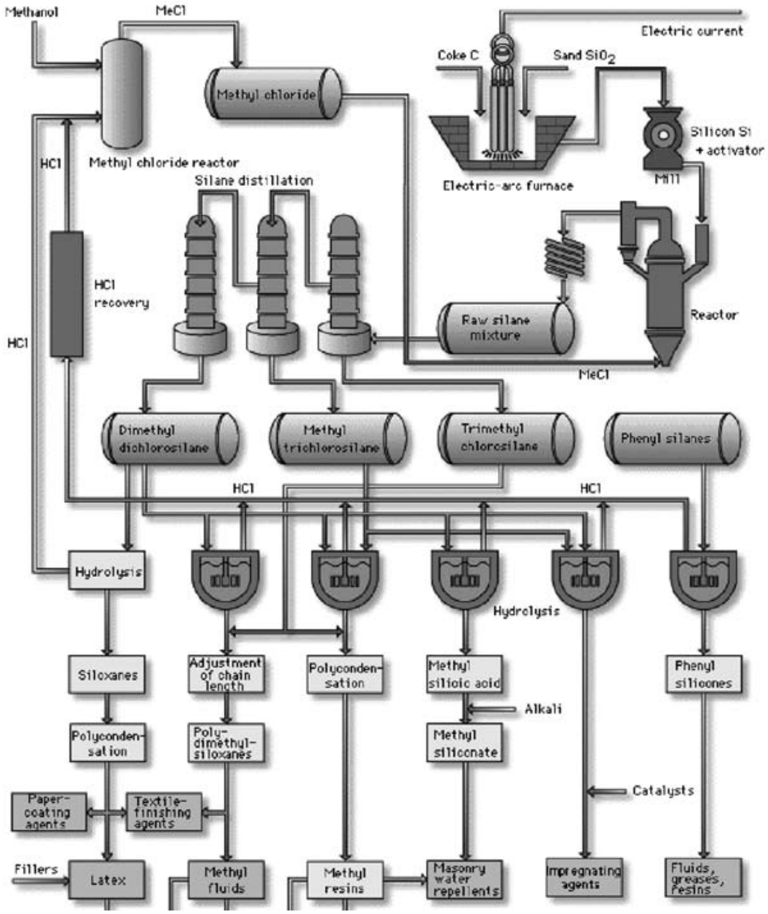
→ Hydrolyzate

Hydrolyzate →

- * Organo-functionals
- * Gums
- * Cyclic Silicones
- * Dimethicone
- * Dimethiconol
- * Silicone Surfactants

construction of plants suitable to practice the chemistry. As a result, few companies actually carry out the Rochow process. Because silicon is crushed prior to reaction in a fluidized bed, the companies practicing this technology are referred to as "silicon crushers." This is an elite group of companies; being referred to as a silicon crusher is considered an honor in the silicone world. **Figure 1.3** shows a silicone flow chart (Wacker).

Figure 1.3. Silicone Flow Chart



Commercially, the Rochow process is the most important route for the preparation of silicone compounds. In this process, methyl chloride is reacted with solid silicon metal in the presence of copper catalysts and certain promoters to produce a mixture of chlorosilanes. Simplistically, the overall reaction is as follows:

$$2\ CH_3\text{-}Cl + Si \xrightarrow[\text{Catalyst}]{300°C} Me_2SiCl_2$$

In fact, a complex mixture of products is actually obtained:

$$Si + 2\ CH_3Cl \rightarrow \begin{array}{l} (CH_3)_2\text{-}Si\text{-}Cl_2 \text{ (Predominant)} \\ (CH_3)_3\text{-}Si\text{-}Cl \\ CH_3\text{-}Si\text{-}Cl_3 \\ Si\text{-}Cl_4 \\ CH_3HSiCl_2 \\ (CH_3)_2HSiCl \\ \text{Others} \end{array}$$

The predominant material obtained is dimethyldichlorosilane (approximately 80% by weight). In order of decreasing concentration, the most abundant compounds are methyltrichlorosilane (approximately 12% by weight), followed by trimethylchlorosilane (approximately 4%) and methylhydrogendichlorosilane (approximately 3% by weight.). This composition information is very important since it drives the economics of the silicone business. Every pound of chlorosilanes produced results in the distribution of hydrolysis derivatives described. The cost of each derivative must be allocated in proportion to the amount produced as well as its commercial demand. To operate business profitably, every pound of product produced must be sold. This, by definition, makes the basic silicone business a commodity business. Specialty producers, on the other hand, make what they can sell and do not have to balance by-product and co-product streams. Since many silicone surfactants are based upon methylhydrogendichlorosilane, a relatively minor component of the silane stream, the cost of these materials is high in relation to silicone fluids based upon dimethyldichlorosilane.

The reaction to make chlorosilanes is quite complex and is carried out at a temperature of about 300°C under pressures of around 3 bars. The mass of starting material must be heated to initiate reaction. Once the reaction temperature is reached, the reaction becomes exothermic and, consequently, requires very stringent temperature control. It is a solid/gas reaction carried out in a fluidized bed reactor. To maximize the reaction efficiency, the solid silicon must be low in other metallic components. The fine residue that is extracted from the process is dependant on the quality of the silicon going into the process but is generally made up of Cu, Fe, Al and Ca. Consequently, silicon with low concentrations of these elements is desired for the process. The nomenclature for chlorosilanes is presented in **Table 1.3**.

Hydrolyzate—Silicone from Chlorosilanes[3]

The preparation of silicone compounds from chlorosilanes is an important synthetic pathway. The hydrolysis process is used to achieve this transformation. During this process, the chlorosilane compounds produced in the Rochow process are reacted with water, converting them into a mixture of linear and cyclic compounds. The exact composition of the Rochow products, the conditions of pH, the concentration of water and the temperature of hydrolysis determine the exact composition of the hydrolysis products produced.

Table 1.3. Chlorosilane Nomenclature

Name	Structure
Trimethylchlorosilane	$(CH_3)_2$-Si-Cl_2
Dimethylchlorosilane	$(CH_3)_3$-Si-Cl
Methyltrichlorosilane	CH_3-Si-Cl_3
Tetrachlorosilane	Si-Cl_4
Methyltrichlorosilane	CH_3HSiCl_2
Dimethylchloro silane	$(CH_3)_2HSiCl$

Since the Rochow process produces primarily dimethyldichlorosilane, the reaction of that component with water is:

Hydrolysis of chlorosilane to produce HCl and siloxanediol

$$(CH_3)_2SiCl_2 + H_20 \rightarrow HCl + (CH_3)_2Si(OH)_2$$

This results in the formation of hydrochloric acid and a siloxanediol. The by-product HCl must be handled with care to avoid corrosion of the equipment.

The following process results in two types of compounds that are used by the industrial chemist: silanol (dimethiconol) and cyclomethicone. The former is used in hair gloss compounds and the latter is commonly used in antiperspirant compositions.

Dehydration of siloxanediol to cyclomethicone and silanols

$$(CH_3)_2Si(OH)_2 \rightarrow H_2O + HO\text{-}(CH_3)_2SiO)nH + \text{cylclomethicone}$$

In his book, The Chemistry of Silicones (1946), Rochow ends with the statement: "With this in mind, it can only be said that a start has been made in organosilicone chemistry and that perhaps something may come of it." 56 years later, we can safely assume that a great deal will be done to utilize this chemistry and the development will continue for years to come.

Table 1.4 outlines the hydrolysis products of the major chlorosilanes produced in the Rochow process.

Table 1.4. Chlorosilane Nomenclature

Chlorosilane Name	Chlorosilane Structure	Silanol Structure
Trimethylchlorosilane	$(CH_3)_2\text{-}Si\text{-}Cl_2$	$(CH_3)_2\text{-}Si\text{-}OH_2$
Dimethylchlorosilane	$(CH_3)_3\text{-}Si\text{-}Cl$	$(CH_3)_3\text{-}Si\text{-}OH$
Methyltrichlorosilane	$CH_3\text{-}Si\text{-}Cl_3$	$CH_3\text{-}Si\text{-}OH_3$
Tetrachlorosilane	$Si\text{-}Cl_4$	$Si\text{-}OH_4$
Methyltrichlorosilane	CH_3HSiCl_2	CH_3HSiOH_2
Dimethylchloro silane	$(CH_3)_2HSiCl$	$(CH_3)_2HSiOH$

Reactions of Chlorosilanes

Chlorosilanes are important reactive materials used to make many commercially important silicone derivatives. Some reactions include:

1. Chlorosilanes react readily with alcohols or phenols to produce alkoxy silanes. Octyl trimethoxysilane is then used to hydrophobize zinc oxide and titanium oxide.

$$CH_3Si\text{-}Cl_3 \quad + \quad 3\,CH_3OH \quad \rightarrow \quad CH_3Si\text{-}(OCH_3)_3 \quad + \quad 3HCl$$

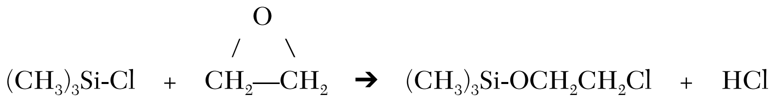
Methyltrichlorosilane Methanol Methyltrimethoxysilane

2. Chlorosilanes react readily with fatty acids to produce acyl derivatives.

$$(CH_3)_3Si\text{-}Cl_3 \quad + \quad R\text{-}COOH \quad \rightarrow \quad (CH_3)_3Si\text{-}O\text{-}C(O)\text{-}R \quad + \quad HCl$$

Trimethylchlorosilane Fatty Acid Acyl Silane

3. Chlorosilanes react readily with ethylene oxide to produce haloethoxysilanes.



$$(CH_3)_3Si\text{-}Cl \quad + \quad \overset{\overset{O}{/\quad\backslash}}{CH_2\text{—}CH_2} \quad \rightarrow \quad (CH_3)_3Si\text{-}OCH_2CH_2Cl \quad + \quad HCl$$

Trimethylchlorosilane Ethylene oxide Trimethylchloroethoxysilane

4. Chlorosilanes are used to make Q resins (which will be addressed in the resin chapter of this book).
5. Chlorosilanes, produced from quartz, are the major materials from which silicones are produced in subsequent processes.

Silicones Properties

Silicone compounds are finding increased utilization in personal care products and must offer unique properties relative to other compounds to justify their cost. Silicone compounds can be divided into two different categories:

1. Silicone homopolymers—This class of compounds is made up of polymers that have only the methyl groups and oxygen and silicon atoms. It includes polymers that lack cross-linking such as silicone fluids, cyclics and gums.
2. Silicone heteropolymers—These are polymers that, in addition to the methyl groups and silicone and oxygen atoms, include other functionalities. These materials are amphilic silicone compounds; they have two different groups that lack solubility in each other and consequently are surface active.

Silicone compounds are used in personal care applications because of the unique properties they possess. These include:

Surface Tension Reduction

In the formulation of personal care products, the ability to alter surface tension and other interfacial properties is critical. Almost every cosmetic that is applied to hair and skin must have a low enough surface tension to facilitate spreading. Consequently, surface tension is important. **Table 1.5** shows the surface tension of a number of pure materials. Surface tension has a direct impact on spreadability, wettability and cosmetic elegance. In terms of the latter, cushion and playtime are most important.

Silicone compounds are interesting materials for use in personal care formulations because their surface tension is different from both oils and water. Silicone compounds have a surface tension of around 20 dynes/cm^2, compared to a surface tension of around 32 dynes/cm^2 for oils and 76 dynes/cm^2 for water. **Table 1.6** shows the reduction of surface tension achieved by the incorporation of a soluble silicone derivative.

Solubility—Group Opposites

Silicone polymers are water-insoluble and oil-insoluble. They are hydrophobic (water-hating) and at the same time oleophobic (oil-hating). This key attribute forces us to think in terms of another classification of hydrophobic materials, namely silicone loving groups, which we have been called siliphillic materials. It is the lack of solubility in oils and water that makes dimethicone a barrier when applied to skin. The use of dimethicone as a barrier on the skin is very common and is considered a drug application by the United States Food and Drug Administration (FDA).

This complexity has resulted in the introduction of the concept of group opposites shown in **Table 1.7**.

Table 1.5. Surface Tension (Pure Materials)

Product	**Surface Tension (dynes/cm)**
Mercury	472.0
Water	72.6
Is paraffin (C12-C14)	53.0
Squalane	46.2
Soap Solution (1%)	38.8
Mineral oil	33.1
Dimethicone (20cs)	26.6
Acetone	23.7
Ethyl Alcohol	22.2
Cyclomethicone (D4)	20.6
Diethyl ether	17.0

Table 1.6. Reduction of Surface Tension with Silicone Derivatives

Solvent	**Surface Tension (as is) Dynes/cm^2**	**Silicone Added (0.5% weight)**	**Surface Tension Dynes/cm^2**
Toluene	28.9	C-26 alkyl dimethicone	25.0
2-butoxy ethanol	29.1	Stearyl dimethicone	22.0
Methanol	23.4	Octyl PEG-8 dimethicone	22.2
Water	72.3	PEG-8 dimethicone	20.1

Table 1.7. Groups Opposites

Hydrophobic (Water Hating)	can be either	Siliphilic (silicone loving)	or	oleophillic (oil loving)
Siliphilic (silicone loving)	is both	oleophobic (oil loving)	and	hydrophobic (water hating)
Oleophilic (oil loving)	is both	siliphobic (silicone loving)	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 hydrophilicity 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 has been rendered hydrophobic (water repelling) by using a silicone coating, (a siliphillic material) both oil and water will be repelled.

The personal care application example relates to coated pigments. Almost all pigments have some sort of coating on them (be it 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. Some pigments 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, over time, the nonbonded pigment can migrate off the pigment into another phase. The result can eventually appear as emulsion instability. The modification of the emulsifier package will not solve this problem. We recommend testing all pigments for the type of coating and its permanence.

Amphilic Materials

While it is interesting that silicone, oil and water are mutually insoluble, the synthesis of organofunctional silicones is key to utilization of materials in the personal care market. By having two different insoluble groups in a molecule, the product becomes surface active. Even when soluble in oil or water, amphilic materials accumulate at the interface and/or form micelles depending upon concentration. Surface activity allows amphilic materials to wet, foam, defoam, emulsify, condition, effect transepidermal water loss, lower surface tension and form films depending upon the exact structure. It is these abilities that make organosilicone materials most interesting.

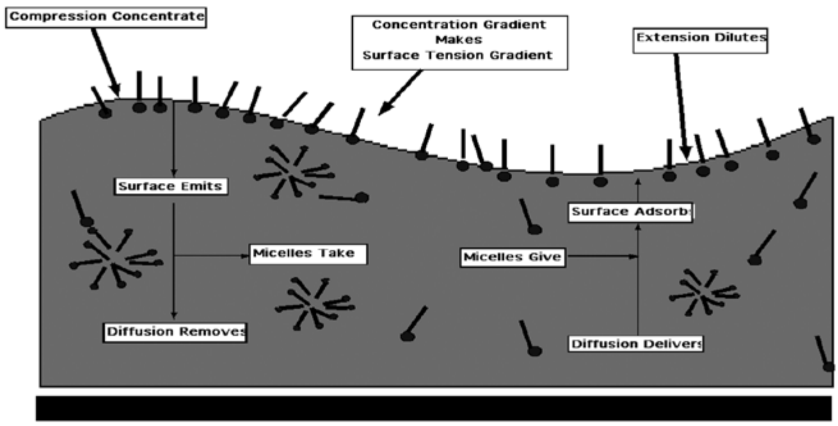
Figure 1.4 shows the complex set of conditions that occur when a liquid containing a surfactant is spread on a surface. This situation occurs with almost all cosmetic products when they are applied to the body.

Silicone Challenges

Anyone that has formulated with silicone compounds knows that this important class of compounds can be a bit problematic. Specifically, many formulators ask:

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

Figure 1.4. Dynamic Surface Tension Amphilic Silicone Molecules



The answers to the first two questions have been already provided in this chapter. The answer to the third question is that the INCI name does not provide all the information needed to fully understand functionality. The performance of a given silicone is dictated by three equally important factors:

Construction is the process by which the polymer backbone is prepared. It determines such important functional attributes as the molecular weight (and consequently surface performance), the ratio of silicone groups to non-silicone groups, and cross-link density.

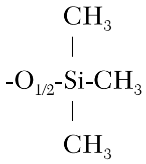
Functionalization is the process by which amphilic silicone compounds are prepared. The specific reaction employed is hydrosilylation, the reaction of a silanic hydrogen polymer made using the construction process with alpha vinyl compounds, to introduce another group of differing solubility.

Derivitization is the process by which organic chemistry is carried out on functional groups like hydroxyl groups introduced into the molecule during hydrosilylation.

Silicone Backbone Nomenclature

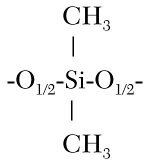
Like doctors, lawyers and technical professionals, silicone chemists have invented a language which makes communication between members of the profession easier. At the same time, however, it makes communication to individuals outside our profession more difficult. The silicone chemists' language is a chemical shorthand developed by Alfred Stock in 19164. The nomenclature is based upon the type of groups present in the backbone of the molecule. The following is a breakdown of that shorthand.

"M unit" is monosubstituted (one oxygen atom on silicon)



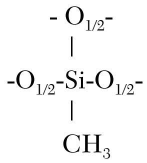
$$\begin{array}{c} CH_3 \\ | \\ -O_{1/2}-Si-CH_3 \\ | \\ CH_3 \end{array}$$

"D unit" is disubstituted (two oxygen atoms on silicon)



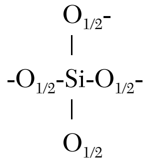
$$\begin{array}{c} CH_3 \\ | \\ -O_{1/2}-Si-O_{1/2}- \\ | \\ CH_3 \end{array}$$

"T unit" is trisubstituted (three oxygen atoms on silicon)



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

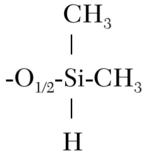
"Q unit" is tetrasubstituted (four oxygen atoms on silicon)



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

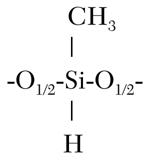
In cases where organofunctional silicone is desired, a process called hydrosilylation is used. It makes use of the Si-H intermediate made in the Rochow process. In the hydrosilylation reaction a double-bonded material (most commonly alpha double-bonded) is reacted with Si-H to form a new Si-C bond. The points at which the organo group is attached contains a Si-H group and has an "*" added to its designation.

"M* unit" is monosubstituted (one oxygen atom on silicon)



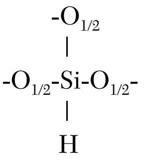
$$\begin{array}{c} CH_3 \\ | \\ -O_{1/2}-Si-CH_3 \\ | \\ H \end{array}$$

"D* unit" is disubstituted (two oxygen atoms on silicon) with organofunctionality



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

"T* unit" is trisubstituted (three oxygen atoms on silicon) with organofunctionality

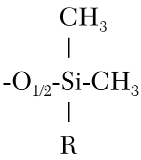


$$\begin{array}{c} -O_{1/2} \\ | \\ -O_{1/2}\text{-Si-}O_{1/2}- \\ | \\ H \end{array}$$

There is no "Q* unit" since there is no possibility of functional groups.

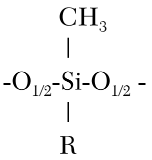
After reaction with the double bond in the hydrosilylation reaction, the "H" is transformed into an "R" group, discussed shortly.

"M* unit" is monosubstituted (one oxygen atom on silicon)



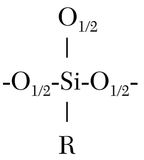
$$\begin{array}{c} CH_3 \\ | \\ -O_{1/2}\text{-Si-}CH_3 \\ | \\ R \end{array}$$

"D* unit" is disubstituted (two oxygen atoms on silicon) with organofunctionality



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

"T* unit" is trisubstituted (three oxygen atoms on silicon) with organofunctionality



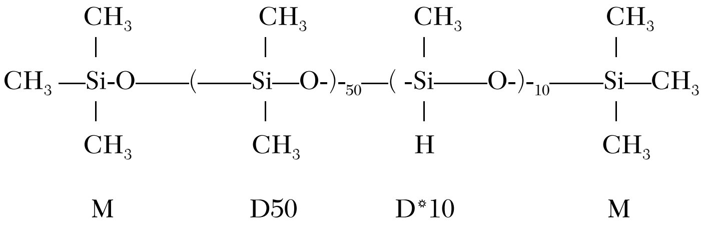
$$\begin{array}{c} O_{1/2} \\ | \\ -O_{1/2}\text{-Si-}O_{1/2}- \\ | \\ R \end{array}$$

Silicone Construction

The "backbone" structure of a silicone molecule is referred to as its construction. This is one critical factor in determining the functional attributes of the molecule. There are three types of construction of silicone polymers. They are comb, terminal and multifunctional.

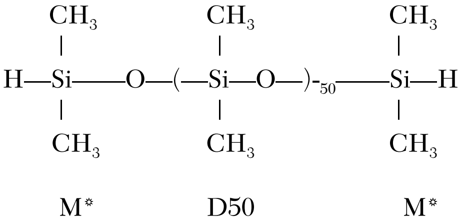
Comb

The "R" groups are internal, resembling a comb.


$$CH_3\text{—}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{——}(\text{——}\overset{CH_3}{\underset{CH_3}{Si}}\text{—}O\text{-})\text{-}_{50}\text{—}(\text{-}\overset{CH_3}{\underset{H}{Si}}\text{——}O\text{-})\text{-}_{10}\text{——}\overset{CH_3}{\underset{CH_3}{Si}}\text{—}CH_3$$

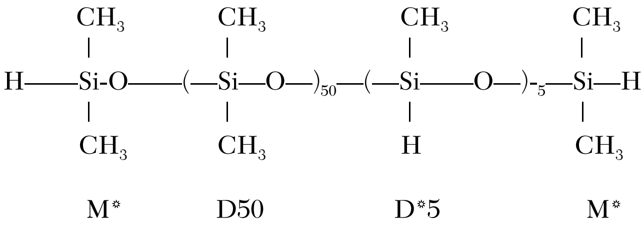
Terminal

The "R" groups are terminal, and there are only two groups possible.


$$H\text{—}\overset{CH_3}{\underset{CH_3}{Si}}\text{——}O\text{—}(\text{—}\overset{CH_3}{\underset{CH_3}{Si}}\text{—}O\text{—})\text{-}_{50}\text{——}\overset{CH_3}{\underset{CH_3}{Si}}\text{—}H$$

Multifunctional

The "R" groups are both internal and terminal, resulting in a high degree of substitution.


$$H\text{——}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{——}(\text{—}\overset{CH_3}{\underset{CH_3}{Si}}\text{—}O\text{—})_{50}\text{—}(\text{—}\overset{CH_3}{\underset{H}{Si}}\text{——}O\text{—})\text{-}_{5}\text{—}\overset{CH_3}{\underset{CH_3}{Si}}\text{—}H$$

Among the functional differences between the comb and the terminal structures, one of the most important is the difference in the number of possible substituents. This number is limited to two in the terminal number of (*) substituents (one at each end) while in the comb polymer, the number can be much larger. The reason is the number of substituents in the terminal compounds can be no more than two (one at each end). The number of functionalized groups in a comb compound can be much larger than two.

The other major difference between terminal and comb structure involves economics. The terminal compounds are more expensive than the comb compounds having the same molecular weight. This is a direct consequence of the fact that the raw material for making the terminal products M*M* is not abundant in the Rochow process and is therefore expensive.

There has been an interest in developing a terminal polymer with a methyl group on one end and an organofunctional group on the other. M*M* is available; however, since the preparation of the silicone polymer is based on equilibration chemistry, even though MM* is used as a raw material, the resulting polymer is a mixture of two parts monosubstituted monomethyl-terminal polymer, one part fluid (dimethyl terminated) and one part difunctional compound having no methyl terminal group. The fluid is not water-soluble and therefore always present in the reaction mixture.

This observation leads to another important concept. To avoid forming a fluid in a polymer equilibration reaction, there must be a certain number of water-soluble functional D* groups in a comb structure relative to D units. The smallest ratio of D* to D can be established experimentally. It is that ratio which leads to a water-soluble product, substantially free of fluid. This observation explains why only a limited number of products in this class are offered commercially.

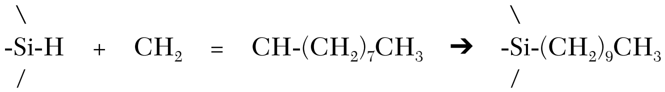
The construction of a silicone molecule can be compared to a knitting machine. The various units M, D, D*, M* and the like are linked together in a backbone with the desired quantity of Si-H groups (the * materials). Since there are no organo groups yet added, the molecule is neither oil-soluble, water-soluble, fluoro-soluble or organo-modified. The ratio of organofunctional to silicone functional groups has been established, as has the total molecular weight. This is one critical step to determining functionality of the molecule. Compounds containing silanic hydrogen groups are used commercially to coat pigments and to waterproof gypsum board.

Functionalization

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 organofunctional products. A single silanic hydrogen polymer can give rise to an entire family of analogs depending on which functional group is placed onto the backbone in the functionalization reaction.

In order to make these products more easily formulated, organofunctional dimethicone compounds have been developed. These include dimethicone compounds with improved oil solubility 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 who 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 avoiding 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.

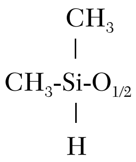
The reaction used to place organofunctionality into silicone compounds is called hydrosilylation. This process is used in the construction part of silicone preparation. The key reaction is one in which a silanic hydrogen (Si-H) is reacted with a terminal double bond resulting in a stable Si-C bond.



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

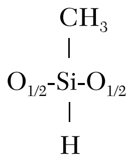
The shorthand for the construction of reactive compound is as follows:

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



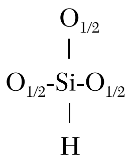
$$\begin{array}{c} CH_3 \\ | \\ CH_3\text{-}Si\text{-}O_{1/2} \\ | \\ H \end{array}$$

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



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

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



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

Silanic hydrogen containing polymers prepared in the equilibration reaction are hydrosilylated in the functionalization reaction to make organofunctional silicones. The vinyl containing groups that are reacted with silanic hydrogen containing silicone polymers include:

Alpha olefin	$CH_2{=}CH\text{-}(CH_2)_7CH_3$
Ally alcohol alkoxylates	$CH_2{=}CH\text{-}CH_2\text{-}O(CH_2CH_2O)_8H$
Fluoro vinyl compounds	$CH_2{=}CH\text{-}CH_2(CF_2)_8CF_3$

The properties of silicone compounds prepared using these raw materials are discussed in the remaining chapters.

Derivatization

Once the hydrosilylation reaction has been conducted, and the organosilicone molecule has been prepared, if there are reactive groups present, they can be used for subsequent chemistry. A number of the known and patented dimethicone coplyol derivatives are shown in Table 1.8.

Table 1.8. Dimethicone Copolyol Derivatives

Raw Material	Process	Product	2nd Process	Product
DMC $-CH_2-OH$ (End Group)	Sulfation	Silicone Sulfates		
	Carboxylation	Silicone Carboxylate	Complexation	Silicone Complexes
	Cyanoethylation	Silicone Amines		Amphoterics
	Phosphation	Silicone Phosphates		Silicone Phospholipid
	Chloroalkyation	Silicone Quats		
	Esterification	Silicone Esters		

Why Amphilic Silicone Compounds?

Amphilic silicone compounds are polymers in which there are at least two groups of functionalities that are insoluble in one another in pure form. These groups can include water-soluble, oil-soluble, silicone-soluble and fluoro-soluble. This amphilic nature results in surface active properties. Understanding these properties requires an understanding of what molecules do at surfaces.

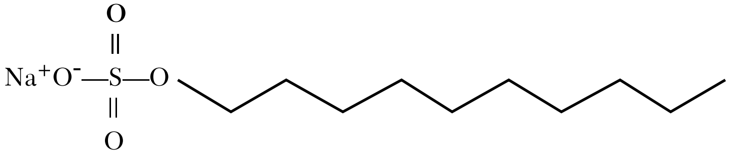
The basic definitions we use need to be examined more closely when considering amphilic materials. Simplistically, the following definitions apply:

1. A solution is a homogeneous mixture composed of one or more substances, known as solutes, dissolved in another substance, known as a solvent.
2. A suspension is a colloidal dispersion in which a finely divided species is combined with another species, with the former being so finely divided and mixed that it doesn't rapidly settle out. In everyday life, the most common suspensions are those of solids in liquid water.

3. An emulsion is a mixture of two immiscible substances. One substance (the discontinuous phase) is dispersed in the other (the continuous phase).

While these are neatly defined, the world of cosmetics is rarely so easy to organize. Consider a fully dissolved 1% solution of sodium chloride in water. This simple system has sodium ions (Na+), chloride ions (Cl-) and water, roughly equally distributed over the entire mass of the system. The solution is clear and homogeneous.

Now consider a 1% solution of a surfactant. The surfactant, or surface active agent, has a water-soluble head and a water-insoluble tail. A very well-known surfactant is sodium lauryl sulfate (CAS 151-21-3). Like NaCl, sodium lauryl sulfate has two opposite ions, but sodium lauryl sulfate in water is very different. The presence of a large fatty portion makes the product surface active. The structure of sodium lauryl sulfate is:



A 1% solution of sodium lauryl sulfate, like that of sodium chloride, is clear but not homogeneous. As one adds sodium lauryl sulfate to water, achieving the lowest overall free energy drives the orientation of the material in the water, in this case minimizing disrupting hydrogen bonding in water. The sodium lauryl sulfate organizes itself at the air/water interface and then begins self-assembly into micelles. **Figure 1.5** shows this.[5] The first box in Figure 1.5 shows pure water, having a surface tension of 72 dynes/cm2. As surfactant is added (second box in Figure 1.5), surface tension is falling as dilute surfactant organizes at the surface. As the surface reaches saturation, a very significant situation develops. The surface tension no longer drops even with additional surfactant. It is at this concentration—critical micelle concentration—that micelles become the dominant form of surfactant (third box in Figure 1.5).

The ability to provide low surface tension surfactant properties for cosmetic formulations is a key reason to use silicones in formulations. Since silicone materials are almost never used alone in formulation, the interaction of silicone with other materials in formulation is critical to their utility. Performance of the silicone alone is almost trivial.

Specifically, the selection of the proper oil-soluble silicone will lower the surface tension of oil-based systems, in exactly the same way that the proper selection of a water-soluble silicone will lower the surface tension of water-based systems, improving spreadability and cosmetic elegance. Selection of the silicone with the proper solubility and surface tension is critical and an often overlooked key to formulating advanced cosmetic products.

An example of surface tension reduction of blends with several ratios of water-soluble silicone (in this case PEG-8 dimethicone) are shown in **Table 1.9**.

Figure 1.5. Surfactant Orientation[5]

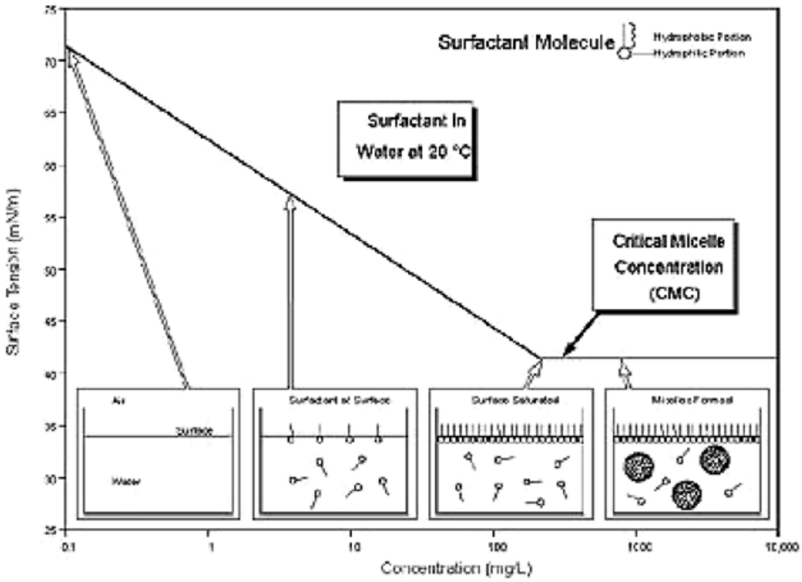


Table 1.9. Surface Tension Reduction Aqueous System

	Cocamidobetaine (% Weight)	PEG-8 Dimethicone (% Weight)	Surface Tension (Dynes/cm^2)
Example 1.1	100%	0%	31.3
Example 1.2	75%	25%	26.0
Example 1.3	50%	50%	23.1
Example 1.4	25%	25%	21.6
Example 1.5	0%	100%	20.1

A few examples of surface tension reduction of blends with several ratios of oil-soluble silicone are shown in **Tables 1.10 and 1.11**.

A few examples of surface tension reduction of using silicone compounds capable of reducing surface tension are blends of water silicone and isopropanol. These are shown in **Table 1.12**.

Table 1.10. Surface Tension Reduction Triglyceride System

	Soybean Oil (% Weight)	Cetyl Dimethicone (% Weight)	Surface Tension (Dynes/cm^2)
Example 2.1	100%	0%	31.4
Example 2.2	75%	25%	25.5
Example 2.3	50%	50%	24.8
Example 2.4	25%	75%	24.1
Example 2.5	0%	100 %	23.6

Table 1.11. Reduction Mineral Oil System

	Mineral Oil (% Weight)	Cetyl Dimethicone (% Weight)	Surface Tension (Dynes/cm^2)
Example 3.1	100%	0%	28.3
Example 3.2	75%	25%	26.1
Example 3.3	50%	50%	25.1
Example 3.4	25%	75%	24.5
Example 3.5	0%	100 %	23.6

Table 1.12. Surface Tension Reduction Mineral Oil System

	Isopropanol (% Weight)	PEG-8 Dimethicone (% Weight)	Surface Tension (Dynes/cm^2)
Example 4.1	100%	0%	21.7
Example 4.2	75%	25%	20.8
Example 4.3	50%	50%	20.5
Example 4.4	25%	75%	20.5
Example 4.5	0%	100 %	20.5

Why is the cosmetic formulator interested in surface tension? Surface tension affects spreadability and cushion, and the addition of different silicones can dramatically alter surface tension and cosmetic acceptability of formulations. The addition of the proper silicone to a high viscosity ester can improve spreadability without effecting the play time (i.e. the time it takes to spread out). The addition of the proper silicone can also improve wetting time and alter bubble structure. A different silicone can improve spreadability and reduce play time. The result is an ability to alter aesthetics in personal care products by adding low concentrations of silicones. This allows one to significantly alter the cosmetic feel of a product without dramatic alteration in the formulation.

Conclusion

Occasionally, a technology is developed which dramatically revolutionizes an industry. The development of silicone technology by Eugene Rochow and a handful of other dreamers has transformed our industry over the last sixty years. The development of this technology seems unlikely when one considers that the materials used start from quartz (a very common mineral).

Rochow states, "The organic compounds of silicon, which have been the subject of many scholarly researches during the past 80 years, at last show promise of emerging from the laboratory and finding a place in industry. An understanding of the behavior of organosilicon materials is necessary to their intelligent use ...." Products have emerged from laboratory curiosities and we still need a better understanding of the behavior of organosilicon materials to intelligently use them.

Please Remember

- ✓ The term "Silicone" as applied to the products used in personal care products describe a very wide class of compounds, having varied solubility, and unique surface tension properties.
- ✓ Silicones, if amphillic (i.e. containing two or more groups which if mixed in pure form will be insoluble), are surface active, assembling in structures which despite their complication provide the lowest free energy to the solution.
- ✓ Silicone compounds are formulated into multi-component formulations, wherein interactions occur, which have an effect on the performance of the silicone. Consequently, evaluation of the pure silicone compound can not only be almost meaningless, but may well lead to false conclusions on performance in mixed systems.
- ✓ When properly used, silicones give unique properties to formulations.

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Chapter 2

Basic Silicone Materials

The basic raw materials used in the personal care market are either products derived from the chlorosilanes process (including cyclomethicone) or products of construction (see **Chapter 1**). The materials are homopolymers of silicone, being composed of silicon and oxygen atoms and methyl groups only. This class of compounds is the oldest and most understood. The compounds of this class also cause formulators to be the most reluctant to incorporate new silicones into formulations. These materials are water- and oil-insoluble and consequently are difficult to formulate.

We need to have a great deal of respect for the pioneering chemists who created a very versatile set of compounds that have their origin in quartz, a ubiquitous mineral. This respect grows even deeper when you look at the steps that were needed to accomplish commercial reality for these products. These pioneers showed insight, persistence and engineering intelligence that allowed for the proper economics for silicones to become the widely accepted products they are today. The basic raw materials, covered in this chapter, were the first steps in achieving commercial reality for silicone compounds. They are the stepping stones for this class of materials.

Cyclomethicone

Cyclomethicone is distilled from the mixture of products found in hydrolsylate, which is produced by the hydrolysis of the chlorosilanes produced in the Rochow process. The predominant cyclomethicone produced is D4, with lesser amounts of D3 and D5.

The ratio of D4 to D5 that is distilled from the hydrolysate reaction is generally 85% D4 to 15% D5. The cyclomethicone mixture distills off the hydrolysis process as an azeotrope. This common azeotrope is the least expensive cyclomethicone composition produced. Since separation of the two from one another requires distillation, the pure D4 is more expensive than the azeotrope and the D5 is even more so. Since D4 has been essentially banned from use[a] in the personal care market, D5 has become the cyclic silicone of choice.

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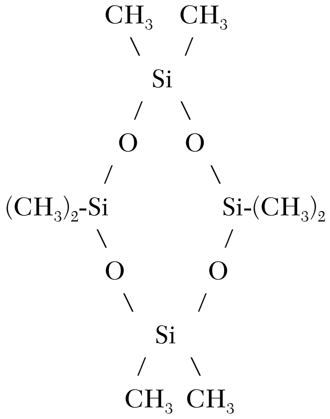
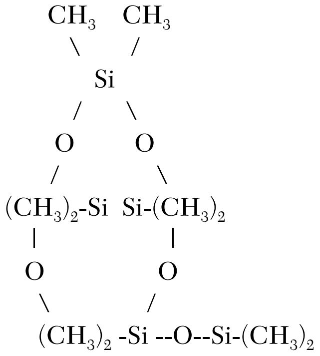
[a] While still being studied, D4 has been shown to have reproductive effects in several reproductive studies including a two-generation study (Stump et al., 2000). These effects include a reduction in the number of implantation sites, the number of live fetuses, and the mean live litter size at the highest inhalation exposure concentrations tested (i.e., 500 and 700 ppm, respectively).

The term cyclomethicone refers to a series of cyclic silicone compounds. The structures for D4 and D5 are:

D4 Cyclomethicone
Cyclotetrasiloxane



D5 Cyclomethicone
Cyclopentasiloxane



The term cyclic refers to a structure; the term cyclomethicone refers to a physical property. Cyclomethicone is available in a variety of compositions. Pure D3, D4, and D5 are available as well as a more common lower cost 85% D4/15% D5 composition. D3 and D4 are used as raw materials in our industry now, and D5 is used as a dry solvent. **Table 2.1** shows the heat of vaporization for several materials. Water takes a lot of energy to vaporize, which explains why clothes take so long to dry in a drier. Ethanol, a rather easily evaporated material, takes less than half the energy. This explains why alcohol-based aftershave formulations feel cool. Finally, D4 and D5 take considerably less energy than ethanol, making them the easiest to evaporate in the series. This explains why cyclomethicone is often used in antiperspirants.

Table 2.1. Heat of Vaporization

Material	Heat of Vaporization (cal/g)
Water (*aqua*)	539
Ethanol	210
D4	31
D5	31

Cyclomethicone requires a low heat for vaporization; additionally, it has low viscosity, a dry skin feel, is easily spread, is noncooling, colorless and essentially odorless. **Table 2.2** shows the assigned INCI names for cyclomethicone compounds.

Table 2.2. Cyclomethicone INCI Nomenclature

# of Si and O Atoms	INCI Name
Mixtures	Cyclomethicone
3	Cyclotrisolxane
4	Cyclotetrasiloxane
5	Cyclopentasiloxane
6	Cyclohexasiloxane

Table 2.3 outlines the properties of the various types of cyclomethicone.

The benefits of using cyclomethicone in skin care products include:

- Imparts a soft and silky feeling to the skin
- Evaporates at room temperature
- Possesses excellent spreading quality
- Leaves no oily residue or buildup
- Detackification
- Feels nongreasy
- Is compatible with a wide range of cosmetic ingredients
- Has low surface tension
- Is a transient emollient; improved rub in and spread

In hair care, the benefits include:

- Transient conditioning
- Lack of build up
- Improved wet comb

Table 2.3. Cyclomethicone Properties

INCI Name Common Name	Cyclotetrasiloxane D4	Cyclopentasiloxane D5	Cyclohexasiloxane D6	Cycloheptasiloxane D7
Viscosity (cSt)	2.5	4.2	4.2	6.8
Molecular Weight	297	371	371	445
Specific Gravity	0.95	0.95	0.95	0.96
Refractive Index	1.394	1.397	1.397	1.399
Solubility Parameter	7.4	7.4	7.4	7.4
Flash Point (°C)	55	76	76	93

Table 2.4. Volatile Non-cyclic silicones

INCI Name Common Name	Hexamethyl-disiloxane MM	Dimethicone 1 visc fluid	Dimethicone 1.5 visc fluid	Dimethicone 2 visc fluid
Viscosity (cSt)	0.65	1	1.5	2
Molecular Weight	162	236	311	385
Specific Gravity	0.76	0.816	0.85	0.872
Refractive Index	1.375	1.382	1.387	1.389
Solubility Parameter	6.7	6.9	7.0	7.0
Flash Point (ºC)	-3	34	56	87

Cyclomethicone is used in the following types of products:

- AP/DO
- Hair sprays
- Cleansing creams
- Skin creams and lotions
- Stick products
- Bath oils
- Suntan products
- Shaving products
- Makeup
- Nail polishes

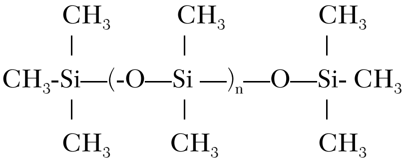
Table 2.4 shows noncyclic silicone compounds that are volatile and provide a dry feeling to the skin.

Molecular Weight of Polymeric Silicones

As one considers silicone polymers, the concept of molecular weight becomes important. Consider pure hexane.

The structure is $CH_3\text{-}(CH_2)_4\text{-}CH_3$. It has six carbon atoms, 14 hydrogen atoms and a molecular weight of 100. If we add another CH_2 group we get heptane with a molecular weight of 114. Easily completed.

Now consider silicone fluid with a viscosity of 200. If one runs a GPC analysis, a molecular weight of 9430 is obtained. The fluid has the following structure:



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

Solving for "n" (the number of repeating units within the parenthesis) we get:

$$n = \frac{\text{Molecular weight of polymer – (molecular weight of the two M units)}}{\text{Molecular weight of the D units i.e. "n"}}$$

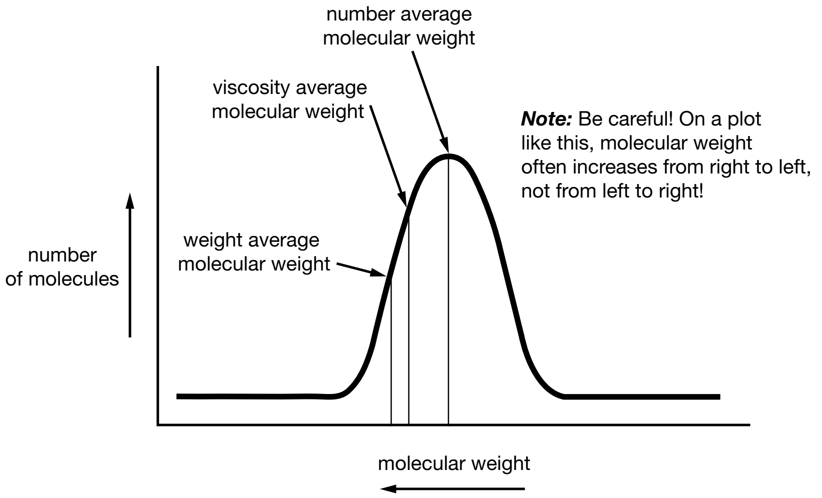
or in this case:

$$n = \frac{9{,}430 - 164 \text{ (M groups)}}{74} = 125.2$$

What does this mean? Is there really a 0.2 n unit? Of course not; it is a consequence of the fact that "n" is an average. The polymer has a range of oligomers in the mixture wherein the average "n" value is 125.5. Oligomer distribution is not unique to silicone compounds. Ethoxylates are also oligomers. An oligomer is a compound with an "n" value that is an integer, in contrast to a polymer that consists of a mixture of many "n" values.

The oligomer distribution is determined in part by the chemistry used to make the polymer, and to some extent the catalyst. This is not the only contributor. Blending is a nonchemical operation in which silicones of different molecular weight are mixed together. The resulting blend often has very different cosmetic properties, most importantly skin feel. Blends of high viscosity and low viscosity fluids can have very elegant skin feel. The high viscosity fluid when used alone can be sticky. The low viscosity fluid aids in spreading the high viscosity fluid and a product with a very interesting skin feel results; consequently, the oligomer distribution that is often critical to performance. Gel permeation chromatography (GPC) is a separation technique involving the transport of a liquid mobile phase through a column containing the separation medium, a porous material. GPC, is also called size exclusion chromatography or gel filtration. The technique provides a rapid method for the separation of oligomeric and polymeric species[1]. A typical GPC for a silicone fluid made without blending is shown in **Figure 2.1**.

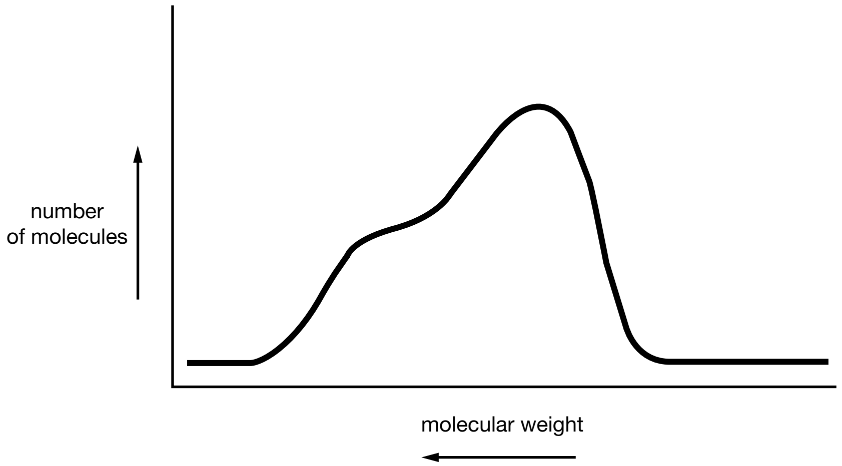
Figure 2.1. Typical GPC for a Silicone Fluid (made without blending)



Note: Be careful! On a plot like this, molecular weight often increases from right to left, not from left to right!

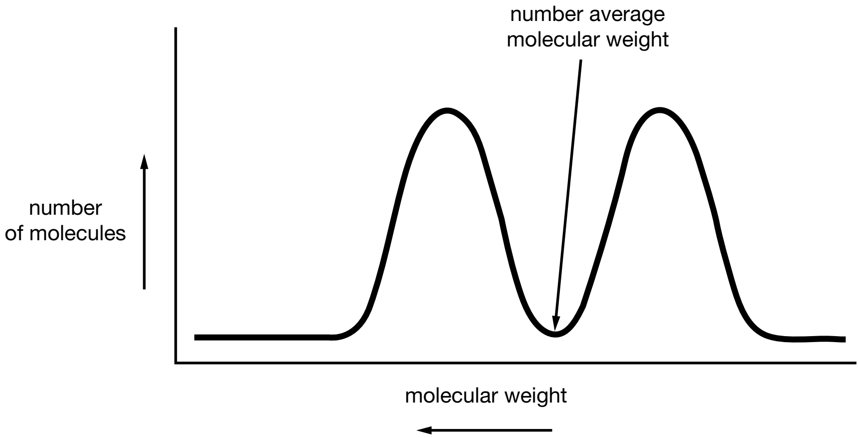
Now consider what happens when one blends two closely related silicones together to obtain a desired viscosity. **Figure 2.2** shows a typical GPC for a silicone fluid made blending two similar molecular weight fluids. One can clearly see the two humps, indicative of the two components.

Figure 2.2. Typical GPC for a Silicone Fluid (made blending 2 similar molecular weight fluids)



Now consider a blend of two very different silicone fluids. **Figure 2.3** shows a typical GPC for a silicone fluid made by blending two very different molecular weight silicone fluids. It is very interesting to note the average molecular weight, for the blend has essentially no concentration.

Figure 2.3. Typical GPC for a Silicone Fluid (made blending 2 different molecular weight fluids)

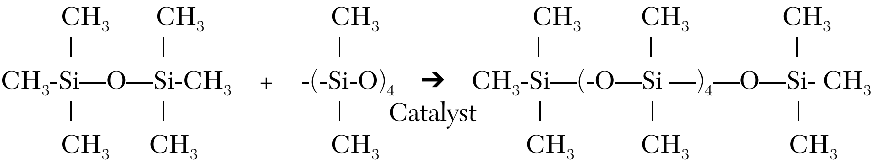


Why is this of interest to the cosmetic chemist? A blend of two very different silicone fluids will have a different feel on the skin in comparison to a single component. The viscosity of the fluid can be very confusing if it is the salient analysis used for a specification. Low molecular weight silicone fluids help spread high molecular weight silicones on the skin. The high molecular weight silicones then provide an outstanding feeling to the skin. Blends function very differently compared to nonblended silicones in application.

Silicone Fluids

Synthesis

Silicone fluids are synthesized by the equilibration reaction of MM and cyclomethicone. The reaction is a ring-opening reaction. Typical of the synthesis of fluids is the following reaction in which one MM is reacted with one D4 compound to make MD_4M, a simple silicone fluid.



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 \;+\; \text{-}(\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_4 \xrightarrow[\text{Catalyst}]{} CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}(\text{-}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—})_4\text{—}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

MM D4 MD4M

The reaction may be run with either an acid or base catalyst. Typically, the reaction is conducted at room temperature for 12 hours with a 2% by weight sulfuric acid as the catalyst, resulting in a mixture of about 10% free cyclic product and 90% linear fluid. If the catalyst is neutralized and the cyclic is stripped off, a stable fluid will result. If the catalyst is not neutralized during stripping, the fluid will degrade back to MM and D4[2,3].

The equilibration process is critical not only to produce stable silicone fluids, but as a means of introducing functional groups into the polymer. This is hydrosilylation, a process used to make organofunctional silicone compounds.

It is also interesting to note that a "finished silicone fluid" may be placed in contact with D4 and catalyst and re-equilibrated to make a higher viscosity fluid. Conversely, a "finished silicone fluid" may be re-equilibrated with MM and catalyst to make a lower viscosity fluid. Finally, silicone rubber may be decomposed into MM and D4 via stripping of the product in the presence of catalyst. This property of silicone polymers makes them decidedly different from organic compounds.

Properties

Silicone fluids, also called silicone oils or simply silicones, are sold by their viscosity and range from 0.65 centistokes (cSt) to 1,000,000 cSt. If blending two different viscosity fluids does not make the product, the viscosity is related to molecular weight. The viscosity allows for an approximate calculation of the value of "n" as shown in **Table 2.5**.

Table 2.5. Approximate "n" Value Based on Viscosity (Non-blended)

Viscosity 25°C (cSt)	Approximate Molecular Weight	Approximate "n" Value
5	800	9
50	3,780	53
100	6,000	85
200	9,430	127
350	13,650	185
500	17,350	230
1,000	28,000	375
10,000	67,700	910
60,000	116,500	1,570
100,000	139,050	1,875

Silicone fluids are classified by their viscosity.

1. Volatile Silicone Fluids

(Linear, noncross-linked silicone having a viscosity of less than 5 cSt)

- 0.65 cSt (CAS# 107-46-0) (MM)
- 1 cSt (CAS# 107-51-7)
- 3 cSt (CAS # 63148-62-9)

Volatile silicone fluids are used in a wide variety of antiperspirants, skin creams, skin lotions, suntan lotions, bath oils, and hair care products. They possess low surface tensions and exhibit excellent spreadability.

2. Low Viscosity Silicone

(Linear, noncross-linked silicone having a viscosity of 5–50 cSt)

CAS# 63148-62-9

- 5 cSt
- 10 cSt
- 20 cSt

Low viscosity silicones are primarily used as an ingredient in a number of personal care products due to their high spreadability, low surface tension and subtle skin lubricity. These fluids are clear, tasteless, odorless and provide a nongreasy feel. They are used in a wide variety of skin creams, skin lotions, suntan lotions, bath oils and hair care products.

3. Regular Viscosity Silicones

(Linear, noncross-linked silicone having a having a viscosity of 50–1,000 cSt)

CAS# 63148-62-9

- 50 cSt
- 100 cSt
- 200 cSt
- 350 cSt
- 500 cSt
- 1,000 cSt

4. High Viscosity Silicones

(Linear, noncross-linked silicone having a viscosity of 10,000–60,000 cSt)

CAS# 63148-62-9

- 10,000 cSt
- 60,000 cSt

5. Ultra High Viscosity Silicone Fluid

(Linear, noncross-linked silicone having a viscosity of over 60,000 cSt)

- 100,000cSt
- 500,000cSt
- 1,000,000cSt

Table 2.6 is provided to give meaning to the viscosity values by relating them to everyday materials.

Silicone fluids, unlike petroleum based products have very good viscosity stability over a wide range of temperatures. This is important in applications where very cold temperatures are encountered, like lubricants for high altitude planes. The viscosity stability can be seen in **Table 2.7**.

See **Figures 2.4** and **2.5** for examples of healthy and damaged hair.

Silicones have a low surface tension so they spread well on the hair. They are highly lubricious; therefore, they lubricate damaged dry hair. Hair damage comes from a variety of sources including:

- Sun damage
- Mechanical damage

Table 2.6. Viscosity Comparison

Reference Object	Viscosity cSt.
water	1 to 5cSt.
kerosene	10cSt.
transformer oil	20cSt.
Sae-5 oil	50cSt.
Sae-10 motor oil	100cSt.
Sae-30 motor oil	350cSt.
Sae-30 motor oil	500cSt.
light syrup	1,000cSt.
pancake syrup	2,500cSt.
honey	10,000cSt.
chocolate syrup	25,000cSt.
ketchup	50,000cSt.
thick molasses	60,000cSt.
hot tar	100,000cSt.
peanut butter	250,000cSt.
paste/caulk	1,000,000cSt.

Table 2.7. Viscosity Change at Different Temperatures Silicone Fluid and Petroleum Oil Viscosity (cSt)

Temperature (°C)	Silicone Fluid	Petroleum Oil
100	40	11
38	100	100
-18	350	11,000
-37	660	230,000

Figure 2.4. Healthy Hair

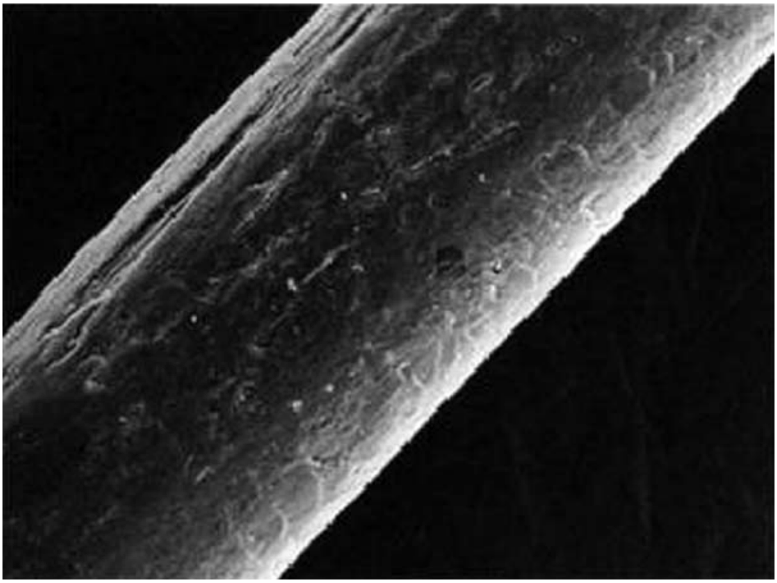
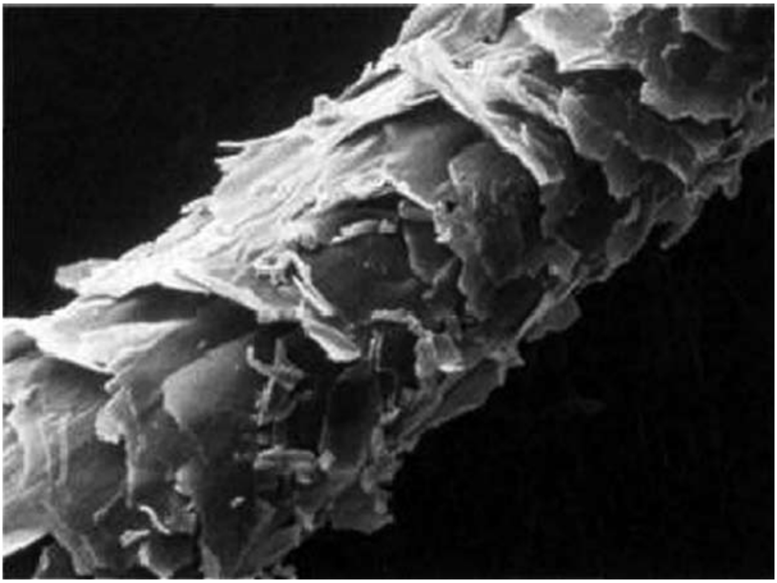


Figure 2.5. Damaged Hair



- Heat damage
- Processing damage

Usually hair damage takes place gradually, stage by stage, as follows:

1. The hair is weakened.
2. The cuticle begins to break down.
3. The cuticle disappears, layer by layer.
4. The cortex is exposed.
5. Split ends appear.
6. The hair breaks.

Silicone fluids applied to the hair can mitigate hair damage. Silicones lock in water and protect hair color from washing out. The problem is making a cosmetically acceptable product that is water-based, like most shampoos, using a water-insoluble silicone fluid. Suspending agents are commonly employed. Many so-called "two-in-one shampoos" contain silicone fluids for conditioning. These products are commonly opaque, as silicone fluid is not soluble in the aqueous shampoo. Additionally, preparation of these types of products requires dispersing the silicone fluid into small droplets and stabilizing the dispersion with thickeners. Such processes have been called "coacervate technology." A coacervate is a spherical aggregation of silicone molecules making up a colloidal inclusion, which is held together by hydrophobic forces. An alternative approach is to use organofunctional materials for clear two-in-one products.

Desirable properties of silicone fluids in conditioners:

- Conditioners that contain dimethicone (a silicone compound deposit mainly at the edges of the cuticle scale—where the damage happens the most easily)
- Micro-fine droplets make the hair surface smooth and shiny (less "fly-away")
- Dimethicone protects the hair from damage by reducing its resistance to brushing, combing and styling, when wet as well as when dry

Dimethicone (a silicone fluid) is an active for topical skin care formulations providing protective coating on skin and acting as an emollient. Barrier use of silicone fluid is a drug and requires regulatory consideration for the type of silicone fluid, and the concentration must meet the Skin Protectancy Monograph (21 CFR 347.10)

Silicone on Substrate

Silicone adheres to substrates, including fiber, fabric, metal surface, hair and skin. It does so by virtue of one or more of several mechanisms, such as hydrophobicity. The hydrophobicity of the molecule results in the insolubility of the silicone in water.

Oil introduced into water disrupts the hydrogen bonding between the water molecules. This disruption is accomplished only when the energy of mixing is sufficient to break the hydrogen bonds. When the mixing is stopped, the oil is forced out of the water by the reformation of the hydrogen bonds between the water molecules. This phenomenon can be used to deliver oil to a surface. Silicone fluids are delivered this way.

Improved adhesion properties are obtained by creating molecules that operate by additional mechanisms including:

- ***Ionic Interactions:*** The charge on the molecule will also have an effect upon the delivery of the oil to substrate. An oil carrying a cationic charge will form ionic bonds with substrates that carry negative surface charges. The two opposite charges together form an ion pair bond. Since ionic charges are quite common in textile fabrics, fibers, glass, hair and skin, this type of bonding becomes quite important.
- ***General Adhesion:*** If an oil delivered to a substrate penetrates and then polymerizes, an interlocking network of polymers will develop. Although not bonded directly to the substrate, this polymer network will adhere to the substrate.
- ***Specific Adhesion:*** If an oil is delivered to a substrate, it will penetrate and then react with groups on these substrates; a chemical bond will then be formed. This is the strongest and most permanent of the adhesion mechanisms.

Silicone fluids react almost exclusively by the mechanism related to hydrophobicity. To the extent the other mechanisms may be introduced, the more strongly and efficiently the benefit to hair can be delivered to substrate. Organofunctional silicones depend on these additional mechanisms to provide thorough and efficient conditioning, lubrication and softness to the substrate.

Cosmetic Usage of Silicone Fluids

There are several cosmetic usages of silicone fluids, as shown in **Table 2.8**.

Silicone fluids are used in low concentrations in many applications. The reason for this relates to their hydrophobicity, which results in their deposition on skin. This deposition has many desirable properties. Silicone fluids can be used to remove tacky organic products, like soaps, from the skin, while providing lubrication and a skin feel that is highly desirable.

While the mechanism of use is the same and independent of the viscosity chosen, the properties of the cosmetic product made with the different viscosity silicones are quite different. The skin feel can be altered significantly by picking the proper silicone fluid. Higher molecular weight products have an oilier feel on the skin, while lower viscosity products have a dryer feel on the skin. Silicone fluids with viscosity over 200 cSt are not soluble in alcohols, while products with lower viscosity are alcohol-soluble.

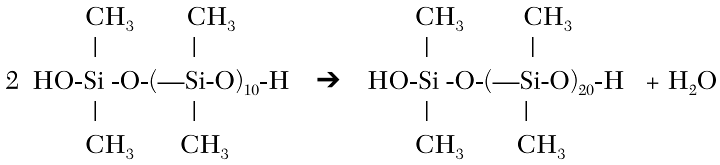
One key limitation on the use of silicone fluids in formulation is the fact that the concentration needs to be kept very low. The very same insolubility that is a consequence of the hydrophobicity and drives the deposition places severe limitations on the useful concentrations. If too much silicone fluid is used, it will result in a product that will separate, have difficulty foaming and lack the most basic aesthetics for a personal care product. Skilled formulation helps, but modification of the product and introducing organofunctionality into the product is a good way to overcome the shortcomings of silicone fluids.

Table 2.8. Cosmetic Use of Silicone Fluids

Product Type	Desired Effect	Use Level
Skin Lotion	Desoaping	0.1%
	Rub-out	1–0.5%
	Protection	1–30%
	Feel	0.5–2%
Skin Cleanser	Lubricity	0.1–0.5%
	Wetting	0.1%
Antiperspirant	Anti-whitening	0.5–2%
	Detackification	0.5–2%
Preshave Lotion	Lubricity	0.5–2%
Aftershave Lotion	Feel	0.5–2%
Makeup	Water Resistance	1–5%
Shaving Cream	Reduce Razor Drag	0.5–2%

Silanol Compounds

Silanol compounds were originally called dimethiconols. These compounds carry Si-OH groups. The Si-OH group can enter many organic reactions and is in many respects analogous to the carbanol group CH_2-OH. There is one major exception. The silanol groups can homopolymerize under many conditions to produce water and a higher molecular weight silanol. The reaction is as follows:



$$2\ \mathrm{HO\text{-}}\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\mathrm{\text{-}O\text{-}(—}\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\mathrm{\text{-}O)_{10}\text{-}H} \rightarrow \mathrm{HO\text{-}}\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\mathrm{\text{-}O\text{-}(—}\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\mathrm{\text{-}O)_{20}\text{-}H} + H_2O$$

Despite the fact that these materials can homopolymerize under certain conditions, they find utilization in a variety of applications, most notably waxes, textiles and personal care applications.

Silanols, like silicone fluids, are available in a range of viscosity from 5,000 to 1,300,000 cSt. As the viscosity increases, the percentage of Si-OH decreases. **Table 2.9** shows the relationship between the percentage of Si-OH and the viscosity of commercial silanol compounds.

Table 2.9. Silanol Compounds

Viscosity (cSt)	Si-OH Weight %	Specific Gravity
	CAS No. [70131-67-8]	
15–35	4.0–6.0	0.95
45–85	0.9–1.2	0.97
100	0.8–0.9	0.97
750	0.2	0.97
1000	0.1	0.98
2000	0.09	0.98
3500	0.08	0.98
8000	0.06	0.98
18,000	0.04	0.98
50,000	0.03	0.98
150,000–200,000	0.03	0.98
380,000–420,000	0.02	0.98
900,000–1,300,000	0.010	0.98

By virtue of their hydroxyl reactive groups, these materials are raw materials for sealants, paints and, more recently, a series of silanol-based esters. High viscosity dimethiconol in cyclomethicone (D5) is used to provide soft feel, spreadability and substantivity, and gloss. Cyclomethicone evaporates readily without a residue. Silanols are more polar than fluids; consequently, they do not build up as much as an equal molecular weight silicone fluid. Silanols are used to protect color on dyed hair by sealing the hair.

High molecular weight silanols in cyclomethicone (D5) provide the following benefits:

- Soft, velvetlike feel
- Long lasting
- Excellent conditioning
- Cyclomethicones evaporate readily without a residue or cooling sensation
- Conditions hair, especially split ends
- Detackifies greasy formulations

Since silanol and carbinol are terms that can both refer to classes of silicone compounds that have hydroxyl groups (OH), there has been confusion in the use of these terms. Both types of compounds are more polar than silicone fluids (dimethicone), but silanol compounds have a Si-OH group. Prior to 1999, they were referred to as dimethiconol. They are commonly found in hair gloss formulations.

Carbinol compounds are a class of polar silicones in which the hydroxyl group is attached to a carbon atom ($-CH_2OH$). They are three types of molecules containing these groups: terminal, comb and multifunctional. The most common is the comb structure. In this type of structure, the organofunctionality is in an internal position.

Carbinol compounds are polar materials that have improved solubility in esters and other polar phases over dimethicone compounds. They are used in skin care applications and pigment grinding. The added polarity makes the performance of these materials stronger than that of dimethicone. Silanol compounds, unlike carbinol compounds, can homopolymerize (increase in molecular weight and liberate water). This makes them materials that require more care in formulation to ensure formulation stability.

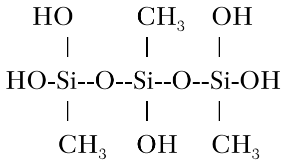
The use of silicone compounds in the synthesis of unique materials is really only limited by imagination. Interestingly, the University of Florida has a patent application (WO/2006/028491), titled "Biocides based on silanol terminated silanes and siloxanes." This patent claims a method of destroying target microorganisms and comprises the step of contacting at least one target microorganism with at least one low molecular weight silanol end group containing molecule.

Bioactive Silanol Derivatives

Silanols are also important since certain multihydroxy materials can complex (hydrogen bond) with bio-actives making them bio-available. Specific silanol derivatives can efficiently protect skin from exterior aggressions, aging and dysfunction of the cell metabolism. They can provide multiple activities (restructuring effects, prevention, protection, reparation and metabolism stimulation) and an excellent skin tolerance (nontoxic and non-allergenic).

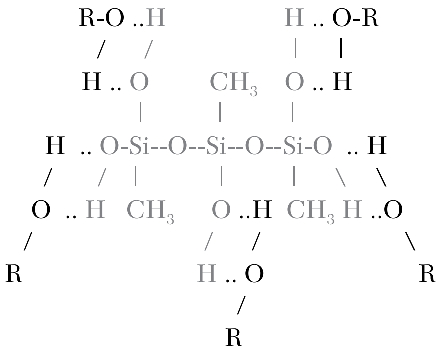
Chemistry and Structure

The silanol compounds of interest in bio-delivery have a silanol group on each Si atom. This allows for complexation (hydrogen bonding) with hydroxyl-containing actives. The silanol structure is:



$$\begin{array}{ccccc} \text{HO} & & \text{CH}_3 & & \text{OH} \\ | & & | & & | \\ \text{HO-Si} & \text{--O--} & \text{Si} & \text{--O--} & \text{Si-OH} \\ | & & | & & | \\ \text{CH}_3 & & \text{OH} & & \text{CH}_3 \end{array}$$

Note the multiple hydroxyl groups and compare this to the standard silanol. An idealized bonding of active to the silanol structure:



The silanol helps deliver the active to the tissue. **Table 2.10** shows the utility of the silanol complexes.

Table 2.10. Activity of Silanol Complexes

INCI Name	**Function**
Methylsilanol Elastinate	• Reduces puffiness, sensations of irritation and inflammation of the skin under the eyes. • Retards the effects of free radical activity.
Methylsilanol Mannuronate	• Retards the symptoms of skin aging.
Ascorbyl Methylsilanol Pectinate	• Used in antiaging and antiwrinkle preparations as an antiradical.
Siloxanetriol Alginate & Caffeine & Butylene Glycol	• Assists in metabolic stimulation. • Used to treat puffy eyes.

cont.

Table 2.10. Activity of Silanol Complexes cont.

INCI Name	Function
Methylsilanol Hydroxyproline Aspartate	• Used as an antistress agent. • Used in the prevention and restructuring of cutaneous aging. • Used in stretch mark cream.
Methylsilanol Carboxymethyl Theophylline Alginate	• Used to assist in metabolic stimulation.

Patents

Silanol compounds are the topic of many patents. The following are two important examples:

(1) U.S. Patent 4,927,952 to Gueyne issued May 22, 1990, titled "Silanol condensation products," discloses the product of condensation of a silanol or a silanol derivative, which comprises an Si atom carrying two organic radicals and two oxygen atoms connected to organic groups other than the radicals; at least one of these organic groups carries at least one NH and a NH_2.

(2) U.S. Patent 4,985,405 to Gueyne issued January 15, 1991, titled "Therapeutic product based on organic silicon derivatives," discloses silanol derivatives, containing as active agents one or more organosilicone compound, more particularly silanols, which are useful therapeutically. They are particularly suitable for the preparation of medicaments which are active as activators and regulators of metabolism and of the growth and the multiplication of cells, in particular those which are involved in the immuno-processes or in the formation of conjunctive and bone tissue.

Several esters and complexes of silanols, having highly interesting therapeutic properties, have been described and used in the past; monomethylsilanetriol salicylate and derivatives of glycerol and polyalkoxysilanes, for example.

It has been observed that the biological activity of silicon atoms, combined in an organic form, can be modified and orientated by the nature of the molecules bonded to these atoms. Thus, the action of an organic complex of silanol is itself all the more physiological, and closer to the natural action of silicon in the living cell, because the silanol is bonded to a natural molecule.

The most interesting products are complexes of organosilicone compounds with monoamino acid or with a pharmaceutically acceptable salt of such an acid. The amino acid is of the type that occurs naturally, either in the free state or combined, particularly in protides. The new product can be a definite compound. A few examples are shown next.

(1) U.S. Patent 5,087,452 to Gueyne et al. issued February 11, 1992, titled "Therapeutic product based on an organic compound of silicon and polycarboxylated

Patents cont.

polyamine, particularly useful in the treatment of atheroma," discloses a therapeutic product formed by the association of an organic derivative of silicon with a polyamine carrying hydrocarbon chains including carboxyl groups. In particular, it includes associations in which the polyamine is a chelating agent of various metals and of calcium in particular. The therapeutic product is more especially in the form of an aqueous solution destined for parenteral administration in humans and animals. It is mainly useful in the treatment of various vascular diseases, particularly for the reduction of atheromatous plaques, inhibition of lipid peroxidation, stimulation of the regeneration of elastic fibers and normalization of cell metabolism. It is possible to regenerate arterial walls with about 20 to 40 injections of 0.05 g of methyl-silane-triol salicylate, at a rate of two injections per week, i.e. over a period of 10 to 20 weeks, but more often over a period of 6 months.

(2) U.S. Patent 5,204,105 to Mausner issued April 20, 1993, titled "Cosmetic composition," discloses an emulsified composition for treatment of the skin under the eye. It comprises means for reducing puffiness of the skin under the eyes and for reducing sensations of irritation and inflammation of the skin under the eyes. The agent for enhancing firmness and elasticity of the skin under the eyes and for minimizing dark circles under the eyes can be selected from the group consisting of silicon derivatives. A preferred silicon derivative is a complex of methylsilanol elastinate and methylsilanol aspartate hydroxyprolinate.

(3) U.S. Patent 5,254,331 to Mausner issued October 19, 1993, titled "Cosmetic composition," discloses a skin cream composition of the present invention comprising: water (*aqua*) and, emulsified and dispersed in the water: (1) a protein complex comprising serum proteins and hydrolyzed animal proteins; (2) a protein-amino acid-vitamin-nucleotide complex comprising propylene glycol, serum proteins, niacinamide, water (*aqua*), adenosine phosphate, and arginine; and (3) dimethylsilanoyl hyaluronate complex, and the dimethylsilanoyl hyaluronate are each present in cosmetically effective quantities. Preferably, the skin cream composition further comprises a highly stable micellar complex.

Conclusion

The basic silicone raw materials include cyclomethicone, silicone fluids and silanols. These materials are insoluble in water and oil. These materials are the oldest and perhaps the most well-understood silicone compounds. Blending, bimodal and other variations in the oligomer distribution dramatically affect performance.

References:
1. *www.answers.com/topic/gel-permeation-chromatography*
2. U.S. Patent 2,384,384, issued September 4, 1945 to McGregor et al. titled Polymeric Silicone and Method of Making it.
3. U.S. Patent 2,443,353, issued June 14, 1948to Hyde et al. titled Production of Organosiloxanes

Chapter 3

Silicone Antifoam Compounds

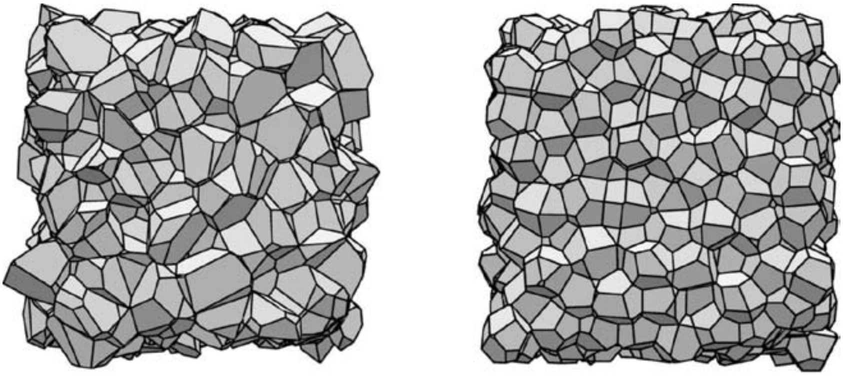
Silicone compounds are effective in lowering the surface tension of water from 72 dynes/cm^2 to 20 dynes/cm^2. This surface activity is one of the reasons why silicones are used commonly in formulation. The effect achieved once surface tension is lowered by the silicone is related directly to the structure of the silicone. Silicone molecules on the surface of water can enhance or destroy foam depending upon how it interacts with other materials on the surface of the water. Hydrophobic silica can disrupt the interface between foam and water, causing pronounced defoaming. In many applications this is not desired but in some it is. Most cosmetic formulations contain surfactants. They provide foam, emulsification, wetting and other desired properties. In some formulations, wetting may be desired, but foam may be a problem. Wetting a surface is an example in which foam generated from this process may interfere, resulting in defects in film uniformity. The first step is to change the surfactant by looking for a lower foam and better wetting. When surfactant selection offers minimal relief, antifoam compounds can be added to many processes.

Foam

Foam refers to a frothy material that is formed by trapping gas bubbles in water. A bubble exists because the surface layer of the water has a surface tension low enough to create a layer that acts like an elastic sheet. The spherical shape of the bubbles is also caused by surface tension. The tension causes the bubble to form a sphere, as a sphere has the smallest possible surface area for a given volume. Ordinary aqueous foams, like suds in a sink, are mostly gas (95%) and a little bit of liquid (5%). The gas subdivides the liquid into a matrix of tiny bubbles. Despite the high concentration of air, foam is a springy material that is quite different from air.

Foam is a direct consequence of surface tension reduction. Not all materials that have low surface tension form foam, but all foaming materials lower surface tension. Since most aqueous cosmetic products contain materials that lower surface tension in order to work in the desired application, foam occurs. Sometimes foam is desired. Shampoos without foam do not receive consumer acceptance, despite the fact that foam and detergency are two different phenomenon. Foam is a very beautiful, complicated structure. **Figure 3.1** shows some common structures.

Figure 3.1. Structure of Foam



There are many instances in which foam is a detriment to the intended application. The application of a film can be disrupted by foam. The foam can cause "fish eyes," areas in which the substrate is not fully covered. The first line of defense in controlling foam is to formulate using surface active agents that maximize the desired effect, like wetting or conditioning, while minimizing the undesired effect, like foam. This requires selection of the proper material. In the world of silicone surfactants, molecular weight plays a major role in determining which material foams and which does not.

Another major area of interest to the cosmetic chemist is the elimination of foam that occurs when cleaning up the mixing tanks and various other pieces of equipment that are used in making cosmetics. Washing out a two thousand gallon "empty" shampoo tank is not accomplished without generating foam, which may also be a problem when the wash water is discharged to the waste treatment plant. The inclusion of a properly selected antifoam agent is important.

The term defoamer and antifoam have different meanings, though the differences have been blurred over the years. The term *antifoam* is generally used to denote a compound with the ability to prevent foam from forming. In contrast, the term *defoamer* generally denotes a material that will knock down existing foam. While some types of compounds are more effective in antifoaming applications and some compounds are more effective in defoaming applications, most compounds have properties that make them useful in both applications.

Antifoam agents are divided into three classes:

1. Those compounds used in industrial applications
2. Those compounds used in applications sanctioned under 21 C.F.R. 173.105, 173.340 or 173.300

3. Those compounds which have been modified to meet specific performance requirements

Since most silicone compounds are water-insoluble, they simply float on water as oily liquids. This behavior makes them useful in destroying or inhibiting foam.

Mechanism of Antifoam

Regardless of the process, there are two mechanisms by which antifoam compounds work.[1] In the first, they destroy interfacial films; and in the second, they impair foam stability. The former is more common and more effective in most applications. A layer of antifoam, by virtue of its insolubility, ends up in between the bubble and its contact points with the water. This dislodges the bubble and breaks it.

Silicone fluids have both antifoam and defoaming attributes. They can be modified by reaction with silica to make significantly more efficient antifoam compounds. Silicone-based antifoam compounds for use in detergents are composed of two major components: silicone fluid and hydrophobic silica. The fluid polymer acts as a carrier to deliver the silica particles to the foam air-water interface, where film rupture occurs.

Efficient silicone-based antifoam compounds can be prepared by the reaction of silanol compounds with silica to form in-situ hydrophobized silica. Many people refer to silanol-based antifoam compounds as "silicone-free." I believe this is misleading. At best, the term "silicone-fluid-free" may be employed.

The performance of silicone-based antifoam compounds is independent of water hardness. They are effective at very low addition levels in all types of surfactant systems normally present in detergent formulations and are effective across a wide range of conditions. Furthermore, silicones cause no yellowing on fabric. Silicone-based antifoam compounds that are 100% active are normally referred to as silicone antifoam compounds. They are generally composed of silicone fluid in the range of 350–1000 cSt into which has been placed 12% hydrophobic silica. Silicone fluid alone does not function well as antifoam.

For well over three decades, tiny particles of silica or relatively high-silica silicates have been used for foam inhibition in aqueous foaming systems. In order to work as antifoam, silica must be treated to make it hydrophobic. The most common treatment is the in-situ hydrophobization, a process that places 12% silica in 88% silicone fluid and heats the dispersion to 150°C for several hours. The exact reasons for the effectiveness of the treated siliceous materials in aqueous foaming systems have been a subject of ongoing debate for years.

One theory is that the silicone fluids with their low surface tension, spontaneous spreading over the bubble surface is primarily responsible for bubble rupture and that the presence of the silica filler increases the spreading pressure and improves dispersibility of silicone oil. The following is known:

- Silicone oil that has no hydrophobic silice present does not act as an efficient foam inhibitor in aqueous foaming systems.
- The combination silicone fluid and hydrophilic silica at normally used ratios is ineffective as antifoam unless it is heat treated at 150°C for two hours

with a base catalyst. Under these conditions the silicone oil presumably reacts with the silica surface.

- A mixture of silicone oil and hydrophobic fine silica is effective as antifoam even without heat treatment.
- Hydrophobic fine silica alone is ineffective as a foam inhibitor, but is capable of defoaming aqueous foams.

Both the hydrophobic fine silica and the silicone oil are necessary for foam inhibition in aqueous foaming systems. This conclusion is rationalized as follows. First, the hydrophobic silica is believed to be a foam breaker, i.e. the fine particles of hydrophobic silica help to rupture foam bubbles. Second, the silicone oil is essentially a carrier fluid that protects the filler particles and brings them into contact with the foam bubble surfaces.

The silica/silicone fluid combination is then combined with an emulsifier, water and a polyacrylate thickener. The result is sometimes called "silicone antifoam emulsion." However the term emulsion applied to aqueous silicone antifoam is a misnomer. The compositions are actually thickened dispersions. Addition of water will cause them to separate into two layers. The dispersion can be rethickened with sodium polyacrylate or a similar thickener.

Foam formation is the result of dissolved molecules in a liquid. The dissolved molecules alter the surface tension of the liquid, and can be viewed as surface active agents (surfactants). The surfactants can be nonionic, cationic, anionic or amphoteric.

- Nonionic surfactant-generated foam is generally depicted as having a hydrophobic head (water-insoluble portion) at the air-liquid interface, and the hydrophilic tail (water-soluble portion) at an aqueous solution. Its orientation would be reversed in non-aqueous liquids.
- Anionic surfactant-generated foam would have a negative charge on the hydrophilic tail. As aqueous liquid is pulled down over the bubble's surface, the negative charges reach a concentration at the bubble at the liquid interface. Most often, the negative charge serves to stabilize the bubble, and the bubbles will begin to repel each other at the interface. This phenomenon is known as an "electrostatic repulsion."
- Cationic surfactant-generated foam would have a positive charge on the hydrophilic tail and exhibit similar behavior as the anionic surfactant in an ideal aqueous liquid.

The liquid can be either aqueous, non-aqueous, or both (some industrial systems may contain dissolved organics which require special consideration). Different surfactants will generate different types of foam and foam stability. When agitated, bubbles will form, which will immediately encounter gravitational effects, pulling liquid along the bubble walls back down into the liquid beneath the bubble.

When the surface tension is high enough, bubble formation becomes more rigid and stable. If a bubble is subjected to mechanical agitation, bubbles caused by entrained air would form very stable lamellar structures. The Marangoni effect is a major stabilizing factor in foam and is driven by osmotic pressure. The Marangoni effect occurs when liquid with a high surface tension pulls more strongly on the surrounding liquid than one with a low surface tension. The presence of a gradient in surface tension will naturally cause the liquid to flow away from regions of low surface tension. In some cases, the aqueous liquid is being pulled through the bubble wall creating regions of high and low surfactant concentrations, which sets up a gradient along the bubble's surface. The gradient would pump liquid back onto the bubble wall. This phenomenon is referred to as a "surface transport."

The bulk viscosity also contributes to foam stability. High viscosity liquids generally produce more stable foam. As the viscosity of liquids increases, the amount of entrained air likewise increases, and bubbles can become trapped below the liquid's surface. Increasing viscosity of the system also reduces the coalescence capability of smaller bubbles merging to become larger bubbles. If the bubbles become large enough (increasing the diameter), bubble stability decreases. The surface viscosity is also important, as it effects the coalescence formation between bubbles. The higher the bulk viscosity becomes, the lower the coalescence formation is between bubbles. When the surface tension is lowered on the bubble, it will burst. The resulting interaction of the defoamer to disperse the foam and its bubble formation is a physical interaction with the aqueous liquid.

Testing Antifoam Performance

Antifoam agents should be tested in an environment that simulates the process in which they will be used. Many different systems have been proposed. The Tramfloc Antifoaming and Defoaming Evaluation Procedure[1] is shown in **Sidebar 1**.

Tramfloc Antifoaming and Defoaming Evaluation Procedure[1]

Required Materials for the Cylinder Shake Test

1. One 250 mL and one 1000 mL beaker
2. Variable speed electrical mixer
3. Low shear mixing blade such as Jiffy Blade
4. Balance
5. 0.4% Kelzan water (0.4% Kelzan S solution in water with preservative)
6. 100 mL graduated cylinders
7. 1% solution of the Sodium salt of Dodecylbenzyl Sulfonic Acid (NaDDBSA)
8. Transfer pipette or syringes
9. Stopwatch

cont.

Tramfloc Antifoaming and Defoaming Evaluation Procedure[1] cont.

METHOD

Prepare 200 g 10% defoamer dispersion in thickened water.

1. Measure in a 250 mL beaker the appropriate amount of thickened water, preferably 0.4% Kelzan S solution (appropriate amount: 200 g minus the amount of defoamer).
2. Add the necessary amount of the defoamer concentrate so you will end up with 200 g 10% solution.
3. Mix it for five minutes at approximately 500 rpm with a low shear mixing blade such as "Jiffy Mixer." Please note that high shear conditions will break any defoamer emulsion causing erroneous results and excessive oiling.

Defoaming

The first part of the measurement is a test for defoaming, also known as quick knockdown. It shows how well the product can destroy foam once it has formed.

1. Pour 45 mL water in the 100 mL graduated cylinder.
2. Add 5 mL of the 1% NaDDBSA to the cylinder so the resulting foaming medium will be 0.1% NADDSBA solution.
3. Shake the cylinder for 60 seconds in such a way that you perform two full shake cycles in every second, 120 shakes total. As a result the foam should reach the top of the cylinder leaving no free airspace. If the foam does not reach the top, it indicates a contaminated cylinder.
4. Remove the stopper and add one drop of the 10% defoamer to the foam using the transfer pipette or syringe, and start the stopwatch at the same time.
5. Record the time when the top of the collapsing foam reaches the 60cc mark and when it goes "flat." "Flat" is when the foam first opens up exposing the liquid surface. Also record the foam height at 60 seconds if there is any foam.
6. Stop and zero the stopwatch after five minutes and record the foam height, if there is any foam at that time.

Antifoaming

The second part of the measurement is to determine the antifoaming properties of the specific Tramfloc compound. Antifoaming is the property of the material that if it is properly dispersed in a foaming medium it can prevent foam formation.

cont.

Tramfloc Antifoaming and Defoaming Evaluation Procedure[1] cont.

1. Replace the stopper in the cylinder and shake it for 60 seconds just as it is described in point 6. After the 60 seconds shake put the cylinder on the counter without delay and start the stopwatch.
2. Record the initial foam height, the time required for the foam to collapse to 60cc, and the time to go "flat." Also record the foam height after five minutes if there is any foam at that time. Repeat the above test two or more times if more accuracy is required.

Conclusion

Foam is a material that will always be of interest to the cosmetic chemist. In some formulations it is highly prized, in others foam is a fatal formulation flaw. Removal of foam during cleaning operations will always offer a challenge. Because they alter surface properties, silicone compounds can be engineered to provide effective foam control properties. The effects silicone compounds have on foam can range from enhancement to destruction. This wide range of possibilities makes silicone compounds effective formulation additives.

References:
1. *http://www.tramfloc.com/defoamer_testproced.pdf*
2. AM Kraynik, Physical Review E 67, 031403, (2003)

Chapter 4

Emulsions

Because the unique solubility that silicone possess, incorporation of silicone fluids is a major challenge to the formulator. Silicone fluids are not soluble in either water or organic oils. The most common solvent used in the personal care industry is water. To make silicone useful in formulations containing water, there are two approaches. The first is to chemically modify the silicone to increase the solubility in water as discussed in other chapters, or to make emulsions of the silicone. This chapter will address emulsions.

An emulsion is a mixture of two insoluble materials, in this case water and silicone. One material is dispersed in the other. The two phases are called the continuous phase and the discontinuous phase. In a standard emulsion silicone is the discontinuous phase and water is the continuous phase. In invert emulsions silicone is the continuous phase and water is the dispersed phase. Emulsions contain emulsifiers. Emulsifiers are surface-active agents that allow the discontinuous phase to be uniformly dispersed through the continuous phase. The surfactant can be of fatty origin (generally nonionic) or silicone (generally alkyl dimethicone copolyol). The nature of the emulsion is dependant upon the interaction of (1) water, (2) silicone and (3) surfactant.

Water is a ubiquitous material in the personal care industry with unique properties. Without water, life as it is known would be impossible. **Table 4.1** shows the properties of water.

Table 4.1. Properties of Water

Name	Water
Molecular formula	H_2O
Molecular Weight	18.0
Density	0.998 g/cm^3 (liquid at 20°C)
Melting point	0°C
Boiling point	100°C
Specific heat capacity	4.184 J/(g•K) (liquid at 20°C)
Surface Tension	72 dynes/cm^2 at 25°C

The interaction between water and oil, while simple in concept, involves complex physical science and mathematics. Water has several unique properties[1]:

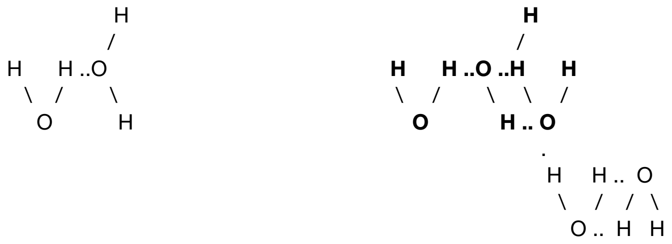
- Water has a partial negative charge (σ-) near the oxygen atom due to the unshared pairs of electrons, and partial positive charges (σ+) near the hydrogen atoms. In water, this happens because the oxygen atom is more electronegative than the hydrogen atoms. That is, it has a stronger "pulling power" on the molecule's electrons; drawing them closer (along with their negative charge) and making the area around the oxygen atom more negative than the area around both of the hydrogen atoms. Hydrogen bonding is a very important concept in understanding why oil and water do not mix.
- Water sticks to itself (cohesion) because it is polar.
- Water also has high adhesion properties because of its polar nature.
- Water has high surface tension caused by the strong cohesion between water molecules. This can be seen when small quantities of water are put onto a non-soluble surface such as polythene; the water stays together as drops. Another surface tension effect is capillary waves. These are the surface ripples that form from the impact of drops on water surfaces and sometimes occur with strong subsurface currents.

Water is the most common solvent used in the personal care market. It is the solvent into which we must get our additives in order to make formulations. Since pure oil, silicone and fluoro compounds are not soluble in water; there are two possible alternatives to allow for their use in water-based systems. First, the insoluble materials can be divided into fine droplets and surfactants and high-energy equipment used to make an emulsion. Secondly, modifications can be made to the molecules to improve their solubility in water. This chapter will deal with making emulsions using silicone fluid.

Silicone fluids are water-insoluble. When silicone fluid and water are mixed together, globules of the oil can be observed in the mixture. Upon cessation of mixing, the silicone fluid comes to the top and two distinct phases develop. As once learned in physical chemistry, systems will develop into their most random, lowest energy state. So, how does oil float on water? It appears to be a highly ordered state. The answer is that this is the lowest free energy system, because any system that has oil in water disrupts hydrogen bonding in water. Because there is a partial negative charge on oxygen and a partial positive charge on hydrogen, water forms intermolecular bonds. **Figure 4.1** shows the association between molecules.

An emulsion is a mixture of two materials that are insoluble in each other. One substance (the discontinuous phase) is dispersed in the other (the continuous phase). Regular emulsions have oil as the discontinuous phase and water as the continuous phase. They are referred to as o/w (oil-in-water) emulsions. Invert emulsions are these emulsions in which water is dispersed in the oil phase. Often the difference between the two is the type of emulsifier used.

Figure 4.1. Association Between Molecules



2 molecules **5 molecules**

Emulsification is the process by which emulsions are prepared. Emulsions are inherently metastable, breaking with time. The best that can be done in masking them is to prolong the time it takes to separate. Emulsions do not form spontaneously; they require the proper surfactant and a source of energy input through shaking, stirring or homogenizers to form an emulsion. In time, emulsions tend to revert to the stable state of oil separated from water. Surface-active substances (surfactants) can increase the kinetic stability of emulsions greatly so that, once formed, the emulsion does not change significantly throughout years of storage.

The most common processing equipment is a homogenizer that uses mechanical energy to break the silicone into small units. This process improves the stability. Proper selection of the surfactant system and the process conditions in homogenization are critical to making good emulsions. Poorly made emulsions will revert to an oil phase and a water phase.

Silicone emulsion products generally contain the following components:

- Water (typically at least 40%)
- Silicone (typically 55%)
- A surfactant

Silicone contained in an emulsion is delivered from a micelle. Since equilibrium exists between silicone on a substrate (fabric, fiber, metal, rubber, hair or skin), and silicone in an emulsion, much of the silicone ends up in the wash water. Not only is this a very costly and inefficient use of expensive raw materials, but it also gives rise to environmental concerns since the wash water ends up in the sewer. Emulsions are susceptible to freeze-thaw instability. Moreover, if additional surfactants are added in making a formulation containing the emulsion, the emulsion may split. The following is a list of emulsion terminology.

Emulsion Terminology[2]

In making emulsions, two materials that are not soluble in each other are required. The phases (discontinuous or continuous) can be oil, water or silicone. The two insoluble phases are combined in the presence of an emulsifier.

Discontinuous Phase. The phase that is dispersed or finely divided within the emulsion.

Continuous Phase. The phase or medium in which the dispersed phase is suspended. The continuous phase is also called the external phase. While it is true in many emulsions that the continuous phase is the larger of the two phases as far as weight percentage is concerned, it does not have to be the larger. Formulation techniques allow for the preparation of emulsions in which the continuous phase is the lower volume. The general rule is that if you can dilute an emulsion with water, without splitting, it is a water continuous emulsion, or an o/w emulsion.

Discontinuous Phase. The discontinuous phase is the phase that is dispersed into the continuous phase.

Dispersion or Emulsion. There has been much confusion generated in the difference between an emulsion and a dispersion. The former is metastable and can be diluted and remain stable, while the latter is only stable in a thickened state. Emulsions are commonly thickened. Thickening can be accomplished with polyacrylates, or sometimes with salt. High viscosity achieved by thickening is highly desirable to keep the emulsion from splitting. Antifoam compounds are dispersions. They stay together by virtue of their viscosity. If diluted they split into two phases but can be made into one phase again only by adding thickener. Care must be exercised to make sure the emulsion is indeed not a dispersion, since use of a dispersion will almost always result in an unstable product. High-viscosity dispersions may not split as prepared, but upon dilution two distinct phases will result. True emulsions can be diluted to low viscosity with the addition of continuous phase, while dispersions will split into two phases.

O/W (Oil-in-Water) Emulsion. An emulsion in which the oil phase is dispersed into a water phase, e.g., mayonnaise, whipped toppings, infant formulas, salad dressings, lotions.

W/O (Water-in-Oil) Emulsion. An emulsion in which the water phase is dispersed into the oil phase, e.g., margarine, icings, some hand creams.

Triple Emulsions. Recently, a series of emulsions has been developed that are the w/o/w emulsions. This is only one type of multiple emulsion. These emulsions are water in oil emulsions that re-emulsified in water. They have unique properties, including outstanding skin feel. Being the most technically sophisticated emulsions made, they can present problems in preparation. The technology has been around since the late 1970s and is now gaining acceptance as more sophisticated technology becomes available. Stability is still a difficulty, however.

Emulsion Equipment. The making of emulsions includes more than the proper selection of discontinuous phase, continuous phase and an emulsifier. It also includes a number of additives such as salt and processing aides, and includes high-energy processing to provide a small particle size. As previously stated, the smaller the particle size the more stable the emulsion.

There are a number of high-energy pieces of equipment, including:

Homogenizer. Homogenization is a mechanical treatment process that lowers particle size of the discontinuous phase. It is brought about by passing the emulsion under high pressure through a tiny orifice. During this process, the oil globules decrease in diameter and increase in number and surface area. The net result, from a practical view, is a reduced tendency to separate. Three factors contribute to this enhanced stability: a decrease in the mean diameter of the globules (a factor in Stokes Law[a]), a decrease in the size distribution of the globules (causing the speed of rise to be similar for the majority of globules so they don't tend to cluster during creaming), and an increase in density of the globules (bringing them closer to the continuous phase).

Colloid Mill. A colloid mill does its work by hydraulic shear, bearing a tremendous amount of energy on a small portion of material in the form of a thin film. This action overcomes the strong polar forces that bind together small clumps of solids or hold together drops of liquid. A colloid mill will not break down hard crystalline particles as an impact type mill would do. It will, however, reduce particles down to their ultimate crystal size by breaking up the agglomerates into which they form. In the case of emulsions, the same principle holds. As the particles of the dispersed phase of the emulsion get smaller and smaller, it requires progressively more energy to overcome the surface tension holding them together. Enormous hydraulic shear is needed to do the job and a colloid mill is the ideal piece of equipment to accomplish it.

Emulsion Stability

The following factors contribute to improved emulsion stability:

Interfacial Tension. At the interface formed between two insoluble liquids, the molecules will interact with each other and produce interfacial tension. In order to produce a stable emulsion, it is desirable to reduce the interfacial tension. Emulsifiers accomplish this task by altering the interaction between the two phases. This occurs because emulsifying agents are amphiphilic compounds. They will concentrate at the oil-water interface, producing a significant reduction of the interfacial tension and will need less energy to form emulsions. Despite a lowering of interfacial tension when surface-active agents are added, the free energy of the interface

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[a] George Gabriel Stokes, was a mathematician, who made important contributions to fluid dynamics.

remains positive, leaving a persisting state of thermodynamic instability.

Repulsion by Electric Charge. Emulsion stability is often explained by the presence of repulsive electrical charges on the surfaces of emulsion droplets. According to the DLVO theory[b], the dispersed particles are subject to two independent forces: the van der Waals force of attraction and the electrostatic force of repulsion arising from the presence of electrical double-layers at the particle surfaces. The net interaction between the particles is obtained by summing these two terms. If the repulsion potential exceeds the attraction potential, an energy barrier opposing collision will result. If the magnitude of this energy barrier exceeds the kinetic energy of the particles, the suspension is stable. The van der Waals negative potential becomes significant only when the distance between the particles is quite small.

At intermediate distances, the repulsive potential is larger than the attractive potential. Attention should be taken on application of the DLVO theory, which was originally developed for inorganic sols (in which the dispersed phase consists of submicroscopic spherical solid particles), to emulsions (where the dispersed phase consists of oil droplets stabilized by adsorbed emulsifying agents). For example, in emulsions, coalescence involves disruption of an adsorbed film around the droplets, and calculations of the potential energy barrier opposing the collision of oil globules must take into account such factors as the distortion or flattening of the oil droplets upon close approach. However, the DLVO theory still provides a good approximation of the electrostatic contribution to emulsion stability.

Ionic surfactants contribute significantly to the stability of o/w emulsions by contributing to the establishment of electric double layers in the aqueous phase adjacent to each oil droplet. Reversibly, this mechanism is of little importance in the stabilization of w/o emulsions, since the oil phase does not generally supply counter ions in sufficient amounts to establish a strong potential gradient.

Stabilization by Finely Divided Solids. Solid particles of very small size, as compared with the size of the dispersed oil droplet, can stabilize an emulsion by adsorbing at the interface to form a physical barrier around the droplets. In addition, energy is required to dislodge solid particles from the interface, since the o/w interface must be increased to do so. Powdered silica, various clays, basic salts and plant cell fragments are examples of such agents.

The emulsion type produced and its stability depend largely on the relative abilities of the two phases to wet the solid particles. The phase that preferentially wets the solid particle tends to become the continuous

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[b] DLVO theory is named after Derjaguin, Landau, Verwey and Overbeek who developed it in the 1940s. The theory describes the force between charged surfaces interacting through a liquid medium. It combines the effects of the van der Waals attraction and the electrostatic repulsion due to the double-layer of counter ions.

phase. If the interfacial tension between solid and oil (g_{SO}) is greater than that between solid and water (g_{SW}), the contact angle (q) of the solid with the aqueous phase is less than 90 degrees, and the major portion of the solid particle resides in the water phase, thus favoring an o/w emulsion. The converse takes place if $g_{SW} > g_{SO}$. Nevertheless, if solid particles remain exclusively in either phase, they have no stabilizing effect. On the other hand, the most stable emulsion is formed when the angle of contact between the two liquids and the solid surface is close to 90 degrees. The surface of the solid and its contact angle may be modified by adjusting pH and by adsorbing various amphiphilic compounds to its surface. Concentration and chain length of the amphiphile's hydrophobic group are important in this regard.

Based on these considerations, it has been recommended that, for the preparation of emulsions stabilized by solid particles, a surface-active substance should be added that is soluble in the least-wetting (discontinuous) phase. Additionally, the concentration of the surface-active agent should be adjusted to give a contact angle in the vicinity of 90degrees between the powder and the two liquids.

Several methods have been introduced to aid in the selection of an appropriate emulsifier, or blend of emulsifiers, for a given purpose. The most prominent of these is the one based on the relative importance of the hydrophobic and hydrophilic properties of the molecules (HLB system).

Silicone Emulsions

Silicone emulsions are used in both hair and skin care products. The preparation of stable emulsions results in a silicone oil in a micelle with a fine particle size. The preparation of a stable emulsion requires the selection of the proper emulsifier pair and the use of a homogenizer. All must be optimized for best performance of the emulsion in the formulation. Many of the complications of using emulsions for the delivery of silicone to substrates relate to the fact that the silicone is delivered out of a surfactant micelle.

When an emulsion is applied to the skin or hair, the silicone oil is delivered to the substrate that has been wetted out by the surfactant at the air-water interface, and the emulsion break and oil are deposited. However, the surfactant, having emulsification properties of its own, re-emulsifies some of the oil. The net result is that silicone ends up on the substrate and in the wash water. This complex equilibrium results in inefficiency in the use of emulsions.

In addition, emulsions are subject to some inherent shear instability and freeze-thaw instability. Finally, there are limitations as to the type of surfactant that can be added to an emulsion-containing system. If the HLB of the formulation is shifted too much, the emulsion will break.

However, with the proper selection of emulsion and the proper formulation techniques, silicone emulsions can be used in the creation of many emulsions that are useful in a plethora of applications. A few of these include mold release agents, automotive tire gloss compounds, textile softeners, antifoam compounds and overspread in web offset printing.

Dimethicone and dimethiconol emulsions are used commonly in many industrial applications. All emulsion products are comprised of water (typically at least 40%), silicone (typically 55%) and the remainder surfactants to facilitate the emulsion. The fact that 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 silicones on the substrate—such as fabric, fiber, metal, rubber, hair or skin—and the silicone in the emulsion, much of the silicone ends up in the wash water which, as stated earlier, is costly, is an inefficient use of expensive raw materials and results in environmental concerns. In order to overcome this limitation, silicone surfactants have been developed that provide non-micelluar delivery to the substrate.

Types of Emulsions

There are two different types of silicone emulsions that exist based upon the raw material used to make the emulsion. Silicone fluids can be prepared and then made into an emulsion, or the silicone fluid can be synthesized in the emulsion from more basic raw materials that have been emulsified.

Silicone emulsions that are prepared by the emulsification of pre-made silicone fluid are the oldest type of product. Early U.S. Patent 2,755,194 issued July 17, 1956, to Volkmann titled Organosilicone emulsions, discloses a stable emulsion having a particle size of 0.5 microns (see **Sidebar** Silicone Emulsion Formulation).

The process includes not only a nonionic emulsifier, but also an anionic material. The repetitive colloid mill treatment is important in getting particle size down. The larger the particle size, the less stable the emulsion. This type of reaction has been used within the last 10 years, when regulatory issues forced the removal of the nonyl phenol ethoxylate. The initial three steps make an invert emulsion (w/o), which is transformed into a regular emulsion (o/w) when the last water is added.

The problem with this technology is that the placement of this type of emulsion into a surfactant containing system like a shampoo will result in a significant increase in the HLB and a split emulsion, despite the small particle size.

Emulsion Polymerization

The basic emulsion polymerization process of silicones has been known for a long time. US Patent 2,891,920 to Hyde issued June 23, 1959, titled Polymerization of organopolysiloxanes in aqueous solution shows this formulation (see **Sidebar** Silicone Emulsion-Emulsion Polymerization).

There have been numerous refinements, improvements and alterations to the above processes through the years to change the rate of addition of the cyclomethicone, including additional nonionic surfactants. Nonionic surfactants useful in the method of the invention include nonionic surfactants with hydrophilic-lipophilic balances (HLB) between 10 and 20. Specifically, the following nonionic surfactants were found useful in the invention method:

- 2,6,8-trimethyl-4-nonyloxypolyethylene oxyethanol (6 EO) (sold as Tergitol TMN-6 by Union Carbide)

Silicone Emulsion Formulation

Step 1—Fluid and Surfactant Blend

Parts	**Material**
35.0 parts	350 viscosity silicone fluid
1.8 parts	Nonylphenol 10
0.15 parts	Alkyl aryl polyether sulfate (Triton W-30)

Mix well, send through a colloid mill

Step 2—First Water

Parts	**Material**
5 parts	Water

Mix well, send through a colloid mill

Step 3—Second Water

Parts	**Material**
10 parts	Water

Mix well, send through a colloid mill

Step 4—Last Water

Parts	**Material**
47.5 parts	Water

Mix well, send through a colloid mill

Total parts **99.45 parts**

- 2,6,8-trimethyl-4-nonyloxypolyethylene oxyethanol (10EO) (Tergitol TMN-10 by Union Carbide); alkylene-oxypolyethyleneoxyethanol (C 11-15 secondary alkyl, 9 EO) (sold by Union Carbide as Tergitol 15-S-9)
- alkylene-oxypolyethylenoxyethanol (C 11-15 secondary alkyl, 15 EO) (sold as Tergitol15-S-15 by Union Carbide)
- octylphenoxy polyethoxy ethanol (40 EO) (sold by Rohm and Haas as Triton X405).

US Patent 4,999,398 issued March 21, 1991, discloses a process for making microemulsions by emulsion polymerization having a droplet size of 0.036 microns (more than an order of magnitude lower than the above emulsion polymerization process). These emulsions are much more stable and of more interest in surfactant-based products.

Silicone Emulsion-Emulsion Polymerization

Material	Grams	%wt
1. Dioctadecyl dimethyl ammonium chloride	8.0	1.5
2. D-4 (cyclomethicone)	283.0	53.0
3. Water	243.0	45.5
Total	534.0	100.0

Procedure

1) Add 1 and 2 together; mix well
2) Add 1 and 2 mixture to 3
3) Add aqueous ammonia to make pH alkaline
4) React at 70°C 10 hours

Deposition of Naturally Derived Hair Color via Reactive Silicone Emulsions

Silicone emulsions have been used to maximize dye deposition on hair. The formulation uses a silanol emulsion as the reactive material that cross-links on dry down to maximize deposition and retention of dye.

Hair color, both permanent and semi-permanent, has become a quickly growing segment of the cosmetic and toiletries market. Although the consumer likes the long-lasting effect of permanent color, the damage that it causes to hair is a major drawback. The semi-permanent colors are gentler though the upkeep is more difficult.

Several naturally derived pigments were treated with reactive silicone to form polymers that were incorporated into a conditioning base and used to treat hair tresses. Various types of tresses were used—virgin, bleached and gray. The deposition and staying power of the colors was examined on the tresses after repeated washings. It appears that the silicone/pigment complex polymerizes with the keratin fibrils in the hair resulting in remarkable deposition and strength of color. The color remains on the hair after repeated washings and even has the ability to cover gray.

Methods

Four natural dyes—indigo, madder, osage and cutch–were combined into a slurry with a reactive silicone at a ratio of one part color, one part silicone and two parts water. This slurry was then incorporated into a conditioner base at 20% concentration by weight. The conditioner/color product was tested at two different pH levels—4.5 and 9.8. Swatches (2.0–2.2g, 8 in. long) of virgin gray and brown hair were washed three times with Prell Oily to Normal Original Shampoo®—two grams of shampoo for two minutes with rinsing in 25°C water. Swatches were then ready for treatment. For coloring treatment, two grams of product was used, left on the swatch for 20 minutes, rinsed with 25°C water and then washed with two grams of the shampoo (following same procedure as above).

The procedure used for treatment is as follows:

1. One swatch as control with no treatment
2. Swatch given one treatment—one application of conditioner/color and one wash with shampoo
3. Swatch treated three times—three conditionings, three washings
4. Swatch treated seven times—seven conditionings, seven washings
5. Swatch treated seven times and then washed an additional 21 times (with no concurrent color treatment)

After treatments, inspection of color was made visually and then chromameter measurements were taken. The formulation for the conditioner base used is shown in **Table 4.2**.

Table 4.2. Conditioner Base

Material	% Wt
Water	67.75
Methylparaben	0.15
Tetrasodium EDTA	0.05
Dimethicone copolyol	1.00
Rice bran oil	4.00
Cetyl alcohol	3.00
Propylparaben	0.10
PEG-100 stearate	1.15
Glyceryl stearate	2.50
Reactive silicone	5.00
Natural color	5.00
Water	10.00
Imidazolidinyl urea	0.30

The increase in deposition of the color can be noted both visually and instrumentally as the number of treatments increases. On the tresses that were treated seven times and then washed an additional 21 times, the intensity of the color remained.

The natural colors also gave excellent gray coverage. One of the most important aspects of the study was the absence of damage to the hair. The presence of the reactive silicone combined with the low pH system resulted in a coloring treatment that is conditioning to the hair. This positive aspect was translated into good wet-combability, minimal buildup or residual, high shine and a soft feel. Also, the color on the hair did not rub off, which means that it would not transfer to fabric. The combination of a reactive silicone with natural coloring agents results in a gentle, conditioning hair color system that does not damage the hair. The colors that were examined fall into the black/blue, red, yellow and brown ranges and can be combined in many different ways to yield all manners of color combinations. The conditioning treatment gives a better and longer-lasting deposition of color than several of the semi-permanent color products currently available on the market.

There is a number of silicone emulsions in which the silicone compound is prepared in the emulsion itself. These in-situ products include specific amino emulsions sold commercially. Specifically, these products are the reaction products of an emulsion containing amino silanes and silanols that react in the emulsion. These compounds are referred to in the chapter on amino silicones and are significant to the personal care market.

While emulsions are an important part of the personal care usage of silicones and are more consumer-friendly in aqueous systems than silicone fluids, there are some significant limitations in their stability. These limitations include splitting over time, freeze-thaw properties, splitting of the emulsion with the addition of surfactants and residual silane in reactive emulsions.

Conclusion

Emulsion technology has been around for many years. It is one of a number of approaches that allows silicone oil to be used in aqueous systems that comprise most of the cosmetic world. While there are challenges, there has been a great deal of advancement in the preparation of useful emulsions. The improvements are generally the result of smaller particle size emulsions. There will continue to be developments in the fine tuning of emulsions for cosmetic applications, offering the formulator greater latitude in preparation of products.

References:
1. *www.biology.arizona.edu/biochemistry/tutorials/chemistry/graphics/water.gif*
2. *http://tooldoc.wncc.nevada.edu/mayo.htm*

Chapter 5

Silicone Surfactants

To overcome the limitations of the use of silicone emulsions or neat silicone oils, silicone surfactants have been developed. These compounds contain a silicone-soluble group and at least one water-soluble or oil-soluble group in the same molecule. The result is a series of compounds with varying solubility in oil, water and silicone.

Since these materials contain both a water-soluble and silicone-soluble portion, they are surface active. Conventional surfactant molecules contain an oil-soluble group (commonly a hydrocarbon chain) and a water-soluble group (commonly a polyoxyethylene glycol group in nonionic surfactants). Silicone surfactants replace hydrocarbon hydrophobicity or add silicone-based hydrophobicity. The combination of a silicone and hydrocarbon hydrophobe as well as a water-soluble group yields a multifunctional surfactant. These surfactants make possible the formulation of a wide variety of products soluble in oil, water and silicone with substantivity, low irritation, skin feel and other attributes of silicone, in addition to the properties expected from conventional surfactants. In molecules where silicone is predominant, the functional attributes of silicone will predominate.

Formulation with these multifunctional materials requires consideration of the balance of silicone/oil and water-soluble portions of the molecule. The so-called 3D HLB has been proposed to allow for a systematic approach to using these surfactants.[1] Since mineral oil, silicone oil and water are mutually insoluble; there is a need for an expanded terminology for surfactants containing these moieties.

A great variety of silicone derivatives, which differ both in structure and functional properties, are now available to the formulator. These derivatives permit great formulation latitude and make possible the creation of products optimized for specific applications.[2] For example, they are very important additives in the urethane field for foam applications, in agricultural applications as super wetters and in personal care products as conditioners, emulsifiers and softeners. The silicone surfactants are amphilic, meaning they have at least two groups that are not soluble in each other in pure form. This results in molecules that are surface active, orientate at surfaces and form micelles if added in sufficient concentration. The incorporation of a variety of ionic and other functional groups results in many formulator friendly products. In fact, there are few classes of fatty surfactants for which there are not silicone analogues. **Table 5.1** shows the parallel universe of silicone surfactants available that are commercial realities.

Of interest for this chapter is how molecules are designed and manufactured. Silicone chemistry, coupled with classical organic chemistry, offers the formulator almost limitless possibilities.

Table 5.1. Comparison of Hydrocarbon-based and Silicone-based Surfactants

Traditional Products	Silicone Products
ANIONIC	
Phosphate esters	Silicone phosphate esters[7,8]
Sulfates	Silicone sulfates[9-11]
Carboxylates	Silicone carboxylates[12,13]
Sulfosuccinates	Silicone sulfosuccinates[11,15]
CATIONIC	
Alkyl quats	Silicone alkyl quats[16]
Amido quats	Silicone amido quats[17]
Imidazoline quats	Silicone imidazoline quats[18]
AMPHOTERIC	
Aminopropionates	Silicone amphoterics[14]
Betaines	Silicone betaines[15]
NONIONIC	
Alcohol alkoxylates	Dimethicone copolyol
Alkanolamides	Silicone alkanolamides[19]
Esters	Silicone esters[20-22]
Taurine derivatives	Silicone taurines[23,24]
Isethionates	Silicone isethionates[25]
Alkyl glycosides	Silicone glycosides[26,27]

Products are chosen for formulation for their specific function. The function has to provide a consumer-perceptible property. The properties most commonly affected by inclusion of silicone products in personal care include (a) conditioning, (b) emulsification, (c) wetting, (d) surface tension reduction, (e) foam, (f) film formation, (g) defoaming properties and (h) spreadability. Obviously (e) and (f) are opposites. How can a silicone do both? A single silicone cannot. But a silicone compound with the proper structure can do one and a different silicone compound with the proper structure can do the other. Some silicone compounds are oil-soluble, water-soluble or silicone-soluble, but no single compound is soluble in more than one. The desire to make "silicone" one material leads to silicone misconceptions, as outlined in **Table 5.2**.

Table 5.2. Silicone Misconceptions

- Silicones are difficult to use in formulations.
- Silicones are water-insoluble.
- Silicones are oil-insoluble.
- Silicones polymerize.
- Silicones are toxic.
- Silicones are difficult to emulsify.
- Silicones are available only at low HLB.
- All silicones are greasy.
- All silicones defoam.

Silicone compounds can be engineered to provide a very wide range of product properties. **Table 5.3** shows the silicone realities.

Table 5.3. Silicone Realities

- Silicone compounds range from defoaming products to highly foaming products.
- Silicone compounds, when properly selected, are easy to use in formulations.
- Some silicone compounds are water-insoluble, some are oil-insoluble, and some are soluble in neither.
- Some silicone compounds polymerize to form elastomeric films.
- Some silicone compounds polymerize to form resinous films.
- Some silicone compounds do not polymerize at all.
- Silicone compounds vary in toxicity based upon structure. Those used in personal care are chosen to be mild.
- Silicones are easy to emulsify if the proper emulsifier is chosen.
- Silicones are available at a wide range of HLB values.
- Silicone compounds range from powder dry to very greasy.

It all depends upon Structure!

The specific properties of the compounds are a direct consequence of the exact structure of the compound chosen. There are three independent steps to making silicone surfactants, all critical to the properties one achieves. **Table 5.4** outlines the steps to making a silicone product.

Table 5.4. Silicone Structure

1. **Construction**

   Determines the specific composition of the silicone backbone. It is determined by the number and location of the so-called M, D, T, Q and M*, D*, T* units present. The latter are the sites to which functionality is added.

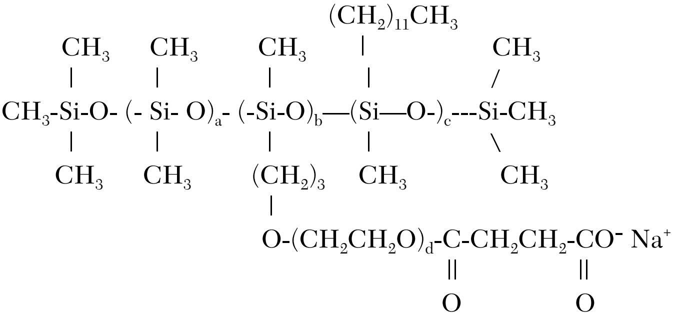
2. **Functionalization**

   Determines the organofunctionality added to the construction product. It is determined by the specific type or mixture of types of olefin added to the M*, D*, T* units present in the construction product.

3. **Derivitization**

   The chemical modifications made to groups introduced in the functionalization step. It determines the chemical modification made to products of functionalization. An example is the improved water solubility obtained by the phosphation of a PEG-8-dimethicone.

Consider lauryl PEG-8-dimethicone copolyol succinate, sodium salt:

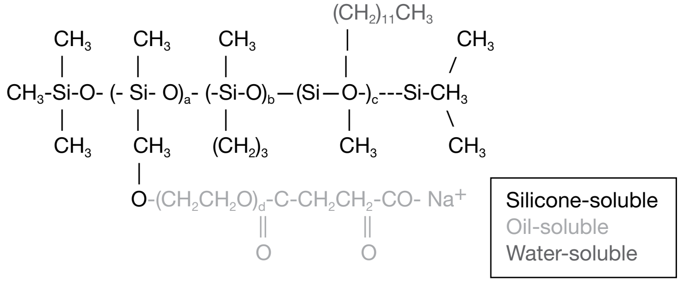


$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{-}(\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O)_a\text{-}(\text{-}\overset{CH_3}{\underset{(CH_2)_3\text{-}O\text{-}(CH_2CH_2O)_d\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}O^-\,Na^+}{Si}}\text{-}O)_b\text{—}(\overset{(CH_2)_{11}CH_3}{\underset{CH_3}{Si}}\text{—}O\text{-})_c\text{---}Si(CH_3)_2\text{-}CH_3$$

The molecule has three groups: silicone-, oil- and water-soluble. **Figure 5.1** shows the three types of groups.

The properties one sees in the compound are due to the type and number of all three elements. This allows for tremendous latitude in making alterations.

Figure 5.1. Type of groups



$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{-}(\text{-}\overset{CH_3}{\underset{\underset{O\text{-}(CH_2CH_2O)_d\text{-}\underset{O}{\overset{\|}{C}}\text{-}CH_2CH_2\text{-}\underset{O}{\overset{\|}{C}}O^-\,Na^+}{CH_3}}{Si}}\text{-}O)_a\text{-}(\text{-}\overset{CH_3}{\underset{(CH_2)_3}{Si}}\text{-}O)_b\text{—}(\overset{(CH_2)_{11}CH_3}{\underset{CH_3}{Si}}\text{—}O\text{-})_c\text{---}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3$$

The molecule has three groups: silicone-, oil- and water-soluble

Alterations include:

1. ***Ratio of silicone- / oil- / water-soluble concentration***
   This alteration is done by varying the ratio of a to b to c in the subscripts in the above structure.
   For example, taking a molecule in which a=1, b=1, c=1, and changing it to a=1, b=5 and c=10.

2. ***Molecular weight***
   This alteration is accomplished by keeping the ratio of a to b to c the same, but lowering or raising the levels.
   For example taking a molecule in which a=1, b=1, c=1, and changing it to a=100, b=100 and c=100.

3. ***Moles of ethylene oxide, propylene oxide or mixtures thereof***
   This alteration is accomplished by changing the value of d.

4. ***Anionic Group***
   The succinate group can be changed to a phthalate (aromatic), alkyl succinate or phosphate.

5. ***Salt counter ion***
   The counter ion can be K, Na, Li, NH_4, amine or many others.

6. ***Combinations***
   All five of the previously listed or any combination of the five can be changed.

It should be clear that silicone materials can be varied widely, which is good in one respect (latitude) but bad in another (understanding). Knowledge of how to engineer molecules is key.

Silicone Molecule Preparation

Construction (Equilibration)

In the construction process, basic silicone monomers are reacted with a suitable catalyst to give the desired polymer. The reactive portions of the molecule include silanic hydrogen-containing materials, capping molecules such as MM and chain extension materials such as cyclomethicone.

The reaction of D4 cyclomethicone with MM is a ring-opening reaction that is the key reaction method used to construct silicones. If silicone fluids are the desired product, MM and D4 and the proper catalyst are the only raw materials used. If, however, organofunctional silicones are desired, silanic hydrogen-containing groups need to be introduced. This is accomplished by reacting MM, D4 and SiH fluid. The exact ratio of the three determines many properties of the molecule, including molecular weight, and ratio of silicone to non-silicone groups.

If there is a desire to make a terminal functional silicone, then M*M* is substituted for MM, giving a terminal Si-H construction. **Figure 5.2** details the raw materials used in the construction of silicone polymers. **Figure 5.3** shows several types of products that can be made using the construction process.

Construction of Silicone Fluids

Silicone fluids are the products of construction only. They are sold by their viscosity, ranging from 0.65 to 1,000,000 cSt. If the product is not made by blending two different viscosity fluids, the viscosity is related to molecular weight. Silicone fluids conform to the structure shown in **Table 5.1**. The viscosity allows for an approximate calculation of the value of "n" as shown in **Table 5.5**.

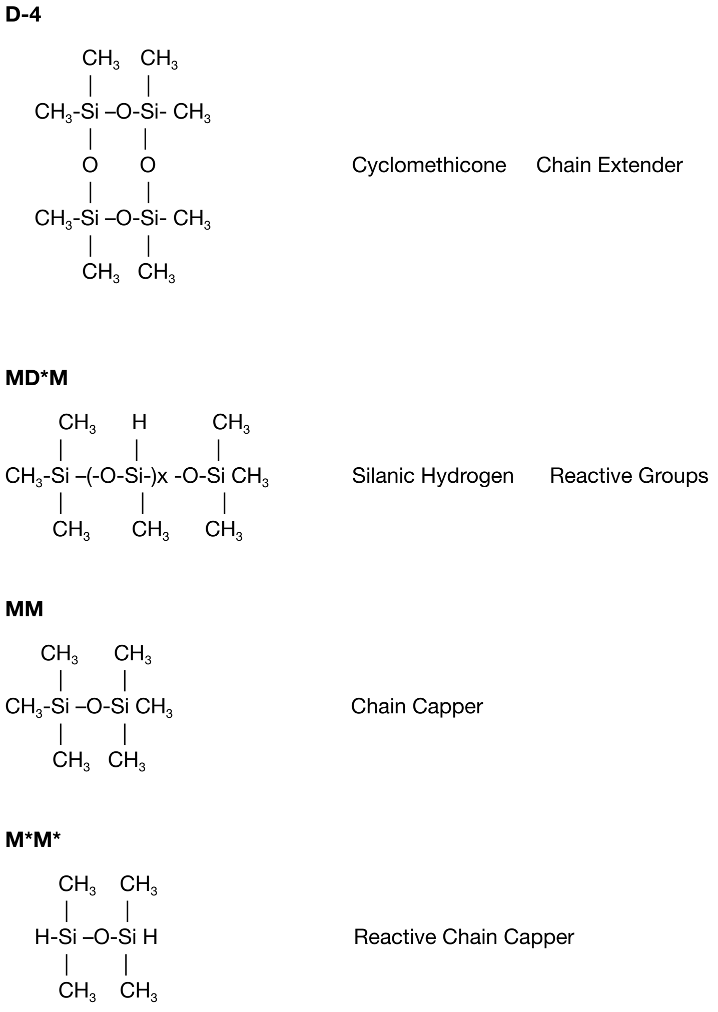
The construction reaction is somewhat unique chemistry, in that it is truly reversible as long as catalyst and proper reaction conditions are available. It is also important to note that the addition of D units is not in increments of four. That is, its MDM is made using D4 and MM. The reaction is truly equilibrium-controlled; each D unit is in equilibrium with all other D units and M units, giving a very reproducible oligomer distribution.

Synthesis

Silicone fluids are synthesized by the equilibration reaction of MM and cyclomethicone (D4). D4 is preferred over D5 since it is a more highly strained ring and opens more rapidly than D5. Typical of the synthesis of fluids is the reaction in which one MM is reacted with one D4 compound to make MD_4M, a simple silicone fluid.

The reaction may be run with either an acid or base catalyst. In one method, the reaction is conducted at room temperature for 12 hours, with sulfuric acid as a catalyst resulting in a mixture of about 95% silicone fluid and about 5% unreacted cyclomethicone. The catalyst is neutralized and the unreacted cyclic is stripped off. Once the catalyst is removed there is no longer an equilibration, so the free cyclic can be removed. However, if the catalyst is not neutralized during stripping, the fluid will degrade back to cyclic compounds D4 and MM.

Figure 5.2. Raw Materials of Construction

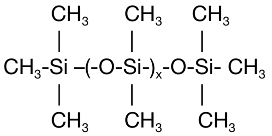


The equilibration process is critical not only to the production of stable silicone fluids, but also as a means of introducing functional groups into the polymer. This is done using a process called hydrosilylation, a process used to make organofunctional silicone compounds.

To demonstrate why the process is called equilibration, one will note that a "finished silicone fluid" may be placed in contact with D4 and catalyst and re-equilibrated to make a higher viscosity fluid. Conversely, a "finished silicone fluid" may be re-equilibrated with MM and catalyst to make a lower viscosity fluid. Finally, silicone rubber may be decomposed into MM and D4 via stripping of the product in the presence of catalyst. This property of silicone polymers makes them decidedly different from organic compounds.[4]

Figure 5.3. Products of Construction

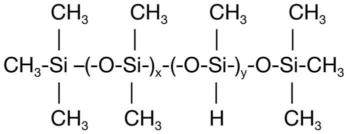
Silicone Fluid



$$\begin{array}{ccccccc} & CH_3 & & CH_3 & & CH_3 & \\ & | & & | & & | & \\ CH_3\text{-} & Si & \text{–(-O-} & Si & \text{-)}_x\text{-O-} & Si & \text{- }CH_3 \\ & | & & | & & | & \\ & CH_3 & & CH_3 & & CH_3 & \end{array}$$

Silicone fluids are homopolymers having an MDxM structure.

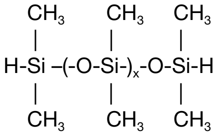
Silicone Reactive Comb Fluid



$$\begin{array}{ccccccccc} & CH_3 & & CH_3 & & CH_3 & & CH_3 & \\ & | & & | & & | & & | & \\ CH_3\text{-} & Si & \text{–(-O-} & Si & \text{-)}_x\text{-(-O-} & Si & \text{-)}_y\text{-O-} & Si & \text{-}CH_3 \\ & | & & | & & | & & | & \\ & CH_3 & & CH_3 & & H & & CH_3 & \end{array}$$

Silicone polymers having a MDD*M structure.

Silicone Reactive Terminal Fluid



$$\begin{array}{ccccccc} & CH_3 & & CH_3 & & CH_3 & \\ & | & & | & & | & \\ H\text{-} & Si & \text{–(-O-} & Si & \text{-)}_x\text{-O-} & Si & \text{-H} \\ & | & & | & & | & \\ & CH_3 & & CH_3 & & CH_3 & \end{array}$$

Silicone polymers having an M*DM* structure.

Equilibration

It is thought that silicone polymers form in equilibrium with their reactants and can be pushed back towards the reactant side of the equation under the correct circumstances. The reactants are Si $(CH_3)_3$-O-Si $(CH_3)_3$ (MM) and $–(Si(CH_3)_2\text{-}O)_4$ or D4. Since D4 is a six-membered ring, having alternate silicon and oxygen atoms, its reaction with MM produces linear polymers in the presence of MM and catalyst.

To be a true equilibrium reaction when MM is added to an already existing linear polymer one might expect to get the equilibrium mixture of D4 and a smaller linear molecule. If an excess of MM is combined with a linear polymer chain one might expect to get a different polymer consuming the MM.

The equilibration reaction was studied[4]. The evaluation included:

1. Reacting MM and D4 and building it up to a viscosity of 350 cSt, and then to 1,000 cSt
2. Adding MM to break down the 1,000 cSt fluid made in step 1 and also to break down a commercially obtained 1,000 cSt fluid
3. Neutralization of the catalyst
4. Analysis via gel permeation chromatography of the products to determine the linear polymer concentration and the concentration of D4 found in each

The composition of product made by build up is the same as the composition made by the break down process. Specifically, the concentration of D4 will be of major interest. One possibility is that there will be a comparable amount of D4 present regardless of whether the process is build up or break down. Another possibility is that since commercial 1,000 cSt product is stripped of D4 after processing, the break down product may be very low in D4.

Table 5.5. The "n" value for selected silicone fluids

Approximate Viscosity at 25°C (cSt)	Approximate molecular weight	"n" Value
5	800	9
50	3,780	53
100	6,000	85
200	9,430	127
350	13,650	182
500	17,350	230
1,000	28,000	376
10,000	67,700	910
60,000	116,500	1,570
100,000	139,050	1,875

The build up reaction is shown in **Table 5.6**. The break down reaction is shown in **Table 5.7**.

Table 5.6. The build up reaction

10 D4 + MM ➔ MD40M

Ring-opening of D4.

Table 5.7. The break down reaction

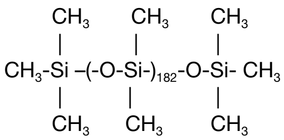
MD40M + MM ➔ 2 MD20M

It has become clear that the equilibrium mixture made by the build up process is the same as that of the break down product. If the reaction is a true equilibrium, it does not matter which path the reaction takes, but is determined by the ratio of reactants introduced.

The average structures of the two silicone fluids used in this study are shown in **Figure 5.4**.

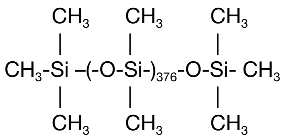
Figure 5.4. Average structures of silicone fluids

350 cSt Dimethicone



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-(-O-\overset{CH_3}{\underset{CH_3}{Si}}-)_{182}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

1,000 cSt Dimethicone



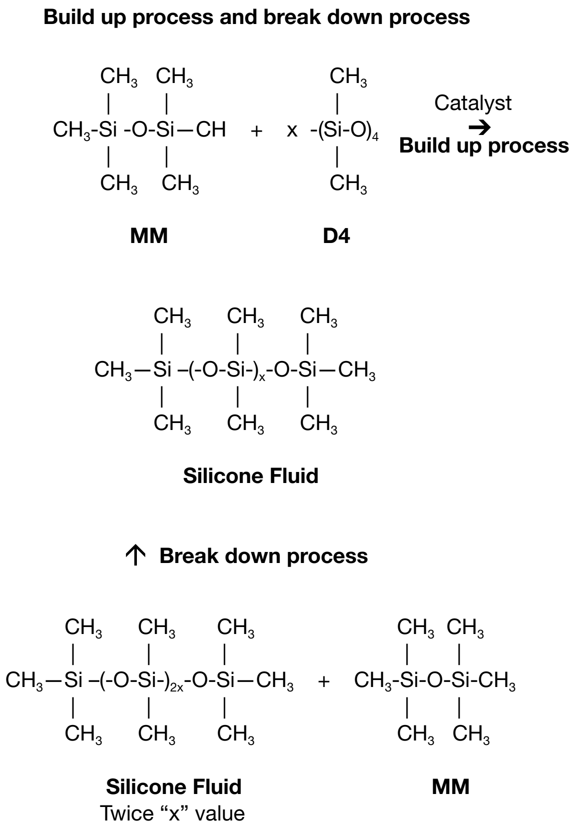
$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-(-O-\overset{CH_3}{\underset{CH_3}{Si}}-)_{376}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

The silicone polymer made by the break down process resulting in D4 is very important to the cosmetic industry because cyclic silicones (D5) are not desirable in cosmetic products.

Methods and Materials

Five samples were studied and are described in **Figure 5.5.**

Figure 5.5. Equilibration Scheme



The equipment used for gel permeation chromatography analysis included an HPLC pump (Waters HPLC Pump Model 515), a differential refractometer detector (Waters Differential Refractometer Detector Model 410) and a column heater module (Waters Column Heater Module). The columns were Styagel HR 3, 1 and 0.5 in series with a flow rate of 1.0 mL/min, a mobile phase THF, a column temperature of 55°C and a detector temperature of 45°C.

Table 5.8. Synthesis of Materials

		Material (in parts)					
Sample	**Description**	**D4**	**MM**	**H_2SO_4**	**$NaHCO_3$**	**C1000***	**C350****
A	1,000 Viscosity Build Up Product	99.4	6.6	5.0	15.0		
B	350 Viscosity Break Down Product from commercial 1,000 viscosity fluid	0.6	5.0	15.0	99.4		
C	1,000 Viscosity Build Up Product broken down to 350 Viscosity	99.4	0.6	5.0	15.0		
D	350 Viscosity Build Up Product	98.8	1.2	5.0	15.0		
E	Commercial 350 Viscosity control						100.0

* = Fluid-1000, a commercial 1,000 cSt silicone fluid
** = Fluid-350 a commercial 350 cSt silicone fluid

Procedures for samples A, B, C, D:

1. Combine the amounts of MM and D4 in a 400 mL flask.
2. Stir well.
3. Add sulfuric acid.
4. Mix for 24 hours (under good agitation for sample A).
5. Slowly add sodium bicarbonate. Foam will be encountered requiring venting of carbon dioxide.
6. Filter.

Both the build up mechanism and the break down mechanism had a comparable quantity of cyclic products present. The break down from 1,000 to 350 had 5.29% cyclic silicones present before distillation, while the build up product had 4.65%. The commercial 350 viscosity product had less cyclic silicones present in it, at 1.58%. This is related to the degree of strip used after the catalyst is neutralized. It is surprising to see that a product that was built up, neutralized but not stripped, followed by a break down had twice as much cyclic silicone as the direct build up.

The build up to 350 had 4.65% and the build up and break down had 10.39%. In the case of this sample, it appears that there were two different mechanisms occurring simultaneously—a build up and a break down—giving different equilibration concentrations of product. One of the other products had MM, D4 and linear silicone present at the same time, representing a different reaction sequence.

Table 5.9. Results of the gel permeation chromatography analysis

Sample	Description	D4	Time	Polymer	Time	Sum
A	F1000 BU	3.05	23.97	96.95	15.29	100.00
B	F350 BD	5.29	23.38	94.71	15.57	100.00
C	BU 1000 BD 350	10.39	23.34	89.61	15.66	100.00
D	F350 BU	4.65	23.45	95.35	15.64	100.00
E	F350 Control	1.58	24.10	98.42	15.76	100.00

Reference to the results in **Table 5.9** suggests several interesting conclusions.

1. There are two different ways to make a 350 viscosity silicone fluid—by build up (Sample D) or break down (Sample B). They result in the same mixture of D4 to polymer.
2. Commercial 350 viscosity silicone is stripped to reduce the % D4 to under 2% (Sample E), from the original level of around 5% (Samples B and D).
3. The equilibrium mixture of silicone fluid having a viscosity of 1,000 (Sample A) has a lower concentration of D4 in the equilibrium mixture than the 350 viscosity product (Sample D).
4. The surprising result is Sample C, the product in which a 350 viscosity silicone fluid was built up to 1,000 viscosity and then broken down to 350 viscosity. That sample had a very high level of D4—twice the expected amount based on Samples B and D.

Functionalization (Hydrosilylation)

The hydrosilylation reaction is the result of the reaction of a silanic hydrogen polymer with an olefinic reactant. This reaction is conducted with specific metal catalysts, most commonly platinum. The preparation of the silanic hydrogen polymer is the first important part of the molecular preparation. We refer to the silanic hydrogen portion as the "construction" part of the molecule. It is well-known that certain silanic hydrogen containing compounds react with carbon-carbon multiple bonds under catalysis by transition metal complexes; this reaction is referred to as hydrosilylation[4-6]. Hydrosilylation is defined simply as the addition of a SiH bond to a C-C double bond.

Construction places the Si-H group along with other silicone groups into the polymer backbone in construction. Once the construction is determined, the reactive groups are used to provide a carbon-carbon bond via hydrosilylation. The type of alpha olefins used in the functionalization process is shown in **Table 5.10**.

Table 5.10. Hydrosilylation Reactants

Class	Structure	Provides
Alpha olefin	CH_2=CH-$(CH_2)_9$-CH_3	Oil solubility
Allyl alcohol alkoxylated	CH_2=CH-CH_2-O-$(CH_2CH_2\text{-}O)_9$H	Water solubility
Fluoro compounds	CH_2=CH-$(CF_2)_8$-CF_3	Fluoro solubility
Allyl alcohol	CH_2=CH-CH_2-OH	Polarity
Alpha omega divinyl	CH_2=CH-$(CH_2)_a$-CH=CH_2	Resins

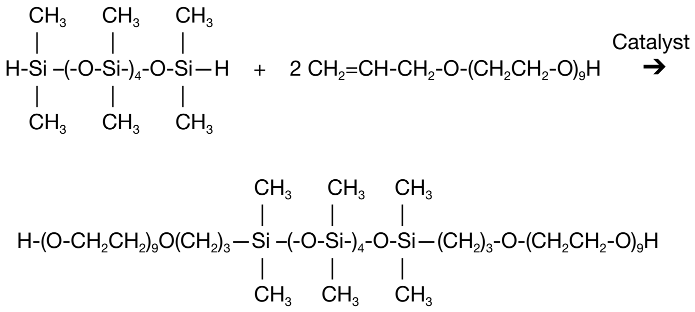
Hydrosilylation Reaction

The hydrosilylation reaction is responsible for functionalization. It allows one to convert a silanic hydrogen compound (Si-H) into an organofunctional product, consuming the Si-H and vinyl group in the reactants. The result is a Si-C bond. It is critical to note that the product of construction has only Si-H groups, therefore it is silicone-soluble. A molecule having the same construction will have different solubility depending upon the group with which it is reacted in the functionalization reaction. Molecules with different solubility made from a common construction are shown in **Figure 5.6**.

Clearly, the functionality of the molecule is determined by both construction and functionalization. INCI names give information on functionalization, but nothing on construction. Two molecules are shown in **Figure 5.7**. Both are cetyl dimethicone, with clearly different structures, amounts of alkyl and silicone, and different molecular weights. Substitution of one for the other, despite the same names, will yield different products. **Figure 5.7** shows two compounds both of which have the name cetyl dimethicone. One has a high percentage of alkyl and the other a very low percentage of alkyl. One would certainly expect different solubility, hardness, cushion and conditioning properties.

Figure 5.6. Hydrosilylation Reaction Functionalization of M*D4M*

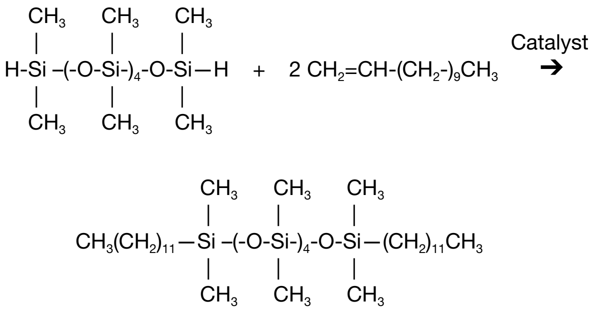
Functionalization 1 (Water-soluble Group Added)



$$\mathrm{H\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{–}(\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_4\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}H \; + \; 2\ CH_2{=}CH\text{-}CH_2\text{-}O\text{-}(CH_2CH_2\text{-}O)_9H \xrightarrow{Catalyst}}$$

$$\mathrm{H\text{-}(O\text{-}CH_2CH_2)_9O(CH_2)_3\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{–}(\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_4\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}(CH_2)_3\text{-}O\text{-}(CH_2CH_2\text{-}O)_9H}$$

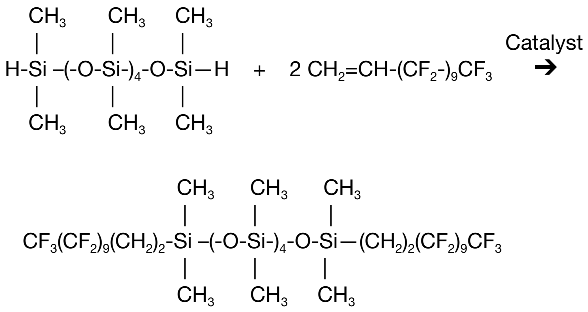
Functionalization 2 (Oil-soluble Group Added)



$$\mathrm{H\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{–}(\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_4\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}H \; + \; 2\ CH_2{=}CH\text{-}(CH_2\text{-})_9CH_3 \xrightarrow{Catalyst}}$$

$$\mathrm{CH_3(CH_2)_{11}\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{–}(\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_4\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}(CH_2)_{11}CH_3}$$

Functionalization 3 (Fluoro-soluble Group Added)

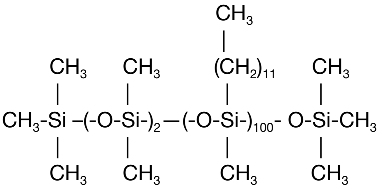


$$\mathrm{H\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{–}(\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_4\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}H \; + \; 2\ CH_2{=}CH\text{-}(CF_2\text{-})_9CF_3 \xrightarrow{Catalyst}}$$

$$\mathrm{CF_3(CF_2)_9(CH_2)_2\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{–}(\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_4\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}(CH_2)_2(CF_2)_9CF_3}$$

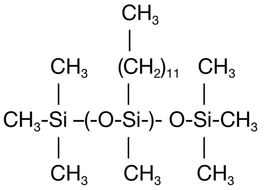
Figure 5.7. Different Compounds "Cetyl Dimethicone"

Cetyl Dimethicone A



$$\begin{array}{cccc}
 & & CH_3 & \\
 & & | & \\
CH_3 & CH_3 & (CH_2)_{11} & CH_3 \\
| & | & | & | \\
CH_3\text{-}Si & \text{-(-}O\text{-}Si\text{-)}_2\text{—} & \text{(-}O\text{-}Si\text{-)}_{100}\text{-} & O\text{-}Si\text{-}CH_3 \\
| & | & | & | \\
CH_3 & CH_3 & CH_3 & CH_3
\end{array}$$

Silicone Reactive Comb Fluid



$$\begin{array}{ccc}
 & CH_3 & \\
 & | & \\
CH_3 & (CH_2)_{11} & CH_3 \\
| & | & | \\
CH_3\text{-}Si & \text{-(-}O\text{-}Si\text{-)-} & O\text{-}Si\text{-}CH_3 \\
| & | & | \\
CH_3 & CH_3 & CH_3
\end{array}$$

Derivitization (Organic Group Reactions)

Derivitization

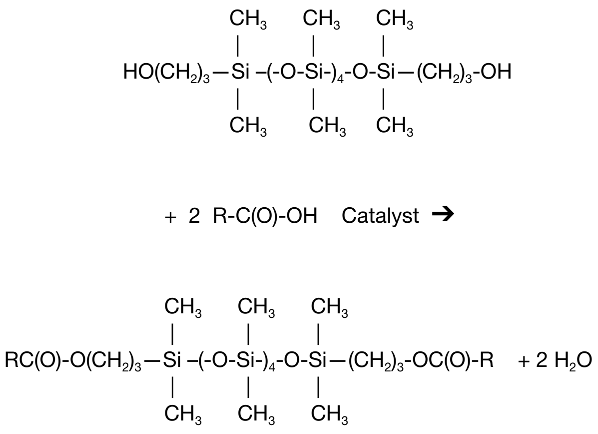
The derivitization step springs from the observation that organic functional groups and the chemistries they enter into will occur even if the groups are attached to silicone via hydrosilylation. Simply stated, hydroxyl groups on pendant groups connected to silicone by hydrosilylation are reactive groups having hydroxyl group reactivity. This includes the ability to esterify phosphate, sulfate, and make urethanes and many others.

The derivitization step allows for a plethora of post reactions for silicone molecules that contain reactive groups. The only limitation is that the reactants need some solubility in one another in order to react and the catalysts and conditions of the reaction must not destroy the silicone backbone. The properties of the compounds made by derivitization are discussed in other chapters. Typical of derivitization of compounds is the esterification reaction shown in **Figure 5.8**.

Conclusion

Silicone surfactants, unlike their organic counterparts, are the result of several steps in the preparation. In predicting the functionality of silicone surfactants that have organofunctionality inserted via the hydrosilylation reaction, there are three key steps to be considered: construction, functionalization and derivitization.

Figure 5.8. Typical Derivitization Reaction



Esterification

$$HO(CH_2)_3-\overset{CH_3}{\underset{CH_3}{Si}}-(-O-\overset{CH_3}{\underset{CH_3}{Si}}-)_4-O-\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_3-OH$$

$$+\ 2\ R-C(O)-OH \quad \text{Catalyst} \rightarrow$$

$$RC(O)-O(CH_2)_3-\overset{CH_3}{\underset{CH_3}{Si}}-(-O-\overset{CH_3}{\underset{CH_3}{Si}}-)_4-O-\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_3-OC(O)-R \quad +\ 2\ H_2O$$

One of the major complaints formulators have with silicone compounds relates to the perceived inability to predict how a product will function in a given formulation. This is due in large part to the lack of specific information on the construction, the functionalization and the derivitization of compounds. When all three are known, the predictability increases.

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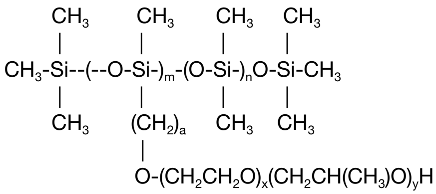
Chapter 6

Dimethicone Copolyol Chemistry

Dimethicone copolyol has been the workhorse of the silicone surfactant industry for many years, during which the INCI names have changed. Dimethicone copolyol is an old name, replaced now by PEG/PPG dimethicone and bis-PEG/PPG dimethicone. **Figure 6.1** shows the structures of these materials. The first nomenclature change for these compounds was in a document called *The Organosilicone Nomenclature Conventions* issued in April of 1999. It called for new nomenclature requiring that the number of moles of PEG (polyethylene glycol) or PPG (polypropylene glycol) be listed with the new name. More recently, the terminal products have been renamed bis-PEG/PPG dimethicone. These changes, however, describe only one aspect of the molecule since only the construction, not the functionalization, is disclosed.

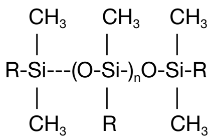
Figure 6.1. Dimethicone Copolyol: Generic Formula

PEG/PPG dimethicone



$$\begin{array}{ccccccccc} & CH_3 & & CH_3 & & CH_3 & & CH_3 & \\ & | & & | & & | & & | & \\ CH_3\text{-} & Si & \text{--}(\text{--}O\text{-} & Si & \text{-})_m\text{-}(O\text{-} & Si & \text{-})_nO\text{-} & Si & \text{-}CH_3 \\ & | & & | & & | & & | & \\ & CH_3 & & (CH_2)_a & & CH_3 & & CH_3 & \\ & & & | & & & & & \\ & & & \multicolumn{6}{l}{O\text{-}(CH_2CH_2O)_x(CH_2CH(CH_3)O)_yH} \end{array}$$

Bis-PEG/PPG dimethicone



$$\begin{array}{ccccccc} & CH_3 & & CH_3 & & CH_3 & \\ & | & & | & & | & \\ R\text{-} & Si & \text{---}(O\text{-} & Si & \text{-})_nO\text{-} & Si & \text{-}R \\ & | & & | & & | & \\ & CH_3 & & R & & CH_3 & \end{array}$$

R is $-(CH_2)_a\text{-}O\text{-}(CH_2CH_2O)_x(CH_2CH(CH_3)O)_yH$

For this reason, despite the change of names, predictions about properties remain elusive. The structure of PEG-12 dimethicone can have no D units (the "n" value in the formula of **Figure 6.1**) or 1,000 D units. The properties of these two PEG-12 dimethicone compounds will be very different.

For purposes of this text, I will refer to dimethicone copolyol as a generic class and the specific compound by its more complete PEG-10 dimethicone name.

Several non-INCI descriptive names for dimethicone copolyol include silicone glycols, silicone surfactants, silicone polyethers, silicone surfactants and silicone nonionic surfactants, among others, and have been used by different industries. Dimethicone copolyol compounds are used to modify the feel on many systems including reduction of the tack in polyacrylate systems. They are co-emulsifiers, plasticizers and foam stabilizers as well as known irritation mitigators for skin and mucous membranes.

The nomenclature was developed to reflect the fact that the molecule is a silicone polymer (dimethicone), a copolymer (copolyol) and an hydroxyl functional (the "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 products dimethicone copolyol, even though they lack the hydroxyl group that originally justified the "ol" ending. Since the capping process is not totally efficient, residual hydroxyl groups are found even in the dimethicone copolyol compounds that claim to be capped.

Reaction

Dimethicone copolyol surfactants are made by a complicated sensitive process called hydrosilylation. A silicone polymer containing a silanic hydrogen moiety is reacted with an allyl ethoxylate. The reaction is described in **Figures 6.2** and **6.3**.[1,2]

The use of allyl alcohol ethoxylates to prepare dimethicone copolyols explains why they carry three CH_2 groups between the silicon atom and the polyoxyalkylene group. When the reaction is conducted there is an excess of allyl alcohol ethoxylate used. It will remain in the product and may be present at concentrations up to 30% by weight.

The raw materials used to synthesize these polymers are polydisperse polymers with an oligomeric distribution. Thus, the resulting polymer structure is an oligomeric distribution of an oligomeric distribution.

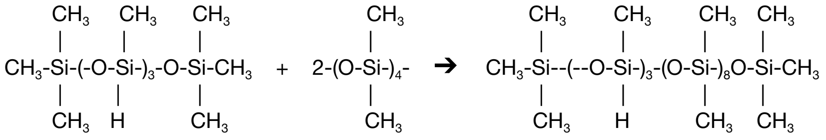
Despite these complications, which are not too unlike those found in carbon-based ethoxylates, silicone polymers can be analyzed and the relation between structure and functional properties can be established.

Dimethicone Copolyol Properties

Dimethicone copolyol compounds are amphilic materials. That is, they possess two or more groups that are present in pure form that would be insoluble in each other. In the case of dimethicone copolyol, the two groups are silicone-soluble (siliphilic) and water-soluble (hydrophilic). The two groups are shown graphically in **Table 6.4**. It is this combination of groups that renders the materials surface active. Surface activity means that despite the fact that these materials are soluble (clear) in water, they do not have a homogeneous distribution of product in water. At concentrations below the CMC (critical micelle concentration), these materials are found at the air-water interface. They lower surface tension from about 72 dynes/cm^2 to between 32 and 20 dynes/cm^2, depending upon structure. What determines the surface tension is the lowest free energy of the molecule at the surface. If the "CH_2" groups present in the ethylene oxide backbone dominate at the interface, the surface tension will range in the 30s. If the "CH_3" groups on silicone dominate at the surface, the surface tension will be in the range of 20 dynes/cm^2. This structure dependency is critical to functionality in foaming and wetting systems.

Figure 6.2. Dimethicone Copolyol: Construction

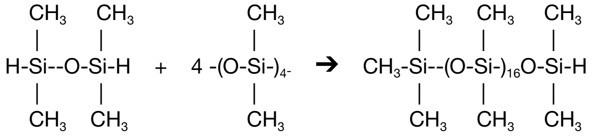
PEG/PPG dimethicone



$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}(\text{-}O\text{-}\overset{CH_3}{\underset{H}{Si}}\text{-})_3\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3 \;+\; 2\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_4\text{-} \rightarrow CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\overset{CH_3}{\underset{H}{Si}}\text{-})_3\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_8O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3$$

MD*M **D4** **MD*3D8M**

Bis PEG/PPG dimethicone



$$H\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{--}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}H \;+\; 4\text{ -}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_4\text{-} \rightarrow CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{--}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_{16}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}H$$

M*M* **D4** **M*D16M***

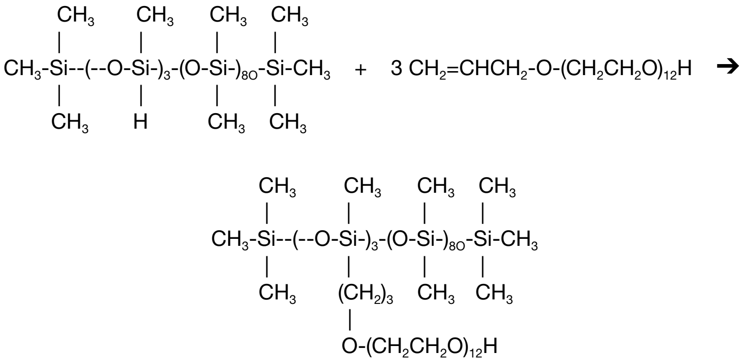
Another factor affecting the orientation of the molecule at the surface and consequently the functional properties[3] of dimethicone copolyol compounds is the molecular weight. Generally, the very low molecular weight polymers are outstanding wetting agents. Because of their proclivity to wet surfaces, they need to be carefully chosen to avoid penetration of tissue and irritation to the skin.

With increasing molecular weight, the wetting properties decrease marginally and the dimethicone copolyol compound becomes a conditioner and emulsifier while wetting properties are lost.

Dimethicone copolyols can be engineered to form microemulsions. Materials that form spontaneous microemulsions without additional surfactants are important

Figure 6.3. DMC Compounds: Functionalization

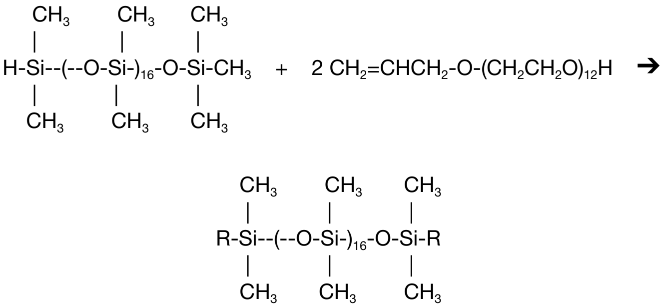
PEG/PPG dimethicone



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_3\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_{8O}\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 + 3\ CH_2{=}CHCH_2\text{-}O\text{-}(CH_2CH_2O)_{12}H \rightarrow$$

$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{\underset{O\text{-}(CH_2CH_2O)_{12}H}{(CH_2)_3}}{\overset{CH_3}{Si}}\text{-})_3\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_{8O}\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Bis-PEG/PPG dimethicone



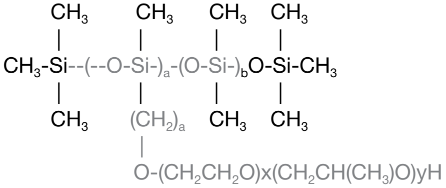
$$H\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_{16}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 + 2\ CH_2{=}CHCH_2\text{-}O\text{-}(CH_2CH_2O)_{12}H \rightarrow$$

$$R\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_{16}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}R$$

R is $\text{-}(CH_2)_3O\text{-}(CH_2CH_2O)_{12}H$

Figure 6.4. Dimethicone Copolyol: Amphilic Materials

PEG/PPG dimethicone



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{\underset{O\text{-}(CH_2CH_2O)x(CH_2CH(CH_3)O)yH}{(CH_2)_a}}{\overset{CH_3}{Si}}\text{-})_a\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_bO\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

to maximize deposition. Microemulsion dimethicone copolyol compounds, when added to water, provide a blue tint, remain clear and add viscosity. These materials deposit on hair and skin because in the deposited form they are in the lowest free energy. This offers the formulator the ability to select the dimethicone copolyol that provides the best combination of solubility and deposition.

One good way to engineer a molecule that will form a spontaneous microemulsion is by varying the "a" and "b" (see **Figure 6.4**). The value of "a" relative to "b" will determine if the product is water-soluble, dispersible or insoluble. A formula exists to determine the point at which a microemulsion will form. The equation is shown in **Table 6.1**.

Table 6.1. Microemulsion Formula

If the value of "D" relative to "D*" is too low, the product will not be soluble regardless of the number of moles of ethylene oxide (the "x" value) because of the concentration of insoluble oligomer present.

Formula to determine microemulsion of dimethicone copolyol

"D*" units = (0.17)(actual number of "D" units)+1

If D* increases, a more water-soluble product will be made.
If D* decreases, a less water-soluble product will be made.

If the line defined by the above equation is plotted, molecules falling on the line will be microemulsions. Those with greater D^* to D values will be water-soluble. Those molecules with greater D to D^* values will be water-insoluble. **Figure 6.5** shows the graph.

The above formula was determined by evaluating a variety of dimethicone copolyol products with eight moles of ethylene oxide. The results are shown in **Table 6.2**.[3]

The observation that D to D^* ratio as well as number of moles of ethylene oxide present in the molecule determines water solubility, along with the fact that this information is not found in the INCI name, explains why the useful range of water-soluble dimethicone copolyol compounds is limited and why INCI names are of limited value in formulation.

Table 6.3 shows several products all having the name PEG-8 dimethicone. They differ in construction, that is the ratio of D to D^* units. The solubility of the products is listed in **Table 6.4**. It should be quite clear from review of this table that construction is critical to solubility.

Figure 6.5. D* Units Needed for Solubility

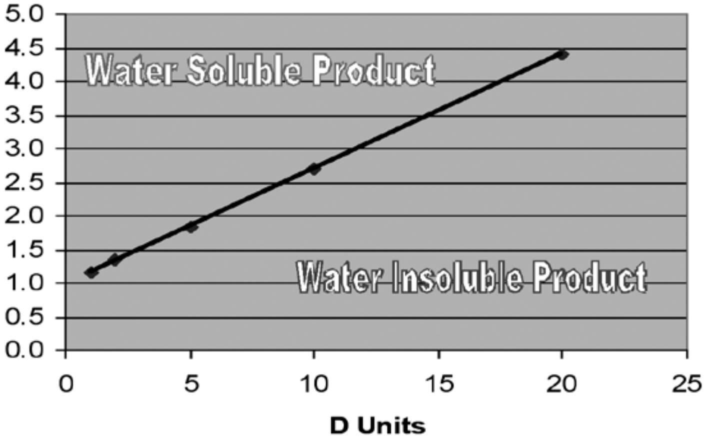


Table 6.2. Solubility of PEG-8 dimethicone (10% in Water)

a	b	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

* using the above formula

"a" is the number of D* units, "b" is the number of "D" units.

Table 6.3. Several PEG-8 Dimethicone Compounds

Product	Old INCI Name	New INCI Name
$MD_{10}D^{*}_{5}M$	Dimethicone Copolyol	PEG 8 Dimethicone
$MD_{10}D_{2}^{*}M$	Dimethicone Copolyol	PEG 8 Dimethicone
$MD_{40}D_{22}^{*}M$	Dimethicone Copolyol	PEG 8 Dimethicone

Table 6.4. Solubility

Product	Old INCI Name	New INCI Name
$MD_{10}D^{*}_{5}M$	Dimethicone Copolyol	PEG 8 Dimethicone
$MD_{10}D_{2}^{*}M$	Dimethicone Copolyol	PEG 8 Dimethiocne
$MD_{40}D_{22}^{*}M$	Dimethicone Copolyol	PEG 8 Dimethicone

Solubility (1%/10% Weight)

Product	Water	Oil	Mineral Glycol	Propylene Methicone	Cyclo Fluid	Silicone IPA
$MD_{10}D^{*}_{5}M$	S/S	I/I	S/S	I/I	D/D	S/S
$MD_{10}D_{2}^{*}M$	I/I	I/I	I/I	I/I	D/I	S/S
$MD_{40}D_{22}^{*}M$	I/I	I/I	D/D	D/I	D/D	S/S

I is insoluble
S is soluble
D is dispersible

Structure Function Study

A structure/function relationship has been established for dimethicone copolyol compounds with a "b" unit containing 8 moles of ethylene oxide, the so-called PEG-8 dimethicone. There was a desire to determine basic surfactant properties like wetting, foam and emulsification. **Table 6.5** shows the molecules studied.

Cloud Point

Like many hydrocarbon-based nonionic surfactants, dimethicone copolyol surfactants exhibit high cloud points when heated in a 1% aqueous solution. The high cloud point phenomenon is related to hydrogen bonding of the polyoxyalkylene portion with water molecules. The cloud point is related to the length of the polyoxyethylene group in the molecule and is rather independent of 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. **Table 6.6** shows the results.

Table 6.5. Dimethicone Copolyol: Compounds Studied

Product Studied	"a units"	"b units"	Molecular Weight (MWU)
A	0	1	632
B	1	1	701
C	2	2	1240
D	5	3	1917
E	7	4	2525
F	8	4	2594

Table 6.6. Cloud Point of Dimethicone Copolyol Compounds

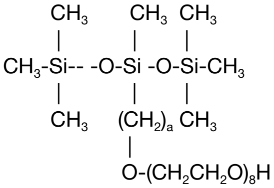
Designation	Molecular Weight	Cloud Point (1% DW)
A	632	58°C
B	701	58°C
C	1240	57°C
D	1917	58°C
E	2525	58°C
F	2594	58°C

Wetting

There are several types of wetting that one may consider when evaluating products. One is called spontaneous wetting, or super wetting. The term super wetting as applied here relates to the ability of a 1% solution of the test surfactant to spread on paraffin without mechanical means. The trisiloxane (**Figure 6.6**) is the only product in the series that demonstrates these properties. However, it also is the material with the most limited hydrolytic stability. Blending this material with another silicone glycol neither overcomes the hydrolytic instability of the trisiloxane, nor does it improve the wetting of the non-trisiloxane component.

While super wetting is very structure specific, Draves Wetting, (the ability to sink a cotton skein in a surfactant solution) is quite different. There is a gradual increase in wetting time as a function if there is increased molecular weight. Eye irritation of the surfactant drops off as molecular weight increases. This means there are a number of compounds that have outstanding Draves Wetting, and at the same time low irritation.

Figure 6.6. Trisiloxane Generic Formula



$$\begin{array}{ccccc} & CH_3 & & CH_3 & CH_3 \\ & | & & | & | \\ CH_3\text{-} & Si\text{-}\text{-} & \text{-}O\text{-} & Si & \text{-}O\text{-}Si\text{-}CH_3 \\ & | & & | & | \\ & CH_3 & & (CH_2)_a & CH_3 \\ & & & | & \\ & & & O\text{-}(CH_2CH_2O)_8H & \end{array}$$

Trisiloxanes have no "D" units.

The compound shown in **Table 6.5** has no D units, and only one D* unit. These compounds have a unique ability to spontaneously wet paraffinic films, spreading out to many times their original droplet size. These compounds are called *super wetters*. They suffer from limited hydrolytic stability and are quite irritating to the eye; consequently they are seldom found in personal care products. If D units are added, this interesting property is lost. They are, however, very important in many applications including spreading compounds on waxy leafed plants in spray applications. Simply put, if the droplet applied to a waxy leaf does not spread, the active in the droplet will not be effective. The testing of super wetting is done without mechanical action, hence is not considered appropriate to many cosmetic applications.

Wetting turns out to be a critical factor in almost every application for silicone surfactants. Silicone surfactants used for conditioning are high molecular weight materials. They are also poor wetting agents. Therefore the ability to spread uniformly on substrates is difficult, resulting in non-uniform films. It is therefore recommended that a lower molecular weight silicone surfactant be added to wet out the higher molecular weight silicone surfactant. This is true for textile fabrics, plastics and hair. Since wetting occurs at or below the CMC, one should add enough to have the product present at that concentration available after the formulation has been cut to use-concentration.

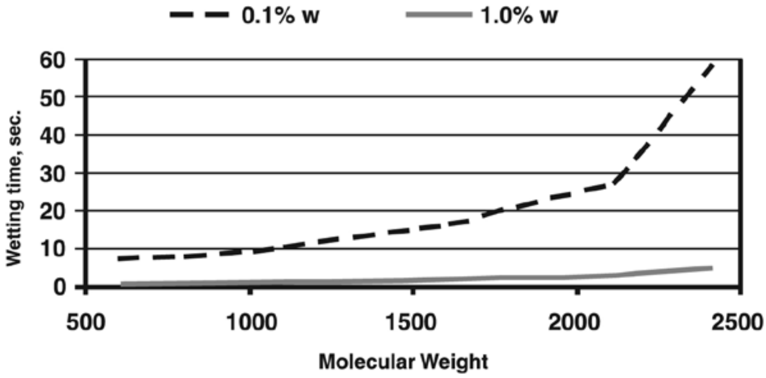
Cosmetic applications are done using the mechanical action of the hands and many times rinsing, making super wetting test methods of limited applications. We have chosen Draves Wetting, which measures the length of time needed to sink a cotton skein (which is very similar to a hair tress) in an aqueous solution (the faster the time, the better the wetting). In the Draves Wetting test, a 0.1% solution of dimethicone copolyol is used to sink a cotton skein (**Table 6.7**).

Table 6.7. Draves Wetting

Designation	Molecular Weight	Wetting @ 0.1%
A	632	7 sec
B	701	8 sec
C	1240	10 sec
D	1917	16 sec
E	2525	27 sec
F	2594	57 sec

The data points to a strong relationship between molecular weight and wetting. The shape of the curve is also important. Specifically, wetting time increases only slightly until the molecular weight of the dimethicone copolyol exceeds 1240 daltons, and then a rapid increase occurs. **Figure 6.7** shows the effect graphically.

Figure 6.7.



Dimethicone copolyol with a molecular weight between 700 and 1,240 is quite an effective wetting agent. Coupled with irritation data, this observation allows for the selection of cost-effective materials with good wetting properties and low irritation. Additional compounds were evaluated for wetting properties. The results are shown in **Table 6.8**.

Table 6.8. Wetting Evaluation

	Type	M.W.	Wetting Time (in seconds)
1	Comb	633	10.5
2	Comb	1400	107
3	Comb	2019	900
4	Comb	2638	2776
5	Comb	6352	23400
6	Comb	12541	28800
7	Terminal	1873	2400
8	Terminal	3272	2700
9	Terminal	2049	4800
10	Terminal	2068	9000

1. In the comb series, the wetting time decreases significantly as the molecular weight of silicone polyether decreases.
2. The wetting power of the terminal series is not as good as the comb series with the same molecular weight.
3. Trisiloxane compounds are the best wetting agent for standard cotton skeins, that is, the lowest molecular weight among all of the tested samples.

CMC and Surface Tension at CMC

The critical micelle concentration (CMC) and the surface tension at the CMC are major properties of surfactants. The lower limit for surface tension for compounds of this type is 20 dynes/cm^2. The observation has been attributed to the portion of the molecule that makes up the bulk of the molecule. Fatty components are very rich in methylene groups (-CH_2-); this limits the surface tension obtainable with fatty surfactants to the range of about 30 dynes/cm^2. Silicone surfactants have a predominance of methyl groups (CH_3), which limits surface tension obtainable from silicone surfactants to the range of about 20 dynes/cm^2. To go below this range fluoro-surfactants are required. **Table 6.9** shows the CMC data.

Table 6.9. Critical Micelle Concentration (CMC)

Designation	Molecular Weight	CMC	Surface Tension@CMC
A	632	20 mg/l	20 dynes/cm^2
B	701	20 mg/l	20 dynes/cm^2
C	1240	19 mg/l	19 dynes/cm^2
D	1917	23 mg/l	21 dynes/cm^2
E	2525	21 mg/l	23 dynes/cm^2
F	2594	21 mg/l	21 dynes/cm^2

Solubility and Percentage Polyoxyethylene

In **Table 6.10**, 10% product in solvent is shown. Solubility in water is directly related to the proportion of ethylene oxide in the molecule.

Table 6.10. Solubility and % EO

Designation	Molecular Weight	Water	Mineral Oil	Methanol	% Ethylene Oxide
A	632	S	D	S	74
B	701	S	D	S	67
C	1240	S	D	S	76
E	2525	S	D	S	74
F	2594	S	D	S	75

S =soluble
D=dispersible

Eye Irritation

Perhaps one of the most interesting properties is the effect of molecular weight upon eye irritation. The data in **Table 6.11** indicates that irritation potential is related to molecular weight with a very sharp drop in irritation as the molecular weight is increased. **Table 6.12** shows the Draize Irritation Rating Scale.

Table 6.11. Eye Irritation Data

Designation	Molecular Weight	1 day	3 days	7 days
A	632	28.3	17.0	4.3
B	701	13.0	9.0	2.0
C	1240	4.7	9.3	2.0
D	1917	4.0	2.0	0.0
E	2525	2.0	0.7	0.0
F	2594	0.0	0.0	0.0

Table 6.12. Draize Primary Irritation Scale

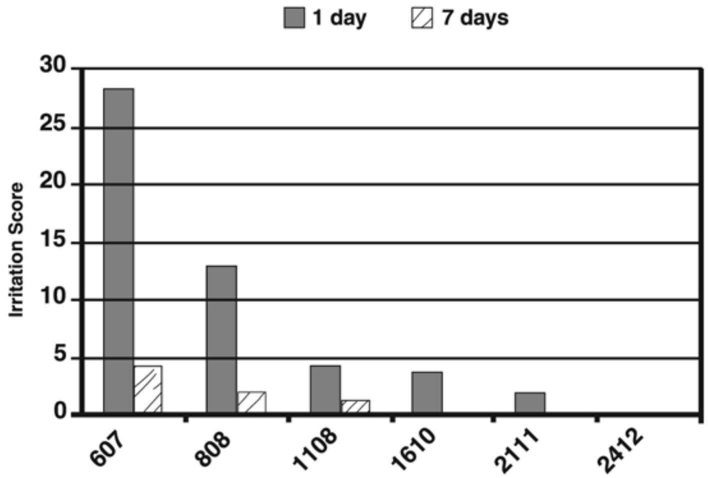
Moderately Irritating	25.1–50.0
Mildly Irritating	15.1–25.0
Minimally Irritating	2.6–15.0
Practically Non-irritating	0.6–2.5
Non-irritating	0–0.5

Proper selection of a dimethicone copolyol can confer a desirable combination of properties to personal care formulations. While low molecular weight dimethicone polyols exhibit the shortest wetting times and the highest eye irritation, a good compromise can be reached with certain dimethicone polyols as low irritation wetting agents (**Figure 6.8**).

Water Solubility

What factors affect the water solubility of a dimethicone copolyol? To anyone with knowledge about HLB, the question seems rather trite. However, as one considers the chemistry, the answer is more complicated.

Figure 6.8. Eye Irritation vs. Molecular Weight



HLB

In order to be clear in water, a PEG dimethicone will need to have an HLB in excess of 9. This, however, does not mean all PEG dimethicone with an HLB of 10 or more will be water-soluble, just that those with lower HLB values will not be soluble.

D/D* Ratio

The second–and perhaps less understood–factor related to the water solubility of PEG dimethicone is the ratio of D to D*. Since silicone polymers, like fatty alcohol ethoxylates, are not pure compounds, but rather are mixtures (referred to as oligomers), there is a "range" of products present in the molecule. Recalling that it is the D* unit that has the EO residue, if there are very few D* units and many D units, there will be some molecules without any D* units present in the oligomeric mixture. If the D* unit is missing in the molecule, the compound is not a PEG dimethicone, but rather a silicone fluid. Therefore, the product will not be soluble regardless of the number of moles of ethylene oxide (the "x" value) because of the concentration of insoluble oligomer present.

This explains why there are so few PEG-dimethicone compounds on the market, and why they have a high HLB and few "D" units present. So, it will be observed:

> *In order to be clear in water, a PEG dimethicone will need to have a D to D* ratio above that called for in the above formula.*

This however does not mean all PEG dimethicone with the specified D to D* ratio will be water-soluble, just that those with lower values will not be soluble. So, it will be observed:

In order to be clear in water, a PEG dimethicone will need to have an HLB in excess of 10 and have a D to D ratio above that called for in the above formula.*

Water Tolerance

Another very interesting functional property of dimethicone copolyol compounds is their ability to bring water into oil phases. This is true even of dimethicone copolyol compounds that are not water-soluble. The proclivity of a dimethicone copolyol to bring water into another phase has been measured by "The Water Tolerance Test." This test uses the fact that even water-insoluble dimethicone copolyol compounds are soluble in isopropanol. The ability of the compound to make the resulting isopropanol/dimethicone copolyol solution water-tolerant is a measurement of the affinity of the dimethicone copolyol compound for water. This turns out to be a very important number for formulators looking to bring some water into their products.

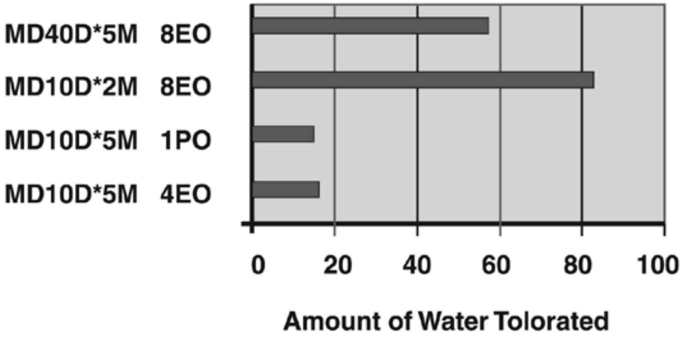
All DMC compounds have "water tolerance" even if they are water-insoluble. Water tolerance was measured by the following test:

1. Dissolve 2.0 g of test dimethicone copolyol in 100 g isopropanol.
2. Begin adding DI water under agitation until cloudiness develops.
3. Record the number of grams of water needed to cloud.*

**Note that water-soluble products will not cloud.*

It is quite interesting and somewhat unexpected that 1 mole of propylene oxide on the dimethicone copolyol compound is a more efficient agent for increasing water tolerance than four moles of ethylene oxide on the same backbone. One area this has been used successfully in is incorporating small amounts of water in pigmented products such lipsticks to improve the feel. The data is shown graphically in **Figure 6.9**.

Figure 6.9. Water Tolerance



Odor

In August of 2002, a US Patent was obtained for a process that removes odor bodies from dimethicone copolyol compounds. The invention provides a simple, effective and nondestructive method to eliminate the odor that is undesirable in the compounds produced by the hydrosilylation reaction. The process is said to effectively remove odor when applied to dimethicone copolyol compounds that have been prepared by hydrosilylation reactions known in the art. The process to deodorize dimethicone copolyol compounds relies upon the ability of water to hydrolyze odor-releasing compounds and to remove the volatile odor causing materials present in the dimethicone copolyol. This development has allowed for the formulation of these compounds into applications where odor is critical.

Other Surfactant Properties

In order to illustrate the properties of DMC polymers, the structures shown in **Table 6.13** were synthesized.

Table 6.13. Compounds Studied

Designation	Molecular Weight	E.M.W.a
MD*M	607	607
MD*DM	808	612
MD_2*D_2M	1108	619
MD_3*D_5M	1610	630
MD_3*D_7M	2111	642
MD_4*D_8M	2412	648

Where D* is $–(CH_2)_3\text{-O-}(CH_2CH_2O)_7\text{-H}$

EMW = Molecular weight divided by number of D* units

Solubility

Solubility was determined by mixing the materials and observing their homogeneity after 30 minutes. Solubility was measured by mixing the sample into the solvent at a given concentration and observing its homogeneity after 24 hours. The solubility was defined as: soluble (S)—clear homogeneous phase; dispersed (D)—translucent or cloudy but homogeneous phase; insoluble (I)—not homogeneous.

The solubility of the DMC materials was measured in polar and nonpolar solvents (**Table 6.14**). All products were soluble in water. As mentioned above in the cloud point discussions, the solubility is related to the length of the polyoxyethylene group. This behavior is similar to that found in ethoxylated alcohols. The average length of the polyoxyethylene group for all the products studied was similar, about 74%, which makes them soluble in water. All products also showed good solubility in methanol, ethanol, i-propanol and propylene glycol.

Products with higher molecular weight dispersed best in nonpolar oils. The larger molecular weight, or longer hydrophobe, seemed to contribute to the enhanced nonpolar media solubilization. The larger molecular weight products will be preferred when formulating using an oil base.

Table 6.14. Solubility in Various Solvents at 1%w and 5%w

Designation	**MD*M**	**$MD_2{}^*D_2M$**	**$MD_3{}^*D_7M$**
Methanol	Soluble/Soluble	Soluble/Soluble	Soluble/Soluble
Ethanol	Soluble/Soluble	Soluble/Soluble	Soluble/Soluble
i-Propanol	Soluble/Soluble	Soluble/Soluble	Soluble/Soluble
Propylene Glycol	Soluble/Soluble	Soluble/Soluble	Soluble/Soluble
Water (*aqua*)	Soluble/Soluble	Soluble/Soluble	Soluble/Soluble
Mineral Oil	Insoluble/Insoluble	Dispersible/Dispersible	Dispersible/Dispersible
Mineral Spirits	Insoluble/Insoluble	Dispersible/Dispersible	Dispersible/Dispersible
Silicone Oil, 350 cps	Insoluble/Insoluble	Insoluble/Insoluble	Dispersible/Dispersible

Surface Tension and Critical Micelle Concentration

Surface tension and CMC were measured at room temperature using a Krüss K-12 automated tensiometer equipped with a Wilhelmy plate. The CMCs were calculated automatically by the K122 program of the tensiometer. We also studied CMC (critical micelle concentration) and the surface tension ( ) at CMC. The data shows that the lower limit for surface tension for compounds of this type is 20 dynes/cm^2. This is due to the surface energy of the methyl groups in the flexible silicon backbone. The lack of significant differences in CMC is not very surprising since the hydrophobe-lipophile content is balanced by EMW considerations. The results can also be understood by the cloud point results, which do not vary much either. **Table 6.15** shows the results.

Table 6.15. Surface Tension and CMC

Designation	CMC, mg/L	at CMC, dynes/cm^2
MD*DM	3	20
$MD_2{}^*D_2M$	4	19
$MD_3{}^*D_5M$	6	23
$MD_3{}^*D_7M$	5	21
$MD_4{}^*D_8M$	14	21

Spreading

The maximum spreading area was measured for various products on a polyester surface. The films were inspected for cleanliness prior to use. These were not used if they showed any signs of fingerprints or debris on the surface. Ten microliters of the sample, prepared with distilled water, were placed on the film using a micropipette and its diameter measured after 45 seconds using a Vernier caliper. Longer times sometimes led to sample evaporation. Experiments were conducted at room temperature (23±1°C) in replicate and averaged. The relative area reported is the area of the sample drop divided by that of distilled water.

Spreading area was studied relative to water on polyethylene films. Trisiloxanes surfactants are well-known for their wetting and spreading properties. These properties make them ideal for use in textiles, coatings, and agricultural adjutants. For example, spreading and wetting properties are directly related to flow in coatings, spread-out area in cosmetics formulations, and leaf coverage in pesticide formulations. Silicones typically spread better than conventional organic and fluorocarbon surfactants.

The spreading properties for the various DMCs are shown in **Figure 6.10**. They indicate that the isomers studied spread slightly better than water. An optimum was observed at $MD_2{}^*D_2M$, clearly outperforming the NP-9EO control. However, none of the samples can be considered super spreaders. These materials are too hydrophilic, as shown by their high cloud point, and thus do not contain the needed subphases (or aggregates) present that provide the necessary surfactant concentration gradient, and diffusion rate, in the droplet spreading front that drives the spreading. Literature states that the larger the molecule the slower the spread of the droplet front, thus the slower the spreading5. This is probably related to monomer size hindrance (molar volume) on packing at the substrate surface, possible higher intrinsic viscosity. However, we believe it is the high cloud point having the major effect.

Foam

The degree of polymerization seems to have an effect on foam height, as shown in **Figure 6.11**. Lower molecular weight material showed higher initial (flash) foam. However, the foam stability was similar for both lower and higher molecular weight.

Figure 6.10. Spreading in Polyester at 24°C

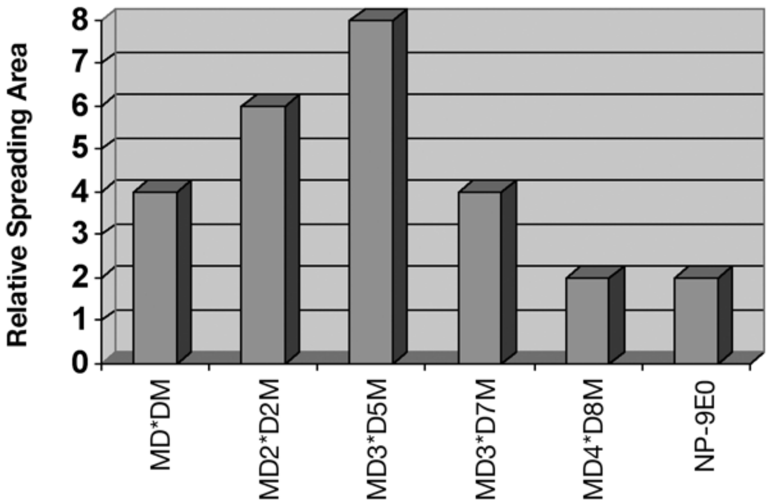
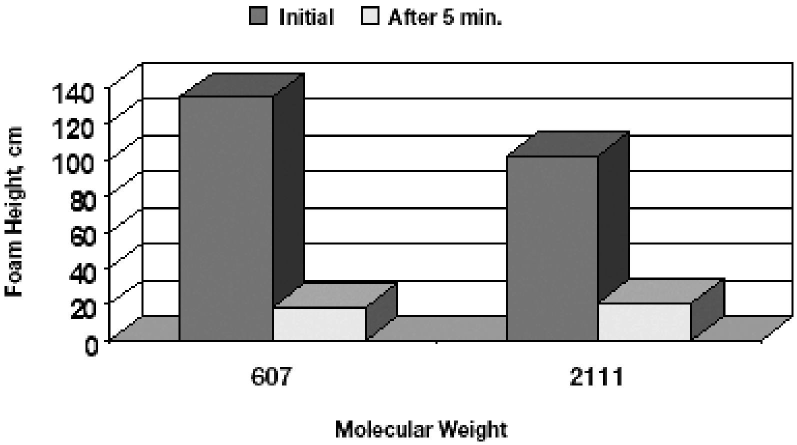


Figure 6.11. Foam at 1% wt.



Emulsification

Emulsification was measured by mixing the materials in a shaker at high speed for five minutes. Each emulsion consisted of 5% w/w DMC and 95% w/w of two of the following phases at a ratio of 1:1 (w=water, O=mineral oil, Si=silicone oil, 350 viscosity). Stability was determined after one hour standing undisturbed. Stability was defined as:

5 = stable/homogeneous milky

4 = appearance of milky layer(s) with the volume of one layer drastically reduced (mostly emulsified)

3 = appearance of milky layer(s) with the volume of each layer shifted to some degree (some dispersion)

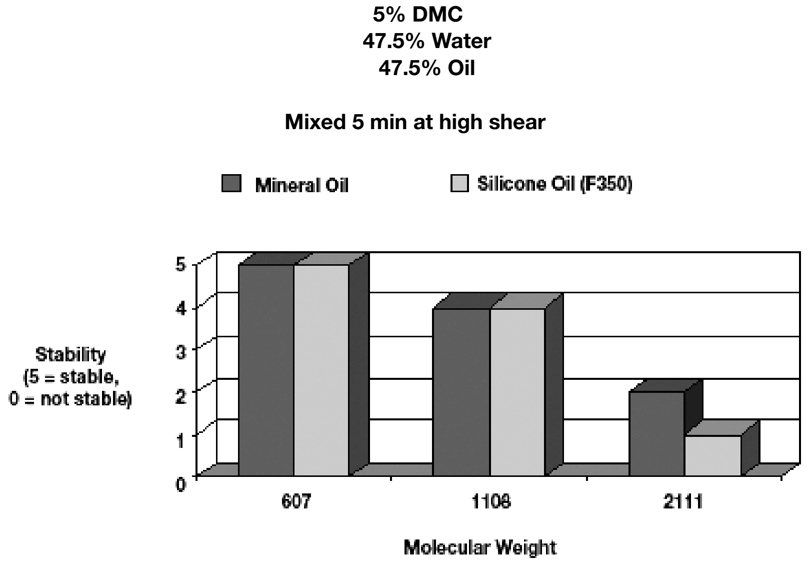
2 = appearance of translucent layer(s) with the volume of each layer shifted to some degree (some dispersion)

1 = appearance of translucent layer(s) with the volume of each layer being approximately the same as originally added to the mixture (slightest degree of dispersion)

0 = no mixing, with two distinct clear layers

The lower the molecular weight the more stable an emulsion of oil in water is. The results are shown in **Figure 6.12**.

Figure 6.12. DMC Emulsification Ability



A summary of properties of selected dimethicone copolyol compounds is shown in **Table 6.16**.

Table 6.16. General Properties

Property	Results					
Molecular weight	607	808	1108	1610	2111	2412
Equivalent weight	588	596.9	610.25	632.5	654.75	668.1
no. D*/no. D	1/0	1.3/0.9	1.75/2.25	2.5/4.5	3/6.75	3.6/8.1
Cloud point, °C, 1%w	58	57	58	58	58	57
Draves Wetting, sec (1.0%w, 24°C)	<1	<1	<1	1	2	4
Draves Wetting, sec (0.1%w, 24°C)	7	8	10	16	27	57
Cmc, mg/l, 24°C	43	3	4	6	5	14
Surface Tension at cmc, dynes/cm^2	20	20	19	21	23	21
Foam power/stab., 1.0%w, 49°C, mm	135/18	--	77/55	--	102/21	--
Foam power/stab., 0.1%w, 49°C, mm	111/21	--	--	--	--	--
Solubility, 24°C, 0.1/1.0%w						
MeOH	S/S	--	S/S	--	S/S	--
EtOH	S/S	--	S/S	--	S/S	--
IPA	S/S	--	S/S	--	S/S	--
Water	S/S	S/D	S/D	S/D	S/S	S/S
Silicone Oil	I/I	--	I/I	--	D/D	--
Mineral Oil	I/I	--	D/D	--	D/D	--
Mineral Spirits	I/I	--	D/D	--	D/D	--
Propylene glycol	S/S	--	S/S	--	S/S	--
Spreading Area relative to water, 0.1% 24°C	3.6	5.9	8.25	2	4.3	1.6
Emulsion - O/Si (5=emulsified), 24°C	--	--	1	--	1	--
Emulsion - o/w	--	--	4	--	1	--
Emulsion - Si/w	--	--	4	--	2	--

S=soluble, D=dispersed, I=insoluble
*none = 3 phases, no emulsion formed

Active Release from an Antiperspirant Stick

The presence and location of propylene oxide, as well as the molecular weight of the polymer in dimethicone copolyol has a profound effect upon the release of antiperspirant actives. PEG/PPG 8 dimethicone is specifically designed to have propylene oxide groups placed throughout the polyoxyalkylene backbone to accelerate the rate of release of antiperspirant actives.

Antiperspirant compositions exist in either the active form, which provides functionality, or in a non-active form. The conversion from the non-active form to the active form is referred to as release. The concentration of active is measured by chloride titration, since the chloride ion is only found in the aqueous phase for active form. The percent release is calculated by the ratio of active divided by the total times 100. **Table 6.17** shows the procedure.

Table 6.17. A.P. Release Methodology

Reagents:

1. Silver nitrate (0.05%N)
2. 10% nitric acid

Apparatus:

1. Constant temperature water bath.
2. Lab stirrer with RPM reading
3. 250 mL beaker
4. Analytical Balance
5. Weighing dish
6. Spatula
7. Filter paper (Whatman #4)
8. Funnel
9. Automatic Chloride titrator (Brinkman)
10. Magnetic Stirrer
11. Thermometer

Procedure:

1. Weigh 199 g of DI water into a 250 mL beaker and heat to 37°C
2. Place the beaker in a constant temperature water bath and mix well at 250 rpm with an overhead mixer.
3. Weigh 1.1 g of antiperspirant stick by shaving with a spatula from the surface of the stick.
4. Mix for 30 min and proceed to step 6.

cont.

Table 6.18. A.P. Release Methodology cont.

5. Repeat steps 1–3 three more times only this time mix for 60, 120 and 240 min.
6. Filter through filter paper and collect liquid for chloride titration.
7. Add 15 mo of 10% nitric acid and mix well.
8. Analyze for chloride ion using the auto titrator.
9. Calculate % chloride

% Chloride titrated 100 = % Active

Theoretical % Chloride

The formulation tested compared PEG-12 dimethicone and PEG/PPG 8/8 dimethicone. The formulation is shown in **Table 6.19**.

Table 6.19. Antiperspirant Formulation

Two different DMCs were evaluated for release in the following formulation:

Material	**Formula A**	**Formula B**
1. Reach AZP-908	24.0	24.0
2. PEG 12 dimethicone	-	2.5
3. PEG/PPG 8/8 dimethicone	2.5	-
4. Cyclomethicone (D5)	30.0	30.0
5. Polydecane	9.0	9.0
6. PPG 14-butyl ether	9.0	9.0
7. Hydrogenated Castor Oil	2.5	2.5
8. PEG-8-Distearate	1.0	1.0
9. Stearyl Alcohol	18.0	18.0
10. Talc	3.0	3.0
11. Cabo-sil-MS	0.5	0.5
12. Fragrance (*parfum*)	0.5	0.5
	100.0	100.0

cont.

Table 6.20. Antiperspirant Formulation cont.

Procedure:

1. Part 1: Combine 1 and either 2 and 3 as specified. Mix well.
2. In a beaker heat 4 to 70°C, slowly add Part 1, followed by 10, and 11, under good agitation.
3. In a separate beaker combine 5, 6, 7, 8, 9, and heat with mixing to 85oC.
4. Cool to 60°C, then add 12.

The result of the release test is shown in **Table 6.21**.

Table 6.21. Release Data

Evaluated using Procedure in Table 6.23.

Example	30 minutes	60 minutes	120 minutes	240 minutes
Formula A PEG 8 /PPG 8 Dimethicone	96.2 %	96.5%	98.8%	-
Formula B PEG-12 dimethicone	43.0%	61.3%	80.5%	90.6%

Clearly the formula containing PEG/PPG has better release.

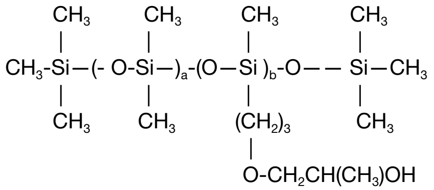
Hydroxypropyl Dimethicone (Carbinol Compounds)

Newer catalyst systems have been developed that allow for the synthesis of dimethicone copolyol compounds that have simple hydroxypropyl groups. In the past, these compounds were elusive since there is a high degree of reaction at both the OH and C=C groups using traditional catalysts. The compounds conform to the structure shown in **Figure 6.13**.

These materials have a hydroxyl group connected to a methylene group. This group is a carbinol compound, rather than a silanol compound, which features a Si-OH bond. These products formulate in a manner very similar to silicone fluids in terms of emulsification requirements but are much more polar and hydrophilic. Their beneficial properties include:

1. ***Polarity on Deposition***—the presence of the hydroxypropyl group introduces polarity into the molecule. When deposited on the hair, the film is more hydrophobic and consequently builds up less.

Figure 6.13. Hydroxypropyl Dimethicone



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}-(\text{-}\,O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}-)_a\text{-}(O-\underset{\underset{O\text{-}CH_2CH(CH_3)OH}{|}}{\underset{(CH_2)_3}{\overset{CH_3}{Si}}}\,)_b\text{-}O-\,-\,\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

2. ***Suspension of Pigments***—the silicone keeps pigments and other active ingredients well dispersed and suspended, while easily wetting and spreading pigments and actives s on skin.
3. **Sensory Properties**—the silicone imparts the sensory performance of higher molecular weight structures and offers moisturization benefits for the skin.
4. ***Altered Solubility*** (See **Table 6.22** and **6.23**.)

Table 6.22. Carbinol Solubility

Material	Carbinol Fluid	DMC	350cSt fluid
Lauryl alcohol	DISP	INSOL	INSOL
Oleyl alcohol	DISP	SOL	INSOL
Glyceryl trioctanate	SOL	SOL	INSOL
Polyglyceryl diisostearate	INSOL	INSOL	INSOL
Mineral Oil	DISP	NSOL	INSOL
Ethanol, 200 proof	DISP	NSOL	INSOL
Propylene glycol	INSOL	DISP	INSOL
Water	INSOL	SOL	INSOL
Dipropylene glycol	INSOL	--	--
Glycol ether	SOL	--	--
Glycerin	INSOL	--	--
Isopropanol	SOL	--	--

cont.

Table 6.22. Carbinol Solubility cont.

Material	Carbinol Fluid	DMC	350cSt fluid
Octyldimethyl PABA	DISP	SOL	NSOL
Octyl methoxycinnamate	DISP	SOL	NSOL
Castor oil	INSOL	SOL	NSOL
Lanolin oil	INSOL	NSOL	NSOL
Sunflower oil	INSOL	NSOL	NSOL
Isododecane	SOL	PSOL	SOL
C11-12 isoparaffin	SOL	NSOL	SOL
Polydecene	INSOL	NSOL	NSOL
D-4/D-5	SOL	NSOL	SOL
Phenyl fluid	SOL	NSOL	SOL

Table 6.23. Carbinol Solubility

Material	Carbinol Fluid	DMC	350cSt fluid
C12-15 alkyl benzoate	SOL	SOL	INSOL
Caprylic/capric triglyceride	SOL	SOL	INSOL
Coco-caprylate/caprate	SOL	PSOL	INSOL
Diisopropyl adipate	SOL	SOL	INSOL
Diisostearyl fumarate	SOL	INSOL	INSOL
Diisostearyl malate	SOL	SOL	INSOL
Isocetyl stearate	SOL	INSOL	INSOL
Isopropyl isostearate	SOL	SOL	INSOL
Isopropyl laurate	SOL	SOL	SOL
Isopropyl myristate	SOL	SOL	SOL
Isopropyl palmitate	SOL	SOL	SOL
Isopropyl stearate	SOL	SOL	SOL

cont.

Table 6.23. Carbinol Solubility cont.

Material	Carbinol Fluid	DMC	350cSt fluid
Myristyl ether acate	SOL	SOL	INSOL
Myristyl lactate	SOL	SOL	NSOL
Octyldodecyl stearoyal stearate	INSOL	INSOL	NSOL
Octylpalmitate	SOL	DISP	DISP
Octylstearate	SOL	DISP	DISP
Tridecyl neopentanoate	SOL	SOL	SOL
Triisocetyl citrate	SOL	INSOL	INSOL

5. ***Fragrance Stabilization***—the carbinol-functional silicone has sustained fragrance capabilities, maintaining fragrances longer than polydimethylsiloxane (PDMS) fluids of similar viscosity (50 cSt) and cyclopentasiloxane.
6. ***Sensory Perspective***—the carbinol fluid has tactile attributes similar to those of baby oil. It is smoother and more substantive than polydimethylsiloxane (PDMS) of equivalent molecular weight.

When applied to hydrophobic fiber-like polyester, they render it more hydrophilic. These molecules will eventually offer the personal care formulator less hydrophobic, nonionic conditioners for use in hair and skin care products.

Patents

There are currently 1,363 patents that have the terms "dimethicone copolyol" and "cosmetic" in them. Some of them are:

(1) U.S. Patent 6,805,855 to Mattai et al. issued October 19, 2004, entitled *Cool and dry antiperspirant stick teaches an antiperspirant and/or deodorant stick composition* is disclosed comprising (a) 10–60 weight % of a volatile silicone such as cyclomethicone; (b) 2–30 weight % of a low melting point wax gelling agent (particularly stearyl alcohol); (c) 1–10 weight % of a high melting point wax (such as hydrogenated castor oil); (d) 0–15 weight % of an emollient which is different from (b) and (c); (e) 0.1–10 weight % of a superabsorbent powder with little or no tack upon wetting such as starch graft homopolymers and copolymers of poly(2-propenamide-co-2-propenioic acid) sodium salt; (f) 0–30 weight % of an antiperspirant active; (g) 0–1 weight % of a dimethicone copolyol; (h) 0.01–0.5 weight % of a selected cooling agent; and (i) 0–5 weight % (particularly 0.1–5 weight %) of a fragrance; wherein the ratio of cooling agent to superabsorbent polymer is in the range of 1:50–1:2.

Patents cont.

(2) U.S. Patent 6,610,279 to Chopra issued August 26, 2003, entitled *Emulsions with naphthalate esters* teaches an anhydrous cosmetic composition comprising: (a) 15–33% of an external phase (also called the oil phase) which is made with at least one selected naphthalate organic ester; a volatile silicone based emulsifier; and a volatile silicone; and (b) 85–67% of an internal phase which is made with an active ingredient, such as an antiperspirant active, in a glycol solvent. For the external phase, all or a major portion of what would have been a nonvolatile silicone component, has been replaced by the naphthalate ester. While a dimethicone copolyol is still included, the use of this particular naphthalate ester obviates the need for the use of any other nonionic emulsifiers.

(3) U.S. Patent 6,491,896 to Rajaiah et al. issued December 10, 2002, entitled *Polybutene containing denture cleanser compositions* teaches denture cleanser compositions comprising polybutene, with a molecular weight of about 300 to about 3,000, an effervescence generator and a bleaching agent. Optionally, denture cleanser compositions may further comprise tablet binders, organic peroxyacid bleach precursors, and surfactants including a dimethicone copolyol, lipophilic compounds such as flavorants and coolants, chelating agents, and other therapeutic and cosmetic active agents.

(4) U.S. Patent 6,468,513 to Murphy et al. issued October 22, 2002, entitled *Low residue liquid antiperspirant composition* teaches antiperspirant compositions, such as those used in roll-on formulations, are disclosed. These compositions do not leave a significant white residue on the skin of the user and exhibit good skin feel when applied. The antiperspirant liquid compositions of the present invention comprise from about 10% to about 70% of an antiperspirant active; from about 20% to about 80% of a volatile solvent; from about 0.5% to about 2% of a high molecular weight silicone material (such as a silicone gum, dimethicone copolyol, or a cross-linked silicone polymer); from about 0.5% to about 5% of a polyethylene wax; and from about 1% to about 8% of hydrophobic organic esters (such as cetearyl ethylhexanoate).

(5) U.S. Patent 6,277,89 to Babenko issued August 21, 2001, entitled *Polysaccharide and dimethicone copolyol as emulsifier for cosmetic compositions* teaches stable o/w emulsion for use in cosmetic compositions comprising an oil phase which contains the combination of a polysaccharide such as animo-mullticarboxylate starch derivative and a dimethicone copolyol as emulsifier, and a water phase.

(6) U.S. Patent 5,858,336 to Graf et al. issued January 12, 1999, entitled *Clear stick deodorant* teaches clear deodorant stick compositions including a solvent, a gelling agent, an odor-controlling agent selected from the group consisting of a germicidal agent, a deodorizing agent, a masking agent and a combination thereof, and a plasticizing/solubilizing agent selected from the group consisting of polyoxyethylene-polyoxypropylene 2-decyltetradecyl ether, ethoxylated dimethicone copolyol and combinations thereof.

(7) U.S. Patent 5,482,703 to Pings issued January 9, 1996, entitled *Hair conditioning compositions* teaches compositions, for conditioning human hair, comprising from about 0.1% to about 10% of a silicone conditioning agent; from about 0.01% to about 10% of a dimethicone copolyol; from about 0.1% to about 10% of a lipid vehicle material; from about 0.05% to about 5% of a cationic surfactant vehicle

Patents cont.

material; and the balance of water. Preferably the lipid vehicle materials are fatty alcohols or fatty esters. Also preferably, the silicone conditioning agent is a non-substituted, amine substituted, or alkoxy substituted polydimethyl siloxane.

(8) U.S. Patent 5,217,625 to Iovanni issued June 8, 1993, entitled *Conditioning shampoo* teaches conditioning shampoo is provided in the form of an aqueous solution having a pH of about 5 to 6 and which includes, in percent by weight of the total composition: (a) about 6% to 20% of at least one anionic surfactant; (b) about 0.1% to about 5% of a dimethicone copolyol having an ethylene oxide/propylene oxide ratio of from about 70/30 to 80/20; and (c) a conditioning component comprising a combination of (i) about 0.1% to 2% guar hydroxypropyltrimonium chloride, (ii) about 0.1% to 2% hydroxypropyl bis-isostearamidopropyldimonium chloride, (iii) about 0.05% to 1.5% of an aluminum salt of a mineral acid, and (iv) about 0.00001% to 0.01% of a fluoroquaternary.

(9) U.S. Patent 4,960,764 to Figeroa issued October 2, 199, entitled *Oil-in-water-in-silicone emulsion* compositions teaches oil-in-water-in-silicone fluid (o/w/s) emulsion composition comprising (a) a silicone fluid continuous phase, (b) an aqueous discontinuous phase comprising an o/w emulsion, and (c) an effective dispersing amount of dimethicone copolyol for dispersing (b) in (a).

(10) U.S. Patent 4,822,602 to Sabatelli issued April 18, 1989, entitled *Cosmetic sticks teaches cosmetic compositions in the form of solid sticks, especially deodorant sticks and antiperspirant sticks* teaches that cosmetic stick compositions of the present invention comprise the essential components: (a) water-soluble active; (b) dimethicone copolyol; (c) volatile silicone oil; (d) propylene glycol; (e) C2 -C4 monohydric alcohol; (f) water; (g) solidifying agent; and (h) coupling agent.

Conclusion

Dimethicone copolyol is a very important class of compounds that will certainly have major applications in the personal care market for many years to come. The ability to make materials that offer different wetting properties, different skin and hair feel, and different conditioning, coupled with the ability to alter solubility, will make these molecules workhorses of the industry. I believe that the incorporation of PPG portions of the molecule will result in more efficient molecules for specific applications.

References:

1. U.S. Patent 2,632,013 issued March 17, 1953 to Wagner, George et al., titled *Process for producing Organosilicone Compounds*.
2. U.S. Patent 2,678,406 issued May 11, 1954 to Francis Foster, titled *Organosilicone Compounds*.
3. N Prieto, and A O'Lenick, Structure Function Relationship of Dimethicone Copolyol, *Journal Surfactants Deterg*, 2(3) 438 (July 1999). Presented as a paper, 1999 AOCS Annual Meeting.
4. U.S. Patent 6,437,162 issued August 20, 2002 to O'Lenick, An-

thony, titled *Process for the manufacture of low odor dimethicone copolyol compounds*.

5. Colloids & Surfaces 44 281(1990).

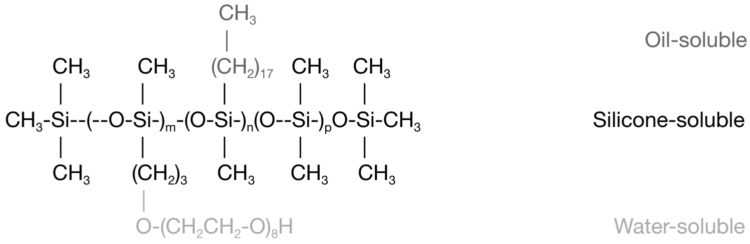
Chapter 7

Silicone Esters

Silicone surfactants are of interest in the cosmetic industry because they are amphiphilic. The fact that two *or more* phases that in pure form would be insoluble are in the same molecule, makes that molecule orientate itself at interfaces to obtain the lowest energy state. This orientation at concentrations below the critical micelle concentration (CMC) results in lowering of surface tension. As the concentration of surfactant is raised, micelles form. Foam, wetting, tactile feel, spreadability and many other properties are affected by the silicones surfactant's ability to alter surfaces. Dimethicone copolyol (water/silicone), alkyl dimethicone (oil silicone), fluoro dimethicone (silicone/fluoro) all have two phases in a single molecule. Alkyl dimethicone copolyol and dimethicone copolyol esters have three groups (oil/water/silicone). It is the ability to prepare molecules that contain both varying amounts of water-soluble, oil-soluble and silicone-soluble groups in the same molecule (homologous series) and the ability to alter the location, type and concentration of the groups within a molecule that offers the potential to obtain different surfactant properties.

Alkyl dimethicone copolyol compounds possess alkyl groups on different silicone molecules in the backbone (**Figure 7.1**). These compounds are free to rotate around the highly flexible Si-O-Si bond. When placed at the water/oil interface, they simply rotate to place the alkyl group in the oil phase and the DMC group in the water phase to achieve lowest energy. These materials are emulsifiers.

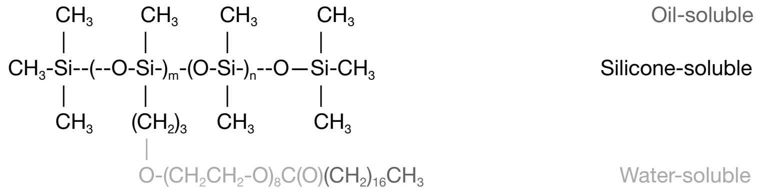
Figure 7.1. Alkyl Dimethicone Copolyol: Generic Formula



$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ CH_3 & CH_3 & (CH_2)_{17} & CH_3 & CH_3 \\ | & | & | & | & | \\ CH_3\text{-Si--} & (\text{--O-Si-})_m\text{-} & (\text{O-Si-})_n & (\text{O--Si-})_p & \text{O-Si-}CH_3 \\ | & | & | & | & | \\ CH_3 & (CH_2)_3 & CH_3 & CH_3 & CH_3 \\ & | & & & \\ & \text{O-}(CH_2CH_2\text{-O})_8H & & & \end{array}$$

Silicone esters are a different story. They have a polar ester group that is attached to the water-soluble group, which is in turn attached to the silicone group. In short, the oil-soluble group cannot rotate away from the water-soluble group. **Figure 7.2** shows the structure. Silicone esters are conditioners, lubricants and emulsifiers.

Figure 7.2. Dimethicone Copolyol Esters: Generic Formula



$$\begin{array}{lllllllll}
 & CH_3 & & CH_3 & & CH_3 & & CH_3 & \\
 & | & & | & & | & & | & \\
CH_3\text{-} & Si & \text{--(--O-} & Si & \text{-)}_m\text{-(O-} & Si & \text{-)}_n\text{--O}- & Si & \text{-}CH_3 \\
 & | & & | & & | & & | & \\
 & CH_3 & & (CH_2)_3 & & CH_3 & & CH_3 & \\
 & & & | & & & & & \\
 & & & \multicolumn{6}{l}{O\text{-}(CH_2CH_2\text{-}O)_8C(O)(CH_2)_{16}CH_3}
\end{array}$$

Silicone esters are prepared by a number of synthetic routes.[1,2,3] One route is the esterification reaction of a dimethicone copolyol with a fatty acid, and another major route is the reaction with natural oils, which are triglycerides. 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

The oldest and most common method of synthesis is esterification of a dimethicone copolyol with a fatty acid or triglyceride. There are construction (polymer backbone preparation), functionalization (hydrosilylation with allyl alcohol alkoxylate) and derivatization (reaction with fatty acid) steps in the process of making dimethicone copolyol esters. These steps are shown in **Figures 7.3**, **7.4** and **7.5** respectively.

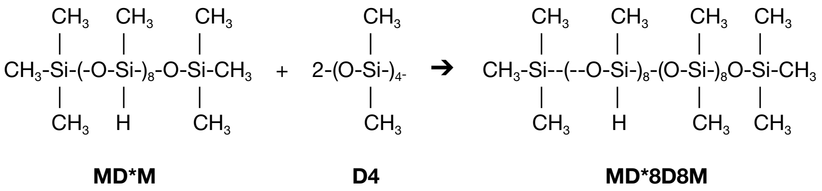
Silicone esters prepared by the esterification reaction of a dimethicone copolyol with a fatty acid results in products that have silicone-soluble groups, oil-soluble groups and water-soluble groups. As such, they are candidates for the so-called "3-D HLB."

Properties

Dimethicone copolyol esters made by the reaction of fatty acid with PEG-8-dimethicone have the following general properties:

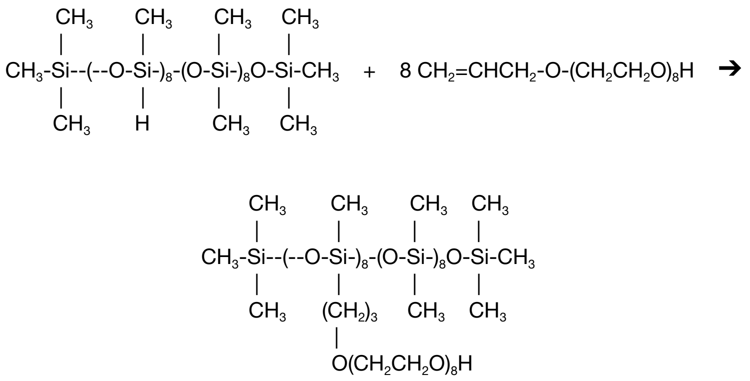
1. Compounds that have less than 12 carbon atoms in the fatty group are liquids at room temperature.
2. Saturated linear compounds that have more than 14 carbon atoms in the fatty group are solids at room temperature.
3. Compounds in which the fatty group is unsaturated or branched are liquids at room temperature.

Figure 7.3. Dimethicone Copolyol Esters: Construction



$$\mathrm{CH_3\text{-}Si\text{-}(\text{-}O\text{-}Si\text{-})_8\text{-}O\text{-}Si\text{-}CH_3} + \mathrm{2\text{-}(O\text{-}Si\text{-})_{4}\text{-}} \rightarrow \mathrm{CH_3\text{-}Si\text{--}(\text{--}O\text{-}Si\text{-})_8\text{-}(O\text{-}Si\text{-})_8O\text{-}Si\text{-}CH_3}$$

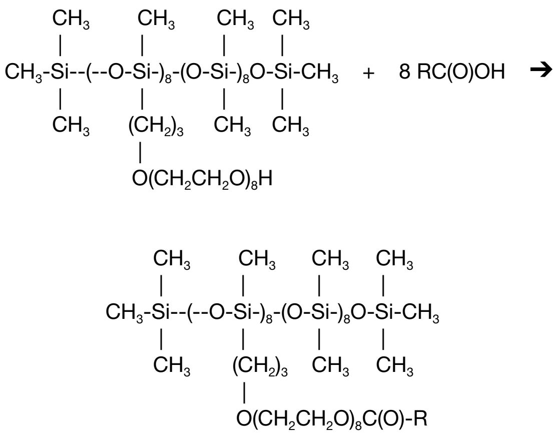
Figure 7.4. Dimethicone Copolyol Esters: Functionalization



$$\mathrm{CH_3\text{-}Si\text{--}(\text{--}O\text{-}Si\text{-})_8\text{-}(O\text{-}Si\text{-})_8O\text{-}Si\text{-}CH_3} + 8\ \mathrm{CH_2{=}CHCH_2\text{-}O\text{-}(CH_2CH_2O)_8H} \rightarrow \mathrm{CH_3\text{-}Si\text{--}(\text{--}O\text{-}Si\text{-})_8\text{-}(O\text{-}Si\text{-})_8O\text{-}Si\text{-}CH_3}$$

$$\mathrm{(CH_2)_3\text{-}O(CH_2CH_2O)_8H}$$

Figure 7.5. Dimethicone Copolyol Esters: Derivitization



$$\mathrm{CH_3\text{-}Si\text{--}(\text{--}O\text{-}Si\text{-})_8\text{-}(O\text{-}Si\text{-})_8O\text{-}Si\text{-}CH_3} + 8\ \mathrm{RC(O)OH} \rightarrow \mathrm{CH_3\text{-}Si\text{--}(\text{--}O\text{-}Si\text{-})_8\text{-}(O\text{-}Si\text{-})_8O\text{-}Si\text{-}CH_3}$$

$$\mathrm{(CH_2)_3\text{-}O(CH_2CH_2O)_8H} \rightarrow \mathrm{(CH_2)_3\text{-}O(CH_2CH_2O)_8C(O)\text{-}R}$$

4. The most hydrophobic products have more than 16 carbon atoms in their fatty group.
5. The greatest spreadability and lubrication is obtained from the liquid products where the fatty group is iso stearic.
6. The 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; many exhibit water tolerance.

Table 7.1 shows properties of these materials.

Table 7.1. Typical Product Properties Dimethicone Copolyol Esters

Product	Description
Silwax WD-IS (Isostearic acid)	Forms a microemulsion in water. Conditions, softens and provides wet comb properties in hair care products. Used as a fiber lubricant for microfibers.
Silwax WS-L (Lauric acid)	A water-soluble product soluble in many polar solvents. It is soluble in both water and propylene glycol and consequently is used in clear deodorant sticks.

Solubility Properties

The incorporation of silicone-, fatty- and water-soluble portions into a molecule results in unique solubility and emulsification properties. In order to illustrate the range of solubility that is achievable using this technology, products were tested at 5 % solids in the solvents shown in **Table 7.2**.

Triglyceride-derived Dimethicone Copolyol Esters

In addition to products that are prepared using fatty acids, there are products made from natural triglycerides. These materials provide conditioning, gloss and softening properties when applied to hair or skin. Some representative products by CTFA designation are:

- Dimethicone copolyol avacodoate
- Dimethicone copolyol almondate
- Dimethicone copolyol olivate
- Dimethicone copolyol cocobutterate
- Dimethicone copolyol meadowfoamate
- Dimethicone copolyol cocoate

Table 7.2. Dimethicone Copolyol Esters: Solubility

Solvent	PEG-8-Isostearate	PEG-8-Laurate
Water	Microemulsion	Soluble
Isopropanol	Soluble	Soluble
Mineral Spirits	Insoluble	Insoluble
350 Visc Silicone	Insoluble	Insoluble
PEG 400	Dispersible	Dispersible
Glyceryl Trioleate	Soluble	Soluble
Oleic Acid	Soluble	Soluble
Tri-octyldodecyl Citrate	Soluble	Soluble
Mineral oil	Insoluble	Insoluble

Products derived from many other triglycerides are also available. Silicone derivatives from these triglycerides function in formulations in the same manner as the silicone products made from the analogous fatty acids and are used predominantly for their name on the label. For example, dimethicone copolyol cocobutterate might be a good additive for after-sun products. Essentially, any triglyceride can be used to prepare a dimethicone copolyol ester. Meadowfoam seed oil, while by no means the only oil useful in making esters, is typical of the properties that can be obtained using this technology.

Dimethicone Copolyol Meadowfoamate

Dimethicone copolyol meadowfoamate is one of the highly studied compounds in this family. Alan Wohlman, PhD of the Fanning Corporation has done this pioneering work.

Meadowfoam seed oil (*Limnanthes alba*)

Before proceeding with the discussion of silicone functionalized meadowfoam seed oil,[4] a discussion of the starting oil is appropriate.

Meadowfoam oil is a triglyceride derived from the herbaceous winter plant (*Limnanthes alba*). It is grown in the southern portion of Oregon in the United States. Since the flowers have an appearance of a canopy of white foam, the name meadowfoam was given to the plant. This material is a relatively new raw material and is unique in that it has both a high concentration of fractions at or above 20 carbons as well as a unique arrangement of double bonds. The fact that the double bonds in the doubly unsaturated product are not conjugated, as in linoleic acid, the oil is liquid to very low temperatures and is stable to oxidation.

This unique oil has an outstanding resistance to odor formation in a process called rancidity. This is due not only to the fact that the double bonds are not conjugated, but also because of the presence of a unique antioxidant, making this oil very valuable in personal care applications. **Table 7.3** shows the carbon distribution.

Table 7.3. Carbon Distribution of Meadowfoam Oil

Component	% Weight
C20:1 (n = 5)	63
C20:2 (n = 5, 13)	12
C22:1 (n = 5)	3
C22:1 (n = 13)	12
C22:2 (n = 5, 13)	10

Meadowfoam Silicone

Conditioning

Dimethicone copolyol meadowfoamate is an effective hair conditioning[5] agent, while the starting dimethicone copolyol is not a conditioner. The following study shows this:

- ***Protocols:*** European blonde hair samples deliberately damaged by processing with permanent wave agents and permanent hair color.
- ***Test materials:*** Dimethiconol meadowfoamate and a water control, both used at 1% in an emulsified leave-in conditioner. Test swatches were completely immersed in the leave-in conditioner for 5 minutes and subsequently air dried at room temperature or rapidly dried with the aid of a commercial blow-dryer.
- ***Measurements:*** Hair samples were mounted onto aluminum scanning electron microscopy (SEM) holders using double-stick tape and colloidal graphite paint. The hair samples were then coated with a thin (about 20 nanometers) conductive film of gold-palladium in a vacuum evaporator. The samples were then examined and photographed using a Philips Model 500 scanning electron microscope.
- ***Elemental microanalysis:*** Elemental composition was studied on thin sections using a Philips Model 711F EDAX microanalyzer (Energy Dis-

> persive Analysis of X-Rays). The atom silicon (atomic number 14) is present in dimethicone copolyol meadowfoamate and, since there is no native silicone present in hair, it can be used as a marker for cuticle substantivity and penetration. The silicone atom, when bombarded with electrons, generates x-rays with a 1740 EV energy peak that shows up slightly to the left of the pronounced 2310 EV sulfur peak present in the hair sulfhydryl groups. Therefore, any detection of Si is clearly indicative of the presence of silicone meadowfoamate. The location can be determined from the EDAX scan. Results are shown in **Figure 7.8**.

The effects of dimethicone copolyol meadowfoamate on cuticular repair confirm earlier studies wherein LIM-1 was used at a 5% level in a simple water rinse. In the present case, LIM-2, at a level of 1% in a leave-in conditioner also clearly demonstrates the ability to facilitate the natural realignment of the cuticular cellular plates.

EDAX measurements confirmed the presence of silicone on the cuticular surface demonstrating the substantive nature of the conditioning agent. After drying with the aid of a conventional blow-dryer, a significant silicone peak was observed in the endocuticle/cortex region of the fiber indicating effective penetration of LIM-2.

Repair of the Hair Shaft

Dimethicone copolyol meadowfoamate is effective in repairing hair shaft,^{5} while the starting dimethicone copolyol is not.

Polarized light microscopy can be used to determine degree of fiber orientation and repair. Considering the lipophilic and hydrophilic nature of the chemical entities that comprise the LIM molecules, one would expect to achieve a certain degree of molecular spatial orientation. In addition, it is likely that orientation of the molecule will influence the alignment of asymmetric molecules in the immediate environment into which the material has penetrated. The present study is designed to determine if the penetration of dimethicone copolyol meadowfoamate into the hair fiber results in a reorientation of the fibrillar structure within the hair shaft.

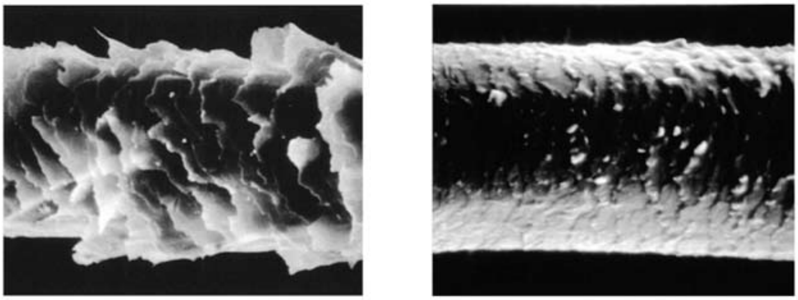
Materials

Single damaged hair fibers were mounted in an immersion microscopic slide. An Olympus polarized light microscope equipped with a full wave filter and photomicrograph equipment was used for time-lapse recording of changes in birefringence in the hair fiber.

Test solutions

Dimethicone copolyol meadowfoamate at 1% in water and, as a control, water alone introduced onto the microscopic slide and allowed to enter the viewing area during photographic recording.

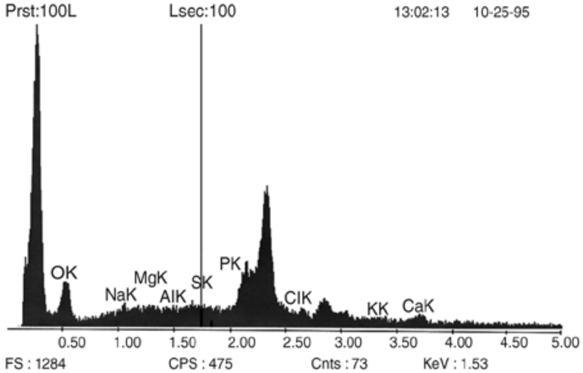
Figure 7.8. SEM Results



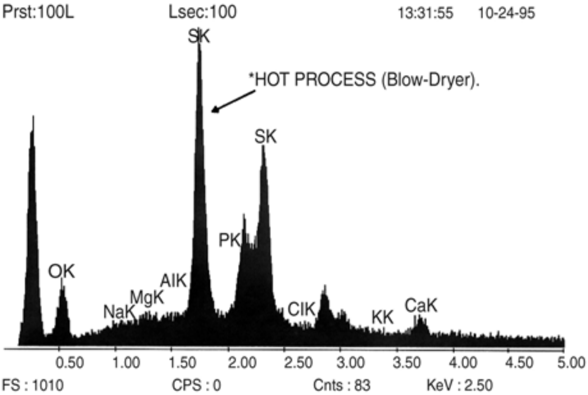
Control: Cuticle Before Treatment

Test Fiber: Cuticle After Treatment

Endocuticle/Cortext Scan



Control EDAX Scan of Damaged Hair Fiber (No Silicon on Cuticle Surface).



EDAX Scan of Endocuticle with Hot Process (Blow Dryer) on "Leave-In" Conditioner Treatment. Dimethicone Copolyol Meadowfoamate serves as a marker to demonstrate the presence of Lim-2 in the endocuticle region of damaged hair shaft.

Results

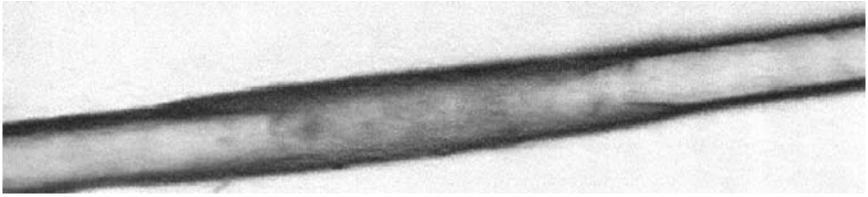
The resulting video clearly demonstrates repair of the damaged fiber as observed by cuticular realignment as well as a return of the overall fiber shape and size to "normal" dimensions.

- A damaged hair fiber as seen in polarized light microscopy (**Figure 7.9**).

Figure 7.9. Damaged Hair

- The same damaged hair fiber, treated with dimethicone copolyol meadowfoamate, as seen in polarized light microscopy (**Figure 7.10**).

Figure 7.10. Damaged hair treated with PEG-8 dimethicone meadowfoamate



Discussion

The still photos in this chapter were obtained from the video. Treatment with 1% dimethicone copolyol meadowfoamate in water or 1% LIM-2 in a leave-in conditioner resulted in the damaged hair fiber undergoing a clearly visible degree of repair as evidenced by the reorientation of structure and return to its normal dimensions ("revolumized"). It appears that during damage, the internal fibrillar structure of the hair shaft is disrupted giving rise to a condensed anisotropic section that is prone to be easily broken. Upon treatment with dimethicone copolyol meadowfoamate, the fiber assumes a more normal isotropic architecture, which is oriented and revolumized.

Table 7.4. Raw Materials Studied

Shorthand	**MD*M**	**MD4*D8M**
Molecular Weight	607	2,612
No. D*/No. D	1/0	4/8
Equivalent Weight	607	653
Trisiloxane	MC	

a) where D* is $–(CH_2)_3\text{-}O\text{-}(CH_2CH_2O)_7\text{-}H$

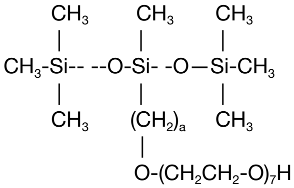
b) EMW = Molecular Weight/number of D* units

Ester Structure/Function

A study was undertaken by Prieto, et al.,[5] to look at the effects of altering the structure of PEG-7 dimethicone in making a series of esters. Two silicone molecules were chosen, a trisiloxane and a dimethicone copolyol. The information on these two raw materials is shown in **Table 7.4**. The specific structure for MD*M is given in **Figure 7.11**. The specific structure for MD8D4*M is given in **Figure 7.12**.

The MD*M and MD4*DM were reacted with a series of commercially available fatty acids, producing esters. The reaction of the MD*M was at equimolar amounts and resulted in the product shown in **Figure 7.13**.

Figure 7.11. MD*M Trisiloxane

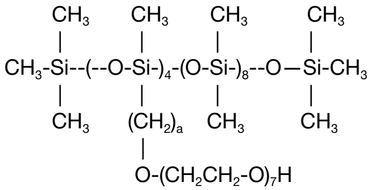


$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-- --}O\text{-}\underset{\underset{O\text{-}(CH_2CH_2\text{-}O)_7H}{(CH_2)_a}}{\overset{CH_3}{Si}}\text{- -}O—\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

The tetra functional MD*4D8M, was reacted with one mole of fatty acid and two moles of fatty acid to give the mixed products shown in **Figure 7.14**.

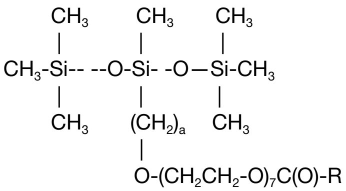
The acids chosen for esterification are listed in **Table 7.5**. The specific acids were chosen to study linearity and branching over a range of molecular weights molecular weights.

Figure 7.12. MD*4D8M Formula



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{\underset{O\text{-}(CH_2CH_2\text{-}O)_7H}{|}}{\underset{(CH_2)_a}{\overset{CH_3}{Si}}}\text{-})_4\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8\text{--}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

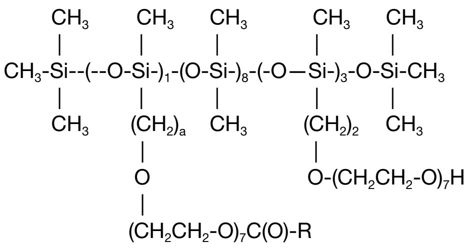
Figure 7.13. PEG-7-dimethicone from MD*M Trisiloxane Ester



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-- --}O\text{-}\underset{\underset{O\text{-}(CH_2CH_2\text{-}O)_7C(O)\text{-}R}{|}}{\underset{(CH_2)_a}{\overset{CH_3}{Si}}}\text{- -}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

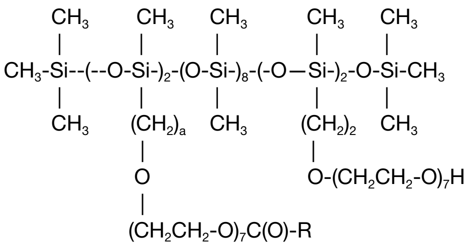
Figure 7.14. MD*4D8M Esters

(a) Monoester, triethoxy-product



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{\underset{\underset{(CH_2CH_2\text{-}O)_7C(O)\text{-}R}{O}}{|}}{\underset{(CH_2)_a}{\overset{CH_3}{Si}}}\text{-})_1\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8\text{-}(\text{-}O\text{—}\underset{\underset{O\text{-}(CH_2CH_2\text{-}O)_7H}{|}}{\underset{(CH_2)_2}{\overset{CH_3}{Si}}}\text{-})_3\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

(a) Diester, diethoxy-product



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{\underset{\underset{(CH_2CH_2\text{-}O)_7C(O)\text{-}R}{O}}{|}}{\underset{(CH_2)_a}{\overset{CH_3}{Si}}}\text{-})_2\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8\text{-}(\text{-}O\text{—}\underset{\underset{O\text{-}(CH_2CH_2\text{-}O)_7H}{|}}{\underset{(CH_2)_2}{\overset{CH_3}{Si}}}\text{-})_2\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Table 7.5. Fatty Acids used in Silicone Esters

Starting Fatty Acid	Adopted Designation
Hexyl	C6
2-Ethylbutyl	2C2C4
2-Ethylhexyl	2C2C6
Pelargonic	C9
Coco	C12
Stearic	C18
iso-Stearic	iC18
Cetyl	C16
Guerbet C16	G16
Guerbet C20	G20

Solubility

The solubility of the silicone esters made with MD*M are shown in **Table 7.6**. The solubility of the silicone esters made with MD4*D8M are shown in **Table 7.7**.

Table 7.6. Solubility of MD*M Esters

Solvent	MD*M	C6	2C2C4	2C2C6	C9	C12	iC18
Methanol	S	S	S	S	S	S	S
Ethanol	S	S	S	S	S	S	S
i-Propanol	S	S	S	S	S	S	S
Propylene Glycol	S	D	S	S	S	S	D
Water	D	I	D	S	S	S	D
Silicone Oil, 350 cps	I	D	D	D	I	I	I
Mineral Oil	I	D	D	D	I	I	S

S = Soluble, I = Insoluble, D = Dispersible

Table 7.7. Effect DMC/acid Mole Ratio on Solubility of MD4*D8M Esters

Solvent (1%W)	MD*4D8M	C9		C12		iC18	
Mole ratio DMC/ester		1	2	1	2	1	2
Methanol	S	S	S	S	S	S	S
Ethanol	S	S	S	S	S	S	S
i-Propanol	S	S	S	S	S	S	S
Water	S	D	D	D	S	D	S
Silicone Oil, 350 cps	S	I	I	I	I	I	I
Mineral Oil	I	I	I	I	I	I	D
Propylene Glycol	S	I	I	I	D	I	I

S = Soluble, I = Insoluble, D = Dispersible

Surface Tension and CMC Data

Surface Tension and CMC data were collected in DI water. **Table 7.8** shows the results.

Table 7.8. Surface Tension and CMC (24°C, DI water)

Designation	CMC, mg/L	ST at CMC, dynes/cm^2
MD*M	31	20
C9	39	24
C12	73	26
iC18	72	27
Monoester		
MD4*D8M	14	21
2C2C6	16	25
C9	21	24
C12	22	26
iC18	28	27

The CMC increases dramatically as the molecular weight of the ester increases. The surface tension (ST) likewise increases with increasing molecular weight. The parent MD*M has a surface tension of 20 dynes/cm^2 a silicone type value (CH_3- at surface) the iC18 is at 27 dyner/cm^2, a value expected for fatty surfactants (CH_3- at surface).

Emulsification

The various silicone esters were evaluated in a simple emulsion test. **Table 7.9** shows the formulation. Three types of emulsion were observed. They are o/si; o/w; and si/w. **Table 7.10** shows the results.

Table 7.9. DMC Esters Emulsification Test

Formulation

Material	**% wt**
1) Silicone emulsifier	5.0
2) Phase 1	47.5
3) Phase 2	47.5

Mixed 5 min. at high shear with a Silverson Blender (9,000 rpm).

Table 7.10. Emulsion stability after 1 hour

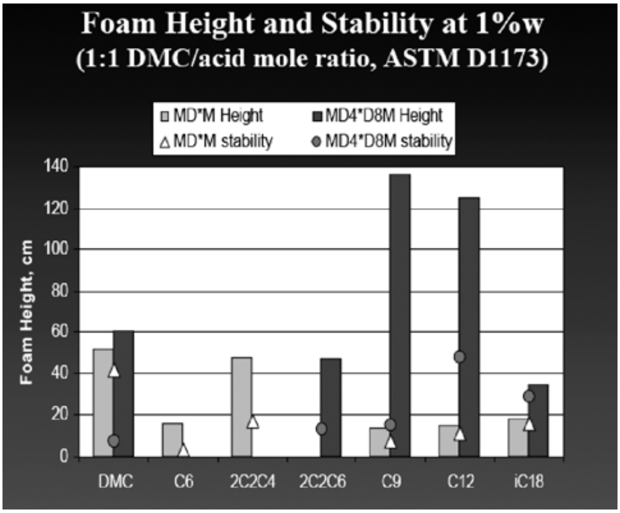
(5 = most stable)

Material	**MD2D*M**			**MD4*D8M**		
Emulsion	O/Si	O/W	Si/W	O/Si	O/W	Si/W
DMC only	1	5	5	1	3	2
C9	1	3	3	1	0	0
C12	1	3	3	2	1	1
iC18	1	5	4	1	1	0

Foam Properties

The various DMC esters as well as the parent DMC were evaluated as foaming agents using ASTM D1173. Results are shown in **Figure 7.15**. The best foaming compound was MD*4D*M - C9 ester.

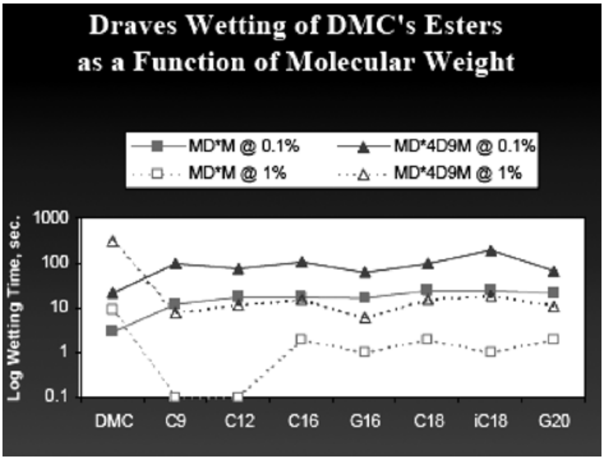
Figure 7.15. Foam height and stability at 1%w



Wetting Properties

Draves Wetting tests were run on the parent DMC and the DMC esters. **Figure 7.16** shows the results. The addition of an ester group onto MD*M, based upon C9 and C12 improved wetting, providing the best wetting in the series.

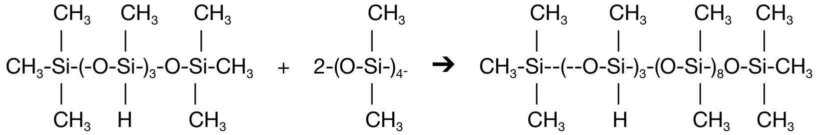
Figure 7.16. Draves Wetting



Other Esterification Methods

Recently, there has been another approach to making dimethicone copolyol esters.[6] This approach makes use of a different reaction sequence. This sequence makes use of an alpha unsaturated ester that is co-hydrosilylated into the silicone backbone, giving a product that has both ester and free hydroxyl moieties present. Construction is shown in **Figure 7.17** and functionalization is shown in **Figure 7.18**.

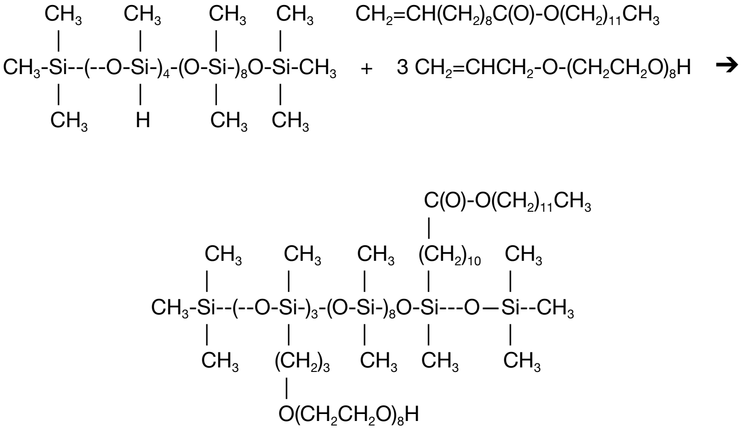
Figure 7.17. Dimethicone Copolyol Esters—Construction



$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}(\text{-}O\text{-}\overset{CH_3}{\underset{H}{Si}}\text{-})_3\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3 \;+\; 2\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_4\text{-} \;\rightarrow\; CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\overset{CH_3}{\underset{H}{Si}}\text{-})_3\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_8O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3$$

MD3*M **D4** **MD*3D8M**

Figure 7.18. Dimethicone Copolyol Esters—Functionalization



$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\overset{CH_3}{\underset{H}{Si}}\text{-})_4\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_8O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3 \;+\; 3\ CH_2{=}CHCH_2\text{-}O\text{-}(CH_2CH_2O)_8H \;\rightarrow$$

$$CH_2{=}CH(CH_2)_8C(O)\text{-}O(CH_2)_{11}CH_3$$

$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\overset{CH_3}{\underset{(CH_2)_3\text{-}O(CH_2CH_2O)_8H}{Si}}\text{-})_3\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_8O\text{-}\overset{C(O)\text{-}O(CH_2)_{11}CH_3\text{-}(CH_2)_{10}}{\underset{CH_3}{Si}}\text{---}O\text{—}\overset{CH_3}{\underset{CH_3}{Si}}\text{--}CH_3$$

These molecules are purported to have better water solubility, less byproduct and the ability to further react the hydroxyl group, allowing for additional functionalization.

Patents

(1) US Patent 6,646,144 to Klein et al. issued Nov. 11, 2003, titled Dimethicone copolyol cranberriate as a delivery system for natural antioxidants teaches that cranberry seed oil derivatives derived by the reaction of dimethicone copolyol and cold-pressed cranberry seed oil. The choice of cold-pressed cranberry seed oil as a raw material in the preparation of the compounds of the present invention is critical, since it has been found that the cold-pressed cranberry seed oil contains antioxidants, antimicrobial compounds and which when reacted with a water-soluble or water-dispersible silicone result in products that deliver said actives to the skin and hair, resulting in protection of the skin and hair from environmental factors such as acid rain, ozone attack and UV degradation.

(2) US Patent 6,630,180 to Klein et al. issued Oct. 7, 2003, titled Dimethicone copolyol raspberriate as a delivery system for natural antioxidants teaches raspberry seed oil derivatives prepared by the reaction of dimethicone copolyol and cold-pressed raspberry seed oil. The choice of cold-pressed raspberry seed oil as a raw material in the preparation of the compounds is critical, since it has been found that the cold-pressed raspberry seed oil contains antioxidants and antimicrobial compounds. When reacted with a water-soluble or water-dispersible silicone, it results in products that deliver said actives to the skin and hair, resulting in protection of the skin and hair from environmental factors such as acid rain, ozone attack and UV degradation.

(3) US Patent 6,552,212 to Walele et al. issued April 22, 2003, titled Benzoate esters of hydroxyl terminated polyether polysiloxane copolyols and process for producing same teaches benzoate esters of hydroxyl terminated polyether polysiloxane copolyols, in particular dimethicone copolyol benzoates, and process for preparing same. The benzoate esters are useful for personal care cleansing products, such as bar and liquid soaps, skin and hair care products and textiles and fibers. The compounds are prepared by reacting benzoic acid with hydroxyl terminated polyether polysiloxane copolyols.

(4) US Patent 6,388,042 to O'Lenick issued May 14, 2002, titled Dimethicone copolyol esters discloses novel dimethicone copolyol ester compounds bearing a fatty group attached through a hydrophobic ester linkage to silicon. This invention also relates a series of such products having differing amounts of water-soluble groups, silicone-soluble groups and fatty-soluble groups. By careful selection of the compounds so constructed, very efficient mild conditioning agents may be achieved.

(5) US Patent 6,358,499 to Hall-Puzio et al. issued March 19, 2002, titled Deodorant with small particle zinc oxide teaches a one-phase cosmetic composition that can be made as a stick, gel or cream and has low residue, low tack and improved fragrance substantivity. The cosmetic compositions are formed by (a) from 0.5–50 weight percent of a dimethicone copolyol ester compound soluble in propylene glycol; (b) from 50–98 weight percent of a gellant/solvent system that comprises a mixture of; (i) 0.5–4.0 weight percent dibenzylidene sorbitol; (ii) 0.05–1.0 weight percent of a co-gellant or structural integrity enhancer; (iii) 0.1–80 weight percent of a polyhydric alcohol solvent; (c) 0.5–10% of a small particle size zinc oxide having a particle size in the range of 20 nanometers–200 microns; and (d) 0.1–3.0% fragrance.

(6) US Patent 6,313,329 to O'Lenick Jr. issued Nov. 6, 2001, titled Silicone functionalized eugenol esters teaches that certain euganol functionalized silicone

Patents cont.

polymers useful to make substantive antimicrobial agents. These compounds allow for the topical delivery of euganol to the skin surface, where it has a variety of desirable effects.

(7) US Patent 6,180,125 to Ortiz et al. issued Jan. 30, 2001, titled Low tack cosmetic composition sticks teaches a one-phase cosmetic composition that is a clear stick or gel having low tack. The cosmetic sticks are formed as a one-phase system by combining: (a) from 0.5–50 weight percent of a dimethicone copolyol ester compound soluble in propylene glycol; (b) from 50–99 weight percent of a gellant/solvent system; which comprises a mixture of: (i) 0.5–4.0 weight percent dibenzylidene sorbitol; (ii) 0.05–1.0 weight percent of a co-gellant or structural integrity enhancer; (iii) 0.1–80 weight percent of a solvent selected from the group consisting of polyhydric alcohols for example, propylene glycol; dipropylene glycol; tripropylene glycol; tetrapropylene glycol; PPG-10 butane diol; 1,3-butane diol; 2-methyl-1,3-propanediol; PEG-6; and PPG-425; optionally including up to 50% of other solvents selected from the group consisting of propylene carbonate, diisopropyl sebacate, methyl pyrrolidone, and ethyl alcohol as a substitute for a portion of the polyhydric alcohol component; and (c) an effective amount of at least one cosmetically active ingredient, for example, an antiperspirant active.

(8) US Patent 5,989,532 to Haning et al. issued Nov.r 23, 1999, titled Hair treatment

Patents cont.

composition and method discloses a hair treatment composition comprising a mixture of polyvinylpyrrolidone and a member selected from the group consisting of an ethoxylated triglyceride, a quaternary ammonium chloride, phenyl trimethicone, an acrylate containing polymer and dimethicone copolyol ester and mixtures thereof. A "component of the present invention is a dimethicone copolyol ester. A preferred dimethicone copolyol ester is that made with meadowfoam oil. The reaction to form the dimethicone copolyol ester is esterification."

(9) US Patent 5,180,843 to O'Lenick Jr. issued Jan. 19, 1993, titled Terminal substituted silicone fatty esters teaches the unique properties of esters based upon M* esters of dimethicone copoylol.

(10) US Patent 5,136,063 issued Aug. 4, 1992, to O'Lenick et al. titled Silicone fatty esters teaches the invention relates to a series of novel silicone fatty esters. This class of compounds provides outstanding softening and lubricating when applied to textiles and fibers. The compounds of the present invention are prepared by reacting a hydroxyl group in a silicone polymer with a fatty carboxylic acid, ester or anhydride.

(11) US Patent 4,724,248 to Dexter et al. issued Feb. 8, 1988, titled Voltage stabilizing esters and urethanes is the first patent to disclose silicone fatty esters.

Conclusion

The ability to modify dimethicone copolyol by reacting the hydroxyl groups partially or completely with fatty acids or triglycerides will offer a method to improve the functionality of amphyllic materials having oil-, water- and silicone-soluble groups. The implications of structural changes upon the surface-active properties of this class of compounds are just now beginning to be fully understood. Optimization is expected to continue.

References:

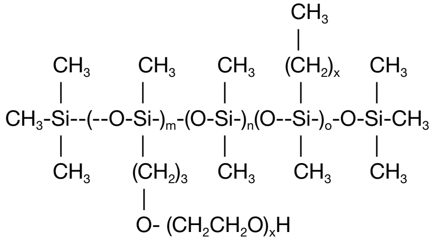
1. U.S. Patent 4,724,248 issued February 9, 1988 to Dexter et al. titled *Voltage stabilizing esters and urethanes*.
2. U.S. Patent 5,180,843 issued January 19, 1993 to O'Lenick, Anthony titled *Terminal substituted silicone fatty esters*.
3. U.S. Patent 6,388,042 issued May 14, 2002, to O'Lenick, Anthony titled *Dimethicone copolyol Esters*.
4. O'Lenick, Anthony, Steinberg, David and Klein, Kenneth, Primary Ingredients, Hansotech Inc., 1998 p. 71.
5. Prieto, Nelson et al. Optimization of Dimethicone Copolyol Ester Structure, website *www.petroferm.com* (2002).
6. US Patent 5,136,063 issued August 4, 1992 to O'Lenick, Anthony titled *Silicone fatty esters*.

Chapter 8

Alkyl Dimethicone Copolyol Compounds

Silicone compounds have been successfully used in a variety of personal care products and were essential in the development of dry antiperspirants, conditioning shampoos and oil-free skin care products. Alkyl dimethicone copolyol compounds are multicomponent compounds that have water-soluble groups, alkyl groups and silicone groups, which in large part contribute to their unique properties vis-à-vis emulsification and skin feel. The structure of alkyl dimethicone copolyol compounds is shown in **Figure 8.1**.

Figure 8.1. Alkyl Dimethicone Copolyol: Generic Formula

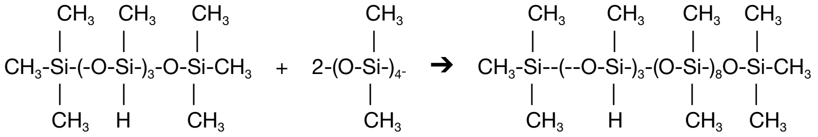


$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\overset{CH_3}{\underset{\underset{O\text{- }(CH_2CH_2O)_xH}{(CH_2)_3}}{Si}}\text{-})_m\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_n(O\text{--}\overset{\overset{CH_3}{(CH_2)_x}}{\underset{CH_3}{Si}}\text{-})_o\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3$$

The processes used to make these materials are made using construction of the silanic hydrogen compound, followed by co-hydrosilylation with allyl alcohol ethoxylate and alpha olefin. This results in a series of compounds that have both alkyl groups and polyoxyalkylene groups which have been promoted in the personal care market as emulsifiers. The processes of construction and functionalization are shown in **Figures** 8.2 and 8.3.

There are significant differences in the structure and function of the dimethicone copolyol, dimethicone copolyol esters and the alkyl dimethicone copolyol compounds. The alkyl dimethicone copolyol compounds have been described as "highly flexible siloxane backbone between two anchor groups. Because of this flexible behavior, the siloxane backbone can adapt to interfaces very easily, without creating steric hindrances.… lower concentrations of silicone emulsifiers are needed than hydrocarbon ones to obtain emulsions with excellent stability."[1]

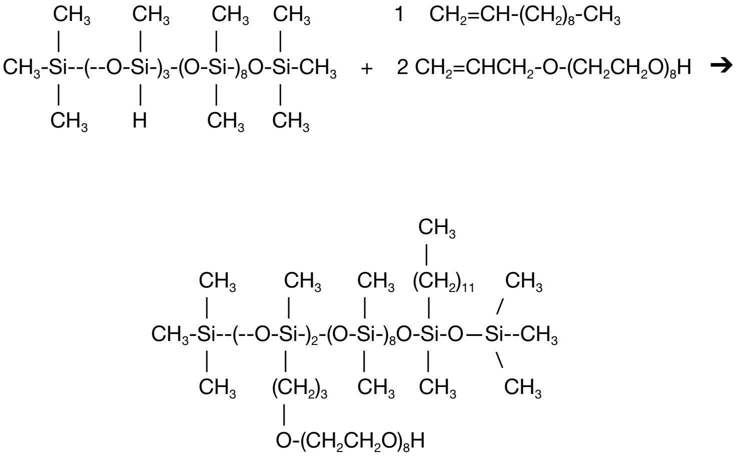
Figure 8.2. Alkyl Dimethicone Copolyol: Construction



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}(\text{-}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_3\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 + 2\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_{4}\text{-} \rightarrow CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_3\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

MD*M **D4** **MD*3D8M**

FIgure 8.3. Carboxy Silicone Compounds: Functionalization



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_3\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 + \begin{array}{l}1\ \ CH_2{=}CH\text{-}(CH_2)_8\text{-}CH_3\\ 2\ CH_2{=}CHCH_2\text{-}O\text{-}(CH_2CH_2O)_8H\end{array} \rightarrow$$

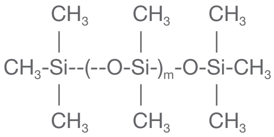
$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{\underset{O\text{-}(CH_2CH_2O)_8H}{|}}{\underset{(CH_2)_3}{\overset{CH_3}{Si}}}\text{-})_2\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8O\text{-}\underset{CH_3}{\overset{\overset{CH_3}{|}}{\overset{(CH_2)_{11}}{Si}}}\text{-}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}CH_3$$

Because of their different structure, silicone esters have different properties. Specifically, the fact that the esters have the fatty-soluble portion connected to the water-soluble portion directly, and the water-soluble portion is in turn linked to the silicone backbone, the free rotation is minimized. This makes the silicone function far more than an anchor group, acting in fact as a full partner in the triad of oil-soluble, silicone-soluble and water-soluble. This makes the esters less efficient emulsifiers, but far better in providing the benefits of silicone on the skin and hair. The ester products provide skin feel and conditioning to the hair and skin and are generally used only as secondary emulsifiers. The structures are shown for comparison in **Figure** 8.4. The silicone-soluble groups are in red, oil-soluble in black and water-soluble in blue.

Figure 8.4. Functional Group Solubility: Silicone Compounds

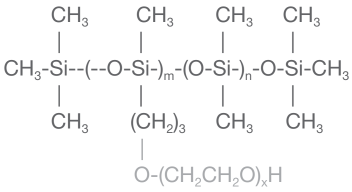
Silicone-soluble Water-soluble Oil-soluble

Dimethicone



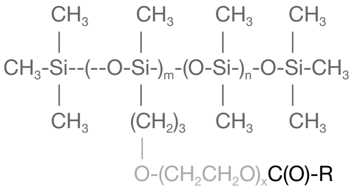
$$\mathrm{CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_m\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3}$$

Dimethicone Copolyol



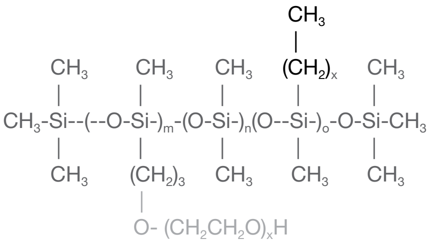
$$\mathrm{CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{\substack{(CH_2)_3\\ |\\ O\text{-}(CH_2CH_2O)_xH}}{\overset{CH_3}{Si}}\text{-})_m\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_n\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3}$$

Dimethicone Copolyol Ester



$$\mathrm{CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{\substack{(CH_2)_3\\ |\\ O\text{-}(CH_2CH_2O)_xC(O)\text{-}R}}{\overset{CH_3}{Si}}\text{-})_m\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_n\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3}$$

Alkyl Dimethicone Copolyol



$$\mathrm{CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{\substack{(CH_2)_3\\ |\\ O\text{-}\ (CH_2CH_2O)_xH}}{\overset{CH_3}{Si}}\text{-})_m\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_n(O\text{--}\underset{CH_3}{\overset{\substack{CH_3\\ |\\ (CH_2)_x}}{Si}}\text{-})_o\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3}$$

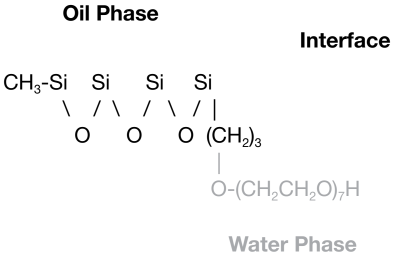
Orientation at the Interface

The physical chemistry that determines orientation at surfaces is a conformation rotation to obtain lowest free energy. This is generally the conformation that disrupts the least hydrogen bonding in the water phase. The orientation at the interface is not made clear from looking at the structure alone, but requires consideration of the ability of the molecule to flex. The tables below show only the pertinent groups and leave off the methyl groups on the Si atom. The groups shown partition themselves in the phase in which they are most soluble and this results in minimal free energy to the system and maximum stability. The key is the ability of the flexible silicone backbone to allow for the rotation.

Orientation of Dimethicone Copolyol at the Interface

Dimethicone copolyol compounds have a silicone-soluble and a water-soluble group. The silicone group provides a flexible chain for the molecule to rotate. This means that the conformation that has the lowest free energy is relatively easily achieved. **Figure 8.5** shows this.

Figure 8.5. Orientation of Dimethicone Copolyol at the Interface



Orientation of Silicone Gemini Dimethicone Copolyol at the Interface

There are some recent compounds on which the water-soluble groups are on the terminal ends. These terminal surfactants have also been called "Silicone Gemini Surfactants (SGS)" having alpha omega functionality. These molecules crowd the interface and thicken. It is quite easy to confuse the thickening phenomenon with emulsification. A thick dispersion will look like an emulsion until it is cut with water, whereupon it splits into two phases. **Figure 8.6** shows this.

Orientation of Alkyl Dimethicone Copolyol at the Interface

Alkyl dimethicone compounds have a silicone-soluble and an oil-soluble group. They are analogues of dimethicone copoylol compounds. The silicone group provides a flexible chain for the molecule to rotate. This means that the conformation that has the lowest free energy is relatively easily achieved. The silicone group provides flexible chain for the molecule to rotate. **Figure 8.7** shows this.

Figure 8.6. Orientation of Dimethicone Copolyol at the Interface

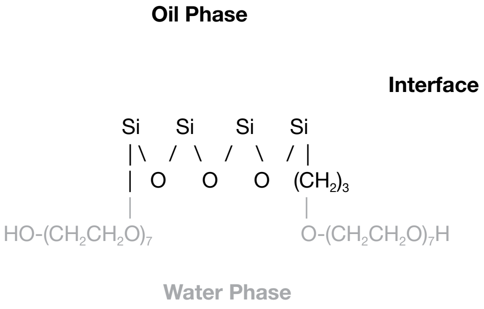
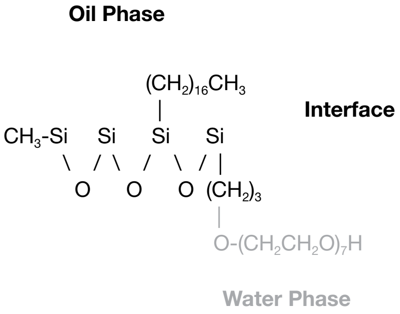


Figure 8.7. Orientation of Dimethicone Copolyol at the Interface

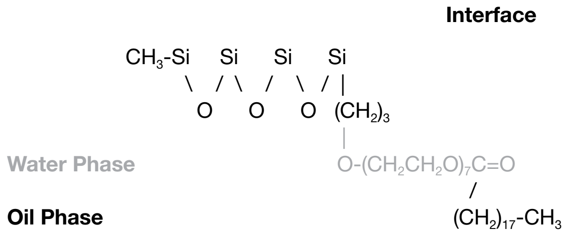


Orientation of Dimethicone Copolyol Ester at the Interface

The orientation of the ester at the interface is quite different. The diagram below shows only the pertinent groups and leaves off the methyl groups on the Si atom. The groups shown partition themselves in the phase in which they are most soluble; however, the silicone group is an equal member in the triad and in order to get least free energy, associates itself with other silicone portions of the molecule. The diagram below shows only the pertinent groups and leaves off the methyl groups on the Si atom. **Figure** 8.8 shows the orientation.

Orientation at the surface is key to functionality and properties. Wetting, emulsification, foam and other properties all are affected by how the molecule interacts with substrate and air at the interface. This chapter is devoted to the alkyl dimethicone copolyol compounds. Another chapter deals with the esters, both are of interest to the formulator of personal care products.

Figure 8.8. Orientation of Dimethicone Copolyol Ester at the Interface



Emulsification Properties

Alkyl dimethicone copolyols are used as emulsifiers in the preparation of water-in-silicone and silicone-in-water emulsions. These products provide advantages over traditional hydrocarbon chemistries since they can be used in the preparation of emulsions without heat. These silicone polymers can be used to prepare products that contain little wax, a large concentration of water, and have a light and spreadable feel on the skin.

The silicone portion of an alkyl dimethicone copolyol compound is flexible in that it can easily undergo rotation along the Si-O-Si bonds to adapt to the lowest free energy state in emulsions. This results in emulsions that have the lowest free energy and consequently the greatest stability.

For many of the aforementioned reasons, these molecules are useful as emulsifiers. While the free rotation of the silicone backbone allows for the lowest entropic state, these alkylated polymers orient or anchor themselves to confer a strong barrier between the oil and water, reduce interfacial tension appropriately against a variety of hydrophobes and hydrophiles and can make for a variety of delivery systems, aesthetics and stability.

Three salient variables determine their emulsification properties of alkyldimethicone copolyols: silicone character (dimethicone chain length or molecular weight), alkyl character (degree of substitution, fatty character chain length), and polyoxyalkylene oxide/polyoxypropylene (EO/PO) content, ratio and location in the polymer. Varying any one of these three will yield significant changes in properties, not the least of which is solubility. Understanding these emulsifiers does not produce traditional micellar structures, but rather lamellar-phased-stabilized sheets, critical to the design and application of these molecules.

As shown in the diagrams, the three variable areas associate with their "likeness" in the emulsion. Starting with an alkyldimethicone copolyol with a very hi EO/PO ratio and content, one expects to see fairly high solubility in water, and a significant reduction in interfacial tension between the oil/silicone phase and water. This will most likely orient in a silicone-in-water manner. Increasing PO content may turn this into more of a coupling agent between silicone and the remainder of the oil phase, rather than making it more hydrophilic. The same can be said for increasing the degree of substitution of the alkyl residue along the silicone backbone. Increasing or decreasing the alkyl residue's chain length at a given degree of substitution has little impact on its ability to make silicone emulsions; rather it plays with the compatibility of the emulsifier with the non-silicone oil content.

Conversely, a dimethicone copolyol (DMC) at a given molecular weight and a given ethylene oxide/propylene oxide ratio with a high alkyl substitution, yields high non-silicone character compatibility, and may yield more traditional emulsion structures.

Less impactful, but still noteworthy is the use of electrolytes to confer or reduce solubility in water. The ability to "salt-out" or "salt-bridge" in w/o emulsions using alkylated DMC as the primary emulsifier confers the ability on the part of the formulator to build rigidity or fluidity without altering content or phase ratios.

Obviously, the character of the alkyl substitution drives the compatibility with non-silicone oil materials. For example, if you were to make an emulsion of a mixture of triglycerides and silicone with water, you work with a DMC with triglyceride substitution. If a hydrocarbon is the non-silicone oil, then an olefin-substituted DMC is the target emulsifier. Traditional methods for resolving balance in these emulsions are insufficient, as the HLB system, the traditional method for resolving and balancing w/o and o/w emulsions of hydrocarbons and triglycerides with water, does not accommodate silicone as either the hydrophobe or the emulsifier, and alkylating the silicone only complicates things further.

Resolution can only be achieved, and true balance to these types of formula can only be realized taking into consideration a more three-dimensional approach, accommodating solubility and compatibility with oil, water and silicone as the three axes.

Alkyl Dimethicone Copolyol as Emulsifiers

Illustrative of the importance of structure is a series of emulsifiers that are designed to be effective in preparing both water continuous and water discontinuous types of emulsions. Specifically, alkyl dimethicone copolyol polymers conforming to the structure in **Figure 8.9** were evaluated.

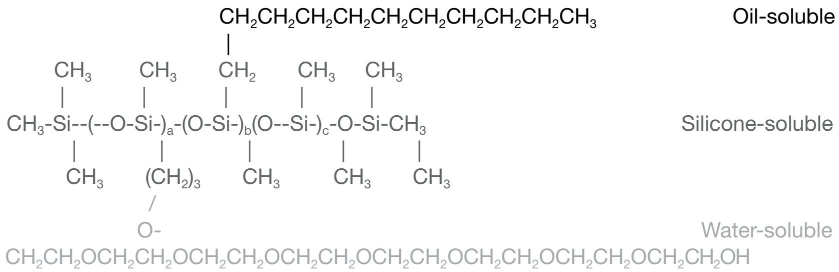
The structures have been color coded to show the orientation in a system containing both water and oil. The orientation is shown in **Figure 8.10**.

Emulsifiers are rarely a single compound, rather they are chosen in pairs to improve emulsion stability. The compounds all have the same construction, but differ in the number of alkyl and water soluble groups. That is the value of b, and c is different, but b + c is constant in the series of products evaluated. This type of series makes the understanding of solubility, formation of emulsions and emulsion stability easier.

The series of products have been designed to have different solubility in a variety of solvents. Additionally, the amount of alkyl in the molecule is reported using the 3D HLB system, since it is much more descriptive than the standard HLB. The composition of the products is disclosed in **Table 8.1**.

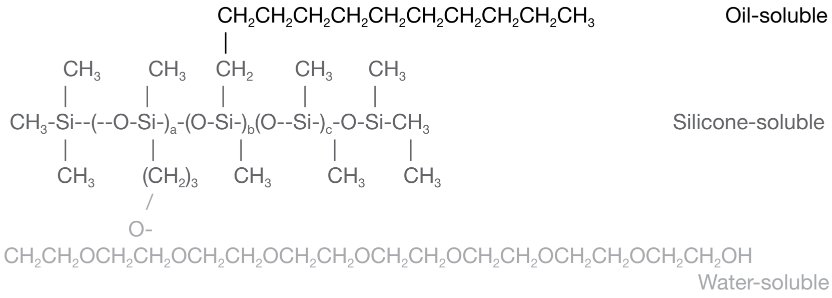
As the ratio of oil-soluble to water-soluble changes so does the solubility. **Table 8.2** shows the difference in solubility.

Figure 8.9. Alkyl Dimethicone Copolyol Emulsifiers



$CH_3\text{-}Si\text{--}(\text{--}O\text{-}Si\text{-})_a\text{-}(O\text{-}Si\text{-})_b(O\text{--}Si\text{-})_c\text{-}O\text{-}Si\text{-}CH_3$

Figure 8.10. Orientation of Alkyl Dimethicone Copolyol Emulsifiers



$CH_3\text{-}Si\text{--}(\text{--}O\text{-}Si\text{-})_a\text{-}(O\text{-}Si\text{-})_b(O\text{--}Si\text{-})_c\text{-}O\text{-}Si\text{-}CH_3$

Table 8.1. Emulsifiers

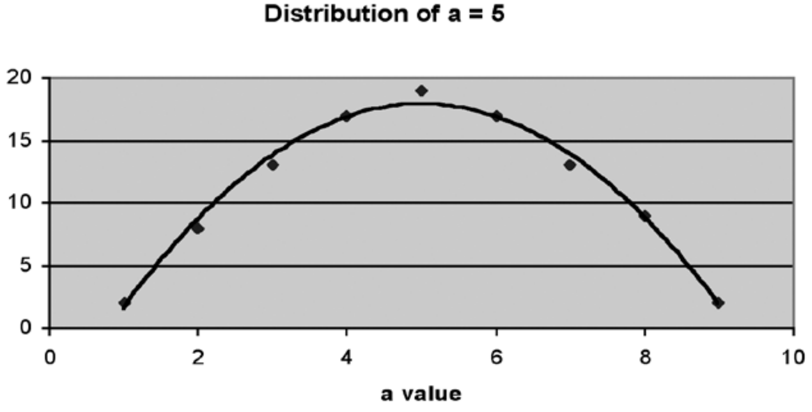
	%		3D HLB	
Product	**EO**	**Alkyl**	**X**	**Y**
J208-212	48	6	9.6	1.2
J208-412	39	13	7.8	2.6
J208-612	28	22	5.6	4.4
J208-812	16	32	3.2	6.4

Table 8.2. Solubility of Silicone Emulsifiers

	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%
J208-212	S	S	S	S	I	I	D	D	S	S	D	D	D	D
J208-412	D	D	S	S	D	D	D	D	S	S	D	D	D	D
J208-612	I	I	S	S	S	S	S	D	S	S	D	D	D	D
J208-812	I	I	S	S	S	S	S	S	S	S	S	S	D	D

An important concept to understand is that silicone polymers, like all polymers, are made up of oligomers. That is there is not one molecular structure, but a range of structures. Unlike simple compounds such as NaCl that have a very clear molecular weight arrived at by simply adding the molecular weight of the Na and Cl, polymers have a range of molecular weights. The values of a b and c are ranges. Typical values are shown in **Figure 8.11**.

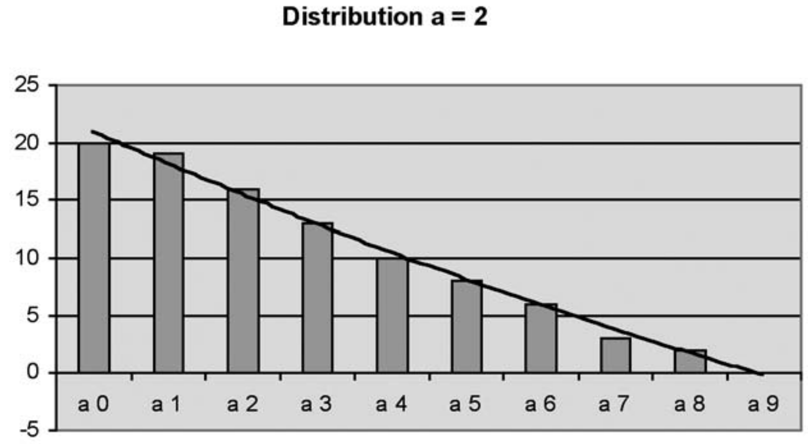
Figure 8.11. Oligomer Distribution



The classical bell-shaped curve for distribution reveals that the range of a value is from 1 to 9 with a maximum at 5.

One must be very careful when using materials with very low values. The lowest value obtainable for a subscript is zero, since there simply is no physical reality to a negative subscript. The distribution is shown in **Figure 8.12**. The difficulty with this type of distribution is there is a considerable amount of material in which a is 0. This can cause major problems with separation of the product, since those materials with zero subscript may well not be soluble in the rest of the composition and form a distinct layer upon exposure to cold. It is important to use emulsifiers that are not homogeneous.

Figure 8.12. Oligomer Distribution



Petrolatum Emulsions

Petrolatum emulsions are of interest in many areas. They have outstanding feel on the skin.

Effects of Varying Ratios of Petrolatum to Water

By varying the ratio of petrolatum to water and using one emulsifier, products with very different properties emerge. The technology can be expanded to cover many other oils including the iso-alkanes and esters. **Table 8.3** shows the effect and results.

Effects of Varying Emulsifier

The study was repeated, only this time to investigate the effect of the other silicone surfactants. The results are shown in **Table 8.4**.

Effects of Varying Oil

The study was repeated, only this time to investigate the effect of the other oil phases. The results are shown in **Table 8.5**. A number of invert emulsions were obtained.

Table 8.3. Petrolatum Emulsions
Effects of Varying Ratios of Petrolatum to Water

Material	**A** **% wt**	**B** **% wt**	**C** **% wt**
Polysurf 67 CS	0.50	0.75	0.25
Tetrasodium EDTA	0.40	0.40	0.40
Water	48.90	70.65	25.00
Propylene glycol	2.00	2.00	—
J208-612	4.00	4.00	4.00
Petrolatum	44.00	22.00	70.15
Propylparaben	0.20	0.20	0.20
	100.00	100.00	100.00

Results:

A is a very heavy lotion, with an outstanding skin feel w/o.
B is a thin lotion with a cooling effect on the skin o/w.
C is a heavy cream with the texture and feel of petrolatum w/o.

Table 8.4. Petrolatum Emulsions
Effects of Varying Emulsifier

Material	**A**	**D**	**E**	**F**
Polysurf 67 CS	0.50	0.50	0.50	0.50
Tetrasodium EDTA	0.40	0.40	0.40	0.40
Water	48.90	48.90	48.90	48.90
Propylene glycol	2.00	2.00	2.00	2.00
J208-612	4.00	—	—	—
J208-412	—	4.00	—	—
J208-212	—	—	4.00	—
J208-812	—	—	—	4.00
Petrolatum	44.00	44.00	44.00	44.00
Propylparaben	0.20	0.20	0.20	0.20
	100.00	100.00	100.00	100.00

cont.

Table 8.4. Petrolatum Emulsions
Effects of Varying Emulsifier cont.

Results:

The emulsions made with J208-612, J208-412 and J208-212 all gave good emulsions. The J208-812 formed a very grainy looking product with visible flecks of petrolatum. Consequently, it appears that the higher HLB material is not suitable to forming good emulsions with petrolatum.

Since the water and petrolatum ration are close to equal the nature of the emulsion (invert or regular) is effected by choice of emulsifier. Clearly, the product made with J208-612 is an invert emulsion, and the product made with J208-212 is a regular emulsion. The product made with the J208-412 has some properties of both.

Table 8.5. Effects of Varying Oil

	1	2	3	4	5	6	7	8	9
Polysurf 67 CS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Water	49.5	49.5	49.5	49.5	49.5	49.5	49.5	49.5	49.5
Propylene glycol	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
J208-612	4.0	2.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Isopropyl palmitate	44.0	46.0	—	—	—	—	22.0	—	11.0
Octyldodecyl neopentanoate	—	—	44.0	—	—	—	22.0	—	33.0
C12-15 Alcohol benzoate	—	—	—	44.0	—	—	—	—	—
Mineral oil	—	—	—	—	44.0	—	—	—	—
Hexamethyl disiloxane	—	—	—	—	—	44.0	—	—	—
Canola oil	—	—	—	—	—	—	—	44.0	—
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Results

1 Lotion
2 Thin Watery
3 Thick Cream
4 Thick Cream
5 Thick Cream
6 Thin Watery
7 Lotion
8 Cream
9 Cream

Two oil Emulsion

Mineral oil and silicone fluid are not soluble in each other, but emulsions can be made from the two using lauryl PEG-8 dimethicone h J-208-612 can be used to make a two immiscible oil emulsion. **Table 8.6** shows the results and formulation.

Table 8.6. Two Oil Emulsions

Material	Phase	% wt
Water	A	60.0
Mineral oil	B	25.0
F-350 Silicone fluid	B	10.0
J208-612	B	5.0

Procedure

1. Heat water to 65°C
2. Combine all ingredients of Phase B in a beaker.
3. Heat Phase B to 65oC, add Phase B to Phase A
4. Cool
5. Siverson 2 min at 5,000 RPM

Remarks

O/W Emulsion thick, good stability and produces a waterproof film.

3D Partition Coefficient

Every student of organic chemistry has worked with partition coefficient. When a separation is run using ether and water, a separation based upon partition coefficient results. Partition coefficient is a measure of the amount of a compound that ends up in each of two insoluble phases after separation. While it is quite true, likes dissolve likes, the reality is that no compound stays entirely in one phase or another.

The term partition coefficient or (distribution coefficient) is a numerical value that relates to the amount of a compound that partitions in one phase or the other. The partition coefficient is a constant. It is defined as the ratio of concentration of compound in aqueous phase to the concentration in an immiscible solvent, as the neutral molecule. **Table 8.7** shows the calculation.

The partition coefficient relates to the ability of a given molecule to be solubilized in a specific solvent when two insoluble solvents are chosen. This concept repeated many times is the key to HLPC.

Table 8.7. Partition Coefficient

Partition Coefficient, P = [Organic]/[Aqueous]

Where [ ] = concentration

Log P= $\log_{10}$ (Partition Coefficient)

NOTE:

Log P = 1 means 10:1 Organic:Aqueous

Log P = 0 means 1:1 Organic:Aqueous

Log P = -1 means 1:10 Organic:Aqueous

Understanding that silicone, oil and water are three mutually immiscible phases, a given molecule will partition to some extent in each of the three, depending upon its composition and orientation in that solvent.

If one now considers a molecule that has a silicone portion, a water-soluble portion and an oil-soluble portion, it will become clear that the so-called "3D partition coefficient" will become interesting. The current practice of the 3D partition coefficient relates to a separation in three phases: mineral oil, water and F-350 silicone fluid. The results are three numbers: the percentage found in the aqueous phase is the first number, the percentage found in the oil phase is the second number and the final number is the percentage found in the silicone phase. 3D partition coefficients then will be 0.3 : 0.5 : 0.2.

The 3D partition coefficient concept not only applies to compounds that have silicone in the molecule, but also organic compounds that have solubility in silicone. Most interestingly, are Guerbet esters, which because of their branching patterns have full solubility in cyclomethicone and partition into silicone fluid. This concept offers to the formulator a numerical method of selecting components for specific phases in their products.

Extraction Technology

A number of techniques are known to those skilled in the art for extracting water-soluble actives. In organic chemistry, extraction is a well-known technique for separating chemical constituents. It is a process by which a solute is extracted from a first solvent into a second solvent, where the two solvents are immiscible. One common extraction methodology used in organic chemistry involves combining in a separatory funnel water and diethyl ether. As is well-known to those skilled in this art, ether and water do not mix; without agitation, they rapidly separate into two phases or layers. For example, hot water extraction removes water-soluble materials, leaving behind oil-soluble materials as well as materials that are insoluble either in water or oil. Tinctures, produced by using hydro-alcoholic solutions, are another extraction vehicle well-known to skilled artisans. Inclusion of alcohol alters the polarity of water, producing different and marginally more efficient (e.g., higher-yield) extracts than water or alcohol alone. Propylene glycol is yet another commonly used vehicle to extract water-and alcohol-soluble materials. Although generally recognized as safe by the U.S. Food and Drug Administration, certain consumer groups have raised health concerns regarding short and long-term health consequences about use of propylene glycolperse, attempting to implicate its use with conditions ranging from skin irritation and sensitization to potential reproductive and development toxicity.

A process has recently been developed for the extraction of actives from botanical materials using a series of silicone compounds having different partition coefficients. The different partition coefficients are obtained by varying the ratio of silicone-soluble, water-soluble, oil-soluble and fluoro-soluble groups on the silicone polymer. The phrase "partition coefficient" is understood to mean the equilibrium distribution of the solute between the two immiscible solvent phases. When an organic compound is placed into a solvent mixture of ether and water, it separates, or partitions, into the water and ether phases. At equilibrium, the ratio of the concentrations of the organic solute in each of the solvent layers is its partition coefficient. As is well-known to those of skill in the art, extracting a compound with an ether/water partition coefficient of 80 will result in 80% extraction of the material during each separation procedure.

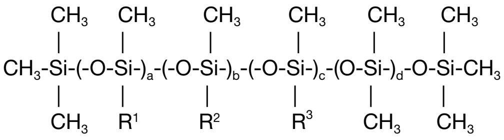
It is also well-known to those of skill in the art that extraction procedures of the type described above are, by their very nature, inefficient, e.g. in terms of maximizing the yield of a desired organic component. In the example of a 1,000 mg sample of botanical material having an ether/water partition coefficient of 80, after a first pass in a separatory funnel, 800 mg of the botanical will be extracted into the ether phase. In order to recover still more botanical material from the remaining 200 mg (e.g., in the water phase), the separation procedure is repeated, each time with fresh ether solvent. The second pass, for example, is expected to remove 140 additional mg, or 80% of the ether-soluble botanical components. However, even with multiple repetitions, some percentage of botanical extract eludes extraction. Thus, there has been and remains a long-felt need to more efficiently and specifically extract actives from botanical materials.

In biochemical applications, partition coefficients are often expressed in terms of an octanol/water coefficient ($K_{o/w}$)—the ratio at equilibrium of the concentration of a nonionized organic compound in an organic solvent (e.g., octanol) versus the concentration of the compound water. $K_{o/w}$ has been correlated with lipophilicity, the affinity of a compound for a lipophilic environment. Compounds having $K_{o/w}$ of greater than one are lipophilic; those below one are hydrophilic. $K_{o/w}$ thus provides an important predictive measure of the ability of a compound to pass through the acid mantle and permeate the lipophilic membranes of cells of the epidermis and dermis. Polar (i.e., hydrophilic) materials extract a different, but also highly-desirable class of compounds from botanical materials. The ability to extract a variety of actives (i.e., both lipophilic and hydrophilic) over a wide range of polarities has heretofore been unattainable.

The silicone polymers based on partition coefficient technology allow for customizing a menstruum to extract not only more materials but also narrower ranges of materials than heretofore has been possible. This specificity offers a number of advantages over the prior art: First, by varying the ratio of silicone-soluble to oil-soluble to water-soluble to fluoro-soluble portions in the molecule (and in so doing creating a series of polymeric materials of differing partition coefficients), many different fractions can be extracted from the same starting plant material. Second, the resulting extracts can each be evaluated for their effects on reducing the signs of biological and/or or photo aging (e.g., appearance of fine lines and wrinkles) as well as analgesic, anti-inflammatory, free radical scavenging, antimicrobial and other desired functional. Based on a range-finding series of silicone polymer extraction vehicles, further refinements can be made to the polymers to maximize the concentration of and/or further isolate compounds of interest. Indeed, many compounds extracted by using the processes of the present invention may have been unavailable. Yet another advantage of the present invention is in terms of environmental stewardship; because extraction of desired actives is more efficient, smaller quantities of plant materials need to be harvested.

The extracting compounds conform to the structure shown in **Figure 8.13**.

Figure 8.13. Silicone Extraction Compounds



$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}(\text{-}O\text{-}\overset{CH_3}{\underset{R^1}{Si}}\text{-})_a\text{-}(\text{-}O\text{-}\overset{CH_3}{\underset{R^2}{Si}}\text{-})_b\text{-}(\text{-}O\text{-}\overset{CH_3}{\underset{R^3}{Si}}\text{-})_c\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_d\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3$$

Wherein:

R^1 is $–(CH_2CH_2O)_e\text{-}(CH_2CH(CH_3)O)_f\text{-}(CH_2CH_2O)_gH$;

R^2 is $–(CH_2)_h\text{-}CH_3$;

R^3 is $\text{-}(CH_2)_2\text{-}(CF_2)_iCF_3$;

a is an integer ranging from 0–20;

b is an integer ranging from 0–20;

c is n integer ranging from 0–20;

d is an integer ranging from 0–200;

e is an integer ranging from 0–20;

f is an integer ranging from 0–20;

g is an integer ranging from 0–20;

h is an integer ranging from 0–35;

i is an integer ranging from 0–9.

The improved extraction efficiencies achieved by using silicone polymer menstrua of the present invention are further illustrated based on extracts of broccoli sprouts, a class of materials that have been reported by researchers at Johns Hopkins University to be effective in protecting against ultraviolet radiation induced skin damage, including cancer. One constituent of particular interest in broccoli sprouts is sulforaphane ($C_6H_{11}NOS_2$), a breakdown product of glucosinolate glucoraphanin. Sulforaphane is also an isothiocyanate, more particularly 4-methylsulfinylbutyl isothiocyanate and (-)-1-isothiocyanato-4(R)-(methylsulfinyl) butane. As discussed below, four silicone polymer menstrua extract four different active fractions with four different FTIR spectra. Spectral subtraction of the menstrua allows identification of groups present in the extracted materials. Menstrua based on partition coefficient technology of the present invention allow for the rapid screening and effective extraction of this class of materials from broccoli sprouts as well as other cruciferous materials.

The silicone menstruum having alkyl-soluble groups extracts 3% of actives. Based on FTIR spectral subtractions are ester, unsaturation, some amine groups and some ketones. The extract changes in color from water-white to pale yellow. The skin feel of the product is quite cosmetically elegant, providing a smooth feel with outstanding glide and spread. The extract of this example can be used as is (i.e., in the menstruum without further modification) as well as in a topical emulsion system by methods known to those in the art.

This menstruum from the silicone-soluble groups extracts 0.9% of the plant material. The functional groups present on the FTIR after spectral subtraction are primarily alcohol and ketones. The extract has no color change. The skin feel is cosmetically appealing, providing a dry powdery feel with outstanding spread. The extract can be used as is or put into topical emulsion systems using methods known to those skilled in the art. This fraction, unlike the starting material, has distinct UV spectra. The extract of this example can be used as is (i.e., in the menstruum without further modification) as well as in a topical emulsion system by methods known to those in the art.

This menstruum, rich in water-soluble groups, is the most effective of the four examples in extracting material; 7% by weight is extracted. The functional groups present on the FTIR after spectral subtraction are alcohols, some esters, a large amount of unsaturation, and some ketones. The extract changes in color from water-white to an intense yellow. The skin feel of the product is cosmetically appealing, providing a smooth feel with outstanding glide and spread. The extract can be used as is or put into water. This extract has a noticeable sulfur smell, which may be an indication of sulforaphane being present.

This menstruum, rich in fluoro-soluble groups, extracts 1.2% of the plant material. The functional groups present on the FTIR after spectral subtraction are ester, and unsaturation. The extract changes in color from a water-white to pale yellow. The skin feel of the product is quite cosmetically appealing, providing a smooth feel with outstanding spread and waterproofing properties.

Patents

(1–3) Early US Patents disclosing how to make alkyl dimethicone copolyols go back to 1956 and include:

- US Patent 2,846,458
- US Patent 3,234,252
- US Patent 3,427,271

(4) US Patent 4,268,499, to Keil issued May 19, 1981, titled Antiperspirant emulsion compositions discloses antiperspirant emulsion compositions are described which comprise an aqueous solution of an astringent agent, a volatile, water-insoluble liquid, a polydiorganosiloxane-polyoxyalkylene copolymer, an oil-in-water type surfactant and a water-in-oil type surfactant. A preferred embodiment comprises an emulsion of aqueous aluminum chlorhydrate in cyclopolydimethylsiloxanes as the volatile fluid. These compositions have improved efficacy as measured by their drying times.

(5) US Patent 4,381,241 to Romenesko et al. issued April 26, 1983, titled Invert emulsions for well-drilling comprising a polydiorganosiloxane and method therefore teaches invert emulsions used on oil drilling.

(6) US Patent 4,698,178, to Huttinger et al. issued Oct. 6, 1987, titled Use of polyoxyalkylene-polysiloxane copolymers with silicon-linked, long-chain alkyl radicals as emulsifiers for the preparation of water/oil emulsions teaches the use of copolymers, as emulsifiers for the preparation of W/O emulsions, whose oily phase consists of or contains silicone oil.

(7) US Patent 6,737,048 to Abend issued May 18, 2004, titled Antiperspirant formulations discloses structured antiperspirant emulsion formulations for topical application to human skin in a cosmetic method for controlling sweat and body odor generation can suffer from problems of impaired sensory properties and impaired efficacy (sweat reduction), which are ameliorated or overcome in structured antiperspirant emulsions in which (%s by weight of the emulsion) a.) the hydrophilic phase comprises 25 to 55%; b.) the hydrophilic phase contains 0 to 15% polyhydric alcohol; c.) the emulsifier comprises an alkyl dimethicone copolyol; d.) the weight ratio of the hydrophilic phase to the emulsifier is selected in the range of at least 60:1 e.) the structurant comprises an acylated sugar and f.) the water-immiscible oil and the structurant are present in a weight ratio of 1.5:1 to 8.5:1.

(8) US Patent 6,967,024 to Scancarella et al. issued Nov. 22, 2005, titled Long wearing composition for making up eyes, skin and lips discloses a composition for making up the eyes and skin comprised of a liquid carrier containing at least one film-forming polymer, and dispersed therein at least one organic pigment forming the main color component of the composition. As well as a method for improving the wear of cosmetic compositions for making up eyes and skin comprising formulating said products with one or more organic pigments in an amount sufficient to improve the wear of the cosmetic composition.

(9) US Patent No. 7,083,800 to Tren et al. issued Aug. 1, 2006, titled Use of a silicone surfactant of alkyl-dimethicone copolyol type for preparing solid water-in-oil cosmetic emulsions and resulting solid water-in-oil emulsions discloses the preparation of a solid water-in-oil emulsion comprising an aqueous phase emulsified by the said surfactant in a fatty phase comprising at least one oil and at least one wax.

Conclusion

Silicone compounds that are organofunctional are amphiphilic surface active materials that offer the formulator opportunities to provide improved properties to formulations. The proper selection will include such variables as solubility, surface tension reduction and desired effect. The formulator is encouraged to look at the physical chemistry of the silicone compound being added to insure that the proper material is chosen to get the desired effect.

References:

1. AJ O'Lenick and JK Parkinson, 3D HLB, *CosmetToilet* 111(10) 37 (1996)
2. AJ O'Lenick and JK, Application of 3D HLB, *CosmetToilet* 112(11) 59 (1997)

Chapter 9

Fluoro Dimethicone

Inclusion of fluoro groups into the silicone backbone results in lower surface tension, increased spreadability and altered solubility when compared to the non-fluoro dimethicone of the same molecular weight. These properties can be very important to the cosmetic formulator. Fluoro dimethicone compounds are very hydrophobic and hence, substantive to skin and hair, and spread out into thin films and, consequently, do not build up.

Surface Tension Reduction

Fluoro compounds are efficient in achieving very low surface tension values compared to silicone surfactants, and are much better than traditional surfactants. **Table 9.1** shows typical surface tension data.

Table 9.1. Surface Tension Values

Surfactant	Surface Tension	Contribution
Standard Surfactants	30 dynes per cm^2	CH_2 contribution
Silicone Surfactants	25 dynes per cm^2	CH_3 contribution
Fluorosilicone Surfactants	20 dynes per cm^2	CH_3 and contribution
Fluoro Surfactants	<20 dynes per cm^2	F contribution

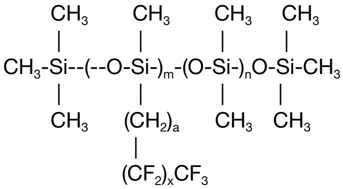
Chemistry

The structure of typical fluoro silicone made by hydrosilylation of a perfluoro vinyl compound is shown in **Figure 9.1**.

The material has both a construction process (**Figure 9.2**) and functionalization step (**Figure 9.3**). In the first step D4 is equilibrated with MM. In the second step perfluoro vinyl compound is hydrosilylated onto the backbone.

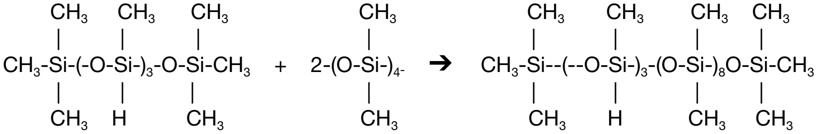
There is considerable latitude in synthesis of fluoro dimethicone compounds. In considering the chemistry of the fluoro dimethicone compounds, one must consider the %F and the number of "D" units present in the molecule. The desired properties are determined by the exact structure. **Table 9.2** outlines the properties obtainable as one alters the ratio of silicone containing portion to the fluoro containing portion.

Figure 9.1. Flurosilicone Compound: Generic Formula



$$CH_3\text{-}Si(CH_3)_2\text{--}(\text{--}O\text{-}Si(CH_3)[(CH_2)_a(CF_2)_xCF_3]\text{-})_m\text{-}(O\text{-}Si(CH_3)_2\text{-})_nO\text{-}Si(CH_3)_2\text{-}CH_3$$

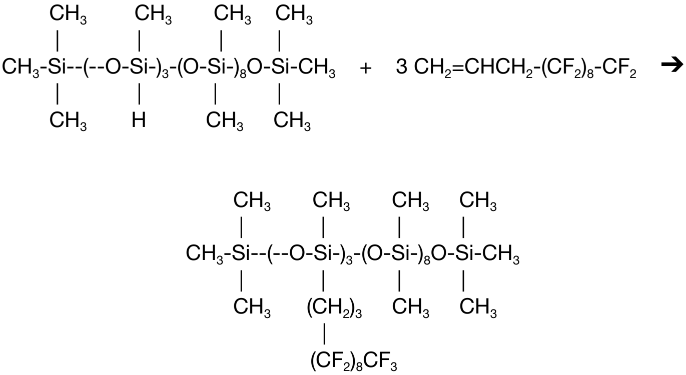
Figure 9.2. Fluorosilicone Compounds: Construction



$$CH_3\text{-}Si(CH_3)_2\text{-}(\text{-}O\text{-}Si(CH_3)(H)\text{-})_3\text{-}O\text{-}Si(CH_3)_2\text{-}CH_3 \; + \; 2\text{-}(O\text{-}Si(CH_3)_2\text{-})_{4\text{-}} \rightarrow CH_3\text{-}Si(CH_3)_2\text{--}(\text{--}O\text{-}Si(CH_3)(H)\text{-})_3\text{-}(O\text{-}Si(CH_3)_2\text{-})_8O\text{-}Si(CH_3)_2\text{-}CH_3$$

MD*M **D4** **MD*3D8M**

Figure 9.3. Silicone Compounds: Functionalization



$$CH_3\text{-}Si(CH_3)_2\text{--}(\text{--}O\text{-}Si(CH_3)(H)\text{-})_3\text{-}(O\text{-}Si(CH_3)_2\text{-})_8O\text{-}Si(CH_3)_2\text{-}CH_3 \; + \; 3\ CH_2{=}CHCH_2\text{-}(CF_2)_8\text{-}CF_2 \rightarrow$$

$$CH_3\text{-}Si(CH_3)_2\text{--}(\text{--}O\text{-}Si(CH_3)[(CH_2)_3(CF_2)_8CF_3]\text{-})_3\text{-}(O\text{-}Si(CH_3)_2\text{-})_8O\text{-}Si(CH_3)_2\text{-}CH_3$$

Table 9.2. Fluorosilicone Properties

Group	Value	Property
Fluoro groups	m	Spreadability and film thickness
Silicone groups	n	Viscosity and play time
Fluoro in each F group	x	Surface tension

Products of this type have CAS number 259725-95-6, EINECS designation Polymer Exempt, and have an INCI Name of Perfluorononyl Dimethicone. The incorporation of fluorine into the silicone backbone results in altered viscosity, altered spreadability and altered solubility. The specific alterations are dependent upon the actual structure.

There are two classes of materials used in the personal care market. The first class consists of those in which the total fluoro content is 5% or below (low fluoro). The second class consists of those fluorosilicone compounds in which the fluoro content is above 5%, typically above 10% (high fluoro).

Low Fluoro Compounds[1]

The low fluoro dimethicone compounds are used in applications where they act as feel modifiers and spreaders. The physical properties of this class of fluorosilicone compounds are shown in **Table 9.3**.

Table 9.3. Low Fluoro Content Silicones
Physical Properties of Fluoro Dimethicone

Trade Name	% F (Weight)	Viscosity		Nominal MW
FSL-150	1.5	1@60	51	5,200
FSH-300	3.0	1@60	60.5	5,200
FSH-150	1.5	1@12	277.5	14,200
FSH-300	3.0	1@12	267.5	14,200
FSU-150	1.5	4@60	9,800	125,200
FSU-300	3.0	4@60	7,750	125,200

Aesthetics

(1–3% F Containing Fluoro dimethicone)

Fluoro dimethicone (FSL and FSH specifically) has a lighter, more lubricious, satiny skin feel compared to the linear polydimethylsiloxane of the same viscosity. The fluoro dimethicone FSU has a high viscosity and leaves a heavy skin feel with a drag and tackiness similar to polybutene.

Gellation of Fluoro-dimethicone

(1–3% F Containing Fluoro dimethicone)

Fluoro dimethicone can be gelled using esters such as behenyl behenate. When the ester is added at 5% by weight to the fluoro dimethicone and heated until dissolved, a homogeneous liquid gel will occur when cooled to ambient temperatures.

Solubility

Fluoro dimethicone, because of the F group, has altered solubility when compared to silicone fluid. For example, fluoro dimethicone compounds are dispersible in mineral oil, while silicone fluids are insoluble and soluble in organic esters. The solubility of compounds tested at 5% by weight are shown in **Table 9.4**.

Table 9.4. Fluorosilicone Solubility

Compounds	FSL-150	FSL-300	FSH-150	FSH-300	FSU-150	FSU-300
Castor Oil	D	D	D	D	D	D
Ethanol	I	I	I	I	I	I
Volatile Silicone	M	M	M	M	M	M
Mineral Oil	D	D	D	D	D	D
Propylene Gylcol	I	I	I	I	I	I
Isopropyl Myristate	M	M	M	M	M	M
Water (*aqua*)	I	I	I	I	I	I
Dimethicone (100 cSt)	M	M	M	M	M	M
Ethylhexyl Ethylhexanoate	M	M	M	M	M	M

D= Dispersible I= Insoluble M= Miscible (soluble at all proportions)

Applications

Fluoro dimethicone are used in a variety of applications listed are shown in **Table 9.5**.

Table 9.5. Applications Properties

Fluoro dimethicone function in skin care as:

- Skin protectants (non-category I)
- Detackifiers for creams and lotions
- Water-repellents
- Skin feel modifiers
- Additives to reduce emulsion soaping
- Epilating agents
- Pore strips
- Improve retention of DEET on skin

Fluoro dimethicone function in hair care as:

- Two-in-one shampoo additives
- Hair laminators to spread the gloss
- Shampoos to improve wet comb

Fluoro dimethicone function in hair care as:

- Lip glosses
- Lipsticks
- Pigment dispersants
- Mascara for spreadability

High Fluoro Compounds

The high fluoro compounds are used in applications where they act as feel modifiers and spreaders. The compounds of this class of fluorosilicone compounds are shown in **Table 9.6**.

The differences in solubility shown in **Table 9.7** result from a variation in structure. A formulator could use these differences to incorporate the silicone into the phase that offers the most benefit.

Fluoro Alkyl Silicones

The incorporation of both fluoro groups and alkyl groups into silicone molecules, results in products in which the benefit of fluoro in terms of spreadability and skin feel is obtained in a solid fluorosilicone wax. The alkyl groups generally have between 18 and 40 carbon atoms, depending upon the desired melt point. These compounds are disclosed in US Patent 5,473,038. They conform to the structure shown in **Figure 9.4**.

Table 9.6. Fluoro Dimethicone (14-35% F containing Fluoro dimethicone)

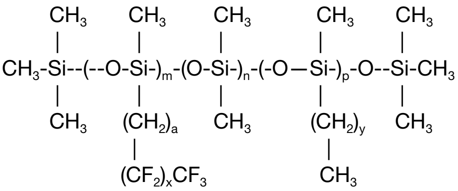
Designation	% F	Nominal MW	Description
A	35	2,000	Low molecular weight, high fluoro content product.
B	32	4,700	Middle molecular weight, high fluoro content product.
C	14	14,000	High molecular weight, lower fluoro content product.

Table 9.7. Solubility (1%/10% Weight)

Product	Water	Mineral Oil	Propylene Glycol	Cyclo Methicone	Silicone Fluid 350 cps	IPA
A	I/I	D/I	S/I	S/S	S/D	S/S
B	I/I	S/S	I/I	S/S	D/D	D/I
C	I/I	I/I	S/I	S/S	S/S	D/D

I =Insoluble D =Dispersible S =Soluble

Figure 9.4. Fluoro Alkyl Silicone Compound: Generic Formula



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{(CH_2)_a(CF_2)_xCF_3}{\overset{CH_3}{Si}}\text{-})_m\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_n\text{-}(\text{-}O\text{—}\underset{(CH_2)_yCH_3}{\overset{CH_3}{Si}}\text{-})_p\text{-}O\text{--}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

There are a vast number of structural changes that can be made to the molecule to affect properties that are of interest to the cosmetic formulator. They include: the variation in the size of the fluoro group (the "m" value), which determines the spreadability and film thickness; the variation of the silicone groups (the "n" value), which determines wax hardness and play time; the amount of fluoro in each F group (the "x" value), which determines surface tension; the number of alkyl groups (the "p" value), which determines wax hardness; and the number of carbon atoms in the alkyl (the "y" value), which determines the melt point of wax.

Table 9.8 shows the possible variations.

Table 9.8. Alkyl Fluoro Silicone Properties

Group	Value	Property
Fluoro Group Thickness	m	Spreadability and film thickness
Silicone Groups	n	Viscosity and play time
Fluoro in each F Group	x	Surface tension
Alkyl Groups	p	Wax hardness
Carbon in Alkyl	y	Melt point of wax

Patents

(1) US Patent 5,473,038 issued Dec. 5, 1995, to O'Lenick, titled "Alkyl fluorinated silicone polymers to a series of novel silicone polymers containing both fluorinated and alkyl side chains." This class of compounds provides very thin breathable barriers which are very durable when applied to textiles and paper. The compounds of the present invention are prepared by reacting a silanic hydrogen containing silicone polymer with a vinyl containing fluoro compound and an alpha olefin.

(2) US Patent 6,280,749 issued August 28, 2001, to Omura, titled "Particles of cured fluorosilicone rubber and cosmetic preparation containing same" discloses is a powder consisting of particles of a cured fluorosilicone rubber having a specified average particle diameter and a specified rubber hardness. The powder is useful as an ingredient in a cosmetic or toiletry preparation to affect improved sustainability of the cosmetic finish and decreased unevenness of coloring on human skin.

(3) US Patent 6,485,731 issued Nov. 26, 2002, to Calello et al., titled "Method for improving integrity of cosmetic films" disclosed a method for improving the integrity of a cosmetic film applied to nails or surrounding cuticle surfaces comprising applying to the surface an effective amount of a composition comprising less than 5% by weight of the total composition of a fluorinated oil, including a fluorosilicone.

(4) US Patent 6,649,173 issued Nov. 18, 2003, to Arnaud, titled "Transfer-free topical composition comprising a fluorinated silicone compound and its use" discloses topical composition, in particular a cosmetic composition, comprising, in a fatty

Patents cont.

phase, at least one wax and/or at least one nonvolatile liquid fatty substance, wherein the fatty phase contains at least one fluorosilicone compound. The composition exhibits good slip, nontightness, softness and/or comfort properties as well as nontransfer and nonmigration properties.

References:

1. Phoenix Chemical Inc. Technical Bulletin *Phenomenon 210*, March 14, 2002
2. Siltech Corporation, Technical Bulletin 26, Jan. 8, 2000

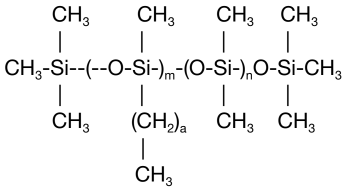
Chapter 10

Alkyl Dimethicone

Alkyl dimethicone compounds are a class of silicones that conform to the structure shown in **Figure 10.1**. **Figures 10.2** and **10.3** show the construction and functionalization of alkyl dimethicone compounds.

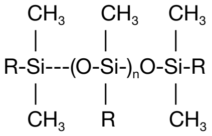
Figure 10.1. Alkyl Dimethicone: Generic Formula

PEG/PPG dimethicone



$$\underset{CH_3}{\overset{CH_3}{CH_3\text{-}Si}}\text{--}(\text{--}O\text{-}\underset{\underset{CH_3}{(CH_2)_a}}{\overset{CH_3}{Si}}\text{-})_m\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_n O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Bis PEG/PPG dimethicone

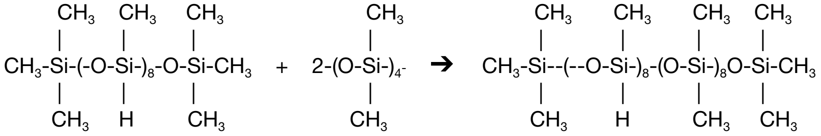


$$R\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{---}(O\text{-}\underset{R}{\overset{CH_3}{Si}}\text{-})_n O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}R$$

R is $-(CH_2)_a-(CH_2)_x-$

FIgure 10.2. Alkyl Dimethicone: Construction

Alkyl Dimethicone

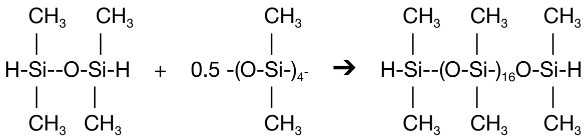


$$\underset{CH_3}{\overset{CH_3}{CH_3\text{-}Si}}\text{-}(\text{-}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_8\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 + 2\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_4\text{-} \rightarrow \underset{CH_3}{\overset{CH_3}{CH_3\text{-}Si}}\text{--}(\text{--}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_8\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8 O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

MD*M **D4** **MD*8D8M** **cont.**

Figure 10.2. Alkyl Dimethicone: Construction cont.

Bis Alkyl Dimethicone

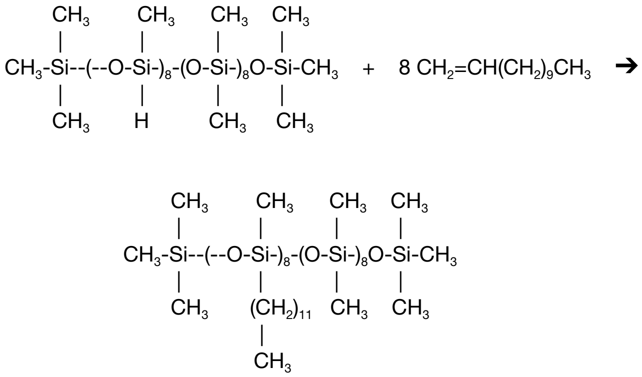


$$H\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{--}O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{-}H \quad + \quad 0.5\ \text{-}(O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{-})_4\text{-} \quad \rightarrow \quad H\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{--}(O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{-})_{16}O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{-}H$$

M*M* **D4** **M*D16M***

Figure 10.3. Alkyl Silicone Compounds: Functionalization

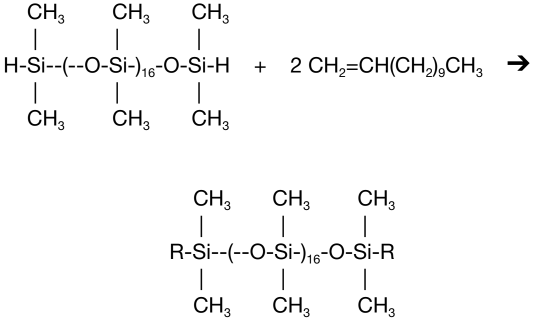
Lauryl Dimethicone



$$CH_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{--}(\text{--}O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{Si}}\text{-})_8\text{-}(O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{-})_8O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{-}CH_3 \quad + \quad 8\ CH_2{=}CH(CH_2)_9CH_3 \quad \rightarrow$$

$$CH_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{--}(\text{--}O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{\underset{\underset{CH_3}{|}}{(CH_2)_{11}}}{|}}{Si}}\text{-})_8\text{-}(O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{-})_8O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{-}CH_3$$

Bis PEG/PPG Dimethicone



$$H\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{--}(\text{--}O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{-})_{16}\text{-}O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{-}H \quad + \quad 2\ CH_2{=}CH(CH_2)_9CH_3 \quad \rightarrow$$

$$R\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{--}(\text{--}O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{-})_{16}\text{-}O\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}\text{-}R$$

R is $(CH_3\text{-}(CH_2)_{12}\text{-}$

Alkyl dimethicone is of interest to cosmetic formulators for two critical reasons: (a) the compounds are soluble inorganic oils and (b) the addition of the compounds to systems in which they are soluble lead to some very important changes to the surface tension and ultimately to the viscosity of the oils to which they are added. In short, alkyl dimethicone offers the formulator some very powerful tools to alter the surface and micelluar properties of oils. Interestingly, these materials are insoluble in water, soluble in mineral oil and insoluble in isopropanol. It only takes a low percentage of alkyl group to obtain mineral oil solubility. However, none are soluble in silicone fluid. This is because the reaction is conducted with a slight excess on alpha olefin, which is insoluble in silicone fluid.

The solubility of alkyl dimethicone is shown in **Table 10.1**.

Table 10.1. Solubility (10% Weight of Alkyl Dimethicone Indicated)

Product	Water	Mineral Oil	PG*	D-5**	Sil Fluid*** 350 Visc	IPA****
D-026 Cerotyl Dimethicone	I	S	I	D	D	I
J-226 Cerotyl Dimethicone	I	S	I	D	D	I
H-418 Stearyl Dimethicone	I	S	I	D	I	I
L-118 Stearyl Dimethicone	I	S	I	I	I	I

* PG is propylene glycol
** D-5 is cyclomethicone
*** Sil Fluid 350 Visc is 350 viscosity silicone fluid
**** IPA is isopropanol

I = insoluble D = dispersible S = soluble

Solubility

As technical people we want to our formulations to be governed by clear, technical rules and to use simple concepts to organize our world. If we organized our world according to simple definitions, we would observe:

- A suspension is a colloidal dispersion in which a finely divided species is combined with another species.
- A solution is a homogeneous mixture composed of one or more substances, known as solutes, dissolved in another substance, known as a solvent, so

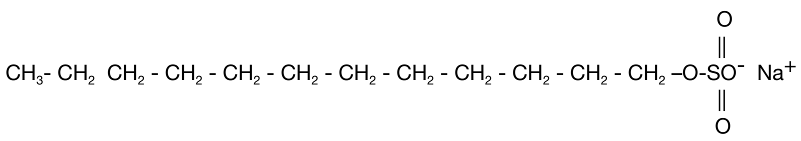
finely divided and mixed that it doesn't rapidly settle out. In everyday life, the most common suspensions are those of solids in liquid water.

- An emulsion is a mixture of two immiscible substances. One substance (the discontinuous phase) is dispersed in the other (the continuous phase).

However, the world of cosmetic chemistry isn't nearly so easy to organize. Consider a fully dissolved 1% solution of sodium chloride in water. This simple system has a sodium ion (Na^+), a chloride ion (Cl^-) and water, roughly equally distributed over the entire mass of the system. The solution is clear and homogeneous.

Now consider a 1% solution of a surfactant. A surfactant or surface active agent has a water-soluble head and a water-insoluble tail. A very well-known surfactant is sodium lauryl sulfate (CAS 151-21-3). Like NaCl, sodium lauryl sulfate has two opposite ions, but sodium lauryl sulfate in water is very different. The presence of a large fatty portion makes the product surface active. The structure of sodium lauryl sulfate is shown in **Figure 10.4**.

**Figure 10.4. Sodium Lauryl Sulfate
A Fatty Amphilic Material**



$$CH_3\text{-}\ CH_2\ \ CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 \text{–}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{SO^-}}\ Na^+$$

A 1% solution of sodium lauryl sulfate, like that of sodium chloride, is clear but not homogeneous. As one adds sodium lauryl sulfate to water, the orientation of the material in the water is driven by achieving the lowest overall free energy; in this case, minimized disrupting of hydrogen bonding in water. The sodium lauryl sulfate organizes itself at the air-water interface and then begins to self-assemble into micelles. **Figure 10.2** shows this[2]. The first box shows pure water, having a surface tension around 72 dynes/ cm^2. As surfactant is added, demonstrated by the second box, surface tension is falling as a dilute surfactant, organizing at the surface. As the surface reaches saturation, a very significant situation develops. The surface tension no longer drops even with additional surfactant. It is at this concentration called critical micelle concentration (CMC) that micelles become the dominant form of surfactant. This situation is shown by the third box in **Figure 10.5**.

Dynamic surface tension is a rather complex situation with a number of equilibrium steps. **Figure 10.6** shows some of them. This type of phenomenon occurs every time we wash our hair, put pigmented products on our skin or simply spread a lotion.

Table 10.2 shows that silicones can be used to reduce surface tension of several materials, making addition of the proper silicone highly desirable.

Figure 10.5. Surfactant Orientation[5]

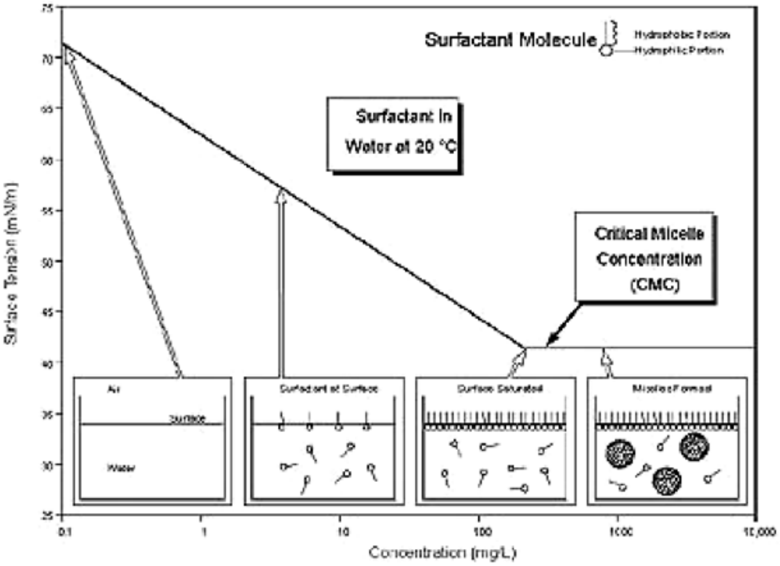


Figure 10.6. Dynamic Surface Tension[5]

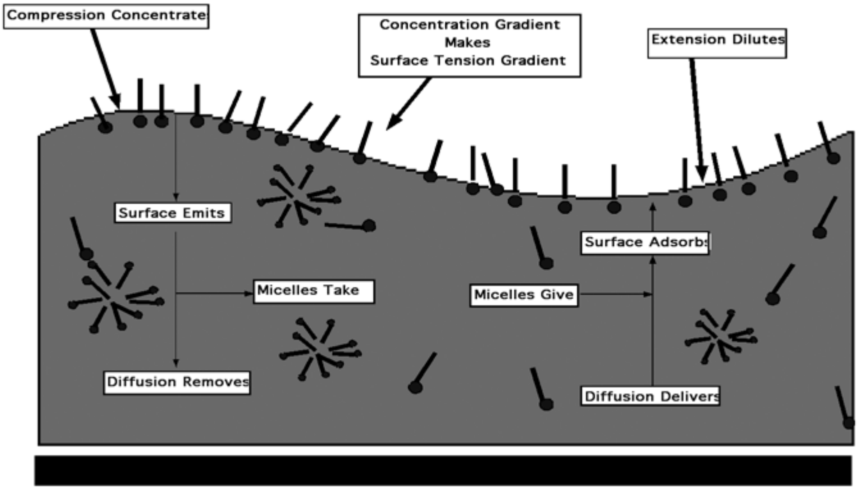


Table 10.2. Reduction of Surface Tension of Oils with Silicone Derivatives

Solvent	Surface Tension (as is) Dynes/cm^2	Silicone Added (0.5% weight)	Surface Tension Dynes/cm^2
Toluene	28.9	C-26 alkyl dimethicone	25.0
2-Butoxy ethanol	29.1	Stearyl dimethicone	22.0
Methanol	23.4	Octyl PEG-8 dimethicone	22.2
Water	72.3	PEG-8 dimethicone	20.1

The concentration of silicone surfactant upon surface tension can be demonstrated with several different oil systems with varying polarity. The surface tension of soybean oil (a relatively polar oil) is reduced from 31.4 to 24.1 by addition of cetyl dimethicone. **Table 10.3** shows the results.

Table 10.3. Concentration Effects on Reduction of Surface Tension of Soybean oil with Alkyl Dimethicone

	Soybean oil (% Weight)	Cetyl Dimethicone (% Weight)	Surface Tension (Dynes/cm^2)
Example 1.1	100%	0%	31.4
Example 1.2	75%	25%	25.5
Example 1.3	50%	50%	24.8
Example 1.4	25%	75%	24.1
Example 1.5	0%	100%	23.6

A similar effect is observed with mineral oil; a much less polar oil. **Table 10.4** shows the results.

The effect of surface tension reduction is not exactly the same as a CMC graph. When CMC is determined, the concentration at which the surface tension stops dropping with added surfactant is the CMC. The term RF_{50} (Reduction Factor 50%) has been defined for each silicone surfactant in each system. The definition is as follows:

RF_{50} = the concentration of silicone surfactant added to reduce the surface tension half of the difference between the fatty surfactant's surface tension and the silicone surfactant's surface tension.

The RF_{50} for cetyl dimethicone in soybean oil is 12.1%.

The RF_{50} for cetyl dimethicone in mineral oil is 24.9%.

The comparison of the two indicates that cetyl dimethicone is more effective at lowering the surface tension of soybean oil than it is at lowering the surface tension of mineral oil. The RF_{50} is half for soybean oil what it is for mineral oil. The most efficient product is the one with the lowest RF_{50}.

The lower the RF_{50} the better able is the silicone surfactant to compete with the fatty surfactant for surface and the more efficient the silicone surfactant will be. This technique allows one to design molecules that will be optimized for a particular formulation. Not only can surfactant systems be evaluated, but complex formulations can also be evaluated, by simply defining the fatty surfactant's surface tension as the formulation's initial surface tension. Not only surface tension, but also foam and the like can be tested and optimized by evaluating foam as the property rather than surface tension.

Table 10.4. Concentration Effects on Reduction of Surface Tension of Mineral Oil with Silicone

	Soybean Oil (% Weight)	Cetyl Dimethicone (% Weight)	Surface Tension (Dynes/cm^2)
Example 2.1	100%	0%	28.3
Example 2.2	75%	25%	26.1
Example 2.3	50%	50%	25.1
Example 2.4	25%	75%	24.5
Example 2.5	0%	100%	23.6

Typical Physical Properties

Typical properties[2] of commercial alkyl dimethicone polymers are shown in **Table 10.5**. As the molecular weight of the alkyl group increases, the melting point increases.

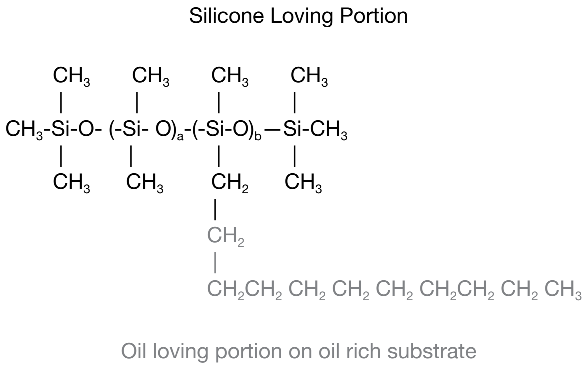
Alkyl Dimethicone Orientation on Surfaces

The way the molecule orientates itself on a specific substrate depends upon the nature of the substrate. If the substrate has a greater affinity for oil than silicone, the orientation will be such that the alkyl group will associate with the substrate, and the silicone portion will repel the substrate, the net effect being that the substrate will be more silicone loving, since it is the silicone portion that is exposed to the outside world. The surface tension will be lower (in the range of 20–25 dynes/cm^2) and the feel will be silicone-like. One example of oil rich substrate is the skin. Alkyl dimethicone polymers of the comb type will orientate themselves as shown in **Figure 10.7**.

Table 10.5. Alkyl Dimethicone Properties

Product	Melting Point (°C)	Molecular Weight	% Alkyl	INCI Designation
Silwax H416	Liquid	4,500	40	Cetyl dimethicone (C-16)
Silwax L118	28–32	4,800	63	Stearyl dimethicone (C18)
Silwax D226	40–44	5,900	62	Cerotyl dimethicone (C-26)

Figure 10.7. Silicone Loving portion of alkyl silicone (Comb Silicone)



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}(\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_a\text{-}(\text{-}\underset{\substack{CH_2\\ CH_2\\ CH_2CH_2\,CH_2\,CH_2\,CH_2\,CH_2CH_2\,CH_2\,CH_3}}{\overset{CH_3}{Si}}\text{-}O)_b\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

A very interesting and often overlooked difference between comb and terminal silicone compounds is their orientation on substrate. Unlike comb silicones, which can rotate freely around the Si-O-Si bonds, the terminal substituted groups cannot, and must therefore assume one of two orientations shown in **Figures 10.8** and **10.9**. The so-called horseshoe orientation occurs primarily on substrate, while the other orientation occurs in emulsions, making lamellar sheets and liquid crystals.

Another interesting and thought-provoking orientation occurs when an alkyl dimethicone polymer is placed on a silicone coated pigment. The application of alkyl dimethicone polymer to coated inorganic pigments such as ZnO results in an orientation that has the oil portion out, increasing the dispersibility in oil. This is shown in **Figure 10.10**.

Figure 10.8. Orientation of Alkyl Silicone Terminal Compounds "Horseshoe Orientation"

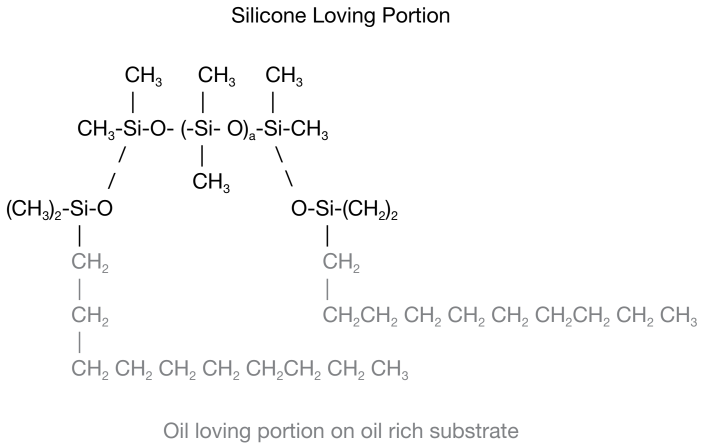


Figure 10.9. Orientation of Alkyl Silicone Terminal Compounds "Interphase Orientation"

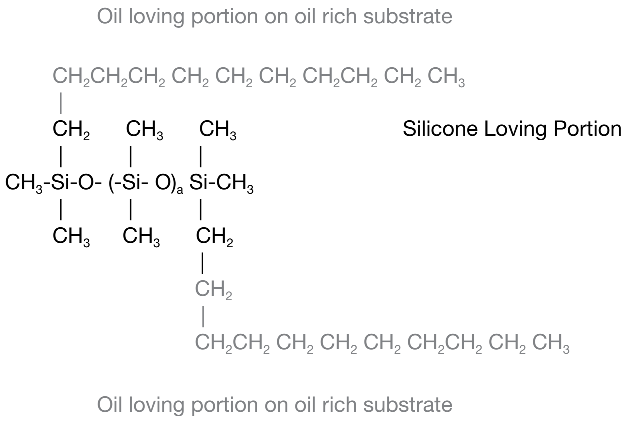
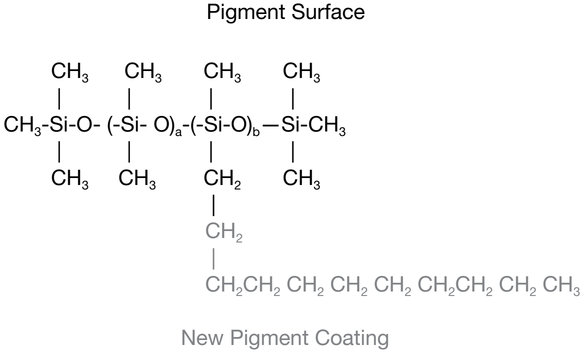


Figure 10.10. Silicone Coated Pigment Treated with Alkyl Silicone (Comb Silicone)



$$\begin{array}{ccccc} & CH_3 & CH_3 & CH_3 & CH_3 \\ & | & | & | & | \\ CH_3\text{-} & Si\text{-}O\text{-} & (\text{-}Si\text{-}O)_a\text{-} & (\text{-}Si\text{-}O)_b\text{—} & Si\text{-}CH_3 \\ & | & | & | & | \\ & CH_3 & CH_3 & CH_2 & CH_3 \\ & & & | & \\ & & & CH_2 & \\ & & & | & \\ & & & CH_2CH_2\,CH_2\,CH_2\,CH_2\,CH_2CH_2\,CH_2\,CH_3 & \end{array}$$

Structure/Function Properties

These compounds are of interest to the cosmetic formulator in products including moisturizers, creams, lotions, antiperspirants and color cosmetics. The challenge is to get the product with the proper attributes for each application. Here again, in order to create a predictive model, one needs to consider both construction and functionalization.

There are two different approaches to studying the properties of alkyl dimethicone polymers. Each results in helpful information for the formulator. One is to keep the construction (silicone backbone) the same and alter functionalization (the number of carbon atoms in the alkyl group). The other approach is to alter the construction (the silicone backbone) and keep the functionalization constant (the number of carbon atoms in the alkyl group).

Alteration of Functionalization (Changes in the Percentage of Alkyl in Molecule)

The changing of the length of the alkyl group in an alkyl dimethicone results in a homologous series of polymers. As the size of the alkyl chain is increased on a given backbone, the weight percentage of alkyl needed to keep the mole ratio correct increases (**Figure 10.11**).

Melt Point

As the carbon number of the alkyl group increases, the melt point increases, as shown in **Figure 10.12**. Alkyl dimethicone compounds having less than 18 carbon atoms in the alkyl chain are liquid at ambient temperatures. Those with more than 18 carbon atoms in their alkyl chain are solids. The higher the number of carbon atoms, the higher the melting point.

Figure 10.11. Alkyl Dimethicone % Alkyl

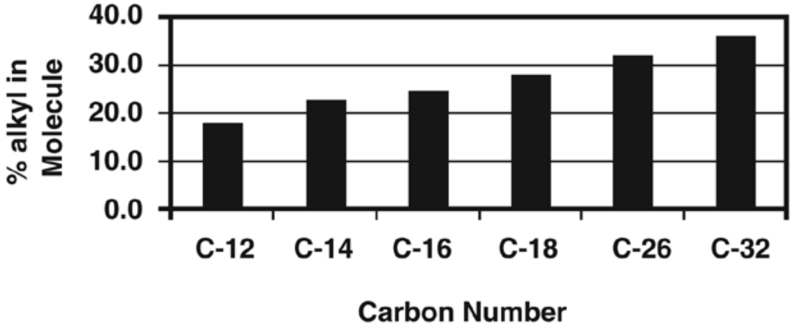
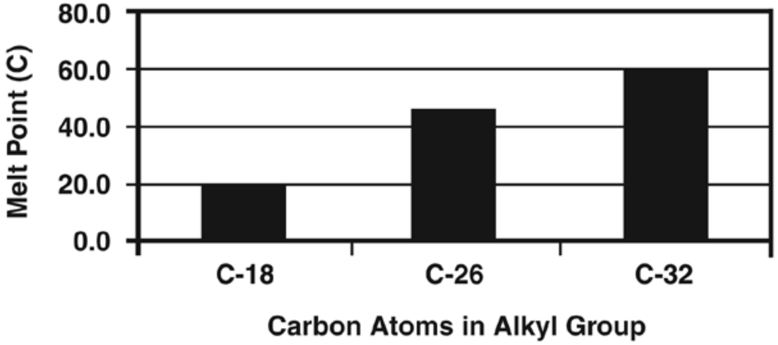


Figure 10.12. Alkyl Dimethicone Melt Point



When there are 18 carbon atoms in the alkyl dimethicone, the melt point is determined by the percentage of alkyl group making up the molecule. **Figure 10.13** shows the differences.

Alteration of Construction (Changes in the Silicone Backbone)

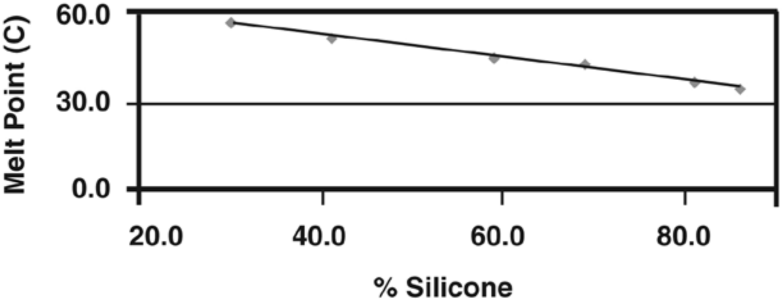
Keeping the alkyl chain at a C-26, the numbers of D units in the backbone is varied. This alteration resulted in a homologous series with the number of D units in the molecule as the variable. As shown in **Figure 10.5**, as the percentage of silicone in the molecule increases, the melt point decreases. This means additional D units lower the melt point. Additionally, the resulting materials are softer as the number of D units increases. **Figure 10.14** shows this.

Figure 10.13. The Melt Point of Stearyl Dimethicone

A= 25% Alkyl B= 48% Alkyl C= 37% Alkyl D= 35% Alkyl

Alkyl silicone compounds having 16 or less carbon atoms in the chain are liquids at ambient temperatute. Those with 20 or more carbon atoms are solids. Those with C18 groups vary in form depending upon the percentage alkyl group in the molecule.

Figure 10.14. Alkyl Dimethicone Melt Point



It will become clear that the number of D units and the size of the alkyl chain can be varied to get the desired melt point and hardness in the compound. The length of the alkyl chain has a dramatic effect upon the melt point of the wax. The amount of silicone in the molecule affects the hardness of the wax, but has a minimal impact on the melting point. **Table 10.6** shows three different C-26 waxes. Despite a wide difference in the percentage of silicone (69% by weight to 86% by weight) the melting points only vary by 6°C. The hardness is quite different however, with the wax having 69% alkyl being a wax hard enough to cut with a knife and the 86% product being soft enough to roll between your fingers. Understanding these trends allows for the selection of a wax for the specific application chosen.

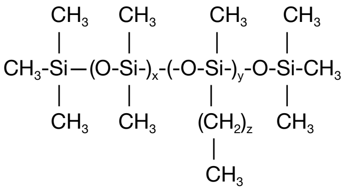
Table 10.6. C-26 Alkyl Silicone

Prod	Alkyl Group	State RT	% Silicone	% Alkyl	MP (°C)	Hardness
D1026	Cerotyl	Solid	69.0	31.0	42.0	Hard
D2026	Cerotyl	Solid	81.0	19.0	37.0	Soft
D3026	Cerotyl	Solid	86.0	14.0	36.0	Soft

Physical Properties

The alkyl dimethicone product so prepared has very interesting solubility. The compounds are insoluble in water and isopropanol. They are soluble in mineral oil, even with low levels of alkyl groups. These products, unlike silicone fluids, can be solids, depending upon the length of the alkyl group (z) or the amount of silicone groups (y). Refer to **Figure 10.15** for the definitions of z and y.

Figure 10.15. Structure Variation Formula Definitions



$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{—}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_x\text{-}(\text{-}O\text{-}\overset{CH_3}{\underset{\substack{(CH_2)_z \\ | \\ CH_3}}{Si}}\text{-})_y\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3$$

In general, the larger the value of z, and the smaller the ration of x/y, the more likely the product will be a paste or solid. Generally, when the value of x/y is less than or equal to one, and the value of z is equal to or greater than 18, the product will be a paste or solid. The greater the value of x/y, the more liquid the product will tend to be. The melt points of these products can be roughly determined using the equation in **Table 10.7**.

Table 10.7. Alkyl Silicone Melt Point Equation

$$\text{Melt point} = (-40.246-2.423) \times A + (4.076) \times B + (0.031) \times A \times A + (0.034)\ (A) \times (B) - (0.018) \times B \times B$$

Where A = ratio of x/y
B = length of alkyl chain

Table 10.8 shows a series of alkyl dimethicone polymers where the value of x/y varies, but the value of z (the alkyl group) remains the same. As can be seen, the melt point decreases as the ratio x/y increases.

Table 10.8. Alkyl Dimethicone Structure / Function

Product	x/y	Length of Alkyl Group	Appearance	Melt Point (°C)
Product 1	2	C26	Hard wax	47
Product 2	6	C26	Hard Wax	45
Product 3	10	C26	Hard wax	43
Product 4	20	C26	Soft Wax	37
Product 5	30	C26	Soft Wax	35

Table 10.9 shows a series of alkyl dimethicone compounds where the value of x/y remains the same, but the value of z (the alkyl group) varies.

As can be seen, as the length of the alkyl group increases, the melt point will increase as well. These properties allow the formulator of pigmented products the ability to modify the ratio of oil to silicone present in the molecule, the melt point of the molecule, the softness of the molecule and still maintain the ability to place the molecule in an oil phase. The viscosity and melt point of the oil will have a dramatic impact upon the feel of the product. The play time, drag and pay off all can be altered by picking a different alkyl dimethicone.

Understanding these trends allows 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 (b) adding differing amounts of silicone to the molecule (hardness).

Table 10.9. Alkyl Dimethicone Structure / Function

Product	x/y	Length of Alkyl Group	Appearance	Melt Point (°C)
Product 6	10	C16	Liquid	Liquid
Product 7	10	C18	Liquid	Liquid
Product 8	10	C22	Gel at RT	20
Product 9	10	C26	Soft Wax	46
Product 10	10	C32	Hard Wax	60

Silicone waxes also have an effect upon the ability of an oil to spread on the skin making them of interest in serum formulations. Those products based upon oils need to spread easily and efficiently on the skin. It is this very same ability to cause oils to spread that makes these materials invaluable aides to the formulation of pigmented products. These materials facilitate the thorough and efficient wetting of pigment coating, resulting in a uniform grinding and a stable emulsion. The ability of these versatile materials to function in the formulation of pigmented products is only now being realized and has not been utilized to the technology's potential.

Alteration of Properties

The addition of 10% stearyl dimethicone to several known esters has an impact on properties. The following four examples are typical of what can be attained with this technology. Two different compounds, both with an INCI name stearyl dimethicone were chosen. One has a high % alkyl group (more D than D*) the other was chosen for its high silicone content (more D*/D).

Ester 1—Poly Glyceryl (6) octa-ricinoleate

The first ester chosen for evaluation was a tacky very substantive ester. The resulting changes in properties after adding 10% of two different stearyl dimethicone compounds were as follows:

Poly Glyceryl (6) octa-ricinoleate	Tacky substantive lipstick ester	Amber liquid
Plus High % Silicone Stearyl Dimethicone	Viscosity increases Reduces tack	Amber slurry
Plus High % alkyl Stearyl Dimethicone	Viscosity increases	Amber gel

In this case the stearyl dimethicone with the high level of silicone was effective in lowering the surface tension, improving spreadability and reducing tack. A gel was also achieved. The high % alkyl product merely increased the viscosity.

Ester 2—Ethylhexyl isononanate

Ethylhexyl isononanate is a highly branched and very dry ester. The resulting changes in properties after adding 10% of two different stearyl dimethicone compounds were as follows:

Ethylhexyl isononanate	Very dry ester	Clear liquid
Plus High % Silicone Stearyl Dimethicone	Improved spread	Clear slush
Plus High % alkyl Stearyl Dimethicone	Great skin feel (Massage Oil)	Clear gel

In this case the stearyl dimethicone with the high level of silicone was effective in lowering the surface tension, making a slush. A clear gel was obtained with the high % alkyl product.

Ester 3—Isostearyl Behenate

The third ester was an isostearyl behenate paste. The resulting changes in properties after adding 10% of two different stearyl dimethicone compounds were as follows:

Isostearyl behenate	Emollient ester	Paste
Plus High % Silicone Stearyl Dimethicone	Improved skin feel	Paste
Plus High % alkyl Stearyl Dimethicone	Reduced melting point	Soft Paste

In this case the stearyl dimethicone with the high level of silicone was effective in lowering the surface tension, improving spreadability. The high % alkyl product reduced the melting point, assumedly by interfering with the formation of the solid network.

Ester 4—Trimethyolpropane Triisostearate

The last and perhaps the most interesting ester was trimethyolpropane triisostearate. The resulting changes in properties after adding 10% of two different stearyl dimethicone compounds were as follows:

Trimethyolpropane triisostearate	Emollient ester	Clear liquid
Plus High % Silicone Stearyl Dimethicone	Increased TEWL	Clear gel
Plus High % alkyl Stearyl Dimethicone	Reduced TEWL	Clear gel

In this case the stearyl dimethicone with the high level of silicone was effective in increasing transepidermal water loss. The solution on the skin acted more like a silicone than the starting ester, allowing more water to pass. The high % alkyl product did the opposite, making the solution more resistant to transepidermal water loss.

The ability to use alkyl dimethicone to alter the properties of oils in anhydrous systems, alcoholic systems and in emulsions is a major reason to consider the use of these materials in cosmetic products.

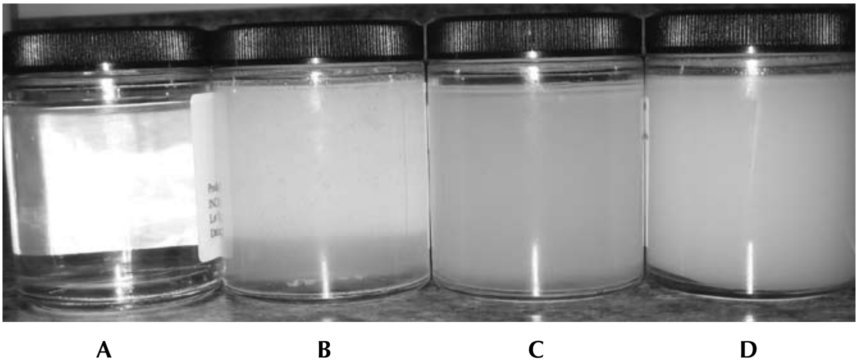
Gelling Esters

Because alkyl dimethicone polymers are amphilic materials in oils, they are soluble; but at low concentrations reduce surface tension from 32 dynes/cm^2 to 22 dynes/cm^2. As the concentration reaches the CMC (critical micelle concentration) the viscosity of the oil increases. As the concentration continues to be increased, a gellation occurs. This gellification of esters is a very interesting property that is the topic of several pending patents. The optimum ester needed to gel a specific oil needs to be determined. The gellification using alkyl silicones is temperature-dependent allowing the remelting and recasting of the thickened oil. This is in stark contrast to resin thickened oils, which do not melt.

Thickened esters are used in skin care and sun care products where there is a desire to control spread time, cushion and play time.

An example of this gel formation is shown in **Figure 10.16**. Stearyl dimethicone added in increasing concentration to pentaeryrthril penta caprate/caprylate (sample A) causes this dry ester to have greater spread and cushion at 0.5% (sample B), form a soft gel at 3% (sample C) and a form a hard gel at 5% (Sample D).

Figure 10.16. Gellation of Esters



Stearyl dimethicone added in increasing concentration to pentaeryrthril penta caprate/caprylate (sample A) causes this dry ester to have greater spread and cushion at 0.5% (sample B), form a soft gel at 3% (sample C), and a form a hard gel at 5% (Sample D).

The melt point, hardness, cushion, play time and cosmetic feel are determined by the percent alkyl, the D to D* ratio and the exact interactions between the oil and the alkyl silicone. Clarity can be achieved by matching refractive index.

Gelling Triglycerides

The reduction in surface tension, followed by gellation as the concentration of alkyl silicone is increased in a triglyceride occurs in exactly the same manner as it does for esters. The gellation of esters has been used in sun care and skin products because of the ability to control cosmetic elegance. The products also can be used in emulsions, both invert (w/o) and regular (o/w), to improve the cosmetic properties of the oil, giving a feel more similar to silicone.

SPF Enhancement

Alkyl silicones have been used to improve wash-off resistance in sun care products3. In fact, a study[4] came to the following conclusion: "Certain alkyl silicones act on the rheology of sun care formations, increasing the thixotropy, resulting in these particular formulations having a higher in vivo SPF. Alkyl silicones with a melting point close to the skin temperature give the best results. These alkyl silicones also appear to form an intimate blend with sunscreen actives as identified by microscopic observation."

This study certainly suggests that the alkyl silicone gives positive effects upon formulation; when optimized, the effects of different additives on the SPF of a nominal 15 SPF formulation were evaluated by substituting out different silicone compounds. It is an invert emulsion.

Table 10.10 shows the formulation used in the evaluation.

Table 10.11 shows the results. Selection of the proper alkyl or aromatic silicone has a dramatic effect upon SPF.

Table 10.10. Sunscreen Formula

Material	%
Polysurf 67 CF	0.50
Water (*aqua*)	49.50
PG	2.00
EDTA	0.40
Silsurf J-208-612	5.00
Sunscreen Combination	18.50
Spider ESO	13.50

cont.

Table 10.10. Sunscreen Formula cont.

Material	%
Test Silicone	10.00
Propyl paraben	0.20
Methyl Paraben	0.40
Total	100.00

Table 10.11. Effects of added Alkyl Dimethicone to SPF

	Description	SPF	UVA Ratio	Wave
Sample 1	Low Aromatic Terminal Dimethicone	17.39	0.49	361
Sample 2	Cetyl Dimethicone (Low Viscosity)	18.68	0.43	359
Sample 3	Cetyl Dimethicone (Higher Viscosity)	19.02	0.44	360
Sample 4	Aromatic Dimethicone Terminal	18.73	0.47	361
Sample 5	Aromatic /Aliphatic Dimethicone (Comb)	19.17	0.44	359
Sample 6	All Aromatic dimethicone (Comb)	20.41	0.43	360
Sample 7	All Aromatic High % Dimethicone comb	20.64	0.45	358
Sample 8	High Aromatic Terminal dimethicone	25.25	0.52	359

Patents

The patent literature related to alkyl dimethicone polymers used in personal care is somewhat limited both in terms of patent number and the length of time alkyl dimethicone compounds have been a topic in patents. The oldest patent was issued in 1986.

(1) US Patent 4,574,082 issued March 4, 1986, to Tietjen et al., titled "One-phase silicone-based cosmetic products containing wax" discloses cosmetic products which do not suffer phase separation, comprise a mixture of a cosmetically acceptable wax with dimethylpolysiloxane and either an organosilane or an organically substituted polysiloxane.

Patents cont.

(2) US Patent 5,194,260 issued March 16, 1993, to Grollier et al., titled "Cosmetic composition for the hair contains a film forming polymer and a silicone incorporated in a wax microdispersion and a cosmetic treatment using the same" discloses a cosmetic composition for the hair contains at least one film-forming polymer and at least one silicone incorporated into a support consisting essentially of a wax micro dispersion in an aqueous liquid vehicle.

(3) US Patent 5,288,482 issued Feb. 22, 1994, to Krzysik, titled "Silicone containing lip care cosmetic composition" discloses a lip care cosmetic composition containing as ingredients an emollient including castor oil, a wax, a suspending agent, a coloring agent, and as an additional ingredient, an organosilicone compound. The improvement resides in increasing the durability of lip care products by including an alkylmethylpolysiloxane.

(4) US Patent 5,478,555 issued Dec. 26, 1995, to Bara et al., titled "Cosmetic composition for the make up of the skin, containing at least one silicone wax and process for its preparation" discloses a composition in which the silicone wax(es) is (are) dispersed in an aqueous phase containing two water-soluble acrylic polymers; the first type of polymer(s) consists of at least one copolymer of a C_3 -C_6 monoethylenic acid or of its anhydride, and the second type of polymer(s) consists of at least one acrylic acid polymer or one of its salts. The presence of these two water-soluble acrylic polymers allows the dispersion of silicone wax(es) to be stabilized.

(5) US Patent 5,556,613 issued Sept. 17, 1996, to Arnaud et al., titled "Anhydrous cosmetic or dermatological composition containing the combination of a silicone oil and a wax made from an ethylene homopolymer or copolymer" discloses a silicone oil-based anhydrous cosmetic or dermatological anhydrous composition having a homogeneous fatty phase wherein said fatty phase contains a silicone having alkyl groups with a range of 1–30 carbon atoms.

(6) US Patent 5,733,533 issued March 31, 1998, to O'Lenick, Jr., et al., titled "Reconstituted silicone wax esters" discloses silicone wax esters, prepared by the reaction of a silicone polymer and a natural high molecular wax ester selected from the group consisting of beeswax, candelillia and carnauba wax. These materials are useful in preparation of cosmetic products where their ability to couple organic silicone and other components into a uniform mass is unsurpassed. One major area for the use of these materials is in lipsticks. In addition, they are useful in antiperspirants and other formulations which contain both oils and silicones.

(7) US Patent 5,750,095 issued May 12, 1998, to Arnaud et al., titled "Anhydrous cosmetic or dermatological composition containing the combination of a silicone oil and a wax made from an ethylene homopolymer or copolymer" discloses a silicone oil-based anhydrous cosmetic or dermatological anhydrous composition having a homogeneous fatty phase wherein said fatty phase contains a silicone oil having alkyl groups with a range of 1–30 carbon atoms, aryl or aralkyl, n represents a whole number between 0 and 100, and m represents a whole number between 0 and 100, provided that the sum of n+m is between 1 and 100; and (ii) a wax in an amount ranging from 3% to 50% by weight based on the total weight of said fatty phase.

(8) US Patent 6,235,292 issued May 22, 2001, to Bara et al., titled "Transfer-free

Patents cont.

makeup or care composition containing an organopolysiloxane and a fatty phase" discloses a transfer-free composition containing an organopolysiloxane and a fatty phase containing at least one oil which is volatile at room temperature, particularly a makeup or care composition for the lips or a makeup foundation composition for the human face and body. This composition is gentle to apply, spreads easily, is nonsticky and does not dry the skin or the lips.

(9) US Patent 6,444,212 issued Sept. 3, 2002, to Cavazzuti et al., titled "Moisturizing and long-wearing make-up composition" discloses a cosmetic composition which can be used for caring for and/or for making up the human face, in particular, the skin, eyelids, or lips, comprising at least one wax, at least one ester and at least one long chain alcohol.

(10) US Patent 6,727,34 issued April 27, 2004, to O'Lenick, Jr., titled "Fluoro alkyl dimethicone copolyol esters" discloses novel dimethicone copolyol ester compounds bearing a fluoro group attached through a hydrophobic ester linkage to silicon. This invention also relates a series of such products having differing amounts of water-soluble groups, silicone-soluble groups and fatty-soluble groups. By careful selection of the compounds so constructed, very efficient mild conditioning agents may be achieved.

Conclusion

Alkyl silicones offer many advantages to formulators of personal care products. These need to be maximized by the proper selection of products, in terms of structure, to meet the ever-changing demand for high performance products.

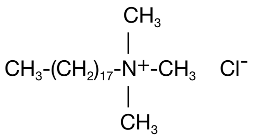
References:
1. J Speier, *J. Amer Chem Soc* 79 974 (1957)
2. Siltech Technical Bulletin 156 (2002)
3. DT Floyd, B Sarnecki, and B McPherson, Getting the most from your sunscreens, SPC, 26–31 (1996)
4. I Van Reeth, F Dahman, and J Hannington, Alkylmethyl-siloxanes as SPF Enhancers, Presented as a poster session at the 19th IFSCC (October 1996)

Chapter 11

Cationic Silicone Compounds

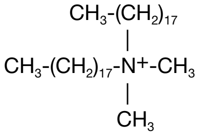
Cationic materials have been used to condition hair for many years. The materials most commonly used are fatty quats. These compounds have a nitrogen group, which has four alkyl groups attached. Most commonly they have either one or two long chain alkyl groups. **Figure 11.1** shows the structure.

Figure 11.1. Fatty Quats



$$CH_3\text{-}(CH_2)_{17}\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}\text{-}CH_3 \quad Cl^-$$

Alkyl trimethyl ammonioum chloride



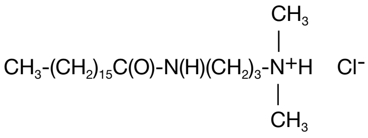
$$\begin{array}{r} CH_3\text{-}(CH_2)_{17} \\ | \\ CH_3\text{-}(CH_2)_{17}\text{-}N^+\text{-}CH_3 \\ | \\ CH_3 \end{array}$$

Dialkyl dimethyl ammonioum chloride

Another class of compounds used commonly for conditioning is the salts of fatty amines. Unlike the quats, these materials have a positive charge on nitrogen as a function of pH. They are generally tertiary amines. Shown in **Figure 11.2**.

Both classes of compounds are used on hair to provide conditioning and softening. There are two sources of substantivity in the molecule. First is the presence of a fatty chain or chains. Hydrophobic materials (oils) will spread out on dry hair providing a film that lubricates. The nature of the fatty hydrophobe will determine the tactile feel of the hair. Stearic materials (C18 saturated) will provide a slick feel; oleyl (C18 unsaturated) will provide a buttery feel. The second point of substantivity is the positive charge. This improves the bindability of the material to the hair. Quats shown in **Figure 11.1** always have a (+) charge, independent of the pH of the formulation. Fatty amidoamine salts have a (+) charge as a function of pH. **Figure 11.3** shows the pH dependence of charge on pH.

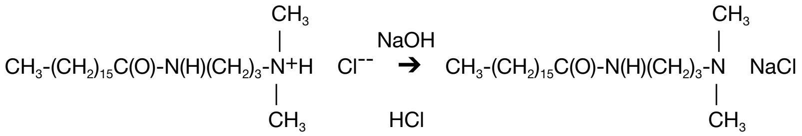
Figure 11.2. Fatty Amine Salts



$$CH_3\text{-}(CH_2)_{15}C(O)\text{-}N(H)(CH_2)_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{N^{+}H}}}}\quad Cl^{-}$$

Stearylamido amine hydrochloride

Figure 11.3. Fatty Amine Salts



$$CH_3\text{-}(CH_2)_{15}C(O)\text{-}N(H)(CH_2)_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{N^{+}H}}}}\quad Cl^{--}\ \xrightarrow[HCl]{NaOH}\ CH_3\text{-}(CH_2)_{15}C(O)\text{-}N(H)(CH_2)_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{N}}}}\quad NaCl$$

Stearylamido amine hydrochloride **Stearylamido amine**

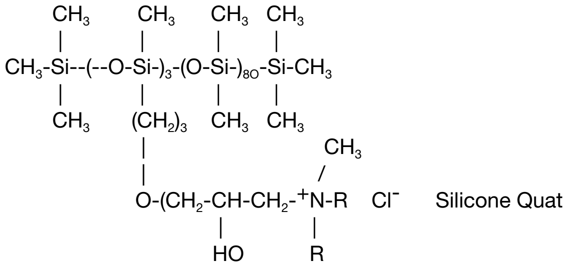
The famous Henderson Hasselbach formulation can be used to calculate the concentration of the protonated (+) charged material and the de-protonated (non-charged) species. Since the pKa of the amine is roughly 10, at that pH there will be roughly equal concentrations of both species. At pH of 9, there will be roughly a 10:1 concentration in favor of the protonated (+) form. At pH 8 the ratio will be 100:1 in favor of the protonated (+) form. Depending upon the pH of the formulation, there will be more or less protonated product. Neutral products will have 1,000:1 ratio.

The nature of the acid used to protonate the amidoamine will also be important. Hydrochlorides are commonly encountered, but many organic acids and multifunctional acids have been used in commercial formulations.

Silicone Conditioners

Silicone conditions mirror the chemistry of products shown above. They can be quaternary compounds (**Figure 11.4**) or amidimethicone (**Figure 11.5**). And finally silicone amido amine salts (**Figure 11.6**). All of the discussions related to pH and formulation above are found in the appropriate silicone group. The salient difference is that silicone is present; weather along or in combination with fatty groups, thereby altering the feel.

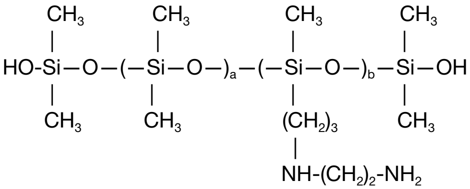
Figure 11.4. Silicone Quaternary Polymer



$$CH_3\text{-}Si\text{--(--}O\text{-}Si\text{-)}_3\text{-(}O\text{-}Si\text{-)}_{80}\text{-}Si\text{-}CH_3$$

$$O\text{-(}CH_2\text{-}CH\text{-}CH_2\text{-}{}^{+}N\text{-}R \quad Cl^{-}$$

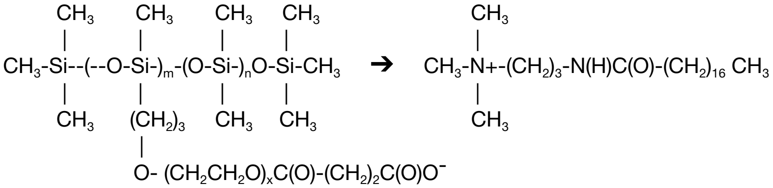
Figure 11.5. Amodomethicone



$$HO\text{-}Si{-}O{-}({-}Si{-}O{-})_a{-}({-}Si{-}O{-})_b{-}Si{-}OH$$

$$NH\text{-}(CH_2)_2\text{-}NH_2$$

Figure 11.6. Carboxy Salt Complex



$$CH_3\text{-}Si\text{--(--}O\text{-}Si\text{-)}_m\text{-(}O\text{-}Si\text{-)}_n O\text{-}Si\text{-}CH_3 \rightarrow CH_3\text{-}N\text{+-}(CH_2)_3\text{-}N(H)C(O)\text{-}(CH_2)_{16}\,CH_3$$

$$O\text{-}\ (CH_2CH_2O)_xC(O)\text{-}(CH_2)_2C(O)O^{-}$$

Amodomethicone

Amodomethicone, a silicone emulsion, has been used successfully as a softener and conditioner when applied to the hair for many years. Amodomethicone is sold commercially as an emulsion, blended together with a fatty quaternary compound and ethoxylated emulsifiers. The product has undergone a number of transformations throughout the years including changing the quat from an animal-derived quat to a plant-derived quat, to changing nonyl-phenol ethoxylates to linear alcohol ethoxylates. What has not changed is the fact that the product is made by is-situ polymerization of an amino silane and a silanol. The typical composition is shown in **Table 11.1**.

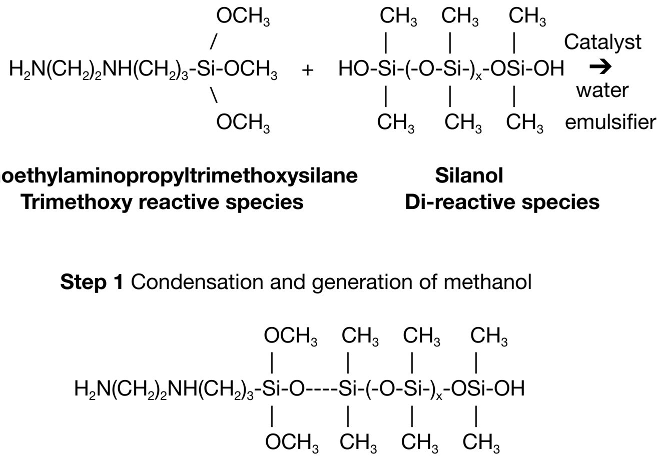
Table 11.1. Amodomethicone: Typical Composition

CAS Number	**Wt %**	**Component Name**
68554-54-1	35	Aminofunctional siloxane
9016-45-9	3	Ethoxylated surfactant
556-67-2	2	Octamethylcyclotetrasiloxane
8030-78-2	4	Quat
	QS	*Water*

Emulsion Polymerization

The most effective process used to make amidimethicone is emulsion polymerization. The process is defined in **Figure 11.7** and a procedure specified in **Table 11.2**.

Figure 11.7. In Sito Amino Reaction



$$H_2N(CH_2)_2NH(CH_2)_3\text{-Si}(OCH_3)_3 + HO\text{-Si}(CH_3)_2\text{-}(\text{-O-Si}(CH_3)_2\text{-})_x\text{-OSi}(CH_3)_2\text{-OH} \xrightarrow[\text{water emulsifier}]{\text{Catalyst}}$$

Aminoethylaminopropyltrimethoxysilane
Trimethoxy reactive species

Silanol
Di-reactive species

Step 1 Condensation and generation of methanol

$$H_2N(CH_2)_2NH(CH_2)_3\text{-Si}(OCH_3)_2\text{-O----Si}(CH_3)_2\text{-}(\text{-O-Si}(CH_3)_2\text{-})_x\text{-OSi}(CH_3)_2\text{-OH}$$

Condensation continues between methoxy (Si-OCH_3) and silanol Si-OH.

Table 11.2. In Situ Aminosilicone Softener Emulsion

Formulation

1. Silanol
2. Amino silane
3. Dibutyl tin dilaurate
4. UCC Terigtol TMN-6
5. GAF Igepal CO-850
6. Water
7. Water

WEIGHT %

20.0
0.2
0.4
2.7
1.8
7.1
68.8

Procedure for Colloid Mill

1. Blend TMN-6 and CO-850. Warm if necessary to melt. Cool to room temperature.
2. Mix silanol, amino silane and dibutyl tin dilaurate at room temperature for one hour.
3. Add TMN-6 and CO-850. Blend into silicone fluid mix.
4. Add 7.1% water slowly and mix until uniform. Do not overmix.
5. Wet colloid mill with small amount of water. Pass emulsion through colloid mill one time at 0.010 inches. Feed thick phase from mill into 67.8% water in mix tank.
6. Mix final emulsion until uniform.

Procedure for Homogenizer

1. Blend TMN-6 and CO-850. Warm if necessary to melt. Cool to room temperature.
2. Mix silanol, amino silane and dibutyl tin dilaurate at room temperature for one hour.
3. Add TMN-6 and CO-850. Blend to silicone fluid and mix until uniform.
4. Add all of water (74.9%) slowly with stirring and mix until uniform.
5. Pass through homogenizer—one pass at 5,000 psi or two passes at 4,000 psi.

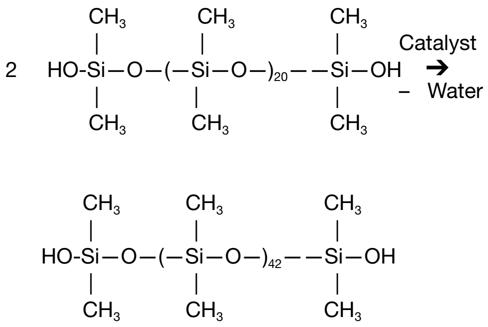
Amodomethicone is a very interesting material for several reasons. There are several structural properties of this material that give it the desirable softening effects. They are silanol groups, amino groups and D units.

Silanol Groups

The molecule is terminated by Si-OH groups. Compounds exhibiting this group were often referred to as dimethiconol compounds by the CTFA, but now are properly called silanol compounds. The preferred nomenclature for this type of group is silanol group. It is most enlightening to compare and contrast this group with the more common carbinol group found on fatty alcohol (CH_2-OH).

Silanol groups, unlike carbinol groups, easily undergo a polymerization reaction, especially in the presence of a catalyst to produce higher molecular weight silicone polymers. See **Figure 11.8**. Carbinol can undergo a reaction with each other to form ethers only under specific conditions, which are unlikely to occur in personal care applications.

Figure 11.8. Silanol Condensation



$$2\ \mathrm{HO{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}(-\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-})_{20}{-}{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}OH} \xrightarrow[-\ \text{Water}]{\text{Catalyst}}$$

$$\mathrm{HO{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}(-\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-})_{42}{-}{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}OH}$$

Since silanol groups are in terminal positions on the molecule, the only way to increase the amount of silanol present in the molecule is to decrease the value of a and b; this results in molecules that have lower total molecular weight.

Amino Groups

The amino group has three very important functions in the molecule:

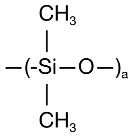
- The amino group provides a slick softening to hair and aides in combability.
- Since the pH of most formulations is below 10, the amino group in aqueous solution will be protonated. This means it will have a positive charge on the amino groups and make the molecule cationic. The cationic nature provides substantivity to the hair.

- The amino group is a catalyst for the condensation of the silanol groups.

D Units

The D units in the polymer are the silicone groups having the structure shown in **Figure 11.9**.

Figure 11.9. D Units



$$-(\text{-}\underset{CH_3}{\overset{CH_3}{|}}\!\!\!\!\!\!\!\underset{|}{\overset{|}{Si}}-O-)_a$$

These groups result in a typical silicone fluid type hand. The hand has been described as greasy. The balance of the amount of amino content, silanol content and the number of D units in a specific polymer determines the functional properties of the resulting polymer. As will become apparent, in addition to structure, the additives placed into the product by the manufacturer, the method of preparation of the polymer and the delivery systems for the polymer are also important variables.

Applications

- Hair softener and conditioner
- Hair color protection
- Allows for an even, long-lasting and gentle coloring of hair
- Gives maximum deposition of color in the minimum amount of time
- Improves hair bounce, manageability and vitality
- Contains silicone for hair shine, combability and softness

While the material has been used in many conditioner formulations, there are several inherent problems with using amidimethicone emulsions in personal care applications. The fact that the product is made by emulsion polymerization limits the latitude of formulations to which the product can be applied. Specifically, amodomethicone cannot be used in clear systems. Additionally, the freeze-thaw stability and HLB of the formulation need to be carefully monitored to prevent formulation separation. Recently a new series of amino-containing compounds have been prepared that offer formulation and performance advantages in these areas over amodomethicone. This chapter addresses the differences between the two types of amino silicones.

The problems are a direct result of the fact that amodomethicone is sold as an emulsion and include:

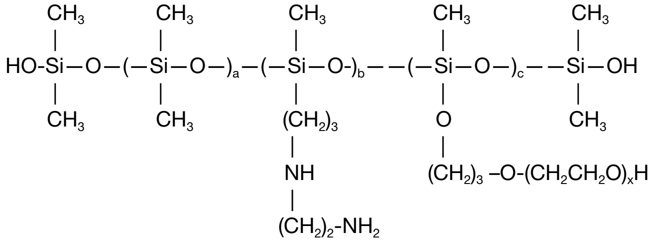
- Products containing amodimethicone emulsions must also be emulsions. Consequently, clear products cannot be prepared.
- The amodomethicone emulsion is stable only over a narrow range of HLB values. This places limitations on the HLB at which a formulation can be prepared. If detergents are added to the system, they cannot alter the HLB of the final product or the amodomethicone emulsion or the emulsion will not be stable and will split out of the formulation. This requirement imposes significant restrictions on the formulator.
- The amodimethicone emulsion has freeze-thaw stability issues.

In order to address these problems and expand the range of formulations into which silicone compounds can be placed, a new series of compounds have been developed and patented.

Dimethicone Copolyol Amine

The synthesis of water-soluble amino compounds is accomplished in several ways. One is the preparation of dimethicone copolyol amine. The structure of dimethicone copolyol amine according to CTFA is shown in **Figure 11.10**.

Figure 11.10. Dimethicone Copolyol Amine



$$HO\text{-}\underset{CH_3}{\overset{CH_3}{Si}}-O-(-\underset{CH_3}{\overset{CH_3}{Si}}-O-)_a-(-\underset{(CH_2)_3-NH-(CH_2)_2-NH_2}{\overset{CH_3}{Si}}-O\text{-})_b--(-\underset{O-(CH_2)_3-O-(CH_2CH_2O)_xH}{\overset{CH_3}{Si}}-O-)_c--\underset{CH_3}{\overset{CH_3}{Si}}-OH$$

The most obvious difference in the structure of dimethicone copolyol amine and amidimethicone is the presence of an additional group, the dimethicone copolyol group. The insertion of this group allows for one to tailor the water solubility of the molecule for specific applications. Molecules have been made that range in water solubility from water-soluble to water-insoluble. The most interesting compounds are those that form microemulsions spontaneously in water without an added surfactant.

The balance of the amount of amino content, silanol content, the number of D units and the number of water-soluble groups in a specific polymer determine the functional properties of the resulting polymer.

Polymerization Process

Unlike amidimethicone, dimethicone copolyol amine is not made by emulsion polymerization. They are made in a process that does not require emulsions. As a result they are water-free as prepared and contain no added surfactants and no added fatty quaternium compounds. This, coupled with the fact that they can be made water-soluble, results in more formulation latitude.

Applications Evaluation

In order to evaluate dimethicone copolyol amine and amidimethicone copolyol amines as conditioners, two formulations were evaluated on virgin brown hair swatches pre-washed with Prell® shampoo. **Table 11.3** and **Table 11.4** show the formulations.

Table 11.3. Formula 1. Conditioning Shampoo (Formulation #98-CS-1)

	Formulation 1	Formulation 2	Formulation 3
A. Deionized water	qs	qs	qs
Sodium laureth-3-sulfate (28%)	30.00	30.00	30.00
B. Cocamidopropyl betaine	7.00	9.00	7.00
Tetrasodium EDTA	0.05	0.05	0.05
Cocamide DEA	3.00	3.00	3.00
C. Dimethicone copolyol amine	2.00	0.00	0.00
Amodomethicone	0.00	2.00	0.00
D. Dowicil 200	0.30	0.30	0.30
Citric acid	Quantity Sufficient to pH 6.3-6.8		

Procedure: In a suitable container, mix together all the components of phases A. In another container, mix together all the components of phase B. Add phase B to phase A. Heat to 40–45°C. Add phase C, under good agitation. Cool to 35°C, add Dowicil and citric acid to pH 6.3–6.8.

Table 11.4. Formula 2. Conditioner (Formulation # 258-CS-1)

	Formulation 1	Formulation 2	Formulation 3
A. Deionized wWater	qs	qs	qs

cont.

Table 11.4. Formula 2. Conditioner (Formulation # 258-CS-1) cont.

	Formulation 1	Formulation 2	Formulation 3
Biosil Basics SPQ	1.00	1.00	1.00
Silsurf WS	1.00	1.00	3.00
Terta sodium EDTA	0.05	0.05	0.05
Methyl paraben	0.15	0.15	0.15
Dimethicone copolyol amine	2.00	0.00	0.00
Amdomethicone	0.00	2.00	0.00
B. Rice bran oil	4.00	4.00	4.00
Cetyl alcohol	3.00	3.00	3.00
PEG-100 stearate	1.15	1.15	1.15
Glyceryl stearate	2.50	2.50	2.50
Propyl paraben	0.10	0.10	0.10
C. Imidazoline urea	0.30	0.30	0.30

Procedure: In a suitable container, mix together all the components of phases A, heat to 75–80°C. In another container, mix together all the components of phase B, heat to 75–80°C. Add phase B to phase A. Heat to 40–45°C. Add phase C, under good agitation.

Evaluation

Each formulation was tested on four, brown, 10-inch virgin hair swatches. The swatches were evaluated individually for each attribute on both wet and dry hair. Each swatch was washed with Prell shampoo and air-dried. Each swatch was treated with two grams of either shampoo or conditioner. The contact time for the application was two minutes. The swatches were then rinsed with de-ionized water at 25°C.

The wet combing properties were evaluated for each swatch tested, and curls were put on the swatches. The curled swatch was then dried. Once dried, the property of the hair in the dry swatch was evaluated. The results were averaged. The evaluation was performed on the hair both wet and dry.

Evaluation Scale

Formulations were prepared using the previously mentioned formulations and applied to hair. The performance was evaluated in several areas using the following scale:

1. Very Poor
2. Poor
3. Satisfactory
4. Good
5. Excellent

Wet Comb Attributes

Wet comb was evaluated using the following classification:

- Residual feel
- Squeaky feel
- Shine wet comb
- Wet comb

Dry Comb Attributes

Dry comb was evaluated using the following classification:

- Residual feel
- Shine
- Curl retention
- Flyaway
- Combability
- Manageability

Results

The results of the shampoo are shown in **Tables 11.5** and **11.6**. The results of the conditioner are shown in **Tables 11.7** and **11.8**.

Dimethicone copolyol amine performs at least at parity with amidimethicone in the formulations tested. It offers several consumer perceptible improvements:

- Dimethicone copolyol amine can be formulated into clear, stable products such as hair gels, shampoos, body washes and toners.
- Dimethicone copolyols amine provides improved shine, softness, manageability and curl retention to hair and does not leave an unpleasant, residual feel.
- Dimethicone copolyol amine is more stable than the emulsion and consequently can be utilized in a wider range of formulations.
- Dimethicone copolyol amine does not contain either an animal-based fatty quat, or a nonyl-phenol-based surfactant, commonly used in the amidimethicone.

Formulators will find that a switch to dimethicone copolyol amine will provide significant improvements for their formulations.

Table 11.5. Wet Comb Evaluation

Formula	Result	Comment
Formula 1 (Dimethicone copolyol amine)	4.6	Good feel, shine and comb
Formula 2 (Amodomethicone)	4.5	Good feel
Formula 3 (Control)	3.6	Satisfactory

Table 11.6. Dry Hair Results

Formula	Result	Comment
Formula 1 (Dimethicone copolyol amine)	4.6	Silky, good curl retention
Formula 2 (Amodomethicone)	4.5	Silky, good curl retention
Formula 3 (Control)	4.0	No curl retention

Table 11.7. Conditioner Wet Hair Evaluations

Formula	Result	Comment
Formula 4 (Dimethicone copolyol amine)	5.0	Silky, smooth and combable
Formula 5 (Amodomethicone)	5.0	Silky smooth and combable
Formula 6 (Control)	4.0	Less combability

Table 11.8. Conditioner Wet Hair Evaluation

Formula 4 (Dimethicone copolyol amine)	4.6	Good shine and softness
Formula 5 (Amodomethicone)	4.3	Good softness
Formula 6 (Control)	3.8	Dry feel, no shine

Silicone aminopolyalkyleneoxide block copolymers

Another alternative to amidimethicone is covered by US Patent 5,807,956, issued Sept. 15, 1998, to Czech, which discloses silicone aminopolyalkyleneoxide block polymers. The patent states that these copolymers are primarily intended as softeners for substrates, especially fiber, hair and textiles. While the copolymers of the present invention can be used neat, for ease of application they are usually applied to the substrates dissolved, dispersed or emulsified to a suitable liquid medium. Preferably, the copolymers of the present invention are applied to a substrate from an aqueous solution, emulsion or suspension. They may also be applied as a solution in a nonaqueous solvent such as isopropanol or in liquid in which the copolymer is miscible. Most preferably, the copolymer is applied to a substrate as an aqueous dispersion.

In general, the dispersion is applied on skin, hair, fiber or textile such that up to 5%, preferably 0.25–2.5% of the copolymer by weight of the dry substrate remains on the substrate. Optionally other additives commonly used to treat hair or textile substrates can be employed along with the copolymers of the present invention, including but not limited to additional surfactants, curing resins, preservatives, dyes, colorants, formularies and/or perfluorinated stain/soil release finishes.

These compositions may be used in personal care formulations, including cleansers, body washes, soaps, lotions, creams, shaving cream, hair sprays, conditioners, shampoos, deodorants, moisturizers and sunscreens.

A typical shampoo formulation contains about 3–30 weight percent of an anionic and/or amphoteric surfactant component, 0.1–10 weight percent of a nonionic surfactant component, together with 0.1–20 weight percent of one or more copolymers of the present invention, and water, preferably also with an effective amount on the order of 0.1–5 weight percent of a thickener. Examples of thickeners include sodium alginate, gum arabic, polyoxyethylene, guar gum, hydroxypropyl guar gum, cellulosics such as methyl cellulose, methylhydroxypropyl cellulose, and hydroxypropylcellulose, starch derivatives such as hydroxyethylamylose, locust bean gum and polysaccharides.

Hair washed with the conditioning shampoo had improved wet and dry combability, provided better gloss and reduced electrostatic charge.

Patents

(1) US Patent 7,048,770 to Azizova et al. issued May 23, 2006, titled Hair coloring and conditioning composition discloses that by providing certain quaternary terpolymers as an integral ingredient in hair coloring formulations, substantially improved and enhanced hair conditioning benefits are attained, providing a highly effective hair coloring composition that also provides conditioning benefits to the hair fibers. In addition, the conditioning benefits and effects are long-lasting and capable of being retained by the hair fibers for up to four weeks.

(2) US Patent 5,854,319 to O'Lenick et al. issued Dec. 29, 1998, titled Reactive silicone emulsions containing amino acids relates to a composition, process for preparation and use of a novel emulsion composition in the personal care indus-

Patents cont.

try. The composition when applied to hair provides outstanding lubrication, and delivers amino acids or proteins to the hair fiber. This aids in the manageability of the hair and remediates damage from treatment processes such as permanent waving, dying and relaxing of the hair as well as environmental effects upon the hair.

(3) US Patent 5,645,822 to Myer et al. issued July 8, 1997, titled Method and apparatus for sunless tanning discloses an apparatus for simulating skin tanning comprises a receptacle containing a fluid comprising dihydroxyacetone, a receptacle containing a fluid comprising a secondary polyamine and dispensing means for simultaneously or sequentially providing desired amounts of dihydroxyacetone and polyamine, such amine can be amodimethicone.

(4) US Patent 5,415,857 to Robbins et al. issued May 16, 1995, titled Hair conditioning shampoos containing aminosilicone conditioning agent teaches a hair conditioning shampoo, of improved fiber conditioning properties, includes an aminosilicone of the amodimethicone type, of a certain formula, and an aqueous medium for the aminosilicone, which serves as a carrier for it. Preferably, the carrier is an aqueous anionic shampoo medium that also contains a cationic surfactant hair conditioning agent, such as a quaternary ammonium salt, and more preferably it also contains hydrocarbon components, such as microcrystalline wax and petrolatum and/or polyethylene and mineral oil, which promote further improvement in conditioning effects on human hair. The invention also contains hair conditioning processes and combined shampooing and hair conditioning operations as well as processes for manufacturing the invented conditioning shampoos.

(5) US Patent 5,154,915 to Weber et al. issued Oct. 13, 1992, titled Dentifrices containing aminoalkyl silicones and sarcosinate surfactants teaches dentifrices, including toothpastes and mouthwashes, are provided that include aminoalkyl silicones and sarcosine surfactants. In the mouth, the aminoalkyl silicones form a lasting hydrophobic film on the teeth for prevention of cavities and stain. Antimicrobial compounds such as chlorhexidine may be included.

(6) US Patent 4,658,839 to Dallal et al. issued April 21, 1987, titled Hair conditioning and enhancing applicator wrap, composition and method discloses a flexible, easily applied carrier that incorporates a combination of cationic hair conditioning agents and a water-soluble or emulsifiable silicone-based compound, a unique hair treatment system is achieved. Preferably, the flexible carrier or applicator is constructed for being wrapped either entirely or partially about a head of hair and also incorporates hair enhancing agents, such as plant and herb extracts and, if desired, coloring agents to further condition and enhance the hair. In the preferred embodiment, the hair treatment applicator is wrapped about the entire head of hair after shampooing, with the hair conditioners and hair-enhancing agent contained therein being transferred to all of the hair fibers by the application of a hot towel to the wrapped applicator and subsequent thorough rubbing.

(7) US Patent 4,529,586 to DeMarco et al. issued July 16, 1985, titled Hair conditioning composition and process discloses a hair conditioning composition containing an amino functional silicone polymer in an aqueous emulsion such as amodimethicone, and an effective amount for increasing the combability of hair of a cationic surfactant-emulsifier containing at least one long chain fatty acid residue that has between 12 and 18 carbon atoms and an effective amount for

Patents cont.

increasing the combability of hair and for improving the durability of the conditioning effect of at least one cationic polymer in an aqueous carrier. The process of the invention involves the application of the aforementioned conditioning composition before or after shampooing whereby the durability of the conditioning effect is further enhanced.

Conclusion

Silicone has many beneficial properties when applied to hair as dimethicone. These include lubrication, softening and detangling. Damage to the hair renders the protein anionic in charge (that is negative). Silicones that possess positive charges (quats and salts) will have improved deposition properties when applied to damaged hair. The ionic interaction not only offers enhanced deposition, it helps improve the efficiency.

The incorporation of amino groups into silicone by many different mechanisms is something that will continue. Many new methods and compounds will be developed to improve the cosmetic elegance, formulatability and properties of these materials.

Chapter 12

Carboxy Silicone Complexes

Hair in its normal state has certain oils, sebum and other components present on its surface. When a detergent is used on the hair, these materials can be removed, leaving the hair stripped of its natural conditioning oils. Stripped hair is generally dried, raspy, and dull and has problems with static electricity that results in a condition called, "flyaway." The ability to treat the hair to remove these undesirable properties is the most basic aspect of conditioning. There are several others. One additional aspect of conditioning is wet comb, which is the ability to effortlessly comb the hair in a wet state. Wet comb relates to wetting of the hair with a surfactant to make combing easier. Another aspect of conditioning relates to providing the hair with a treatment that the consumer perceives as soft and conditioned many hours after the hair has been treated. The advent of two-in-one systems that provide this type of advanced conditioning has been made possible by inclusion of polymers, often silicone polymers into hair care products[1–3]. In recent years this type of conditioning has been achieved by inclusion of oil soluble esters[4] and making complexes of anionic and cationic surfactants that contain silicone[5]. It is expected that this area will be a growth area as the structure/function rules related to this type of long-term conditioning are better understood. Yet another desirable effect of a conditioner is "dry comb," which is the ability to comb the hair effortlessly and without entanglement after the hair is dry. Materials that function in wet comb are not necessarily the same as those that function as dry comb agents.

The isoelectric point of untreated hair is 3.7. Using the Henderson Hasselbasch equation, it is clear that when the pH is below this 3.7, the hair is cationic, and when the pH is above 3.7, the hair is anionic. Therefore it is safe to assume that when using products having a pH above 3.7, the hair coated with aqueous product can be considered as anionic. This means that cationic materials will have an attraction to the hair and, by virtue of ionic charge, be substantive to the hair.

Fatty quaternaries (quats) have been known for many years. Because of their fatty nature and positive charge, these compounds find application in a variety of areas including conditioners for hair. The proper selection of quat can result in a conditioner that addresses the most basic aspects of conditioning, dryness, raspiness, dullness and static buildup.

The use of quats in hair care products can be problematic, since many of these materials are not compatible with anionic materials. This incompatibility can be manifested as a precipitate, or as cloudiness in formulation. Some quats are very insoluble when added to an anionic surfactant; others have improved compatibility. The ability to select quats that have optimum compatibility with anionic systems offers the formulator flexibility in formulating heretofore unavailable. The nature of the anionic/cationic interaction is key to the functionality, or lack of functionality of conditioners.

The situation is further complicated by testing methodology. Historically, deposition of cationic material onto hair was measured by a number of dye uptake tests. These tests merely measure the presence of cationic material on the surface of the hair. Since deposition on hair made from a solution containing a cationic and anionic molecule, contains no free cationic, no red color is observed with these tests. This does not mean there is no deposition and no conditioning. Correctly interpreted, it simply means the deposited material does not have an overall positive charge and consequently does not bind dye.

Anyone who has added stearylalkonium chloride to sodium lauryl sulfate and observed the white sticky solid that results knows anionic and cationic surfactants can be incompatible. Anionic and cationic materials that produce a white gunky solid when mixed together are referred to as hard complexes.[5] As the expression implies, the cationic and anionic compounds possess properties that when combined form insoluble complexes (salts). The nature of the cationic/anionic interaction can be altered to make the complex compatible. The terms used here for quats and anionic materials are an adaptation of the work of Pearson (*J Am Chem Soc* **85**, 3533 [1963]) used to describe acids and bases. Pearson proposed that "hard acids bind strongly to hard bases and soft acids bind softly to soft bases,"[5] the anionic and cationic interactions are exactly analogous.

The structural changes that can be made to cationic molecules can "soften" them, making them more compatible with anionic systems. Additionally, the cationic material can be combined with an anionic silicone compound to make a soft combination. Once an anionic and cationic surface-active agent is placed together in a solution, the ions dissociate and belong to the solution and not each other. Sodium lauryl sulfate and stearyl trimethyl ammonium chloride, when added to water, become chloride ion, sodium ion, sodium lauryl sulfate ion and stearyl trimethyl ammonium ion.

Carboxy silicones, created by the reaction of an anhydride with a dimethicone copolyol, have been known for some time.[5,6] An exciting and growing area in cosmetic chemistry is the formation of complexes between carboxy functional silicone polymers and fatty quaternary compounds and their use in personal care applications.

Hair is the most visible physical attribute and, therefore, deserves special attention. Nearly everyone wants their hair to be clean, to look natural, to have gloss and to be easy to comb and style. In other words, people want their hair to be in good condition. Silicones are good materials for hair care, but how does a consumer choose the proper one?

Cats wash their fur, ducks preen their feathers and humans groom their hair. From early records, it's known that people washed, scented and styled their hair, and I am sure that part of this process involved the use of materials to improve its condition. At first it was probably animal fat, neat or emulsified as hair cream, bay rum and brilliantine. These materials were, and often still are, added to hair separate from the cleansing process. Until the second half of the last century, hair cleansing was achieved by using various soaps, and claims were made that some soaps left the hair in better condition than others. When detergents started to replace soap, the hair was left much cleaner and was not affected by precipitated hard water deposits. However, the anionic shampoo created its own problem—flyaway. To counteract this, the hair conditioner was born. Typically, this was an emulsion of fatty alcohols with a cationic surfactant that was applied after the shampoo process and was then itself washed from the hair. The cationic surfactant was intended to neutralize the positive charge left by the anionic shampoo, and the fatty alcohols were deposited as a thin film on the hair shaft, making it glossy, soft, slippery to the touch and easy to comb. Another popular product of the time was the acid rinse; lemon juice and vinegar had long been used and were eventually replaced by citric, lactic or tartaric acid, usually in aqueous-alcoholic solution.

Shampoos have changed from strong cleansers designed to be used weekly to mild formulations for daily use. Some have simply reduced the active levels, others have increased the amphoteric content and many have included conditioning aids. Cationic polymers, together with anionic silicones, are commonly used as conditioning additives. Used at levels of 0.1– 0.5%, the complex is soluble in the large excess of anionic surfactant present. The complex is adsorbed onto the hair with sufficient attraction to resist being lost at the rinse stage.

Consumer expectations have changed throughout the years. Consumers now demand conditioning products for hair.

Energetics of Complex Formation

The existence of anionic/cationic complexes is not something new. Many times the complex between an anionic (for example, sodium lauryl sulfate) and a cationic (for example, stearalkonium chloride) is a white gooey precipitate. If the complex is a precipitate, the complex is not an effective conditioner.

Considerable work has been performed throughout the years on the interaction of large oppositely charged molecules in aqueous solution. Textile dyes are commonly leveled by forming a complex. In fact, in the days of shag rugs, many dyes applied directly to the carpet would result in a nonuniform deposition and some carpet fiber that remained white in color. Forming the complex of an anionic dye and a tallow amine ethoxy-quat resulted in the phenomenon called dye leveling.

Stellner, Amante, Scamehorn and Harwell[6] published the now classical work done on the physical chemistry of the complex in 1988.[4] In this paper the authors explore the physical chemistry and prove that the complex is preferentially adsorbed out of water, because its absorption results in the lowest free energy of the system. What a great situation—the very product we want to place on the hair or skin is in fact the one that is preferentially absorbed. Additional information on this can be seen in the paper by Lucassen-Reyndes, Lucassen and Giles published in 1981.[7]

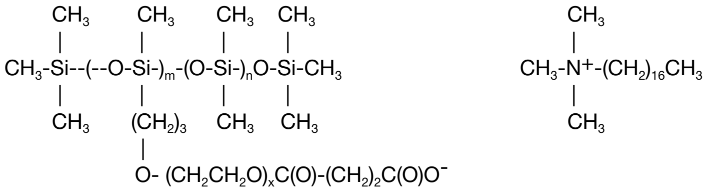
Mild Conditioning Products

Cationic polymer complexes are effective as conditioners in shampoos based on anionic surfactants. Surprisingly, they do not need to have a high positive charge, but molecular structure is important if properly complexed. The silicone polymer/surfactant complex is more readily precipitated and deposited on the hair upon dilution of the shampoo, and a coiled polymer is less strongly adsorbed on hair than a straight polymer and is, therefore, easier to remove if necessary.

All silicone complexes are effective to differing amounts in reducing combing forces on wet and dry hair and a very low level of silicone. Low concentrations of complexes greatly reduce the forces exerted on the hair when it is being combed. The synergy between anionic silicone and cationic guars can double the amount of silicone deposited and greatly improve the efficacy of the system. The conditioning effect of silicone anionic compounds in shampoos and conditioners is dependent on high molecular weight, and it is essential to disperse the silicones uniformly within the product. It is important to select the correct silicone for the product. Complexation is key to efficiency.

Carboxy silicone polymers useful in making the complexes have a terminal carboxy group present and, consequently, are anionic. These compounds by themselves are substantive to the surface of hair and textile fiber and provide some lubricity. Carboxy silicone complexes conform to the structure in **Figure 12.1**.

Figure 12.1. Carboxy Silicone Complex: Generic Formula



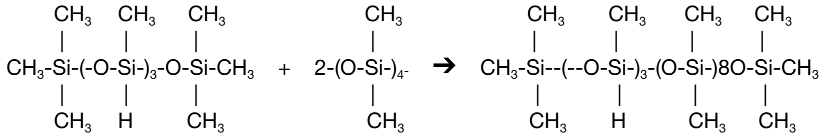
$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{\underset{O\text{- }(CH_2CH_2O)_xC(O)\text{-}(CH_2)_2C(O)O^-}{(CH_2)_3}}{\overset{CH_3}{Si}}\text{-})_m\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_nO\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 \qquad CH_3\text{-}\underset{CH_3}{\overset{CH_3}{N^+}}\text{-}(CH_2)_{16}CH_3$$

Carboxy silicone polymers used in the preparation of the complexes are made using a sequence of construction, functionalization and two derivitization steps; this is shown in **Figures 12.2–12.5**.

Fatty Quaternary Ammonium Compounds

The other necessary component for making the complex is the cationic quat compound. Fatty quaternary compounds, commonly called quats, are tetra-substituted ammonium compounds where each of the four groups on nitrogen is a group other than hydrogen. If any hydrogen groups are present, the compounds are not quaternary amines, but rather are primary or secondary amines.

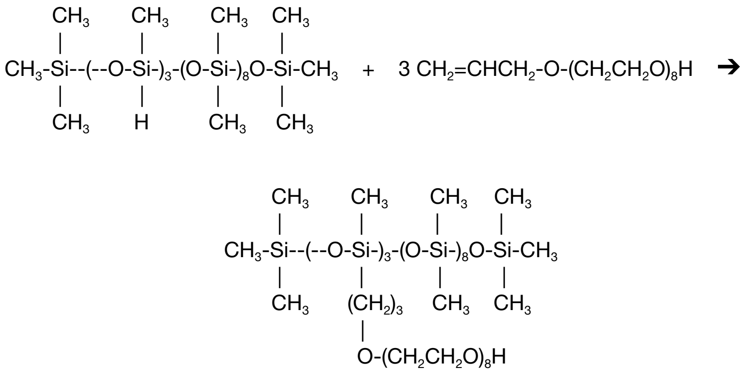
Figure 12.2. Carboxy Silicone Complex: Construction



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}(\text{-}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_3\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 \; + \; 2\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_{4}\text{-} \rightarrow CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_3\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})8O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

MD*M **D4** **MD*3D8M**

Figure 12.3. Carboxy Silicone Complex: Functionalization

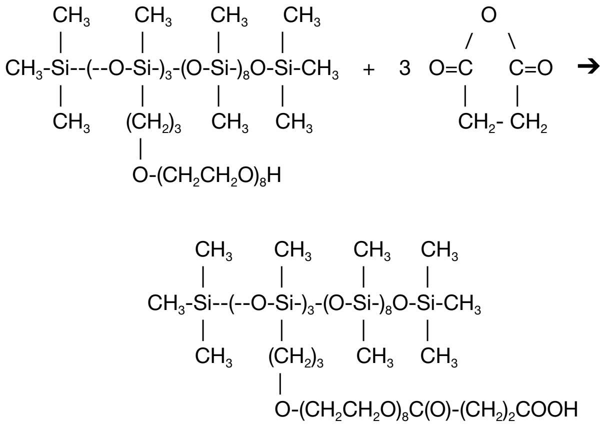


$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_3\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 \; + \; 3\; CH_2{=}CHCH_2\text{-}O\text{-}(CH_2CH_2O)_8H \rightarrow$$

$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{\substack{(CH_2)_3\\|\\O\text{-}(CH_2CH_2O)_8H}}{\overset{CH_3}{Si}}\text{-})_3\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Figure 12.4. Carboxy Silicone Complex: Derivitization

Step 1

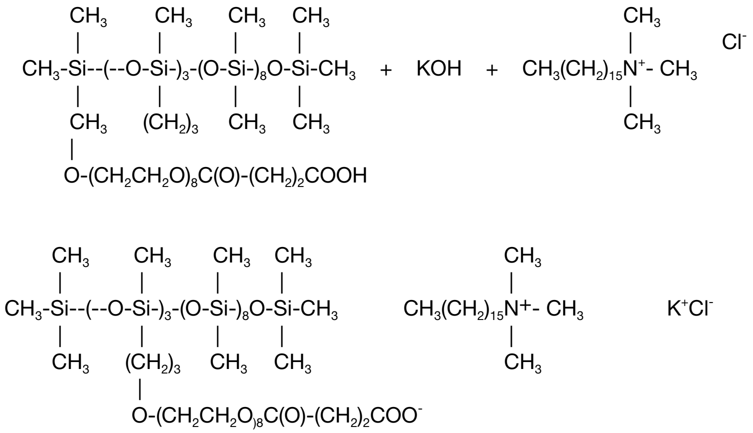


$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{\substack{(CH_2)_3\\|\\O\text{-}(CH_2CH_2O)_8H}}{\overset{CH_3}{Si}}\text{-})_3\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 \; + \; 3 \; \begin{array}{c} O \\ / \quad \backslash \\ O{=}C \qquad C{=}O \\ | \qquad | \\ CH_2\text{-}\;CH_2 \end{array} \rightarrow$$

$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{\substack{(CH_2)_3\\|\\O\text{-}(CH_2CH_2O)_8C(O)\text{-}(CH_2)_2COOH}}{\overset{CH_3}{Si}}\text{-})_3\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Figure 12.5. Carboxy Silicone Complex: Derivitization

Step 2



$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{--(--O-}\overset{CH_3}{\underset{(CH_2)_3\text{-}O\text{-}(CH_2CH_2O)_8C(O)\text{-}(CH_2)_2COOH}{Si}}\text{-)}_3\text{-(O-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-)}_8\text{O-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3 + KOH + CH_3(CH_2)_{15}\overset{CH_3}{\underset{CH_3}{N^+}}\text{-}CH_3 \quad Cl^-$$

$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{--(--O-}\overset{CH_3}{\underset{(CH_2)_3\text{-}O\text{-}(CH_2CH_2O)_8C(O)\text{-}(CH_2)_2COO^-}{Si}}\text{-)}_3\text{-(O-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-)}_8\text{O-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3 \quad CH_3(CH_2)_{15}\overset{CH_3}{\underset{CH_3}{N^+}}\text{-}CH_3 \quad K^+Cl^-$$

The most commonly encountered substituents are alkyl and alkyl amido groups. There are several classes of quats. One scheme to classify quats is shown in **Table 12.1**.

Table 12.1. Carboxy Silicone Complex: Derivitization

INCI Name	**Fatty Quat**
Stearalkonium dimethicone Copolyol succinate (Stearyl complex)	Stearalkonium chloride
Cetrimonium dimethicone Copolyol Succinate (Cetyl complex)	Cetyltrimonium chloride

There are several undesirable attributes of fatty cationic products.

- Fatty quaternary compounds are incompatible with anionic surfactants since an insoluble complex frequently is formed when the two types of materials are combined.
- Many fatty quaternary compounds are eye irritants. The material is minimally irritating to the eyes at concentrations of 2.5 %[8] that limits the concentration at which they are useful if low irritation is a requirement.

- Fatty quats are generally hydrophobic and when applied to substrate can cause a loss of absorbance of the substrate. It is not an uncommon situation for a hotel guest to encounter a very soft towel that totally fails to absorb water. This is because the fatty quaternary gives softness but being hydrophobic also prevents re-wet. This situation also can be observed on hair: the conditioner becomes gunky on the hair and has a tendency to build up.

Silicone complexes with carboxy silicone compounds mitigate many of these negative attributes. The carboxy silicone complexes with quaternary compounds have altered properties, which make them highly desirable in personal care applications.

Complexes are made from to two well-known quats. Stearalkonium chloride is an excellent conditioning agent, with outstanding substantivity to hair. It has detangling properties and improves wet comb when applied after shampooing. The US Food and Drug Administration formulation data reports the use of this material in 78 hair conditioners, eight at less than 0.1 %, 18 at between 0.1 and 1.0%, and 52 at between 1 and 5%.

Cetyltrimonium chloride (CTAC) is a very substantive conditioner that also has a nongreasy feel, improves wet comb and provides a gloss to the hair. It is classified as a severe primary eye irritant. Therefore, its use concentration is generally at or below 1%.

Chemistry

Fatty quaternary carboxy silicone complexes are clear water-soluble complexes, providing outstanding wet comb properties, antistatic properties and nongreasy softening properties to hair, fiber and skin. In addition, they are minimally irritating to the eye and can be used to formulate clear conditioners. They are effective at as low as 0.5% concentration!

The complexes commercially available are shown in **Table 12.2**.

Table 12.2. Fatty Quat Classification

Group	Description	Example
A	Alkyl trimethyl	Cetyltrimonium Chloride
B	Alkylamidopropyl, dimethyl	Stearylamidalkonium Chloride
C	Di alkyl, dimethyl	Dicetyldimonium Chloride
D	Alkyl, benzyl, Dimethyl	Stearalkonium Chloride
E	Polymerics	Polyquaternium 10

Desirable Properties of Cationic Silicone Complexes

The development and understanding of the importance of making complexes will become more of a major factor in formulation of personal care products. All formulators learn that sodium lauryl sulfate and stearylalkonium chloride form an insoluble complex. It will gum up the bottom of the beaker and be of little practical use. This particular anionic/cationic complex is insoluble. However, the proper selection of the anionic and cationic, and the inclusion of silicone in the combination, result in very desirable properties.

Compatible with Anionic Surfactants

Traditional fatty quats, such as stearalkonium chloride and cetyltrimonium chloride, form water-insoluble complexes when combined with sodium lauryl sulfate in aqueous solution. This is due to the formation of an anionic/cationic complex, which is insoluble.

Cetyl complex like the traditional quats form an insoluble complex but, surprisingly, the stearyl complex is compatible and clear over a range of concentrations.

Anionic Compatibility Test

A 10% solids solution of sodium lauryl sulfate was prepared. Separately, a 10% solids solution of the quat compound was prepared. The quat was titrated into 100 mL of the sulfate solution. The formation of a white insoluble complex or the formation of a haze is considered the endpoint of the titration (**Table 12.3**).

Table 12.3. Anionic Compatibility Text

Quat	End Point	Observation
Stearalkonium chloride	0.3 ml	White solid
Cetyltrimonium chloride	0.2 ml	White solid
Cetyl complex	0.5 ml	White solid
Stearyl complex	35.8 ml	Haze develops

As can be seen from the data, the stearyl complex is unique in that it has compatibility with anionic systems.

Eye Irritation

Eye irritation is a major concern in the formulation of personal care products, particularly when working with quats. Primary eye irritation was tested using the protocol outlined in FHSLA 16 CFR 1500.42. The products were tested at 25% actives. The results are shown in **Table 12.4**.

Table 12.4. Eye Irritation Results

Product	Score	Interpretation
Cetyltrimonium Chloride	106.0	Severely Irritating
Cetyl complex	8.3	Minimally Irritating
Stearalkonium Chloride*	116.5	Severely Irritating
Stearyl complex	11.3	Minimally Irritating

* At a concentration of 0.5 % stearalkonium chloride was minimally irritating. This rating of minimally irritating was the same rating of Cetyl complex and Stearyl complex at 25% (or 50 times the concentration). As the data clearly shows, the irritation potential of the complex is dramatically reduced, when compared to the starting quat.

Re-wet

When fatty quaternary compounds complexed with carboxy silicone are used to treat textile fabrics, they make the substrate soft but do not make them hydrophobic. This makes them different from the standard fatty quats, which make the substrate hydrophobic.

This property carries over to hair in that the hair treated with the complexed quat does not build up. This will be demonstrated with several formulations later in this chapter.

Conditioning/Combability

The following test was performed to determine the conditioning and combability properties.

Test Method

The test hair used was 7-inch dark brown virgin hair from the well-known supplier DeMeo Brothers. Five two-gram tresses were used per product evaluated. All tresses were pre-washed three times with Prell® original shampoo, rinsed in water at 25°C, and air-dried. The test scale was:

1 = Very poor
2 = Poor
3 = Satisfactory
4 = Good
5 = Excellent

The materials and formulations tested are shown in **Table 12.4**.

Wet Comb

The evaluations were made using both visual and tactile observations. All raw materials were evaluated in the base at 2% as provided, except the formula with di (C12-C13 alkyl) malate, which was added at 0.5%. A commercial product was also evaluated as a positive control. Evaluation of the formulations can be found in Table 12.5.

Table 12.4. Materials and Formulation Tested

Materials Tested

1. Base formulation (147-CS-1)
2. Commercial conditioner product
3. 2.0% stearyl complex added to base formula
4. 2.0% CETAC 30 added to base formula
5. 2.0% stearalkonium chloride added to base formula
6. 2.0% cetyl complex added to base formula
7. 2.0% cetyl complex & 0.5% di (C12-C13 alkyl) malate added to base formula.

Formula Tested
Base Formulation 147-CS-1

A	
Water (*aqua*)	qs 100.00
Methylparaben	0.15
Tetrasodium EDTA	0.05
Biosil Basic SPQ	0.50
B	
Rice bran oil	4.00
Cetyl alcohol	3.00
Test ingredient	2.00
Glyceryl stearate	2.50
Propylparben	0.10
C	
Germall 115	0.20

Procedure:

1. In a suitable container, weigh A in order. Mix well and heat to 75°C.
2. In a separate container, weigh and combine B in the order.
3. Heat B to 75°C.
4. Add B to A at 75°C, agitating for at least 15 min.
5. Add C and cool to 25-30°C.

Table 12.5. Wet Comb Evaluation

Formulation 1 (Base Formula) (147-CS-1)

Residual feel	2
Squeaky feel	1
Shine	1
Wet combing	4
Product spreadability	4
Smoothness of product	3

Formulation 2 (Commercial Product)

Residual feel	4
Squeaky feel	2
Shine	2.5
Wet combing	5
Product spreadbility	4.5
Smoothness of product	3.5

Formulation 3 (Stearyl complex formula)

Residual feel	4
Squeaky feel	1
Shine	1
Wet combing	5
Product spreadbility	4
Smoothness of product	4

Formulation 4 (CETAC Formula)

Residual feel	1
Squeaky feel	1
Shine	1
Wet combing	4
Product spreadability	3
Smoothness of product	3

Formulation 5 (Stearalkonium chloride formula)

Residual feel	1
Squeaky feel	1
Shine	1
Wet combing	4
Product spreadablity	3
Smoothness of product	3

cont.

Table 12.5. Wet Comb Evaluation cont.

Formulation 6 (Cetyl complex formula)	
Residual feel	2
Squeaky feel	3
Shine	2
Wet combing	2.5
Product spreadbility	3
Smoothness of product	3
Formulation 7 (Cetylcomplex with di (C12-C13 alkyl) malate formula)	
Residual feel	2
Squeaky feel	1
Shine	3.5
Wet combing	4
Product spreadbility	4
Smoothness of product	4

Wet Comb Conclusions

Comparing Formulas 1, 3 and 5, the following trends emerge:

- Putting stearakonium chloride into the base formula did not improve the base at all. (Formula 1 and Formula 5)
- Putting stearyl complex into the base formula improved residual feel and wet combability. (Formula 1 and Formula 3)

Comparing Formulas 1, 6 and 4, the following trends emerge:

- Putting CETAC into the base formula did not improve the base at all. (Formula 1 and Formula 4)
- Putting cetyl complex into the base formula, improved residual feel and wet combability. (Formula 1 and Formula 6)
- Putting cetyl complex and dialkyl (C12-C13 Malate) into the base formula along with cetyl complex, improved the shine over the formula lacking the malate.

Dry Comb

The previous formulations were also evaluated on dry hair. The results are shown in **Table 12.6**.

Dry Comb Conclusions

Comparing Formulas 1, 3 and 5, the following trends emerge:

- Putting stearakonium chloride into the base formula did result in only a marginal improvement. (Formula 1 and Formula 5)

Table 12.6. Dry Comb Evaluation

Formulation 1 (Base Formula)	
Residual feel	3
Shine	2
Dry combing	3
Fly away	2
Curl retention	3
Fullness	2
Manageability	3
Formulation 2 (Commercial Product)	
Residual feel	3
Shine	3
Dry combing	3
Fly away	2
Curl retention	2
Fullness	2
Manageability	3
Formulation 3 (Stearyl complex formula)	
Residual feel	3
Shine	3.5
Dry combing	4
Fly away	2
Curl retention	2
Fullness	4
Manageability	2
Formulation 4 (CETAC Formula)	
Residual feel	3
Shine	2.5
Dry combing	5
Flyaway	2
Curl retention	3
Fullness	2.5
Manageability	2

cont.

Table 12.6. Dry Comb Evaluation cont.

Formulation 5 (Stearalkonium chloride formula)	
Residual feel	3
Shine	3
Dry combing	3
Fly away	2.5
Curl retention	2
Fullness	3
Manageability	2
Formulation 6 (Cetyl complex formula)	
Residual feel	4
Shine	3.5
Dry combing	3.5
Fly away	2.5
Curl retention	3
Fullness	3
Manageability	3
Formulation 7 (Cetylcomplex with di (C12-C13 alkyl) malate formula)	
Residual feel	3
Shine	3.5
Dry combing	4
Fly away	3
Curl retention	3.5
Fullness	4.5
Manageability	3

- Putting Stearylsil into the base formula improved shine, dry comb, and showed a significant improvement in fullness of the hair. (Formula 1 and Formula 3)

Comparing Formulas 1, 6 and 4, the following trends emerge:

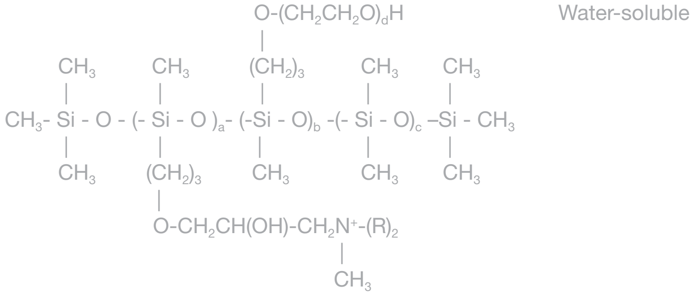
- Putting CETAC into the base formula resulted in an improvement in shine and dry comb. (Formula 1 and Formula 4)
- Putting cetyl complex into the base formula improved all properties measured except curl retention. (Formula 1 and Formula 6)
- Putting cetyl complex and Dialkyl (C12-C13 Malate) into the base formula along with Cetylsil, improved the hair fullness over the formula lacking the malate.

The incorporation of stearyl complex, or cetyl complex into the base resulted in significant improvements in the formulations.

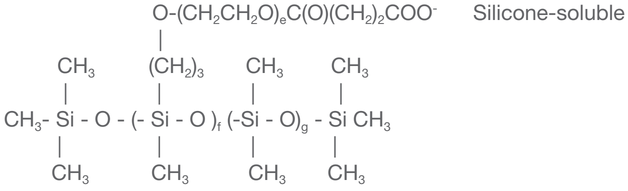
Silicone/Silicone Complexes

A new series patented conditioning agent based upon complexation chemistry has been described wherein the fatty quat is replaced in a complex with a silicone quat. The result is a very high molecular weight complex with outstanding conditioning properties. Specifically, silicone quaternium 20 combines anionic and cationic silicone polymers conforming to the structure shown in **Figure 12.6**.

Figure 12.6. Silicone Carboxy Silicone Complex



Silicone Quat



Silicone anionic

The product has been designed to be soluble in water and compatible with anionic surfactants and provide outstanding conditioning at low concentrations. The nature of water and the hydrogen bonding that occurs between molecules of water makes water a unique material and one necessary to life as it's known. The interaction of ionic surfactants in dilute aqueous solution is important in formulation and utilization of personal care products.

Since anionic and cationic materials have an opposite charge, they will attract each other and form a salt complex. It is the nature of this complex rather than the properties of the polymers themselves that determines how the formulations function. As ionic materials are added to water, opposite charges attract and the same charges repel. As the concentration of point charges are increased, the solution becomes so ordered that either: (a) the solubility product of the salt is exceeded and a precipitate occurs. (b) the viscosity of the solution increases or (c) the complex becomes insoluble. It is the nature of this interaction that is of interest to the present study. These complexes (that are made up on anionic and cationic surfactants in aqueous solution that thicken and remain clear) are referred to as soft complexes, while insoluble complexes are referred to as hard complexes. The chemical structure of each determines the hardness or softness of the complex. As the number of anionic and cationic species becomes equal, the number of interaction complexes will be greatest and the concentration of uncomplexed surfactant becomes lowest. It is for this reason that the highest viscosity of the blends of anionic and cationic surfactant occurs at equal amounts.

Silicone Quaternium 20 has been developed to maximize the disruption of the hydrogen bonding between water molecules, yet still maintain water solubility. The result is a complex that despite its water solubility achieves lowest free energy by deposition on the hair and skin. The result is a very effective conditioning of the hair and skin. Silicone quaternium 20 and the quat upon which it is based were evaluated in the formulation in **Table 12.7.**

Table 12.7. Materials and Formulation Tested

Compounds Evaluated

1. Silicone quat (see Table 12.13)
2. Silicone complex (see Table 12.13)

Shampoo Base

Ingredients	**%**
Water	Qs
Sodium laureth-2 sulfate	30.00
Cocamidopropyl betaine	7.00
Cocamide DEA	4.00
Na_2EDTA	0.10
Siltech materials	2.50
Germaben II	1.00
Citric Acid (25% soln)	as Required

All formula pH adjustments ranged from 6.65 to 6.80, specs being 6.3 to 6.8.

Comments:

- All products were yellow in color.
- The product made with silicone complex was crystal clear; the one made with silicone quat was slightly hazy.
- The product with the silicone quat was crystal clear and did not affect the viscosity.
- The product with the silicone complex was similar in both foam and viscosity to the control.
- The product with silicone quat had lower foam and viscosity indicating interaction between the cation and anion.

EVALUATIONS:

These two products were then evaluated for wet and dry combing on 10-inch virgin brown hair. Three-2-gram swatches were used with one gram of shampoo for each swatch. The water temperature used for wetting and rinsing the hair was a constant 25°C. All the swatches were rinsed until squeaky clean or for at least 1 min e. After the wet hair evaluation, the swatches were left to air dry then the dry comb evaluation was performed.

The scale used for all evaluations is from 1–5, 5 being best. **Table 12.8** shows the evaluation of the wet comb properties and **Table 12.9** shows the dry comb properties.

Table 12.8. Wet Combing Evaluation

	(Control) Water only	Silicone quat	Silicone Complex
Wet Comb	1	4	5
Rinse off	3	4	5
Clean feel	1	4	5
Shine	3	4	5
Average	2	4.0	5

Silicone quaternium 20 is a notable product for use in a 2-in-1 shampoo and for adding sheen and softness to color-treated hair. It left the hair silky soft with no residual feel and the combing was without any tugging or pulling. The comb slipped right through the swatches. Best of all was the shine, which was far superior to the silicone quat upon which silicone quaternium is based for the wet or dry combing. The product provides conditioning comparable to high molecular weight dimethicone in a clear product.

Table 12.9. Dry Combing Evaluation

	(Control) Water only	Silicone quat	Silicone Complex
Dry comb	2	4	5
Feel	2	4.5	5
Manageability	2	4	5
Shine	3	5	5
Clean look	2	4	5
Flyaway	2	3	4.5
Static	2	3	4.5
Residual feel	3	4.5	5
Average	2.25	4.00	4.875

Conclusion

The ability to use complexation chemistry to make quats more water-soluble, provide more conditioning and shine and to lower irritation is a major step for the hair care industry. The expansion of the approach is expected.

References:

1. RG Pearson, *J Am Chem Soc*, 85, 335 (1963)
2. US Patent 4,374,825 ,issued February 22, 1983 to Bolich et al titled "Hair conditioning compositions".
3. US Patent 4,728,457 , issued March 1, 1988 to Fieler et al titled "Process for making a silicone-containing shampoo".
4. US Patent 5,932,203 ,issued August 3, 1999 to Cottindaffer et al titled "Conditioning shampoo compositions containing select hair conditioning esters".
5. US Patent 6,498,263 ,issued December 24, 2003, to O'Lenick et al , entitled "Alkoxylated silicone carboxylate--amido cationic complexes used in personal care applications."
6. K StellnerJ Amante, J Scamehorn and J Harwell, *J Colloid and Interface Science*, 123(1) 186–200 (1988)
7. EH Lucassen-ReyndesJ Lucassen and D Giles, *J Colloid and Interface Science*, 81(1) 150-157 (1981)
8. A Hunter, *Encyclopedia of Shampoo Ingredients* Micelle Press, 1983, p. 174–175.

Chapter 13

Silicone Phosphate Esters

Fatty Phosphate Esters

Fatty phosphate esters are used in many applications because of the various surfactant properties they possess. Of the desirable surface active properties, alkali stability and wetting properties are key. Phosphate esters are part of a class of anionic surface active agents, made by phosphation of hydroxyl groups. The process produces a mixture of monoester, diester, triester and free fatty alcohol. Monoallkyl phosphate compounds are the most interesting for personal care applications. The alkali metal salts of monoalkyl phosphates of long-chained alkyl alcohols are excellent as detergents since they are water-soluble, have satisfactory foaming and cleaning performance, and are less toxic and thus less irritative to skin. Dialkyl phosphates are scarcely soluble in water and have no substantial foaming performance. Rather, the dialkyl phosphates show foam suppressing properties, and accordingly, said sesqui-phosphates containing monoalkyl phosphates cannot be used as highly foaming detergents.

In a given alkyl phosphate mixture, other important properties such as water miscibility, Krafft point and foam production also are a function of the relative amounts of monoalkyl and dialkyl phosphate. As the dialkyl phosphate content increases, the solubility, foaming ability and detergency decrease, and the Krafft point increases. The desirable range for a monoalkyl phosphate composition has been defined to be wherein the ratio of monoalkyl to dialkyl phosphate is at least 80:20 weight percent (US Patent 4,139,485). Acceptable performance was found at 70:30, and relatively little additional improvement was obtained above 90:10.

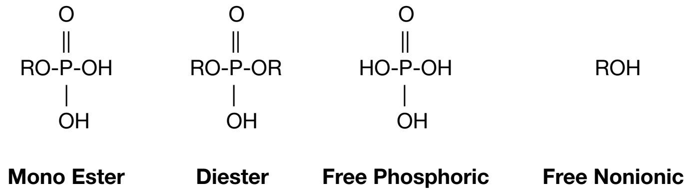
Typical phosphation processes do not produce product mixtures with the high monoalkyl phosphate together with the low dialkyl phosphate, low phosphoric acid and low residual alcohol contents necessary to obtain the above advantages. The two commonly used phosphating agents produce two extremes in the compositional range.

The commercial products are complex mixtures of three components shown in **Figure 13.1**. The mixture is reproducible when (1) the phosphation reagent, (2) the mole ratio of reactants, (3) the dimethicone copolyol and (4) the process used are controlled.

Silicone Phosphates

The derivitization of a dimethicone copolyol to include a phosphate group is a major step in developing an analogue to fatty phosphate esters, and just like the products based upon fatty alcohol, monoesters of dimethicone copolyol compounds are the preferred material for personal care use. There are two different approaches that result in somewhat different molecules. The older series of silicone surface active agents containing an ionizable phosphate group are prepared by the phosphation of dimethicone copolyol. These silicone-based phosphate esters have been compared to traditional fatty phosphate esters. **Figure 13.2** shows the structure.

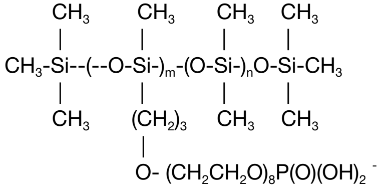
Figure 13.1. Products of the Phosphation Reaction



$$\mathrm{RO\text{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}OH} \qquad \mathrm{RO\text{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}OR} \qquad \mathrm{HO\text{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}\text{-}OH} \qquad \mathrm{ROH}$$

Mono Ester **Diester** **Free Phosphoric** **Free Nonionic**

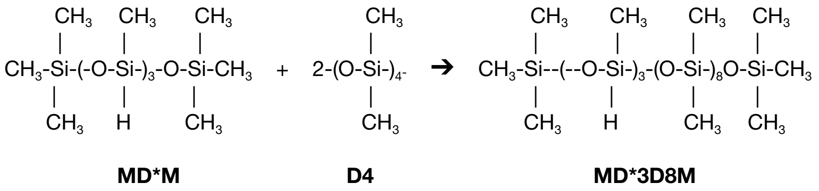
FIgure 13.2. Silicone Phosphate: Generic Formula



$$\mathrm{CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{--}(\text{--}O\text{-}\underset{\underset{\underset{\underset{O\text{-}\ (CH_2CH_2O)_8P(O)(OH)_2^{\ -}}{|}}{(CH_2)_3}}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-})_m\text{-}(O\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-})_nO\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-}CH_3}$$

The products are made by the phosphation of a dimethicone copolyol. This is a derivitization step. The construction, functionalization and derivitization step for making silicone phosphates is shown in **Figures 13.3**, **13.4** and **13.5**[1].

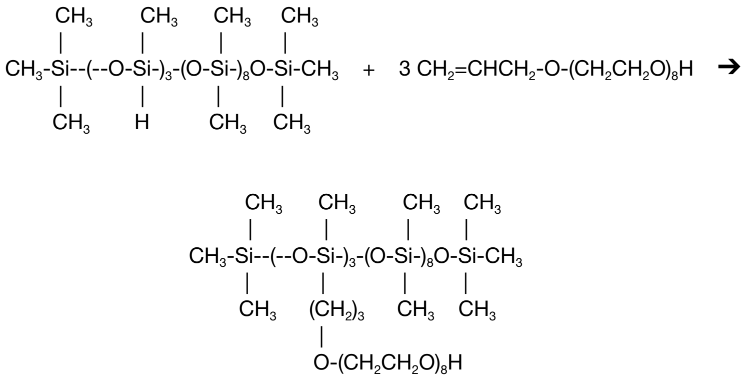
Figure 13.3. Silicone Phosphate: Construction



$$\mathrm{CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-}(\text{-}O\text{-}\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-})_3\text{-}O\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-}CH_3} \ + \ \mathrm{2\text{-}(O\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-})_{4^-}} \ \rightarrow \ \mathrm{CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{--}(\text{--}O\text{-}\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-})_3\text{-}(O\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-})_8O\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-}CH_3}$$

MD*M **D4** **MD*3D8M**

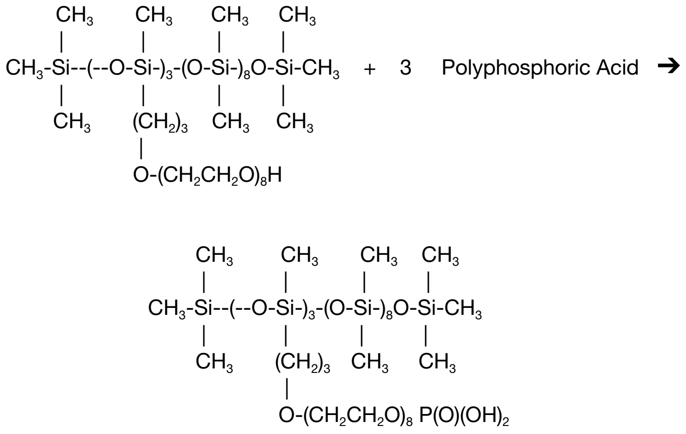
FIgure 13.4. Silicone Phosphate: Functionalization



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--(--O-}\underset{H}{\overset{CH_3}{Si}}\text{-)}_3\text{-(O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-)}_8\text{O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 \ + \ 3\ CH_2{=}CHCH_2\text{-O-}(CH_2CH_2O)_8H \rightarrow$$

$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--(--O-}\underset{\substack{(CH_2)_3\\ |\\ O\text{-}(CH_2CH_2O)_8H}}{\overset{CH_3}{Si}}\text{-)}_3\text{-(O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-)}_8\text{O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Figure 13.5. Carboxy Silicone Compounds: Derivitization



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--(--O-}\underset{\substack{(CH_2)_3\\ |\\ O\text{-}(CH_2CH_2O)_8H}}{\overset{CH_3}{Si}}\text{-)}_3\text{-(O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-)}_8\text{O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 \ + \ 3 \ \text{Polyphosphoric Acid} \rightarrow$$

$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--(--O-}\underset{\substack{(CH_2)_3\\ |\\ O\text{-}(CH_2CH_2O)_8\ P(O)(OH)_2}}{\overset{CH_3}{Si}}\text{-)}_3\text{-(O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-)}_8\text{O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

The reaction of the dimethicone copolyol to make the phosphate is conducted using PPA, which stands for polyphosphoric acid. It is used because there is a desire to obtain maximum monoester. This approach results in 90% monoester. The monoester, or MAP, is the most desirable for personal care applications.

Properties

The product evaluated for the preparation of the property data is described in Table 13.1.

Table 13.1. Silicone Phosphate Evaluated

INCI:	Dimethicone PEG-7 Phosphate
Molecular Weight:	3,000
CAS No:	132207-31-9
EINECS:	Polymer Exempt

Despite its low pH (range of 2–4), the silicone phosphate ester has an outstanding safety profile, outlined in **Table 13.2**.

Table 13.2. Safety Profile Silicone Phosphate 100% Active

Eye Irritation	NON-IRRITATING
Skin Irritation	NON-IRRITATING
Oral Toxicity	NON-TOXIC
Comedogenicity	NON-COMEDOGENIC

Silicone phosphate esters have solubility properties shown in **Table 13.3**.

Table 13.3. Silicone Phosphate Solubility

Solvent	10% wt
Castor Oil	d
Ethanol	s
Volatile Silicone	d
Mineral Oil	d
Propylene Glycol	s
Isopropoyl Myristate	i
Water	s

s = soluble i = insoluble d = dispersible

Silicone-based phosphate esters are substantive to hair, skin and fiber and provide antistatic properties. Since these compounds contain a pendant ionizable phosphate group, they provide antistatic and lubrication properties to the hair or fiber.

Silicone phosphate esters are acidic and can be neutralized to any desired pH with alkaline materials. The pH of the final formulation not only affects the solubility of the phosphate ester, but also has a profound effect upon other surfactant properties such as wetting, foaming and emulsification. The partially neutralized phosphate ester has solubility characteristics intermediate between those of the free acid and the completely neutralized phosphate ester.

PEG-7 dimethicone phosphate finds application in hair care, skin care and color cosmetics. It provides the following attributes to formulations:

- Emulsification
- Water-soluble emollient
- Foaming agent for body washes and shampoos
- Pigment wetting and dispersing agent
- Mild detergent/surfactant for facial cleansers and shampoos
- Hair conditioner to enhance combability and promote shine
- SPF booster
- Irritation reduction

Emulsifiers

As emulsifiers, silicone-based phosphate esters are efficient, producing emulsions of the o/w type, and quite useful as emulsifiers for personal care products such as moisturizing creams and lotions. They are particularly effective in producing creams and lotions containing sunscreens (both organic and inorganic), pigments, skin protectants and medicaments. Their emulsification properties allow for the use of these materials in one-step shampoos and other applications, including emulsion polymerization processes.

Dimethicone copolyol phosphates have been shown to be effective in making o/w emulsions of fluoro solvents that are transparent or translucent cosmetic emulsions.[4] The emulsions comprise an aqueous phase, a fatty phase and a surfactant, with the fatty phase containing a miscible mixture of at least one cosmetic oil and at least one volatile fluoro compound. These products find use of the emulsion in skin care, hair conditioning, sunscreens and/or artificial tanning.

When it is desired to obtain an emulsion as described of the o/w type, the use of an anionic or silicone surfactant comprising at least one phosphate is preferable.

Water-soluble Emollients

As water-soluble emollients, silicone phosphate esters can be used in aqueous systems. For example, they can be added to carbomer gels for emolliency without diminishing the clarity of the gel. Phosphating dimethicone copolyol renders the molecule more water-soluble, necessitating fewer moles of ethylene oxide for the same degree of water solubility. This allows for retention of much of the favorable aesthetics associated with the increased content of the dimethylpolysiloxane portion of the molecule.

Foaming Agents

As foaming agents, silicone-based phosphate esters produce higher levels of copious foam than what are produced by dimethicone copolyol polymers. The sodium and potassium salts of the phosphate esters tend to be slightly better foaming agents than the phosphate esters in their free acid or amine salt forms. Salts formed by the neutralization of dimethicone copolyol phosphate and myristamidopropyldimethyl amine are excellent foam boosters and conditioners in shampoo systems. Salts formed by the neutralization of dimethicone copolyol phosphate and linoleylamidopropyldimethyl amine are excellent emulsifiers for dimethicone in shampoo systems.

Silicone-based phosphate esters show good detergency, surface tension reduction, wetting, emulsification, dispersing properties and solubilization. Their detergent properties are generally considered to be equal to those of nonionic surfactants. However, the presence of the silicone moiety in the molecule results in improved mildness, substantivity and conditioning properties over conventional fatty-based phosphate esters. These properties make the products excellent candidates for incorporation into shampoos and other detergent systems for personal care products.

Silicone-based phosphate esters function as hair conditioners and have been found to have outstanding conditioning effects when applied to permanent waved hair.

SPF (Sun Protection Factor) Improvement

Inadequate dispersal of TiO_2 will result in agglomeration of TiO_2 particles leading to reduced sun protection factor (SPF). PEG-7 dimethicone phosphate has been found to be an excellent dispersant for inorganic sunscreens and other pigments. Substituting PEG-7 dimethicone phosphate for C12-15 alkyl benzoate and sorbitan isostearate (commonly used TiO_2 dispersants) increases SPF by more than 17%. Microscopic examination confirms the improved dispersion showing better uniformity of particles and more homogeneity. TiO_2 dispersions consisting of PEG-7 dimethicone phosphate are more uniform, preventing TiO_2 agglomeration compared to dispersion made with C12-15alkyl benzoate and sorbitan isostearate. **Table 13.4** shows the formulation evaluated for SPF studies and **Table 13.5** shows the SPF values obtained.

Dimethicone PEG-7 Phosphate has been found to be an SPF enhancing silicone by Phoenix Chemical.[5] PEG-7 dimethicone phosphate is a clear, 100% active, water-soluble silicone phosphate ester. It has been shown to be effective in boosting SPF of certain sunscreen formulations shown in **Table 13.6**. The results of the testing are shown in **Table 13.7**.

Comparing the corrected SPFs of test condition "A" and "B," the addition of PEG-7 dimethicone phosphate increased the SPF of the vehicle plus sunscreen by more than 47%. Furthermore, a comparison of test condition "C" and "D" (without sunscreen) indicates that PEG-7 dimethicone phosphate has no effect on the SPF

Table 13.4. SPF Formula

Premix 1	**Formulation 11-55-1**	**Formulation 11-56-1**
(a)		
PEG-7 Dimethicone Phosphate	60.00	--
C_{12-15}, Alkyl Benzoate	--	54.00
Sorbitan isostearate	--	6.00
(b)		
Titanium Dioxide	40.00	40.00
A		
Water (*aqua*)	61.45	61.45
Magnesium aluminum silicate	1.00	1.00
Methyl glueth 20	2.50	2.50
PEG20- Methyl glucose sesqusterate	0.75	0.75
Disodium EDTA	0.05	0.05
B		
Premix 1	12.50	12.50
Hvdroxvlated lanolin	3.00	3.00
Methvl glucose sesquisterate	4.00	4.00
Mineral oil (and) lanolin alcohol	5.00	6.00
PEG-100 stearate	5.00	5.00
PPG-3 Myristyl ether	3.00	3.00
C		
Propylene glycol (and) diazolidinyl urea (and) methylparaben (and) propyl paraben	1.50	1.50
Fragrance (parfum)	0.25	0.25

Procedure:

The compositions above were prepared as follows:

1. Premix (a) under a high shear homogenzier (e.g., a Silverson).
2. Slowly add (b) to (a) and homogenize for five minutes at 4,000 revolutions per minute.
3. Combine A and heat to 72-77°C with adequate agitation.
4. Separately combine B and heat to 75-80°C with adequate agitation.

cont.

Table 13.4. SPF Formula cont.

Procedure (cont.):

5. Add B to A with adequate agitation.
6. Pass AB through a colloid mill for five minutes or until completely recirculated.
7. With adequate agitation, the resulting emulsion is allowed to cool to 45°C.
8. Add C to AB with adequate agitation.
9. Adjust pH to 5.5 - 6.0 with 10% phosphoric acid.
10. Maintain adequate agitation is continued until the emulsion reaches 35°C.

Table 13.5. Comparison of SPFs of TiO_2

TiO_2 Dispersant	**Measured SPF**	**Formula**
C12-15 Alkyl benzoate and sorbitan isostearate	11.22	11-56-1
PEG-7 Dimethicone phosphate	13.14	11-55-1

Table 13.6. Formulations Tested

Test Formulations

A	A	B	C	D
Water (*aqua*)	qs	qs	qs	qs
Propylene glycol	5.00	5.00	5.00	5.00
Glycerin	2.50	2.50	2.50	2.50
PEG-7 Dimethicone phosphate	–	3.00	–	3.00
B	A	B	C	D
Ethylhexyl p-ethoxycinnamate	7.50	7.50	–	–
Oxybenzone	2.00	2.00	–	–
Isosteraryl behenate	4.00	4.00	4.00	4.00
Ceteraryl alcohol (and) ceteareth-20	1.50	1.50	1.50	1.50
Cetaryl alcohol	3.50	3.50	3.50	3.50
C	A	B	C	D
Propylene glycol (and) diazolidinyl urea (and) methylparaben (and) propylparaben	1.00	1.00	1.00	1.00

cont.

Table 13.6. Formulations Tested cont.

Procedure:

Combine and heat A to 70-75°C with an adequate agitation. Combine and heat B 70-75°C with adequate agitation. Add B to A with adequate agitation and cool to 45°C under adequate agitation. Add C to AB with adequate agitation cool to 35°C under adequate agitation.Irritation Reduction of SLS/SLES:

Table 13.7. Increased SPF

Formula	Description	Measured SPF	Corrected SPF*
A	Vehicle + Sunscreens	8.15	5.92
B	Vehicle + Sunscreens + 3% PEG-7 Dimethicone phosphate	10.86	8.74
C	Vehicle alone	2.23	–
D	Vehicle + 3% PEG-7 Dimethicone phosphate	2.12	–

*Corrected for Vehicle and Vehicle PEG-7 Dimethicone phosphate

of the vehicle. Therefore, it appears that PEG-7 dimethicone phosphate mode of action is to enhance the performance or efficiency of the vehicle rather than having a direct effect on UV-absorption or scattering.

Irritation Reduction of Sodium Lauryl Sulfate

PEG-7 dimethicone phosphate has shown the effectiveness of silicone phosphate esters in reducing irritation to the eye and skin as described in a patent.[3] It was determined that silicone phosphate esters can reduce eye and skin irritation of fatty alcohol sulfates or fatty alcohol ether sulfates by a factor of three.

Irritation Reduction of Alpha Hydroxy Acids (AHA)

Recently, independent studies indicate that PEG-7 dimethicone phosphate can significantly reduce the primary irritation index (PII) of glycolic acid by as much as 58%. The results are presented in **Table 13.8**.

Cosmetic Properties

- Silicone phosphate esters provide conditioning properties in hair care products, and are recommended for inclusion in products designed for use on damaged, chemically treated and ethnic hair. They improve wet and dry combing properties, reduce static and impart a soft, smooth feeling to hair, while enhancing luster and shine.

- The anionic characters of silicone phosphate esters form complexes with cationic conditioning agents, such as quaternary ammonium compounds and polyquaterniums. Silicone complexes are effectively used in rinse-off conditioners, shampoos, and styling products.
- Silicone phosphate esters are effective co-emulsifiers and emulsion stabilizers when used in the preparation of o/w emulsions, providing conditioning and emolliency in skin care formulation and can be used in creams, lotions and clear products (such as gels based on polyacrylate¨ polymers), where it will also improve spreading properties and reduce tack.
- Silicone phosphate esters are foaming products and are effective additives for use in skin cleansing formulations, including facial cleansers.
- Silicone phosphate esters are recommended for use in other clear, water-based systems, such as body washes and bath gels, where they provide a smooth, nongreasy skin feel and promote the soft, moisturized sensation that is generally associated with silicone additives.

Table 13.8. Reduction of Primary Irritation Index (PII) of Glycolic Acid

10% Glycolic acid solution alone	**10% Glycolic acid solution with 10% PEG-7 dimethicone phosphate**
PII* 3.88	PII* 1.63

<u>PII Scale</u>

0.0 – 0.5	Non-irritating
0.6 - 2.0	Mild
2.1 - 5.0	Moderate
> 5.1	Severe

Higher Molecular Weight Silicone

A new higher molecular weight silicone phosphate ester has been prepared and patented.[4] Applications and use levels for the product are described in **Table 13.9**.

The new material features a molecular weight of 9,000 and offers several advantages over the older 3,000 MW products. **Table 13.4** shows that the surface tension of the higher molecular weight silicone phosphate is higher than the surface tension for the lower molecular weight silicone phosphate ester. Likewise, the surface tension of the higher molecular weight PEG-7 dimethicone, from which the silicone phosphate esters, were made is higher in surface tension than the lower molecular weight PEG-7 dimethicone. Finally, the phosphation of the dimethicone copolyol reduces the surface tension in both the high molecular weight and the low molecular weight model.

Table 13.9. Dimethicone Copolyol Phosphate Application

Applications

Applications for this high performance, functional, silicone ingredient include:

Product Type	Use Level	Function
Shower gels	2.5-5%	Irritation Mitigation
Shampoos	1-3%	Foam Modifier/Conditioner
Facial Cleaners/ Make-up Remover	2.5-5%	Irritation Mitigation Surfactant
Lotions	1-5%	Emulsifier
Creams	5-12%	Emulsifier
Hair Conditioners	2-10%	Emulsifier/Conditioner
Foundations	1-12%	Emulsifier/Pigment Wetter
Sun Screens (Organic)	2-10%	SPF Enhancement
Sun Screens (Inorganic)	2-10%	SPF Enhancement/Pigment Wetter

Table 13.10. Surface Tension Data
Silicone Phosphate Esters of Different Molecular Weight

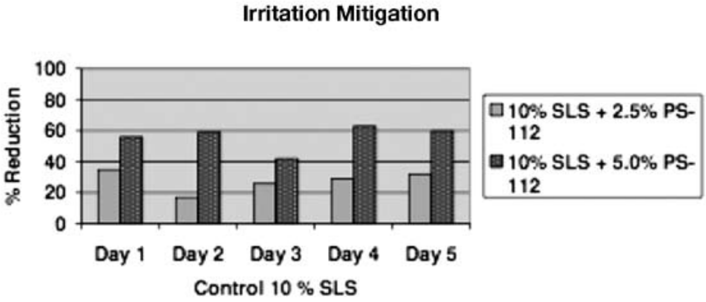
Sample I.D.	MW	Concentration	Surface Tension (mN/m)
PEG-7 Dimethicone A	3,000	0.1%	25.2
PEG-7 Dimethicone B	9,000	0.1%	28.9
PEG-7 Dimethicone Phosphate A	3,000	0.1%	23.5
PEG-7 Dimethicone Phosphate B	9,000	0.1%	26.9

The higher molecular weight product offers some distinct advantages in many applications.

Irritation Mitigation

Figure 13.6 outlines the irritation mitigation of sodium lauryl sulfate (SLS) and sodium lauryl ether sulfate.

Figure 13.6. Dimethicone Copolyol Phosphate

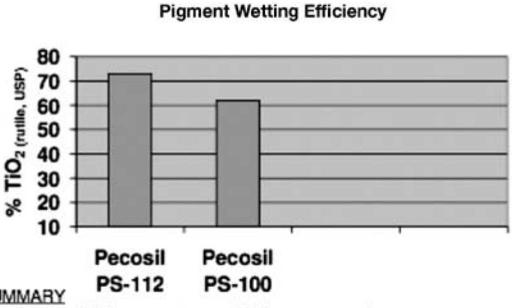


SUMMARY
At 2.5% **PECOSIL PS-112**, erythema reduction averaged 27%.
At 5.0% **PECOSIL PS-112**, erythema reduction averaged 55%.
Irritation mitigation continued after 5-days of repeated insult.

Pigment Wetting

Figure 13.7 shows that Pecosil PS-112, the higher molecular weight silicone phosphate ester, is a better pigment wetter than Pecosil PS-100, the lower molecular weight silicone phosphate ester.

Figure 13.7. Dimethicone Copolyol Phosphate



PS-100 is lower molecular weight than PS-112.

SUMMARY
Pecosil PS-112 demonstrates a 16% improvement for pigment wetting over Pecosil PS-100.

Emulsification

Using the formulation and procedure outlined in **Table 13.11**, the emulsification ability of the two different molecular weight silicone phosphate esters were evaluated. **Figure 13.8** shows the results. The higher molecular weight silicone phosphate ester is a better emulsifier than the lower molecular weight silicone phosphate ester.

Table 13.11. Emulsification Efficacy Test Method

Objective:

Determine the emulsification efficacy of a raw material.

Materials:

- Pelemol GTIS (INCI: Glyceral Triisosterate)
- Lanette 16NF (INCI: Cetyl Alcohol)
- 60mL B.D. Disposable Syringes with Luer Lock tip (x2) (B.D. REF# 309653)
- Three way male needle-lock luer to female luer to side female luer (Aldrich REF# 250658-3)

Method of Measurement:

Visual subjective evaluation

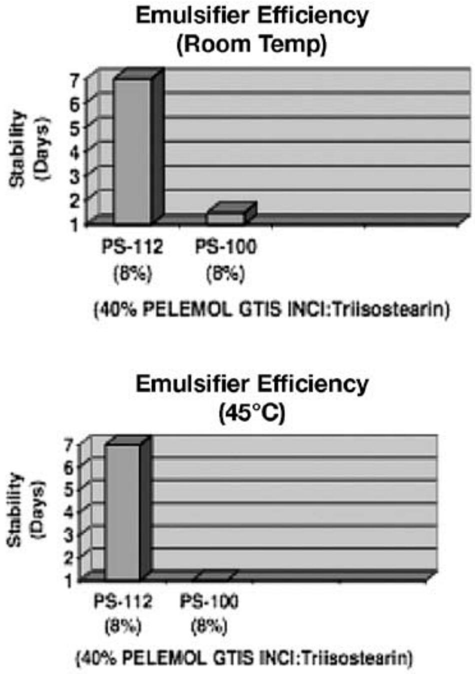
Procedure:

1. Prepare 50g of a test emulsion according to test formula
2. Combine phase A and heat to 65-75°C to liquefy cetyl alcohol. Mix until uniform.
3. Fill the first disposable, 60mL B.D. syringe with phase A.
4. Combine phase B and heat to 65-75°C.
5. Fill second syringe with phase B.
6. Attach both syringes with the luer lock valve and ensure they form a tight seal.
7. Slowly dispense contents of one syringe through the valve into the other. Repeat vigorously 10 times until uniform. Cool to 20-30°C with continued dispensing.

Test Formula Emulsion

Phase	Trade Name	%W/W
A	Pelemol GTIS (INCI: Glyceral Triisosterate)	40.00
A	Lanette 16 NF (INCI: Cetyl Alcohol)	1.00
B	Test Material (Active)	8.00
B	Deionized Water	51.00
	Total	100.00

Figure 13.8. Dimethicone Copolyol Phosphate



SUMMARY

Pecosil PS-112 demonstrates superior stability performance over Pecosil PS-100 for a primary emulsifier of a Triglyceride. (PELEMOL GTIS). Emulsions formulated with **Pecosil PS-112** demonstrated stability beyond 1 week at R.T./45°C while Pecosil PS-100 versions separated under 12 hours.

Patents

(1) US Patent 7,153,493 issued Dec. 26, 2006, to Nelson titled "Clear oral compositions containing potassium salt" teaches oral cavity, comprising an effective amount of a soluble potassium salt, a sodium alkylsulfate in an amount effective to remove or loosen debris and/or stains from a surface, and a polar surfactant, said surfactant comprising a hydrophobic portion selected from a alkyl group and a polymeric silicone group. Some specific examples of derivatized polydimethylsiloxane copolyols including dimethicone copolyol phosphate.

(2) US Patent 6,986,809 issued Jan. 17, 2006, to Spencer, titled "Erasable inks, writing instruments, and methods" discloses erasable inks provided for use in a writing instruments. In one aspect, the inks include a solvent, and, dispersed in the solvent as a colorant, a pigment having a flake-like morphology, the ink being

Patents cont.

substantially free of other colorants. Examples of suitable dispersants include, but are not limited to, anionic dimethicone copolyol phosphates.

(3) US Patent 6,733,798 issued May 11, 2004, to Heeg, titled "Cranberry seed oil, cranberry seed flour and a method for making" discloses that when used as a skin care product, such as a sunscreen or treatment for lesions, the cranberry oil may be blended with other ingredients. These other ingredients include emulsifiers. The emulsifiers may be used to make an o/w emulsion or a w/o emulsion. Emulsifiers may be anionic, cationic or nonionic and either in a liquid or a solid phase at room temperature. A suitable emulsifier is dimethicone copolyol phosphate.

(4) US Patent 6,602,515 issued August 5, 2003, to Chandri, titled "Photostable organic sunscreen compounds with antioxidant properties and compositions obtained therefrom" discloses the incorporation of dimethicone copolyol phosphate in photostable sunscreens.

(5) US Patent 6,287,582 issued Sept. 11, 2001, to Gott, titled "Towelette product" discloses a disposable towelette product, which includes a flexible water-insoluble substrate such as a tissue impregnated with an alpha-or beta-hydroxycarboxylic acid in a cosmetically acceptable carrier vehicle. Impregnated cosmetic composition in water will have a pH no higher than 6.8. A silicone microemulsion is present to minimize any stickiness resulting from deposition of the hydroxycarboxylic acid by the towelette onto the skin. An example of a derivatized polydimethylsiloxane copolyol is dimethicone copolyol phosphate.

(6) US Patent 5,993,832 issued Nov. 30, 1999, to Lorant, titled "Oil-in-water emulsion, a composition comprising this emulsion and use of this emulsion in cosmetics and in hygiene" discloses an o/w emulsion comprising an aqueous phase, a fatty phase, at least one silicone surfactant comprising at least one anionic group and at least one acidic compound other than the silicone surfactant and a composition comprising such an emulsion. The invention also relates to the use of a silicone surfactant comprising at least one anionic group for the preparation of a stable emulsion comprising at least one acidic compound other than the silicone surfactant.

(7) US Patent 5,908,619 issued June 1, 1999, to Scholz, titled "Hydroalcoholic compositions thickened using surfactant/polymer complexes" teaches hydroalcoholic compositions and methods of preparation are provided. The composition includes a lower alcohol and water in a weight ratio of at least 20:80, and a thickener system comprising a complex of at least one charged polymer and at least one oppositely charged surfactant. Suitable acidic polymers include acidic functionality such as hydrogen sulfate, sulfonic acid, hydrogen phosphate, phosphonic acid, and carboxylic acid. Examples of suitable polymers with acidic functionality include polymers containing free acid groups; dimethicone copolyol phosphate is also suitable.

(8) US Patent 5,362,484 issued Nov. 8, 1994, to Wood, titled "Hair care composition for conditioning hair with silicone oil" discloses a hair care composition for conditioning hair with silicone oil comprising a stable emulsion of water-insoluble hair conditioning silicone oil dispersed in a liquid carrier composed essentially of polyoxyalkylene glycol and an emulsifier consisting of a silicone phosphate salt, in which the anionic moiety comprises a copolymer of dimethylpolysiloxane and polyoxyethylene.

Patents cont.

(9) US Patent 5,332,569 issued July 26, 1994, to Wood, titled "Hair care composition for conditioning hair with silicone oil" discloses a liquid hair care composition for conditioning hair with silicone oil comprising a stable emulsion of a water-insoluble hair conditioning silicone oil dispersed in a liquid carrier composed essentially of polyoxyalkylene glycol and an effective emulsifying amount of a complex formed from (i) an anionic copolymer of dimethylpolysiloxane and polyoxyethylene, wherein the siloxane chain contains from 20–40 dimethylsiloxy units and the oxyethylene chain contains from 3–15 oxyethylene units, and terminates in an anionic phosphate or sulfate group; and (ii) a cationic hair conditioner compound containing at least one cationic quaternary nitrogen or amido amine group and at least one hydrophobic aliphatic or silicone polymer chain.

(10) US Patent 5,302,378 issued April 12, 1994, to Crotty, titled "Self-tanner cosmetic compositions" discloses a composition and method for self-tanning of skin is provided which includes an alpha-hydroxy substituted ketone or aldehyde such as dihydroxyacetone, an anionic silicone copolyol such as dimethicone copolyol phosphate and a pharmaceutically acceptable carrier. Advantageously, at least 15% propylene glycol may also be incorporated to improve color intensity.

(11) US Patent 5,232,688 issued August 3, 1993, to Ziegler, titled "Self-tanner cosmetic compositions" discloses a composition and method for self-tanning of skin is provided which includes an alpha-hydroxy substituted ketone or aldehyde such as dihydroxacetone, a polyacrylamide and a pharmaceutically acceptable carrier. Advantageously, there may also be incorporated at least 15% propylene glycol to improve color intensity, containing a dimethicone copolyol phosphate.

Conclusion

The introduction of an anionic phosphate group onto a dimethicone copolyol introduces a number of desirable properties. These properties, as in all silicones, are related to the structure. The comparison of silicone phosphate esters with different molecular weights offers insights into the importance structure to function. The abundance of applications patents over a range of time (1993–2006) is an indicator of the level of interest in these materials.

References:

1. US Patent 5,149,765 issued September 22, 1992 to O'Lenick, Anthony, titled "Terminal phosphated silicone polymers".
2. US Patent 6,175,028 issued Jan 16, 2001 to to O'Lenick, Anthony, titled "Silicone alkyl phosphate esters".
3. US Patent 5,859,161issued Jan 12, 1999 to Imperante, John et al, titled "Silicone phosphate esters as irritation mitigants"
4. US Patent 6,419,909., issued July 16, 2002, to Lorant et al titled "Transparent or translucent emulsions, process for preparing them and cosmetic use thereo".

Chapter 14

Silicone Resins

This chapter deals with elastomers and resins. This is one of the newer areas of growth in the silicone market. These products find use in skin care products to provide a powdery feel, in hair care applications for volumizing effects and substantivity, and most recently in transfer-resistant pigmented products.

There is a great deal of confusion as to the proper meaning of the terms “fluid,” “elastomer,” “resin” and “gum.” This is due in part to patent litigation. In the patent litigation process, words are used within the context of a patent, are defined by that patent and have meaning only within the patent. This is due to the ability of the patent writer to draft and define words, and as long as those definitions are used consistently, that is authors of patents can use words with a different than commonly used meaning.

Fortunately, most of us do not live in the *Alice through the Looking Glass* world of patent litigation. A world where words mean exactly what the inventor wants them to mean, no more, no less. Words used by chemists need proper definitions.

According to the Wikipedia entry for silicone, “Silicone resins are a type of silicone material which is formed by branched, cage-like oligosiloxanes with the general formula of $R_nSiX_mO_y$, where R is a nonreactive substituent, usually Me or Ph, and X is a functional group of H, OH, Cl or OR. These groups are further condensed in many applications, to give highly cross-linked, insoluble polysiloxane networks.

When R is methyl, the four possible functional siloxane monomeric units are described as follows:

- “M” stands for Me_3SiO
- “D” for Me_2SiO_2
- “T” for $MeSiO_3$
- “Q” for SiO_4

Answers.com defines silicone resins as “polymers composed of alternating atoms of silicon and oxygen with organic substituents attached to the silicon atoms. Silicones, also called organopolysiloxanes, may exist as liquids, greases, resins or rubbers. Silicone polymers have good resistance to water and oxidation, stability at high and low temperatures and lubricity.”

Chenguang-chemi.com states that “silicone resins are mixtures of solvent (toluene or xylene) with combined hydrolyzates of methyl chlorosilanes and phenyl chlorosilanes containing some amount of hydroxyl groups. The hydroxyl can be further condensed into a hard film under heating.”

Clearly, what is meant by resin in the personal care world is something different. Other definitions are needed.

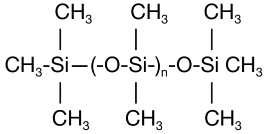
Definitions

A. Silicone Fluid

Silicone fluids are linear polymers; structures are shown in **Figure 14.1**.

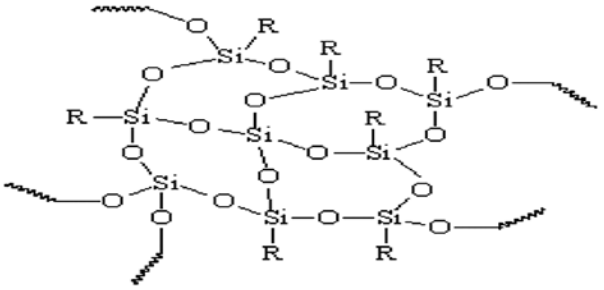
Figure 14.1. Silicone Fluid and Resin

Silicone Fluid



$$CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-(\text{-}O\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-})_n\text{-}O\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\ CH_3$$

Silicone Resin



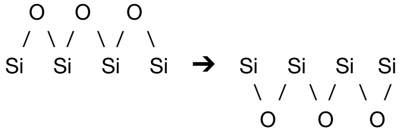
R= Me, OH, H.

They have no cross-linking and as such are free to rotate. This free rotation makes them liquid. Silicone fluids can have increased viscosity, but are never solid. They can have very high viscosity, but are still liquid. **Figure 14.2** shows a graphic of the free rotation around a Si-O-Si backbone with no cross-linking. Since the rotation is merely a change in confirmation, it proceeds with a low level of energy, in a rather common manner.

B. Silicone Gum

As the number of "D" units is increased, the viscosity of the fluid increases. At a certain viscosity (will be system dependant), the fluid becomes too thick to pour. It has no cross-linking but simply has high viscosity. This thick silicone fluid is referred to as a gum. Gums may have organic functionality on them, but no cross-linking. It is therefore proper to refer to an alkyl silicone with a very high viscosity as an alkyl gum, or a vinyl containing material that has a high viscosity but no cross-linking as a vinyl gum. If the vinyl group were to be reacted with silanic hydrogen (Si-H), the material would cease to be a fluid or gum and become either an elastomer or resin. The difference between a gum and a fluid therefore is physical, not chemical. The term gum is applied to a material with a viscosity that renders it impossible to pour. Since a gum refers to the viscosity at which pouring becomes impossible, the molecular weight at which this occurs for a fluid will be a different molecular weight than the one at which an alkyl becomes a gum. Consequently, the term gum refers to a physical property, not a chemical one.

Figure 14.2. Silicone Fluid Rotation



The Encyclopedia of Chemical Technology suggests that silicones with no functionality become gums with a molecular weight range of about 140,000 to 350,000.

US Patent 6,328,983 to Afriat states: "For the purposes of the present invention, the term 'silicone gum' is applied to linear noncross-linked polydimethyl siloxanes which may be hydroxylated or phenylated, and which have the consistency of a thick oil or transparent solid, in contrast to the alkyl-and alkoxy dimethicones which, when solid, have an opaque waxy appearance, but which may also have the appearance of a clear oil when their melting point is lower than room temperature. Silicone gums preferably have a viscosity equal to or greater than 200,000 cSt (0.2 m.sup.2/s) and, preferably, greater than 300,000 cSt (0.3 m.sup.2/s), this viscosity being measured on a Brookfield viscometer at 25°C."

C. Cross linked Silicone

As cross-linking is introduced into the molecule, either cross-linking through silicone (as in Q or T compounds) or with organic compounds (as in -(CH_2)n-), the ability to freely rotate in the fluids is compromised. The material becomes an elastomer or resin. The INCI name will change from dimethicone to names specified in "Organosilicone Nomenclature Conventions" issued August 13, 1999. The section related to polymers is in **Table 14.1** and the entire work is contained in **Appendix A**. The convention, by and large, allows for the assignment of an INCI name for cross-linked silicones.

Table 14.1. Organosilicone Nomenclature Conventions

August 13, 1999

****

The conventions for the definitions, INCI name classifications,
and recommendations for changes to existing INCI names

****

Silsesquioxanes

Silsesquioxanes are based on the T siloxane unit (the empirical formula is $RSiO_{3/2}$). If the R group is anything other than methyl, it must be specified by a prefix (e.g. if R = phenyl, then it would be phenylsilsesquioxane). The presence of a third polymerization site on silicon leads to a variety of three-dimensional structures such as ladder, cage and partial cage structures. The condensation of T units to form these structures is reversible and depends strongly upon processing conditions. Because of this, it is impossible to write definite structures for these compounds. The size of the silsesquioxane polymer is often controlled by the introduction of M (terminal) units (e.g. trimethylsiloxy, vinyl dimethylsiloxy), and this must be indicated in the name. For example, a polymer made up of M and T units where all the organic substituents are methyl would be called Trimethylsiloxymethylsilsesquioxane. Co-polymerization with D units is also possible, and these are named according to established INCI rules (e.g. Dimethiconol/Silsesquioxane Copolymer).

The only exception to this rule is for pre-existing Phenyl Trimethicone and Caprylyl Trimethicone. The current definition would not change and will reflect the M and T unit in structure of this silsesquioxane.

Silicates

Silicates are based on the Q 3-dimensional structure as random, ladder, cage and partial cage structures. They have empirical formulas of $SiO_{4/2}$. Silicates may be reacted with M, D, and T units which must be indicated in the name (e.g., Trimethylsiloxysilicate)

Copolymer and Crosspolymer

The terms Copolymer and Crosspolymer are used in the same way as in the naming of organic polymers.

Other

When there is a question about how to name a new silane or silicone and it does not fall into one of the categories set forth above, then the default will be silyl ($\equiv$Si-) or siloxy ($\equiv$Si-O) root as part of the nomenclature and conventional INCI protocol for organic containing portion.

In certain cases, Polysilicone-X will be used for complex silicon-containing polymers.

It is important to note that the terms "gum," "elastomer," "resin" or "fluid" do not appear in the INCI document, meaning it is chemistry, not physical properties, that dictate INCI names. This approach seems proper. However, the terms are sometimes misused in the literature.

The terms elastomer and resin refer to properties of silicone produced during the cross-link process. An elastomer is a cross-linked silicone that is rubbery. Unlike a silicone fluid, an elastomer has its ability to rotate limited by cross-linking. **Figure 14.3** shows a graphic of this. The methyl groups have been omitted. A resin is a hard cross-linked silicone polymer. **Figure 14.4** shows a graphic of a resin. The methyl groups have been omitted. The degree of cross-linking is high and a "crumbly" solid product results.

Figure 14.3. Silicone Elastomer Rotation
(Presence of crosslink limits free rotation)

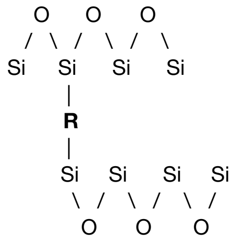
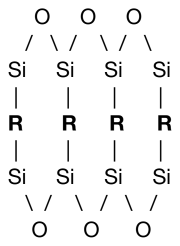


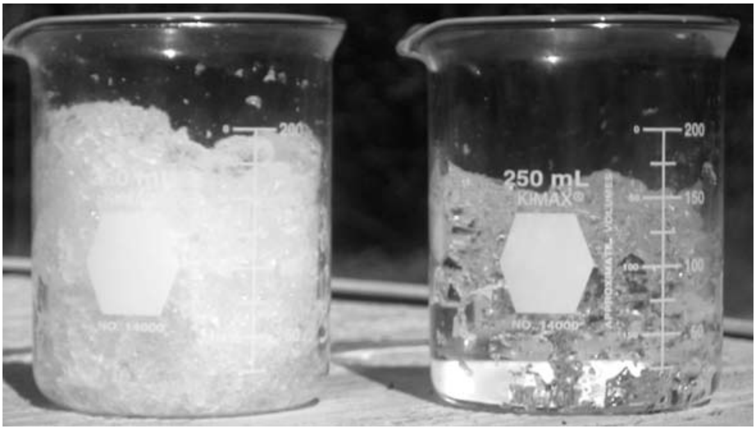
Figure 14.4. Silicone Resin Rotation
(Presence of high level crosslink stops rotation)



The number and length of the cross-linking groups will determine if the resulting polymer is a resin or elastomer. If the cross-linking group (the "R" group in **Figure 14.3**) is very long or the silicone backbone is very long then the number of cross-linking groups needed to form an elastomer or resin will be higher than if the cross-linking group is short or the number of cross-linking groups per silicone group is low. The difficulty here is that the terms describe a physical property not a chemical one. The presence of organic functional groups on the silicone backbone can also alter the point at which a molecule is either an elastomer or resin.

Figure 14.5 contains a picture of a resin and an elastomer. The elastomer is a soft rubbery material which will maintain its shape when dumped onto a table, will seal when cut and will have a sticky feeling. The resin will be much harder and crumble to the touch. The material will be resilient and bounce.

Figure 14.5



Silicone resins (right) are powdery and crumble when put under pressure. Silicone Elastomers are rubbery (left). *Photo by Kevin O'Lenick*

Table 14.2 describes properties of silicone fluids, elastomers and resins.

Table 14.2. Properties

Material	Crosslink	Physical State	Play Time	Use
Silicone fluid	None	Liquid	Long	Pigment dispersant
Silicone elastomer	Low	Gel	Short	Sebum removal
Silicone resin	High	Solid	None	Lipstick film

Cross-linking Groups

Cross-linking groups are used to make elastomers and resins. There are a number of cross-linking materials that are commonly encountered. They fit into two categories: silicone cross-linkers and organo-cross-linkers.

Silicone Cross-linkers

a. T groups
b. Q groups

The structures of the "T" and "Q" groups are shown in **Figures 14.6** and **14.7**, respectively. Since "T" groups provide one cross-link per group and "Q" groups provide two, in order to get a resin more "T" groups per molecule are needed than if "Q" groups are used. "T" groups are commonly used in elastomer and "Q" groups in resins.

Figure 14.6. "T" Cross-Linked Silicone

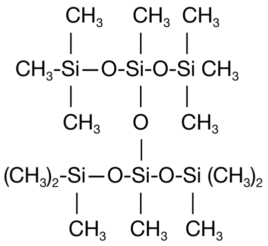
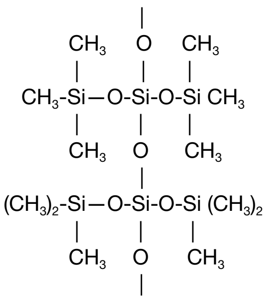


Figure 14.7. Q Cross-linked Silicone



Organo-cross-linkers

The organo cross-linkers are generally added by hydrosilylation (functionalization). In this particular version of functionalization, a divinyl compound is reacted with a silanic hydrogen containing compound. The result is a new Si-C bond.

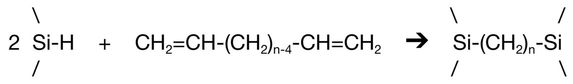
a. Methylene groups

The cross-linking group is -$(CH_2)n$-; the value of "n" ranges from two to 20. The value of two comes from the reaction of acetylene. The higher values come from the reaction of alpha omega divinyl compounds shown in **Figure 14.8**. The reaction is shown in **Figure 14.9**.

Figure 14.8. Methylene Cross-linking Reagent

$CH_2{=}CH{-}(CH_2)_n{-}4{-}CH{=}CH_2$

Figure 14.9. Methylene Cross-linking Reaction

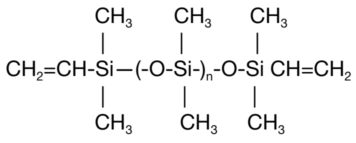


$$\begin{array}{cccccc} & \backslash & & & & \backslash \qquad\qquad / \\ 2 & Si{-}H & + & CH_2{=}CH{-}(CH_2)_{n-4}{-}CH{=}CH_2 & \rightarrow & Si{-}(CH_2)_n{-}Si \\ & / & & & & / \qquad\qquad \backslash \end{array}$$

b. Vinyl silicone groups

The cross-linking moiety is generally an alpha omega double bond. One of the compounds that meet this requirement is either a comb or a terminal silicone vinyl compound. Multifunctional vinyl materials lead to greater cross-link density if they contain more than two such bonds. **Figure 14.10** shows terminal silicone vinyl compounds ($M^*(D)_xM^*$). **Figure 14.11** shows comb vinyl silicone compounds.

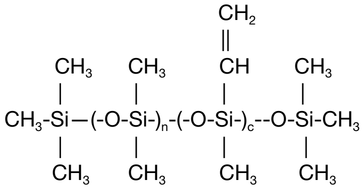
Figure 14.10. Terminal Vinyl Silicone Fluid



$$\begin{array}{lcccc} & CH_3 & & CH_3 & CH_3 \\ & | & & | & | \\ CH_2{=}CH{-}&Si & {-}({-}O{-} & Si{-})_n{-}O{-} & Si\ CH{=}CH_2 \\ & | & & | & | \\ & CH_3 & & CH_3 & CH_3 \end{array}$$

The reaction of silanic hydrogen polymer (shown as Si-H) with terminal vinyl silicone is shown in **Figure 14.12** and the reaction with comb vinyl silicone is shown in **Figure 14.13**.

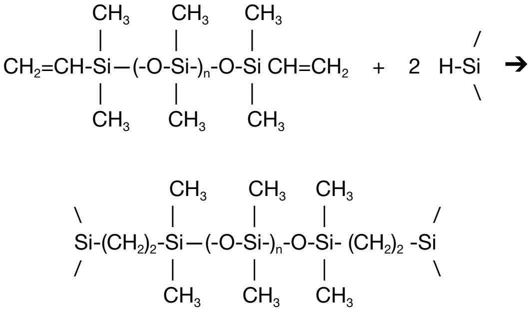
Figure 14.11. Comb Vinyl Silicone Fluid



$$CH_3\text{-}Si(CH_3)_2\text{—}(\text{-}O\text{-}Si(CH_3)_2\text{-})_n\text{-}(\text{-}O\text{-}Si(CH_3)(CH{=}CH_2)\text{-})_c\text{--}O\text{-}Si(CH_3)_2\text{-}CH_3$$

"c" is 2 or greater.

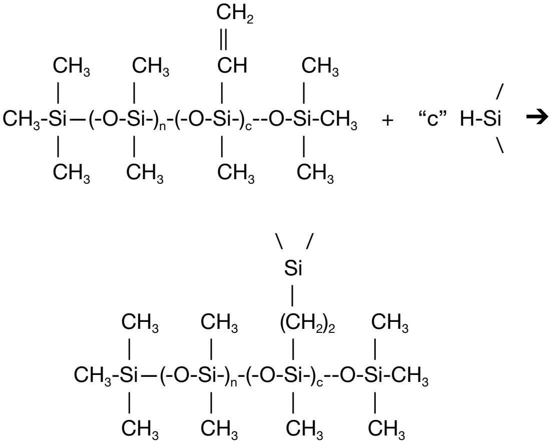
Figure 14.12. Crosslink Reaction of Terminal Vinyl Silicone Fluid



$$CH_2{=}CH\text{-}Si(CH_3)_2\text{—}(\text{-}O\text{-}Si(CH_3)_2\text{-})_n\text{-}O\text{-}Si(CH_3)_2\,CH{=}CH_2 + 2\ H\text{-}Si{<} \rightarrow$$

$${>}Si\text{-}(CH_2)_2\text{-}Si(CH_3)_2\text{—}(\text{-}O\text{-}Si(CH_3)_2\text{-})_n\text{-}O\text{-}Si(CH_3)_2\text{-}(CH_2)_2\text{-}Si{<}$$

Figure 14.13. Comb Vinyl Silicone Fluid



$$CH_3\text{-}Si(CH_3)_2\text{—}(\text{-}O\text{-}Si(CH_3)_2\text{-})_n\text{-}(\text{-}O\text{-}Si(CH_3)(CH{=}CH_2)\text{-})_c\text{--}O\text{-}Si(CH_3)_2\text{-}CH_3 + \text{"c"}\ H\text{-}Si{<} \rightarrow$$

$$CH_3\text{-}Si(CH_3)_2\text{—}(\text{-}O\text{-}Si(CH_3)_2\text{-})_n\text{-}(\text{-}O\text{-}Si(CH_3)((CH_2)_2\text{-}Si{<})\text{-})_c\text{--}O\text{-}Si(CH_3)_2\text{-}CH_3$$

"c" is 2 or greater.

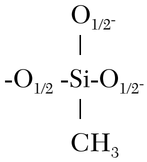
Clearly, the comb silanic hydrogen will result in a greater cross-link density than the terminal. Also, it is important to note that the reaction with a terminal vinyl group results in a different cross-link group than by reaction with an alkyl group. The cross-link group in the case of a terminal vinyl silicone is a silicone chain, not an alkyl chain.

Chemistry

Siloxysilicates "T compounds"

These compounds are branched compounds consisting of T units. The most common products are called by the INCI name polymethylsilsesquioxane.

"T unit" is trisubstituted (three oxygen atoms on silicon)



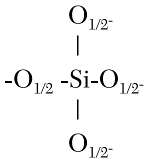
$$\begin{array}{c} O_{1/2}- \\ | \\ -O_{1/2}\text{-Si-}O_{1/2}- \\ | \\ CH_3 \end{array}$$

This class of compounds is commonly made from chlorosilane (Cl_3SiCH_3).

Siloxysilicates "Q compounds"

These compounds are highly cross-linked resins and are seen commonly in cosmetic formulations.

"Q unit" is tetrasubstituted (four oxygen atoms on silicon)



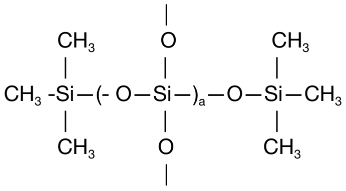
$$\begin{array}{c} O_{1/2}- \\ | \\ -O_{1/2}\text{-Si-}O_{1/2}- \\ | \\ O_{1/2}- \end{array}$$

This class of compounds is commonly made from tetrachlorosilane (Cl_4Si) or silicates.

MQ Compound

The structure of this type of product is shown in **Figure 14.14**.

Figure 14.14. MQ Compound



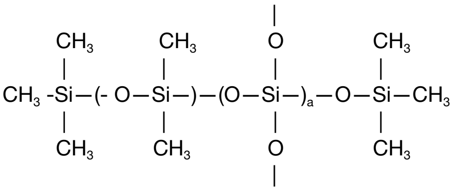
$$\begin{array}{ccccc} & & | & & \\ & CH_3 & O & CH_3 & \\ & | & | & | & \\ CH_3 & \text{-Si}-(\text{- O}- & \text{Si} & -)_a-O-\text{Si}- & CH_3 \\ & | & | & | & \\ & CH_3 & O & CH_3 & \\ & & | & & \end{array}$$

The molecule has only "M" and "Q" groups, hence the name "MQ compound." This type of product has the highest cross-link density and consequently is a resin (plastic-like). These compounds are commonly drying to the skin and often are formulated with silicone fluids as plasticizers.

MDQ Compound

This type of product has the following structure. It has not only "M" and "Q" groups, but also "D" groups, hence the name "MDQ resin." This type of product has lower cross-link density than the MQ resin and can be engineered to be either a resin (plastic-like) or an elastomer (rubbery) depending upon the Q to D ratio. Shown in **Figure 14.15**.

Figure 14.15. MDQ Compounds



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}-(\text{-}\,O-\underset{CH_3}{\overset{CH_3}{Si}}-)-(O-\underset{\underset{|}{O}}{\overset{\overset{|}{O}}{Si}}-)_a-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

Copolymers

Alpha omega alkyl divinyl based polymers

The hydrosilylation reaction allows for cross-linking of silanic hydrogen compounds using alpha omega containing di-olefins. This gives a very different linkage, resulting in products with different properties. If the number of carbon atoms between the olefinic linkages is high, the resin will have better hydrocarbon solubility. The reaction is depicted in **Figure 14.16**.

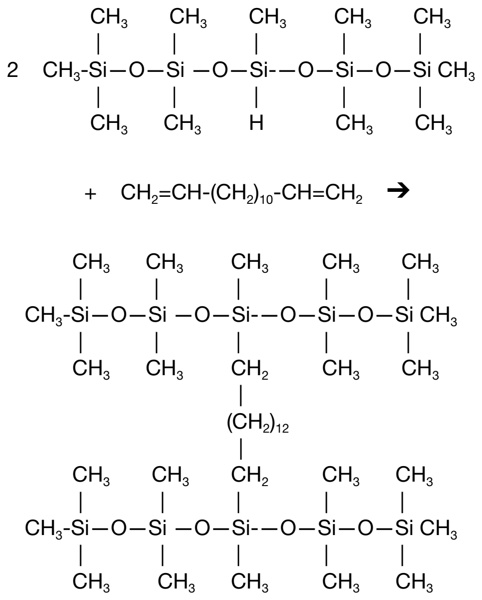
A wide variety of cross-linking agents are available to make these materials, ranging from a short group ($\text{-}CH_2CH_2\text{-}$) to a much longer–$(CH_2)_8$-. Clearly the number of methylene groups will have an impact upon hydrocarbon solubility (the greater the alkyl % of the molecule, the greater the oil solubility), and the hardness, (the fewer the methylene groups, the harder the polymer).

Alpha omega divinyl silicone based polymers

The hydrosilylation reaction allows for cross-linking of silanic hydrogen compounds using alpha omega containing silicones. The reaction is depicted in **Figure 14.17**. Despite the ability to alter the number of Si groups in the cross-linker, there are always exactly two methylene groups between the Si that bear the Si-H and that which are on the vinyl compound. This is because the cross-linker is a vinyl silicone.

A wide variety of "D" units in the cross-linking agents are available to make these materials, giving very different polymers.

Figure 14.16. Alkyl Divinyl Reaction



$$2\ CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{H}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\ CH_3$$

$$+\ CH_2{=}CH\text{-}(CH_2)_{10}\text{-}CH{=}CH_2 \rightarrow$$

$$\begin{array}{c} CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{CH_2}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\ CH_3 \\ | \\ (CH_2)_{12} \\ | \\ CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{CH_3}{\overset{CH_2}{Si}}\text{—}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}O\text{—}\underset{CH_3}{\overset{CH_3}{Si}}\ CH_3 \end{array}$$

Applications

The list where these types of products find applications is both long and growing. It is perhaps one of the fastest growing areas of silicone chemistry today.

Silsesquioxanes

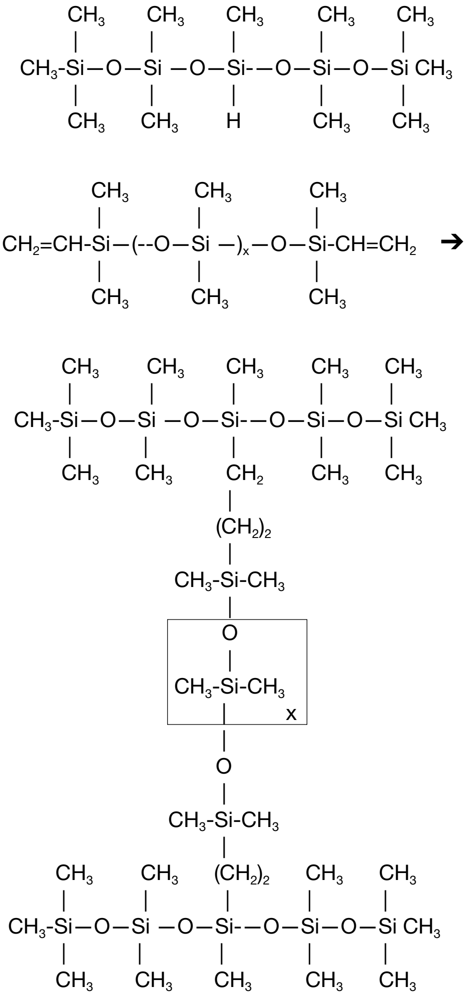
These compounds are used in pigment grinding applications. They allow for better uniformity of grind and subsequently better pigment dispersibility. They are used in hair set holding agents. In these applications the compounds provide outstanding hold and humidity resistance, and can be formulated easily. Finally, this class of compounds is incorporated into powders to maintain a free-flow attribute.

Siloxysilicates

MQ resins can find use in transfer-resistant lipsticks[1] and have some of the following characteristics:

- M/Q ration 0.7 to 1.0
- Molecular weights of 1,000 to 10,000
- This product is soluble in organic solvents, but not in silicone
- Forms a rather brittle film that holds pigment well but needs placticizers like silicone fluid
- Generally sold in a solvent

Figure 14.17. Silicone Divinyl Reaction



MDQ resins are generally provided in solutions like cyclomethicone, have a powdery feel, and find applications in skin care for this reason. In addition, they increase deposition on hair, are reported to be volumizing agents, and have been put into emulsions and can be delivered into aqueous systems in this form.

Copolymers

These compounds can be made in MD*M versions or MD*DM versions, and as such can be thought of as more organic-friendly versions of the MQ resin and the MDQ resin. Pigmented products and skin care are two very active areas of research in this area.

Patents

Typical of the patents related to the cosmetic industry including silicone elastomers and resins are:

(1) US Patent 7,175,836 issued Feb. 13, 2007, to Hart et al., titled "Oil continuous phase cosmetic emulsions with conjugated linoleic acid" discloses a cosmetic w/o composition that includes a w/o emulsifying silicone surfactant, cross-linked silicone elastomer and conjugated linoleic acid. The conjugated linoleic acid functions to improve radiance on facial surfaces to which the composition is topically applied.

(2) US Patent 7,118,733 issued Oct. 10, 2006. to Butts et al., titled "Topical silicone compositions and method for making" discloses a silicone composition which comprises at least one polysiloxane or silicone resin, and at least one molecular hook wherein the molecular hook comprises a hexafluorophosphate counterion, a tetrafluoroborate counterion, a triflate counterion, or combinations thereof. Silicone compositions of the present invention that include at least one polysiloxane or silicone resin provide benefits in products such as hair care products, but also include textile care, cosmetic, oral care and animal care products. A particular advantage of the present invention is that many of the described linkers provide solubility in consumer relevant media to the silicone composition as well as the potential for additional hair care benefits, which may or may not be typically associated with the functional groups of the linker. In particular, the molecular hook of the present invention is thermally and hydrolytically stable.

(3) US Patent 7,166,276 issued Jan. 23, 2007, to Stephens et al., titled "Silicone elastomer emulsion cosmetic composition comprising colorant inclusive internal phase" discloses silicone elastomer emulsion cosmetic compositions that comprise an internal phase and include a colorant. These compositions are intended to deliver colorant ingredients to the skin of the user in such a manner as to provide a smooth and even color appearance. In particular, the present invention relates to a cosmetic composition comprising an emulsion of: a) a continuous aqueous phase comprising approximately 0.1% to about 10% by weight of a non-emulsifying cross-linked siloxane elastomer; b) a dispersed oil phase comprising approximately 1% to 25% by weight of an oil compatible colorant and approximately 0.01% to 20% by weight of a binder; and c) approximately 0.01% to 15% by weight of an emulsifier.

(4) US Patent 7,056,496 issued June 6, 2006, to Pate et al., titled "Sunscreen composition and a process for preparing it" discloses a process of preparing an advanced cosmetic product by combining a high internal phase ratio (HIPR) emollient-in-water emulsion with a partial cosmetic formulation that typically contains water, a coloring agent, a fragrance, and a rheology modifier or pH adjuster, or combination thereof. The present invention also includes compositions directed to two particular subclasses of HIPR emollient-in-water emulsions, namely an HIPR silicone elastomer-in-water emulsion and an HIPR sunscreen-in-water emulsion, and water-diluted dispersions thereof. The use of an HIPR emulsion of a cosmetic emollient provides a simple and flexible method of formulating the cosmetic product, due in part to the long shelf-stability of the HIPR emulsion (greater than 1 year), and the low quantity of water in the emulsion (typically less than 20% by volume based on the volume of emollient and water). The HIPR sunscreen-in-water emulsion can be formulated into an advanced cosmetic product with an improved sun protection factor (SPF) and critical wavelength.

Patents cont.

(5-8) A series of patents related to the preparation of globular particles of a silicone resin or, in particular, a polyorganosilsesquioxane resin having properties suitable as an adjuvant in hair-care toiletry preparations by the hydrolysis condensation reaction of an organotrialkoxy silane compound, such as methyl trimethoxysilane in an aqueous alkaline medium, are disclosed in the following:

- US Patent 6,849,265 issued October 10, 2006 to Butts et al, titled"Silicone compositions for personal care products and method for making"
- US Patent 6,849,264 issued February 1, 2005 to Butts et al, titled "Silicone compositions for personal care products and method for making"
- US Patent 6,844,002 issued Janusry 18, 2005 to Butts et al, titled "Silicone compositions for personal care products and method for making"
- US Patent 6,841,164 issued January 11, 2005 to Butts et al, titled "Silicone compositions for personal care products and method for making"

(9) US Patent 6,737,444 issued May 18, 2004, to Liu, titled "Method of making silicone resin emulsions" discloses a method for making aqueous silicone resin containing emulsions by (i) mixing a silicone resin or a blend of a silicone resin and a nonresinous silicone polymer, with an inversion assisting polymer to form a homogeneous oil phase; (ii) mixing one or more surfactants with the homogenous oil phase in (i) to form a mixture; (iii) adding sufficient water to the mixture in (ii) to cause an inversion of the continuous phase and the dispersed phase, and forming an o/w emulsion; (iv) diluting the o/w emulsion in (iii) by adding more water; and (v) recovering an o/w emulsion containing silicones having a particle size in range of 100 nm to 5,000 nm (0.1 to 5.0 microns). The inversion assisting polymer is a silicon-functional or an organofunctional polysiloxane having in its molecule a silicon-functional or an organofunctional group such as hydroxyl, alkoxy, amino, epoxidized amino, glycidyl, polyoxyethylene oxypropylene, carboxyl, mercapto, quaternary ammonium or combinations thereof.

(10) US Patent 6,793,915 issued Sept. 21, 2004, to Guenin et al., titled "Cool and dry soft solid antiperspirant" discloses a stable, high efficacy, low residue surfactant-free, soft solid cosmetic composition (especially an antiperspirant and/or deodorant) comprising: (a) 40–75 weight % of a volatile silicone; (b) 0.5–20 weight % of a non-emulsifying silicone elastomer; (c) 0.1–10 weight % of a of a superabsorbent powder with little or no tack upon wetting; (d) 0.01–0.5 weight % of a cooling agent selected from the group consisting of L-menthol; menthyl lactate; menthone glycerine; menthone glycerin acetal; (-)-isopulegol, N-ethyl-5-methyl-2-(1-methylethyl)-cyclohexanecarboxamide; N-ethyl-p-menthane-3-carboxzamide; 4-methyl-3-(1-pyrrolidinyl)-2[5H]-furanone; N,2,3-trimethyl-2-isopropylbutanamide; menthoxypropanediol; methanediol; and vanillyl butyl ether; (e) 0–20 weight % of an emollient or a mixture of two or more emollients; (f) 0–30 weight % of an antiperspirant active based on an anhydrous, buffer-free antiperspirant active; (g) 0–8 weight % of polyethylene beads having a particle size in the range of 5–40 microns and a density in the range of 0.91–0.98 g/cm.sup.3; (h) 0–5 weight % fragrance; (j) 0–5 weight % of an antimicrobial agent; wherein the ratio of cooling agent to superabsorbent polymer is in the range of 1:5–1:2.

(11) US Patent 6,685,921 issued Feb. 3, 2004, to Lawlor, titled "Dental care compositions" discloses nonvolatile oral care compositions that comprise: i) from

Patents cont.

about 0.5% to about 60%, by weight, of a silicone resin; ii) from about 0.1% to about 30%, by weight, of a silicone gum; iii) from about 0.1% to about 95%, by weight, of a nonvolatile polysiloxane fluid which has a viscosity from about 1 cSt to about 1,000 cSt; and iv) from about 0.01% to about 50%, by weight, of an oral care active selected from teeth color modifying substances, anti-tartar agents, antiplaque agents, fluoride ion sources, antimicrobial agents, nutrients, antioxidants, H-2 antagonists, analgesics, antiviral agents, mucosally absorbed pharmacological agents and mixtures thereof. A second aspect of the present invention relates to the use of nonvolatile oral care silicone compositions in the oral cavity to treat the hard and soft tissue surfaces wherein the composition comprises: (i) from about 0.5% to about 60%, by weight, of a silicone resin; (ii) from about 0.1% to about 30%, by weight of a silicone gum; (iii) from about 0.1% to about 95%, by weight, of a nonvolatile polysiloxane fluid which has a viscosity from about 1 cSt to about 1,000 cSt. Compositions of the present invention are useful for providing a substantive composition on the surfaces of the oral cavity which can provide prophylactic, therapeutic or cosmetic benefits.

(12) US Patent 6,589,561 issued July 8, 2003, to Inokuchi et al., titled "Aqueous dispersion of globular silicone elastomer particles" discloses an aqueous slurry of globular particles of a silicone-based composite elastomer consisting of titanium dioxide particles and a cross-linked silicone elastomer as its matrix. The aqueous dispersion comprises from 10% to 60% of the globular elastomer particles of 0.1 to 100 .mu.m diameter, from 0.1% to 30% by weight of a surfactant which is preferably an anionic surfactant such as a salt of a dialkyl sulfosuccinate, and the balance of water. The aqueous dispersion of the globular elastomer particles is quite satisfactory as an ultraviolet-shielding adjuvant in water-based cosmetic or toiletry preparations with respect to good stability of dispersion, high ultraviolet-shielding power and surface lubricity.

(13) US Patent 6,548,074 issued April 15, 2003, to Mohammadi, titled "Silicone elastomer emulsions stabilized with pentylene glycol" discloses cosmetic compositions that include a silicone elastomer, a volatile siloxane, water (*aqua*) and pentylene glycol. These compositions are emulsions that have improved phase stability as a result of the presence of pentylene glycol. The systems are also microbiologically preserved without the need for other added traditional preservatives.

(14) US Patent 6,488,918 issued Dec. 3, 2002, to Hess et al., titled "Powdery cosmetic composition and method of making same" discloses a powdery bleaching composition with storage stability that contains from 25% to 70% by weight of at least one solid per-compound as effective bleaching agent and from about 0.1% to about 20% by weight of at least one cross-linked silicone elastomer. This elastomer is made by cross-linking with an alpha, omega-diene or a vinyl-polysiloxane, and preferably is a dimethicone/vinyl-dimethicone crosspolymer or a cyclopentasiloxane and dimethicone crosspolymer. Simple methods of making the powdery cosmetic compositions are also described.

(15) US Patent 6,284,941 issued Sept. 4, 2001, to Cox et al., titled "Bandage having a scar treatment pad for scar management and scar repair" discloses a bandage for the treatment of dermal scars, keloids, wounds or abrasions by contacting the skin of the user. The bandage includes a flexible member having an adhesive

Patents cont.

located on the first side. A scar treatment pad such as a layer of silicone elastomer is attached by the adhesive to the first side of the flexible member. The bandage is used by placing the first side of the flexible member in contact with the skin of the user such that the layer of silicone elastomer substantially contacts a scarred area of the skin. The adhesive removably attaches the first side of the flexible member substantially in contact with an unscarred area of the skin of the user. The layer of silicone elastomer attached to the first side of the flexible member improves the cosmetic and functional aspects of the scarred area of the skin of the user.

(16) US Patent 5,845,336 issued Dec. 29, 1998, to Divone et al., titled "Process for preparing silicone elastomer compositions" discloses a process for preparing a silicone elastomer composition for cosmetic products, which includes the steps of feeding the silicone elastomer composition comprising a silicone rubber in a carrier fluid into a reactor, mixing the composition in the reactor, delivering the composition from the reactor into a high pressure pump, pumping the fluid into a device for reducing particles of rubber into smaller sizes and recirculating the resultant size reduced particles back to the reactor. The device for reducing particle size is preferably a high pressure fed homogenizer, most advantageously a sonolator.

(17) US Patent 5,505,937 issued April 9, 1996, to Castrogiovanni et al., titled "Cosmetic compositions with improved transfer resistance" discloses a transfer-resistant cosmetic composition comprising: a) 1%–70% volatile solvent; b) 0.1%–15% silicone resin; c) 10%–45% wax; d) 5%–50% powder; and e) 1%–30% oil.

(18) US Patent 5,496,544 issued March 5, 1996, to Mellul et al., titled "Powdered cosmetic composition containing a silicone fatty binder" discloses a cosmetic composition for skin consisting of an anhydrous powder and mainly including a solid particulate phase mixed with a fatty binder containing a silicone mixture which consists of (a) at least one silicone oil, (b) at least one silicone wax, (c) at least one silicone resin, (d) optionally at least one silicon gum and (e) optionally at least one phenyldimethicone; wherein components (a), (b), (c), (d) and (e) are present in the binder in concentrations of 12%–98.9%, 1%–60%, 0.1%–25%, 0%–3% and 0%–20% by weight respectively in relation to the overall weight of the silicone mixture. The composition may be used as face makeup, as eye shadow or as a makeup foundation or powder.

(19) US Patent 4,906,459 issued March 6, 1990, to Cobb et al., titled "Hair care compositions" discloses hair care compositions that give both improved style retention and hair conditioning properties, as well as easier processing. The compositions comprise from about 0.01% to about 10.0% of a filler reinforced silicone gum, from about 0.01% to about 10.0% of a silicone resin and a volatile carrier.

(20) US Patent 3,770,648 issued Nov 6, 1973 to Mackels et al, titled " Anhydrous Areosol Foam" discloses an anhydrous aerosol foam composition for external use that incorporates a silicone resin in a solution of organic solvents to produce a stable "quick breaking" foam when the foam is rubbed into or spread onto a surface on which it has been deposited.

(21) US Patent 2,512,192 issued May 24, 1948, to Yen et al., describes a silicone resin medication coating.

Future Developments

As previously stated, this is a rapidly growing area in silicone chemistry, one that is not often discussed. Products are being custom tailored for specific applications at the present time.

Perhaps the most interesting thing about resin chemistry is that all of the derivatives discussed in the previous chapters can be applied to the resin chemistry. Resin-based dimethicone copolyol, alkyl silicones and fluoro compounds are more than mere laboratory curiosities at the present time. The creative formulator will find many new areas of applications for these materials throughout the personal care market.

References:

1. G Odian, *Principles of Polymerization*, Wiley Interscience 2nd edn, p 35 (1981)
2. US Patent 6,139,823 issued October 31, 2003 to Drechler et al, titled "*Transfer resistant cosmetic compositions*".

Chapter 15

Silicone Phospholipids

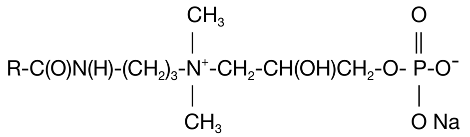
In order to develop an appreciation for silicone phosphobetaines and silicone phospholipids, a discussion of the chemistry of nonsilicone compounds is necessary.

Phosphobetaines

The first set of materials of interest in this class are phosphobetaines. These compounds are true amphoterics with a net charge of zero. This makes them quite different from the products called phospholipids that are compounds with net + charges. The differences between phosphobetaines and phospholipids will become apparent not only vis-à-vis structure, but also as relates to function in formulation.

Phosphobetaine compounds were first described in 1981 in US Patent 4,283,542. The patent, now expired, dealt with compounds that have the structure shown in **Figure 15.1**.

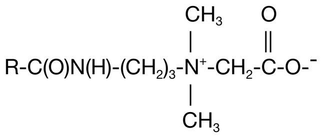
Figure 15.1. Alkylamido Phosphate



$$R\text{-}C(O)N(H)\text{-}(CH_2)_3\text{-}\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{N^+}}\text{-}CH_2\text{-}CH(OH)CH_2\text{-}O\text{-}\ \underset{\substack{|\\O\ Na}}{\overset{\substack{O\\||}}{P}}\text{-}O^-$$

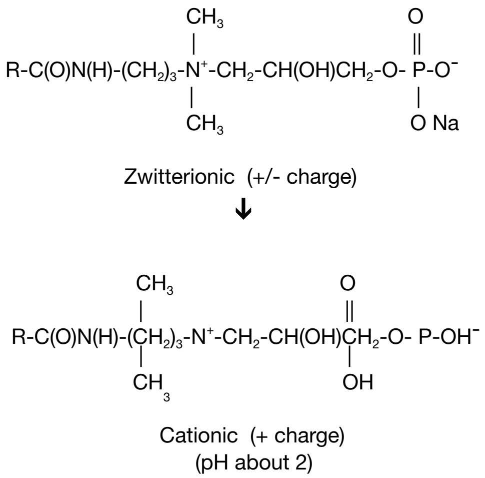
The products are amphoteric materials, because they have a (+) charge on nitrogen and a (-) charge on phosphate. Phosphobetaines are the phosphorus analogue of betaines (**Figure 15.2**). They are capable of existing in two forms: cationic and zwitterionic (**Figure 15.3**).

Figure 15.2. Alkylamido Betaine



$$R\text{-}C(O)N(H)\text{-}(CH_2)_3\text{-}\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{N^+}}\text{-}CH_2\text{-}\overset{\substack{O\\||}}{C}\text{-}O\text{-}^-$$

Figure 15.3. Alkylamido Phosphobetaine Ionic Forms



$$R\text{-}C(O)N(H)\text{-}(CH_2)_3\text{-}\underset{CH_3}{\overset{CH_3}{N^+}}\text{-}CH_2\text{-}CH(OH)CH_2\text{-}O\text{-}\ \underset{O\,Na}{\overset{O}{\overset{\|}{P}}}\text{-}O^-$$

Zwitterionic (+/- charge)

↓

$$R\text{-}C(O)N(H)\text{-}(\underset{CH_3}{\overset{CH_3}{C}}H_2)_3\text{-}N^+\text{-}CH_2\text{-}CH(OH)\underset{OH}{\overset{O}{\overset{\|}{C}}}H_2\text{-}O\text{-}\ P\text{-}OH^-$$

Cationic (+ charge)
(pH about 2)

There are a number of additional patents (see **Table 15.1**).

Table 15.1. Patents for Phosphobetaines and Phospholipids

Number	Date of Issue	Topic
4,209,449	24-Jun-80	Phosphate Quats
4,215,064	29-Jul-80	Phosphobetaines
4,243,602	06-Jan-81	Phosphate Quat
4,261,911	14-Apr-81	Phosphitaines
4,283,542	11-Aug-81	Phosphobetaine Process
4,336,385	22-Jun-82	Phosphate Quats from Imidazolines
4,336,386	22-Jun-82	Phosphite Quaternaries
4,380,637	19-Apr-83	Imidazoline Phosphobetaines
4,503,002	05-Mar-85	Phosphate Quat Compounds

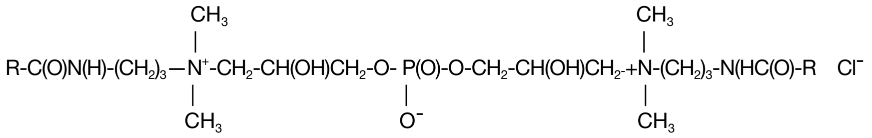
The products from this class differ in the "R" composition. The common attribute is that the products are all mono-substituted and are amphoteric products because they bear only one (+) charge and only one (-) charge in the same molecule.

The phosphobetaines are detergent systems that are mild and have good foam. They form anionic/cationic complexes with sulfates and ether sulfates. These complexes are more substantive to hair, very mild and good for personal care products (such as baby products) where mildness is of importance.

Phospholipids

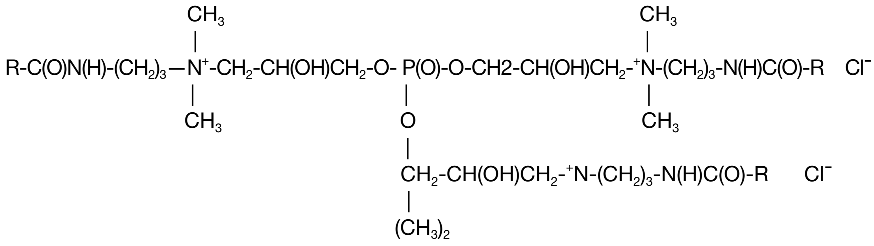
The term phospholipid is properly reserved for compounds in which there is more than one functional group. While at first this sounds unimportant, looking at the structure, one becomes aware of the differences. The ability to alter the ratio of mono-, di-, and trifunctional product is determined in the stage of reacting the phosphate salt with epichlorohydrin. Unlike phosphobetaines that are balanced with one (+) and one (-) charge, phospholipids have an overall (+) charge. This makes them cationic. **Figures 15.4** and **15.5** show the sifunctional (overall charge +1), and the trifunctional, (overall charge +3). No class of product is completely mono, di or tri, but is a mixture—inherently self-preserving.

Figure 15.4. Alkylamido Phospholipid Structures
Difunctional



$$R\text{-}C(O)N(H)\text{-}(CH_2)_3\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}\text{-}CH_2\text{-}CH(OH)CH_2\text{-}O\text{-}\ \underset{\displaystyle O^-}{P}(O)\text{-}O\text{-}CH_2\text{-}CH(OH)CH_2\text{-}{+}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}\text{-}(CH_2)_3\text{-}N(HC(O)\text{-}R \quad Cl^-$$

Figure 15.5. Alkylamido Phospholipid Structures
Trifunctional



$$\begin{array}{l} R\text{-}C(O)N(H)\text{-}(CH_2)_3\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}\text{-}CH_2\text{-}CH(OH)CH_2\text{-}O\text{-}\ \underset{\displaystyle O}{P}(O)\text{-}O\text{-}CH2\text{-}CH(OH)CH_2\text{-}{}^+\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}\text{-}(CH_2)_3\text{-}N(H)C(O)\text{-}R \quad Cl^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad |\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \underset{\displaystyle (CH_3)_2}{CH_2}\text{-}CH(OH)CH_2\text{-}{}^+N\text{-}(CH_2)_3\text{-}N(H)C(O)\text{-}R \quad Cl^- \end{array}$$

As the degree of substitution around the phosphate group increases, the product is no longer amphoteric and becomes more and more cationic. It has two (+) charges and one (-) charge, leaving a net charge of +1.

This change in charge has a profound affect on the properties of the material. As the product becomes more functionalized, the following changes occur:

- The molecular weight increases
- The skin penetration decreases
- The cationic nature increases
- The skin and hair substantivity increases
- The amount of fatty material in the molecule increases
- The skin feel improves

This explains why the phospholipids are used in skin care as emollients and conditioners and not as detergents.

Complexation with Anionic Surfactants

One of the critical functionalities observed with phosphobetaine and phospholipid technology is the interaction between the products and sodium laureth sulfate. When the two are combined, a complex forms. The more cationic the phosphobetaine, the less soluble the complex with ether sulfate.

Cocamidobetaine

The first material to consider is an ampholyte, namely a cocamidobetaine. Sodium trideceth sulfate (STDES) and cocamidobetaine were combined at differing ratios. All solutions were prepared at 10% active in water (**Table 15.2**). Over all ranges, the mixture was clear and homogeneous, indicating any action that occurs to be likewise clear and homogeneous.

Table 15.2. Betaine/STDES Interaction

STDES/Cocamidobetaine	Result
90/10	Clear, high foam, low viscosity
80/20	Clear, high foam, low viscosity
70/30	Clear, high foam, low viscosity
60/40	Clear, high foam, low viscosity
50/50	Clear, high foam, low viscosity
40/60	Clear, high foam, low viscosity
30/70	Clear, high foam, low viscosity
20/80	Clear, high foam, low viscosity

Phosphobetaine (Mono-product)

The mono-substituted product functions like the cocamidobetaine (**Table 15.3**). Over all ranges, the mixture was clear and homogeneous, again indicating little or no interaction.

Table 15.3. Phosphobetaine Interaction with STDES

STDES/Cocamido phosphobetaine	Result
90/10	Clear, high foam, low viscosity
80/20	Clear, high foam, low viscosity
70/30	Clear, high foam, low viscosity
60/40	Clear, high foam, low viscosity
50/50	Clear, high foam, low viscosity
40/60	Clear, high foam, low viscosity
30/70	Clear, high foam, low viscosity
20/80	Clear, high foam, low viscosity

Phospholipid (Di-product)

A distinct difference is noted with the di-product, due to the greater amount of cationic charge (**Table 15.4**). The anionic/cationic charge results in a cloudiness at equal molar concentrations. As can be clearly seen, the net (+) charge on the phospholipid makes the product much less compatible with anionics.

Silicone Products

Phosphobetaines and phospholipids are important classes of surfactants, so it is not surprising that there has been a desire to add silicone functionalization to them. Silicone phosphobetaines were first made in the early 1990s.[1, 2] Silicone phosphobetaines made according to the referenced patents[3] are reported to provide the following beneficial attributes to cosmetic formulations:

- Emulsification
- Pigment wetting
- Irritation mitigation
- Conditioning properties

- Water-soluble emollient
- Mild detergent
- Foam booster

Additional variations of silicone phosphobetaines were made later.[4]

Table 15.4. STDES/Diamido Phospholipids

STDES/Cocamido diphosphate	Result
90/10	Clear, high foam, low viscosity
80/20	Cloudy, moderate foam, low viscosity
70/30	Clear, high foam, low viscosity
60/40	Cloudy, moderate foam, low viscosity
50/50	Cloudy, moderate foam, low viscosity
40/60	Cloudy, moderate foam, low viscosity
30/70	Clear, moderate foam, low viscosity
20/80	Clear, moderate foam, low viscosity

Chemistry

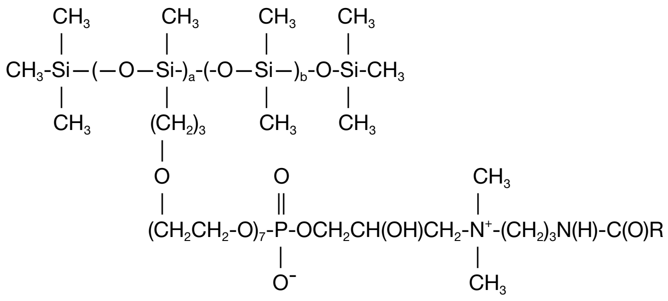
A product was developed that combined the desirable properties of phosphobetaines and silicone. The higher molecular weight, improved skin feel and improved conditioning effects the silicone product provides is a direct result of the inclusion of silicone into the molecule. The silicone phosphobetaine conforms structure is shown in **Figure 15.6.**[1, 2]

As specified by our definition, the overall charge is zero, making this an amphoteric and a phosphobetaine. As mentioned earlier, nonsilicone and phosphobetaine are good detergents but not conditioning compounds. However, these silicone analogues exhibit good conditioning effects, as will become clear.

Complexation of silicone phospholipid with anionic surfactants

The silicone phosphobetaine product functions like a phosphobetaine. Specifically, stearimonium hydroxypropyl PEG-7 dimethicone phosphate was the silicone phosphobetaine evaluated. It is sold as Pecosil PSQ-418. The results of the evaluation are shown in **Table 15.5**.

Figure 15.6. Silicone Phosphobetaines



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—(—O—}\underset{\substack{(CH_2)_3\\ O\\ (CH_2CH_2\text{-}O)_7\text{-}\underset{O^-}{\overset{O}{\overset{\|}{P}}}\text{-}OCH_2CH(OH)CH_2\text{-}\underset{CH_3}{\overset{CH_3}{N^+}}\text{-}(CH_2)_3N(H)\text{-}C(O)R}}{\overset{CH_3}{Si}}\text{-})_a\text{-(-O—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—)}_b\text{-O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Table 15.5. STDES/Silicone Phosphobetaine Interaction

STDES/Silicone Phosphobetaine	Result
90/10	Clear, high foam, low viscosity
80/20	Clear, high foam, low viscosity
70/30	Clear, high foam, low viscosity
60/40	Clear, high foam, low viscosity
50/50	Clear, high foam, low viscosity
40/60	Clear, high foam, low viscosity
30/70	Clear, high foam, low viscosity

Cylinder shake foam test

Formulas 1 and 2 are clear water white liquids as prepared. Both formulas were diluted to 0.5% solids and tested for foam height using a cylinder shake foam test. The incorporation of the silicone quat into the formulation both increased the initial foam and provided enhanced foam stability. The formula is shown in **Table 15.6**. The results are shown in **Figure 15.7**.

Salt curve response

Figure 15.8 indicates the resulting viscosities achieved when salt (NaCl) was added at 2%, 3%, 4% and 5% to Formulas 1 and 2. The presence of the silicone quat lowered the viscosity only minimally, from a peak viscosity of 15,000 cps to about 14,000 cps. The percentage added of salt to reach peak viscosity was not altered.

Table 15.6. Formulation for Foam Test

With Silicone Phosphobetaine

Ingredient	% Weight	Function
Water	41.4	
Sodium lauryl sulfate (Standapol WAQ-LC) (28% Active)	53.6	Anionic Surfactant
Cocamide DEA (Standamid KD)	3.0	Alkanolamid
Stearimonium hydroxypropyl PEG-7-dimethicone phosphate (Pecosil PSQ-418) (40% Active)	2.0	Silicone Phosphobetaine

Without Silicone Phosphobetaine (control)

Ingredient	% Weight	Function
Water	43.4	
Sodium lauryl sulfate (Standapol WAQ-LC) (28% Active)	53.6	Anionic Surfactant
Cocamide DEA (Standamid KD)	3.0	Alkanolamid

Figure 15.7. Foam Data Silicone Phosphobetaine

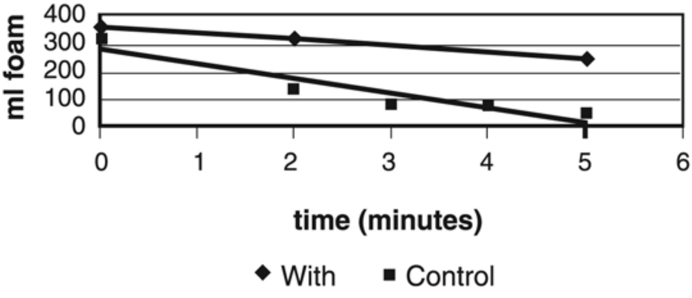
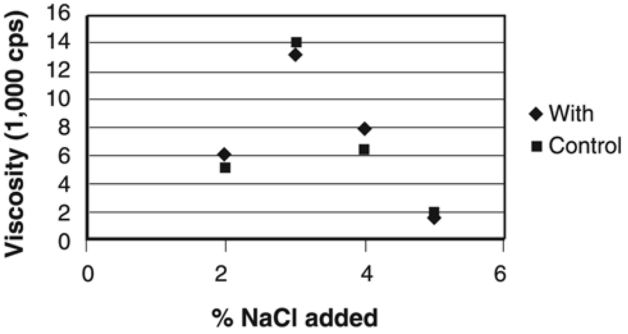


Figure 15.8. Salt Curve Silicone Phosphobetaine



Wet comb test

The silicone phosphobetaine functions like its nonsilicone-based relative in foam, salt curve response and compatibility with anionic surfactants. However, as the data will show, the silicone phosphobetaine is an exceptional additive for wet comb properties.

A laboratory test is conducted to screen the wet comb properties of a representative member of the family of novel compounds. Hair swatches are purchased from a supply of human hair from the same head. Each test swatch contains 7 g of hair and is 11 inches in length. The hair is tied tightly one inch from one end with string. The swatch is pre-cleaned with a 3% solution of ammonium lauryl sulfate. Subsequently, the swatch is washed under running tap water. The hair is then squeezed out and, while still damp, dipped into a 200 mL solution of 0.2% active quaternary. Another rinse is made, and then the swatch is blotted dry. Holding the hair swatch, the hair is combed as rapidly as possible while alternating the side of the swatch and then the swatch is treated. The time needed to get one smooth free stroke without tangling is recorded. Typical results for the standard quaternary compounds used in hair conditioning (stearyldimethylbenzyl ammonium chloride) range 12– 14 seconds. Selected results are shown in **Table 15.7**.

Table 15.7. Rinse Conditioner Wet Comb Test

Product	Time in Seconds
Stearimonium hydroxypropyl PEG-7-dimethicone phosphate	9
Stearyldimethylbenzyl ammonium chloride	12

Conclusion

The incorporation of the silicone phosphobetaine allows for the formulation of a conditioning shampoo that is clear, viscous, and has desirable foam properties and outstanding wet comb properties.

References:

1. US Patent 5,091,493, issued Feb 25, 1992 to O'Lenick et al., titled "Silicone phosphobetaines".
2. US Patent 5,237,035, issued Aug 17, 1993 to O'Lenick et al., titled "Silicone phospholipid polymers".
3. Technical Bulletin Phenomenon #200, Phoenix Chemical Inc. 6/2001
4. US Patent 5,623,043, issued April 12, 1997 to Fost et al., titled "Silicone modified phospholipid compositions".

Chapter 16

HLB

As should by now be clear, many molecules are multifunctional, containing water-soluble, oil-soluble and silicone-soluble groups. The balance results in the ability to make unique emulsions. The compounds presented here are esters, but recently, the use of the 3D HLB[1, 2] concept has been expanded to the more hydrolytically stable alkyl dimethicone copolyols.

Despite the fact that the basic HLB system has been around for about 50 years, the ability to predict the performance of specific emulsifiers in the preparation of emulsions remains a challenge to the formulator. The HLB system works best in predicting emulsification for alcohol ethoxylates, which are surfactants based upon fatty alcohols that have been modified by reaction with ethylene oxide. The system is also most useful for emulsions in which water is a component.

HLB System

The HLB system was proposed by Griffin[3] and has been widely promoted by ICI.[4] Through the years it has proven to be a very valuable aide to the formulator. Within the HLB system, hydrophilic refers to the portion of the surfactant that is soluble in the aqueous phase, while lipophilic refers to the oil-soluble portion of the surfactant. The value of HLB ranges from 1–20. Low HLB emulsifiers are soluble in oil while high HLB emulsifiers are soluble in water. Bancroft's rule tells us that the type of emulsion (i.e. o/w or w/o) is dictated by the emulsifier and that the emulsifier should be soluble in the continuous phase. Low HLB emulsifiers are soluble in oil and give rise to w/o emulsions. The value of HLB is calculated by:

$$\text{HLB} = 20(1-(S/A))$$

…where S is the saponification number* of the ester and A is the acid number of the resulting acid. The saponification number is the mass in mg of potassium hydroxide required to saponify. "Saponify" comes from the French term "saponifier," which means to make fat from soap (one gram of the acid plus ester). The acid number is the number of mg of potassium hydroxide required to neutralize one gram of acid plus ester

HLB, the Hydrophile-Lipophile Balance, is the ratio of oil-soluble and water-soluble portions of a molecule. The system was originally developed for ethoxylated products. Listed in **Table 16.1** are some approximations for the HLB value for surfactants as a function of their solubility in water. Values from **Table 16.2** are used to define a one-dimensional scale ranging from 0 to 20.

Table 16.1. Approximate HLB Values for Surfactants

Solubility in water	HLB value	Description
Insoluble emulsifier	4–5	w/o
Poorly dispersible (milky appearance)	6--9	wetting agent
Translucent to clear	10–12	detergent
Very soluble emulsifier	13–18	o/w

Table 16.2. HLB Properties

A	B	C	D
HLB 4–5	HLB 6–9	HLB 10–12	HLB 13–16

Despite the fact that surfactants can be made to have virtually any HLB, they function in certain ways at very specific HLB Values. This was part of the genius of the Griffin system.

Solubility in water	HLB value	Description
A. Insoluble emulsifier	4–5	w/o emulsifier
B. Poorly dispersible	6–9	wetting agent
C. Translucent to clear	10–12	detergent
D. Very soluble emulsifier	13–18	o/w emulsifier

We will use the generic term "hydrocarbon" to designate the oil-soluble portion of the molecule. This generic term includes the more specific terms *fatty*, *lipid* and *alkyl*.

Two basic types of emulsions are envisioned by the current HLB system: o/w and w/o. The phase listed first is the discontinuous phase; that is, the discontinuous phase is the phase that is emulsified into the other phase. Bancroft[5] postulated that upon mixing of the two phases with a surfactant present, the emulsifier forms a third phase as a film at the interface between the two phases being mixed together.

Bancroft also predicted that the phase in which the emulsifier is most soluble will become the continuous phase. The continuous phase need not be the predominant quantity of material present. There are emulsions in which the discontinuous phase makes up a greater weight percent than the continuous phase. A simple test is: if the emulsion is readily diluted with water, water is the continuous phase.

It has been said, "The HLB system has made it possible to organize a great deal of rather messy information and to plan fairly efficient systematic approaches to optimize emulsion preparation. If one pursues the concept too far, however, the system tends to lose itself to complexities."[6] We agree with this and believe the first objective is a system that provides direction in the selection of an emulsifier. A mathematical model has been developed to allow for approximations of HLB.

Calculation of HLB

The HLB system, in its most basic form, allows for the calculation of HLB using the following equation:

$$\text{HLB} = \%\ \text{hydrophile} \div 5$$

Where % hydrophile is the % hydrophile by weight of molecule.

For example, oleyl alcohol has five ethyl oxides weighing 44 mwu each. In this case, the molecular weight of the hydrophile is 5 x 44 = 220. The total weight of the molecule is 489. The % hydrophile or % hydrophile by weight of molecule is 220 ÷ 489 = 45.0%. Therefore, for oleyl alcohol: HLB = 45% ÷ 5 = 9.0.

Application of HLB

One can predict the approximate HLB needed to emulsify a given material and make more intelligent estimates regarding which surfactants or combinations of surfactants are appropriate to a given application. When blends are used, the HLB can be estimated by using a weighted average of the surfactants used in the blend. **Table 16.3** gives approximate HLB values needed to emulsify selected materials.

For those materials not listed in **Table 16.3**, it is recommended that the oil be tested using specific blends of known emulsifiers. This allows the formulator to calculate the HLB needed to emulsify the nonlisted oil.

The appearance of the emulsion is dependent upon the particle size of the discontinuous phase, as shown in **Table 16.4**.

Applicability of the HLB System to Surfactant Types

Traditional nonionic surfactants

The selection of a traditional nonionic surface active agent for a specific emulsification application has been made simpler and more systematic by the development of the HLB System.

Silicone/polyoxyethylene-based surfactants

In recent years, there has been a greater acceptance of silicone surfactants in the preparation of emulsions. The direct application of the HLB concept to these materials has resulted in an approximate value. Many manufacturers of silicone

Table 16.3. Approximate HLB Needed to Emulsify (oil-in-water)

Material	HLB
Acetophenone	14
Acid, lauric	16
Acid, oleic	17
Beeswax	9
Benzene	15
Butyl stearate	11
Carbon tetrachloride	16
Castor oil	14
Chlorobenzene	13
Chloronated paraffin	8
Cottonseed oil	6
Cyclohexane	15
Kerosene	14
Lanolin	12
Lauryl amine	12
Mineral spirits	10
Nonylphenol	14
Orthodichlorobenzene	13
Petrolatum	7
Pine oil	16
Toluene	15
Xylene	14

Table 16.4. Emulsion Appearance as a Function of Particle Size

Particle Size (nanometers)	Appearance
> 1	white
0.1–1.0	blue white
0.05–0.1	translucent
< 0.05	transparent

surfactants, rather than dealing with the differences between calculated and observed HLB, have dropped specific values and adopted the use of high, middle or low as a classification of HLB values. Determining the HLB of surfactants containing silicone groups, alkyl groups and polyoxyethylene groups does not work in predicting emulsion performance.

Silicone surfactant/fatty polyoxyethylene surfactant blends

Most formulations that use silicone-based surface active agents also have traditional hydrocarbon surfactants present. The presence of these blended systems has offered challenges for the predictability of emulsification properties. In a recent paper, Bancroft discussed the difficulties in predicting the behavior of silicone-based surfactants when used in combination with hydrocarbon surfactants.[6] He came to the conclusion that even when low molecular weight silicone compounds are evaluated, there is "varying non-ideal behavior," depending on the type and concentration of the surfactants used. This type of conclusion, while supported by the data, is not helpful to the formulator.

Silicone/fatty/polyoxyethylene-based surfactants

To further complicate the situation, the market has seen a virtual explosion of new silicone compounds that combine polyoxyethylene (water-soluble), silicone (silicone-soluble) and hydrocarbon (oil-soluble) portions into one molecule. The introduction of these types of molecules and the inability to fit them into the HLB concept has resulted in confusion about how to use the compounds.

Three-dimensional HLB

The current HLB system has been used successfully for some time in helping to predict how to make w/o and o/w emulsions. It has been less than satisfactory for predicting the performance of silicone-based molecules and has been unsuccessful in predicting the performance of surfactants having silicone, hydrocarbon and polyoxyalkylene portions present.

Any attempt to expand the current HLB system must be able to assign meaningful values to surfactants containing the three components, because each group is insoluble in the other. This mutual insolubility led us to consider an HLB system in which oil, water and silicone were all considered in the determination of the emulsion properties of surfactants. Because our system considers three components (silicone, oil and water), we have called our system "three-dimensional HLB" (3D HLB). As you will see, the mathematics of the system evolved, so we need to determine only two components, from which the third (silicone) is determined by a different calculation. **Figure 16.1** shows the 3D HLB system in graphic form.

The reference compounds for the three points of the triangle are shown in **Table 16.5**.

The triangle model

The first efforts to build a new HLB model attempted to use a cube, having x, y and z coordinates. This type of system is difficult from a conceptual point of view and the mathematics are difficult to handle. Fortunately, experimental data solved this problem and we could work with a triangle instead.

Figure 16.1. HLB Evolutions Three Dimensional HLB

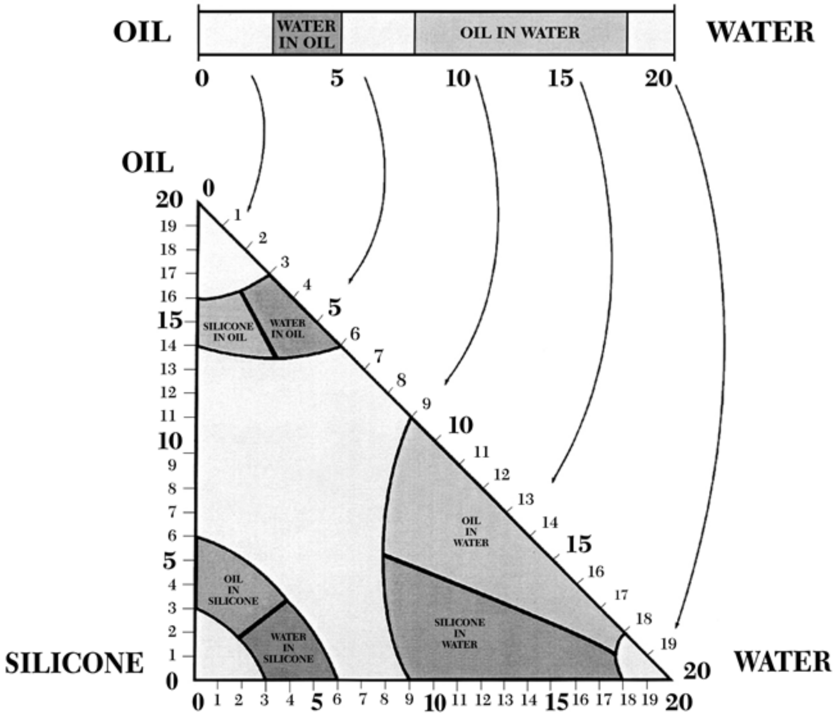


Table 16.5. Triangle References in the 3D HLB System

Material	x	y	x,y
Mineral oil	0 ÷ 5	100 ÷ 5	0,20
Silicone oil	0 ÷ 5	0 ÷ 5	0,0
Silicone oil	100 ÷ 5	0 ÷ 5	20,0

As we made the many compounds, some of which are outlined in **Table 16.6**, and evaluated their properties to make emulsions, we found that the system we needed was not as complex as envisioned. Because the original HLB system has proven over time to be very helpful, it was our desire to use its concept and expand it to include a molecule with silicone present. In fact, we retained both the scale used by the current system (0–20) and one of the calculations (% hydrophile ÷ 5). One of the lines in our triangle system is the current HLB system.

Table 16.6. 3D HLB Values for Selected Silicone Surfactants (Calculated)

Compound tested	% Water-sol.	% Oil-sol.	3D HLB x	3D HLB y
Dimethicone copolyol isostearate "A"	47/5	24/5	9.5	4.8
Dimethiconol stearate	0/5	15/5	0.0	3.0
Dimethicone copolyol isostearate "B"	32/5	20/5	8.0	4.0
Cetyl dimethicone	0/5	20/5	0.0	4.0
Dimethicone copolyol amine	19/5	0/5	3.8	0.0
Dimethicone copolyol isostearate "C"	55/5	10/5	11.0	2.0
Dimethicone copolyol isostearate "D"	48/5	16/5	9.6	3.2
Dimethicone copolyol amine "B"	28/5	5/5	5.5	1.0
Dimethicone copolyol amine "C"	20/5	75/5	4.0	15.0
Dimethicone copolyol amine "D"	19/5	30/5	3.8	6.0
Dimethiconol stearate steareth (2) alcohol blend	22/5	70/5	4.3	14.0
Dimethiconol stearate steareth (2) alcohol blend	6/5	55/5	1.2	11.0
Dimethiconol stearate steareth (2) alcohol blend	0/5	79/5	0.0	15.8

One of the major discoveries was that in a molecule in which oil, water and silicone are present, we need only calculate two values; their difference would give us the third value. This is true because the calculations are based upon % by weight of oil-soluble and % by weight of water-soluble portions of the molecule.

If one subtracts the sum of those two values from 100, the remainder is the % silicone-soluble by weight.

The same observation applies in the current system, which is the calculation of the % by weight of water-soluble ÷ 5. The calculation of % oil-soluble is therefore 100 minus the % water-soluble. We simply make one more calculation. Since our system is based upon the current HLB system, molecules that have no silicone present can be easily accommodated. They fall on the hypotenuse of the triangle.

Our first attempt to develop a system was to evaluate an equilateral triangle with one of the corners representing oil, one corner water and the third silicone. While this was appealing in that it gave equal weight to each component, the experimental data did not support the equilateral triangle. The generated values were best accommodated by a right triangle. The hypotenuse, representing the current HLB system, is the longest line. That line connects the oil and the water portions. The hypotenuse is labeled 0–20 like the other sides. However, the distance between units is longer than for the other two lines, which are of equal length. Initially, this seemed unsettling. However, as we worked with the system, we discovered that this explains why the current HLB is not directly applicable to silicone-based surfactants. The physical significance of this is the fact that silicone and hydrocarbon compounds are not equally as hydrophobic per % by weight. As we considered this experimental observation, it became clear that this made sense. The right triangle (**Table 16.1**) was generated using the experimental data and appears to best predict which molecules will give the indicated emulsions.

The line connecting points (0,0) and (0,20) is the silicone/water HLB line (X axis). All points falling on this line have no fatty portion. Traditional dimethicone copolyol compounds fall on this line.

The line connecting points (20,0) and (0,20) is the traditional HLB line (the hypotenuse). All points falling on this line have no silicone portion. Traditional surfactants fall on this line. This line represents the standard HLB line.

The last line connecting points (0,0) and (20,0) is the oil/silicone HLB line (Y axis). This line predicts that emulsifiers allow for the emulsification of silicone oil and fatty oil. This concept was not clear to us until the system was developed and we anxiously tried to make molecules predicted to give these types of emulsions.

It is significant that the triangle used is not equilateral, although we originally thought to use an equilateral. As one looks at the right triangle that we propose, one sees clearly that the hypotenuse representing the standard HLB is longer that the other two sides. This difference in length is not artifact. It helps explain why the predictions of HLB for dimethicone copolyols based upon the standard formula (% hydrophile ÷ 5) do not result in numbers that match the observed values. Our system addresses this problem.

Calculating the 3D HLB

The calculation of the x and y points within our system are as follows:

X coordinate = % water-soluble ÷ 5
Y coordinate = % oil-soluble ÷ 5

This calculation gives the two values that describe the point. Essentially the amount of silicone is the difference.

For example, for a standard fatty surfactant, % oil-soluble is 50.0% and the % water-soluble is 50.0%. Therefore:

$$x = 50.0 \div 5 = 10.0$$
$$y = 50.0 \div 5 = 10.0$$

For a standard silicone surfactant, % oil-soluble is 0% and the % water-soluble is 50.0%. Therefore:

$$x = 0 \div 5 = 0$$
$$y = 50.0 \div 5 = 10.0$$

For a three-dimensional surfactant, % oil-soluble is 30.0% and the % water-soluble is 20.0%. Therefore:

$$x = 30.0 \div 5 = 6.0$$
$$y = 20.0 \div 5 = 4.0$$

References in the system

The corners of the graph are defined by the references previously shown in **Table 16.5**.

Testing the 3D HLB System

The test surfactants

The predictive value of the **Table 16.1** triangle was tested by making a variety of surface active agents, the results of which are shown in **Table 16.6**. The predictions were then compared to the actual properties. The performance of the surfactants studied allowed for the definition of the boundaries of the system.

The test emulsions

The 3D HLB System predicts six types of emulsions as shown in **Table 16.7**.

The formulation for each type of emulsion is in **Table 16.8**.

Emulsion Procedure

Procedure: In each case, the test surfactant was added to the discontinuous phase under good agitation for 5 min. The continuous phase was added slowly.

Evaluation: Emulsions were evaluated on a scale of 1 to 5, where 5 was a stable emulsion and 1 was a completely unstable emulsion.

Results

The results of the stability evaluations are shown in **Table 16.9**.

Table 16.7. Emulsions for Evaluation

1. Silicone-in-water (s/w) (Formula A)
2. Oil-in-water (o/w) (Formula B)
3. Water-in-silicone (w/s) (Formula C)
4. Water-in-oil (w/o) (Formula D)
5. Oil-in-silicone (o/s) (Formula E)
6. Silicone-in-oil (s/o) (Formula F)

Table 16.8. Formulations for Test Emulsions

	Emulsion Type / Formula					
	S/W	**O/W**	**W/S**	**W/O**	**O/S**	**S/O**
Material	**A**	**B**	**C**	**D**	**E**	**F**
Silicone oil	15.0	--	80.0	--	80.0	15.0
Mineral oil	--	15.0	--	80.0	15.0	80.0
Test surfactant	5.0	5.0	5.0	5.0	5.0	5.0
Water (*aqua*)	80.0	80.0	15.0	15.0	--	--

Table 16.9. Stability of the Test Emulsions Rated on a 1 to 5 Scale

	Emulsion Type / Formula					
	S/W	**O/W**	**W/S**	**W/O**	**O/S**	**S/O**
Material	**A**	**B**	**C**	**D**	**E**	**F**
Dimethicone copolyol isostearate "A"	4	5	0	0	0	0
Dimethiconol stearate	0	0	0	3	5	0

cont.

Table 16.9. Stability of the Test Emulsions Rated on a 1 to 5 Scale cont.

	Emulsion Type / Formula					
	S/W	O/W	W/S	W/O	O/S	S/O
Material	**A**	**B**	**C**	**D**	**E**	**F**
Dimethicone copolyol isostearate "B"	5	2	0	0	0	0
Cetyl dimethicone	0	0	0	0	5	2
Dimethicone copolyol amine	0	0	5	0	0	0
Dimethicone copolyol isostearate "C"	4	2	0	0	0	0
Dimethicone copolyol isostearate "D"	5	3	0	0	0	0
Dimethicone copolyol amine "B"	0	0	5	3	0	0
Dimethicone copolyol amine "C"	0	0	3	4	0	0
Dimethicone copolyol amine "D"	0	0	0	0	0	0
Dimethiconol stearate steareth (2) alcohol blend	0	0	0	0	4	5
Dimethiconol stearate steareth (2) alcohol blend	0	0	0	0	0	0
Dimethiconol stearate steareth (2) alcohol blend	0	0	0	0	3	5

Conclusions

The following conclusions can be drawn:

- The evaluation of the surfactant systems has resulted in a modification of the standard HLB system.

- This modified system appears to have applicability to a broad range of emulsifiers and emulsion types.
- The ability to select emulsifiers to emulsify mineral oil and silicone oil, with either being the continuous phase in the absence of water, was unexpected by the authors.
- The Three-dimensional HLB System predicts that there will be overlap in those materials that make the two closely related emulsions. For example, surfactants that are on the cusp between o/w and silicone-in-water emulsions will have properties for both. This implies these materials will be good emulsifiers for systems containing both oil and silicone co-emulsified in water.

References:
1. AJ O'Lenick, JK Parkinson, *Cosm Toil*, 111 10, 37 (1996)
2. AJ O'Lenick, JK Parkinson, *Cosm Toil*, 112 11, 26 (1997)
3. WC Griffin, *J Soc Cosm Chem*, 1, 311 (1949)
4. ICI Bulletin, HLB System, 8 (1984)
5. WO Bancroft, *J Phys Chem*, 17, 514 (1913)
6. A Adamson, *Physical Chemistry of Surfaces*, Wiley Interscience, 506 (1976)

Chapter 17

Applying the Three-dimensional HLB System

Formulators in the personal care field have a vast number of traditional surfactants from which to choose in the preparation of new products. There are nonionic, cationic, amphoteric and anionic products available. Each product class is composed of products with different functional properties. Within each class there are numerous products with specific formulation nuances. A novice formulator might ask, "Why are there so many types of surfactants?" The answer is clear. The structure of the surfactant determines the functionality. It is, therefore, not surprising that when scientists developed a series of surfactants containing silicone, they found that the structure determined the properties of these new materials, just as it did with the traditional surfactants.

Silicone is unique when placed into molecules. It confers substantivity, lowers irritation and alters the feel on skin and hair. When silicone is incorporated into water, an emulsifier pair, water and silicone are added and the resulting mixture is exposed to high sheer to develop small particles. Small particle size is critical to product stability.

With the addition of silicone into surfactants, an expansion to the 50-year-old hydrophile/lipophile balance (HLB) system appears necessary. Silicone is not soluble in either oil or water, making it a third phase. Incorporating silicone as one of the components to make the three-dimensional HLB system, or 3-D HLB system, expands the utilization of the system to a new class of surfactants.[1-4] In an effort to investigate the system further, the effect of introducing a fatty ester group onto specific dimethicone copolyol compounds was evaluated, specifically changes in solubility and emulsification properties that result as a consequence of the introduction of the fatty group into the molecule. The types of emulsions predicted by 3-D HLB are shown in **Table 17.1**.

The prior chapter introduced the concept of 3-D HLB. This chapter will investigate the predictive value of the 3-D HLB model, discuss an emulsifier kit for 3-D surfactants and look at the petrolatum emulsions. The study tested molecules with no fatty group as well as molecules with a fatty ester group. The standard HLB system has been found to work well with these types of molecules.[2]

The 3-D HLB System

The 3-D HLB system uses a right triangle to predict the effectiveness of various compounds in making emulsions. The 3-D HLB system assigns an x and y value to a compound. The x coordinate is the old HLB value. The new y coordinate is calculated using the percent oil soluble in the molecule. The calculations for 3-D HLB are shown in **Table 17.2**.

Table 17.1. Emulsions for Evaluation

1. Silicone in water (S/W) (Formula A)
2. Oil in water (O/W) (Formula B)
3. Water in silicone (W/S) (Formula C)
4. Water in oil (W/O) (Formula D)
5. Oil in silicone (O/S) (Formula E)
6. Silicone in oil (S/O) (Formula F)

Table 17.2. 3D HLB Calculation

The calculations of the x and y points for 3D HLB are as follows:

X coordinate = %water-soluble ÷ 5

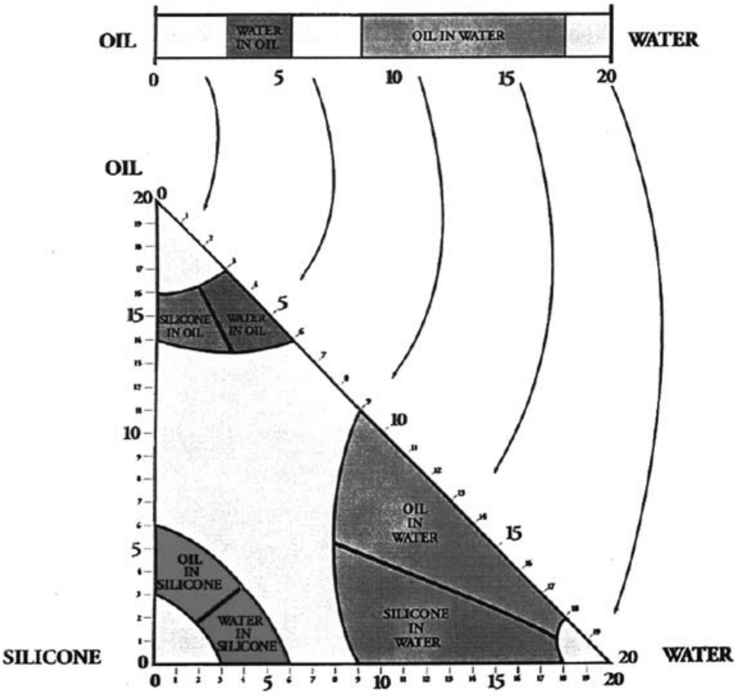
Y coordinate = %oil-soluble ÷ 5

This calculation gives the two values that define a point on the 3-D graph. The point will fall into a region that specifies a type of emulsion for which the molecule is predicted to be applicable. Using the x and y coordinates calculated above and the three-dimensional HLB chart on the facing page, the specific surfactant is pinpointed on the graph. The areas shown predict the type of emulsifier that results. **Figure 17.1** shows the 3-D HLB graphic.

Compounds

In order for the third dimension of the 3-D HLB system to be useful, there need to be three phases: silicone, water and oil. When silicone is lacking, the HLB system is very satisfactory. There are two types of molecules that have the three present: dimethicone copolyol esters and alkyl dimethicone copolyol. **Figure 17.2** shows the structure of the two classes of 3-D compounds.

Figure 17.1. HLB Evolutions 3D HLB



Concept: Top is old system - drops to be hypotenuse of new system

Dimethicone copolyol compounds

Dimethicone copolyol compounds can be esterified, making 3-D surfactants. The esterification reaction of dimethicone copolyol is shown in **Figure 17.3**. Such an esterification is classified as a derivitization. This means it occurs after construction of the polymer backbone and functionalization with allyl alcohol alkoxylates.

The combination of surfactant properties and liquidity are best when branched acids are used. Isostearic and 2 ethylhexanoic acids are best.

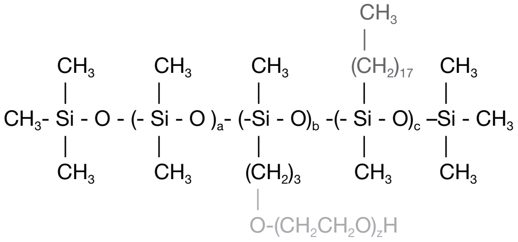
Dimethicone copolyol esters

To obtain the best comparisons, we used esters that were based upon the same polymer backbone as the dimethicone copolyols and also conformed to the structure shown in **Figure 17.4** where R is isostearic.

The use of a common silicone backbone for both the dimethicone copolyol and the ester results in molecules that vary only with the presence or absence of the isostearic portion. Dimethicone copolyol compounds are referred to as DMC A through DMC E, and the ester compounds as Ester A through Ester E. The nomenclature

Figure 17.2. 3D HLB Surfactants

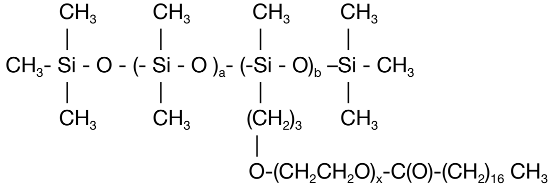
Class 1
Alkyl Dimethicone Copolyol Surfactants



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}(\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_a\text{-}(\text{-}\underset{\underset{O\text{-}(CH_2CH_2O)_zH}{(CH_2)_3}}{\overset{CH_3}{Si}}\text{-}O)_b\text{-}(\text{-}\underset{CH_3}{\overset{\overset{CH_3}{(CH_2)_{17}}}{Si}}\text{-}O)_c\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Oil soluble Water soluble Silicone soluble

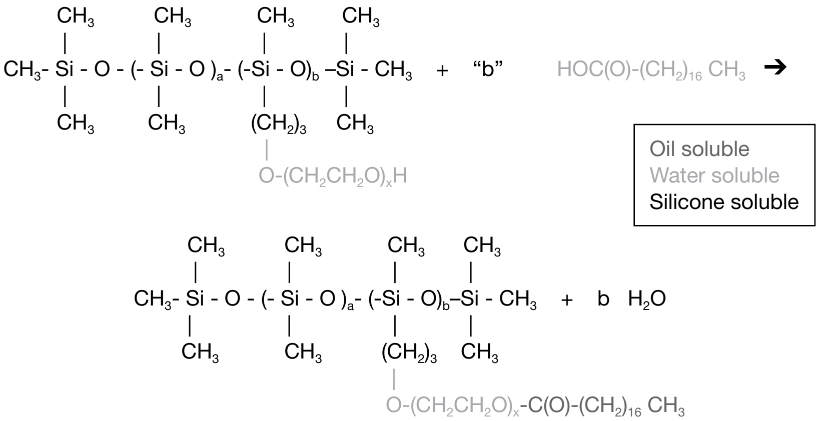
Class 2
Dimethicone Copolyol Esters



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}(\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_a\text{-}(\text{-}\underset{\underset{O\text{-}(CH_2CH_2O)_x\text{-}C(O)\text{-}(CH_2)_{16}CH_3}{(CH_2)_3}}{\overset{CH_3}{Si}}\text{-}O)_b\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Oil soluble Water soluble Silicone soluble

Figure 17.3. Esterification of Dimethicone Copolyol



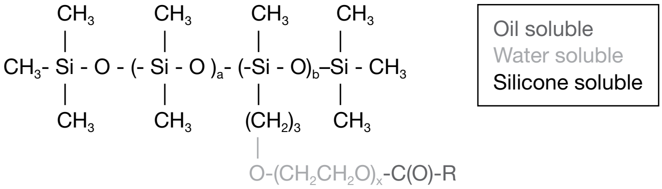
$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}(\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_a\text{-}(\text{-}\underset{\underset{O\text{-}(CH_2CH_2O)_xH}{(CH_2)_3}}{\overset{CH_3}{Si}}\text{-}O)_b\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 + \text{“b”}\ HOC(O)\text{-}(CH_2)_{16}CH_3 \rightarrow$$

$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}(\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_a\text{-}(\text{-}\underset{\underset{O\text{-}(CH_2CH_2O)_x\text{-}C(O)\text{-}(CH_2)_{16}CH_3}{(CH_2)_3}}{\overset{CH_3}{Si}}\text{-}O)_b\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 + b\ H_2O$$

allows for a direct comparison. The compounds with the same letter designation are prepared from the same silicone backbone. Therefore, DMC A had the same silicone backbone as Ester A; the only difference being that the ester has the added isostearic portion of the molecule.

The percentages of water-soluble, oil-soluble and silicone-soluble were calculated to ascertain the 3-D HLB values for each molecule. Then we compared the observed solubility properties of the resulting molecules, as well as their emulsification properties. Finally, we compared the emulsification properties to the predictions made by the 3-D HLB system.

Figure 17.4. Dimethicone Copolyol Isostearate



$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{-}(\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O)_a\text{-}(\text{-}\overset{CH_3}{\underset{(CH_2)_3\text{-}O\text{-}(CH_2CH_2O)_x\text{-}C(O)\text{-}R}{Si}}\text{-}O)_b\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3$$

R is derived from iso-stearic acid.

The compounds are shown in **Table 17.3**. The compounds as prepared were all clear yellow liquids.

Table 17.3. Compounds Evaluated

Compound	% Silicone soluble	% Fatty soluble	% Water soluble	3D-HLB	
				x	y
DMC A	40.0	0.0	60.0	12	0
DMC B	60.0	0.0	40.0	8	0
DMC C	70.0	0.0	30.0	6	0
DMC D	75.0	0.0	25.0	5	0
DMC E	80.0	0.0	20.0	4	0

cont.

Table 17.3. Compounds Evaluated cont.

Compound	% Silicone soluble	% Fatty soluble	% Water soluble	3D-HLB x	3D-HLB y
Ester A	30.0	25.0	35.0	7.5	5.0
Ester B	48.8	19.2	32.0	6.5	4.8
Ester C	58.5	16.5	25.0	5.0	3.3
Ester D	65.2	13.0	21.8	4.4	3.2
Ester E	72.0	10.0	18.0	3.6	2.0

Testing

Solubility testing

The solubility of each of the ten compounds listed in **Table 17.4** were determined at 5% by weight in the following solvents:

- Water (*aqua*)
- Mineral oil
- Cyclomethicone
- Dimethicone

Table 17.4. Solubility of Compounds (Compounds listed in Table 17.3)

Compound	Water	Mineral oil	Cyclo-methicone	Dimethicone (visc 350)
DMC A	sol	disp	disp	ins
DMC B	micro	disp	disp	ins
DMC C	disp	disp	sol	disp
DMC D	ins	disp	sol	disp
DMC E	ins	disp	sol	disp

cont.

Table 17.4. Solubility of Compounds cont.
(Compounds listed in Table 17.3)

Compound	Water	Mineral oil	Cyclo-methicone	Dimethicone (visc 350)
Ester A	micro	disp	disp	ins
Ester B	disp	trans	disp	disp
Ester C	disp	trans	sol	disp
Ester D	ins	trans	sol	disp
Ester E	ins	disp	sol	disp

sol describes a soluble material (clear)

insol describes an insoluble material (2 layers)

disp describes a dispersible material (one phase milky)

trans describes a translucent material, not clear but not milky.

micro describes a microemulsion (thick, clear with blue tint)

Emulsion testing

Emulsions were prepared for each of the ten compounds listed in **Table 17.4** using the formulations in **Table 17.5**. In each, the formulation was prepared by adding the test surfactant to the discontinuous (internal) phase under good agitation for five minutes. Following this, we slowly added the continuous phase.

Table 17.5. Formulations for Test Emulsions

Material	S/W	O/W	W/S	W/O	O/S	S/O
Silicone oil (350 visc.)	15.0	--	80.0	--	80.0	15.0
Test Surfactant	5.0	5.0	5.0	5.0	5.0	5.0
Water	80.0	80.0	15.0	15.0	--	--
Mineral oil	--	15.0	--	80.0	15.0	80.0
Total	100.0	100.0	100.0	100.0	100.0	100.0

The emulsions were evaluated on a scale with 5 being a stable emulsion and 0 being completely unstable. One note of interest is that very thick materials may look stable but may not be emulsions. Oils can be stabilized in thick dispersions simply because they cannot settle. There have been several patent applications that confuse the two concepts. Emulsions will remain stable when the concentration is lowered by addition of continuous phase, whereas thicker dispersions will not.

Table 17.6 summarizes the results for emulsification properties.

Table 17.6. Emulsion Stability of Compounds Tested (Emulsion Formulation from Table 17.5)

Compound	S/W	O/W	W/S	W/O	O/S	S/O
DMC A	3	1	0	0	0	0
DMC B	0	0	0	0	0	0
DMC C	0	0	4	0	0	0
DMC D	0	0	5	0	0	0
DMC E	0	0	4	0	0	0
Ester A	4	3	0	0	0	0
Ester B	0	0	0	0	0	0
Ester C	0	0	4	0	3	0
Ester D	0	0	5	0	4	0
Ester E	0	0	5	0	2	0

Evaluation Criteria

0 split into two layers, 5 Stable emulsion 3 hours at ambient.

Discussion

Solubility

The tested compounds reveal several interesting trends.

As the percentage of silicone in the molecule increases, the water solubility decreases. Molecules go from soluble to microemulsions to dispersible and, finally, to insoluble. This trend occurs both in the dimethicone copolyol compounds and in the ester compounds. However, the presence of the fatty group in the ester further lowers water solubility of the molecule.

As the percentage of silicone in either set of compounds increases, there is no effect upon solubility in mineral oil. Incorporation of the fatty group into the molecule changes the mineral oil surfactant blend from milky white to translucent in stable emulsions. Incorporation of fatty groups into the molecule improves oil compatibility.

As the percentage of silicone in the molecule increases, the solubility in cyclomethicone increases. Molecules go from dispersible to soluble. This is true in both esters and dimethicone copolyol compounds. One compound (DMCC) is dispersible in water and soluble in cyclomethicone and another (Ester B) is dispersible in both.

As the percentage of silicone in the molecule increases, the dispersibility in 350 viscosity dimethicone increases. Molecules go from dispersible to insoluble. This trend occurs both in the dimethicone copolyol compound and in the ester compounds. However, the presence of the fatty group in the ester improves dimethicone compatibility.

The ratio of the silicone-, fatty- and water-soluble portion of the molecule alters solubility of compounds in various solvents. The trends are predictable; consequently, it is possible to choose molecules for specific applications.

Emulsification properties

Figure 17.1 presents a graph based on the 3-D HLB theory. The figure shows the lines that are generated by connecting the 3-D HLB values of the dimethicone copolyol and the ester made from the same silicone backbone. The 3-D HLB value for a lettered dimethicone copolyol is joined with the 3-D HLB value for a similarly lettered ester.

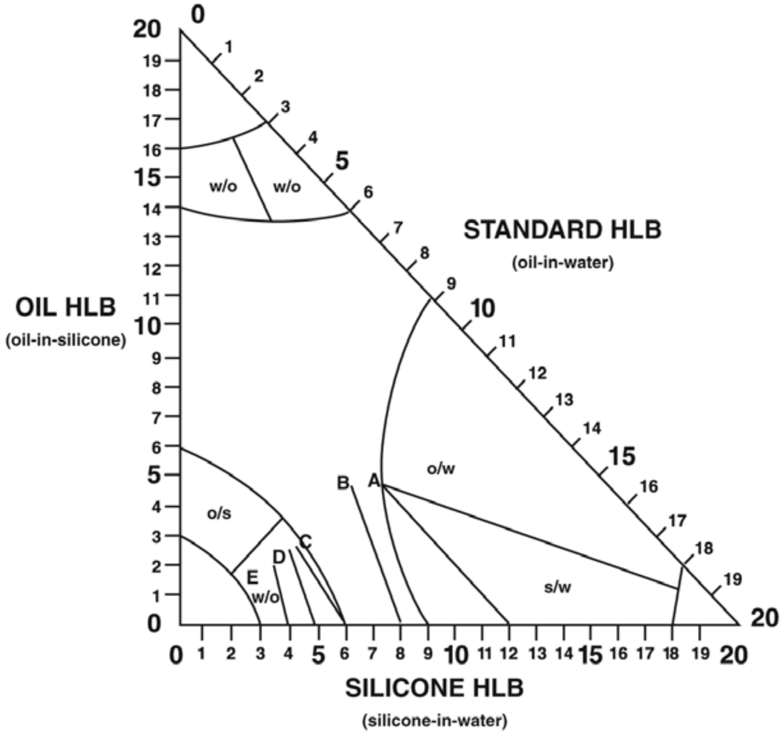
Figure 17.5 shows the inclusion of the fatty group not only increases the amount of fatty from zero, it also dilutes the other percentages. This is why the lines slope upward to the left. The slope of the lines decreases as one looks at lines A through E. The reason for this is that as you go from A to E the polymers have an increasing amount of silicone in the molecule. Consequently, there is less isostearic needed to react on a mole-to-mole basis. This is also why the percentage of fatty continues to be lower as one progresses from A to E.

Figure 17.5 also predicts the effects of the alteration of structure on the emulsification properties. It is significant to look at what we call the "cusp surfactants. " In each corner of the triangle there are two regions that have a common line between them. These three pairs share a common border. They are (o/w: s/w), (o/s: w/s) and (s/o: w/o). A surfactant whose 3-D HLB value falls on these border lines is called a cusp surfactant. Cusp surfactants are predicted to be good as emulsifiers in both types of emulsions that share the common border.

The inclusion of the fatty groups into the molecules shifts the emulsification properties, in some instances resulting in some near cusp surfactants. Cusp surfactants allow for the emulsification of two different insoluble oils into an emulsion. The technology is currently used in making mineral oil and silicone fluid co-emulsions, in which the two oils are blended prior to emulsification. The closest to the border line is ester A. This material, as predicted, is good for making both s/w and o/w emulsions; unlike the dimethicone copolyol based upon the same silicone backbone (DMC A), esters C, D, and E are all closer to the cusp than the dimethicone copolyol sharing the common backbone. Consequently, they are predicted to be better emulsifiers for o/s than the dimethicone copolyol based upon the same backbone. The way one would make esters C, D, and E true cusp surfactants is to increase the amount of fatty in the molecule to fall on the border line between the o/s and the w/s regions.

The results of the modifications are shown in **Figure 17.5**.

Figure 17.5. 3D HLB Plot



3D HLB plot of five pairs of a dimethicone copolycol and an isostearic ester with the same polymer backbone.

Line A joins DMC A and ester A
Line B joins DMC B and ester B
Line C joins DMC C and ester C
Line D joins DMC D and ester D
Line E joins DMC E and ester E

Emulsifier Kits

The ability to successfully make emulsions is the desire of the formulator; while theory might be interesting, a practical program to make the emulsion is needed. To this end, a series of four related emulsifiers have been made into an emulsifier kit, ranging in solubility, 3-D HLB and emulsion properties. Emulsifier kits for hydrocarbon-based surfactants are a very valuable formulation tool and have been available for many years. The concept is now available for 3-D Surfactants. **Table 17.7** shows the surfactants available.

Table 17.8 shows the solubility of the 3-D emulsifiers in several solvents. As the HLB increases, oil solubility is lost and water solubility gained.

Table 17.7. 3D Surfactants in Kit Form

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

Table 17.8. Solubility of 3D Emulsifiers

	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%
J208-212	S	S	S	S	I	I	D	D	S	S	D	D	D	D
J208-412	D	D	S	S	D	D	D	D	S	S	D	D	D	D
J208-612	I	I	S	S	S	S	S	D	S	S	D	D	D	D
J208-812	I	I	S	S	S	S	S	S	S	S	S	S	D	D

Petrolatum Emulsions

For emulsion systems that contain roughly the same amount of oil and water, the type of emulsion that forms is due only to the emulsifier.

Regular emulsions are o/w emulsions. Invert emulsions are what's called "backwards emulsions." The aqueous phase is dispersed in the non-aqueous phase. While this type of emulsion has largely taken a back seat to a more common standard emulsion, some of the oldest cosmetic formulas are invert emulsions. The classic beeswax/borax cold cream formula has been around forever. Invert emulsions have advantages over the o/w type. There are many ingredients that can be used in the external phase, as opposed to water being the only external phase allowed in an o/w emulsion. Mineral oil, vegetable oils, esters and silicone waxes, and liquids have all been used in invert emulsions. Properties like initial feel, spreadability and substantivity can be tailored more precisely to the needs of the product. There are still more o/w emulsifiers available than w/o emulsifiers, but the need for improved performance that comes with invert emulsions has encouraged many companies to develop many new, effective invert emulsifiers. Silicone based emulsifiers are one of the new breed. Silicone surfactants allow the formulator to tailor external phases to the precise needs of new and improved products such as substantive sunscreens.

The ratio of oil to water used in many emulsions is often 1:1, meaning that the emulsifier is often the deciding factor in the type of emulsion formed. There are metastable emulsions in the market invert from o/w to w/o as the water phase evaporates on the skin. The resulting product gives improved water-resistance. There is still a great potential for creative cosmetic chemists to develop improved emulsions that provide consumer perceivable advantages over what is already out there.

Effects of Varying Ratios of Petrolatum to Oil

Table 17.9 shows the formulations evaluated to show the effect of emulsifier concentration on an invert emulsion of petrolatum.

Table 17.9. Formulations
Varying Ratio of Emulsifiers

Material	A % wt	B % wt	C % wt
Polysurf 67 CS (Thickener)	0.50	0.75	0.25
Tetrasodium EDTA	0.40	0.40	0.40
Water	48.90	70.65	25.00
Propylene Glycol	2.00	2.00	--
J208-612 (3HLB see above)	4.00	4.00	4.00
Petrolatum	44.00	22.00	70.15
Propylparaben	0.20	0.20	0.20
	100.0	100.0	100.0

The results of the change in concentration are as follows:

A is a very heavy lotion, with an outstanding skin feel.

B is a thin lotion with a cooling effect on the skin.

C is a heavy cream with the texture and feel of petrolatum.

This demonstrates that the cosmetic aesthetics of an emulsion is dramatically affected by concentration of surfactant.

Effects of Varying Emulsifier

Formula A repeated, only this time to investigate the effect of the other 3-D surfactants. **Table 17.10** shows the formulations for varying emulsifiers.

**Table 17.13. Formulations
Varying Emulsifiers**

Material	5-A	5-D	5-E	5-F
Polysurf 67 CS (Thickener)	0.50	0.50	0.50	0.50
Tetrasodium EDTA	0.40	0.40	0.40	0.40
Water	48.90	48.90	48.90	48.90
Propylene Glycol	2.00	2.00	2.00	2.00
J208-612	4.00	--	--	--
J208-412	--	4.00	--	--
J208-212	--	--	4.00	--
J208-812	--	--	--	4.00
Petrolatum	44.00	44.00	44.00	44.00
Propylparaben	0.20	0.20	0.20	0.20
	100.0	100.0	100.0	100.0

J208-612, J208-412 and J208-212 all gave good emulsions. The J208-812 formed a very grainy looking product with visible flecks of petrolatum. Consequently, it appears that the higher HLB material is not suitable to forming good emulsions with petrolatum. Since the water and petrolatum ration are close to equal, the nature of the emulsion (invert or regular) is affected by the choice of emulsifier.

The product made with S J208-612 is an invert emulsion, and the product made with S J208-212 is a regular emulsion. The product made with the J208-412 has some properties of both. Clearly, the type of emulsifier chosen has a dramatic affect upon emulsion properties.

Conclusion

The 3-D HLB system is helpful in engineering emulsifiers that will allow for the formulation of complex emulsions. Making an emulsion using the 3-D surfactants, the emulsion can be emulsified into mixed emulsions using our system in two easy steps. This simplified process makes multiple phase emulsions by making two simple emulsions one after another. A more sophisticated process is shown in the chapter titled "Silicone Emulsions." The process described therein will produce a more elegant emulsion with a smaller particle size.

References:
1. WC Griffin, *J Soc Cos Chem* 1 311 (1949)
2. Hill, ACS Symposium Series, No 501 (1992) p 278
3. HLB System, ICI Bulletin (1984) p 8
4. O'Lenick, AJ and JK Parkinson, *Cosmet Toil* 111(10) 37-44 (1996)

Chapter 18

Silicone Quats

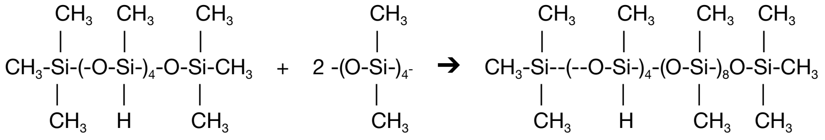
Traditional cationic compounds, referred to as quats, are used very commonly in the personal care industry as conditioners and softeners on the hair and skin. This is due to the fact that hair and skin have a net negative charge and as a result of ionic interactions, the positively charged quats become substantive to the hair and skin.[1]

It is therefore not surprising that the silicone analogues of traditional quats are likewise important compounds in personal care vis-à-vis conditioning and softening. The structure of the compound and the balance of silicone-, fatty- and water-soluble groups determines the properties of silicone quats, as is the case with all other silicone compounds. In the instance of these compounds the cationic group is a water-soluble group.

Numerous silicone quats have been produced over the years, differing in structure and properties.[2-4] The silicone quaternary compounds in Chapter 19 are made significantly different in structure from those covered in this chapter. The compounds in this are derived from dimethicone copolyol polymers. They are water-soluble and consequently easy to use in formulation. The quats in this chapter are new to the personal care market, but are receiving growing acceptance. They include (1) dialkyl quats, (2) amido quats based upon aminoethyl ethanolamine (AEEA), and (3) diamido quats based upon diethylene triamine (DETA). They are less water-soluble, more oil-soluble and more substantive. They are also more difficult to place into formulations, particularly aqueous formulations due to the fact they are less soluble in water than the compounds derived from dimethicone copolyol.

Figures 18.1, 18.2 and 18.3 show the construction, functionalization and derivitization reactions used to make the silicone quats in this chapter.

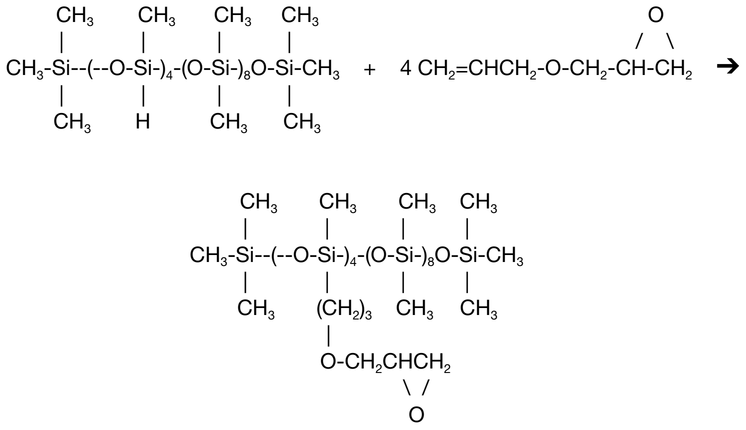
Figure 18.1. Silicone Quats Compounds: Construction



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}(\text{-}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_4\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 \quad + \quad 2\ \text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_4\text{-} \quad \rightarrow \quad CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_4\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

MD*M **D4** **MD*3D8M**

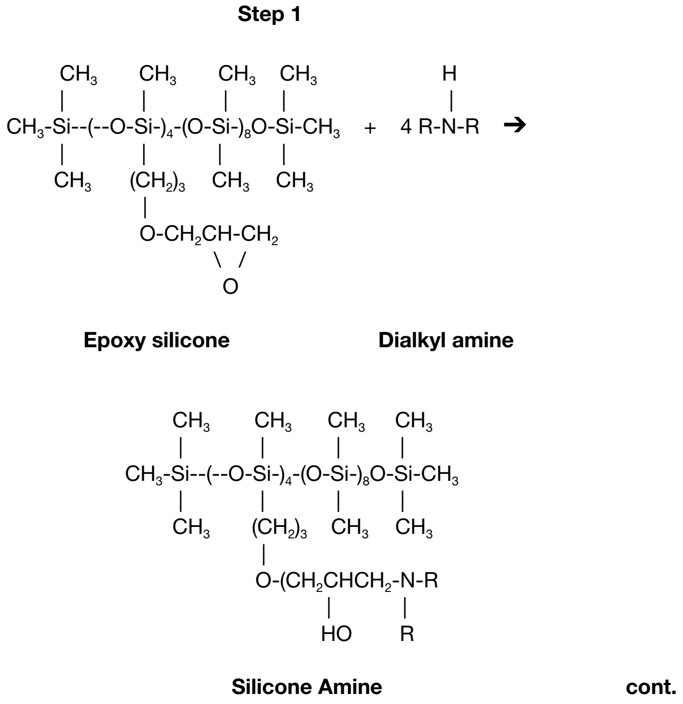
Figure 18.2. Silicone Quats Compounds: Functionalization



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--(--O-}\underset{H}{\overset{CH_3}{Si}}\text{-)}_4\text{-(O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-)}_8\text{O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 \;+\; 4\;CH_2{=}CHCH_2\text{-O-}CH_2\text{-}\overset{O}{\overbrace{CH\text{-}CH_2}} \rightarrow$$

$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--(--O-}\underset{(CH_2)_3\text{-O-}CH_2\underset{O}{\underbrace{CHCH_2}}}{\overset{CH_3}{Si}}\text{-)}_4\text{-(O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-)}_8\text{O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

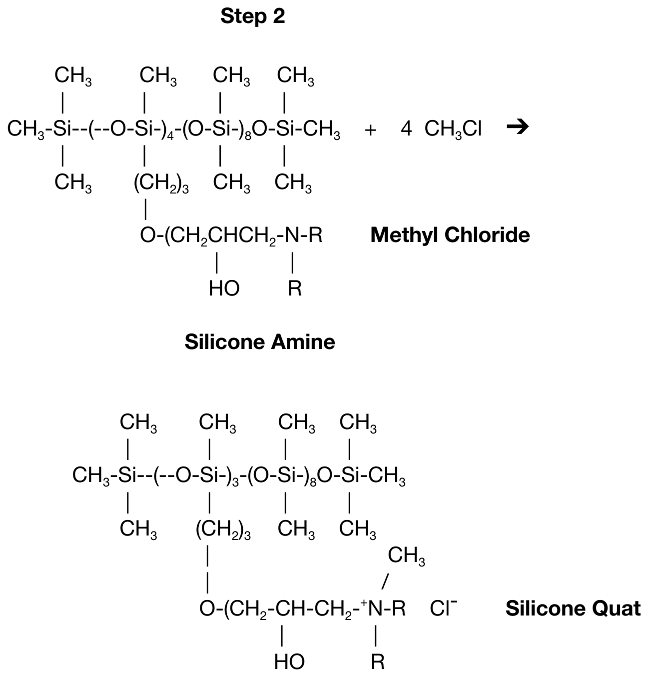
Figure 18.3. Silicone Quat Compounds: Derivitization Steps



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--(--O-}\underset{(CH_2)_3\text{-O-}CH_2\underset{O}{\underbrace{CH\text{-}CH_2}}}{\overset{CH_3}{Si}}\text{-)}_4\text{-(O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-)}_8\text{O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 \;+\; 4\;R\text{-}\overset{H}{N}\text{-}R \rightarrow$$

$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--(--O-}\underset{(CH_2)_3\text{-O-(}CH_2\underset{HO}{CH}CH_2\text{-}\underset{R}{N}\text{-}R}{\overset{CH_3}{Si}}\text{-)}_4\text{-(O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-)}_8\text{O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Figure 18.3. Silicone Quat Compounds: Derivitization Steps cont.



$$\underset{CH_3}{\overset{CH_3}{CH_3\text{-}Si}}\text{--(--O-}\underset{(CH_2)_3\text{-O-}(CH_2\underset{HO}{CH}CH_2\text{-}\underset{R}{N}\text{-R}}{\overset{CH_3}{Si}}\text{-)}_4\text{-(O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-)}_8\text{O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-CH}_3 + 4\ CH_3Cl \rightarrow$$

$$\underset{CH_3}{\overset{CH_3}{CH_3\text{-}Si}}\text{--(--O-}\underset{(CH_2)_3\text{-O-}(CH_2\text{-}\underset{HO}{CH}\text{-}CH_2\text{-}\underset{R}{\overset{CH_3}{{}^{+}N}}\text{-R}\ Cl^{-}}{\overset{CH_3}{Si}}\text{-)}_3\text{-(O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-)}_8\text{O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-CH}_3$$

Structure

The following compounds were chosen to illustrate the structure of silicone quats:

Class 1

Dialkyl Quats

The silicone dialkyl quats have the structure shown in **Figure 18.4**.

There are two different types of compounds within this group. The first class of compounds has methyl or ethyl "R" groups. The second class of compounds has higher alkyl C12 or C19.

The lower alkyl products have the following properties:

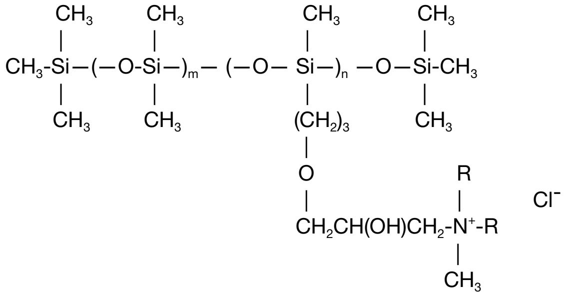
- Less oleophilic than the higher alkyl products
- Better antistatic properties than the higher alkyl products
- More water compatible than the higher alkyl
- Less build up on hair than the higher alkyl

The higher alkyl products have the following properties:

- More buttery (fatty) feel on hair

- More oleophobic than the lower alkyl products
- More intensively conditioning

Figure 18.4. Class 1. Di-alkyl Quats



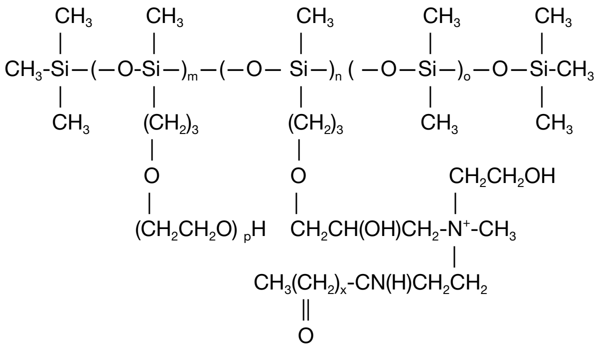
R ranges from CH_2CH_3 to $C_{18}H_{37}$.

Class 2

FattyAmido Quats from AEEA

This class of compounds contains only one amido group and a hydroxy ethyl group on the quaternary group. The molecules also have PEG groups present. These materials are traditional textile, wool and fabric softeners. There are hydrophobic, but less hydrophobic than those materials in Class 3. This class of compounds has found utility in the softening of textile fabrics and fibers. **Figure 18.5** shows the structure.

Figure 18.5. Class 2. Amido Quats from AEEA



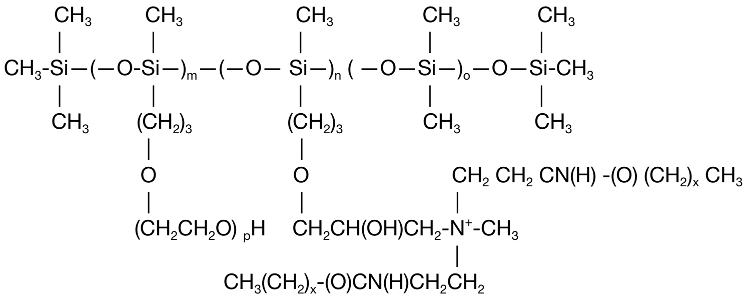
x=10 for coco products x=16 for stearic

Class 3

Fatty Diamido Quats from DETA

Compounds from this class have more oil-soluble amido groups than Class 2. They provide outstanding wet comb and are used primarily in conditioners. **Figure 18.6** shows the structure.

Figure 18.6. Class 3. Amido Quats from DETA



$$CH_3\text{-}Si(CH_3)_2-(-O\text{-}Si(CH_3)[(CH_2)_3O(CH_2CH_2O)_pH]-)_m-(-O-Si(CH_3)[(CH_2)_3O\,CH_2CH(OH)CH_2\text{-}N^+(CH_3)(CH_2CH_2CN(H)\text{-}(O)(CH_2)_xCH_3)(CH_2CH_2N(H)C(O)\text{-}(CH_2)_xCH_3)]-)_n(-O-Si(CH_3)_2-)_o-O-Si(CH_3)_2\text{-}CH_3$$

x=10 for lauryl

x=16 for stearyl

Properties

The compounds evaluated are shown in **Table 18.1**.

The identification numbers in the result section are described in **Table 18.2**.

Physical properties

Table 18.3 shows the solubility of these compounds in various fluids.

Application properties

The properties of silicone quats are determined by the amount of silicone present, the number of cationic groups present in the molecule, the carbon number of the alkyl groups around nitrogen, the molecular weight of the compound and the class of compound (i.e. structure).

The critical functional attributes that allow for the utilization of these compounds in personal care products include the water solubility of the compound, hydrophobicity of the compound when applied to the substrate and hydrophobicity of the compound on the hair or skin.

Table 18.1. Physical Properties and Softness Results for Selected Silicone Quats

Group	Silicone	Degree of Softness	% Silicone	% Cationic Charge	Alkyl group	Mol. Wt.
1	Silquat D2	2.6	53	6.0	Ethyl	1,960
1	Silquat J2	2.6	49	6.5	Ethyl	4,400
1	Silquat J15AO	4.8	75	3.0	Ethyl	11,000
2	Silquat D208-B	3.3	36	1.0	Stearyl	2,900
2	Silquat J208-2B	3.8	33	0.84	Stearyl	6,900
2	Silquat Di 008 – 2B	3.8	11	1.7	Stearyl	1,700
3	Silquat D208 CA	2.5	39	1.02	Coco monoamide from aminoethylethanolamine	2,700
3	Silquat D208 CDA	3.7	36	0.96	Coco diamide from diethylenetriamine	2,900

Table 18.2. Designation of Silicone Quats

Compound	Class	Name
1.	1	Silquat D2
2.	1	Silquat J2
3.	1	Silquat J15AO
4.	2	Silquat D208-B
5.	2	Silquat J208-2B
6.	2	Silquat Di 008-2B
7.	3	Silquat D208 CA
8.	3	Silquat D208 CDA

Table 18.3. Solubility of Silicone Quats

	Water		IPA		Mineral Spirits		Mineral Oil		Aromatics		Cyclo Methicone		350 Visc. Silicone Fluid	
Quat 10%	1%	10%	1%	10%	1%	10%	1%	10%	1%	10%	1%	10%	1%	
1.	S	S	S	S	I	I	S	S	I	I	I	I	I	I
2.	S	S	S	S	I	I	I	I	I	I	I	I	I	I
3.	D	D	S	S	D	I	I	I	I	I	I	I	D	D
4.	D	D	S	S	I	I	I	I	S	S	I	I	D	D
5.	S	S	S	S	I	I	I	I	S	S	I	I	D	I
6.	D	D	S	S	S	I	I	I	S	S	I	I	D	D
7.	D	D	S	S	I	I	I	I	S	S	I	I	D	D
8.	D	D	S	S	I	I	I	I	S	S	I	I	D	I

1. Silquat D2
2. Silquat J2
3. Silquat J15AO
4. Silquat D208-B
5. Silquat J208-2B
6. Silquat Di 008-2B
7. Silquat D208 CA
8. Silquat D208 CDA

Softness

A protocol for measuring softness

The similarity of cotton fabric to hair makes cotton a good model for predicting the performance of silicone quats in personal care applications. The following data was taken from evaluations made on textile softeners[5] evaluated on cotton fabric. It represents one of the most thorough evaluations of silicone quats carried out to date.

The cotton was cut into 4-by-4 inch squares and weighed. Originally, the amount of water used for the test was 10 times the weight of the cotton; however it was found that this would not be enough to fully cover the surface area of the cloth. Hence, the value was increased to 40 times the weight of the cloth.

The ratio of grams of quat to grams of water is 0.06:100. The desired amount of quat was added to the water and the pH of the mixture was adjusted to 5–6. The mixture was heated to 55–60°C and the cotton was added. After stirring the cotton in the mixture for 10 minutes, the cotton was squeezed dry and then air dried.

After completion of all the samples, 10 people were asked to test the softness of each cotton piece against a control on a scale from 1 (the control) to 5 (most soft).

Results

Table 18.4 ranks the silicone quats from softest to least soft with the respective average grade given by each of the 10 people.

Table 18.4. Softness of Silicone Quats

Quat	Degree of Softness
3	4.8
5	3.8
6	3.8
8	3.7
4	3.3
1	2.6
2	2.6
7	2.5

Table 18.4 shows the silicone quats in each of these groups and the softness results for the selected silicone quats.

In the Group 1 quats, the J15AO has by far the highest degree of softness. The molecular weight is very large and so is the silicone percentage, whereas the percentage of cationic charge is smaller than the D2 and J2 quats. The J2 and D2 quats, although differing in molecular weight, have relatively the same percentages of silicone and cationic charge. This suggests that molecular weight may not be a factor in determining softness. The higher percentage of cationic charge also is a factor since the higher the cationic charge, the more water-soluble the silicone becomes and, therefore, may be easier to wash off.

The Group 2 distearyl amines show promising results for softness. The J208 and D208 quats were fairly similar, with the J208 having a higher degree of softness.

Although the diethyl amine quats in Group 1 show no difference in softness with increasing molecular weight, there does seem to be a correlation between degree of softness and molecular weight with the distearyl amine quats. This could be due to the high degree of branching that may make the quats more substantive.

The Group 3 coco amide quats show that the silicone quat D208-CA gave a small increase in softness compared to the control, but not as great as the silicone quat D208-CDA. This is as would be expected because the percentage of silicone in both molecules is similar, but there is a higher percentage of coco amide. The increase in fatty coco diamide would help in softness, because amides have been used quite commonly in the personal care and textile market for softness and conditioning.

Comparing the three groups, it appears that overall the distearyl quats give consistently higher softness than the coco or tallow amide quats. The coco amides have the lowest degree of softness followed by the tallow amide quats. The degree of softness provided by the water-soluble diethyl amine quats is fairly low, but when the amount of silicone is increased and the product is dispersible in water, the degree of softness is excellent.

Surface Tension Silicone Quats

The ability to lower a surface tension is critical to the utilization of silicone quats. The polymers need to lower surface tension to (a) wet, (b) spread out, and (c) condition the hair. Recalling that water has a surface tension of 72 dynes/cm^2, fatty surfactants 32 dynes/cm^2 and silicone surfactants 22 dynes/cm^2, the value obtained for the silicone quat will allow for the determination if the product orients itself with the fatty or silicone portion at the surface. The change in surface tension over time and as a function of pH is an important determination, since it will be indication of instability.

Table 18.5 shows the methodology used for surface tension analysis. The products all have surface tension values of around 30, showing little change over seven days. (See **Table 18.6**.) The test results for the product adjusted to different pH values are shown in **Figures 18.7**, 18.8, **18.9** and **18.10**. To the extent the surface tension changes (increases) the polymer is experiencing instability. The conclusion from these charts is that the quats should be used at pH values of below 10.

Table 18.5. *Surface Tension* Test Methodology
All the surface tension measurements were done with 0.1% solution of Silicone quat in deionized water at room temperature. Sigma 70 with software version 2.52 was used for the measurements. The 0.1% solution was made by mixing 0.6 g of silicone polyether with 600 mL of deionized water. The solution was then divided into three parts in 4 oz bottles. The first part was used "as is" without any pH adjustment. The second part was adjusted to a pH value of 10 with diluted ammonium hydroxide. And the third part was adjusted to a pH value of 4 with diluted acetic acid. The pH of the solution was re-adjusted to the desired value after the first week, when needed.

Table 18.6. Surface Tension of Silicone Quats (neutral pH)

Day	Silquat D-2 #1	Silquat J2 #2	Siliquat J-208-2B #5	Silicone Quaternium 8 Silquat AD
0	30.2	30.1	29.0	30.1
7	29.5	29.0	29.0	30.0

Figure 18.7. Surface Tension of Silquat D2, Quat #1

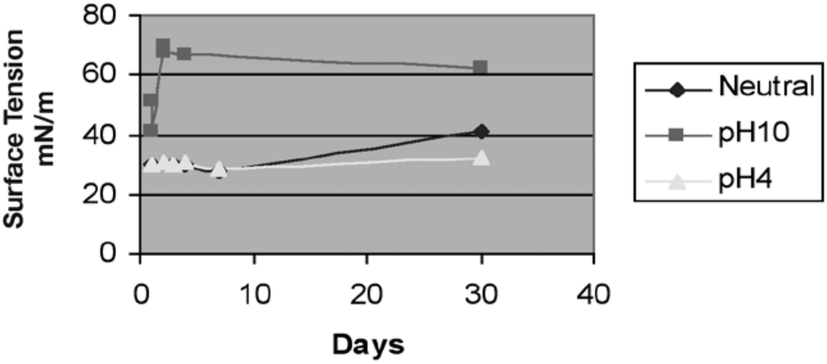


Figure 18.8. Surface Tension of Silquat J2, Quat #2

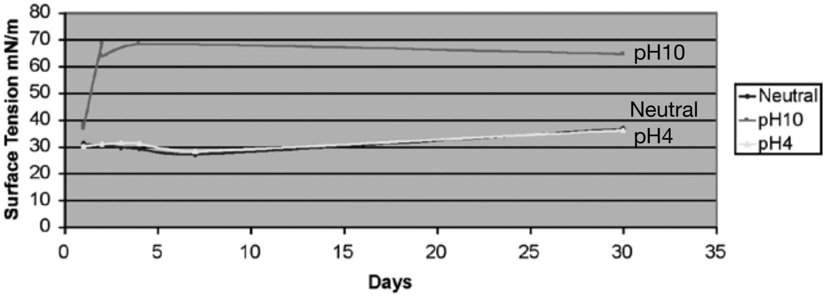


Figure 18.9. Surface Tension of Silquat J208-2B, Quat #5

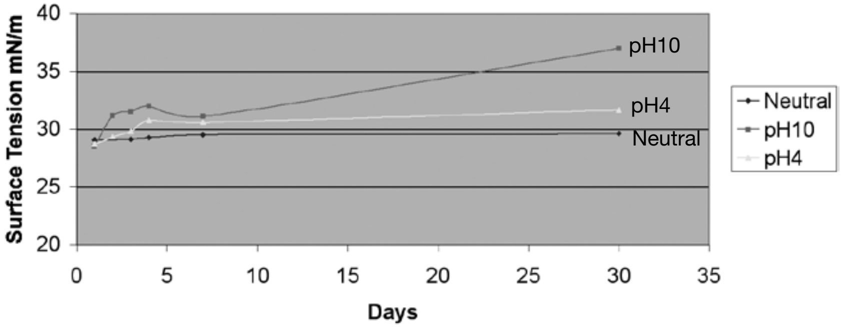
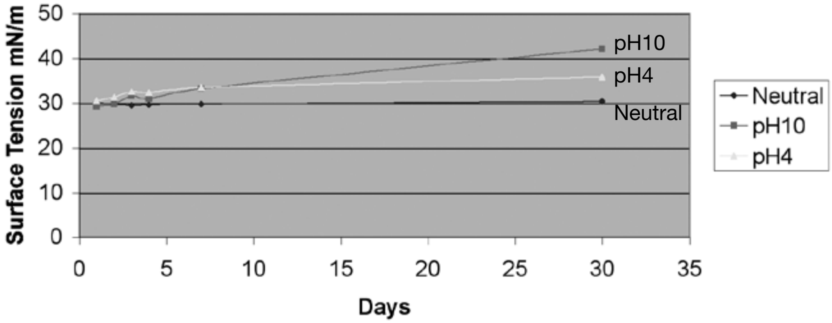


Figure 18.10. Surface Tension of Silquat AD Silicone Quaternium 8



Conclusion

It can be seen from the above analysis that incorporating silicone quats onto fiber will increase the degree of softness. The higher the percentage of silicone and fatty amine in the molecule, the greater the degree of softness. It can also be seen that the larger the alkyl groups, the better the increase in softness as well. The silicone quat J15AO gave the highest degree of softness, mainly due to the high percent of silicone in the molecule. The silicone quat D208-2TDA (tallow diamide) also gave a high degree of softness due to the large percent of tallow diamide in the molecule. The silicone quat D208-CDA (coco diamide) and silicone quat J208-2B (distearyl quat) also gave higher degrees of softness due to the larger amount of fatty alkyl groups in the molecule.

Solubility also plays an important factor in determining the substantivity and degree of softness. If the quat is too soluble, it can be easily washed off. The quats need to have a degree of dispersibility in water in order to better deposit onto the substrate. In the Group 1 silicone diethylamine quats, the solubility is provided by the diethylamine quat group. Therefore, the higher the cationic charge, the more water-soluble the product. In the Group 2, 3 and 4 quats, the alkyl group is much larger (C12-C18) and therefore the quats are hydrophobic as is. A polyether moiety must be included in the molecule to provide water dispersibility or solubility.

Although these tests were incorporated on cotton fibers, one can assume that this correlation will apply to hair fibers as well. We expect that these compounds will find applications in personal care in the near future.

References:

1. A O'Lenick, *Surfactants Chemistry and Properties*, Allured Publishing, (2002)
2. US Patent 4,891,166 issued January 2, 1990 to Schaeffer et al. titled "Diquaternary polysiloxanes, their synthesis and use in cosmetic preparations"
3. US Patent 5,098,979 issued March 24, 1992 to O'Lenick, Anthony, titled "Novel silicone quaternary compounds".
4. US Patent 5,602,224 issued February 11, 1997 to Vrckovnik et al., titled "Silicone alkyl quats".
5. Siltech Technical Bulletin, 2003.

Chapter 19

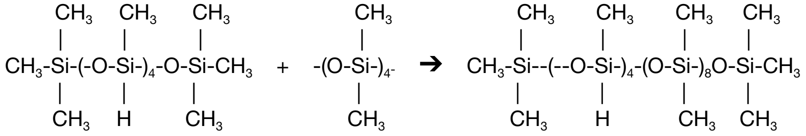
Silicone Ester Amido Quaternary Compounds

When the first edition of this book was written in 2003, this class of compounds was new and just being introduced. Over the last five years the references to the use of these materials in formulated products has grown significantly. A number of the silicone amido quaternium compounds, dubbed silicone quaternium compounds, are covered by various US patents.[1,2] These materials are based on the reaction of dimethicone copolyol with chloracetic acid followed by reaction with an amido amine to produce an ester amido quat. These compounds have been found to have good compatibility with anionic systems, provide outstanding wet comb properties, antistatic properties and nongreasy softening properties to hair, fiber and skin. **Figure 19.1** shows the construction, **Figure 19.2** the functionalization and **Figure 19.3** derivitization steps to make these compounds.

The compounds have an ester group, an amid group and a cationic group with a chloride counter ion. This results in some interesting properties. The amido group renders the compounds more compatible with anionic materials. The ester group renders the molecule both more biodegradable and less stable in high or low pH formulations. The quats of this type are water-soluble and consequently easy to use information.

The products can have a varying amount, type and location of polyoxyalkylene in the polymer backbone. This ability to regulate the type of alkylene oxide and amount present in the silicone polymer results in a series of products with a range of water/oil solubility. The technology used to produce the compounds of the present invention is very flexible and allows for performance-tailored molecules for specific applications.

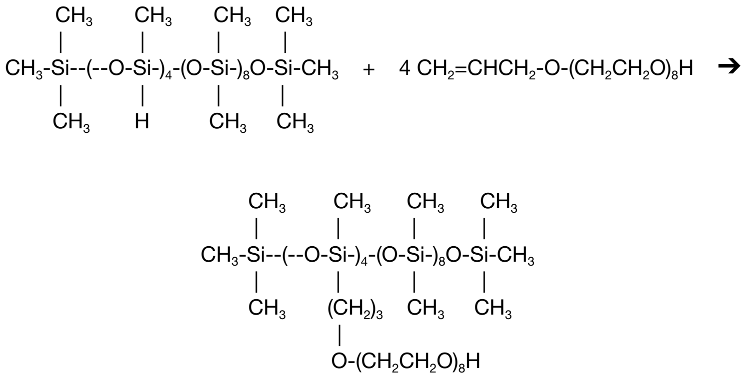
Figure 19.1. Silicone Quaternium Compounds: Construction



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}(\text{-}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_4\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 \;+\; \text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_4\text{-} \;\rightarrow\; CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_4\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

MD*M **D4** **MD*4D8M**

Figure 19.2. Silicone Quaternium Compounds: Functionalization



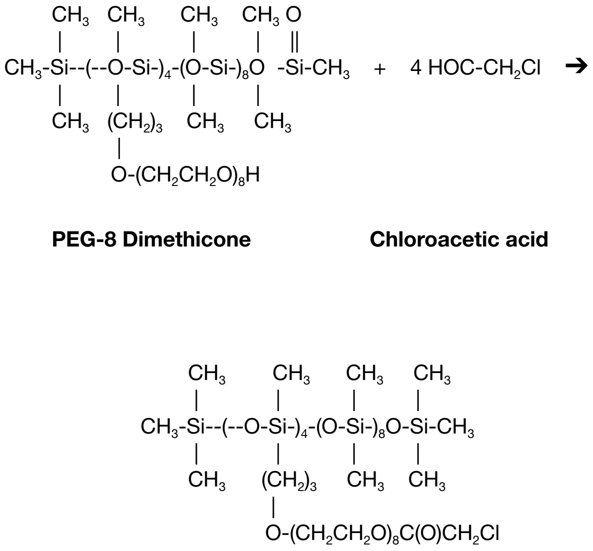
$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\overset{CH_3}{\underset{H}{Si}}\text{-})_4\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_8O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3 \;+\; 4\ CH_2{=}CHCH_2\text{-}O\text{-}(CH_2CH_2O)_8H \rightarrow$$

$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\overset{CH_3}{\underset{\underset{O\text{-}(CH_2CH_2O)_8H}{(CH_2)_3}}{Si}}\text{-})_4\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_8O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3$$

PEG-8 Dimethicone

Figure 19.3. Silicone Quaternium Compounds: Derivitization Steps

Step 1



$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\overset{CH_3}{\underset{\underset{O\text{-}(CH_2CH_2O)_8H}{(CH_2)_3}}{Si}}\text{-})_4\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_8\overset{CH_3}{\underset{CH_3}{O}}\ \text{-}\overset{O}{\overset{\|}{Si}}\text{-}CH_3 \;+\; 4\ HOC\text{-}CH_2Cl \rightarrow$$

PEG-8 Dimethicone **Chloroacetic acid**

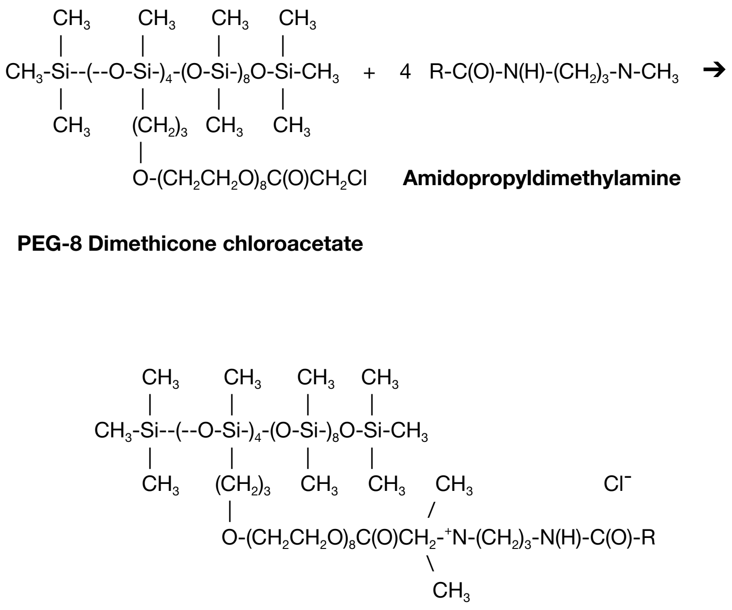
$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\overset{CH_3}{\underset{\underset{O\text{-}(CH_2CH_2O)_8C(O)CH_2Cl}{(CH_2)_3}}{Si}}\text{-})_4\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_8O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3$$

PEG-8 Dimethicone chloroacetate

cont.

Figure 19.3. Silicone Quaternium Compounds: Derivitization Steps

Step 2



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{(CH_2)_3O(CH_2CH_2O)_8C(O)CH_2Cl}{\overset{CH_3}{Si}}\text{-})_4\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 + 4\ R\text{-}C(O)\text{-}N(H)\text{-}(CH_2)_3\text{-}N\text{-}CH_3 \rightarrow$$

Amidopropyldimethylamine

PEG-8 Dimethicone chloroacetate

$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--}(\text{--}O\text{-}\underset{(CH_2)_3O(CH_2CH_2O)_8C(O)CH_2\text{-}{}^{+}N(CH_3)_2\text{-}(CH_2)_3\text{-}N(H)\text{-}C(O)\text{-}R}{\overset{CH_3}{Si}}\text{-})_4\text{-}(O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_8O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 \quad Cl^-$$

Silicone Quaternium

The application of this class of compounds is found in aqueous systems like shampoos, body washes and wipes. The products are water-soluble, and contribute a soft conditioning effect and a cosmetically elegant skin feel.

There are now 21 silicone quaternium compounds currently listed in the CTFA dictionary, shown in **Table 19.1**.

Table 19.1. Silicone Quaternium Compounds

Name	**Supplier(s)**
Silicone Quaternium-1	Corum Corporation
Silicone Quaternium-2	Elgin Corporation
Silicone Quaternium-3	Phoenix Chemical, Inc.

Table 19.1. Silicone Quaternium Compounds cont.

Name	Supplier(s)
Silicone Quaternium-4	Phoenix Chemical, Inc.
Silicone Quaternium-5	Phoenix Chemical, Inc.
Silicone Quaternium-6	Phoenix Chemical, Inc.
Silicone Quaternium-7	Phoenix Chemical, Inc.
Silicone Quaternium-8	Siltech LLC. Noveon
Silicone Quaternium-9	Phoenix Chemical, Inc.
Silicone Quaternium-10	Phoenix Chemical, Inc.
Silicone Quaternium-11	Phoenix Chemical, Inc.
Silicone Quaternium-12	Phoenix Chemical Inc.
Silicone Quaternium-15	CHT R. Beitlich GmbH
Silicone Quaternium-16	CTFA currently has no supplier
Silicone Quaternium-17	CHT R. Beitlich GmbH
Silicone Quaternium-18	CTFA currently has no supplier.
Silicone Quaternium-20	Siltech LLC.
Silicone Quaternium-21	CTFA currently has no supplier.

The amido groups of the commonly encountered silicone quaternium compounds are cocamido, myristamido and dilinoleylamido propyl based. The nomenclature is shown in **Table 19.2**.

Table 19.2. Silicone Quaternium Compounds

Name	CTFA Name	Alkyl Amido Group
Silquat* AC	Silicone Quaternium 1	Cocamidopropyl dimethyl
Silquat* AM	Silicone Quaternium 2	Myristamidopropyl dimethyl
Silquat* AD	Silicone Quaternium 8	Di-linoleylamidopropyl dimethyl

*Silquat is a registered trademark of Siltech LLC, Dacula, Ga.

Table 19.3 shows the solubility and surfactant properties of silicone quaternium 8.

Table 19.3. Silicone Quaternium 8 Surfactant Properties

Surface Tension 0.1%	Draves Wetting 0.1%	Water	Solubility 5% wt Propylene glycol fluid	Mineral oil	Silicone
30.0 dynes/cm^2	300 sec	S	D	I	I

Formulation

Many two-in-one shampoos make use of micro emulsions of silicone fluids to provide conditioning effects. While it is quite true that silicone fluids can be used to condition hair, the formulations need to have elaborate thickening systems (in order to remain homogeneous) and must be opaque. Additionally, it is quite possible to break the emulsions when the products are formulated into anionic systems. The existence of various silicone quats has resulted in improved formulation latitude in making conditioning systems.

Despite their cationic character, alkylamido ester quats can be formulated into clear products without emulsification at concentrations that provide outstanding skin feel and conditioning. For example, 3% silicone quaternium 3 can be incorporated into 15% sodium lauryl sulfate with simple mixing. The result is a clear product that can be further formulated into shampoo, body wash or many other personal care products.

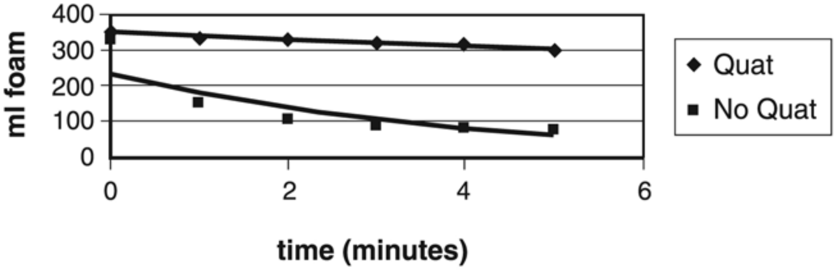
Applications Data—Foam

The formulation shown in **Table 19.4** was evaluated for foam properties for the two formulations diluted to 0.5% solids and tested for foam height using the cylinder shake foam test. **Figure 19.4** shows that both initial foam and foam stability were improved by the addition of the silicone quat.

Table 19.4. Formulation for Foam Evaluation

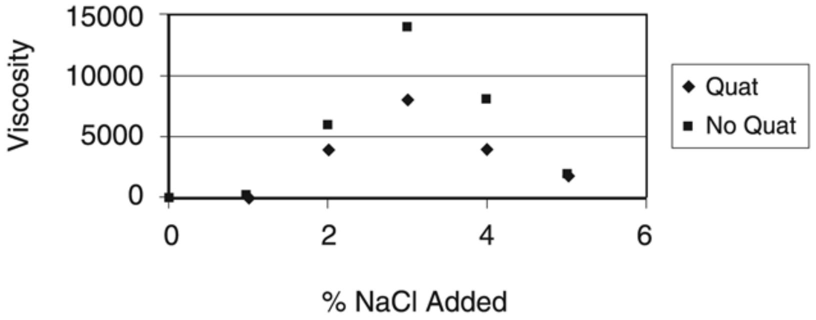
Ingredient	With Quat	No Quat
Water (*aqua*)	41.4	43.3
Sodium Lauryl Sulfate (28% active)	53.6	53.6
Cocamid DEA	3.0	3.0
Silicone Quaternium 8 (40% Active)	2.0	3.0

Figure 19.4. Foam Heights, Formulation 1



The viscosity data shown in **Figure 19.5** clearly indicates that the peak viscosity of the formulation is reduced from 14,000 cps to 8,000 cps. The amount of salt to reach peak viscosity does not change, nor does the shape of the salt curve.

Figure 19.5



Viscosity achieved by the addition of salt to the formulation (Table 19.6)

Wet Comb Test

A laboratory test was conducted to screen the wet comb properties, and the silicone quats were compared to other quats. Hair swatches were purchased from a supply of human hair from the same head. Each test swatch contained 7 g of hair and was 11 inches in length. The hair was then tied tightly 1 inch from the end with string. The swatch was then pre-cleaned with a 3% solution of ammonium lauryl sulfate. Subsequently, the swatch was washed under running tap water.

The hair was then squeezed out and, while still damp, dipped into a 200 mL solution of 0.2% active quaternary. Another rinse was made and then the swatch was blotted dry. Holding the hair swatch, the hair was combed as rapidly as possible while alternating the side of the swatch combed and then the swatch was treated. The time needed to get one smooth free stroke without tangling was recorded. Typical results for the standard quaternary compounds used in hair conditioning (stearyldimethylbenzyl ammonium chloride) ranged from 12–14 seconds.

Table 19.5. Rinse Conditioner (Wet Comb)

Product	Time in Seconds
Silicone quaternium 8	9
Silicone quaternium 2	10
Stearyldimethylbenzyl ammonium chloride	12

As can be seen from the data in **Table 19.5**, the silicone quaternium compounds provide good wet comb properties to the hair, whilst providing a clear formulation. The mildness of the silicone quaternary compounds makes them outstanding candidates to make baby shampoos and family use products by providing needed conditioning without irritation.

Silicone ester amido quats are an interesting class of compounds for the formulation of personal care products. Care must be exercised, however, to use the products at pH ranges between 6 and 9 and to avoid the hydrolysis of the ester bond.

Commercial Acceptance

Dove Advanced Care Therapy makes use of silicone quaternium 8 "to help repair dryness and brittleness with its patented Silicone Technology that seeks out the damaged area of the hair, where treatment is needed." **Table 19.6** shows the products that contain silicone quaternium 8.

Table 19.6. Silicone Quaternium 8 in Commercial Product Lines

Dove Advanced Care Therapy to help repair dryness and brittleness with its patented Silicone Technology that seeks out the damaged area of the hair, where treatment is needed.

The following products contain Silicone Quaternium 8:

cont.

Table 19.6. Silicone Quaternium 8 in Commercial Product Lines cont.

- Deep Moisture Facial Cleansing Cloths
- Cool Moisture Facial Cleansing Cloths
- Sensitive Skin Facial Cleansing Cloths
- Silky Dry Aerosol
- Advanced Care Therapy for Severely Damaged Hair
- Advanced Color Care Conditioner for Lightened Hair
- Extra Volume Conditioner
- Beautiful Care Conditioner
- Cool Moisture Conditioner
- pro•age Conditioner
- Intense Moisture Conditioner

Source: *http://search.dove.us/*

Patents Mentioning Silicone Quaternium Compounds

One of the best ways to evaluate the commercial interest in new products is reviewing the patent literature. Silicone quaternium 8 is the most commonly encountered in the literature.

(1) A series of three patents were issued to Brain et al.

- US Patent 7,196,049, titled "Encapsulated fragrance chemicals," issued March 27, 2007
- US Patent 7,122,512, titled "Encapsulated fragrance chemicals," issued Oct. 17, 2006
- US Patent 7,119,057, titled "Encapsulated fragrance chemicals," issued Oct. 10, 2006

"Polymeric encapsulated fragrance is disclosed, which is suitable for use in personal care and cleaning products. In a preferred embodiment of the invention, the fragrance is encapsulated by a first polymer material to form a fragrance-encapsulated polymer; the polymer-encapsulated shell is then coated with a mixture of cationic polymers."

The patents state:

Also included are "Suitable silicone materials include amodiemthicone, polymethylalkyl siloxanes, polydimethylalkyl siloxanes, dimethicone, dimethicone copolyol, dimethiconol, disiloxane, cyclohexasiloxane, cyclomethicone, cyclopentasiloxane, phenyl dimethicone, phenyl trimethicone, silicone quaternary materials including silicone quaternium-8, and silicone quaternium-12, trimethylsiloxyamidodimethicone, trimethylsiloxysilicate and the like."

(2) US Patent 7,122,238 issued Oct. 17, 2006, to Macedo, titled "Cleansing article for personal care"

Patents cont.

A disposable personal care cleansing article is provided having a cleansing composition adjacent to a water-insoluble substrate formed of a fibrous web. A plurality of slits having a length ranging from 6–40 mm are cut into the web. The slits allow the article to expand when a consumer applies the article to cleanse the body under a flow of water.

Most preferred is Silquat AD designated by the CTFA as **Silicone Quaternium** 8.

(3) US Patent 7,074,747 issued July 11, 2006, to Lukenbach, titled "Cleansing compositions"

Cleansing compositions suitable for use in personal cleansing applications, and in particular makeup removal applications, which not only impart superior cleansing properties, but are also relatively non-irritating (and thus suitable for use by people having sensitive skin and eyes), comprised of esters, liquid silicones and water-dispersible components. Also disclosed are compositions for effectively depositing various benefit agents into and onto the skin.

An example of a suitable hair softener nonexclusively includes silicone compounds, such as those that are either nonvolatile or volatile and those that are water-soluble or water-insoluble. Examples of suitable silicones include organo-substituted polysiloxanes, which include cetyl dimethicone; cetyl triethylammonium dimethicone copolyol phthalate; cyclomethicone; dimethicone copolyol; dimethicone copolyol lactate; hydrolyzed soy protein/dimethicone copolyol acetate; **silicone quaternium** 13; stearalkonium dimethicone copolyol phthalate; stearamidopropyl dimethicone; and mixtures thereof.

(4) US Patent 7,045,491 issued May 16, 2006, to Hourigan, titled "Bar soap composition with reduced bar wear properties"

A non-clear (translucent to opaque) cleansing bar comprising: (a) about 3–40 weight % anionic soap; (b) about 4–40 weight % of at least one synthetic surfactant; (c) from 0.1–10 weight % of a gelling agent from the group consisting of dibenzylidene sorbitol, dibenzylidene xylitol, dibenzylidene ribitol, and mixtures thereof; (d) about 5– 60 weight % of a humectant provided that glycerin is a component of the humectant and is present in an amount of about 2–10 weight %; and (e) water; wherein all amounts are in % by weight based on the weight of the entire composition.

More particular examples of skin feel conditioning agents that maintain translucency and provide a nice skin feel when added to a translucent composition of the invention at a level of 2 weight % are those selected from the group consisting of: soybean oil, PEG 6 caprylic/capric triglycerides, PEG 80 glyceryl cocoate, PEG 40 glyceryl cocoate, PEG 35 soy glycerides, caprylic/capric triglycerides, PEG 8 dimethicone, PEG/PPG-22/24 dimethicone, **silicone quaternium** 8, dimethicone PEG-7 isostearate, petrolatum, lanolin quat (quaternium-33), capric/caprylic triglycerides, PEG-7 glyceryl cocoate and mixtures of the foregoing.

(5) US Patent 6,992,054 issued January 31, 2006, to Lee et al., titled "Damp cleansing wipe"

Disposable substantially damp cleansing article is disclosed having a cleansing composition impregnated onto a flexible substrate such as a nonwoven cloth. The impregnated compositions include lathering surfactants and water, and a water-binding agent resulting in a composition having a water activity less than

Patents cont.

0.977 but no lower than 0.001. Amounts of water range from greater than 15% to no higher than about 40% by weight of the total article. Speed of lather formation and foam volume increases within the window of the stated water activity and water range.

Amino silicone quats may be similarly employed. Most preferred is Silquat AD designated by the CTFA as **Silicone Quaternium** 8, available from Siltech Inc.

(6) A series of two patents were issued to Niemiec et al.

- US Patent 6,908,889, titled "Detergent composition with enhanced depositing, conditioning and softness capabilities," issued June 21, 2005
- US Patent 6,858,202, titled "Detergent compositions with enhanced depositing, conditioning and softness capabilities," issued Feb. 22, 2005

Novel two-in-one detergent compositions comprised of at least one water-soluble silicone agent, at least one cationic conditioning agent and a detergent. These compositions are suitable for use in shampoos and bath and shower gels. Also described is a novel delivery system for depositing benefit agents into and onto the skin, nails and/or hair, comprised of at least one water-soluble silicone and at least one cationic conditioning agent.

A method for enhancing the deposition of benefit agents that comprises topically administering to a human or animal a composition comprised of: a) a delivery system comprised of i) at least two cationic conditioning compounds selected from the group consisting of guar hydroxypropyltrimonium chloride, acrylaminopropyltrimonium chloride/acrylamide copolymer, and mixtures thereof; ii) at least one water-soluble silicone compound comprised of silicone quaternium-13; and b) an effective amount of a benefit agent to a desired location on the skin, hair and/or nails.

Another embodiment of the present invention is directed to a method for enhancing the deposition of benefit agents that comprises, consists essentially of, and/or consists of topically administering to a human or animal a composition comprised of, consists essentially of, and/or consists of: a) a delivery system comprised of i) at least two cationic conditioning compounds selected from the group consisting of guar hydroxypropyltrimonium chloride, acrylaminopropyltrimonium chloride/acrylamide copolymer, and mixtures thereof; ii) at least one water-soluble silicone compound comprised of **silicone quaternium-13**; and b) an effective amount of a benefit agent.

(7) US Patent 6,838,420, issued Jan. 4, 2005, to Sachdev, titled "Soap composition"

A translucent or transparent composition soap is described. It contains emollients. Other emollients can also be in the composition. Examples of these materials include silicone quats such as **silicone quaternium** 8, and the like; lanolin quats such as quarternium 33 and cationic polymers such as polyquat-6 and polyquat-7.

(8) US Patent 6,808,701, issued Oct. 26, 2004, to Duden et al., titled "Conditioning compositions"

A conditioning composition comprising: 5%–20% based upon the total weight of said conditioning composition of a surfactant portion comprising: 1. a nonionic surfactant; 2. an amphoteric surfactant; and 3. an anionic surfactant; and from

Patents cont.

about 0.1%–6.0% based upon the total weight of the conditioning composition of a conditioner portion comprising: 1. at least one vinylpyrrolidoine/vinylimidazolium copolymer; and 2. a nonvolatile silicone selected from the group consisting of cetyl dimethicone; cetyl triethylammonium dimethicone copolyol phthalate; dimethicone copolyol; dimethicone copolyol lactate; hydrolyzed soy protein/dimethicone copolyol acetate; **silicone quaternium 13**; stearalkonium dimethicone copolyol phthalate; stearamidopropyl dimethicone; phenyl trimethicone; amodimethicones; polyalkylarylsiloxanes; and mixtures thereof; wherein the weight ratio of branched quaternary cationic polymer to silicone ranges from about 1:4 to about 1:6.

(9) US Patent 6,762,158, issued July 13, 2004, to Lukenbach et al., titled "Personal care compositions comprising liquid ester mixtures"

Personal care compositions suitable for use in skin care applications that effectively deliver and/or deposit various benefit agents into and onto the skin and that are relatively non-irritating, comprising at least one ester and a water dispersible component, and thus suitable for use by people having sensitive skin and eyes.

An example of a suitable hair softener nonexclusively includes silicone compounds, such as those that are either nonvolatile or volatile and those that are water-soluble or water-insoluble. Examples of suitable silicones include organo-substituted polysiloxanes, which are either linear or cyclic polymers of monomeric silicone/oxygen monomers and which nonexclusively include cetyl dimethicone; cetyl triethylammonium dimethicone copolyol phthalate; cyclomethicone; dimethicone copolyol; dimethicone copolyol lactate; hydrolyzed soy protein/dimethicone copolyol acetate; **silicone quaternium 13**; stearalkonium dimethicone copolyol phthalate; stearamidopropyl dimethicone; and mixtures thereof.

(10) US Patent 6,743,760, issued June 1, 2004, to Hardy et al., titled "Transparent conditioning shampoo"

A conditioning shampoo comprising: (a) 8–18 weight % of an anionic surfactant; (b) 0.5–0.8 weight % of a conditioning system comprising: (i) 0.1–0.75 weight % of **silicone quaternium 8**; (ii) 0.1–0.5 weight % of a low molecular weight guar gum with a molecular weight less than 100,000 centipoise as an aqueous clear cationic solution of a modified polysaccharide clear cationic solution; and (iii) 0.1–0.5 weight % of polyquaternium-10; (c) 1.0–6.0 weight % of an amphoteric surfactant; (d) 0.5–5.0 weight % of a member selected from the group consisting of cocodiethanol amide, and cocomonoethanol amide; and (e) the remainder as water.

(11) US Patent 6,696,068, issued February 24, 2004, to Crotty et al., titled "Cosmetic cream cleanser"

A cosmetic cream cleansing composition is provided based on the presence of a silicate, a cross-linked carboxyvinyl polymer, a silicone copolyol sulfosuccinate and a carrier. The composition has a viscosity of approximately 20,000–500,000 centipoise. The combination of components achieves a product with good viscosity, pleasant skin feel, rich lather and phase stability.

Amino silicone quats may be similarly employed. Most preferred is Silquat AD designated by the CTFA as **Silicone Quaternium 8**, available from Siltech Inc.

Patents cont.

(12) US Patent 6,660,282, issued Dec. 9, 2003, to Crotty et al., titled "Self foaming cosmetic product"

A foaming cosmetic product is provided packaged in a non-aerosol mechanical dispenser. The dispenser includes a container for holding a liquid composition, a dispensing head with a housing enclosing a pump mechanism and a screen material in the flow path to convert liquid composition into a foam, and a diptube for delivering liquid from the container to the dispensing head. The cosmetic composition is an opaque creamy, relatively non-viscous fluid; its creamy appearance is imparted by a latex with suspended polymer particles compatible with the foaming mechanism.

Amino silicone quats may similarly be employed. Most preferred is Silquat AD designated by the CTFA as **Silicone Quaternium** 8, available from Siltech

(13) US Patent 6,607,717, issued August 19, 2003, to Johnson et al., titled "Silicon based quaternary ammonium functional compositions and their applications"

There are disclosed novel **quaternary ammonium functional silicone**-based emulsions and other formulations, as well as methods to make such emulsions and formulations. These materials have uses in personal care and other applications.

(14) US Patent 6,638,527, issued October 28, 2003, to Gott et al., titled "Substantially dry cleansing product of improved latherability and wet flexibility"

A disposable, single-use, substantially dry cleansing article is disclosed having wet flexibility, and a lathering surfactant in one embodiment and having an apertured fabric and a specific lather volume coefficient in a second embodiment.

Amino silicone quats may similarly be employed.

(15) US Patent 6,634,037, issued October 21, 2003, to Turbett et al., titled "Personal cleansing system"

A personal cleansing system for substantially dry wiping articles is described as suitable for use in a shower environment, utilizing a shell enclosing the wiping articles and having a dispensing slot formed along the shell, a closure means, and a support device secured to the shell.

Cationic conditioning agents in monomeric and polymeric type are also useful for purposes of this invention. Examples of the polymeric type include: cationic protein derivatives (e.g. Mackpro WWP manufactured by McIntyre Co.), cationic cellulose derivatives, cationic starches, copolymers of a diallyl quaternary ammonium salt and an acryl amide, quaternized vinylpyrrolidone, vinylimidazole polymers, polyglycol amine condensates, quaternized collagen polypeptide, polyethylene imine, cationized silicone polymer (e.g. Amodimethicone), cationic silicone polymers provided in a mixture with other components under the trademark Dow Corning 929 (cationized emulsion), copolymers of adipic acid and dimethylaminohydroxypropyl diethylenetriamine, cationic chitin derivatives, cationized guar gum (e.g. Jaguar C-B-S, Jaguar C-17, Jaguar C-16, etc. manufactured by the Celanese Company), and quaternary ammonium salt polymers (e.g. Mirapol A-15, Mirapol AD-1, Mirapol AZ-1, etc., manufactured by the Miranol Division of the Rhone Poulenc Company). Amino silicone quats may similarly be employed. Most preferred is Silquat AD designated by the CTFA as **silicone quaternium** 8, available from Siltech Inc. Amounts of each cationic agent may range from about 0.01% to 5%, preferably from about 0.1% to about 4%, optimally from about 0.3% to about 3.5% by weight of the composition impregnated in the substrate.

Patents cont.

(16) US Patent 6,524,594, issued February 25, 2003, to Santora et al., titled "Foaming oil gel compositions"

A gelled oil composition containing an emulsifier, a gelling agent, an oil and a surfactant that, when applied to the skin in the presence of water, produces a significant amount of foam. After the composition is rinsed from the skin, a non-greasy oil residue remains.

An example of a suitable hair softener nonexclusively includes silicone compounds, such as those that are either nonvolatile or volatile and those that are water-soluble or water-insoluble. Examples of suitable silicones include organo-substituted polysiloxanes, which are either linear or cyclic polymers of monomeric silicone/oxygen monomers and which nonexclusively include cetyl dimethicone; cetyl triethylammonium dimethicone copolyol phthalate; cyclomethicone; dimethicone copolyol; dimethicone copolyol lactate; hydrolyzed soy protein/dimethicone copolyol acetate; **silicone quaternium 13**; stearalkonium dimethicone copolyol phthalate; stearamidopropyl dimethicone and mixtures thereof.

(17) US Patent 6,495,498, issued December 17, 2002, to Niemiec et al., titled "Detergent compositions with enhanced depositing, conditioning and softness capabilities"

Novel two-in-one detergent compositions comprised of at least one water-soluble silicone agent, at least one cationic conditioning agent, and a detergent. These compositions are suitable for use in shampoos, baths, and shower gels. Also described is a novel delivery system for depositing benefit agents into and onto the skin, nails, and/or hair, comprised of at least one water-soluble silicone and at least one cationic conditioning agent.

Another embodiment of the present invention is directed to a method for enhancing the deposition of benefit agents that comprises, consists essentially of, and/or consists of topically administering to a human or animal a composition comprised of, consists essentially of, and/or consists of: a) a delivery system comprised of i) at least two cationic conditioning compounds selected from the group consists of guar hydroxypropyltrimonium chloride, acrylaminopropyltrimonium chloride/acrylamide copolymer, and mixtures thereof; ii) at least one water-soluble silicone compound comprised of **silicone quaternium 13**; and b) an effective amount of a benefit agent to a desired location on the skin, hair, and/or nails.

(18) US Patent 6,391,835, issued May 21, 2002, to Gott et al., titled "Alkyl diol impregnate dry cleansing wipe"

A disposable substantially dry cleansing article is disclosed having a lathering surfactant and a C5-C12 alkyl diol impregnated into a flexible substrate such as a nonwoven cloth. The alkyl diol primarily is a process aid which may concurrently improve aesthetics and increase latherability. Hexylene glycol is the preferred diol. Best performance is achieved with an alkyl diol to total lathering surfactant weight ratio from about 1:1 to about 1:8.

(19) US Patent 6,284,234, issued September 4, 2001, to Niemiec et al, titled "Topical delivery systems for active agents".

This invention relates to a method for enhancing the transmembrane penetration of benefit agents using a certain nonionic lipid/surfactant-containing formulation as an enhancing agent, and the compositions used therein. Various active

Patents cont.

agents, such as antidandruff agents, hair growth agents, hair inhibitor agents, antiacne agents, antiaging agents, depilatory agents and depigmentation agents may be effectively delivered into the skin, hair follicles and sebaceous glands using the compositions of the present invention.

An example of a suitable hair softener nonexclusively includes silicone compounds, such as those that are either nonvolatile or volatile and those that are water-soluble or water-insoluble. Examples of suitable silicones include organo-substituted polysiloxanes, which are either linear or cyclic polymers of monomeric silicone/oxygen monomers and which nonexclusively include cetyl dimethicone; cetyl triethylammonium dimethicone copolyol phthalate; cyclomethicone; dimethicone copolyol; dimethicone copolyol lactate; hydrolyzed soy protein/dimethicone copolyol acetate; **silicone quaternium 13**; stearalkonium dimethicone copolyol phthalate; stearamidopropyl dimethicone and mixtures thereof.

(20) US Patent 6,120,753, issued September 19, 2000, to Vinski et al., titled "Conditioning cosmetic cleanser compositions"

An aqueous cleansing composition cleanser with moisturizing properties is disclosed including an anionic surfactant, a urethane siloxane copolymer and a nonionic water-insoluble emollient.

Amino silicone quats may similarly be employed. Most preferred is Silquat AD designated by the CTFA as **silicone quaternium** 8, available from Siltech Inc.

(21) US Patent 6,030,931, issued February 29, 2000, to Vinski et al., titled "Foaming cleansing skin product"

A foaming cleansing product is provided as a cleansing composition packaged in a non-aerosol mechanical dispenser. The dispenser includes a container for holding a liquid composition, a dispensing head with a housing enclosing a pump mechanism and a screen material in the flow path to convert liquid composition into foam, and a dip tube for delivering liquid from the container to the dispensing head.

Amino silicones quats may similarly be employed. Most preferred is Silquat AD designated by the CTFA as **silicone quaternium** 8, available from Siltech Inc.

(22) US Patent 5,747,435, issued May 5, 1998, to Patel, titled "Mild foaming and conditioning detergents"

Composition useful as two-in-one cleansing products are disclosed that are extremely mild to skin and hair, which use neutralized, essentially chargeless ionic complexes of fatty amines and fatty acids to deliver various levels of conditioning; neutralized, essentially chargeless ionic complexes of a detersive surfactant comprising a water-soluble cationic surfactant and/or polymer complexed with one or more anionic surfactants; or an amphoteric surfactant complexed with one or more anionic surfactants; or a water-soluble cationic surfactant and/or polymer complexed with one or more amphoteric surfactants; or a water-soluble cationic surfactant and/or polymer complexed with one or more anionic surfactants and an amphoteric surfactant; detersive surfactant-soluble but water-insoluble silicones or derivatives thereof; and water. These products exhibit true two-in-one conditioning properties, and are lower in cost than current equivalent products. Clear or opacified products can be formulated.

(23) US Patent 6,607,717, issued August 19, 2003, to Johnson et al., titled "Silicon

Patents cont.

based quaternary ammonium functional compositions and their applications"

There are disclosed **novel quaternary ammonium functional silicone**-based emulsions and other formulations, as well as methods to make such emulsions and formulations. These materials have uses in personal care and other applications.

References:

1. US Patent 5,166,297, issued November 24, 1992 to O'Lenick, Anthony, titled "Silicone ester quaternary compounds."
2. US Patent 5,153,294, issued to October 6, 1992, to O'Lenick, Anthony, titled "Silicone ester quaternary compounds".

Chapter 20

Silicones for Coating Pigments

Background

Color Pigment Manufacturers Association defines pigments as "colored, black, white or fluorescent particulate organic and inorganic solids which usually are insoluble and essentially physically and chemically unaffected by the vehicle or substrate in which they are incorporated. They alter appearance by selective absorption and/or by scattering light. Pigments are usually dispersed in vehicles or substrates for application. Pigments retain a crystal or particulate structure throughout the coloration process."

This chapter deals with pigments and how they can be modified using silicone. The fact that pigments are solids, that they contain reactive sites and adsorb oils is critical to the understanding of the modification of the pigments for use in personal care products.

In recent years, the coating of pigments with various materials, including silicones, waxes, fatty acids and fluoro-polymers has become popular. These coatings make pigments more compatible with formulations, making them important to formulators. The application of the correct coating can result in a pigment that has:

- Improved dispersibility in oil or silicone
- Improved tactile feel
- Lessened agglomeration in formulation
- Easier wetting

These improvements can be attained either as a result of physical or chemical bonding depending upon the technique employed to apply the coating. The methods used for application include chemical, electrostatic and mechanical.

In fact, many of today's pigmented products would not exist were it not for the ability to coat pigments used in them.

Historical Perspective

Pigments are solid particles in a solvent matrix. Over time, gravity will cause the pigments to settle. Minimizing this settlement of particles is a challenge that formulators of pigmented products face on a daily basis.

There are various methods available to improve the dispersibility of the pigment. These include decreasing the size of the particle, providing the particle an ionic charge and adding a coating.

The larger the particle, the more rapidly it settles from a dispersion. Regulating the size of a pigment in a product is accomplished by a number of mechanical means including milling of the pigment. In this process, the pigment is ground into smaller particles. Many types of machines are employed in this processing.

Often, the milling of a particle is done in an "oil phase," resulting in a grind that is more easily formulated in pigmented products. These "oil phases" include esters, silicones, mineral oils and similar materials. The proper choice of the "oil phase" is an important consideration in the ultimate formulation properties of the pigment. Many times the "oil phase" is adsorbed onto the pigment, improving its dispersibility in a similar oil phase in the pigmented product. This is a clever application of the old chemical adage "likes dissolve likes." If the oil phase has an ionizable group on it, the result is a pigment with an adsorbed ionic charge, leading to an ionic matrix. Because like charges repel, the pigments do not agglomerate rapidly. Examples of ionizable oils include fatty acids, such as oleic and erucic.

Silicone Coatings for Pigments

The ability to go beyond adsorbed pigments and achieve truly coated pigments was the goal in the industry.

The next important step in making more permanent coatings for pigments came in 1992 with a true pigment coating.[1] This patent claimed a product "consisting essentially of finely divided particles of pigment (inorganic or organic) whose surfaces are chemically bonded to, and physically completely coated by, polysiloxane, which coating renders the particles hydrophobic." This type of product makes use of a silanic hydrogen reactive silicone.

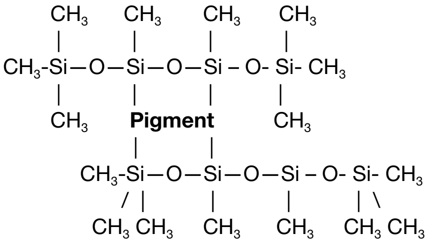
A subsequent series of patents[2-7] was based upon an alternative reactive silicone. This polymer was an alkoxy silicone. The patents disclosed a process for making metal oxide hydrophobic by coating the metal oxide with an alkoxy silicone polymer. The hydrophobic metal oxide is prepared by contacting the metal oxide with a reactive silicone compound and subsequently heating the coated metal oxide.

Pigment Reactive Binding Mechanisms

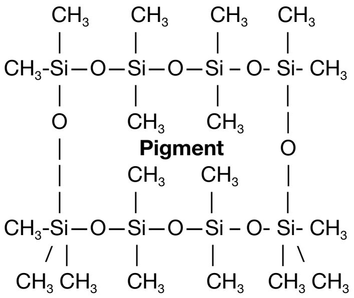
In order to get a chemically reacted coating on pigment, one must choose a silicone that is reactive with the pigment. This simple fact is key to the chemistry of coatings. There are three reactive binding mechanisms: (1) reaction of coating reagent with active sites on the pigment, (2) the self condensation reaction of the coating reagent with itself and (3) both. The best case is (3), since coverage is maximized. Pigments lacking reactive sites can only be chemically coated by mechanism (2), which may result in efficient coverage and coating durability, depending upon the reagent and process used to coat. **Figure 20.1** shows the various binding mechanisms by which pigments may be coated.

Figure 20.1. Pigment Binding Mechanisms

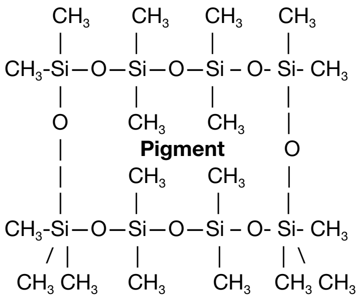
(1) Reaction of coating reagent with active sites on the pigment.



(2) Self condensation reaction of the coating reagent with itself



(3) Both (1) and (2)



Active sites are those groups on a pigment that are reactive. "Coatable" pigments have active sites. In fact the number of active sites can be monitored using infrared (IR) absorption, at 2335 cm^{-1}. Nitrogen adsorbed on high area titanium dioxide samples is measured for untreated TiO_2. The intensity of the absorption, at 2335 cm^{-1} progressively decreases as the amount of inorganic coating increases. In fact, the concentration needed to coat can be determined by the amount of coating reagent at which further uptake by the pigment stops. This corresponds to 0.2% of oxide per square meter of TiO_2. The optimum coating concentration varies for each pigment. At lower coating levels, silica coating reduces adsorption of IR-active nitrogen more effectively than the same weight of alumina. Rates of photooxidation decrease as the amount of coating increases.[7]

Silicone Structure

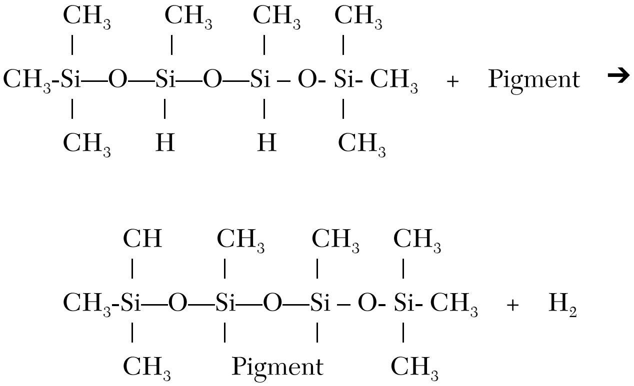
The number of active sites on the pigment is a very important factor in binding. But, clearly the structure of the silicone is critical. The two critical issues are shown in **Figure 20.2**. They are the number of reactive sites in the silicone molecule, (the "a" to "b" ratio), the location of the binding sites (D* or M*) and the overall size of the silicone molecules. Short molecules give different coating properties than long ones.

With the number of variables that effect coating efficiency and pigment properties, none of which are in the control of the formulator, controlling the properties of the coated pigment become critical. The recommendations that follow in this chapter are intended to allow for better control over coated pigments making their use easier and more predictable.

Chemistry

Silanic hydrogen

The first class of reactive silicones are those that contain silanic hydrogen. The reaction proceeds with the liberation of hydrogen gas and the attachment of the silicone to the pigment. A simplified reaction sequence is shown below.



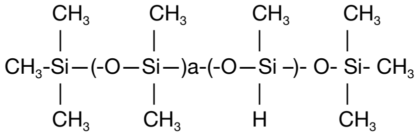
$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—O—}\underset{H}{\overset{CH_3}{Si}}\text{—O—}\underset{H}{\overset{CH_3}{Si}}-O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 + \text{Pigment} \rightarrow$$

$$CH_3\text{-}\underset{CH_3}{\overset{CH}{Si}}\text{—O—}\underset{\text{Pigment}}{\overset{CH_3}{Si}\text{—O—}\overset{CH_3}{Si}}-O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3 + H_2$$

The resulting pigment has much better dispersibility in silicone, is more hydrophobic and settles much more slowly in oil phases including organic and silicone oils. The generation of hydrogen needs to be carefully controlled during the process as it is flammable and under some concentrations it is an explosive gas. The quantity of gas generated can be used as a measure of the completion of the reaction. The above reaction shows the reaction of active sites on the pigment with silanic hydrogen. Active sites on the metal are reacted with Si-H liberating H_2 gas.

Figure 20.2. Silicone Structure Effecting Binding

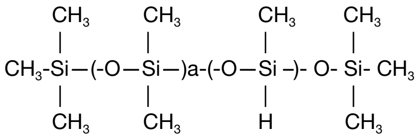
(1) The number of reactive sites in the silicone molecule (the "a" to "b" ratio),



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—(-O—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—)a-(-O—}\underset{H}{\overset{CH_3}{Si}}\text{ –)- O- }\underset{CH_3}{\overset{CH_3}{Si}}\text{- }CH_3$$

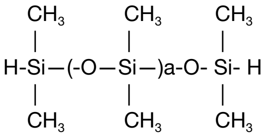
(2) The location of the binding sites (D* or M*)

D* Si-H



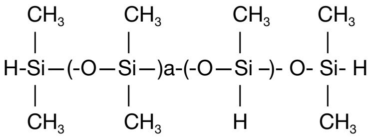
$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—(-O—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—)a-(-O—}\underset{H}{\overset{CH_3}{Si}}\text{ –)- O- }\underset{CH_3}{\overset{CH_3}{Si}}\text{- }CH_3$$

M* Si-H



$$H\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—(-O—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—)a-O- }\underset{CH_3}{\overset{CH_3}{Si}}\text{- }H$$

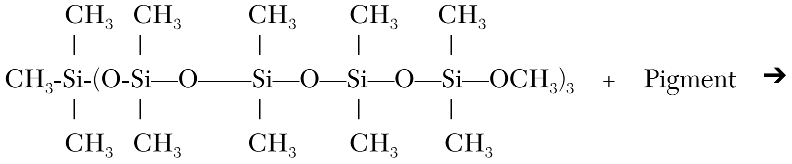
Both M* and D* Si-H



$$H\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—(-O—}\underset{CH_3}{\overset{CH_3}{Si}}\text{—)a-(-O—}\underset{H}{\overset{CH_3}{Si}}\text{ –)- O- }\underset{CH_3}{\overset{CH_3}{Si}}\text{- }H$$

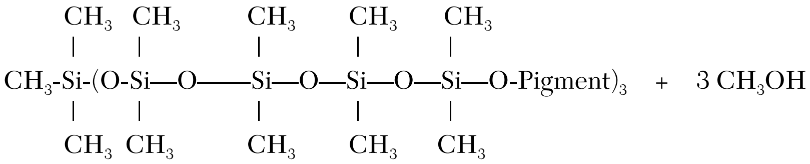
Alkoxy silicone

In the second class of reactive silicones are those that contain alkoxy groups. The reaction proceeds with the liberation of alcohol and the attachment of the silicone to the pigment. A simplified reaction sequence is shown below.



$$CH_3\text{-}Si\text{-}(O\text{-}Si—O——Si—O—Si—O—Si—OCH_3)_3 + \text{Pigment} \rightarrow$$

Methyl trimethoxy silicone



$$CH_3\text{-}Si\text{-}(O\text{-}Si—O——Si—O—Si—O—Si—O\text{-Pigment})_3 + 3\,CH_3OH$$

The resulting pigment—like the pigment treated with silanic hydrogen—has much better dispersibility in silicone, is more hydrophobic and settles much more slowly in oil phases including organic and silicone oils. The generation of methanol needs to be carefully controlled during the process because it, too, is flammable.

Other Functional Groups

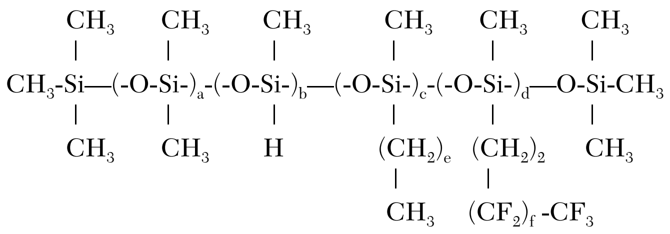
Regarding the molecules mentioned in this chapter, it should be clear to the reader that replacing the methyl group with alkyl, fluoro or other functional groups included in the molecule as part of its construction will allow for the preparation of coated pigments with other added attributes, such as spreadability and fatty compatibility. These materials will be commercially available shortly.

Reactive silicones can be modified to deliver desired surface properties to pigments. This will be a key area of research for specialty silicone companies for some time to come. This is particularly true for transfer-resistant lipsticks, because minimizing syneresis means the pigment needs to be compatible with the silicone resin system and the various waxes and oils present.

Multifunctional Coatings

The development of coatings for pigments will be driven as the formulator needs pigments that disperse more easily in specific formulation phases. These phases include oil, water, silicone and fluoro.

An example of one such development is a patent[7] that was recently issued covering a multifunctional silanic hydrogen-containing compound having the following structure:



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{—}(\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-})_a\text{-}(\text{-}O\text{-}\underset{H}{\overset{CH_3}{Si}}\text{-})_b\text{—}(\text{-}O\text{-}\underset{\underset{CH_3}{(CH_2)_e}}{\overset{CH_3}{Si}}\text{-})_c\text{-}(\text{-}O\text{-}\underset{\underset{(CF_2)_f\text{-}CF_3}{(CH_2)_2}}{\overset{CH_3}{Si}}\text{-})_d\text{—}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Wherein:

- a is an integer ranging from 0 to 100
- b is an integer ranging from 1 to 20
- c and d are independently integers ranging from 0 to 20, with the proviso that c or d is at least 1
- e is an integer ranging from 9 to 31
- f is an integer ranging from 1 to 20

If c is zero and d is not, a perfluoro compound results.
If d is zero and c is not, an alkyl coating results.

It is said to be effective in coating. A variety of metal oxides may be processed using the invention including zinc oxide, titanium dioxide, iron oxide, cesium oxide, zirconium oxide, silicon dioxide and antimony oxide.

The functionality of each group in the molecule is critical to the functionality. The "a" group is the silicone-soluble group. If c, d, and e are all zero, the molecule will improve the dispersibility of the pigment in silicone fluid. Consequently, if one is making a long-wear lipstick that contains silicone, the selection of a product having a large "a" it is not recommended to use b, c, or d.

The "b" group is the reactive group. If it is 1, then the molecule is loosely bonded; if it is 20, then a more rigid resin coating forms. The other groups result in altered solubilities as shown in **Table 20.1**.

Table 20.1. Coating Solubility

Group	Type	Solubility
"a"	Siloxane	Silicone fluid
"b"	Silanic hydrogen	Reactive group
"c"	Alkyl	Mineral oil soluble
"d"	Perfluoro ether	Fluoro-soluble

The result is a coated pigment with improved dispersibility in the specific class of compound that is contained in the pigment group. Coating promotes dispersibility in the shown type of compound results.

If c or d are non-zero values, the ability for the pigment to complex the component with the lower value is enhanced. For example, if c is 3 and d is 20, the resulting treated pigment will disperse well in fluoro solvents and have the ability to complex oils into the resulting dispersion, rendering it thicker and more stable.

The reaction occurs using titanium dioxide; which is a representative metal oxide. It is believed that the reaction occurs at the active sites on the metal oxide—in this case, titanium dioxide, reacting with the silianic hydrogen (Si—H) to result in a covalent bond between silicone and titanium dioxide, and the formation of hydrogen gas. Since no water is present in this process, the metal oxide crystals remain intact and "frozen" in shape by the silicone, which acts like a matrix for the titanium dioxide crystals. The silicone preserves the structure of the titanium dioxide crystals, eliminates the reactivity in water, and modifies the surface making the pigment more dispersible in the desired solvent.

Longevity of Coatings

The mechanism affecting coating on the pigment can be of three types, based on: (a) hydrophobic interactions, (b) ionic bonds and (c) covalent bonds. The latter cases have three variations: those in which (1) pigment reacts with a coating reagent at active sites on the pigment; (2) a coating reagent that self condenses; or (3) both. All will respond differently, especially in emulsions. The key to understanding pigment coatings is the fact that while a coating may be very stable on a pigment when only the two materials are present, the longevity of the coating on the pigment in a formulation is what dictates product stability.

Coatings bonded to pigments by hydrophobic interaction are the least stable and cause the most problems in formulations. Sometimes, however, the hydrophobic coating is enough in formulation to obtain the desired effect. Often an emulsion is made with this type of pigment and over time the coating is stripped off into the oil phase, leaving a noncoated pigment and an oil. The inexperienced formulator may well go back to optimize the formulation by adjusting the emulsifier, but the pigment, in time, may lose its coating, resulting in a nonstable emulsion.

The second mechanism of coating is based upon ionic bonding between the pigment and the coating; their charges must be opposite. An example of this is a quaternary coated clay. This type of bonding is stronger, based upon a cationic/anionic interaction. This added benefit may overcome the problem in formulation but is sometimes ineffective.

The strongest type of bond is achieved with reactive coating. There are two variations: the first is when the coating bonds by reaction with the pigment, and the second when the coating penetrates the pigment and reacts with itself to form an interpenetrating network. The first results in a new molecule; the latter in an encapsulated pigment. This pigment is very tenacious and seldom migrates in a formulation.

There are a number of extraction techniques that allow for the analysis of the type of coating found on the pigment. The formulator should discuss the nature of the coating with the supplier. This will make the selection process more efficient and it is particularly important when formulating lipsticks, makeup or sunscreens.

Why Coat Pigments?

The reason to coat pigments is to make them more effective in the preparation of cosmetic products. The making of products that the consumer will purchase is the ultimate goal of the exercise. The technology supports that goal. Pigments are coated to improve the ability to make a stable formula. Improved stability in finished product, which is often a pigmented emulsion, is a key reason to coat a pigment. A pigment can be coated to:

- Make it more hydrophobic
- Make it more compatible with the oil phase
- Make it less likely to agglomerate
- Make the emulsion more stable

The selection of a transient coating can cause the following problems with formulations:

- Color Shift
- Unpredictable pigment appearance on skin
- Stability issues especially pigmented emulsions (W/Si)

Chemisorbed Coatings for Pigments

If one applies an oil to a powdered pigment in a proper blend, the oil will coat the pigment. It will spread over the surface and in some instances wet out the pigment. This approach alters the pigment by providing a physical coating of oil to the pigment. This makes the pigment more hydrophobic. The lowest energy state for the oil on the pigment is spread over the surface. This approach can result in a transient coating when the pigment is formulated into product. The reason for this is that the lowest energy of the coated pigment in the formulation may not be the same as the lowest energy state for the oil coated pigment alone.

ne major area of concern is that is the coating may be removed by emulsifiers and end up in the oil phase. Over time, the lowest energy state is attained and the pigment is uncoated and the coating oil is in the oil phase. The time frame for this removal of the oil from the pigment is determined by the nature of the coating and can require a long time to occur. This manifests itself in poor product stability over time. The change can be accelerated by increased temperature, making oven stability key.

Reacted Coatings for Pigments

The reaction of the coating to the surface of the pigment results in improved permanence of the coating. Generally, one prefers at least some reaction of active sites with pigment coating over just self condensation of the coating reagent. The degree of coating and the coating stability depend upon the reactivity of the coating reagent and the extent to which the reaction is conducted each time a coated pigment is produced. If the percent reaction is not controlled batch to batch, variation may result.

Pigment Coating Studies

Case Study 1

A pigment is coated with oleic acid in a ribbon blender. The result is an organo modified pigment on which the oleic acid is roughly uniform. There is no reaction. The oleic acid stays on the pigment simply by wetting it out and assuming the lowest free energy. The pigment is hydrophobic. The oleic-coated pigment is placed in an invert emulsion along with an emulsifier, an oil, water and other additives, including thickener. The product looks great in the lab and scale up occurs. The first batch runs well. Several months later the formulator gets a call saying, "We have a bad emulsion product, creaming is occurring in the bottle. There is a color shift in the product."

Analysis

The coating is merely chemisorbed and is an oil-soluble material (oleic acid). There is emulsifier present, and the pH was adjusted in processing, making sodium oleate (soap). Under normal conditions the emulsifier would remove the acid and the acid would end up in the oil phase—the phase in which it is most stable. Since the formulation is thickened and the emulsion has stability the whole process is delayed. What went in as a coated pigment, over time becomes a naked pigment and soap. The product lacks predictability since the product is thick and separation that would normally take minutes to occur could take weeks. Another problem is that heat accelerates manifestation of the effect.

Corrective Steps

The formulator in this instance would probably look to the emulsifier first.

- Change emulsifier
- Change process for emulsion

If the problem is in fact caused by the coating on the pigment, there would be no improvement. A detailed procedure for evaluating pigment coatings with modifying emulsifiers is offered in the chapter on alkyl dimethicone copolyols.

The formulator should then look to the pigment.

Making an emulsion with and without pigment, and evaluating the stability, will reveal instability when pigment is present and offer a possibility to correct the problem.

There remains another concern. To the extent that the coating process is not correctly run, there can be batch to batch variation in the pigment, a fluctuating problem made all the worse by its random nature, which is out of the control of the formulator. The lack of performance results in unpredictable batch to batch variation which drives production and QC people crazy!

What to Do?

A. Get full disclosure from the pigment manufacturer.

- Is the coating reacted or chemosorb?
- What is the type of coating?
- What concentration is on the pigment?
- What analytical tests are used to confirm?

B. Impose QC Test

A Soxhelt Extraction prior to use can reveal the longevity of the coating and the chemical or chemicals used to coat. It will make life easier if this is a required test from the vendor. Of course it will be better if there is a more specific test offered by the pigment coater specific for the type of coating applied. **Figures 20.3** and **20.4** show both a Soxhlet Extractor and set up respectively.

A Soxhlet extractor (**Figure 20.3**) is a glass apparatus invented in 1879 by Franz von Soxhlet. It is designed for the extraction of liquid from a solid test material, but can be used whenever it is difficult to extract any compound from a solid. The laboratory set up is shown in **Figure 20.4**.

Figure 20.3. Soxhlet Extractor Glassware

Procedure

The coated pigment is placed inside a "thimble" made from filter paper, which is loaded into the Soxhlet extractor. The extractor is attached to a flask containing a solvent and a condenser. The solvent is heated, causing it to boil. The boiling solvent reaches the condenser and drips back through the thimble. The liquid solvent removes the coating from the pigment and drips into the solvent bath below, whereupon the solvent boils again, leaving the higher boiling coating in the flask. Because the solvent boils and the coating does not, only clean warm solvent is used to extract the solid in the thimble. This increases the efficiency of the extraction when compared with simply heating up the solid in a flask with the solvent.

Figure 20.4. Soxhlet Extractor Setup

Case Study 2

Emulsifier

Emulsifiers can be a source of problems in manufacturing. A particularly difficult problem is using emulsifiers that separate into phases when cold. Emulsifiers are complex oligomeric mixtures and care must be used when working with them. Invert emulsions are by far the most complicated regular emulsions and are far more likely to cause problems.

History

1. R&D develops a new invert emulsion
2. Scale up occurs with no problem
3. The emulsion from R&D appears robust giving acceptable product every time
4. First few production batches are fine

5. Soon product is not working well, some batches work well others split rapidly
6. Production complaints that product is not performing and is out of control
7. Production becomes convinced that R&D has a haunted formula
8. R&D is convinced that production is haunted

R&D never had a bad batch; production sometimes has a bad batch.

After much investigation, it is realized that the silicone emulsifier that is critical to the product when cooled separated into layers. The layers have different compositions, and consequently HLB, if used in formulation, can result in unpredictable quality. Since all batches made in the lab were made with emulsifier in glass bottles, there is no possibility of using a split emulsifier. Production quantity of surfactant comes in metal drums. Since operators do not have X-ray vision, they do not know if separated material is in the drum. Depending upon how much material is removed and from what layer, the emulsifier is different with every batch.

The separation of the emulsifier occurs in the cold, but it requires a much higher temperature and mixing to reconstitute. This means that product that separated in the winter will remain separated in the summer.

Solution?

Buy an emulsifier that does not split when cold.

Approach

When approaching the problem of instability, correct one situation at a time. Multivariable analyses are difficult to do.

- Leave out pigment and evaluate stability
- Check emulsion with different emulsifiers
- Optimize for oil
- Run pigment extraction test
- Put pigment back in formulation
- Re-check

Pigment Wetting

When processing pigments, wetting is a critical step. This is true for both coated and noncoated pigments. Pigment wetting agents historically include hydroxylated lanolin or acetylated lanolin alcohol, and an oily material to reduce tackiness such as isopropyl myristate (preferably), isopropyl palmitate, squalene, oleyl alcohol, mineral oil, liquid lanolin, and/or sesame oil.

The wetting stage involves the removal from the surface of the pigment particles of adsorbed molecules of gas, liquid and other materials and their replacement with molecules of the vehicle. This is accomplished through preferential adsorption. The efficiency of wetting depends primarily on the comparative surface tension properties of the pigment and the vehicle, as well as the viscosity of the resultant mix. **Figure 20.5** shows the steps in pigment wetting.

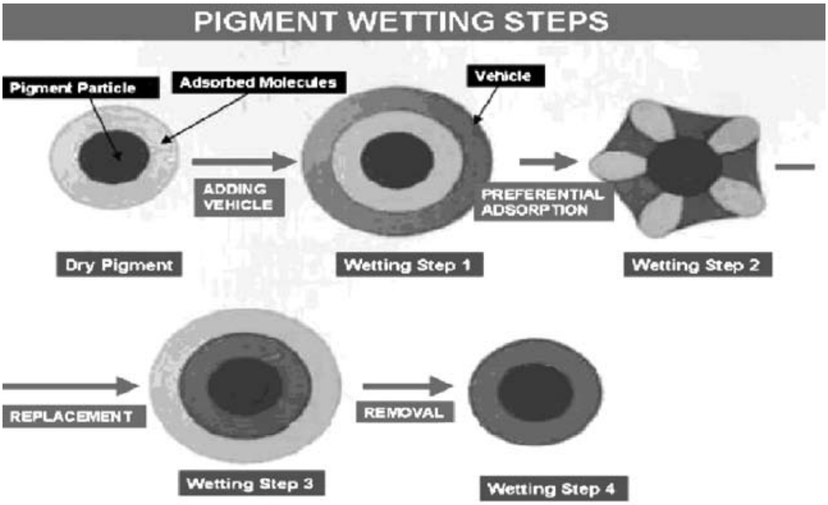


Figure 20.5. Pigment Wetting Steps

Alkyl silicones are very efficient pigment wetting agents. The properties are discussed in the chapter covering these materials.

Conclusion

Coated pigments are an important class of materials. The efficient utilization of these materials requires a higher level of technical understanding than many other raw materials. The coatings offer the potential for improved formulation. At the same time, these improved properties come at a cost of difficulty in optimizing the formula. The optimization can be achieved by approaching the formulation in steps; eliminating problems each step along the way. There is still a great deal of work that can be done to optimize coating technology.

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Chapter 21

Silicone Surface Tension in Formulation

Up to this point, we have concentrated on looking at the properties of silcone compounds in water and oil. In the real world, cosmetic products are complex mixtures of materials. More and more silicone surfactants and traditional fatty surfactants are used in formulations to provide the asethetics consumers demand. The physical chemistry of interactions between these two classes of very different materials is a complicated matter. Even clear solutions can be complex in terms of the distributon of species at the surface and within the solution. This chapter investigates some of the interactions between silicone surfactants and ingredients often found in personal care formulations.

Silicone in Mixed Systems

As technical people we want our formulations to be governed by clear, technical rules and to use simple concepts to organize our world. If we organize our world according to simple definitions,[1] we would observe:

1. A **solution** is a homogeneous mixture composed of one or more substances, known as solutes, dissolved in another substance, known as a solvent.
2. A **suspension** is a colloidal dispersion in which a finely divided species is combined with another species, with the former being so finely divided and mixed that it doesn't rapidly settle out. In everyday life, the most common suspensions are those of solids in liquid water.
3. An **emulsion** is a mixture of two immiscible substances. One substance (the discontinuous phase) is dispersed in the other (the continuous phase).

However, the world of cosmetic chemistry is rarely so easy to organize. Consider a fully dissolved 1% solution of sodium chloride in water. This simple system consists of a sodium ion (Na^+), chloride ion (Cl^-) and water, roughly equally distributed over the entire mass of the system. The solution is clear and homogeneous.

Now consider a 1% solution of a surfactant. Surfactant, or surface active agent has a water-soluble head and a water-insoluble tail. A very well-known surfactant is sodium lauryl sulfate (CAS 151-21-3). Like NaCl, sodium lauryl sulfate has two opposite ions, but sodium lauryl sulfate in water is very different. The presence of a large fatty protion makes the product surface active.

A 1% solution of sodium lauryl sulfate, like that of sodium chloride, is clear but not homogeneous. As one adds sodium lauryl sulfate to water, the orieitation of the material in the water is driven by achieving the lowest overall free energy, in this case through minimizing disrupting hydrogen bonding in water. The sodium lauryl sulfate organizes itself at the air-water interface and then begins to self assemble into micelles. **Table 21.2** shows this.[2] The first box shows pure water, having a surface tension of approximately 72 dynes/ cm.[2] As surfactant is added, demonstrated by the second box, surface tension is falling as dilute surfactant organizes at the surface. As the surface reaches saturation, a very significant situation develops. The surface tension no longer drops even with additional surfactant. It is at this concentration called cririal micelle concentration (CMC) that micelles become the dominant form of surfactant.

The above situation occurs when a surface active material is added to water.[3] The surface active agent, while soluble has a structural attribute that causes the lowest free energy level to be at the interface or in micelles rather than uniformily distibuted throughout the solution. This very same phenomonen occurs in non-aqueous systems, if the surface active agent is soluble and has a structural attribute that causes the lowest free energy level to be at the interface or in micelles, rather than uniformily distibuted throughout the solution. The world of cosmetic chemistry has water, oil and silicone phases, all mutually imicible. So, is it proper to ask, "What happens when an alkyl silicone is added to an oil?" Or to ask "What is the critical micelle concentration of cetyl dimethicone in an ester?" These are very proper and important questions for the cosmetic chemist.

The introduction of surfactants based upon silicone hydrophobes offers another dimension to surfactant technology. Often called the 3D HLB system,[4] the altered solubility allows the cosmetic formulator an opportunity to take advantage of silicones' unique properties to achieve a desired benefit. One such benefit is derived from the fact that the solubility of silicone can be modified by the addition of alkyl groups for water soublity, water-soluble groups for water solubility, or even fluoro solubility by addition of fluoro groups. Silicone surfactants and fatty surfactants differ fundamentally in their surfact tension properties. While fatty surfactants generally have aqueous surface tensions of around 32 dynes/cm,[2] their silicone-based cousins have surface tension values of around 20 dynes/cm^2. Since most organic oils have surface tensions below 30 dynes/cm^2 only silicone surfactants are able to alter the surface tension, spreadability, cushion and play time of oil phases. Silicones can be engineered to be both soluble in and surface active in oil phases. Even at 0.5% by weight surface tensions can be reduced by using a properly selected silicone. The use of fatty surfactants is not effective due to insolubility and/or the fact that the fatty surfactant has a higher surface tension than the solvent.

The type of products the cosmetic formulator generally encounters are those in which dynamic surface tension is important. That is, we are generally creating new surface area as we spread color cosmetics on the lips, spread shampoo on the hair or spread fragrance on the skin. This means surfact tension, wetting, cushion and play time are critical to an elegant feel. Dynamic surface tension is a rather complex situation with a number of equlibrium steps.

Table 21.1 shows that silicones can be used to reduce surface tension of several materials, making the addition of the proper silicone highly desirable. The reduction of surface tension confirms the surface activity of a material in solution.

Table 21.1. Reduction of Surface Tension of Oils with Silicone Derivatives

Solvent	**Surface Tension (as is) Dynes/cm²**	**Silicone Added (0.5% weight)**	**Surface Tension Dynes/cm²**
Toluene	28.9	C-26 alkyl dimethicone	25.0
2-butoxy ethanol	29.1	Stearyl dimethicone	22.0
Methanol	23.4	Octyl PEG-8 dimethicone	22.2
Water (*aqua*)	72.3	PEG-8 dimethicone	20.1

The effect of a concentration of amphillic material on surface tension is important. **Table 21.2** shows concentration effects on reduction of surface tension of oils with silicone.

Why is the cosmetic formulator interested in surface tension? Surface tension affects spreadbility and cushion. The addition of the proper silicone to a high viscosity ester can improve spreadability without effecting the play time (i.e. the time it takes to spread out). A different silicone can improve spreadability and reduce playtime. The result is an ability to alter aesthetics in personal care products by adding low concentrations of silicones. This allows one to significantly alter the cosmetic feel of a product without dramatic alteration in the formulation. The addition of the proper silicone can also improve wetting time and alter bubble structure. **Table 21.3** shows this effect.

Simple Surfactant Systems

Since silicones generally do not get used in systems as the sole surface active agent, how they interact with the ominpresent fatty surfactants is critical to effective usage.

Fatty Surfactants

The most commonly used surfactants in the cosmetic industry for cleansing products are SLS (sodium lauryl sulfate) and SLES-2 (sodium lauryleth sulfate). The CMC graph for sodium lauryl sulfate is observed in **Figure 21.1** and the CMC graph for sodium laureth-2-sulfate is observed in **Figure 21.2**.

Table 21.2. Concentration Effects on Reduction of Surface Tension of Oils with Silicone

Blends of several ratios of different materials were evaluated for surface tension reduction. The results are as follows:

	Cocamidobetaine (% weight)	**PEG-8 Dimethicone (% weight)**	**Surface Tension (Dynes/cm^2)**
Example 1.1	100%	0%	31.3
Example 1.2	75%	25%	26.0
Example 1.3	50%	50%	23.1
Example 1.4	25%	25%	21.6
Example 1.5	0%	100%	20.1

	Soybean Oil (% weight)	**Cetyl Dimethicone (% weight)**	**Surface Tension (Dynes/cm^2)**
Example 2.1	100%	0%	31.4
Example 2.2	75%	25%	25.5
Example 2.3	50%	50%	24.8
Example 2.4	25%	75%	24.1
Example 2.5	0%	100 %	23.6

	Mineral Oil (% weight)	**Cetyl Dimethicone (% weight)**	**Surface Tension (Dynes/cm^2)**
Example 3.1	100%	0%	28.3
Example 3.2	75%	25%	26.1
Example 3.3	50%	50%	25.1
Example 3.4	25%	75%	24.5
Example 3.5	0%	100 %	23.6

	Isopropanol (% weight)	**PEG-8 Dimethicone (% weight)**	**Surface Tension (Dynes/cm^2)**
Example 4.1	100%	0%	21.7
Example 4.2	75%	25%	20.8
Example 4.3	50%	50%	20.5
Example 4.4	25%	75%	20.5
Example 4.5	0%	100 %	20.5

Table 21.3. Effects of Added PEG-8 Dimethicone upon Cocamidobetaine

	Draves Wetting (seconds)	Ross Miles Foam (Initial)	Ross Miles Foam (5 minutes)
Example 1.1	9.6	175	150
Example 1.2	7.5	170	145
Example 1.3	4.8	155	135
Example 1.4	3.6	145	115
Example 1.5	2.0	135	110

Figure 21.1. CMC for SLS

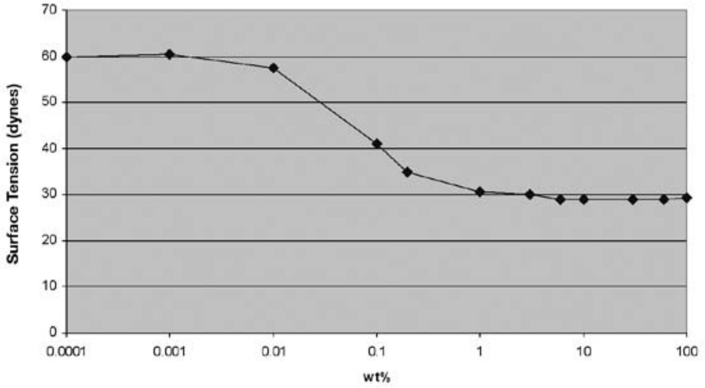
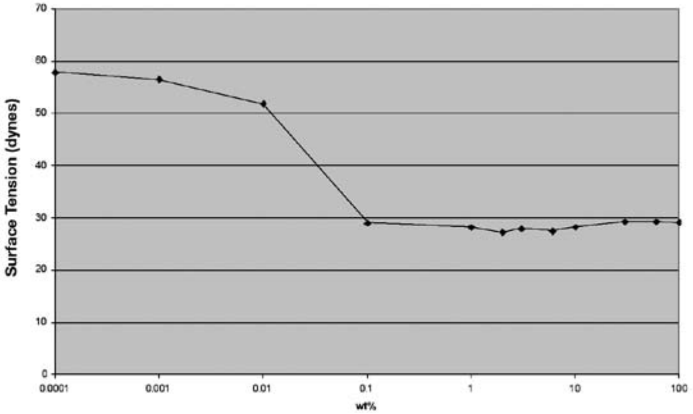


Figure 21.2. CMC for SLES-2



Silicone Surfactants

A very commonly used silicone surfactant is PEG-8 dimethicone. The CMC graph can be generated for silicone surfactants. Two variations were studied, one with a molecular weight of 700 and another with a molecular weight of 2,700. **Figures 21.3 and 21.4** display CMC for the two compounds.

Figure 21.3. CMC graph for low molecular weight PEG-8-dimethicone

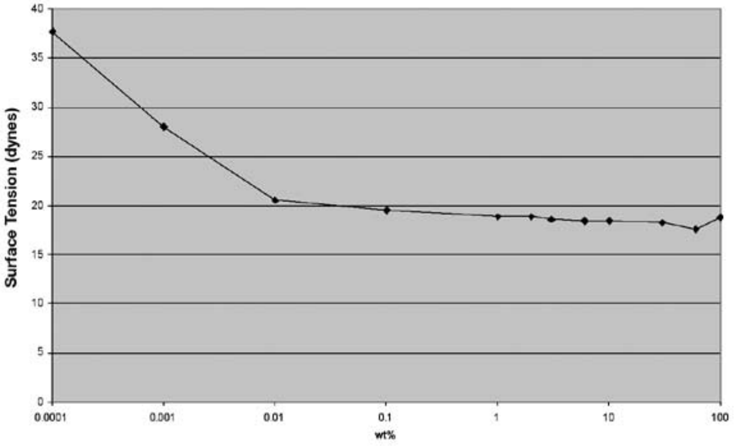
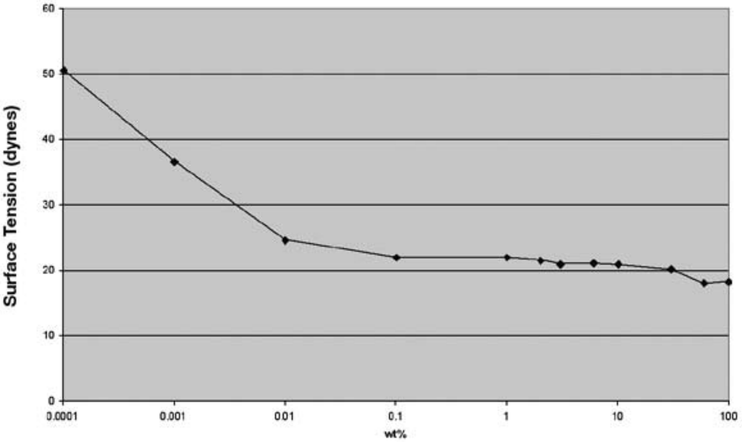


Figure 21.4. CMC graph for high molecular weight PEG-8-dimethicone



Mixed Systems

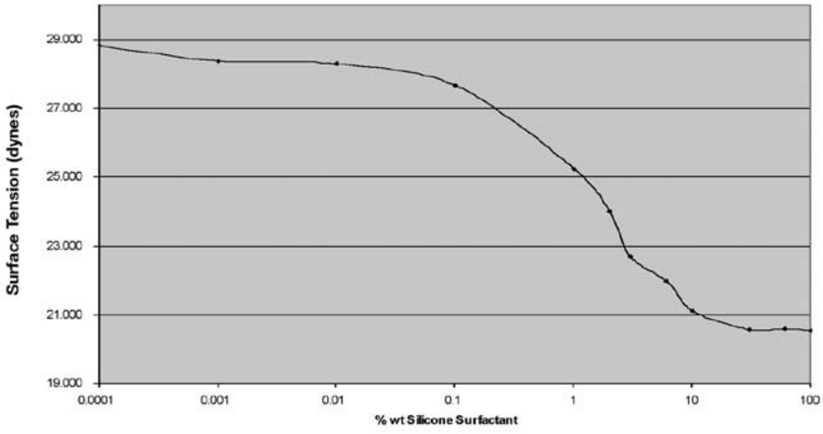
However, silicone surfactants are seldom used in systems as the sole material. As stated above, "Silicone surfactants and fatty surfactants differ fundamentally in their surface tension properties. While fatty surfactants generally have aqueous surface tensions of around 32 dynes/cm,[2] their silicone based cousins have surface tension values of around 20 dynes/cm.[2]" What happens to mixed systems?

One can pretty well predict the starting surface tension with no added silicone surfactant (the surface tension of the fatty surfactant) and the ending surfact tension (the surface tension of the silicone surfactant). The shape of the intermediate points (that is the surface tension of the blends) was not predictable.

Test Methodology

In order to study the effect of adding silicone surfactant to fatty surfactant, a 1% solution of either sodium lauryl sulfate or sodium laureth sulfate was used as the solvent, replacing water in running a standard CMC analysis. To a 1% solution of the fatty surfactant was added different amounts of silicone surfactant and the surface tension was measured. The starting surface tension was around 30 (the surface tension of the pure fatty surfactant) and the surface tension of the pure silicone surfactant was likewise around 30. **Figures 21.5** through **21.8** show the results.

Figure 21.5. Surface Tension of blends of Silsurf A-208 and SLS



The concentration of SLS and SLES in the system exceeds the CMC for those materials in all evaluations. In fact, the 1% solution of fatty surfactant is significantly over the CMC. This situation was chosen because the surface is saturated with surfactant at this concentration. Any reduction in surface tension beyond the CMC surface tension for the fatty surfactant is a direct result of competition between the fatty surfactant and the silicone surfactant. The fact that there is a significant lowering of the surface tension by the addition of low concentration of silicone surfactant, indicates the silicone surfactant competes well with the fatty surfactant for surface at the interface.

Figure 21.6. Surface Tension of blends of Silsurf C-208 and %SLS

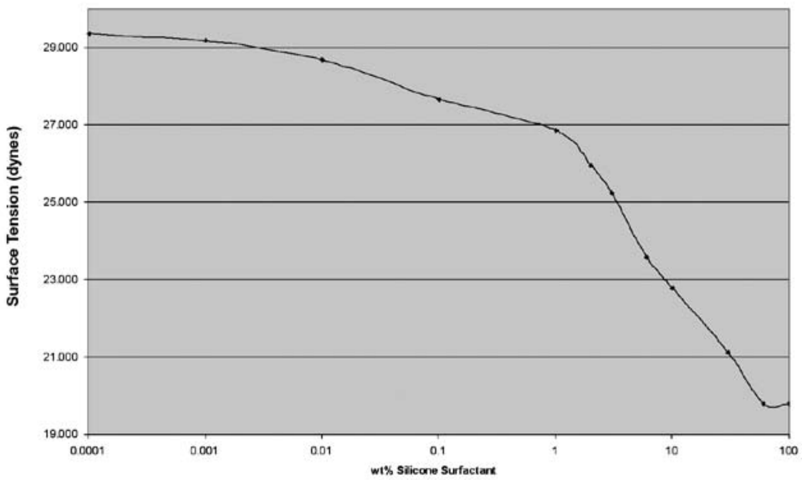


Figure 21.7. Surface Tension Silsurf A-208 and SLES-2

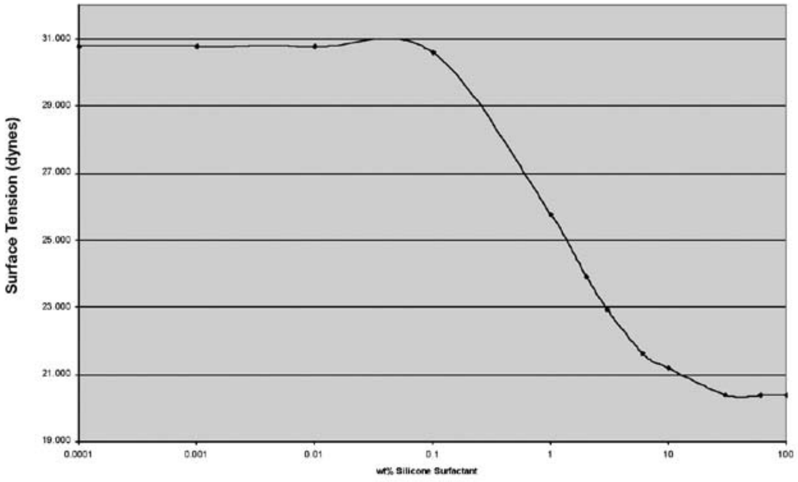
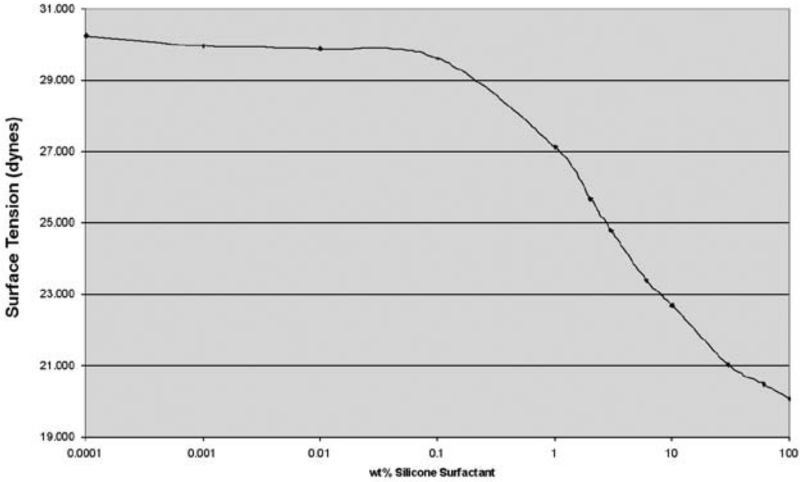


Figure 21.8. Surface Tension SilSurf C-208 and SLES-2



We suggest looking at what we call the RF_{50}, that is the ***Reduction Factor 50%*** for each silicone surfactant in each system. The definition is as follows:

RF_{50} = the concentration of silicone surfactant added to reduce the surface tension half of the difference between the fatty surfactant's surface tension and the silicone surfactant's surface tension.

The lower the $\mathbf{RF_{50}}$ the better able is the silicone surfactant to compete with the fatty surfactant for surface and the more efficient the silicone surfactant will be. This technique allows one to design molecules that will be optimized for a particular formulation. Not only can surfactant systems be evaluated but complex formulations can be evaluated, by simply defining the fatty surfactant's surface tension as the formulation's initial surface tenison. Not only surface tension, but also foam and the like can be tested and optimized by evaluating foam as the property rather than surface tension.

Silicone Surfactant	Fatty Surfactant	RF_{50}
A-208	SLS	1.2
A-208	SLES-2	1.2
C-208	SLS	1.5
C-208	SLES-2	3.5

For SLES-2 systems the A-208 and C-208 models have about the same RF_{50}, meaning the molecular size is not the controlling issue in the system. We assume the interaction between the polyoxyalkylene groups is controlling. In SLS systems, removing the polyoxyalkylene interactions, molecular size is most important.

Conclusions

1. By understanding the properties obtained by mixing different ratios of silicone surfactants with traditional surfactants, one can maximize the effect in formulation and minimize cost. This property can be defined by RF_{50}, a technique which allows for the evaluation of the effectiveness of silicone surfactants in a variety of formulations for a variety of applications.
2. It is also quite possible to use surface active silicone compounds in oil phases to alter surface tension, spreadability, cushion and play time in formulations. These oils can be used as is or in emulsions.
3. The alteration of surface tension of products offered by incorporating the proper amount of silicone into products allows the formulator to obtain altered aesthetics from formulations that are already developed, minimizing development time and maximizing lab efficiency.

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Chapter 22

Properties of Silicone Compounds

Silicone compounds vary in terms of their construction, functionalization and derivitization. These changes will produce materials with altered properties. There is a tendency to lump together the properties of silicones.

Refractive Index

Refractive index is a topic of interest to cosmetic chemists for a number of reasons. These include (1) production of so-called clear emulsions via refractive index matching and (2) gloss production, which is related to refractive index. An analytical method for measuring refractive index is at the end of this chapter. The refractive index is a constant for a given pair of materials. It can be defined as:

Speed of light in material 1/ speed of light in material 2

By definition, the refractive index of a vacuum is 1. In practice, air makes little difference to the refraction of light with an absolute refractive index of 1.0008, so the value of the absolute refractive index can be used assuming the incident light is in air.

Refractive Index Silicone Fluid

Table 22.1 shows the refractive index for common materials. It is noteworthy that silicone fluid has a refractive index that changes only marginally as the viscosity increases.

Table 22.1. Refractive Index for Common Materials

Material	Refractive Index	
Vacuum	1.0000 (exactly)	
Air (STP)	1.0003	
Ice	1.309	
Water (20°C)	1.333	**cont.**

Table 22.1. Refractive Index for Common Materials cont.

Material	Refractive Index
Alcohol	1.33
Acetone	1.36
Ethyl Alcohol	1.36
Dimethicone (50 visc)	1.402
Dimethicone (350 visc)	1.403
Dimethicone (1,000 visc)	1.403
Dimethicone (10,000 visc)	1.403
Dimethicone (60,000 visc)	1.404
Silica	1.47
Polymethacrylate	1.49
Polyethylene	1.51
Nylon	1.53

Refractive Index Organofunctional Silicone

The refractive index for organosilicone can vary between a value of 1.39 to 1.50 by changing the functionality. **Table 22.2** and **Table 22.3** show this.

Table 22.2. Refractive Index Organofunctional Silicone

1.386	Silicone Fluid	1.44	Aromatic
Fluoro	1.403	PEG-dimethicone	1.50

Table 22.3. Refractive Index Organofunctional Silicone

Fluoro Dimethicone

Product	% F	RI
A	35	1.3757
B	32	1.3864
C	14	.3895

cont.

Table 22.3. Refractive Index Organofunctional Silicone cont.

PEG Dimethicone

Product	% EO	RI
D	52.1	1.4419
E	47.0	1.4345
F	44.3	1.4316

Aromatic Dimethicone

Product	% Aromatic	RI
G	17	1.4701
H	48	1.5123

Surface Tension

PEG Dimethicone

The surface tension of a water-soluble amphilic silicone surfactant ranges between 21–32 dynes/cm^2. The surface tension is determined by how the molecules orientate themselves at the interface. That is influenced by molecular weight, % EO and structure. Those relationships are rather complicated, as is seen in **Table 22.4**.

Table 22.4. Surface Tension PEG Dimethicone

	M.W.	% EO	Surface Tension
1. PEG-4 Comb	602	82	27.9
2. PEG-8 Comb	12541	71	30.8
3. PEG-8 Comb	633	70	20.9
4. PEG-8 Comb	6352	70	28.1
5. PEG-8 Comb	2638	68	28.3
6. PEG-8 Comb	2019	67	27.3
7. PEG-8 Comb	1400	65	23.5
8. PEG-8 Linear	2049	64	29.4

cont.

Table 22.4. Surface Tension PEG Dimethicone cont.

	M.W.	% EO	Surface Tension
9. PEG-8 Linear	1400	65	27.0
10. PEG 10 Linear	1873	60	27.6
11. PEG-8 Comb	781	59	22.0
12. PEG-12 Linear	3087	48	35.0
13. PEG-8 Linear	2067	46	27.3
14. PEG-8 Comb	4740	50	31.9

PEG/PPG Dimethicone

Introduction of EO and PO results in molecules with surface tension values between 29–32 dynes/cm^2. These surface tension values are comparable to fatty surfactants indicating that the methylene groups are at the interface. **Table 22.5** shows the data.

Table 22.5. Surface Tension PEG/PPG Dimethicone

Product	M .W.	% EO	% PO	EO+PO	ST
15. PEG/PPG Comb	24059	36	43	78.67	32.0
16. PEG/PPG Comb	3272	55	23	78.07	29.8
17. PEG/PPG Comb	13223	31	38	69.27	29.6
18. PEG/PPG Comb	7166.4	25	30	54.44	33.3
19. PEG/PPG Linear	6647	26	32	57.86	29.7
20. PEG/PPG Comb	3374	34	15	49.8	31.4
21. PEG/PPG Comb	6240	32	13	44.79	32.3

Alkyl PEG Dimethicone

Introduction of EO and alkyl results in molecules with surface tension values between 31–35 dynes/cm^2. These surface tension values are comparable to fatty surfactants indicating that the methylene groups are at the interface. **Table 22.6** shows the data.

Table 22.6. Surface Tension Alkyl PEG Dimethicone

Sample	M.W.	%EO	% Olefin	ST
22. C16 PEG 8	17004	62	11	35.4
23. C12 PEG 8	5869	61	6	32.0
24. C12 PEG 8	5387	51	14	31.1

Foam

In order to get a feel for the relative foam of Siltech materials, we evaluated them for foam potential. The materials are not intended as primary surfactants, but an understanding of their foaming potential is very helpful in selecting a proper product for a given application.

Procedure:

All products were evaluated with the same procedure. A 500 mL cylinder with 2 mL increments with a glass stopper was used. All samples and distilled water were sampled at 25°C. One gram of material was used, and distilled water was poured to the 100 mL line. The cylinder was then shaken in the left and right motion, back and forth, 20 times total, 10 shakes to the left and 10 shakes to the right. Each material had an "initial" reading and then a "two minute" reading, at which foam heights were documented. Each material was evaluated three times and their averages were then calculated.

The foam results are noted in **Table 22.7**. None of the compounds foamed as well as cocamidobetaine, in fact the best foaming material produced ½ the foam of the betaine.

Table 22.7. Foam Silicone Surfactants

Product	Initial	2 minute
PEG 12 Dimethicone	240	230
PEG-8 Dimethicone	235	212
PEG-8 Dimethicone Succinate	225	217
Lauryl PEG 8 Dimethicone Quat	225	213
PEG-8 Dimethicone	222	127
PEG-8 dimethicone isostearate	175	156
Cocamidopropyl betaine	500	500

Shampoo Study

Several water-soluble silicones were evaluated in a shampoo to look for performance differences. All were based upon PEG-8 dimethicone.

Product	Designation
A	PEG-8 Dimethicone
B	Cetyl PEG-8 Dimethicone
C	Lauryl PEG-8 Dimethicone
D	Stearyl PEG-8 Dimethicone Quat

Shampoo Base

Ingredients	%
1. Water (*aqua*)	Qs
2. Sodium Laureth Sulfate	30.00
3. Cocamidopropyl Betaine	7.00
4. Cocamide DEA	4.00
5. Na_2EDTA	0.10
6. Silicone materials	2.50
7. Germaben II	1.00

All formula pH adjustments ranged from 6.70 to 6.80, specs being 6.3 to 6.8. All products were yellow in color and crystal clear.

Foam

The shampoo containing each of the silicone compounds described above were subjected to the cylinder shake foam test described above. The results are shown in **Table 22.8**.

Table 22.8. Foam Quality

1. PEG-8 Dimethicone in a shampoo base:

Foam: 325 mL

Foam Quality: The foam was tight and creamy

2. Cetyl PEG-8 Dimethicone in a shampoo base:

Foam : 350 mL

Foam Quality: The foam was tight with small bubbles

3. Lauryl PEG-8 Dimethicone in a shampoo base:

Foam 350 mL

Foam Quality: The foam was tight with small bubbles

cont.

Table 22.8. Foam Quality cont.

4. Stearyl PEG-8 Dimethicone Quat in a shampoo base

Foam: 385 mL

Foam Quality: The foam was very creamy and abundant and with small bubbles

Hair Evaluation

The four products were then evaluated for wet and dry combing on 10-inch virgin brown hair. Three two-gram swatches were used with one gram of shampoo for each swatch. The water temperature used for wetting and rinsing the hair was a constant 25°C. All the swatches were rinsed until squeaky clean or for at least one minute. After the wet hair evaluation, the swatches were left to air dry then the dry comb evaluation was performed. The scale used for all evaluations is from 1 to 5, 5 being the best. **Tables 22.9** and **22.10** show the results of wet comb and dry comb respectively.

Table 22.9. Wet Combing Evaluation

	Control Water only	PEG-8 Dimethicone	Cetyl PEG-8 Dimethicone	Lauryl PEG-8 Dimethicone	Stearyl PEG-8 Dimethicone Quat
Wet comb	1	4	4.5	4.5	5
Rinse off	3	5	4	4.5	5
Clean feel	1	5	4	4.5	4.5
Shine	3	4	4	4	4.5
Average	2	4.5	4.125	4.375	4.75

Table 22.10. Dry Combing Evaluation

	Control Water only	PEG-8 Dimethicone	Cetyl PEG-8 Dimethicone	Lauryl PEG-8 Dimethicone	Stearyl PEG-8 Dimethicone Quat
Dry comb	2	4	4.5	4	4
Feel	2	4	4	4	4
Manageability	2	4	3	4	4

cont.

Table 22.10. Dry Combing Evaluation cont.

	Control Water only	PEG-8 Dimethicone	Cetyl PEG-8 Dimethicone	Lauryl PEG-8 Dimethicone	Stearyl PEG-8 Dimethicone Quat
Shine	3	5	4	4.5	4.5
Clean look	2	4	4	4	4
Flyaway	2	3	3	3	4
Static	2	3	3	3	4
Residual feel	3	4	4	4	4.5
Average	2	4.5	4.125	4.375	4.75

Evaluation

1. Upon the comparative evaluation of these materials, they all performed quite well from foam heights to wet and dry combing.
2. The material that stands out as the best is stearyl PEG-8 dimethicone quat. The foam height was superior to the rest and the dry combing left the hair soft, shiny and very manageable with no residual after feel which otherwise could give the impression of weighing down the hair, or of the hair being dirty or greasy. This material enhanced, without a doubt, all the attributes for hair treatment. It also left the skin feeling very soft and silky.
3. The PEG-8 dimethicone performed quite well on all attributes, except it did not seem to build up on the foam height. The lauryl PEG-8 dimethicone performed well also, except it fell slightly short with the static and flyaway evaluation. The foam height was very good. The cetyl PEG-8 dimethicone did slightly poorer with the static and manageability evaluation.

Conclusions

The proper selection of silicone for use in an application is formulation- and structure-dependant.

ANALYTICAL METHOD

Refractive Index

Scope: This method is applicable to all normal oils and liquid fats.

Summary: The index of refraction of oil is characteristic within certain limits for each kind of oil. Using the refractometer's light, take the most distinct reading possible by centering the horizon on the crosshairs. Take at least three readings and calculate the average of all of the readings.

Apparatus:

1. Refractometer, any standard refractometer equipped with the Abbe, Butyro or any other standard scale. A dipping type refractometer is satisfactory.

2. Light source. If the refractometer is equipped with a compensator, a tungsten lamp or day-light is permissible. Otherwise, a monochromatic light such as an electric sodium vapor lamp is required.

3. Lens tissue or cotton.

Reagents:

1. Toluene, technical grade.
2. Isopropyl alcohol (IPA), technical grade.

Procedure:

1. Using a thermostatically controlled water bath and motor-driven pump to circulate water through the refractometer, control the temperature of the instrument to within ±0.1°C of the desired temperature.

2. Verify that the instrument has been calibrated within the previous two weeks. If not, calibrate the instrument using the calibration procedure.

3. Clean the prism with toluene or IPA. Allow to dry completely.

4. Place a few drops of sample on the lower prism (Remark 1).

5. Close the top prism and tighten firmly.

6. Allow the sample to equilibrate to temperature (about one minute) before taking a reading.

7. Adjust the instrument and light to focus the horizon on the

crosshairs. Determine the most distinct reading for the refractive index. Record the refractive index to four decimal place accuracy.

8. Repeat Step 7 until three readings have been made. Using Equation 1 in the Calculations section of this method, calculate the average refractive index. Report the refractive index to four decimal place accuracy (Ex. 1.4014).

Calculations: *Equation 1*

$$\text{Avg. Refractive Index} = \frac{(\text{RI \#1}) + (\text{RI \#2}) + (\text{RI \#3})}{3}$$

Safety: Isopropyl alcohol is flammable and a dangerous fire risk. Only handle in well ventilated areas.

Toluene is toxic and flammable. Do not inhale and use in a well ventilated fume hood. The TLV is 100 ppm in air.

Remarks: 1. If the sample is not liquid, melt the sample and filter through filter paper to remove any impurities and last traces of moisture.

References: 1. A.O.C.S. Official Method Cc 7-25.

Chapter 23

Reactive Silicone Compounds

The ability to derivitize silicone compounds has become more and more important. Initially, the modification of organic groups on silicone was limited. The chemistry available to make new organic materials using silicone compounds with reactive pendant groups is constantly expanding.

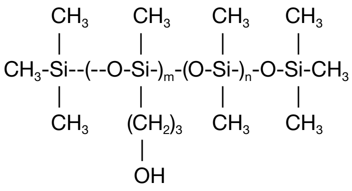
The reactive groups, when placed on silicone, display reactivity as though silicone were not present, with solubility and stability being the two issues. In other words, a silicone with a reactive group on it can participate in any reactions that the group alone can participate in, if the silicone compound is soluble in the other reactant and if the reaction conditions do not degrade the silicone.

Silicone with hydroxyl groups

Hydroxyl groups are reactive to make a variety of materials. They can be simple hydroxypropyl groups as shown in **Figure 23.1**. They can also be alkoxylated with either ethylene oxide, propylene oxide butylene oxides or mixtures thereof. Typical compounds available are shown in **Table 23.1**.

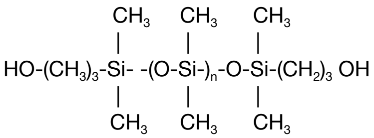
Figure 23.1. Silicone Compounds with Hydroxyl Groups

Comb



$$CH_3\text{-}Si(CH_3)_2\text{--}(\text{--}O\text{-}Si(CH_3)((CH_2)_3OH)\text{-})_m\text{-}(O\text{-}Si(CH_3)_2\text{-})_n\text{-}O\text{-}Si(CH_3)_2\text{-}CH_3$$

Terminal



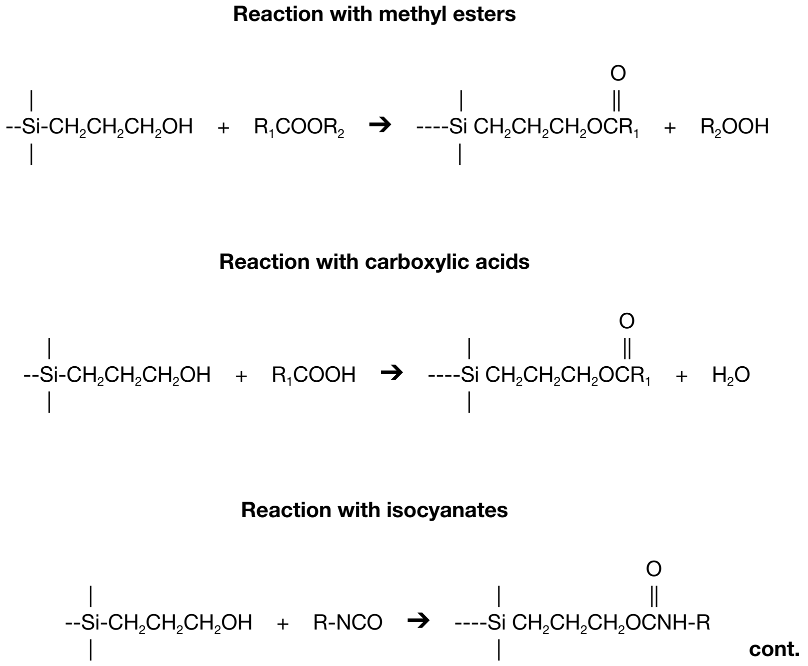
$$HO\text{-}(CH_3)_3\text{-}Si(CH_3)_2\text{-}\ \text{-}(O\text{-}Si(CH_3)_2\text{-})_n\text{-}O\text{-}Si(CH_3)_2\text{-}(CH_2)_3\,OH$$

Table 23.1. Hydroxyl Functional Silicone

Designation	Type	Functional Groups	MW	EMW MW/Groups
OH-A0	Comb	1	280	280
OH C-50	Comb	3	11,600	3,800
OH J10	Comb	10	8,800	880
OH Di50	Terminal	2	4,000	1,980
OH Di100	Terminal	2	7,700	3,800

The reaction of the hydroxyl group provides esters, polyesters (if multifunctional silicone hydroxyls are reacted with multifunctional acids), and urethanes or polyurethanes. **Figure 23.2** shows the chemistry.

Figure 23.2. Reaction with Silicone Compounds having Hydroxyl Groups



Reaction with methyl esters

$$\text{--}\overset{|}{\underset{|}{Si}}\text{-}CH_2CH_2CH_2OH + R_1COOR_2 \rightarrow \text{----}\overset{|}{\underset{|}{Si}}\ CH_2CH_2CH_2O\overset{\overset{O}{\|}}{C}R_1 + R_2OOH$$

Reaction with carboxylic acids

$$\text{--}\overset{|}{\underset{|}{Si}}\text{-}CH_2CH_2CH_2OH + R_1COOH \rightarrow \text{----}\overset{|}{\underset{|}{Si}}\ CH_2CH_2CH_2O\overset{\overset{O}{\|}}{C}R_1 + H_2O$$

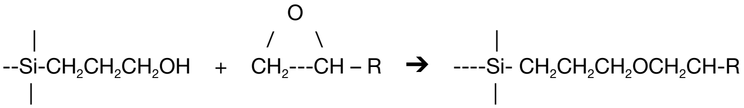
Reaction with isocyanates

$$\text{--}\overset{|}{\underset{|}{Si}}\text{-}CH_2CH_2CH_2OH + R\text{-}NCO \rightarrow \text{----}\overset{|}{\underset{|}{Si}}\ CH_2CH_2CH_2O\overset{\overset{O}{\|}}{C}NH\text{-}R$$

cont.

Figure 23.2. Reaction with Silicone Compounds having Hydroxyl Groups cont.

Reaction with epoxides



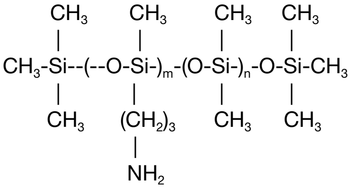
$$\text{--}\underset{|}{\overset{|}{\mathrm{Si}}}\text{-}CH_2CH_2CH_2OH \;+\; \overset{O}{\overbrace{CH_2\text{---}CH}} - R \rightarrow \text{----}\underset{|}{\overset{|}{\mathrm{Si}}}\text{- }CH_2CH_2CH_2OCH_2CH\text{-}R$$

Silicone compounds with amino groups

Amino groups are reactive to make a variety of materials. They can be simple amino groups as shown in **Figure 23.3** or polyamine groups. Typical compounds available are shown in **Table 23.2**.

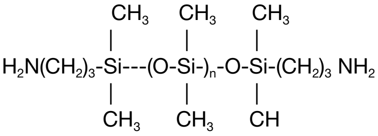
Figure 23.3. Silicone Compounds with Amino Groups

Comb



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\text{--(--O-}\underset{\underset{NH_2}{(CH_2)_3}}{\overset{CH_3}{\mathrm{Si}}}\text{-)}_m\text{-(O-}\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\text{-)}_n\text{-O-}\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\text{-}CH_3$$

Terminal



$$H_2N(CH_2)_3\text{-}\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\text{---(O-}\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\text{-)}_n\text{-O-}\underset{CH}{\overset{CH_3}{\mathrm{Si}}}\text{-}(CH_2)_3\ NH_2$$

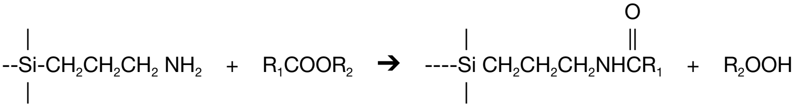
Table 23.2. Amino Functional Silicone

Designation	Type	Functional Groups	MW	EMW MW/Groups
NH Di-8	Terminal	2	850	425
NH Di-50	Terminal	2	3,600	1,800

The reaction of the amino group provides amide, polyamides (if multifunctional silicone amino are reacted with multifunctional acids), urethanes and substituted silicone amines. **Figure 23.4** shows the chemistry.

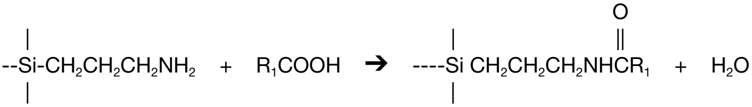
Figure 23.4. Reaction with Silicone Compounds having Amino Groups

Reaction with Methyl Esters to make Amides



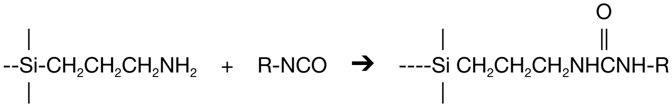
$$\text{--}\overset{|}{\underset{|}{\mathrm{Si}}}\text{-}CH_2CH_2CH_2\ NH_2 + R_1COOR_2 \rightarrow \text{----}\overset{|}{\underset{|}{\mathrm{Si}}}\ CH_2CH_2CH_2NH\overset{O}{\overset{\|}{C}}R_1 + R_2OOH$$

Reaction with Carboxylic Acids to make Amides



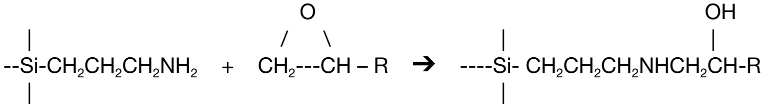
$$\text{--}\overset{|}{\underset{|}{\mathrm{Si}}}\text{-}CH_2CH_2CH_2NH_2 + R_1COOH \rightarrow \text{----}\overset{|}{\underset{|}{\mathrm{Si}}}\ CH_2CH_2CH_2NH\overset{O}{\overset{\|}{C}}R_1 + H_2O$$

Reaction with Isocyanates to make Urethanes



$$\text{--}\overset{|}{\underset{|}{\mathrm{Si}}}\text{-}CH_2CH_2CH_2NH_2 + R\text{-}NCO \rightarrow \text{----}\overset{|}{\underset{|}{\mathrm{Si}}}\ CH_2CH_2CH_2NH\overset{O}{\overset{\|}{C}}NH\text{-}R$$

Reaction with Epoxides to make Amines



$$\text{--}\overset{|}{\underset{|}{\mathrm{Si}}}\text{-}CH_2CH_2CH_2NH_2 + \overset{O}{\overset{/\quad\backslash}{CH_2\text{---}CH}} - R \rightarrow \text{----}\overset{|}{\underset{|}{\mathrm{Si}}}\text{-}\ CH_2CH_2CH_2NHCH_2\overset{OH}{\overset{|}{C}}H\text{-}R$$

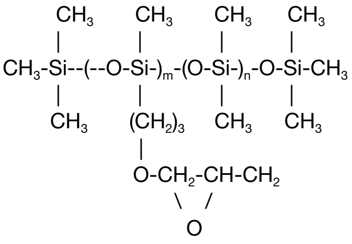
Silicone Compounds with Epoxy Groups

Epoxy groups are reactive to make a variety of materials. They can be simple glycidyl groups as shown in **Figure 23.5**, or cycloepoxy compounds. Typical compounds available are shown in **Table 23.3**.

The reaction of the epoxy group reacts with hydroxyl groups or amino groups. **Figure 23.6** shows the chemistry.

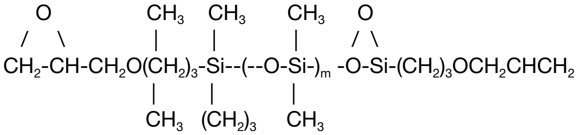
Figure 23.5. Silicone Compounds with Epoxy Groups

Comb



$$CH_3\text{-}Si(CH_3)_2\text{--}(\text{--}O\text{-}Si(CH_3)[(CH_2)_3\text{-}O\text{-}CH_2\text{-}\underset{\setminus\ O\ /}{CH\text{-}CH_2}])_m\text{-}(O\text{-}Si(CH_3)_2)_n\text{-}O\text{-}Si(CH_3)_2\text{-}CH_3$$

Terminal



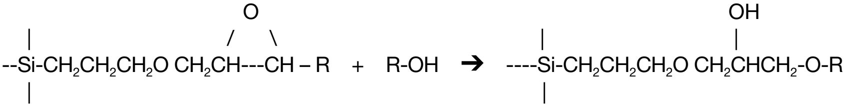
$$\overset{O}{\overbrace{CH_2\text{-}CH}}\text{-}CH_2O(CH_2)_3\text{-}Si(CH_3)_2\text{--}(\text{--}O\text{-}Si(CH_3)(CH_2)_3)_m\text{ -}O\text{-}Si(CH_3)\text{-}(CH_2)_3OCH_2\overset{O}{\overbrace{CHCH_2}}$$

Table 23.3. Epoxy Functional Silicone

Designation	Type	Functional Groups	MW	EMW MW/Groups
EP-C50	Comb	3	11,800	3,900
EP-J10	Comb	10	9,300	930
EP-Di-50	Terminal	2	4,100	2,050
EP Di-100	Terminal	2	78,800	3,900

Figure 23.6. Reaction with Silicone Compounds having Epoxy Groups

Reaction with Alcohols

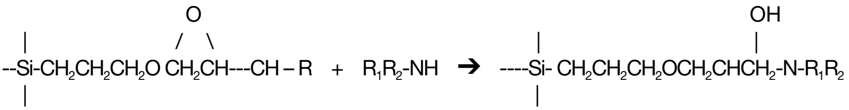


$$\text{--}\overset{|}{\underset{|}{Si}}\text{-}CH_2CH_2CH_2O\ CH_2\overset{O}{\overbrace{CH\text{---}CH}}-R\ +\ R\text{-}OH \rightarrow \text{----}\overset{|}{\underset{|}{Si}}\text{-}CH_2CH_2CH_2O\ CH_2\overset{OH}{\overset{|}{C}}HCH_2\text{-}O\text{-}R$$

cont.

Figure 23.6. Reaction with Silicone Compounds having Epoxy Groups cont.

Reaction with Amines



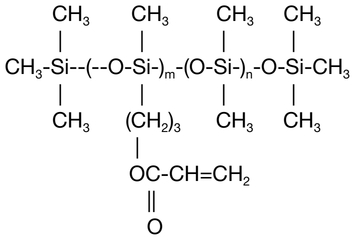
$$\text{--}\underset{|}{\overset{|}{Si}}\text{-}CH_2CH_2CH_2O\,CH_2\overset{\overset{O}{/\ \backslash}}{CH\text{---}CH}\text{ - }R + R_1R_2\text{-}NH \rightarrow \text{----}\underset{|}{\overset{|}{Si}}\text{- }CH_2CH_2CH_2OCH_2\overset{\overset{OH}{|}}{CH}CH_2\text{-}N\text{-}R_1R_2$$

Silicone compounds with acrylate groups

Acrylate groups or methacrylate groups on silicone are reactive to make a variety of materials. They can be simple hydroxypropyl acrylate groups as shown in **Figure 23.7**. They can also be alkoxylated with either ethylene oxide, propylene oxide butylenes oxides or mixtures thereof. Typical compounds available are shown in **Table 23.4**.

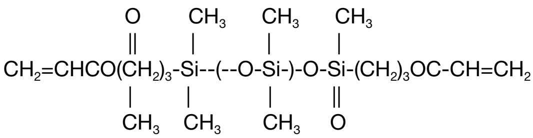
Figure 23.7. Silicone Compounds with Acrylate Groups

Comb



$$CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{--(--O-}\underset{\underset{\underset{\underset{\underset{O}{\|}}{OC\text{-}CH=CH_2}}{|}}{(CH_2)_3}}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-)}_m\text{-(O-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-)}_n\text{-O-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-}CH_3$$

Terminal



$$CH_2=CH\underset{\underset{CH_3}{|}}{\overset{\overset{O}{\|}}{C}}O(CH_2)_3\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{--(--O-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-)-O-}\underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{Si}}\text{-}(CH_2)_3OC\text{-}CH=CH_2$$

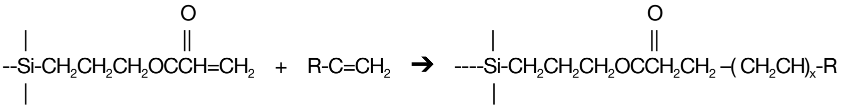
Table 23.4. Acrylate Functional Silicone

Designation	Type	Functional Groups	MW	EMW MW/Groups
ACR D-2	Comb	4	1,790	700
ACR Di-50	Terminal	2	4,100	2,050
ACR-Di-100	Terminal	2	7,800	3,900

The reaction provides polyacrylates and a variety of hetero radical polymers. **Figure 23.8** shows the chemistry.

Figure 23.8. Reaction with Silicone Compounds having Acrylate Groups

Reaction with Vinyl Monomers



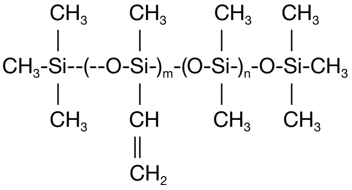
$$\text{--}\overset{|}{\underset{|}{Si}}\text{-}CH_2CH_2CH_2O\overset{\overset{O}{\|}}{C}CH{=}CH_2 \quad + \quad R\text{-}C{=}CH_2 \rightarrow \text{----}\overset{|}{\underset{|}{Si}}\text{-}CH_2CH_2CH_2O\overset{\overset{O}{\|}}{C}CH_2CH_2\text{-(}CH_2CH)_x\text{-}R$$

Silicone compounds with vinyl groups

Vinyl groups on silicone are reactive to make a variety of condensation polymeric materials. They can be simple vinyl groups as shown in **Figure 23.9**. They can be M* (terminal vinyl groups). Typical compounds available are shown in **Table 23.5**.

Figure 23.9. Silicone Compounds with Vinyl Groups

Comb

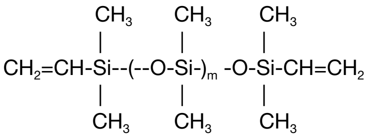


$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--(--O-}\underset{\underset{CH_2}{\overset{\|}{CH}}}{\overset{CH_3}{Si}}\text{-)}_m\text{-(O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-)}_n\text{-O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

cont.

Figure 23.9. Silicone Compounds with Vinyl Groups cont.

Terminal



$$CH_2{=}CH\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{--(--O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-)}_m\text{-O-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH{=}CH_2$$

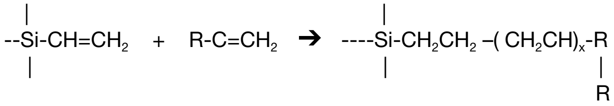
Table 23.5. Acrylate Functional Silicone

Designation	Type	Functional Groups	% Vinyl	millimoles/gm
Vin-C50	Comb	3	0.7	0.26
Vin-J10	Comb	10	3.2	1.18
Vin-70	Terminal	2	1.4	0.51
Vin-100	Terminal	2	0.9	0.33

The reaction of the hydroxyl group provides esters, polyesters (if multifunctional silicone hydroxyls are reacted with multifunctional acids), and urethanes or polyurethanes. **Figure 23.10** shows the chemistry.

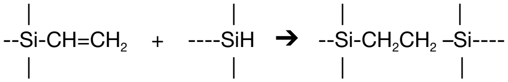
Figure 23.10. Reaction with Silicone Compounds having Vinyl Groups

Reaction with Vinyl Monomers



$$\text{--}\underset{|}{\overset{|}{Si}}\text{-}CH{=}CH_2 \;+\; R\text{-}C{=}CH_2 \rightarrow \text{----}\underset{|}{\overset{|}{Si}}\text{-}CH_2CH_2\text{–(}CH_2\underset{R}{CH})_x\text{-}R$$

Reaction with SiH



$$\text{--}\underset{|}{\overset{|}{Si}}\text{-}CH{=}CH_2 \;+\; \text{----}\underset{|}{\overset{|}{Si}}H \rightarrow \text{--}\underset{|}{\overset{|}{Si}}\text{-}CH_2CH_2\text{–}\underset{|}{\overset{|}{Si}}\text{----}$$

Conclusion

Reactive silicone compounds offer the possibility of making derivatives based upon customized raw materials. This type of material was generally used in a captive manner in the production of silicone polymers, but is now available as a formulator-friendly material to make the availability of products more flexible.

Chapter 24

Methods in Silicone Chemistry

This chapter will address several methods used to evaluate silicone compounds, including instrumental methods like FTIR and GPC, as well as methods for use in the evaluation of formulated silicone compounds.

Instrumental Methods

The evaluation of silicone compounds generally involves two distinct steps: separation and group identification. The fact that silicone compounds may be blends of different materials or pure compounds can only be determined by separation science. Separation science deals with techniques that "separate" the components, most often based upon molecular weight. Only by separation of the mixture into its components prior to looking at functional groups on the molecule will the composition of the mixture be known. A functional group analysis of blended materials will result in an average of groups present on the mixture, without identifying if the groups are on the same or different molecule.

FTIR

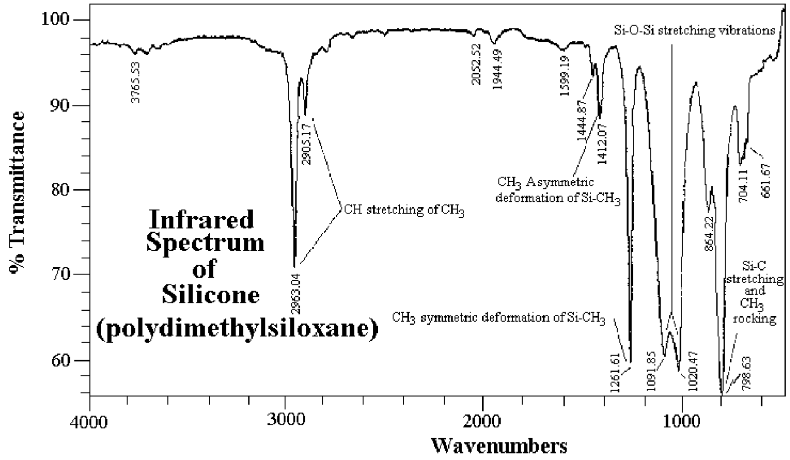
Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint." This fingerprint is very valuable because it provides an easy yet powerful analytical method for verification of the salient group. FTIR is most useful for identifying chemicals that are either organic or inorganic.

The term Fourier Transform Infrared Spectroscopy (FTIR) refers to the manner in which the data is collected and converted from an interference pattern to a spectrum. The methodology makes use of many different scans that are averaged by the computer to produce a spectrum free of noise that can be seen in single scan analysis.

FTIR will be very important in the identification of functionalization and derivatization, since the groups added with these processes are easily identified by FTIR. NMR, the next technique discussed, will reveal very important information on construction.

Figure 24.1 shows a typical FTIR of a silicone containing compound.

Figure 24.1. FTIR Spectrum



http://www.wcaslab.com/tech/tbftir.htm

Figures 24.2–24.4 show typical FTIR evaluations for silicone materials.

Figure 24.2. FTIR of Dimethicone

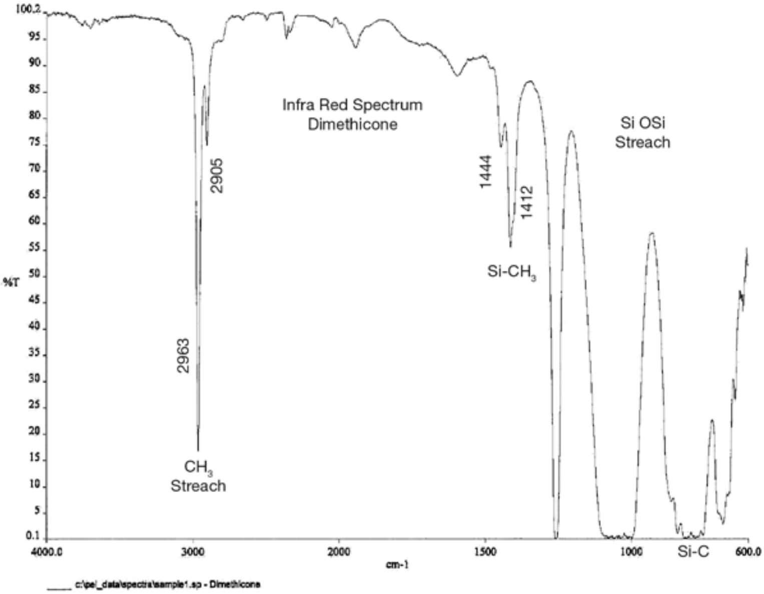


Figure 24.3. FTIR PEG 12 Dimethicone

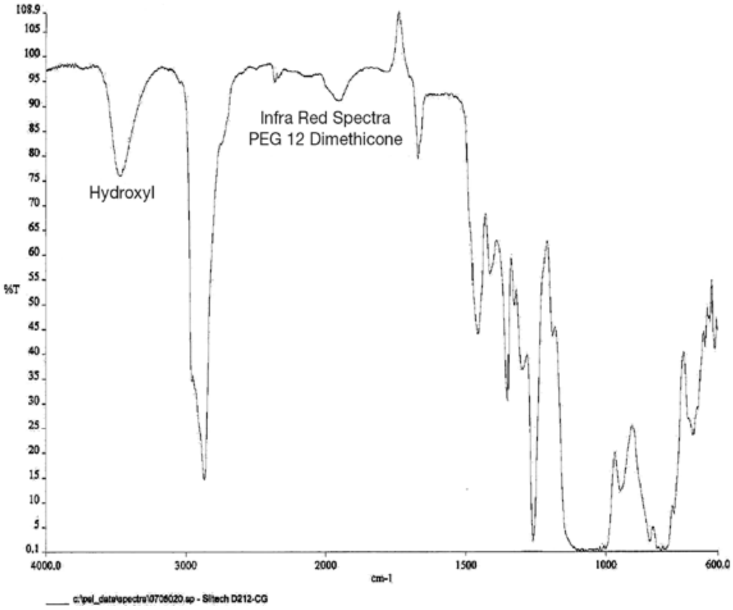
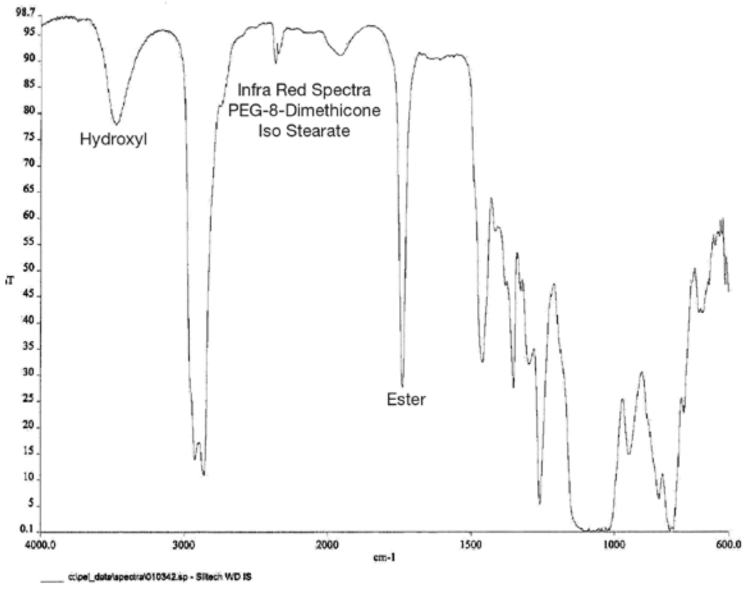


Figure 24.4. FTIR PEG-8 Dimethicone isostearate



NMR

Nuclear magnetic resonance (NMR) is a phenomenon that occurs when the nuclei of certain atoms are immersed in a static magnetic field and exposed to a second oscillating magnetic field. Some nuclei experience this phenomenon, and others do not; this depends upon whether they possess a property called spin. Si^{29}, a natural isotope of silicon, is such a molecule. **Figure 24.5** shows the relative abundance of the isotopes found in silicon.

Figure 24.5. Isotopes of Si

Silicon is element number 14.

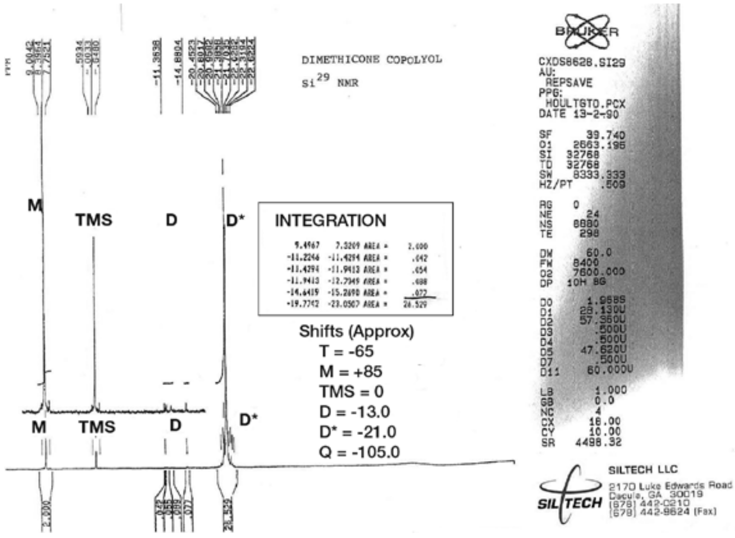
It has a molecular weight of 28.0855 and occurs in three isotopes:

Si^{28} (92%),
Si^{29} (5%),
Si^{30} (3%).

Because of Si^{29}, silicon has an NMR spectra.

Figure 24.6 shows silicone NMR.

Figure 24.6. Silicon^{29} NMR



INTEGRATION

```
  9.4967    7.3209 AREA =     2.000
-11.2246  -11.4294 AREA =      .042
-11.4294  -11.9413 AREA =      .654
-11.9413  -12.7349 AREA =      .688
-14.6419  -15.2690 AREA =      .072
-19.7742  -23.0507 AREA =    24.529
```

Shifts (Approx)
T = -65
M = +85
TMS = 0
D = -13.0
D* = -21.0
Q = -105.0

```
CXDS8628.SI29
AU:
 REPSAVE
PPG:
 HOULTGTO.PCX
DATE 13-2-90

SF      39.740
O1    2663.195
SI   32768
TD   32768
SW    8333.333
HZ/PT     .509

RG    0
NE       24
NS     8880
TE      298

DW      60.0
FW    8400
O2    7600.000
DP   10H BG

D0       1.968S
D1      28.130U
D2      57.360U
D3        .500U
D4        .500U
D5      47.620U
D7        .500U
D11     60.000U

LB       1.000
GB       0.0
NC       4
CX      18.00
CY      10.00
SR    4498.32
```

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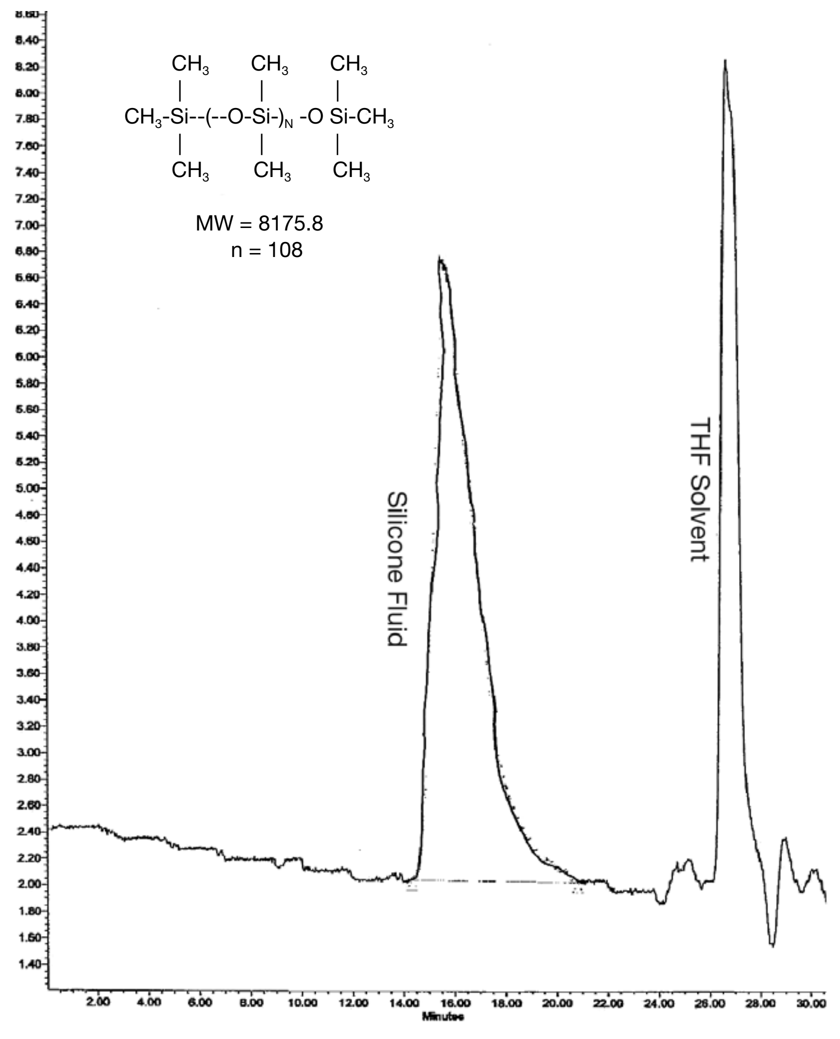
(678) 442-9624 (Fax)

NMR will allow for the establishment of the ratio of the different silicone groups found on the construction. **Figure 24.7** shows a typical NMR.

Figure 24.7. GPC Silicon Fluid



GPC

Size exclusion chromatography (SEC) is a chromatographic method in which particles (usually large molecules or macromolecular complexes) are separated based upon size. When the chromatographic medium is a gel, the technique is more specifically known as gel permeation chromatography.

Theory and Method

The underlying principle of SEC is that particles of different sizes will elute (filter) through a stationary phase at different rates. This results in the separation of a solution of particles based on size. Provided that all the particles are loaded simultaneously or near simultaneously, particles of the same size should elute together.

This is usually achieved with a column, which consists of a hollow tube tightly packed with extremely small porous polymer beads designed to have pores of different sizes. These pores may be depressions on the surface or channels through the bead. As the solution travels down the column some particles enter into the pores. Larger particles cannot enter into as many pores. The larger the particles are, the less overall volume to traverse over the length of the column, and therefore, the faster the elution. The use of this type of analysis results in some important information on the composition of the silicone material being investigated as to the molecular weight and distribution of materials over a range of molecular weight. **Figure 24.8** and **Table 24.1** show two very different but not atypical GPC for commercial dimethicone products.

Figure 24.8. GPC of Blended Silicone

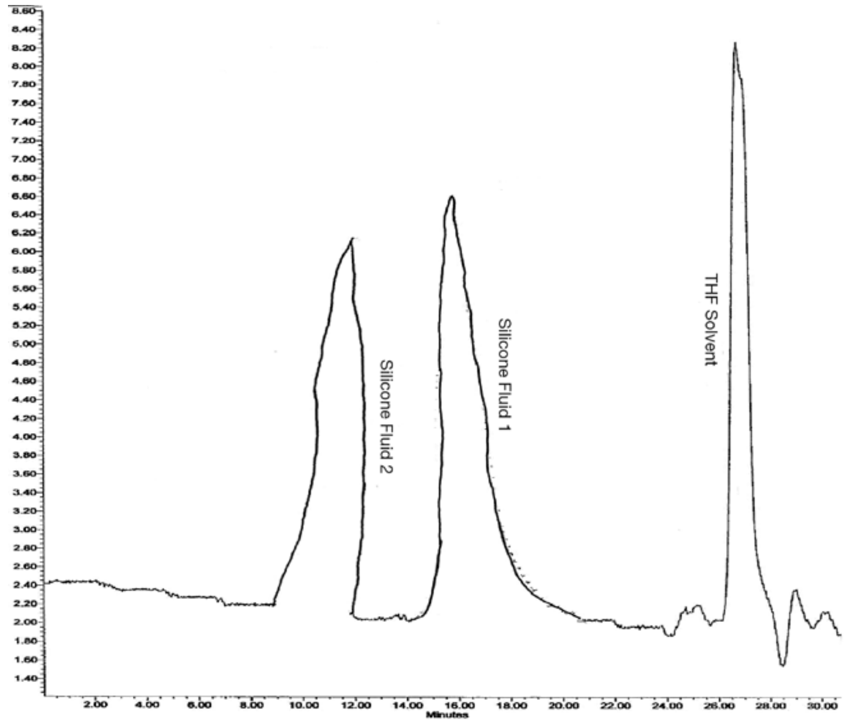


Table 24.1. Draves Wetting PEG-8 Dimethicone

	Samples	M.W.	Cotton Wetting Time (Sec)
1	A008	633	10
2	A208	781	37
3	B208	1,400	107
7	D208	2,638	2,776
8	J208	6,352	23,400
9	T208	12,541	28,800

Wetting Test Methodology

Wetting is a property that is always of interest to the cosmetic chemist. This is due to the fact that application of cosmetic products to the hair or skin always includes spreading on a substrate and formation of new surface area. Shampoos spread a layer of detergent on the hair, lipsticks spread pigment on the lips, and sunscreen formulations spread UV absorbers on the skin.

Despite the major differences in their formulations, they all have a common need for a wetting agent. Wetting provides a uniform surface that does not have voids or imperfections. Wetting is generally thought of as a water phenomenon; however, wetting also occurs in the oil phase. Silicones by virtue of their exceptionally low surface tension can provide wetting to pigments when placed in oil. This is important for uniform coatings.

Standard Methodology

Most methodologies used in the personal care market were developed for other industries. The standard Draves Wetting Method was developed for use in the textile market; the methodology evaluates the ability of a surfactant to wet out cotton skeins.

Scope: To determine the efficiency of a silicone wetting compound.

Summary: The silicone wetting compound is added to a liter of water and mixed thoroughly. A 22 cm skein is placed at the surface and dropped into water. The time it takes for the cord to slacken and the skein to collapse is observed.

Apparatus

a) Beaker, 1000 mL

b) Drave 40/2 Cotton Skein, (5 g/45 cm)
c) Stopwatch
d) 40 g weight with wire loop and attached to copper S hook with lined thread.

Note: Skeins and lead weight assembly as outlined in AATCC Test Method 117-1994 from Testfabrics, Inc.

Reagents: Tap water

Procedure

1. Add 0.5 g of wetting material to one liter of tap water in a 1000 mL beaker. Mix thoroughly.
2. Obtain a 45 cm skein and fold in two to make a length of approximately 22 cm. Attach the bound end to the wire hook on the lead weight and cut the other end with scissors to leave it open.
3. Gently place the lead weight just at the water surface and drop it into the beaker while starting the stopwatch. Observe the thread between the lead weight and the wire hook and stop the watch once it begins to slacken.
4. Repeat with 2 other skeins and take the average time of all three runs. The average wetting time should be less than 20 sec for a 0.5 g sample.

The Draves Wetting Times (DWT) varies as a function of molecular weight on PEG-8 dimethicone. As the molecular weight increases so too does the wetting times. For comparison the wetting times for some typical fatty surfactants is shown in **Table 24.1**.

For comparison **Table 24.2** outlines wetting times for some fatty surfactants typically found in cosmetic products.

The data clearly shows that silicone surfactants are more effective wetting agents than the traditional surfactants.

Table 24.2. Draves Wetting
Wetting time of fatty surfactants

Sample	Unit	Wetting Time
Cocamidopropyl betaine	sec	>39,600
Sodium Dooctylsulfosuccinate	sec	398
Sodium Lauryl Sulfate (Technical grade, 95%)	sec	108

Wetting of Hair

In the cosmetic industry, wetting of cotton may or may not be proper. Since it is hair, not cotton, that is the substrate of interest in wetting, a modified methodology has been developed to replace cotton with hair.

For this exercise, use the same procedure as in the Draves Wetting Test, but instead of using cotton swatches, use virgin European dark hair swatches and measure the wetting properties of several dimethicone copolyol products (PEG-8 dimethicone) products:

Test Method:

The Draves Wetting Test Method (SAM 140) is used with the following modification:

1. Add 0.5 g of wetting agent to one liter of tap water in a 1000 mL beaker and mix thoroughly.
2. Gently pour the above solution in Step #1 to a 1000 mL graduated cylinder and then let it sit for one hour or until all bubbles below the surface of the solution rise to the top.
3. Measure and record the temperature of the solution.
4. Remove any foam bubbles on the top of the liquid surface.
5. Cut a small piece of nylon/polyester thread and tight a small loop at the bottom of the hair swatches. The total weight of the hair swatches is about 50 g.
6. Attach a wire hook with a 20 g lead weight to the hair swatches through the loop at the bottom of the swatches.
7. Hold the hair swatches with one hand and hold a stopwatch in the other; then gently place the hanging lead weight just at the water surface.
8. Release and drop the hair swatches into the solution while starting the stopwatch.
9. Observe the thread between the lead weight and the wire hook; stop the watch once it begins to slacken and then record the wetting time.
10. Clean the hair swatches with Johnson's baby shampoo, rinse with three gallons of tap water three times and then dry in a 50°C oven for 16 hours or until the weight of the hair swatches is unchanged.
11. Repeat the above steps with different wetting agents.

Table 24.3 shows the results.

Comparison of Methodology

Clearly, the wetting method using the standard Draves Wetting Methodology was more discriminating in determining differences in the wetting agents. The use of cotton skeins provides results that show differences in the wetting agents more than can be seen using hair. However, the cosmetic formulator is not interested in wetting cotton skeins; the substrate of interest is hair and skin. The methodology that shows the performance on the substrate of interest to the cosmetic formulator of shampoos is hair, and consequently it is submitted that it is that very same substrate that should be used for testing.

Table 24.3. Hair Wetting Results

Sample I.D.	MW	Hair Wetting Time (Sec)
A008	633	4
A208	781	8
B208	1,400	10
C208	2,638	11
D208	6,352	22
No wetting Agent		60

Table 24.4 compares the results of the two methodologies. The salient difference is that samples 4 and 5 (higher molecular weight products) would be considered good hair wetting agents, but poor cotton wetting agents. This information is of interest to the cosmetic and textile formulator as it provides different conclusions.

Table 24.4. Comparison of Wetting Methodology

	Samples	Hair Wetting Time (Sec)	Cotton Wetting Time (Sec)
1	A008	4	10.5
2	A208	8	37.3
3	B208	10	107
4	D208	11	>2,776
5	J208	22	>23,400

Additional Silicone Information

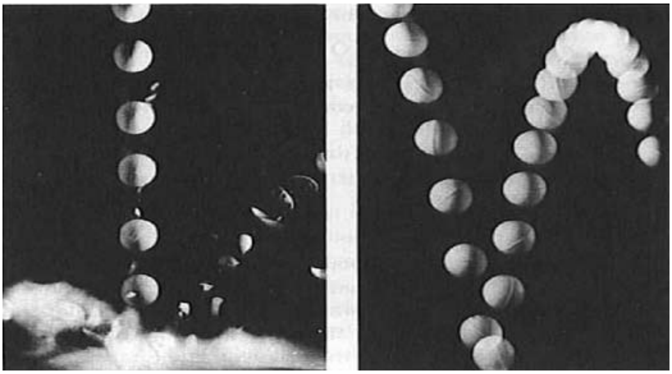
Silicone Thermal Properties

Silicone compounds have very good thermal stability when compared to carbon-based products. There are two specific examples: one is the fact that silicone changes very little in viscosity when temperature drops significantly (**Table 24.5**) and the other that silicone rubber remains non-brittle when compared to its carbon-based brother. This is shown in **Figure 24.9**.

Table 24.5. Silicone Fluid and Petroleum Oil Viscosity

Temperature (°C)	Viscosity (cs) Silicone Fluid	Petroleum Oil
100	40	11
38	100	100
-18	350	11,000
-37	660	230,000

Figure 24.9. Silicone Rubber and Carbon-based Rubber at Low Temperatures



A graphic example of the retention of physical properties at low temperatures brought about by low intermolecular attraction, in this case due to the high degree of internal motion within the dimethylsiloxane chains of silicone rubber. At -80°C a ball made of natural rubber (left) shatters when dropped, but one made of silicone rubber (right) bounces readily despite its low temperature.

Surface Tension

The relatively high surface tension of water relative to its molecular weight is well-known to the scientist. This property of water, which is essential to life, also is essential to the ability of certain insects to float on water. Surface tension, like viscosity, is, however, something many scientists understand the logistics of but lack a point of reference for. **Table 24.6** shows surface tension values for common materials.

Table 24.6. Surface Tension Values

Product	Surface Tension (dynes/cm)
Mercury	472.0
Water (*aqua*)	72.6
Isoparaffin (C12-C14)	53.0
Squalane	46.2
Soap Solution (1%)	38.8
Mineral oil	33.1
Dimethicone (20cs)	26.6
Acetone	23.7
MM (0.65 Visc)	22.7
Ethyl Alcohol	22.2
Cyclomethicone (D4)	20.6
Diethyl ether	17.0

Source: KF De Polo, A Short Textbook of Cosmetology,
Verlag fur Chemische Indusrtie, (1998)

Emulsification Kit

A series of alkyl dimethicone copolyol compounds have been developed and packaged in a kit to allow for the development and optimization of emulsions. Previously, ethoxylated fatty alcohols have been packaged in kits by Union Carbide to allow for the development of emulsions. Today a kit of silicone emulsifiers is available.

The chemistry of alkyl dimethicone copolyols has been covered in Chapter 8. This section will describe the use of a kit to make emulsions. **Figure 24.10** outlines the emulsifiers in the kit. There are four, available in a range of HLB from 3.2 to 9.6. The chemical properties of the products are defined in **Table 24.7**.

Table 24.7. Silicone Emulsifiers

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

Because these differ in concentration of both alkyl and water-soluble groups, these materials are used to make emulsions either alone or in combination.

Approach

Five 250 mL beakers are labeled A through E. To each beaker is added 48.5 g of the oil or mixture of oils of interest in the emulsion and 48.5 g of water, 1 g of NaCl and the emulsifier as shown in **Table 24.8**.

Table 24.8. Emulsification Kit Evaluation

Beaker	Emulsifier Type	Emulsifier Grams	Oil Grams	Water Grams	NaCl Grams
A	None	0.0	48.5	48.5	1.0
B	J-208-212	3.0	48.5	48.5	1.0
C	J-208-412	3.0	48.5	48.5	1.0
D	J-208-612	3.0	48.5	48.5	1.0
E	J-208-812	3.0	48.5	48.5	1.0

The contents of the beaker are heated to 50°C under agitation. Once at 50°C, the contents are mixed at high setting with a handheld mixer shown in **Figure 24.10**, on high for two minutes. The resulting materials are allowed to cool under agitation and evaluated after 30 minutes.

Figure 24.10. Sheer Mixer

Sheer apparatus for lab evaluation. *Picture by Kevin O'Lenick*

Results of several different tests are shown for Spider Ester® GEC, a polar ester. The results are shown in **Figure 24.11**.

Optimization of Emulsion

Emulsifier Blends

If the good results were obtained with two emulsifiers, it might well indicate the best performance might be with an emulsifier having an HLB between the two. Blends of emulsifiers should be used to learn which is superior. We recommend a 75/35, 50/50 and a 25/75, of the two different emulsifiers. Using these rations repeat the above experiment.

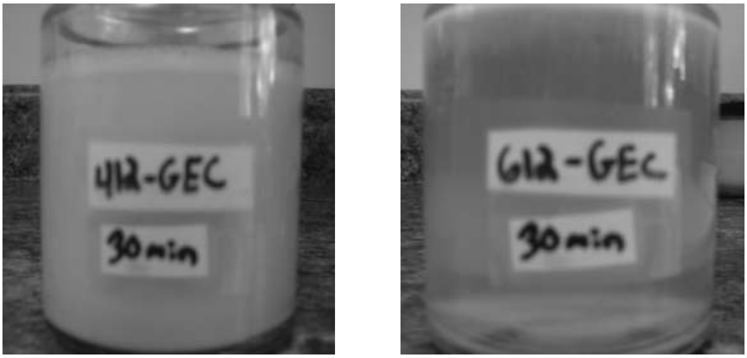
Emulsifier Concentration

Ken Klein, an expert in emulsion technology, has often pointed out that, generally, formulators have a tendency to use too much emulsifier. A repeat of the best one or two results above should be made using a 1.5% emulsifier to observe any improvement in emulsion stability or properties.

Figure 24.11. Emulsion Results

A. Ester Alone
30 min after Mix

B. Ester plus J-208-212
30 min after Mix



C. Ester plus J-208-412
30 min after Mix

D. Ester plus J-208-612
30 min after Mix

Salt concentration

The concentration of salt should also be evaluated. We recommend picking the best emulsifier from B to D and remaking it using 0,0%, 0.5%, 1.0% and 3.0% by weight salt, observing any improvement in emulsion stability or properties.

Conclusion

The use of silicone compounds effectively in formulations requires not only an understanding of the chemistry, but the composition of the silicone being used, as well as establishing test methodologies that are appropriate for the industry and for the materials being tested. Additionally, the effective use of products requires a comfort with the properties, which is improved by understanding how the values we encounter relate to real world items. I have a long time chemist friend who did not realize a spatula used in the lab was the same word for the one used to flip eggs in the kitchen. In fact, he pronounced the words for each differently, the kitchen version was pronounced normally and the lab version as "spa-too-ula". Naturally the lab version was more mystical and more feared.

The formulator is encouraged to see the tests, materials and procedures used in formulation as normal, everyday experiences related to other activities in one's life. By this approach the formulation will become easier.

Chapter 25

Future Trends

Silicone polymers, processing and technology is truly a very flexible and growing technology platform. It is amazing to think that it all starts with SiO_2. The first transformation from quartz to silicon, while a first and important step, is only one small step in the promise of silicone technology.

As important as the technology is to growth, intellectual property is also a major factor that will continue to impact upon silicone technology.

Patents

One of the most interesting areas to develop in the five years since this book was initially published is the importance of patents in the development and use of silicones in the personal care market. The sheer number of patents and the small but apparent differences between prior art and new patents is staggering. The importance of using patents to plan research cannot be overstated. The importance of understanding the patent landscape and planning development activities to avoid infringement is key to success. In the years since the publication of the first edition of this book, "design around" and "five legged chair" have become terms researchers know and understand.

The concept of design around is an approach by which after a full evaluation of the patent literature, a chemist, accompanied by a patent attorney, develops a design of formulations or molecules that can be commercialized. The approach saves a great deal of time and is far more productive than the old process of researching first and getting legal advice later.

The concept of five legged chair is that a modification of an existing patented technology that provides an unobvious advantage (a fifth leg) is subsequently patented to prevent others from obtaining patent coverage. Many companies are using the approach as a defensive tool and more are expected to adopt the strategy.

As patents control more and more of the business, there will more than likely be licensing agreements allowing for development of formulations that would be blocked if not for a patent. Raw material manufacturers and formulation companies are already doing this. Raw material manufacturers are doing more formulation and applications patents, which they license to customers. This is done in large part to prevent formulators from patenting the raw material and preventing the raw material manufacturer from selling the product.

Technology

Due to the important place the function of a new molecule holds in formulation, more emphasis will be placed upon understanding the properties of additives within formulations and not merely as stand alone ingredients. This will lead to the knowledge that the understanding of the complicated surface physical chemistry of formulations is critical to efficient product development. Formulation modifications and the effect of multivariable analysis will be key to optimizing products. Much of this will be automated and computerized.

The development of synergistic blends of dimethicone copolyol compounds with traditional fatty compounds to provide new products that achieve a benefit that was not possible with either compound alone is yet another area of commercial interest. One such series of compounds is the Zenicone[1] family of products, which claim to be blends of a very high molecular weight PEG dimethicone and specific castor ethoxylates. The PEG dimethicone compounds are too high in molecular weight to provide spreadability of the PEG dimethicone on the hair, but if spreadability were possible, a unique conditioning effect would be achieved. The castor ethoxylate, with its unique structure, having a hydroxyl group in the 12 position provides the needed wetting and spreadability. The result is a series of products that have a very unique feel on hair and skin.

Resins, elastomers and gums will continue to be very important growth areas. Not just for the formulation of film formers in transfer-resistant makeup, but for use in more traditional areas like hair and skin care. These materials will become commonly used as conditioners, pigment coatings and body wash additives. The important technology will have the ability to control particle size and formulation stability. These materials will also become critical to skin care, where they will be to alter the delivery of actives to the skin. Sunscreens, antioxidants, colors and the like will be delivered by advanced systems out of aqueous solutions using this technology.

Creativity can take many forms in our industry; molecular changes, blends and formulation technologies all offer possibilities of improving products.

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

- The synthesis skills of the organosilicone chemist
- The formulating and engineering skills of the chemists and engineers who design formulations and processes using these materials
- The ability of both groups to modify molecules for specific applications and formulate the products to meet consumer expectations

Increasingly, the more interesting developments will be those that are made one-on-one with the organosilicone chemist and the skilled formulation chemist. Together these two will unravel the hidden but present rules and regulations that allow for the prediction of the behavior of these complex molecules. The marketing of such materials will be less and less a selling of a product line and more and more a development of highly functional materials for the specific high demand application.

The first 60 years of silicone chemistry have been marked first by slow growth and more recently by a technology explosion. The next 50 will experience an even more dramatic growth and specialization as computer modeling becomes more prevalent. I am most amused with the words of Eugene Rochow, known as "the father of silicone chemistry," who ends his now famous 1946 book *The Chemistry of Silicones* with this statement about silicone chemistry: "With this in mind, it can only be said that a start has been made in organosilicone chemistry and that perhaps something may come of it." How far we have come and how far we have to go.

References: 1. Zenicone is a registered trademark of Zenitech LLC, Old Greenwich, CT. (www.zenitech.com)

Appendix A

Organosilicone Nomenclature Conventions

August 13, 1999

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The conventions for the definitions, INCI name classifications, and recommendations for changes to existing INCI names

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In 1997, the CTFA INC determined that the nomenclature protocol for silicon containing substances was inadequate for new emerging complex compounds. The attached recommended protocol is designed to clarify nomenclature conventions. In addition, this protocol is designed to meet international harmonization objectives.

Silicon-containing substances have been classified into 8 groupings as listed below:

1. Silanes
2. Hydroxyl-containing compounds (silanols)
3. Cyclic Dimethyl Siloxanes
4. Linear Polysiloxanes (trimethylsiloxy end-blocked)
5. Linear Polysiloxanes (non-trimethylsiloxy end-blocked)
6. Silsesquioxanes
7. Silicates
8. Copolymers & Crosspolymers

The key difference from pre-existing nomenclature, and requiring notification of change for some existing products, is full disclosure of the chain length for alkoxylated products (current all lumped into Dimethicone Copolyol). It will be required to rename certain silanes and siloxanols to conform to this protocol.

BACKGROUND:

The conventions for naming silicon-containing ingredients should follow those for conventional carbon compounds as related in the INCI dictionary and those proposed by Eaborn and Bott[1]:

1. functional organic substituents
2. organic substituents
3. functional substituents

Within each grouping alphabetical order applies. Further, where there is an existing nomenclature convention for organic compounds, it will take precedent. Chains are numbered as in organic chemistry, starting from a key atom and considering the longest chain as the parent compound.

Additionally, silicone nomenclature will be applied to any compound containing at least one silicon atom and falling within the generic family of silanes and silicones. Silanes are monomeric compounds containing one silicon atom or two or more silicon atoms bonded directly to each other. Silicones, or more precisely, organo-substituted (poly)-siloxanes have a backbone with alternating silicon and oxygen atoms. These occur in the form of linear, cyclic, branched, or three-dimensional oligomers and polymers.

The nomenclature system for siloxanes is based upon recommendations by Sauer[2], which were subsequently developed and adopted by the American Chemical Society[3], the IUPAC[4], and the Chemical Society[5]. A convenient shorthand notation is sometimes used to designate the degree of functionality of the silicon atom as shown below:

M	**D**	**T**	**Q**
(Monofunctional)	(Difunctional)	(Trifunctional)	(Quadfunctional)

For siloxanes, the prefix designates the number of silicon atoms in the molecules: disiloxane, trisiloxane, and polysiloxane. Substituted siloxanes ($R_2SiO_{2/2}$) are named in the same manner as silanes: Hexamethyldisiloxanes, Tris (trimethylsiloxy) silane, poly (dimethylsiloxane). Monosubstituted silicon-oxygen polymers ($RSiO_{3/2}$) are generally called silsesquioxanes and non-substituted silicon-oxygen polymers ($SiO_{4/2}$) are generally called silicates. The silicon analogs to organic alcohol=s are called silanols. Metal salts of the silanols are termed silanolates.

The various Silicon-containing INCI classifications are grouped as follows:

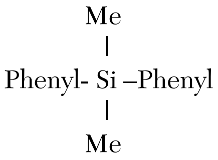
1. Silanes
2. Hydroxyl-containing compounds (silanols)
3. Cyclic Dimethyl Siloxanes
4. Linear Polysiloxanes (trimethylsiloxy end-blocked)
5. Linear Polysiloxanes (non-trimethylsiloxy end-blocked)
6. Silsesquioxanes
7. Silicates
8. Copolymers & Crosspolymers

Below is the protocol for developing a nomenclature for each of these categories and root terminology that applies.

1. Silanes

Silanes are the basic building block to most silicon-containing molecules. They are based on either a single silicon atom or two or more silicon atoms joined together. Nomenclature protocol would list in alphabetical order the different groups attached to the silicon. A numerical prefix will indicate the number of silicon atoms present (e.g., a compound with two silicon atoms bonded together would be named as a disilane).

Example: Dimethyldiphenylsilane

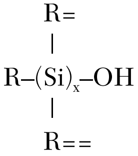


$$\begin{array}{c} \text{Me} \\ | \\ \text{Phenyl- Si –Phenyl} \\ | \\ \text{Me} \end{array}$$

2. Hydroxyl-containing compounds

This broad category is meant to classify all hydroxyl containing species. There are a number of subclassifications that require different roots based on their structure.

(a) Silanols



$$\begin{array}{c} R= \\ | \\ R\text{–}(Si)_x\text{–}OH \\ | \\ R== \end{array}$$

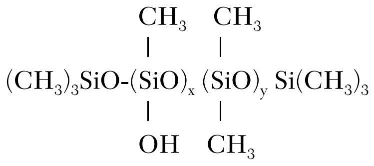
Applied when x equals one and there is at least one hydroxyl group.

Examples:

- When R groups are not hydroxyl groups, then compound would be named as a silanol.
- When one of the R groups is a hydroxyl group, then compound would be named as a silanediol.
- When two of the R groups are hydroxyl groups, then compound would be named as a silanetriol.
- Replacing R, R= and/or R== with another substituent would require naming them as prescribed in standard INCI nomenclature. For example, when R=phenyl, R==R=== hydroxyl, the compound would be Phenyl Silanetriol.

(b) Siloxanols

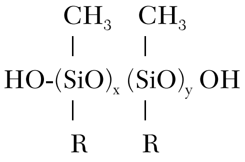
This nomenclature is used when x is greater than or equal to one; the default would be the methyl (poly) siloxane protocol, but would also need to include the number of hydroxyl groups in nomenclature:



$$(CH_3)_3SiO\text{-}(\underset{OH}{\overset{CH_3}{Si}}O)_x\,(\underset{CH_3}{\overset{CH_3}{Si}}O)_y\,Si(CH_3)_3$$

Examples:

- When two hydroxyl groups occur on the siloxane backbone (x=2), the compound would be named as a *siloxanediol*.
- When three hydroxyl groups occur along the siloxane backbone (x=3), the compound would be named as a *siloxanetriol*.
- When the hydroxyl groups occurs on the terminal position, the root would be assigned the nomenclature of *methiconol* (y=0) or *dimethiconol* (y>0) plus proper designation of other functional substituents:

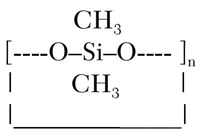


$$HO\text{-}(\underset{R}{\overset{CH_3}{Si}}O)_x\,(\underset{R}{\overset{CH_3}{Si}}O)_y\,OH$$

(c) Derivatives of Silanol-functional Silicones

If one or more hydroxyl groups were further derivatized, such compounds would be named as a derivative (e.g. ester) per standard INCI protocol.

3. Cyclic Dimethyl Siloxanes



$$\left[\text{----}O\text{–}\underset{CH_3}{\overset{CH_3}{Si}}\text{–}O\text{----}\right]_n$$

Cyclomethicone is currently assigned to mixtures of cyclic dimethyl siloxanes where n = 3-

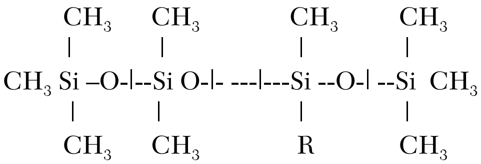
7. Nomenclature for pure components (=99%) would be assigned for each as follows:

n = 3	Cyclotrisiloxane
n = 4	Cyclotetrasiloxane

n = 5 Cyclopentasiloxane
n = 6 Cyclohexasiloxane
n = 7 Cycloheptasiloxane

Replacement of methyl groups with another organic group would be indicated by using the appropriate organic substituent name as a prefix. Example: if one of the methyl groups on Cyclotetrasiloxane were replaced with a hexyl group, this would be called Hexyl Cyclotetrasiloxane.

4. Linear Polysiloxanes (trimethylsiloxy end-blocked)



$$\begin{array}{lllll} & CH_3 & CH_3 & CH_3 & CH_3 \\ & | & | & | & | \\ CH_3 & Si\text{ –O-|--} & Si\text{ O-|- ---|---} & Si\text{ --O-| --} & Si\ \ CH_3 \\ & | & | & | & | \\ & CH_3 & CH_3 & R & CH_3 \end{array}$$

(a) Methicones:

When x = 0, y > 0, and R= hydrogen, the name is *Methicone*.

When x= 0, y >0, and R = functional substituent group (e.g., alkyl), then the name of the organic substituent would be included as a prefix or suffix (depending on the substituent).

Examples:

R= phenyl: Phenyl Methicone

R= polyether (PEG, PPG, PEG/PPG): PPG-Y Methicone where Y = average number of moles of PPG.

R= stearyl: Stearyl Methicone.

(b) Dimethicones

When x>2 and y=0, the name is *Dimethicone*.

Two names have been established for oligomers (short chain Dimethicone):

When x and y =0, then the assigned name is *Hexamethyldisiloxane*.

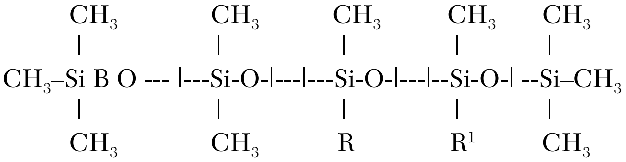
When x=1 and y = 0, then the assigned name is *Octamethyltrisiloxane*.

(c) Other Linear Polysiloxanes
When x and y >1, and functional groups other than hydrogen are present on the

siloxane backbone, these polysiloxans are named as derivatives of Dimethicone. The substituent groups are generally named according to existing INCI conventions, however there are three special cases: polyether, ethylene diamine, and quaternary nitrogen substituents, as noted below.

Example:

When R = cetyl, then the name is *Cetyl Dimethicone.*



$$\begin{array}{ccccc} CH_3 & CH_3 & CH_3 & CH_3 & CH_3 \\ | & | & | & | & | \\ CH_3\text{–Si B O --- |} & \text{---Si-O-|---} & \text{|---Si-O-|---} & \text{|--Si-O-|} & \text{--Si–}CH_3 \\ | & | & | & | & | \\ CH_3 & CH_3 & R & R^1 & CH_3 \end{array}$$

TERPOLYMERS: (more than one non-methyl substituent) are named using multiple prefixes or suffixes. For example (referring to the structure above), if x, y, and z are =1 and R = cetyl and R= = phenyl, the name would be *Cetyl Phenyl Dimethicone.*

POLYETHERS: There are a large number of derivatives of Dimethicone where the substituents are polymers of ethylene oxide (PEG), propylene oxide (PPG), or copolymers of ethylene and propylene oxide (PEG/PPG). These silicones were previously designated as Dimethicone Copolyols. In an effort to provide nomenclature that is more descriptive, these materials will be named as follows:

When the substituents are PEG and are connected to the silicone by a Si-O-C bond, the material will be named in a manner analogous to ethoxylated fatty alcohols. In other words, they will be named as derivatives of the silanol-functional starting material. For example, if Dimethicone were ethoxylated with 18 moles of ethylene oxide, it would be named Dimethiconeth-18

When the substituents are PEG, PPG or PEG/PPG and are connected to the silicone through a short chain alkyl group (C1-C3), these materials will be named as derivatives of dimethicone or methicone.

Examples:

In the structure above, when x and y > 1, and R is $-CH_2CH_2CH_2-(OCH_2CH_2)_{12}-OH$, then the material would be named: *PEG-12 Dimethicone.*

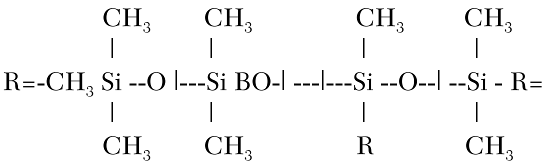
In the structure above, when x = 0 and y > 1, and R is $-CH_2CH_2CH_2-(OCH_2CH_2)_{12}-OH$, then the material would be named: *PEG-12 Methicone.*

In the structure above, when x and y > 1, and R is $-CH_2CH_2CH_2-(OCH_2CH_2)_{18}-(OCH_2CHCH_3)_{18}-OH$, then the material would be named: *PEG/PPG-18/18 Dimethicone.*

ETHYLENE DIAMINE: According to established precedent, when the organic substituent on the polysiloxane is aminoethylaminopropyl ($-CH_2CH_2CH_2$-$NHCH_2CH_2NH_2$), this is indicated by the use of the Amo prefix (e.g. Amodimethicone)

QUATERNARY-NITROGEN: Due to the complexity of naming polysiloxanes containing organic substituents with quaternary nitrogen groups, these ingredients are named using the generic term Silicone Quaternium-X, where X is the next available number.

5. Linear Polysiloxanes (non-trimethylsiloxy end-blocked)



$$\begin{array}{lllllllll} & CH_3 & & CH_3 & & CH_3 & & CH_3 & \\ & | & & | & & | & & | & \\ R{=}\text{-}CH_3 & Si & \text{--}O\ |\text{---} & Si & BO\text{-}|\ \text{---}|\text{---} & Si & \text{--}O\text{--}|\ \text{--} & Si & -\ R{=} \\ & | & & | & & | & & | & \\ & CH_3 & & CH_3 & & R & & CH_3 & \end{array}$$

It is possible for linear polysiloxanes to be end-blocked with groups other than trimethylsilyl groups. In this case, the substituents at each end of the polymer are named according to established INCI nomenclature rules. The prefix Bis will be used to denote which substituents occur at the end of the polymers.

Examples:

In the structure above, if $x > 0$, $y = 0$, and R= is phenyl, then the material would be named *Bis-Phenyl Dimethicone*

In the structure above, if $y = 0$ and $x > 0$, and R= is $-CH_2CH_2CH_2$-$(OCH_2CH_2)_{12}$-OH, then the material would be called *Bis-PEG-12 Dimethicone*

In the structure above, if $x > 0$, $y > 0$, R is stearyl, and R= is isobutyl, then the material would be named *Bis(Isobutyl) Stearyl Dimethicone*

6. Silsesquioxanes

Silsesquioxanes are based on the T siloxane unit (the empirical formula is $RSiO_{3/2}$).

If the R group is anything other than methyl, it must be specified by a prefix (e.g. if R = phenyl, then it would be phenylsilsesquioxane). The presence of a third polymerization site on silicon leads to a variety of three-dimensional structures such as ladder, cage and partial cage structures. The condensation of T units to form these structures is reversible and depends strongly upon processing conditions. Because of this, it is impossible to write definite structures for these compounds. The size of the silsesquioxane polymer is often controlled by the introduction of M (terminal) units (e.g. trimethylsiloxy, vinyl dimethylsiloxy), and this must be indicated in the name. For example, a polymer made up of M and T units where all the organic substituents are methyl would be called Trimethylsiloxymethylsilsesquioxane. Copolymerization with D units is also possible, and these are named according to established INCI rules (e.g. Dimethiconol/Silsesquioxane Copolymer).

The only exception to this rule is for pre-existing Phenyl Trimethicone and Caprylyl Trimethicone. The current definition would not change and will reflect the M and T unit in structure of this silsesquioxane.

Silicates

Silicates are based on the Q 3-dimensional structure as random, ladder, cage and partial cage structures. They have empirical formulas of $SiO_{4/2}$. Silicates may be reacted with M, D, and T units which must be indicated in the name (e.g., Trimethylsiloxysilicate)

Copolymers & Crosspolymers

The terms Copolymer and Crosspolymer are used in the same way as in the naming of organic polymers.

OTHER

When there is a question about how to name a new silane or silicone and it does not fall into one of the categories set forth above, then the default will be silyl (=Si-) or siloxy (=Si-O) root as part of the nomenclature and conventional INCI protocol for organic containing portion.

In certain cases, Polysilicone-X will be used for complex silicon-containing polymers.

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