# Silicone Chemistry Overview
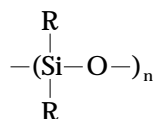
**DOW CORNING**

# Silicone Chemistry Overview

## 1. Introduction

By analogy with ketones, the name silicone was given in 1901 by Kipping to describe new compounds of the generic formula $R_2SiO$. These were rapidly identified as being polymeric and actually corresponding to polydialkylsiloxanes, with the formulation:

$$-(\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O-)_n$$

The name silicone was adopted by the industry and most of the time refers to polymers where R = Me (polydimethylsiloxane). The methyls along the chain can be substituted by many other groups, e.g., phenyl, vinyl or trifluoropropyl. The simultaneous presence of "organic" groups attached to an "inorganic" backbone gives silicones a combination of unique properties and allows their use in fields as different as aerospace (low and high temperature flexibility), electronics (high electrical resistance), medical (excellent bio-compatibility) and construction (resistance to weathering).
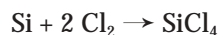
## 2. Historic

The principal steps in the development of silicone chemistry are[1,2]:

- The discovery of silicon by Berzelius in 1824 from the reduction of potassium fluorosilicate with potassium:

$$4\ K + K_2SiF_6 \rightarrow Si + 6\ KF$$
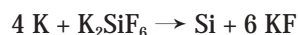
Reacting silicon with chlorine gave a volatile compound later identified as tetrachlorosilane, $SiCl_4$:

$$Si + 2\ Cl_2 \rightarrow SiCl_4$$

- The next step was made by Friedel and Craft with the synthesis of the first silicon organic compound in 1863, tetraethylsilane:

$$2\ Zn(C_2H_5)_2 + SiCl_4 \rightarrow Si(C_2H_5)_4 + 2\ ZnCl_2$$
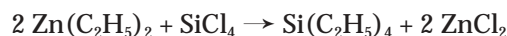
- In 1871, Ladenburg observed that, in the presence of a diluted acid, diethyldiethoxysilane, $(C_2H_5)_2Si(OC_2H_5)_2$, gave an oil that decomposed only at a "very high temperature."

- Kipping laid the foundation of organosilicon chemistry with, among other things, the preparation of various silanes by means of Grignard reactions and the hydrolysis of chlorosilanes to yield "large molecules"; the polymeric nature of the silicones was confirmed by the work of Stock.

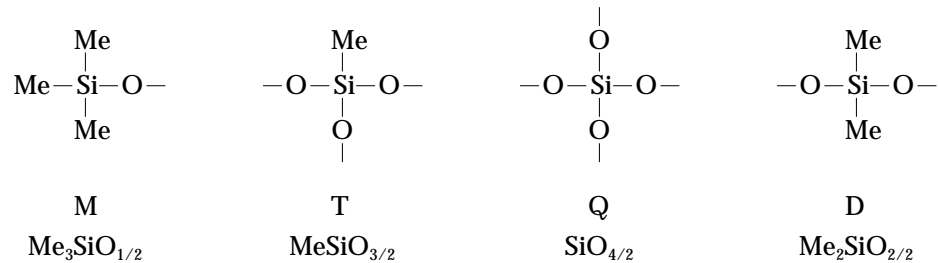- In the 1940s, silicones became commercial materials after Hyde of Dow Corning demonstrated the thermal stability and high electrical resistance of silicone resins, and Rochow of General Electric found a direct method of preparing silicones from Si and MeCl.

### 3. Nomenclature

The most common silicones are the polydimethylsiloxanes trimethylsilyloxy terminated, with the following structure:

$$\text{Me}-\underset{\underset{\text{Me}}{|}}{\overset{\overset{\text{Me}}{|}}{\text{Si}}}-\text{O}-(\underset{\underset{\text{Me}}{|}}{\overset{\overset{\text{Me}}{|}}{\text{Si}}}-\text{O})_n-\underset{\underset{\text{Me}}{|}}{\overset{\overset{\text{Me}}{|}}{\text{Si}}}-\text{Me} \quad \text{or} \quad \text{Me}_3\text{SiO}(\text{SiMe}_2\text{O})_n\text{SiMe}_3 \quad (n = 0, 1, ...)$$
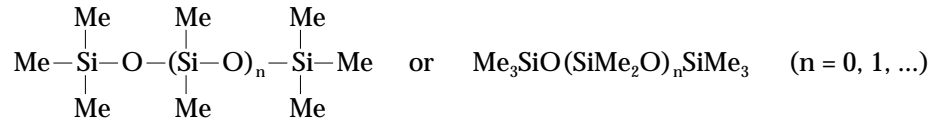
These are linear polymers and liquids, even for large values of n. The main chain unit, — $(\text{SiMe}_2\text{O})$ —, is often shortened by the letter D because, as the silicon atom is connected with two oxygen atoms, this unit is capable of expanding within the polymer in two directions. In a similar way, M, T and Q units can be defined corresponding to[3]:

| M | T | Q | D |
|---|---|---|---|
| $\text{Me}-\underset{\underset{\text{Me}}{|}}{\overset{\overset{\text{Me}}{|}}{\text{Si}}}-\text{O}-$ | $-\text{O}-\underset{\underset{\text{O}}{|}}{\overset{\overset{\text{Me}}{|}}{\text{Si}}}-\text{O}-$ | $-\text{O}-\underset{\underset{\text{O}}{|}}{\overset{\overset{\text{O}}{|}}{\text{Si}}}-\text{O}-$ | $-\text{O}-\underset{\underset{\text{Me}}{|}}{\overset{\overset{\text{Me}}{|}}{\text{Si}}}-\text{O}-$ |
| $\text{Me}_3\text{SiO}_{1/2}$ | $\text{MeSiO}_{3/2}$ | $\text{SiO}_{4/2}$ | $\text{Me}_2\text{SiO}_{2/2}$ |

The above polymer can also be described as $\text{MD}_n\text{M}$. It is possible to simplify the description of various structures like $(\text{Me}_3\text{SiO})_4\text{Si}$ or tetrakis(trimethylsilyloxy)silane, which becomes $\text{M}_4\text{Q}$ (superscripts are sometimes used to indicate groups other than methyl).

### 4. From Sand to Silicones

Silicones are obtained in a three-step synthesis:
- chlorosilane synthesis
- chlorosilane hydrolysis
- polymerization and polycondensation

### 4.1 Chlorosilane Synthesis

Today, silicones are obtained commercially (± 500,000 t/y) from chlorosilanes prepared following the direct process of Rochow[2] and using Si metal obtained from the reduction of sand at high temperature:

$$\text{SiO}_2 + 2\,\text{C} \rightarrow \text{Si} + 2\,\text{CO}$$
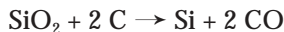
and methylchloride obtained by condensation of methanol with hydrochloric acid:

$$\text{CH}_3\text{OH} + \text{HCl} \overset{\text{cat}}{\rightarrow} \text{CH}_3\text{Cl} + \text{H}_2\text{O}$$
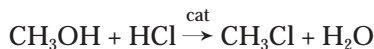
The reaction giving chlorosilanes takes place in a fluidized bed of silicon metal powder in which a stream of methylchloride flows, usually at temperatures of 250 to 350 °C and at

pressures of 1 to 5 bars. A mixture of different silanes is obtained containing mainly the dimethyldichlorosilane, $Me_2SiCl_2$[3]:

| | Yield (weight %) | Bp (°C) |
|---|---|---|
| x Si + y CH$_3$Cl $\xrightarrow{cat}$ Me$_2$SiCl$_2$ [1] | > 50 | 70.0 |
| MeSiCl$_3$ | 10-30 | 66.4 |
| Me$_3$SiCl | < 10 | 57.9 |
| MeHSiCl$_2$ | < 5 | 41.0 |
| other silanes | 5 | - |

The reaction is exothermic and has a yield of 85 to 90%. A copper-based catalyst is used. The reaction mechanism is not completely understood. Chemisorption phenomenons on active sites seem preferred to the radical-based mechanism originally proposed. The various silanes are separated by distillation. As the boiling points are close together, long distillation columns are always seen at silicone factories. The dimethyldichlorosilane [1] which is separated becomes the monomer for the preparation by hydrolysis of polydimethylsiloxanes (see further). Redistribution reactions can be used to convert the other silanes and increase the commercial yield of the production equipment[4].

Ethyl- and phenylchlorosilanes can also be obtained through similar reactions to the direct process described above. Phenylchlorosilanes can also be prepared through a Grignard reaction[3]:

$$MeSiCl_3 + C_6H_5MgBr \rightarrow Me(C_6H_5)SiCl_2 + MgClBr$$

Other chlorosilanes are prepared from an existing silane, e.g., the methylvinyl-dichlorosilane is obtained by the addition of methyldichlorosilane on acetylene using a Pt complex as catalyst[4]:
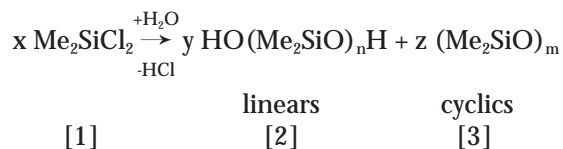
$$MeHSiCl_2 + HC \equiv CH \xrightarrow{Pt} MeViSiCl_2$$
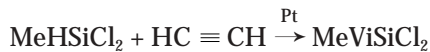
It is also possible to replace the chlorine groups by alcoholysis:

$$-\overset{|}{\underset{|}{Si}}Cl + ROH \rightarrow -\overset{|}{\underset{|}{Si}}OR + HCl$$
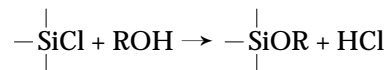
In this way, various silanes with different functionalities can be prepared, e.g., alkoxy and vinyl. These allow coupling reactions to take place between inorganic surfaces and polymers in composite manufacturing[5].

## 4.2 Chlorosilane Hydrolysis

Polydimethylsiloxanes are obtained by the hydrolysis of the dimethyldichlorosilane in the presence of an excess of water according to[3]:

$$x\ Me_2SiCl_2 \overset{+H_2O}{\underset{-HCl}{\rightarrow}} y\ HO(Me_2SiO)_nH + z\ (Me_2SiO)_m$$

| | linears | cyclics |
|---|---|---|
| [1] | [2] | [3] |

with n = 20 - 50 and m = 3, 4, 5, ... (mainly 4).

This heterogeneous and exothermic reaction yields a disilanol, $Me_2Si(OH)_2$, which readily condenses, with HCl acting as a catalyst, to give a mixture of linear [2] or cyclic [3] oligomers by inter- or intramolecular condensation. This mixture separates from the

aqueous acid phase, with the ratio between the two oligomers depending on the hydrolysis conditions (concentrations, pH, solvents). These oligomers are water-washed, neutralized and dried. The HCl is recycled and reacted with methanol to give the methylchloride used in the direct process described above.

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**4.3
Polymerization
and
Polycondensation**

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The linear [2] and cyclic [3] oligomers obtained by hydrolysis of the dimethyldi-chlorosilane have too short a chain for most applications. They must be condensed (linears) or polymerized (cyclics) to give macromolecules of sufficient length[6].

### 4.3.1 Cyclic polymerization

Opening and polymerizing cyclics, $(R_2SiO)_m$, to form long linear chains is catalyzed by many acid or base compounds[4] and gives at equilibrium a mixture of cyclic oligomers plus a distribution of  polymers. The proportion of cyclics will depend on the substituents along the chain, the temperature and the presence of a solvent. Polymer chain length will depend on the presence of substances capable of giving chain ends. For example, in the polymerization of $(Me_2SiO)_4$ with KOH, the average length of the polymer chains will depend on the KOH concentration:

$$x\ (Me_2SiO)_4 + KOH \rightarrow (Me_2SiO)_y + KO(Me_2SiO)_zH$$

[3]

A stable and $^-$OH terminated polymer, $HO(Me_2SiO)_zH$, can be isolated after neutralizing and stripping the above mixture, under vacuum, of the remaining cyclics. In fact, a distribution of chains with different lengths is achieved.

The reaction can also be made in the presence of $Me_3SiOSiMe_3$, which will act as a chain endblocker according to:

$$\sim\!\sim\!\sim Me_2SiOK\ +\ Me_3SiOSiMe_3 \rightarrow\ \sim\!\sim\!\sim Me_2SiOSiMe_3\ +\ Me_3SiOK$$

where $\sim\!\sim\!\sim$ is the main chain.

The $Me_3SiOK$ formed will attack another chain to reduce the average molecular weight of the linear polymer formed.

The copolymerization of $(Me_2SiO)_4$ in the presence of $Me_3SiOSiMe_3$ with $Me_4NOH$ as a catalyst displays a surprising viscosity change over time[6]. First, a peak or viscosity maximum is observed at the beginning of the reaction. With such a base catalyst, the presence of two oxygen atoms on each silicon in the cyclics makes them more susceptible to a nucleophilic attack by the catalyst than the silicon of the endblocker, which is substituted by one oxygen atom. The cyclics are polymerized first in very long, viscous chains that are subsequently reduced in length by the addition of terminal groups provided by the endblocker, which is slower to react. This reaction can be described as follows:

$$Me_3SiOSiMe_3 + x\ (Me_2SiO)_4 \xrightarrow{cat} Me_3SiO(Me_2SiO)_nSiMe_3$$
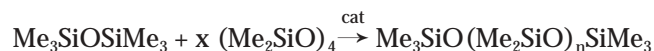
The ratio between D and M units will define the average molecular weight of the polymer formed.

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