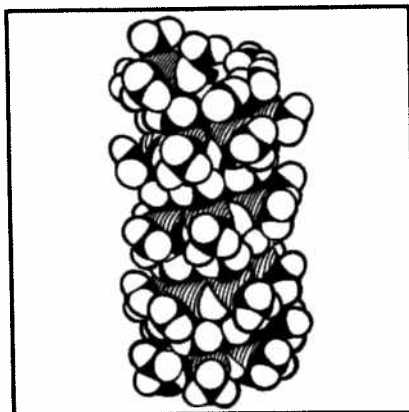


EDITORS:  
Bayer AG, Leverkusen  
Th. Goldschmidt AG, Essen  
Wacker-Chemie GmbH,  
München  
Haus der Technik e.V., Essen



# **SILICONES**

## **Chemistry and Technology**



CRC Press  
Boca Raton · Ann Arbor  
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## Preface

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Silicones have been produced commercially since the beginning of the 1940's. Starting in the United States of America, this group of products has conquered the world market quite rapidly, and all signs indicate that this trend will continue at a growth rate clearly above that of general industrial growth.

The reason for this development is to be found in the molecular structure of the silicones. The connexion of silicon and oxygen atoms leads to a stable basic structure in which the remaining valences of silicon are bound to hydrocarbon radicals (mostly methyl groups). This structure results in outstanding properties of the products which cannot be obtained with other compounds. Furthermore, many basic compounds (silanes) of different functionality make it feasible to create an enormous number of products which are used in nearly all industries and economic spheres as oils, greases, rubbers and resins. It is surely not exaggerated to state that, at present, there are several thousand silicone products available worldwide. The associated business volume is approximately 6 billion DM (approx. US\$ 3 billion) per year. One-quarter of this is the share of the German silicone manufacturers.

With this background, it is surprising that no in-depth summarizing presentation of this field has become available since W. Noll's treatise "Chemie und Technologie der Silicone" from the 1960's. Now, however, there is a considerable need for just such a publication in view of the immense increase in the number of individual contributions in specialty journals and thousands of patent applications.

The German silicone manufacturers therefore were glad to accept the proposal by the Haus der Technik to hold a one-day symposium on present-day knowledge of the chemistry and technology of silicones from the industrial point of view to give the attendants from user industries and universities a deeper understanding of this class of materials. Clearly, such a symposium can only give an abridged, and therefore incomplete, picture of the considerably greater variety of the industrial silicone scene.

This monograph contains all lectures that were presented on April 28, 1989 at the Haus der Technik on the topic "Chemistry and Technology of Silicones". The publishers hope that it will pave the way to the understanding of this part of organic silicon chemistry for a large group of experts and interested persons from universities and industry.

G. Koerner, Th. Goldschmidt AG  
M. Schulze, Bayer AG  
J. Weis, Wacker-Chemie GmbH

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# Introductory Remarks on the Peculiarities of Silicone Chemistry

by G. Koerner

The purpose of this meeting is to give an overview of modern, industrially realized, silicone chemistry. Commercially produced silicones have grown into a product group with many branches. These special polymers are used today in nearly all industrial sectors, from the pharmaceutical and cosmetic industries to metal manufacturing or the electrical industry. Therefore, we decided to forgo to a large extent going into application details. So that the lectures will appeal to a larger audience.

As is well-known, silicones originated in the United States which today still represent the most important location of production. In a comparison of countries, the German Federal Republic is in second place. Thus, the share of the three German producers of silicones represents 20–25 % of the annual silicone production in the Western World of 5–6 billion DM (approximately US\$ 3 billion). In spite of this magnitude, silicones have not reached the volume of the bulk polymers. Nevertheless silicones enjoy a steady growth due to the variety of different product types and applications.

In my introduction, I should like to consider the variety of these products as well as the reasons for its development.

Silicones, as commercially available products, cover a broad physical spectrum of low-viscosity liquids, oils and greases, rubbers and resins. This stems from the different application characteristics of these products. However, this broad range of products is possible only because, in comparison with other polymers, a large number of different building blocks—mostly chlorosilanes — are commercially available.

The four most important synthetical paths to this abundance of different silanes are shown schematically in Fig 1. By far the most significant one is the so-called direct synthesis of methylchlorosilanes. The direct synthesis of phenylchlorosilanes or the dehydrochlorinating synthesis of phenylchlorosilanes is quantitatively less important but does open a path to the important product group of phenylsilanes which can be produced commercially also by the Grignard synthesis.

Finally, an extraordinarily broad range of starting compounds for silicone chemistry is opened by the hydrosilylation of hydrogensilanes which makes feasible practically every important organo-function. Therefore, the hydrosilylation reaction is especially responsible for the commercially realized diversity of silicones. Figure 1 gives only a brief survey of the actually available diversity of silane monomers.

A further basis for this variety lies in the synthetic potential of silicone chemistry. It is generally known that polar silicon functions normally exhibit a markedly higher reactivity than equivalent carbon compounds. So, polar Si-functions, such as SiCl-, SiOalkyl- or SiH-groups bonded to siloxane, are readily transformed almost quantitatively by esterification, transesterification or hydrosilylation reactions, as shown in Fig. 2.

This special reactivity in the so-called polymeranalogous transformations plays a key role for the synthesis of copolymers which contain siloxanes as polymeric components and

Production Path	Products
Direct or Rochow Synthesis of Methylchlorosilanes	
$\text{CH}_3\text{Cl} + \text{Si}$	$\longrightarrow$ $(\text{CH}_3)_2\text{SiCl}_2$ (Main Product) $(\text{CH}_3)_3\text{SiCl}$ , $\text{CH}_3\text{SiCl}_3$ , $\text{SiCl}_4$ $\text{CH}_3\text{HSiCl}_2$ , $(\text{CH}_3)_2\text{HSiCl}$
Direct Synthesis of Phenylchlorosilanes	
$\text{C}_6\text{H}_5\text{Cl} + \text{Si}$	$\longrightarrow$ $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$ , $\text{C}_6\text{H}_5\text{SiCl}_3$
Dehydrochlorinating Synthesis of Phenylchlorosilanes	
$\text{C}_6\text{H}_5\text{Cl} + \text{HSiCl}_3$	$\longrightarrow$ $\text{C}_6\text{H}_5\text{SiCl}_3$
$+ \text{CH}_3\text{HSiCl}_2$	$-\text{HCl}$ $\text{C}_6\text{H}_5(\text{CH}_3)\text{SiCl}_2$
Hydrosilylating Synthesis of Silanes	
$\text{HSiX}_3 + \text{CH}_2 = \text{CH} - \text{CH}_2 - \text{R}$	$\longrightarrow$ $\text{R}(\text{CH}_2)_3\text{SiX}_3$
$\text{CH}_3\text{HSiX}_2$	$\text{R}(\text{CH}_2)_3\text{Si}(\text{CH}_3)\text{X}_2$

Fig. 1: Synthesis of various silane building blocks

for the synthesis of modified siloxanes. The great variety of these products is basically related to their ease of production. An important example of the high reactivity of polar Si-functions is the reaction of polymer-bonded SiOH-groups with tri- or tetra-functional silanes. This reaction is used for room temperature cross-linking of silicone rubber. Pure organic chemistry in comparison offers very few reactive groups to achieve room temperature cross-linking such as isocyanate or epoxy groups.

A special role in technical silicone chemistry is played by the equilibration reaction. During this reaction the Si-O-Si bonds of a siloxane are cleaved and reformed so that, in the end, a polymer distribution results which corresponds to the thermodynamic equilibrium. This possibility of equilibration is an outstanding peculiarity of silicone chemistry. The equilibration is achieved with either strong bases or strong acids. It is here that the SiOSi bond shows its janus nature. Generally, the Si-O-Si bond is thermally highly stable and under normal conditions also hydrolytically resistant but can be broken by the attack of strong acids or bases. The equilibration reaction enables the unusually highly reproducible synthesis of corresponding products (Fig. 3 a).

Thus, equilibration enables the production of  $\alpha,\omega$ -bistrimethylsiloxypolydimethylsiloxanes, that is, silicone oils of desired chain length or viscosity by equilibrating dimethylpoly-siloxanes with the appropriate amount of hexamethyldisiloxane.

Equilibrating synthesis of siloxanes containing SiH-groups is shown in Fig. 3 b. Such products are particularly suitable as starting compounds for further transformations using the hydrosilylation reaction. The resulting copolymers are linked via SiC-bonds.



Polymer-bonded Si-function	Products	Type of Reaction
$\text{Si}-\text{Cl} + \text{ROH}$	$\longrightarrow \text{Si}-\text{O}-\text{R} + \text{HCl}$	Esterification
$\text{Si}-\text{O}-\text{Alkyl} + \text{ROH}$ (Alkyl = $\text{CH}_3$ oder $\text{C}_2\text{H}_5$ )	$\longrightarrow \text{Si}-\text{O}-\text{R} + \text{Alkyl}-\text{OH}$	Transesterification
$\text{Si}-\text{H} + \text{CH}_2=\text{CH}-\text{CH}_2-\text{R}$	$\longrightarrow \text{Si}-(\text{CH}_2)_3\text{R}$	Hydrosilylation
$3 \text{ Si}-\text{OH} + \text{R}-\text{SiX}_3$	$\longrightarrow \text{Si}-\text{O}-\overset{\text{R}}{\underset{\text{OSi}}{\text{Si}}}-\text{O}-\text{Si} + 3\text{HX}$	Room Temperature Vulcanisation

(X =  $\text{C}_2\text{H}_5\text{O}-$ ,  $\text{CH}_3\text{COO}-$ ,  $\text{C}_6\text{H}_{11}-\text{NH}-$ ,  $\text{Ph}-\text{CO}-\underset{\text{CH}_3}{\text{N}}-$  etc.)

Fig. 2: Polymer-analogous reaction of functional Si-compounds

### Production of silicone oils by equilibration

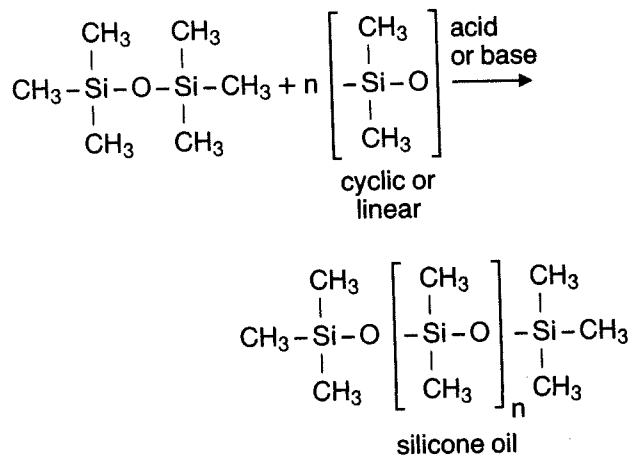


Fig. 3a: Equilibration as key reaction for the production of silicone oils and functional siloxanes

### equilibrating synthesis of comb-like siloxanes containing SiH-groups

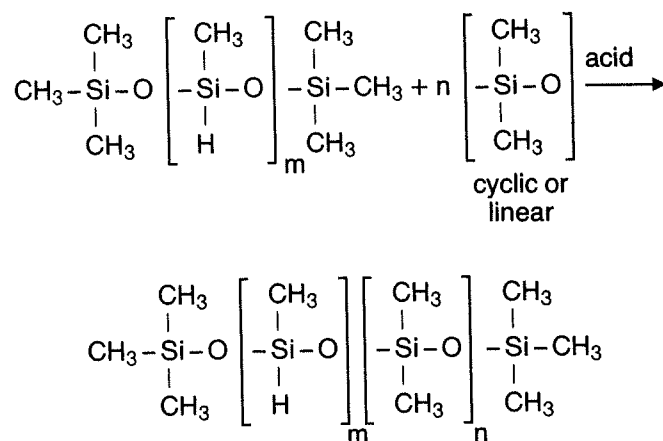


Fig. 3b: Equilibration as key reaction for the production of silicone oils and functional siloxanes

In contrast, alkoxysiloxanes can be produced by alkaline equilibration as shown in figure 3c. These alkoxysiloxanes can be transesterified with low or high-molecular organic hydroxy functional compounds; this leads to the formation of copolymers with SiOC-bonds.

Finally, the formulae of Fig. 3d show the synthesis of chlorosiloxanylsulfates. Here, the chlorosilanes are hydrolyzed with less than stoichiometric amounts of water and simultaneously or subsequently equilibrated with sulfuric acid. The chlorosiloxanyl sulfates formed can also be reacted with organic hydroxy functional compounds. Thus, via esterification again copolymers linked by SiOC-bonds are obtained.

The formulae for the subject of equilibration presented here give only a portion of the much more extensive industrial practice. To repeat: equilibration does not only control the chain length very precisely but is also the chemical tool of choice for the insertion of reactive functional groups into the polymer structure. It is therefore the key reaction for the synthesis of reactive siloxane constituents.

To summarize: the specific characteristics of silicone chemistry represent an important basis for the industrial success of these products. These characteristics include primarily:

1. The various processes of synthesis that are used for production of many different silicone raw materials,
2. The high reactivity of polar Si-functional groups, and
3. The equilibration reaction as the key for the synthesis of both final products and constituents.

### synthesis of alkoxy siloxanes by alkaline equilibration

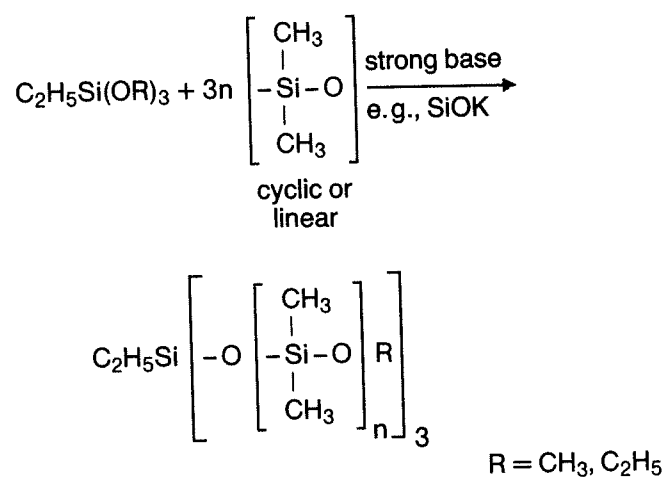


Fig. 3c: Equilibration as key reaction for the production of silicone oils and functional siloxanes

### synthesis of branched chlorosiloxanyl sulfates by hydrolysis of chlorosilanes and equilibration with sulfuric acid

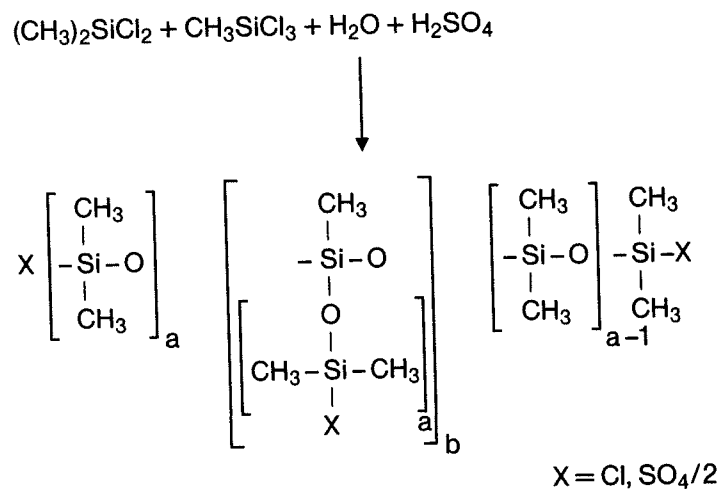


Fig. 3d: Equilibration as key reaction for the production of silicone oils and functional siloxanes

A further important reason for the industrial success of silicones is the fact that they exhibit a whole range of highly interesting and often unique properties (Fig. 4). Among these are their excellent thermal stability and weather resistance which can be further improved by the introduction of phenyl groups into the methylsilicones. These are decisive preconditions for their use as thermally stable oils as well as heat and weather resistant rubbers and resins.

The viscosity of silicone oils is considerably less influenced by changes in temperature than the viscosity of organic oils. Also the freezing point of silicone oils is unusually low. Silicone rubbers retain their rubber elasticity down to very low temperatures. That means that the physical constants of typical silicones exhibit a relatively small temperature dependence.

Silicones, particularly methylsilicones, show a low surface tension which accounts for the water-repellant effect of silicone impregnations and also for their ability to work as the lyophobic part of highly active surfactants. The low surface tension reflects the low intermolecular interaction of silicone oils. This is an essential requirement for the use of these products as release agents and lubricants.

Apart from a few exceptions, silicones are biologically inert. They are therefore generally nontoxic. They cannot be decomposed by biological means but they can be chemically degraded in the environment, by the action of certain clay minerals and in aqueous media under the influence of sun light in the presence of nitrate ions.

- thermal stability
- weather resistance
- small temperature dependence of the viscosity of methylsilicone oils
- low freezing point
- maintenance of rubber elasticity down to low temperatures
- little intermolecular interactions
- low surface tension of methylsilicones
- hydrophobicity, surface activity
- release and lubrication properties
- good dielectric properties

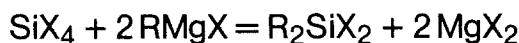
Fig. 4: Properties of silicones

# Chemistry and Technology of Direct Synthesis

by K. Feldner

My contribution will first give an overview of the chemistry and technology of direct synthesis of organochlorosilanes. These are the most important starting compounds for silicones which originally permitted the technical breakthrough for this class of materials. The most important ones are the **methylchlorosilanes** followed by the phenylchlorosilanes.

Kipping, at the University of Nottingham, was the first to investigate organosilicon compounds systematically. He also was the first to find an industrially feasible method of synthesis of organohalogenosilanes [1]. We deal here with a synthesis with the aid of Grignard compounds, starting, for example, with silicon tetrachloride. The general scheme is shown in Fig. 1.



R = organic radical, e.g.  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$

X = Cl, Br

Fig. 1: Grignard synthesis

Besides finding the flexible "Grignard-Synthesis path" to a great many organohalogenosilanes, Kipping is also credited with the realization that hydrolysis of dimethyldichlorosilane does not yield the acetone analog – silicone – , but polymer compounds of an oily nature (Fig. 2). Nevertheless, the name silicones has become accepted for polymers with

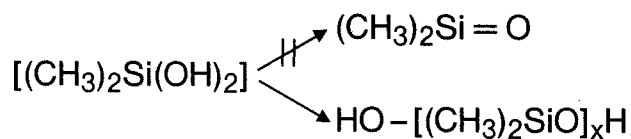


Fig. 2: Chlorosilane hydrolysis

the typical constituent group  $\begin{array}{c} \text{R} \\ | \\ \text{[Si-O]} \\ | \\ \text{R} \end{array}$  -, although these compounds should be identified correctly as polysiloxanes. Because of their special properties, the importance of these compounds was recognized in subsequent years; with the discovery of direct synthesis by Müller and Rochow in the early 1940's, the industrial silane- and silicone chemistry started to grow because it became possible to make large quantities economically available.

Direct synthesis (today generally known as Rochow Synthesis) is now understood to be the reaction of silicon with methylchloride according to the equation shown in Fig. 3. With this synthesis, which is represented in the figure in a simplified form, the 1985 world production of methylchlorosilane was about 610,000 t/yr.

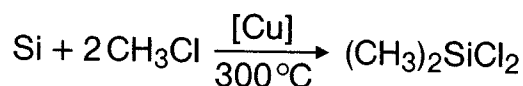


Fig. 3: Direct synthesis

Current estimates are near 800,000 t/yr with worldwide sales of silicones in 1988 of approximately US\$  $3.5 \times 10^9$ .

The silicone market is distributed approximately as follows: USA 40 %, Europe 30 %, Japan 20 %, other trading countries 10 %.

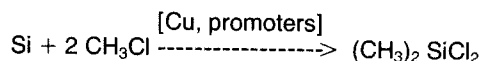
Manufacturers of silicones in the Western world are

- USA: Dow Corning, General Electric, Union Carbide, Wacker;
- Great Britain: Dow Corning, Rhône-Poulenc (formerly ICI);
- France: Rhône-Poulenc;
- German Federal Republic: Bayer, Goldschmidt, Wacker, Nünchritz;
- Japan: Shin-Etsu, Toray (DC), Toshiba (GE).

In other trading countries, known manufacturers are

- Factories in Czechoslovakia, People's Republic of China, USSR.

Most of the listed companies also use the direct synthesis and thus obtain their own raw materials. According to the equation for the reaction



one requires for the direct synthesis:

Silicon  
Methylchloride

and a copper catalyst as well as promoters (Fig. 4).

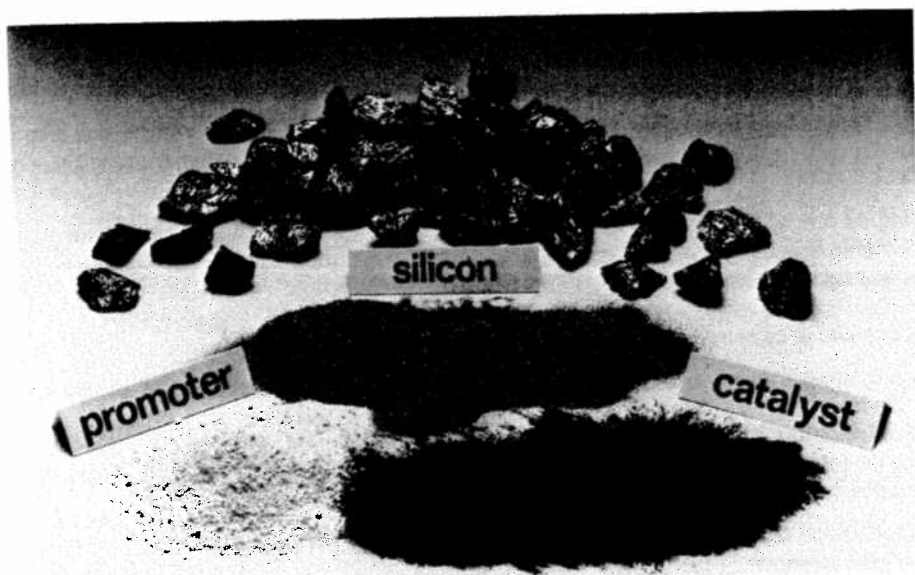


Fig. 4: Raw materials

## 1. Silicon

The required silicon is mostly obtained by electro-thermal reduction of silicon dioxide (quartz) with carbon. There are silicon manufacturers in all countries where cheap electrical energy is available, for example, Norway, Switzerland, South Africa, Sweden, Canada and Brazil. By appropriate selection of raw materials, and relatively simple metallurgical operations, the manufacturers obtain silicon with a purity of better than 99 %, so-called chemical quality. Typical impurities are, among others, Al, Ca, Fe and Ti.

Since the direct synthesis is carried out in a fluidized bed as a gas-solid reaction, the particle size of silicon is of considerable importance. Published information and personal investigations indicate that particle sizes in the range of 30–350  $\mu\text{m}$  are particularly suitable. To produce such a fine powder requires that the silicon must be crushed and ground.

## 2. Methylchloride

Methylchloride is gaseous at room temperature (its boiling point is  $-24.2^{\circ}\text{C}$ ). The classical methods of production are:

- Chlorination of methane and
- reaction of methanol with hydrogen chloride.

Since formation of Si–O–Si bonds by reaction of methylchlorosilanes with water (hydrolysis) necessarily produces hydrogen chloride, most silane manufacturers use this hydrogen chloride to produce methylchloride as discussed in the following presentation.

### 3. Copper catalyst and promoters

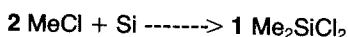
Suitable **catalysts** are materials from the copper-oxygen system with a **mean** composition approximately in the range of  $\text{Cu}_2\text{O}$ . The particle size is under  $10\text{ }\mu\text{m}$ ; one deals therefore with a fine powder. Such catalysts are often used in the form of spheres with a small copper nucleus, surrounded by an intermediate  $\text{Cu}_2\text{O}$ -layer and finally a layer of  $\text{CuO}$ . Particular emphasis is placed on a low degree of impurities.

**Zinc** as metal, oxide or chloride, is used as promoter. Recent literature indicates other elements that can be used as promoters, such as tin, phosphorous, arsenic, aluminium as well as alkali- and alkaline earth-metals [2].

#### Technical process of direct synthesis

The synthesis requires reaction of a mixture of solids (contact material) with the gas methylchloride. Reaction takes place at about  $300^\circ\text{C}$  and is exothermic. It produces about 725 kcal (about 3,000 kJ) per kg of crude silane mixture. Therefore, fluidized bed or vortex reactor technology is in world-wide use because of the advantages of good thermal process control.

At a reaction temperature of about  $300^\circ\text{C}$ , the reaction products, methylchlorosilanes, are also gaseous. The reaction involves a reduction in the quantity of gaseous constituents, as indicated by the equation



Application of pressure is therefore technically feasible (see Fig. 5).

$$T = 280 - 330^\circ\text{C}$$

$$p = 2 - 4\text{ bar}$$

$$\Delta H_R = 725\text{ Kcal/kg crude silane}$$

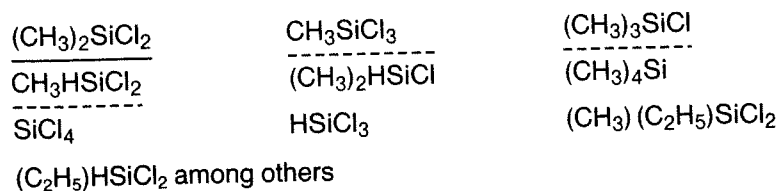
fluidized-bed technology

Fig. 5: Reaction conditions

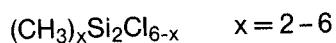
One obtains then a mixture of all imaginable methylchlorosilanes of which dimethyl-dichlorosilane represents more than 80 %. The second-largest fraction is methyltrichlorosilane with about 10–15% followed by trimethylchlorosilane and methylhydrogen-dichlorosilane which both represent at most 3–4%. All other compounds appear only in insignificant amounts (Fig. 6). The indicated fractions are only guidelines, because manufacturers, on one hand, try to influence the spectrum of the products during the reaction and, on the other hand, correct the product composition by appropriate measures. These additional measures for correction of the product composition can be the reactions shown in Fig. 7.



## monomer silanes:



## disilanes:



## trisilanes, siloxanes

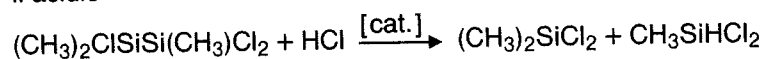
## silicon-free compounds:

$\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2$ - to  $\text{C}_4$ -carbohydrates among others

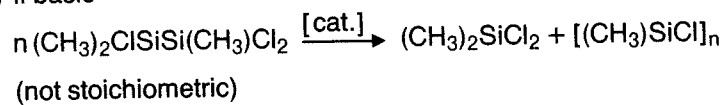
Fig. 6: Product composition

## disilane cleavage reactions

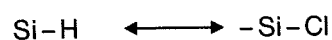
a) if acidic



b) if basic



## ligand replacement reactions



according to e.g.:



Fig. 7: Follow-up reactions to correct the product spectrum

### What is known about the chemistry of direct synthesis?

If one takes all the information from the literature, one can now state that the individual steps of the solids reactions can be rather well described and are sufficiently clarified; in contrast, the actual reaction with methylchloride, as well as the action of the promoters, is largely not understood and therefore must be described empirically [3]. It is just these problems that are of special interest because it is here where the composition of the crude silane mixture can be and is influenced. However, this knowledge is treated as confidential "know-how" and is not published.

For qualitative understanding, I should like to present the following partial steps:

- The essential metallochemical process is the formation of  $\text{Cu}_3\text{Si}$  on the surface of silicon which can be effected in several ways.

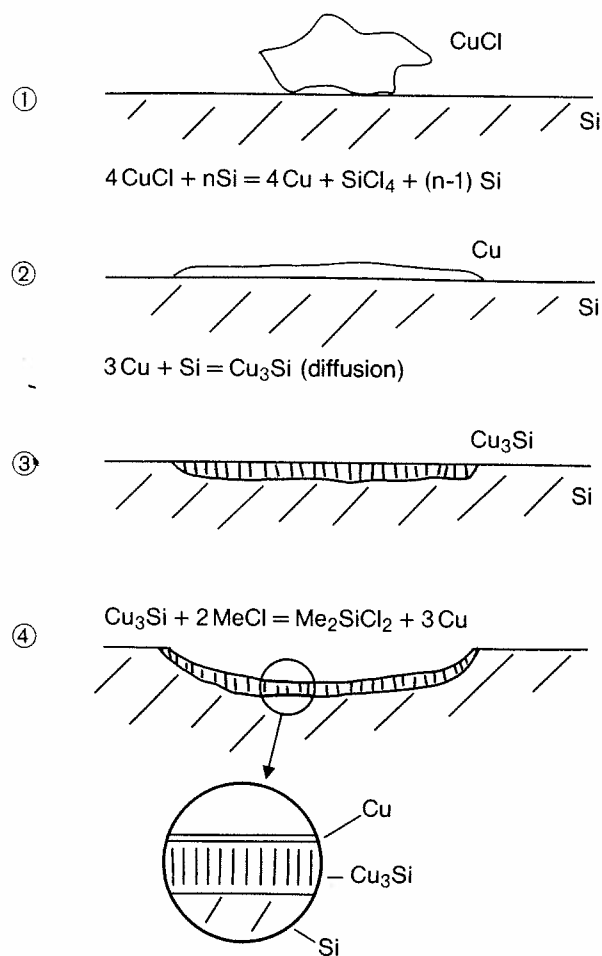
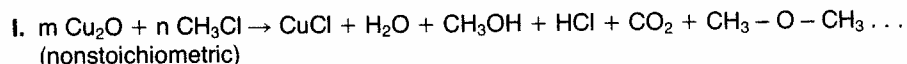


Fig. 8: Copper catalysis

Reaction of oxidic catalysts in the presence of  $\text{CH}_3\text{Cl}$  is of industrial importance according to:

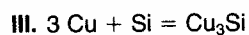


It is essential here to go from a Cu-Oxide to a Cu-Chloride system.

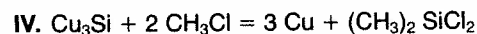
Then, in the presence of silicon, the following reaction step takes place:



Because of good reproducibility, this reaction often is preferred in the laboratory as a preparative method for making the contact material. The copper thus precipitated on the silicon surface has a sufficiently intimate contact with the silicon (Fig. 9) to form the intermetallic phase  $\text{Cu}_3\text{Si}$  by diffusion at about  $300^\circ\text{C}$  according to:



The silicon grains thus become superficially covered with specks of  $\text{Cu}_3\text{Si}$ . Then, the  $\text{Cu}_3\text{Si}$  reacts with methylchloride to form methylchlorosilanes and leaves an excess of copper on the surface according to:



These steps are indicated in Fig. 8. In this manner, the surface is intermittently in a state that corresponds to Eq. III.

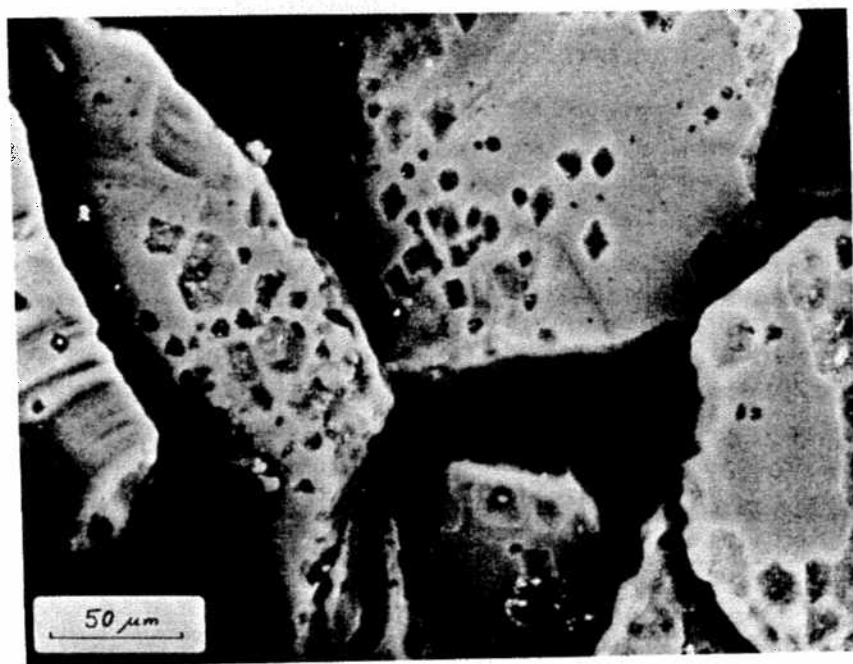


Fig. 9: Silicon contact

Because excess copper diffuses through the  $\text{Cu}_3\text{Si}$  layer, the  $\text{Cu}_3\text{Si}$  surface becomes reexposed and fresh  $\text{Cu}_3\text{Si}$  is formed at the silicon/ $\text{Cu}_3\text{Si}$  boundary. Formation of the silanes gradually produces holes and the silicon grains are consumed until they become so small that they can be swept out of the reactor with the reacting gas.



Fig. 10: Reactive center

### progression of selectivity

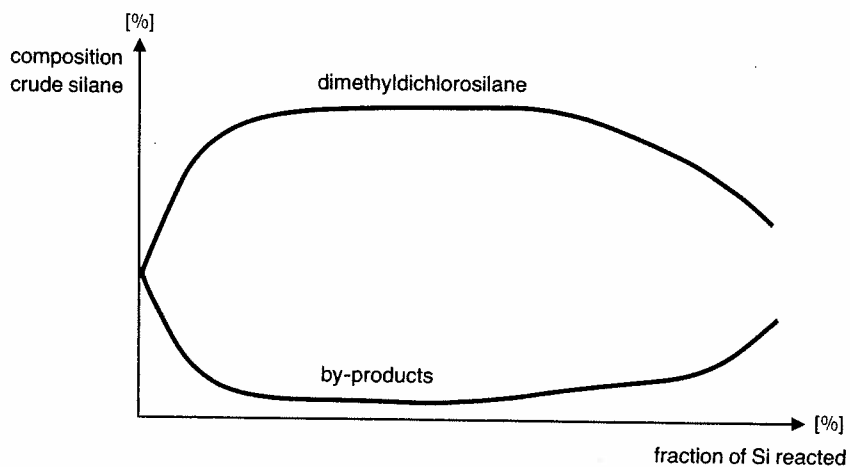


Fig. 11: Progression of selectivity

The composition of the crude silane mixture depends on the fraction of silicon reacted and also on the contact composition. At first, one reaches a high selectivity for dimethyl-dichlorosilane which lasts for an appreciable time. Formation of by-products increases strongly only when a high fraction of the silicon has reacted (Fig. 11).

Since a continuously operating reactor contains particles of all degrees of Si depletion, it is not possible, in principle, to realize the maximum selectivity that can be achieved in laboratory experiments.

**What does the reaction vessel look like and what must be considered for a large-scale process [4]?**

Reactors are cylindrical vessels of several meters height and several meters diameter (Fig. 12). Important aspects are the gas distribution, heat exchange and a cyclone for separation and return of solids. For the construction of fluidized-bed reactors, it is essential to achieve the following aims (Figs. 13 and 14):

**Rochow synthesis:**

silicon + methylchloride  $\xrightarrow{\text{copper catalyst}}$  methylchlorosilane

technical process: fluidized-bed reactor

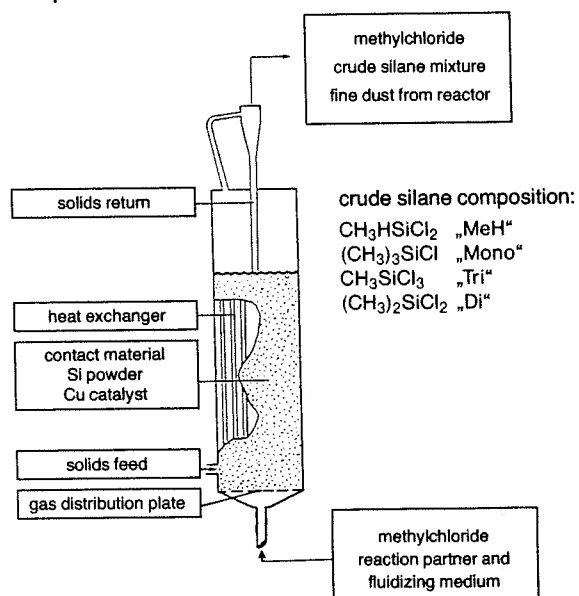


Fig. 12: Fluidized-bed reactor

### Construction Specification:

- uniform fluidization of the contact material, bubble-free as much as possible
- precise temperature control in the range of about 300°C
- prevention of baking-on in the reaction vessel

Fig. 13: Specifications for construction

### Aims for operation of the reactors:

- highest possible selectivity for dimethyldichlorosilane relative to methyltrichlorosilane
- reduction of the contents of methyldichlorosilane or di- and polysilanes with higher boiling points
- highest possible yield of silicon
- continuous operation

Fig. 14: Aims for operation of the reactors

Data about actual size of the reactors, content of dimethyldichlorosilane in the raw silanes, excess of methylchloride with respect to silicon, operating pressure, yield with respect to silicon, etc. represent the know-how of silane manufacturers and therefore are not published.

The following parameters are important for uniform continuous operation of reactors with high output and selectivity (Fig. 15). Adjustment of these parameters is so important because, on the one hand, the smallest particles (used-up silicon enriched with non-volatile impurities) must be removed, and on the other hand, not too much usable silicon should be lost.

- quality and particle size of the silicon
- quality and particle size of the copper catalyst
- kind and quantity of the promoters
- separation limit of the cyclone
- flow velocity of the methylchloride

Fig. 15: Important parameters for reactor operation

The finely dispersed residue, which is removed from the reactor, contains, in addition to silicon, other elements including up to

about 20 % Cu  
 about 5–7 % Fe  
 about 4 % Al  
 and about 3 % Ca

and must be separated from the gas stream.

A number of suggestions have been made to separate these fine particles by chemical and/or physical means into useable silicon and a useless residue thereby increasing the amount of useable silicon. The same considerations apply to copper, which is of importance as a raw material and also the disposal of which can create environmental problems.

After separation of the finely dispersed residue, the gas mixture which flows through the cyclone contains the excess of methylchloride as well as the already-mentioned product mixture of organosilicon and other organic compounds. Thus, there follows a complex processing scheme:

- separation of the methylchloride;
- separation of the monomer silanes;
- separation of the distillable oligomer silanes,

followed by

- purification of the methylchloride (removal of the hydrocarbons that are within the boiling range of methylchloride);
- separation of the monomer silanes by multistage distillation;
- cleavage of the disilanes;
- disposal of the solids containing residues that cannot be distilled.

Let me briefly consider the last item:

### Treatment of residues [5]:

The above-mentioned finely dispersed reactor residues frequently occur in the form of sludge combined with organosilicon compounds which cannot be distilled and which have high boiling points. It is clear that such a reactive, sometimes self-ignitable, material cannot be easily disposed of. One possibility is incineration of the residue, but the problems of purification of the combustion gases, removal of hydrogen chloride and finely distributed silica, as well as the treatment of metal-containing combustion residues must be solved.

Another possibility is hydrolysis of the residue which transforms the Si-Cl-bonds into Si-O-Si-bonds and hydrochloric acid. If this process is followed by treatment with oxidizing agents, such as sodium hypochlorite or oxygen (under pressure), the copper contained in the residue is dissolved as  $\text{CuCl}_2$ , and the Si-Si- and the Si-H-bonds are partially transformed into Si-OH- and Si-O-Si-bonds (Fig. 16).

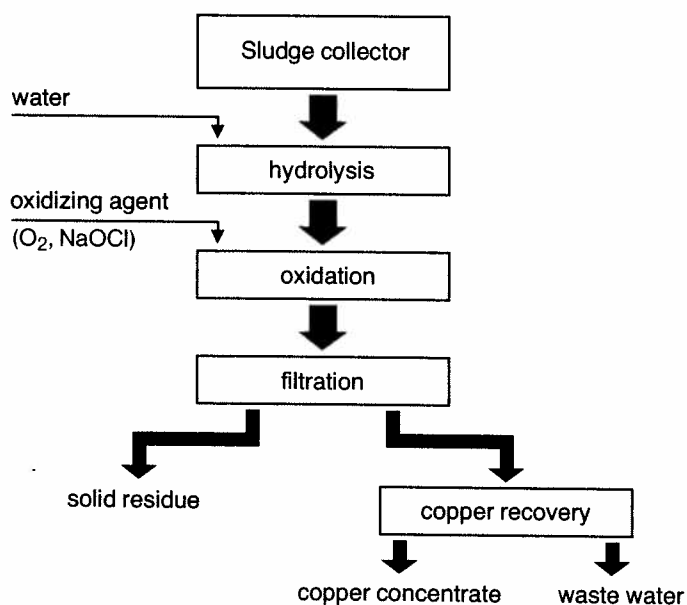


Fig. 16: Oxidation of the residue

The solid organosilicon residues, after filtration from the suspension, can be disposed of without problems. Copper can be recovered from the filtrate by well-known processes, for example, by extraction or by precipitation using an alkaline reduction process. The ideal aim here is to realize a nearly complete recycling of copper.

The preceding discussion has shown that under present-day conditions, economic and ecological considerations require the combination of process units shown in Fig. 17.



### Direct synthesis installation:

- 1) synthesis with recovery and purification of the unused methylchloride
- 2) multistage product distillation
- 3) equipment for cleavage of higher boiling point di- and polysilanes
- 4) installation for treatment of solids-containing residues with incorporated recycling of copper
- 5) recycling of chlorine by methanolysis or hydrolysis with subsequent methanol esterification and formation of methylchloride
- 6) combustion of waste gases

Fig. 17: Considerations for a modern synthesis installation

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# Chemistry and Technology of Polysiloxanes

by J. Burkhardt

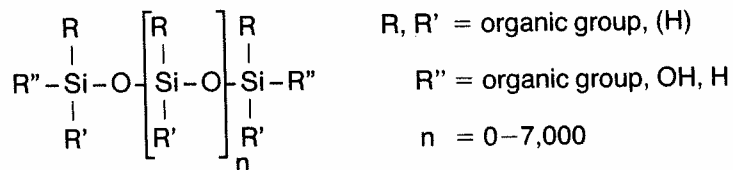
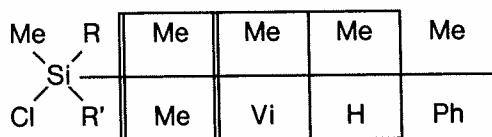
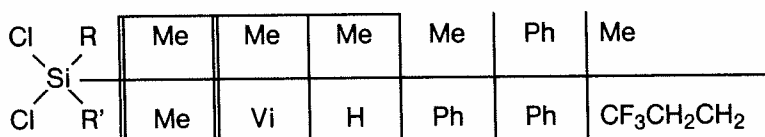


Fig. 1: POLYDIORGANOSILOXANE

In Polydiorganosiloxanes the most important organic group is the methyl group. To a minor extent, other substituents are employed.

Organochlorosilanes (Fig. 2) are the starting materials for the production of organosiloxanes (Fig. 1).



Silanes mainly used for producing silicone elastomers

Fig. 2: Organochlorosilanes important for polymer production

Polydimethylsiloxanes are obtained from dimethyldichlorosilane in a two-step process (Fig. 3).

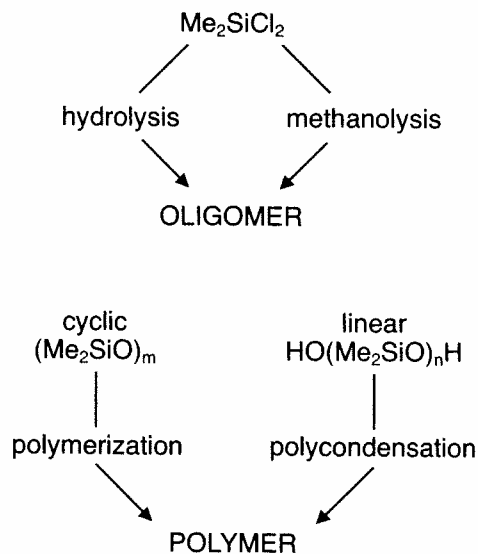


Fig. 3: Production of polydimethylsiloxane

The first step is hydrolysis or methanolysis of dimethyldichlorosilane to cyclic and/or linear oligodimethylsiloxanes. The various polymers then are produced in a second step by polymerization of the cyclic or polycondensation of the linear oligomers.

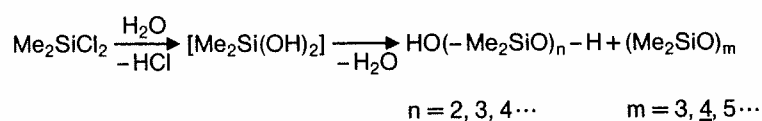
#### Hydrolysis, Methanolysis

Hydrolysis is the classical method for converting dimethyldichlorosilane into dimethylsiloxane. Mixtures of cyclic and linear oligomers are obtained. The ratio of cyclic to linear compounds as well as the chain length of the linear siloxanes may be controlled by the conditions of hydrolysis. Thus, concentration and duration of the contact of hydrochloric acid with the formed siloxanes play a decisive role. Rapid removal or neutralization of HCl leads to short-chained siloxanediols. The smallest molecule, which is obtained by rapid mixing of dimethyldichlorosilane with an ice-cold aqueous solution of  $\text{NaHCO}_3$ , is the crystalline tetramethyldisiloxanediol ( $n = 2$ ). Dimethylsilanediol ( $n = 1$ ) cannot be recovered. Among the cyclic oligosiloxanes octamethylcyclotetrasiloxane ( $m = 4$ ) dominates (Fig. 4).

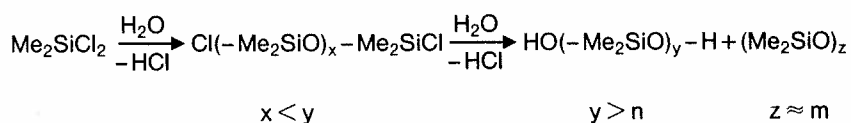
The complete conversion of dimethyldichlorosilane into linear siloxanediols may be realized by continuous hydrolysis (Fig. 5). This is possible because the siloxane bond is easily cleaved by catalysts. Thus, the cyclosiloxanes, distilled continuously from the mixture of oligomers, can be cleaved by an acid catalyzed reaction with dimethyldichlorosilane to yield  $\alpha, \omega$ -dichlorosiloxane (Fig. 5).

The HCl resulting from the hydrolysis is converted by methanol into methylchloride which then is reused for the silane synthesis. Thus, the chlorine goes through a cycle in which oligosiloxanes and methylchloride are formed in separate processes.

## 1) Silane in water (excess water)



## 2) Water in silane ("reverse" hydrolysis)



The ratio of linear to cyclic oligomers, as well as  $n$ ,  $y$  and  $z$ ,  $m$  depend on the hydrolysis conditions.

Fig. 4: Production of oligodimethylsiloxanes  
Hydrolysis

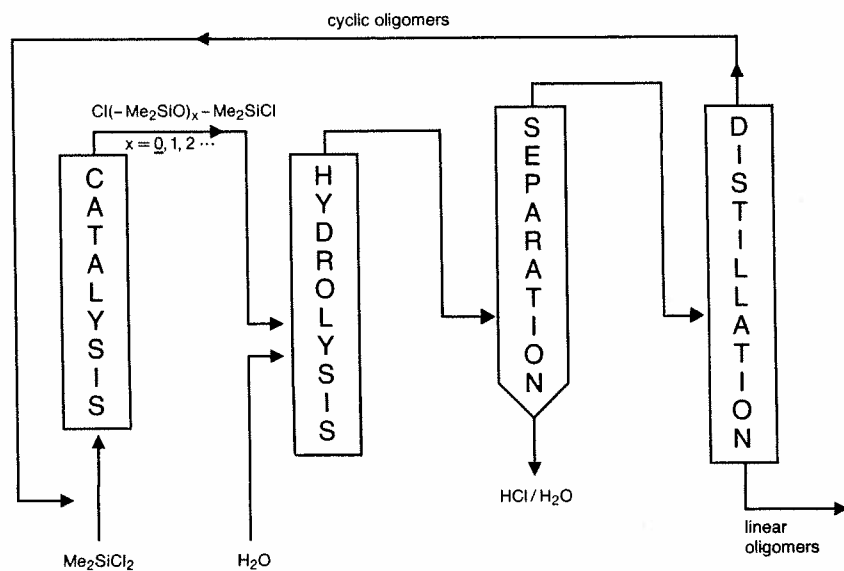
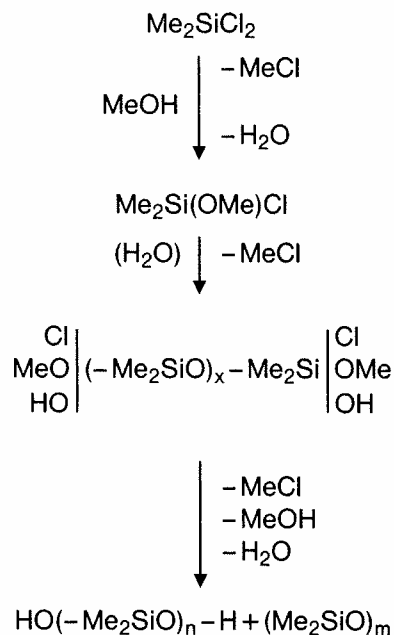


Fig. 5: Continuous hydrolysis of dimethyldichlorosilane

A process where the Si-bound chlorine is directly transformed into methylchloride is methanolysis (Fig. 6). Here, the chlorosilane reacts with methanol to yield the mixture of cyclic and linear oligosiloxanes.

As in the case of hydrolysis, continuous operation may yield quantitatively linear oligomers by recycling the distillable cyclosiloxanes.



MeCl is reused in silane synthesis

Fig. 6: Production of oligodimethylsiloxanes  
Methanolysis

If the linear oligomer that results from hydrolysis or methanolysis is to be used for the production of high molecular weight polymer ( $n > 1000$ ), then extreme purification of the  $\text{Me}_2\text{SiCl}_2$  by distillation is required. The content of  $\text{MeSiCl}_3$ , whose boiling point is only  $4^\circ$  lower, must definitely be less than 0.01% because hydrolysis or methanolysis of  $\text{MeSiCl}_3$  leads to trifunctional methylsiloxane units. In dimethylsiloxane gums, these cause undesirable branches or even cross-links. If the  $\text{Me}_2\text{SiCl}_2$  does not have the indicated purity, then the mixture of oligosiloxanes obtained by hydrolysis or methanolysis must be purified. This may be achieved by alkaline- or acid-catalyzed depolymerization to cyclosiloxanes which are removed from the reaction mixture by distillation. Trifunctional impurities remain in the distillation flask.

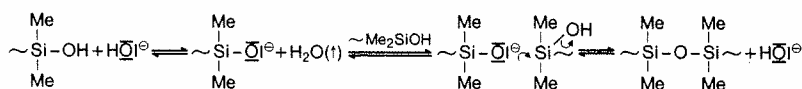
### Polymerization, Polycondensation

The acid-catalyzed reactions which follow hydrolysis and methanolysis of  $\text{Me}_2\text{SiCl}_2$ , that is, condensation of silanol groups and cleavage of siloxane bonds, occur also during polycondensation of OH-terminated linear and polymerization of cyclic oligomers. In both cases, one deals with ionic reactions. The initial step is the attack of a proton ( $\text{H}^+$ ) on the oxygen of the siloxane bond or the silanol group. All strong acids ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{CF}_3\text{SO}_3\text{H}$ , etc.), as well as Lewis acids, act as catalysts. Solid catalysts such as acid-activated fuller's earth may also be used.

Polymerization and polycondensation may also be catalyzed by alkali. Strong bases can be used, such as  $\text{KOH}$ , or quaternary ammonium- or phosphonium hydroxides. The initial step is the nucleophilic attack of the anion on the silicon (Fig. 7).

In all cases one has to deal with equilibrium reactions, that is, one may use alkaline or acid catalysts for both growth and degradation of the siloxane chain. The direction of the reaction depends on the conditions. This process of simultaneous cleavage and recombination of siloxane bonds is called equilibration.

#### 1. Polycondensation of linear oligomers $\text{HO}(\text{--Me}_2\text{SiO})_n\text{--H}$



#### 2. Polymerization of cyclic oligomers $(\text{Me}_2\text{SiO})_m$

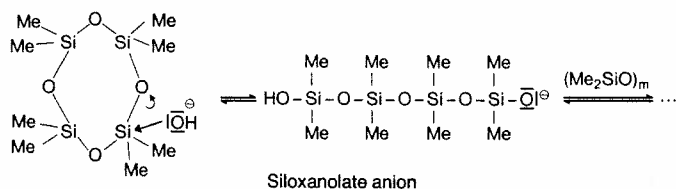


Fig. 7: Production of polydimethylsiloxane  
Alkaline catalysis

### Equilibration

If one catalyzes a cyclic oligodimethylsiloxane or a linear polydimethylsiloxane, then an equilibrium is established between cyclic oligomers and linear polymers. After deactivation of the catalyst, the 15–20% cyclosiloxanes, mostly tetramer, can be removed by vacuum distillation. If the catalyst is not deactivated, the removed cyclosiloxanes are permanently regenerated until the polymer is completely used up (Fig. 8). This depolymerization is suitable for recycling of polysiloxanes of any degree of polymerization. So octamethylcyclotetrasiloxane can be recovered even from silicone rubber waste with good yields.

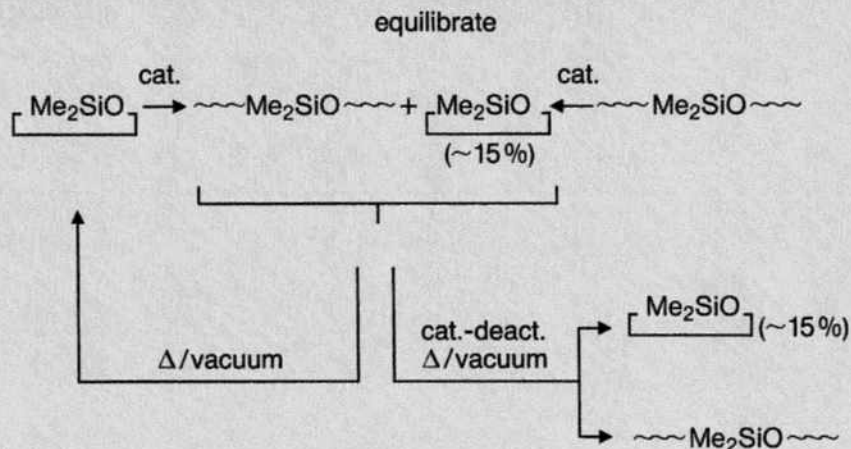
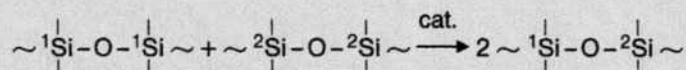


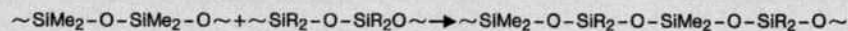
Fig. 8: Polymerization – Depolymerization  
Equilibration

These equilibration reactions, which proceed under constant cleavage and recombination of siloxane bonds also play a role in the preparation of copolymers and the regulation of chain length during polymerization (Fig. 9).

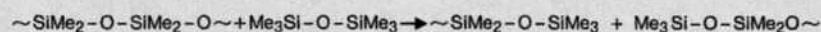
Catalysis: acid or alkaline

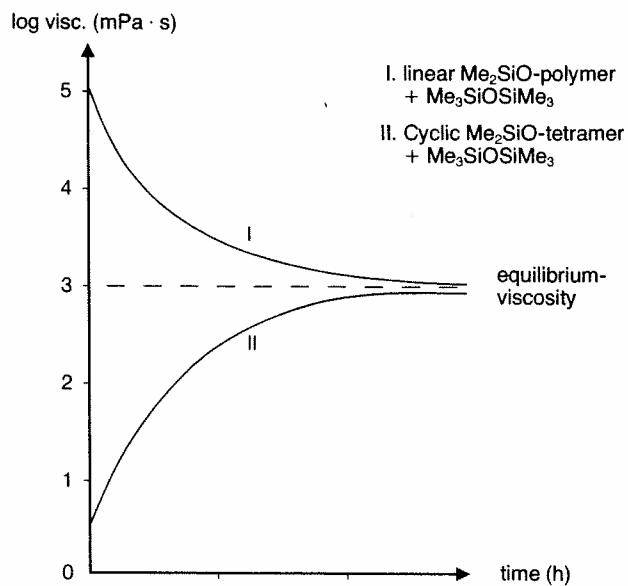


#### 1) Preparation of copolymers



#### 2) Regulation of chain length





The equilibrium viscosity is predetermined by the ratio  $\text{Me}_2\text{SiO}/\text{Me}_3\text{SiO}$  independent of starting material

Fig. 9: Equilibration reactions

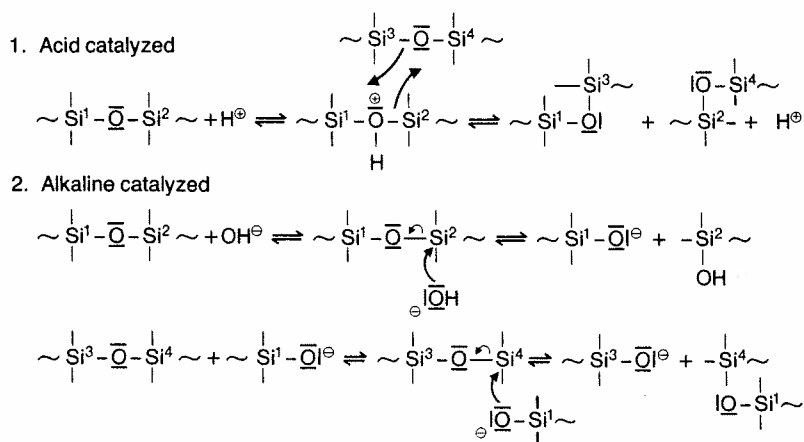


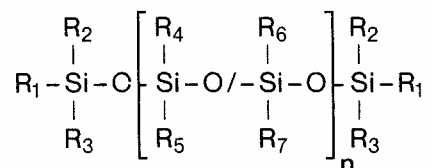
Fig. 10: Mechanism of equilibration



### Special Polysiloxanes

Production, properties and use

There are many possible variations for the preparation of special siloxanes (Fig. 11).



1. Substituents on silicon (homopolymer-copolymer)
2. Distribution of the substituents on silicon (random – block-like)
3. Chain length
4. Distribution of chain lengths (narrow – wide – homogeneous – heterogeneous)

Fig. 11: Possible variations

Polysiloxanes can be divided into two groups with respect to their use:

1. Silicone oils which can be used either directly or after modification for special applications -
2. Polysiloxanes for production of elastomers

#### Silicone Oils

The technically most important silicone oils are the  $\alpha,\omega$ -trimethylsiloxypolydimethylsiloxanes. They are produced by the reaction of oligodimethylsiloxanes with  $\text{Me}_3\text{SiO}$ -terminated short-chained dimethylsiloxanes, in the simplest case with hexamethyldisiloxane.

The reaction is catalyzed by strong acids or bases. A desired viscosity, or average chain length of the siloxane, is adjusted according to the ratio  $\text{Me}_2\text{SiO}/\text{Me}_3\text{SiO}$  in the reacting mixture (Fig. 9). It is remarkable that there is a linear relation between the logarithm of the average chain length and the logarithm of the viscosity (Fig. 12).

This relationship applies to a wide range of the viscosity and shows that dimethylsiloxanes with molecular weights over 100,000 still are capable of flowing. Organic polymers are already solid at considerably lower molecular weights. The reason for the low viscosities at relatively high molecular weights are the low intermolecular forces in the dimethylsiloxanes. This also explains the small temperature dependence of physical and mechanical properties of silicone oils and elastomers which is important for many technical applications. Similarly to the viscosity dependence on average chain length, a linear relationship for the temperature dependence of viscosity ( $\log \text{visc. [mPa} \cdot \text{s]} \sim 1/\text{temp. [K]}$ ) may be formulated (Fig. 13).

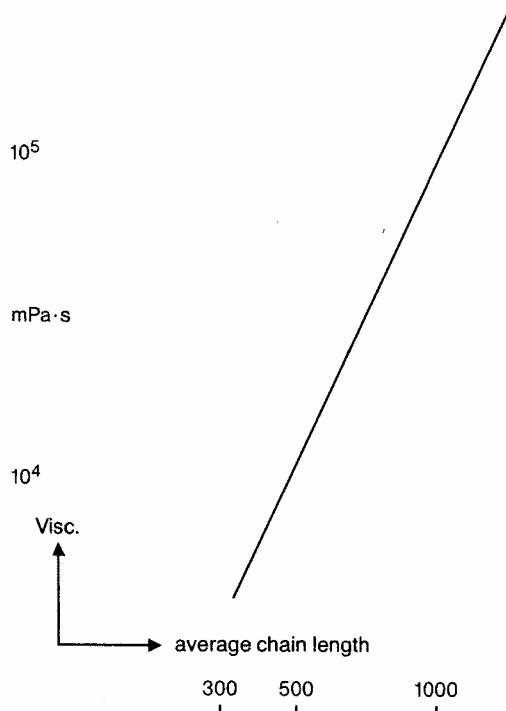


Fig. 12: Polydimethylsiloxane  
Average chain length – viscosity

The gradients of the straight lines are a measure of the intermolecular forces. If some of the methyl groups of dimethylsiloxane are replaced by phenyl or trifluoropropyl the temperature dependence of the viscosity is enhanced because the intermolecular forces increase markedly. This also applies, more or less, to other organic groups.

Therefore, if one speaks of the low intermolecular forces of siloxanes, one refers primarily to dimethylsiloxane. This may also be demonstrated by comparison of viscosity and average chain length for diorganosiloxanes with different substituents (Fig. 14).

A high viscosity at relatively low molecular weight implies strong intermolecular forces.

The intermolecular forces also affect the boiling points of distillable compounds. This may be demonstrated on the series  $\text{Me}_3\text{SiOSiMe}_3$ ,  $\text{Me}_3\text{SiOH}$ ,  $\text{HOH}$ . Although these three compounds have considerably different molecular weights, their boiling points are close to  $100^\circ\text{C}$  (Fig. 15).

The reason for this effect is the increase of intermolecular forces in the form of hydrogen bonds.

Finally, the low surface tension of  $21 \text{ mN/m}$  may be cited as an indication of the low intermolecular forces in polydimethylsiloxanes.

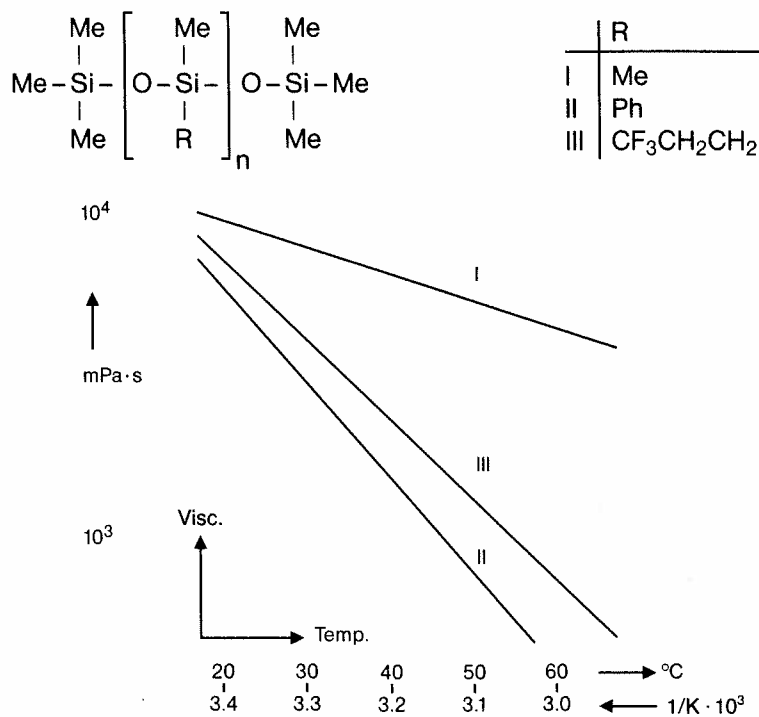


Fig. 13: Temperature dependence of the viscosity of polydiorganosiloxanes

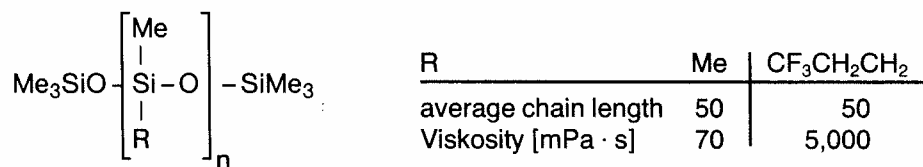


Fig. 14: Intermolecular forces – influence on the viscosity

	Me <sub>3</sub> Si-O-SiMe <sub>3</sub>	Me <sub>3</sub> Si-O-H	H-O-H
Mol. weight	162	90	18
Boiling point	~100°C	~100°C	100°C

Fig. 15: Intermolecular forces – influence on the boiling point

Of technical importance is the high thermal stability of dimethylsiloxane which is a consequence of the very strong siloxane bond. In the absence of oxygen, dimethylsiloxanes withstand temperatures above 200°C. By replacing some of the methyl groups by phenyl, the thermal stability may be considerably increased both in the presence and absence of air. The reason is the lower susceptibility to oxidation of phenyl relative to methyl and additional stabilization of the siloxane bond.

The low-temperature properties of polydimethylsiloxanes also are worth noting. High molecular weight dimethylsiloxane has a melting point near -40°C and a glass transition temperature of about -120°C. A few percent of bulky radicals can be used to break up the regularity of the dimethylsiloxane chain such that crystallization is inhibited. For example, this can be achieved with a small number of phenyl groups in the form of phenylmethyl- or diphenylsiloxane units or with a low content of siloxane branching on the siloxane chain.

Of technical importance are the good dielectric properties of silicone oils. The volume resistivity of dimethylsiloxane lies at  $10^{15} \Omega \cdot \text{cm}$  and the dielectric strength is 15 kV/mm.

Finally, the physiological inertness of silicone oils should be mentioned. Experiments with feeding to animals or skin tests caused no irritations or symptoms of intoxication.

The most important properties and applications of silicone oils are summarized in Fig. 16.

In addition to the applications in pure form, silicone oils also can be used in the formulation of emulsions, pastes and greases.

One group of silicone oils of growing importance may only be mentioned. These are the organofunctional siloxanes which will be discussed by Dr. Wewers.

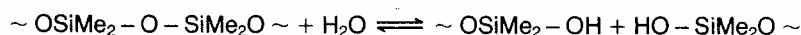
Properties:	thermal stability
	low-temperature flowability
	low viscosity changes vs. temperature
	high compressibility
	low surface tension
	hydrophobicity
	dielectric properties
	physiological inertness
Applications:	heat transfer medium
	dielectric fluid
	brake fluid
	hydraulic fluid
	water repellent agent
	antifoam additive
	release agent
	additive in skin creams

Fig. 16: Properties and applications of silicone oils

### Polymers used in silicone elastomers

For the conversion of a polymer into an elastomer by cross-linking of the siloxane chains, functional groups attached to the silicon directly or via organic radicals are required. Since subsequent articles will deal with the chemistry and technology of room temperature and elevated temperature cure, I shall restrict myself to a description of the production of the basic polymers required for these two types of vulcanization.

The silanol terminated polydimethylsiloxanes usually employed in room temperature vulcanized formulations (RTV), represent quantitatively the largest polymer group. Here, only the chain length which determines the density of cross-links is varied. Preferably, these polymers are produced by catalytic condensation of silanol terminated oligo-siloxanes. But high molecular weight  $\alpha,\omega$ -siloxanediols may be produced also by catalytic cleavage of siloxane links with water. As already mentioned, an equilibrium is established (Fig. 17).



linear or cyclic siloxane

Fig. 17: Siloxanol/H<sub>2</sub>O-equilibrium

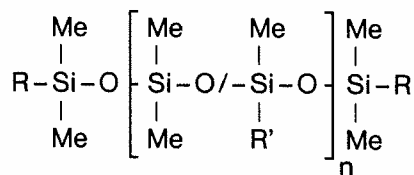
The reaction may proceed in either direction e.g., by removal of water (evaporation) or by water addition. Once the desired viscosity is achieved, the catalyst is deactivated.

Vinyl-functional polydimethylsiloxanes represent the second large polymer group for the production of silicone elastomers. The vinyl groups attached to the silicon may be located at the end and/or within the siloxane chain. What is varied is the vinyl content and the chain length of the polymers. Polymers with extremely high molecular weights with few vinyl groups are used for high temperature vulcanized silicone rubber (HTV), while polymers with shorter vinyl terminated chains are mainly employed in low temperature vulcanized rubber (LTV, RTV) (Fig. 18).

Polymers, which usually contain less than 1% ViMeSiO in the Me<sub>2</sub>SiO chain, are produced, for instance, by copolymerization of cyclic oligomeric dimethylsiloxanes and vinylmethylsiloxanes or by cocondensation of linear, OH-terminated oligomeric dimethylsiloxanes and vinylmethylsiloxanes. A random distribution of the few ViMeSiO units in the siloxane chain is provided by equilibration. Also, the introduction of terminal groups, and therewith the control of chain length, takes place by equilibration (Fig. 9). Short-chained RMe<sub>2</sub>SiO-terminated dimethylsiloxanes serve to supply the end groups – in the simplest case the corresponding disiloxanes (R = Vi, Me; n = 0) are used.

Polydimethylsiloxanes which have at least two methyl groups replaced by hydrogen atoms also play an important role in the formulation of silicone rubber. These SiH-functional siloxanes together with the vinyl-functional polymers are the basic materials for addition curing silicone rubber.

The employment of copolymers leads to silicone rubbers with special properties. Elastomers with increased thermal stability and improved low-temperature properties are obtained with phenyl containing copolymers, as previously discussed for silicone oils.



- |  |  |
|--|--|
| 1) R = Vi, Me<br>R' = Vi<br>$\text{Me}_2/\text{ViMe} > 100$<br>$\bar{N} = 4\,000 - 7\,000$ | HTV polymers<br>cross-linking by radicals    |
| 2) R = Vi<br>R' = <u>Me</u> , Vi<br>$\bar{N} = 200 - 1\,000$                               | RTV (LTV) polymers<br>addition cross-linking |

Partial substitution of  $\text{Me}_2\text{SiO}$  by  $\text{PhMeSiO}$ ,  
 $\text{Ph}_2\text{SiO}$  or  $\text{CF}_3\text{CH}_2\text{CH}_2(\text{Me})\text{SiO}$  leads to special  
 properties of the vulcanizates

Fig. 18: Vinyl-functional siloxanes for the production of elastomers

Dimethylsiloxane rubbers lose their elasticity below  $-40^\circ\text{C}$ , while elastomers with 8%  $\text{PhMeSiO}$  or 5%  $\text{Ph}_2\text{SiO}$  in the siloxane chain remain elastic to  $-100^\circ\text{C}$ . Since the thermal stability is improved up to  $250^\circ\text{C}$ , the range of application is about  $350^\circ\text{C}$ .

Another organic group of technical importance is the 3,3,3-trifluoropropyl group which increases the solvent resistance of silicone rubber.

The copolymers are produced, as already mentioned in the case of  $\text{ViMeSiO}$ , by equilibration of oligodimethylsiloxane with oligomers containing these special siloxane units.

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