The Fascinating World of **Silicones**

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Silicones were commercialized in the 1940s in the United States and ever since their introduction, they have expanded remarkably not only in terms of economic growth but also by an amazingly diverse assortment of product types and applications. Silicones represent a class of compounds that are based on silicon and they exist in a variety of forms including oils, fluids, high viscosity polymers, gums, elastomers, resins, and silanes. Silicones' involvement in coatings began with the early stages of silicone product development and today they are used extensively in coatings mainly as either modifiers or additives. Typical modified coatings contain around 30% of the binder as silicone and these coatings exhibit improved weatherability, increased moisture vapor transport, and improved heat stability. Silicone additives are used in small amounts in coatings, usually less than one percent and even lower, to achieve various enhanced properties such as improved flow and leveling, slip and antimar, improved abrasion resistance, improved adhesion, foam control, and water repellency. Although silicones are useful for eliminating or diminishing surface defects, they are also capable of producing surface defects. An understanding of phenomena surrounding surface defects can aid the coatings formulator in avoiding surface defects caused by silicones. Part I of this two-part article presents a brief history of silicone development and describes silicones. Part II, to be published in the May 2012 issue of CoatingsTech, *will detail how silicones are used in coatings.*

INTRODUCTION

The term *silicone* as it is used today was coined by Professor Frederic Stanley Kipping in 1905 as part of his noteworthy and extended investigations of organosilicon compounds.[1] The name silicone described the empirical composition, R_2SiO, of compounds obtained from the hydrolysis of disubstituted silicon chlorides, as it was believed to be similar to its carbon analog, the ketone: R_2CO ($R_2C=O$). Silicones actually have no resemblance to the carbonyl group of organic chemistry, but the name stuck and it has been used ever since to describe oligomers and polymers of organosiloxanes and their precursors.

Kipping pioneered the use of the newly discovered Grignard reagent to prepare organosilicon compounds; he reported in 1904 the first silicone polymers and described them as "sticky messes with no particular use."[2] Over a period of some 45 years (1899–1944), Kipping and his coworkers at University College, Nottingham, England, published a series of 57 scientific papers on organosilicon compounds.[3] During an address he gave to the Royal Society in

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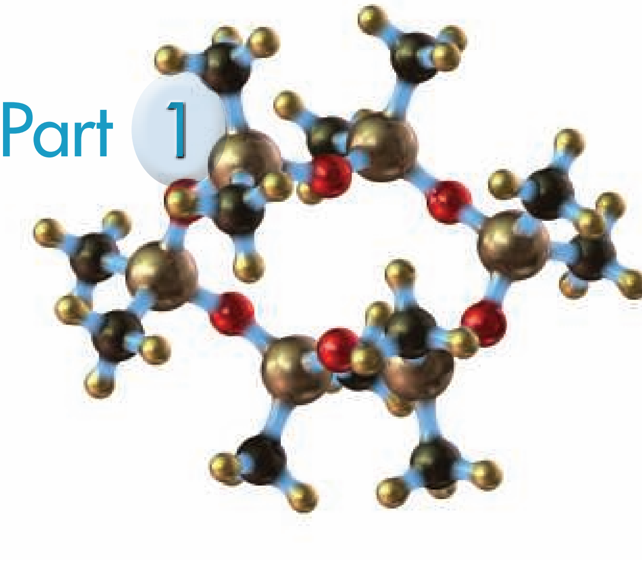
Presented as the Plenary Lecture at the 39th Waterborne Symposium, sponsored by the School of Polymers and High Performance Materials, The University of Southern Mississippi, February 13–17, 2012, in New Orleans, LA.

and Their Impact on Coatings: Part 1



1937, Kipping was not very optimistic about the future of silicones as he pronounced at the conclusion of his Bakerian Lecture " . . . the prospect of any immediate and important advances in this section of organic chemistry does not seem to be hopeful."[4] Fortunately, Professor Kipping was wrong in his outlook because the commercial silicone industry started in 1943 and it has it been growing robustly ever since. Today, global silicone consumption is in excess of $10 billion USD annually.[5]

The utility of silicones is primarily due to their unusual surface properties, their resistance to the effects of weather, and their ability to accommodate wide temperature extremes. Chief industries where silicones find widespread use are in aerospace, automotive, construction, electrical, food, medical, paper, personal care, plastics, paint, and textiles.[6-13] In numerous applications, silicone is vital as no other substance can match the silicone's performance and, in many of these applications, very small levels of silicone are used. Silicones are used in thousands of different ways that touch practically everyone's lives in the developed world. This article will cover a brief history of silicones, their manufacture, and their conversion into different forms. Part II will focus on the use of silicones in coatings with an emphasis on waterbased coatings.

DISCUSSION

Silicon

The element silicon (atomic number 14, atomic weight 28) from which silicones are derived, is the second most abundant element on earth (after oxygen) and it occurs natively as its oxide, silica, in sand and quartz, and also as metal silicates in most rocks. Although silicates have been used in ceramic arts and crafts (clay pottery) for the past 5,000 years or so, silicon was not known as an element until Jons Berzelius first reported its isolation in 1824 by reducing potassium fluorosilicate with potassium[14]:

$$K_2SiF_6 \;+\; 4K \longrightarrow Si \;+\; 6KF$$

Today, silicon is prepared commercially by reducing silicon dioxide, usually in the form of white quartz, with carbon in an electric arc furnace[15]:

$$SiO_2 \;+\; 2C \longrightarrow Si \;+\; 2CO$$

The elemental silicon thus obtained is on the order of 99% pure and is commonly referred to as metallurgical grade silicon. Its chief impurities are iron, aluminium, and calcium and its main use is in preparing alloys of aluminum and iron. It is metallurgical grade silicon that is also used to prepare silicones. Semiconductor grade silicon, used for electronic semiconductor devices and also in some solar modules, is in a separate class of purity and it is prepared by decomposition of certain purified silanes that in turn are derived from metallurgical grade silicon.

Soon after preparing elemental silicon in 1823, Berzelius prepared $SiCl_4$ by igniting his Si in a stream of chlorine gas.[7] In 1857, Wohler reported several important compounds of silicon including SiH_4 (silane) and $SiHCl_3$ (trichlorosilane).[16] Those compounds are very useful today especially in the electronics industry. Although Wohler was actually the first to use the term *silicone*, he used it to describe something other than what Kipping described and something other than what silicones have become known as today.[17] In 1863, Friedel and Crafts announced the preparation of tetraethylsilane, $(C_2H_5)_4Si$, by reacting $SiCl_4$ with diethyl zinc.[18] This was the first example of an organosilicon compound, since it possessed at least one Si–C bond.

Commercialization of Silicones

The commercial silicone industry had its start in the 1930s with a visionary leader, Dr. Eugene Sullivan, who was employed at the Corning Glass Works in Corning, NY. Dr. Sullivan believed that somehow combining the chemistry of glass or ceramics and organic-based plastics would lead to substances having very desirable properties, namely higher thermal stability than plastics and more flexibility than glass.[19] As the director of Research at Corning Glass Works, Dr. Sullivan hired Dr. J. Franklin Hyde, an organic chemist, in 1930 to pursue this idea. Hyde picked up Professor Kipping's work on silicones and soon he was preparing lab size quantities of silicone polymers using the Grignard route, which Kipping pioneered. A meeting was held between

General Electric and Corning Glass Works in 1938 and during that meeting some of Dr. Hyde's samples of silicone resin impregnated glass cloth aroused interest at General Electric.[20]

By 1942, Dr. Hyde's progress with silicone development had reached such a critical stage that Corning Glass Works launched a joint partnership with the Dow Chemical Company to commercialize some of Hyde's silicone resins.[21] The joint venture was formally finalized on February 9, 1943, and called the Dow Corning Corporation and was located in Midland, MI, near the Dow Chemical Company plant.[22] The very first commercial silicone product was a silicone grease called DC 4 Compound that was used successfully during World War II to coat allied aircraft ignition wire harnesses and prevent them from arcing at high altitudes.[23]

After the war, the government cancelled all silicone orders, so the fledgling company had no products to sell. Fortunately, that soon changed and the first peacetime commercial silicone product developed was an aqueous emulsion of polydimethylsiloxane fluid that was used as a tire mold release compound.[24]

After the important Corning Glass Works—General Electric meeting that occurred in 1938, General Electric initiated research into silicones as the company was most interested in determining what benefits silicone resins could provide to electric motors. Dr. Eugene Rochow at General Electric began experimenting with silicones and also on a practical route towards methyl silicones. On May 10, 1940, he struck gold in the laboratory when he invented the direct synthesis of methyl chlorosilanes from a reaction of methyl chloride gas and elemental silicon in the presence of copper.[25] Prior to this discovery and for some time afterwards, all silicones were prepared by the Grignard route, which utilized magnesium. Since Dow was the only domestic producer of magnesium at the time, General Electric was at a severe disadvantage for competing in the silicones business.[26] Rochow's discovery changed that completely. Not only did it allow General Electric to enter the silicones business competitively, it also provided a route to many silicone products that otherwise would have been far too expensive to have succeeded in the market as they have so done. General Electric publicly announced on November 14, 1944 that it was entering the commercial silicones business.[27]

Table 1—Comparison of Chemical Bonding Parameters

Silicon		Carbon	
Bond Energies:		Bond Energies:	
Si–O	445 kJ/mol	C–O	358 kJ/mol
Si–C	306 kJ/mol	C–C	346 kJ/mol
Bond Angles:		Bond Angles:	
Si–O–Si	143°	C–C–C	112°
O–Si–O	110°	C–O–C	112°
Bond Lengths:		Bond Lengths:	
Si–O	1.65 Å	C–O	1.43 Å
Si–C	1.92 Å	C–C	1.54 Å
Rotational Energies:		Rotational Energies:	
Si–O–Si	~ 0 kJ/mol	C–C	14 kJ/mol

Ever since the two companies launched commercial silicones in the 1940s, the market has continued to flourish not only in terms of overall silicone consumption, but also in terms of the diverse uses that silicones serve, the number of products developed, and the number of enterprises and employees who invent, produce, and distribute these fascinating materials.

Silicones

The repertoire of different silicone products that silicone manufacturers have developed over the past 70 years is astounding. From medical syringe needle lubricants to food grade antifoams to premier hair conditioners to luxurious feeling fabrics to high performance airbag coatings to leather coatings that feel exquisite—to even silicone rubber boots that walked on the moon, silicones have become an integral part of people's lives.

The reason for the extraordinary versatility of silicone products lies in silicones' properties, which in turn are due to a large extent to the chemistry of the siloxane bond in polyorganosiloxanes.[28] Thus, the electronic character of the siloxane bond significantly affects both chemical reactivity and physical properties of polysiloxanes. Interestingly, an adequate description of the nature of the siloxane bond is still a matter of scientific debate.

Although silicon lies just below carbon in group IV of the Periodic Table, its properties are quite different from those of carbon. Silicon is normally tetra coordinate like carbon; however, unlike carbon, silicon does not readily form multiple bonds with itself or other atoms.[29] Also, silicon possesses *d* orbitals in its outer valency shell that are at an energy level convenient for bonding. This makes pentacoordinate and hexacoordinate silicon compounds possible.[30]

Silicon is more electropositive than carbon and this gives rise to the siloxane bond having a fairly significant degree of ionic character; it is empirically calculated to be 40–50%.[31]

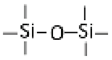
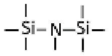
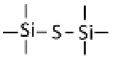
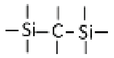
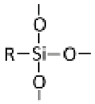
Electronegativity:	**Si**	**C**	**O**
	1.8	2.5	3.5

Earlier investigators attributed siloxanes' behavior to electron delocalization from oxygen *p* orbitals to empty silicon *d* orbitals $[p(O)–d(Si)]\pi$.[32] Theoretical calculations later showed that the contribution of silicon *d* orbitals to the total distribution of electrons is small. This led to a model called negative hyperconjugation that was

Table 2—Some Silicon-Containing Substances

Name	Symbol	Description
Silicon	Si	Element no. 14; at. wt. 28.086
Silica	SiO_2	Silicon dioxide; sand
Silicone	$-(Me_2SiO)_n-$	Polydimethylsiloxane
Silane	$MeSi(OMe)_3$	Methyltrimethoxysilane
Silicate	Na_2SiO_3	Sodium metasilicate
Siliconate	$MeSi(ONa)_3$	Sodium methylsiliconate

Table 3—Some Silicon-Containing Structures

Siloxane	 $-\mathrm{Si}-\mathrm{O}-\mathrm{Si}-$	
Silazane	 $-\mathrm{Si}-\mathrm{N}-\mathrm{Si}-$	
Silthiane	 $-\mathrm{Si}-\mathrm{S}-\mathrm{Si}-$	
Silcarbane	 $-\mathrm{Si}-\mathrm{C}-\mathrm{Si}-$	
Silsesquioxane	 $\mathrm{R}-\mathrm{Si}(\mathrm{O})(\mathrm{O})-\mathrm{O}-$	$RSiO_{3/2}$

based on *p* oxygen orbitals interacting with silicon sigma antibonding orbitals.[33,34] The calculations, however, have not provided unequivocal results about the character of the silicon–oxygen bond, so the (*p*–*d*)π model cannot be totally ruled out.[35]

The siloxane bond is unusually non-reactive and this is due mainly to electron delocalization along the O–Si–O linkage.[36] Ionic bonding and electron delocalization contribute to a high siloxane bond energy, which is considerably higher than its carbon analog, as can be seen in *Table* 1.[29,34,36] This high energy of the siloxane bond gives rise to its strong resistance to homolytic cleavage. On the other hand, the siloxane bond is highly susceptible to heterolytic cleavage from reactions with nucleophiles.[29] This is due to the strongly polarized siloxane bond, the relatively large size of the silicon atom, and its accessibility within a siloxane chain as every other atom is silicon.[32,36]

The siloxane chain possesses a unique degree of mobility due to the electronic structure of the Si–O–Si linkage and low steric hindrance of side groups as the side groups are attached at every other atom within the siloxane chain. Although the siloxane backbone in silicone polymers is highly polar, it is effectively shielded by non-polar side groups such as methyl that result in low intermolecular forces in polysiloxanes.[37] These circumstances give rise to polysiloxanes having very low glass transition temperatures, to low polymer viscosities at high molecular weight, and to polymer viscosities that change very little with temperature.[38]

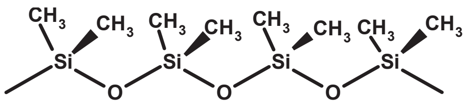
Weak intermolecular forces of polysiloxanes also give rise to poor mechanical properties of polysiloxanes.[39] Although polysiloxane polymers (elastomers) are inherently weak, reinforcement with resins or suitable fillers significantly improves mechanical properties.[40] The very low intermolecular forces of polysiloxanes are also a factor in the exceptionally high permeability of silicones to gases as silicone polymers are perhaps the most permeable polymers known.[41]

The high mobility of the polysiloxane chains also plays a role in another of silicones' unique characteristics which is its surface properties. Extremely low rotational barriers allow polysiloxanes to easily orient to thermodynamically favored conformations in a variety of environments such as at interfaces. This feature, combined with weak intramolecular interactions, gives rise to very low surface tension (21 mN/m for PDMS). Silicones have the lowest surface tension of all polymers excluding fluoropolymers.[42] Silicone fluids readily spread over the surfaces of many substances, making them useful in a variety of applications such as surfactants, antifoams, lubricants, release agents, and water repellents. In some cases silicones can serve in seemingly paradoxical functions, for example, silicone release agents versus silicone adhesives or silicone antifoams versus silicone foam stabilizers.[43]

Thus, the remarkable properties of polysiloxanes have been the reason behind silicones' extraordinary success and diverse uses and they can be attributed in large part to the chemistry of the siloxane bond.

What Are Silicones?

Silicones are compounds of silicon that possess at least one silicon—carbon bond and have a siloxane linkage. The most common silicone material is poly(dimethylsiloxane), or PDMS:



Silicones exist in a variety of forms that encompass fluids or oils, high viscosity polymers, gums, elastomers, resins, and silanes. Although silanes do not possess a siloxane unit, they form siloxanes when they undergo their typical reactions, so they too are considered silicones. These forms of silicones are discussed individually.

Nomenclature

Silicon, silica, silicone, silicate, siliconate, siloxane, silazane, silsesquioxane—these are names describing different substances that are all related to silicon, the element, and not all of them are generally known. *Tables* 2 and 3 describe some of these silicon compounds and structures.

In the early phase of silicone commercial development, a nomenclature system arose out of General Electric and this "silicone shorthand" is extensively used to this day to conveniently describe siloxane

Table 4—Silicone Shorthand

Symbol	Bonding Capacity	Meaning	Example
M	1	terminating	$Me_3SiO_{1/2}$
D	2	chain extension	Me_2SiO
T	3	X-linking	$MeSiO_{3/2}$
Q	4	X-linking	$SiO_{4/2} = SiO_2$

structures.[44] *Table* 4 explains the M, D, T, and Q shorthand. Thus, for example, D_4 is $(SiMe_2O)_4$ and $MD_{100}M$ is $Me_3Si(OSiMe_2)_{100}OSiMe_3$. In silicone shorthand, methyl groups (Me, CH_3-) are the default; if other groups are bonded to silicon, some means of identifying those units should be used to avoid confusion.

Manufacture of Silicones

Preparation of most silicones involves four general steps:

1. Preparation of organochlorosilanes
2. Hydrolysis of organochlorosilanes to siloxane intermediates
3. Polymerization of siloxane intermediates into polysiloxanes
4. Formulation of polysiloxanes into finished products

Formation of Organochlorosilane

Chlorosilanes are the basic building blocks of most silicones. The most common chlorosilanes are given in *Table* 5. Methyl chlorosilanes are manufactured by the Rochow process, or direct process whereby silicon reacts with methyl chloride at an elevated temperature[45]:

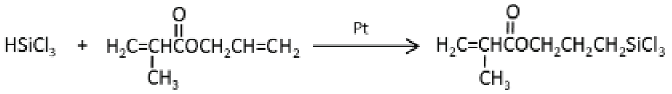
$$Si \quad + \quad 2MeCl \xrightarrow[320°C]{Cu\ catalyst} Me_2SiCl_2$$

A number of other products are formed along with Me_2SiCl_2, namely $MeSiCl_3$, Me_3SiCl, and $MeHSiCl_2$ in addition to small amounts of numerous other byproducts, but Me_2SiCl_2 is the most significant and it can reach as much as 90% of the product mixture.[46] The chlorosilanes are separated from each other by fractional distillation. Phenyl chlorosilanes are obtained by direct reaction of chlorobenzene and silicon at an elevated temperature and also by alkylation via the Grignard reaction.[47]

Table 5—The Most Common Chlorosilanes

Me_2SiCl_2	Dimethyldichlorosilane
Me_3SiCl	Trimethylchlorosilane
$MeSiCl_3$	Methyltrichlorosilane
$MeHSiCl_2$	Methyldichlorosilane
$PhSiCl_3$	Phenyltrichlorosilane
Ph_2SiCl_2	Diphenyldichlorosilane
$PhMeSiCl_2$	Phenylmethyldichlorosilane
$HSiCl_3$	Trichlorosilane

Another important preparative method of silicones involves an addition reaction of silicon hydrides to terminally unsaturated organic compounds. Reaction can be initiated by peroxides, UV radiation, or more commonly by Pt catalysis, the most common being the soluble H_2PtCl_6 as described by Speier[48]:



$$HSiCl_3 \quad + \quad H_2C{=}\underset{CH_3}{C}H\overset{O}{C}OCH_2CH{=}CH_2 \xrightarrow{Pt} H_2C{=}\underset{CH_3}{C}H\overset{O}{C}OCH_2CH_2CH_2SiCl_3$$

Hydrolysis

Chlorosilanes, of which dimethyldichlorosilane is the most common, are converted into siloxane intermediates by hydrolysis with water:

$$Me_2SiCl_2 \quad + \quad 2H_2O \longrightarrow Me_2Si(OH)_2 \quad + \quad 2HCl$$

The primary hydrolysis product, dimethylsilanediol $[Me_2Si(OH)_2]$, is too unstable to be isolated under the typical hydrolysis conditions used and it readily condenses spontaneously into oligomeric siloxanes[49]:

$$nMe_2Si(OH)_2 \longrightarrow HO\text{-}(Me_2SiO)_n\text{-}OH \quad + \quad n/2H_2O$$

Normally, a mixture of cyclic and linear oligomers is formed. The byproduct HCl is recovered and reacted with methanol to regenerate methyl chloride:

$$HCl \quad + \quad MeOH \longrightarrow MeCl$$

The chloride used to produce silicones is recycled and remains in a closed loop. Thus, the basic raw materials for silicone manufacture are silica (quartz), carbon, and methanol. Methanol is produced today primarily by steam reforming of natural gas.[50] As methanol is a commodity chemical that is produced and consumed in enormous quantities, price fluctuations of both methanol and natural gas significantly impact costs of producing silicones.

Linear Siloxanes; Siloxane Fluids

Polydimethylsiloxane is produced in a wide range of molecular weights (and hence viscosities) primarily by acid or base catalyzed polymerization of dimethyl cyclosiloxanes or linear siloxanes followed by neutralization:

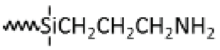
$$(Me_3Si)_2O \ + \ x(Me_2SiO)_4 \xrightarrow{catalyst} Me_3Si\text{-}(OSiMe_2)_n\text{-}OSiMe_3$$

$$HO\text{-}(SiMe_2O)_m\text{-}OH \xrightarrow{catalyst} H\text{-}(OSiMe_2)_n\text{-}OH$$

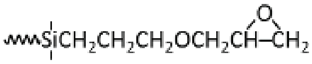
$$n = 0 \longrightarrow 10{,}000$$

Cyclosiloxanes that are also formed during polymerization (mainly D_4 and D_5) are volatile and are typically removed by vacuum stripping. Gaussian molecular weight distributions of polymers are normally produced; degree of polymerization can reach as high as 10,000.[51] Poly(dimethylsiloxane) is available in a variety of molecular weights and exists as low viscosity fluids, medium viscosity oils, higher molecular weight viscous polymers, and still higher molecular weight gums. Viscosities of polydimethylsiloxane fluids range from 0.65 centistokes for the lowest viscosity silicone oil to tens of millions of centistokes for silicone gum.

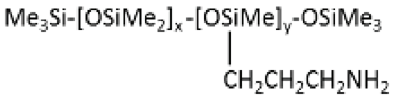
Although the majority of siloxane polymer chains are capped with inert trimethylsiloxy groups (Me_3SiO-), they can also be capped with reactive organic functional groups. Some examples are: OH (silanol), amino, vinyl, epoxide, and acryl esters; several examples are shown:



$$\sim\sim\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$$



In numerous commercially available siloxane polymers, inert chain ends are used and organic functionality is incorporated into the polymer at pendant locations along the siloxane polymer chain. In many of these compounds, only a few percent of the siloxane units are functionalized; the remainder are non-functional dimethyl siloxane units:



$$Me_3Si\text{-}[OSiMe_2]_x\text{-}[\underset{\displaystyle CH_2CH_2CH_2NH_2}{OSiMe}]_y\text{-}OSiMe_3$$

X = 98
Y = 2

Thus, the molecules retain the properties of polydimethylsiloxane while possessing reactive organic functional groups that can be utilized in various ways like reaction with organic substances or to enhance silicone deposition. It should be understood that non-functional polydimethylsiloxane is the lowest cost silicone oil. Adding functionality increases cost and in many cases cost is directly associated with what type of functionality is used as some organic functional groups can be more expensive and/or more difficult to attach to silicon than others.

Another class of silicone fluids is phenyl fluids. Poly(phenylmethylsiloxane) and copolymers of dimethyl siloxane and phenyl methyl fluid are the most common. Phenyl siloxane fluids are more thermally stable than dimethyl siloxane fluids.[52] However, since phenyl siloxane fluids are considerably more expensive than dimethyl siloxane fluids, they are used in coatings only to a limited extent.

Silicone Resins

When alkyl or aryl trichlorosilanes are hydrolyzed, silsesquioxanes are the result:

$$2RSiCl_3 + 3H_2O \longrightarrow 2RSiO_{3/2} + 6HCl$$

Silsesquioxanes are branched siloxanes that are the basis of silicone resins and also provide crosslinking sites for some siloxane elastomers.[53] Although practically any organic substituent can make up the R group in silsesquioxanes, the most common groups in silicone resins are methyl and phenyl and, to a limited extent, propyl. In addition to preparation from chlorosilanes, silsesquioxane resins can be prepared from trialkoxysilanes, which are usually obtained from chlorosilanes and alcohol:

$$RSiCl_3 + 3MeOH \longrightarrow RSi(OMe)_3 + 3HCl$$
$$RSi(OMe)_3 + 1.5H_2O \longrightarrow RSiO_{3/2} + 3MeOH$$

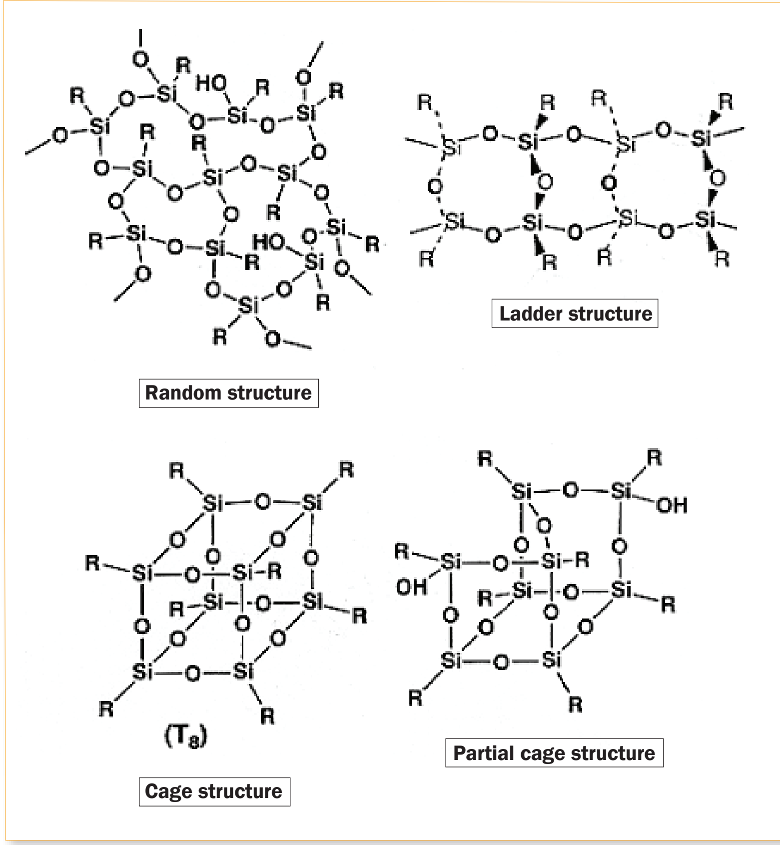


Figure 1—Some structures of silsesquioxanes.

When silicone resins are prepared, usually some silanol groups remain; typical resins normally contain from about 0.5 to 3.0% SiOH.[54] These silanols are used to crosslink or cure the resin in coatings and also to react with carbinols present in organic resins, such as alkyd resins.

Silicone resins used in coatings are in the form of flake or powder solids, solvent solutions, and, in some cases, aqueous emulsions. It should be realized that not all silicone resins are available in all of these forms and especially emulsions, as only a limited number of silicone resins are available as aqueous emulsions.

POS or POSS®—polyhedral oligomeric silsesquioxane—is another type of silsesquioxane that has become a topic of considerable interest during the past 25 years. POS materials are generally fully condensed silsesquioxane $R_8Si_8O_{12}$ cubic cage structures with R groups being organic radicals such as Me, Ph, or *i*-Bu and either all of the substituents or a portion of them can also be functionalized with organic functional groups.[55] These silsesquioxanes can be used to modify polymers having low friction surfaces.[56,57] Some different types of silsesquioxanes are shown in *Figure* 1.

In addition to T structures, silicone resins can be formed using all of the silicone building blocks: M, D, T, and Q. Thus, silicone resins can exist practically as an infinite variety of structures and compositions. Methyl and phenyl substituents on silicon influence resin properties differently;

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Table 6—Contribution of Groups to Silicone Resin Properties

$PhSiO_{3/2}$	Hard, moderately fast cure
$MeSiO_{3/2}$	Brittle, hard, fast cure
Ph_2SiO	High modulus, tough, slow cure
PhMeSiO	Tough, moderate modulus, flexible
Me_2SiO	Soft, flexible

these are shown in *Table* 6.[58] It is possible to prepare silicone resins with combinations of substituents to achieve properties that are desirable for a particular application.

Another important silicone resin is that based on M units and Q units, or a resin comprised of $Me_3SiO_{1/2}$ and SiO_2 units. Sometimes, this resin is referred to as "trimethylsiloxy capped silica." It is an important resin and it is used in a large variety of silicone products; however, MQ resins are not used so much as resin modifiers in coatings.

As mentioned previously, most silicone resins will contain residual silanol (SiOH), which allows them to react further at some point, either with themselves or with other organic polymeric systems. Normally, some type of stimulus is used to complete these reactions, such as heat or addition of catalysts or other reactive compounds. Silicone resins are used extensively in coatings either as pure silicone coatings for bakeware or as a binder in high temperature coatings or as combinations with organic polymer binders to obtain improved weatherability and improved water vapor transmission.[59]

Silicone Elastomers

Silicone elastomers (silicone rubber) are formed by vulcanizing or crosslinking PDMS of varying molecular weight. Typically, siloxane molecular weight is above 5,000 and higher; however, it is possible to form elastomeric siloxanes using molecular weights lower than this value. Vulcanizing siloxane polymers to form elastomers can occur by a number of different methods, which are usually divided into either heat vulcanization or room temperature vulcanization (RTV).

Heat vulcanization is usually accomplished by using organic peroxides.[60] Another method of heat vulcanization involves addition reactions of functionalized siloxanes containing silicon hydrides (SiH) and vinyl functional siloxanes ($SiCH{=}CH_2$) in the presence of a noble metal catalyst, usually platinum.[61] Numerous coatings systems rely on Pt cured siloxanes, in particular paper coatings for making release liners for pressure sensitive adhesives.[62]

Room temperature vulcanization of siloxanes is usually accomplished by using reactive leaving groups on silicon; some leaving groups are alcohol (Si–OR), acid ($Si{-}O_2C{-}$), oxime ($Si{-}N{=}CR_2$) and ketone [$Si{-}OC(Me){=}CH_2$]. These curing compositions can be designed to cure as a two-part or one-part system.[63] Two-part systems might consist of reactive siloxane polymers in one part and a catalyst in the other part. One-part systems typically consist of reactive polymer compositions that react with ambient moisture in air and are packaged in air-tight containers. Exposure of the composition to air results in crosslinked siloxane polymer. This method is the basis for the popular silicone sealants available in the consumer market.

Another type of silicone elastomer is water-based silicone elastomers which consist of aqueous emulsions of siloxane polymers that are either pre-cured (pre-vulcanized) or cure after application.[64] Usually the latter involves a two-part system. These water-based silicone elastomers are discussed further in the section on 100% Silicone (Elastomeric) Coatings.

Silanes

Organofunctional silanes are typically monomeric organosilicon compounds that contain reactive or hydrolyzable groups (usually alkoxy) on silicon and some type of organic functional group[65]:

$$(RO)_3SiCH_2CH_2CH_2{-}X$$

$$R = CH_3\text{-};\ C_2H_5\text{-};\ X = \text{organic functional group}$$

Over many decades of commercial silicone development, quite a number of organofunctional silanes have become commercially available. The most common organofunctional silanes are based on the following functional groups: amino, epoxide, and unsaturated such as vinyl or acryl. Organofunctional silanes are used extensively in mineral/organic composites such as fiberglass composites and in glass wool insulation. In such applications, a high degree of stable, covalent bonding between polymer molecules and mineral surfaces can be achieved by the use of silanes.[66] In particular, good chemical bonding is achieved and retained under wet conditions.[67] Silanes can also be used to achieve improved adhesion in some coatings.[68,69] Organofunctional silanes are also used to effect crosslinking in siloxanes and in coatings that contain siloxanes as well as in some organic polymers.[70,71] Silanes are also used in waterproofing applications.[72]

SUMMARY

Silicones are a class of compounds or their precursors that possess at least one silicon–carbon bond and a siloxane unit. Silicones exist in a large variety of forms that include oils or fluids, high viscosity polymers, gums, elastomers, resins, and silanes. First commercialized in the United States in the early 1940s, silicones have experienced strong growth ever since. In Part I of this article, some of the illustrative history of silicones, as well as their preparation and properties, have been discussed. In Part II, the use of silicones in coatings will be detailed.

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