THE CHEMISTRY OF SILICON POLYMERS

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In 1937, the Royal Society's Bakerian Lecture [1] was given by Professor F. S. Kipping on the organic chemistry of silicon. This interesting review of a lifetime of arduous and careful research concluded with the following words :

" Most if not all of the known types of organic derivatives of silicon have now been considered and it may be seen how few they are in comparison with those that are entirely organic : as moreover the few which are known are very limited in their reactions, the prospect of any immediate and important advance in this section of organic chemistry does not seem to be very hopeful."

From the standpoint of pure chemistry this conclusion was not unduly pessimistic, but it is now known that the academic work of this English scientist had already fired the imagination of several groups of industrial workers. This renewal of interest in organosilicon compounds may be traced to the following three factors : (1) the new ideas concerning the structure of high polymers, particularly the importance of functionality as enunciated by R. H. Kienle [2] and applied so fruitfully by W. H. Carothers ; [3] (2) the development of colourless, transparent polymers capable of being used as organic glasses ; (3) the need for electrical insulating materials capable of withstanding higher operating temperatures than the conventional organic varnishes so greatly relied upon by the electrical industry.

In the light of these factors, it was but natural and logical to re-examine the glue-like and glassy materials which Professor Kipping had so frequently observed, and which he recognised to be products of high molecular weight. Moreover, the high electrical resistance of quartz and the natural silicates, *e.g.*, mica, must have directed attention to the organosilicon compounds as promising dielectrics. These factors are seen to provide the background for the work of K. Andrianov,[4] M. Kotov,[5] E. G. Rochow and W. F. Gilliam,[6] and J. F. Hyde and R. C. DeLong,[7] each of which was sufficient to demon-

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[1] *Proc. Roy. Soc.*, 1937, *A*, **159**, 193.

[2] *J. Soc. Chem. Ind.*, 1936, **55**, 229T.

[3] *Trans Faraday Soc.*, 1936, **32**, 43.

[4] K. Andrianov and O. Gribanova, *Zhur. Obs. Khim.*, 1938, **8**, 552, 558 ; K. Andrianov, *J. Gen. Chem.* (*U.S.S.R.*), 1938, **8**, 1255 ; *Org. Chem. Ind.* (*U.S.S.R.*), 1939, **6**, 203.

[5] *Zhur. Prikl. Khim.*, 1939, **12** (10), 1435.

[6] *J. Amer. Chem. Soc.*, 1941, **63**, 798.

[7] *Ibid.*, p. 1194.

strate that a new and important development was at hand. It was not, however, until 1943 that the appearance of silicon-based polymers with certain novel properties indicated the measure of success attained in the United States. The new materials, called " silicones ", were marketed in the form of fluids, greases, resins, and elastomers. Methods of manufacture were not divulged for military and commercial reasons, but a large number of secret patent specifications was filed both here and in the United States. Further specifications continue to appear and from the mass of information contained therein the truth can only be approached by intelligent conjecture. Nevertheless, the appearance during the last two or three years of many scientific and technical publications makes it less difficult to survey the production, constitution, and properties of the new silicon polymers and the industrial materials which are derived therefrom. Reference is directed in particular to a recent book by E. G. Rochow, " An Introduction to the Chemistry of Silicones " (John Wiley, 1946).

Nomenclature.—The word " silicone " was originally used by Kipping to denote the silicon analogues of ketones (RR'Si:O, cf. RR'C:O) but he soon recognised that monomeric silicones are incapable of existence ; in fact, no compound containing the group Si:O is yet known. The original meaning is therefore misleading, for there is no chemical resemblance between the ketones and the silicones. By usage, the term silicone is now applied to almost all organosilicon compounds which contain at least one pair of silicon atoms linked by an oxygen atom. The accepted structure for the silicones consists of alternating silicon and oxygen atoms, in chains, rings, or networks, and as in all true organo-compounds the necessary hydrocarbon radicals must be linked directly to the silicon atoms. This definition excludes the partial hydrolysis products of ethyl silicate and silicon tetrachloride [8] which are known to contain such siloxane structures.

The nomenclature of organosilicon compounds has been confused owing to the common practice of deriving names from carbon analogues (*e.g.*, silicochloroform) and the use of both " silane " and " silicane " as roots. The American Chemical Society [9] has recently recommended a system of nomenclature, substantially that advocated by R. O. Sauer,[10] which is based on the following generalisations :

1. Silicon compounds of the general formula $R\cdot[R_2Si]_n\cdot SiR_3$, where R may be an organic radical, hydrogen, halogen, or an alkoxy- or aryloxy-group, and $n = 0, 1, 2, 3 \ldots$, are named as *silane* derivatives.
2. Organosilicon compounds containing the group Si–O–Si are named as *siloxane* derivatives.
3. Cyclic organosilicon compounds of the general formula $[R_2SiO]_n$ are named *cyclosiloxanes* (in English usage, cyclo*siloxanes*).
4. Organosilicon compounds containing one or more hydroxyl groups attached to silicon are named by adding the suffixes *-ol*, *-diol*, *-triol*, etc.
5. Organosilicon compounds of the general formula $R\cdot[R_2Si\cdot NH]_n\cdot SiR_3$ are named as *silazane* derivatives.

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[8] W. C. Schumb and A. J. Stevens, *J. Amer. Chem. Soc.*, 1947, **69**, 726.

[9] *Chem. and Eng. News*, 1946, **24**, 1233.

[10] *J. Chem. Educ.*, 1944, **21**, 303.

The following examples illustrate the application of these general principles :

Formula of compound.	Systematic name.
$SiMe_3Et$	Trimethylethylsilane
$SiMe_2Cl_2$	Dimethyldichlorosilane
$SiEt_3{\cdot}OH$	Triethylsilanol
$SiPh_2(OH)_2$	Diphenylsilanediol
$SiEt_3{\cdot}O{\cdot}SiEt_3$	Hexaethyldisiloxane
$SiPh_3{\cdot}OEt$	Triphenylethoxysilane
$SiPh_2(OH){\cdot}O{\cdot}SiPh_2{\cdot}OH$	Tetraphenyldisiloxane-1 : 3-diol
$[SiEt_2O]_3$	Hexaethyl*cyclo*trisiloxane

The proposed system of nomenclature has several advantages in addition to that of uniformity, for it is not only euphonious but usually shorter than any of the previously employed systems. It will be employed throughout this review.

Early Work on Organosilicon Compounds.—Before 1938, knowledge of organosilicon compounds was based principally on the work of Friedel, Crafts, and Ladenburg, and the Kipping research team at Nottingham. A detailed account is to be found in Newton Friend's text-book,[11] and reviews have been made by B. N. Dolgow,[12] F. S. Kipping,[1] and A. Bygdén.[13] This early work was concerned chiefly with the preparation and characterisation of a large number of representative organosilicon compounds and with the determination of their more obvious properties. Theoretical interest centred mainly in the degree of similarity between organosilicon compounds and their carbon analogues, and it is apparent that Kipping commenced his work purely with the object of preparing an asymmetric organosilicon compound suitable for resolution into its optical antipodes.

Methods of Preparation.—The methods for preparing organosilicon compounds are comparatively few and mostly consist in treating a silicon halide or an alkyl silicate with an organometallic compound or its equivalent. C. Friedel and J. M. Crafts [14] originated the use of silicon tetrachloride and diethylzinc for the preparation of tetraethylsilane and the various ethylchlorosilanes. The latter can be caused to react with other zinc alkyls to attach two or more dissimilar groups to the silicon atom :

$$1.\quad 2SiCl_4 + ZnEt_2 \longrightarrow 2SiEtCl_3 + ZnCl_2$$

$$2.\quad SiCl_4 + 2ZnEt_2 \longrightarrow SiEt_4 + 2ZnCl_2$$

$$3.\quad 2SiEtCl_3 + ZnMe_2 \longrightarrow 2SiMeEtCl_2 + ZnCl_2$$

A. Ladenburg [15] showed that alkyl orthosilicates can be employed in place of silicon tetrachloride :

$$Si(OMe)_4 + ZnEt_2 \longrightarrow SiEt_2(OMe)_2 + Zn(OMe)_2$$

and he also employed diphenyl- and ditolyl-mercury to prepare the corresponding arylchlorosilanes :

$$2SiCl_4 + HgPh_2 \longrightarrow 2SiPhCl_3 + HgCl_2$$

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[11] " A Text Book of Inorganic Chemistry ", edited by J. Newton Friend, Vol. XI, Part I, by Goddard and Goddard.

[12] *Uspekhi Khim.*, 1932, **1**, No. 5, 626.

[13] Inaug. Diss., Upsala, 1916.

[14] *Annalen*, 1863, **127**, 28.

[15] *Ber.*, 1873, **6**, 1029.

Tetra-arylsilanes[16] can be prepared from silicon tetrachloride and the appropriate aryl halide in presence of sodium, a process which doubtless depends on the intermediate formation of sodium aryls:

$$2Na + PhCl \longrightarrow NaPh + NaCl$$
$$SiCl_4 + 4NaPh \longrightarrow SiPh_4 + 4NaCl$$

The preparation of organosilicon compounds was greatly facilitated when F. S. Kipping[17] introduced the use of Grignard reagents in conjunction with silicon tetrachloride. This method permitted the introduction of a great variety of organic radicals, and enabled the highly reactive chlorosilanes to be prepared in quantity:

$$MgEtI + SiCl_4 \longrightarrow SiEtCl_3 + MgClI$$

By substituting ethyl silicate for silicon tetrachloride, the ethoxysilanes are obtained with equal facility:

$$Si(OEt)_4 + 2MgEtI \longrightarrow SiEt_2(OEt)_2 + 2Mg(OEt)I$$

In this reaction the Grignard reagent can be formed in contact with ethyl silicate without the agency of ether.[4]

It will be seen that all these methods permit the introduction of up to four hydrocarbon radicals either in one operation or by successive treatment with the same or different reagents. As a direct consequence, it follows that the products are usually mixtures of the possible compounds, and the separation of these mixtures is frequently difficult.

Vapour-phase alkylation has recently been effected by D. T. Hurd,[18] who passed the mixed vapours of silicon halides and alkyl halides over heated aluminium and zinc. For example, in contact with aluminium at 375° dimethyldichlorosilane and methyl chloride gave trimethylchlorosilane in 30% yield. It is suggested that alkylation involves the formation of zinc and aluminium alkyls.

Several novel methods of preparing organosilicon compounds have recently come to light. I. I. Shtetter[19] claims that under high pressure in presence of metallic chlorides and oxychlorides, silicon tetrachloride reacts with olefins:

$$CH_2{:}CH_2 + SiCl_4 \longrightarrow Cl{\cdot}CH_2{\cdot}CH_2{\cdot}SiCl_3$$

and with acetylene to give 2-chlorovinyltrichlorosilane:

$$CH{\vdots}CH + SiCl_4 \longrightarrow CHCl{:}CH{\cdot}SiCl_3$$

He also states that carbon monoxide reacts with silicon tetrachloride under similar conditions:

$$CO + SiCl_4 \longrightarrow Cl{\cdot}CO{\cdot}SiCl_3$$

These reactions would be of value for producing intermediates, but so far they have not been confirmed. However, it has been shown[20] that *n*-octyltrichlorosilane is obtainable in 99% yield from trichlorosilane and

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[16] A. Polis, *Ber.*, 1885, **18**, 1540.

[17] *Proc.*, 1904, **20**, 15.

[18] *J. Amer. Chem. Soc.*, 1945, **67**, 1545.

[19] Russian Cert. of Invention, 44934, filed 12.6.1935.

[20] L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 1947, **69**, 188.

oct-1-ene in presence of diacetyl peroxide. The following free-radical mechanism is advanced :

$$(CH_3{\cdot}CO{\cdot}O)_2 \longrightarrow 2CH_3{\cdot}CO{\cdot}O{\cdot} \longrightarrow 2CH_3^{\bullet} + 2CO_2$$

$$CH_3^{\bullet} + H{\cdot}SiCl_3 \longrightarrow CH_4 + Cl_3Si^{\bullet}$$

$$CHR{:}CH_2 + Cl_3Si^{\bullet} \longrightarrow R{\cdot}\dot{C}H{\cdot}CH_2{\cdot}SiCl_3$$

$$R{\cdot}\dot{C}H{\cdot}CH_2{\cdot}SiCl_3 + H{\cdot}SiCl_3 \longrightarrow R{\cdot}CH_2{\cdot}CH_2{\cdot}SiCl_3 + Cl_3Si^{\bullet}$$

Various claims[21] are made concerning reactions between silicon tetrachloride and hydrocarbons in the vapour phase and at elevated temperature.

An outstanding contribution to organosilicon chemistry has been made by W. I. Patnode and E. G. Rochow[22] in the discovery of a so-called direct synthesis. This consists in passing the vapour of an alkyl or aryl halide over a heated contact mass consisting of an intimate mixture of silicon with either copper or silver. The process is most successful with methyl chloride which yields a mixture of methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, and methyldichlorosilane ($SiHMeCl_2$), of which the first two comprise by far the greater proportion. The reaction temperature in this case is 280—350°, and in general, the lowest possible reaction temperature favours the production of compounds of the type SiR_2X_2. Copper is the most efficient agent for producing the methylchlorosilanes, and silver for the phenylchlorosilanes.[23] D. T. Hurd and E. G. Rochow have described convincing experiments[24] which show that methylcopper has a transient existence in the process, and its decomposition provides the methyl radicals for methylation :

$$2Cu + CH_3Cl \longrightarrow Cu{\cdot}CH_3 + CuCl$$

$$Cu{\cdot}CH_3 \longrightarrow Cu + CH_3^{\bullet}$$

Cuprous chloride, the other product of the initial reaction, is reduced by silicon at the temperature employed, and it is assumed that subchlorides of silicon are formed and that these accept methyl radicals to give the various methylchlorosilanes :

$$CuCl + Si \longrightarrow \equiv SiCl + Cu$$

$$\equiv SiCl + 3CH_3^{\bullet} \longrightarrow (CH_2)_3SiCl$$

The process can also be applied to the synthesis of vinyl- and allyl-chlorosilanes,[25] and methylbromosilanes.[26]

Separation of the methylchlorosilanes is particularly difficult on account of the proximity of their boiling points :

	$SiMe_4$.	$SiMe_3Cl$.	$SiMe_2Cl_2$.	$SiMeCl_3$.	$SiHMeCl_2$.	$SiCl_4$.
B.p. . . .	26°	57·6°	70°	66°	42°	57·6°

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[21] H. C. Miller and R. S. Schreiber, U.S.P. 2,379,821.

[22] W. I. Patnode, U.S.P. 2,380,997 ; E. G. Rochow and W. I. Patnode, U.S.P. 2,380,996 ; E. G. Rochow, *J. Amer. Chem. Soc.*, 1945, **67**, 963.

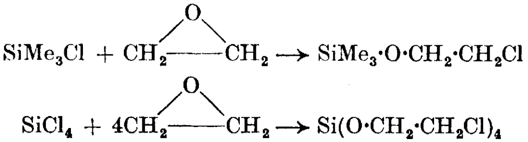
[23] E. G. Rochow and W. F. Gilliam, *ibid.*, p. 1772.

[24] *Ibid.*, p. 1057.

[25] D. T. Hurd, *ibid.*, p. 1813.

[26] W. F. Gilliam, R. N. Meals, and R. O. Sauer, *ibid.*, 1946, **68**, 1161.

Highly efficient fractionation (80—100 theoretical plates) is necessary to effect a separation. Another method for achieving this end depends on a general reaction of silicon halides with ethylene oxide. The corresponding 2-halogenoethoxysilanes are readily formed :[27]



$$SiMe_3Cl + CH_2\overset{O}{—}CH_2 \rightarrow SiMe_3{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$$

$$SiCl_4 + 4CH_2\overset{O}{—}CH_2 \rightarrow Si(O{\cdot}CH_2{\cdot}CH_2Cl)_4$$

and these can readily be separated by distillation owing to their widely different boiling points.

Much attention has been given to the halogenation of alkylchlorosilanes. The methylchlorosilanes are readily chlorinated photochemically or in the vapour phase at elevated temperature,[28] progressive substitution occurring at the same carbon atom. Fission of the carbon–silicon bond with alkaline hydrolytic agents occurs with increasing ease as the number of chlorine substituents is increased. Alkylfluorosilanes are obtainable from the corresponding chlorosilanes by treatment with antimony trifluoride [29] and zinc fluoride,[30] and also with hydrogen fluoride.[31] They can also be prepared from silicon tetrafluoride and Grignard reagents,[32] and by the direct method from alkyl fluorides.[30b] The alkylfluorosilanes are very stable thermally and are less readily hydrolysed than the corresponding chlorides.[31]

Such are the available methods for producing primary organosilicon compounds. Their suitability in any given instance depends on a combination of factors both technical and economic, and, although the Grignard synthesis has proved suitable for manufacture on an industrial scale, the direct method of production is likely to become increasingly important within its own range of utility.

It will be appreciated that primary organosilicon compounds can be produced in large number, and considerable progress in that direction has already been made. Organosilicon compounds containing one or more hydrolysable atoms or groups (commonly Cl or OEt) attached to the silicon atom are the essential intermediates for the production of silicones.

The organochlorosilanes are highly reactive and corrosive. They can only be preserved in complete absence of moisture, and special methods must therefore be employed when working with them. On the other hand, the organoethoxysilanes are pleasant materials to work with, and are particularly well adapted to small-scale investigation. They are accessible not only by synthesis from ethyl silicate using any of the standard methods, but also by the treatment of organochlorosilanes with alcohol.

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[27] R. O. Sauer and W. I. Patnode, *J. Amer. Chem. Soc.*, 1945, **67**, 1548.

[28] R. H. Krieble and J. R. Elliot, *ibid.*, p. 1810.

[29] H. S. Booth *et al.*, *ibid.*, 1946, **68**, 2650, 2652, 2655, 2658, 2660, 2662.

[30] (*a*) H. J. Emeléus and C. J. Wilkins, *J.*, 1944, 454 ; (*b*) A. E. Newkirk, *J. Amer. Chem. Soc.*, 1946, **68**, 2736.

[31] W. H. Pearlson, T. J. Brice, and J. H. Simons, *ibid.*, 1945, **67**, 1769.

[32] J. A. Gieurut, F. W. Sowa, and J. A. Nieuwland, *ibid.*, 1936, **58**, 897.

Hydrolysis of Pure Intermediates.—Monofunctional intermediates (R_3SiX) hydrolyse to the corresponding silanols which may be liquid, like trimethyl- and triethyl-silanols (b.p.s 98·6° and 154° respectively), or crystalline, like triphenylsilanol (m.p. 150—151·5°). Such silanols exhibit basic and acidic characteristics. For example, trimethylsilanol forms a sodio-derivative not only with sodium but also with 12N-sodium hydroxide solution, and it reacts with phosphoric and sulphuric acids to give tris(trimethylsilyl) phosphate (b.p. 85—87°/4 mm.)[33] and bis(trimethylsilyl) sulphate (b.p. 170°/12 mm.).[34] With more or less ease, the silanols pass into the corresponding disiloxanes:

$$SiR_3X \longrightarrow SiR_3{\cdot}OH \longrightarrow SiR_3{\cdot}O{\cdot}SiR_3$$

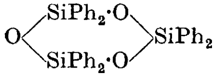
The simpler hexa-alkyldisiloxanes are mobile liquids which are attacked by phosphoric and sulphuric acids to give trialkylsilyl phosphates and sulphates.

The hydrolysis of aliphatic bifunctional intermediates (SiR_2X_2) normally leads to a complicated mixture of linear and cyclic condensation products of dialkylsilanediols, but these compounds can sometimes be isolated if the hydrolysis and subsequent treatment are carried out under suitably mild conditions:[35]

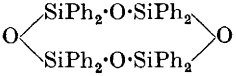
$$SiEt_2Cl_2 + 2H_2O \longrightarrow SiEt_2(OH)_2 + 2HCl$$
$$nSiEt_2(OH)_2 \longrightarrow HO{\cdot}SiEt_2{\cdot}[OSiEt_2]_n{\cdot}O{\cdot}SiEt_2{\cdot}OH + [SiEt_2{\cdot}O]_n$$

Dimethylsilanediol appears to be incapable of existence: its highly complex condensation products will be described in a later section.

Aromatic bifunctional intermediates are similarly hydrolysed, but it is comparatively easy to isolate the simple silanediols. The nature of the condensation products of diphenylsilanediol (m.p. 148°) was determined by F. S. Kipping.[36] When the silanediol is heated at 180° until effervescence ceases, hexaphenyl*cyclo*trisiloxane (I) is produced, but if a drop of pyridine is added to an acetone solution of the diol, crystals of octaphenyl*cyclo*tetrasiloxane (II) are gradually deposited.



(I; m.p. 188°.)



(II; m.p. 200°.)

$$HO{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}OH$$

(III; m.p. 113°.)

$$HO{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}OH$$

(IV; m.p. 112°.)

$$HO{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}OH$$

(V; m.p. 128·5°.)

Addition of ammonia solution to an acetone solution of diphenylsilanediol yields tetraphenyldisiloxanediol (III) and hexaphenyltrisiloxanediol (IV). These have almost identical melting points but they can be separated owing to the solubility of the simpler compound in 5% potassium hydroxide solution. All these compounds can be degraded, ultimately to the potas-

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[33] R. O. Sauer, *ibid.*, 1944, **66**, 107.

[34] L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *ibid.*, 1946, **68**, 2282.

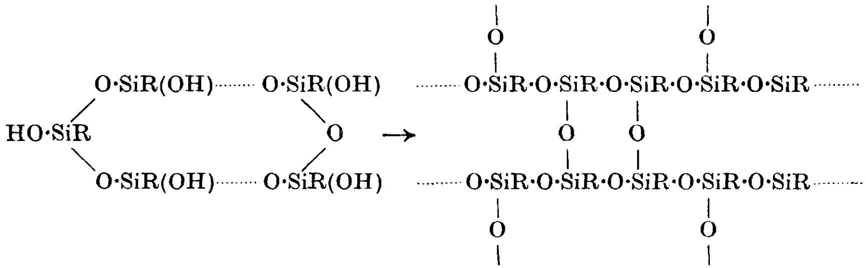
[35] P. A. DiGiorgio, L. R. Sommers, and F. C. Whitmore, *ibid.*, p. 344.

[36] *J.*, 1912, **101**, 2108; F. S. Kipping and R. Robison, *J.*, 1914, **105**, 484.

sium derivative of diphenylsilanediol, by hydrolysis with potassium hydroxide solution; by stopping the process of hydrolysis at an early stage, (IV) can be obtained from (I), and octaphenyltetrasiloxanediol (V) from (II). These observations have been confirmed and extended by C. A. Burkhard *et al.*[37] and by J. F. Hyde *et al.*[38] *X*-Ray diffraction methods have established the nature of (I) and (II) beyond any shadow of doubt. It was shown by J. F. Hyde *et al.*[38] that (I) exists in orthorhombic and monoclinic forms, and that (II) has three distinct modifications and also forms a crystalline compound with benzene.

The trifunctional organosilicon intermediates ($SiRX_3$) are hydrolysed to amorphous powders or hard brittle solids which have no definite melting point. Some are in fact described as being infusible. The work of J. A. Meads and F. S. Kipping[39] shows that these substances are condensation products derived from the hypothetical monosubstituted silanetriols, $SiR(OH)_3$. It must be concluded that they will consist of linear, cyclic, and cross-linked structures depending on the conditions of hydrolysis, and that the end-product of the dehydration process (VII) must be cross-linked, insoluble, and infusible:

$$SiRX_3 \longrightarrow (HO)_2SiR{\cdot}[O{\cdot}SiR(OH)]_n{\cdot}O{\cdot}SiR(OH)_2 \longrightarrow$$



(VI.) (VII.)

The facility with which cross-linked structures are formed may be judged by observations due to W. I. Patnode and D. F. Wilcock.[40] They obtained ether-soluble products by treating a dilute ethereal solution of methyltrichlorosilane with water, but their attempts to remove the solvent, even by evaporation at low temperature, caused the formation of insoluble material.

It will be seen that by judicious admixture of intermediates, having various functionalities, it must be possible to vary the nature of the hydrolysis products and to obtain industrially useful materials. This is the fundamental principle of silicone chemistry.

The Methylsiloxane Polymers.—On hydrolysis, both dimethyldichloro- and dimethyldiethoxy-silanes give rise to colourless oils having the empirical

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[37] C. A. Burkhard, *J. Amer. Chem. Soc.*, 1945, **67**, 2173; C. A. Burkhard, B. F. Decker, and D. Harker, *ibid.*, p. 2174.

[38] J. F. Hyde, L. K. Frevel, H. S. Nutting, P. S. Petrie, and M. A. Purcell, *ibid.*, 1947, **69**, 488.

[39] *J.*, 1914, **105**, 679.

[40] *J. Amer. Chem. Soc.*, 1946, **68**, 358.

formula C_2H_6OSi.[40, 41] These contain roughly equal amounts of cyclic polymers $[Me_2SiO]_n$ and polymeric linear diols $HO{\cdot}SiMe_2{\cdot}[O{\cdot}SiMe_2]_n{\cdot}O{\cdot}SiMe_2{\cdot}OH$, which may be separated by distillation up to 250°/1 mm. The more volatile material is substantially of cyclic character and by careful fractionation can be split up into polymers containing from 3 to 9 or more units in the ring (see Table I). The proportion of cyclic to linear polymers varies somewhat according to the conditions of hydrolysis ; for example, hydrolysis in presence of concentrated hydrochloric acid promotes the formation of cyclic polymers, whereas ammonia solution leads to a greater proportion of linear products.[40] The viscous linear polymerides (b.p. > 250°/1 mm.) cannot be distilled, for at high temperature they undergo rearrangement and minor dehydration to give the simpler cyclic polymers. This change occurs from 350° upwards in an inert atmosphere and may be taken virtually to completion. The distribution of the cyclic polymers obtained by pyrolysis is different from that in the initial distillate (see Table II), and it will be seen that pyrolysis of the non-volatile dimethylsiloxane polymers provides a good method for preparing the lower cyclic polymers and particularly the trimer.[40] J. F. Hyde *et al.*[41] claim that the thermal rearrangement is facilitated by addition of a small amount of sodium or potassium hydroxide. The lower polymers can be converted into higher polymers by treatment with sulphuric acid.[40] The latter attacks the siloxane bonds, doubtless by formation of readily hydrolysable sulphates, and it follows that the proportion of sulphuric acid governs the ultimate average molecular

TABLE I

Cyclic polymers of dimethylsiloxane, $[(CH_3)_2SiO]_n$

No. of units in polymer:	3.	4.	5.	6.	7.	8.	9.
M.p.	64·5°	17·4°	− 44°	− 3·0°	− 3·2°	31·5°	
B.p./760 mm. . . .	133°	171°	204·5°	236°			
B.p./20 mm.. . . .					147°	168°	188°
$d^{25°}_{4°}$			0·9531	0·9613	0·9664	Solid	
$n^{25°}$			1·3958	1·3996	1·4118	1·4139	
η (centistokes at 25°) .			3·87	6·62	9·47	13·23	

TABLE II

Distribution of polymers

No. of units in polymer :	3.	4.	5.	6.	> 6.
Initial distillate (% by volume) .	1	82	12	3	2
Pyrolysate (% by volume) . . .	44	24	9	10	13

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[41] M. J. Hunter, J. F. Hyde, E. L. Warwick, and H. J. Fletcher, *ibid.*, p. 667 ; R. McGregor and E. L. Warwick, U.S.PP. 2,380,057, 10.7.1945 ; 2,384,384, 26.2.1945.

weight of the product, which is a rubbery gel. D. W. Scott[42] has examined this rubbery gel by fractional precipitation from a mixture of ethyl acetate and acetone, followed by osmotic-pressure measurements. He concluded that the molecular weights of the highest linear polymers (see Table III) are much higher than would be expected from their plastic properties arguing by analogy with other polymers such as poly*iso*butylene.

Partial hydrolysis of dimethyldichlorosilane yields a series of linear $\alpha\omega$-dichloropolydimethylsiloxanes[40] (see Table IV). These compounds still contain reactive chlorine atoms and so may be hydrolysed by water to linear and cyclic polydimethylsiloxanes. They appear to be valuable intermediates for synthesising more complicated silicones.

TABLE III

High linear polymers of dimethylsiloxane

Fraction.	Nature.	% of whole.	Number average mol. wt.
A. . . .	Elastic	17	$2{\cdot}8 \times 10^6$
B. . . .	Soft and plastic	14	$1{\cdot}5 \times 10^6$
C. . . .	,, ,, ,,	18	$6{\cdot}1 \times 10^5$
D. . . .	Very plastic	27	$2{\cdot}9 \times 10^5$
E. . . .	Viscous liquid	15	

TABLE IV

Properties of αω-dichloropolydimethylsiloxanes

Compound.	B.p. (760 mm.).	B.p. (20 mm.).	M.p.
$Cl{\cdot}[SiMe_2O]_1{\cdot}SiMe_2Cl$	138°	41°	− 37°
$Cl{\cdot}[SiMe_2O]_2{\cdot}SiMe_2Cl$	184	79	− 53
$Cl{\cdot}[SiMe_2O]_3{\cdot}SiMe_2Cl$	222	111	− 62
$Cl{\cdot}[SiMe_2O]_4{\cdot}SiMe_2Cl$	—	138	*ca.* − 80
$Cl{\cdot}[SiMe_2O]_5{\cdot}SiMe_2Cl$	—	161	*ca.* − 80

When a mixture of trimethylchlorosilane, $SiMe_3Cl$, and dimethyldichlorosilane, $SiMe_2Cl_2$, is hydrolysed, hexamethyldisiloxane and cyclic dimethylsiloxane polymers are formed, but a considerable proportion of intercondensed products is also produced. These have the general formula $SiMe_3{\cdot}[O{\cdot}SiMe_2]_n{\cdot}O{\cdot}SiMe_3$ and consist of chains of dimethylsiloxane units terminated by trimethylsilyl units.[40] The proportion of trimethylchlorosilane in the original mixture plays an important part in governing the average molecular complexity of the hydrolysis product. A more satisfactory method of preparing these chain-stoppered compounds is by equilibrating a mixture of dimethylsiloxane polymers and hexamethyldisiloxane in presence of sulphuric acid. This process is carried out simply

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[42] *J. Amer. Chem. Soc.*, 1946, **68**, 1877.

by agitation in the cold for sixteen hours, and it is apparent that the siloxane bonds are broken and reformed until an equilibrium distribution of chain length has been established. This distribution is of a narrow order, and is governed by the relative proportions of the initial silicones. Some properties of the first members of this series of polymers are shown in Table V, which includes hexamethyldisiloxane as the first member.

TABLE V

Chain-stoppered dimethylsiloxane polymers, $SiMe_3{\cdot}O{\cdot}[SiMe_2{\cdot}O]_n{\cdot}SiMe_3$

Polymer (values of n) :	0.	1.	2.	3.	4.	5.	6.	7.
B.p./mm.	99·5°/760	152°/760	192°/760	229°/760	142°/20	165°/20	153°/5·1	173°/4·9
M.p.	− 68°	− 86°	− 76°	− 84°	− 59°	− 78°	− 63°	
$\eta^{25°}$ (c.-stks)	0·65	1·04	1·53	2·06	2·63	3·24	3·88	
$d^{25°}_{25°}$	0·7606	0·8182	0·8516	0·8710	0·8873	0·9004	0·9078	
$n^{25°}$	1·3478	1·3822	1·3872	1·3902	1·3922	1·3940	1·3952	
$\gamma^{25°}$ (dynes/cm.)	14·82	16·05	16·52	17·08	17·42	17·61	18·03	

The higher members of the series have been described by M. G. Hunter, E. L. Warwick, J. F. Hyde, and C. C. Currie.[43]

TABLE VI

Higher chain-stoppered dimethylsiloxane polymers

Polymer (approx. value of n):	14.	23.	48.	90.	150.	210.	250.	350.
M	1200	1900	3700	6700	11,300	15,800	19,000	26,400
$\eta^{25°}$ (c.-stks)	10	20	50	100	200	350	500	1000
$d^{25°}_{4°}$	0·937	0·947	0·952	0·965	0·968	0·969	0·969	0·970
$n^{25°}$	1·399	1·400	1·402	1·403	1·4031	1·4032	1·4033	1·4035
A.S.T.M. pour-point	− 67°	− 60°	− 55°	− 55°	− 53°	− 50°	− 50°	− 50°

The molecular weights were estimated by A. J. Barry [44] from measurements of intrinsic viscosity, osmotic pressure, and light scattering.

D. F. Wilcock [45] has examined the effect of chain-branching upon the properties of these polymers. Branched-chain polymers were obtained by hydrolysing mixtures of trimethylchlorosilane, dimethyldichlorosilane, and methyltrichlorosilane, care being taken to include an additional amount of trimethylchlorosilane to counterbalance the greater functionality contribution due to methyltrichlorosilane. The product was then equilibrated with sulphuric acid, and fractionally distilled. The branched-chain polymers have lower melting points and viscosities than the corresponding straight-chain polymers.

Various condensed ring methylpolysiloxanes have been prepared by

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[43] *Ibid.*, p. 2284.

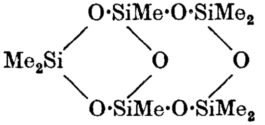
[44] *J. Appl. Physics*, 1946, **17**, 1020.

[45] *J. Amer. Chem. Soc.*, 1947, **69**, 477.

D. W. Scott,[46] who hydrolysed an equimolecular mixture of dimethyldichlorosilane and methyltrichlorosilane, and submitted the resultant viscous, translucent liquid to thermal rearrangement. Between 350° and 600° two-thirds of the material volatilised to give an amber liquid together with some crystalline solid. The latter was separated and the liquid fractionally distilled to give the following compounds:

Compound:	$Si_5O_6Me_8$.	$Si_6O_7Me_{10}$.	$Si_6O_8Me_8$.	$Si_7O_9Me_{10}$.	$Si_8O_{11}Me_{10}$.	$[CH_3{\cdot}SiO_{3/2}]_{2n}$.
M.p. . .	118°	51°	119°	150°	139°	Sublimes

All of these compounds must contain two or more fused siloxane rings, and alternative structures are possible for all except the first, which is

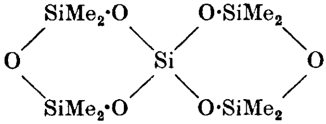


(VIII.)

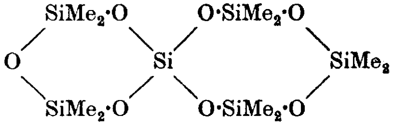
octamethyl*bicyclo*[5 : 3 : 1]pentasiloxane (VIII). Similar treatment of a mixture of dimethyldichlorosilane (5 mols.) and silicon tetrachloride (1 mol.) gave four compounds:

Compound:	$Si_5O_6Me_8$.	$Si_6O_7Me_{10}$.	$Si_7O_8Me_{12}$.	$Si_8O_9Me_{14}$.
M.p.	121°	57°	31°	− 12°

The first two are considered to be octamethyl*spiro*[5 : 5]pentasiloxane (IX) and decamethyl*spiro*[5 : 7]hexasiloxane (X) respectively.



(IX.)



(X.)

Methyldichlorosilane ($SiHMeCl_2$), a product of the direct synthesis, can be hydrolysed in presence of an inert solvent to cyclic liquid polymers of general formula $(CH_3{\cdot}SiHO)_n$. The tetramer (b.p. 135°), pentamer (b.p. 169°), and hexamer (b.p. 93°/21 mm.) have been isolated by R. O. Sauer, W. J. Schieber, and S. D. Brewer,[47] but not the trimer. These materials are less stable than the cyclic polydimethylsiloxanes, and are easily transformed into higher polymers. Chain-stoppered linear compounds of general formula $SiMe_3O{\cdot}[SiHMeO]_n{\cdot}SiMe_3$ can also be prepared by treating the cyclic polymers with hexamethyldisiloxane in the presence of sulphuric acid.

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[46] *J. Amer. Chem. Soc.*, 1946, **68**, 356.

[47] *Ibid.*, p. 962.

The physical properties of methylsiloxane fluids have been extensively studied,[48] and notable differences have been observed between them and ordinary liquids. The influence of temperature on the viscosity of methylsilicone fluids is surprisingly small; for example, the viscosities at 38° and 100° are in the ratio of 5 : 2 whereas the corresponding ratio for a petroleum oil of viscosity index 100 is 10 : 1. This suggests that the molecular cohesive forces are of a low order, a conclusion which may also be drawn from the low boiling points of the cyclic dimethylsiloxane polymers compared with those of hydrocarbons of similar molecular weight, and from their low surface tensions.

H. A. Kierstead and J. Turkevitch [49] have derived an Arrhenius type of equation for fluidity, $\phi = Ae^{-E/RT}$, from which J. F. Hyde *et al.*[41] have calculated the energy of activation for viscous flow in the case of the cyclic dimethylsiloxane polymers (see Table VII).

TABLE VII

Energy of activation of cyclic dimethylsiloxane polymers

Dimethylsiloxane units.	$A \times 10^{-3}$.	E (cals.).	M.
4	7·94	3060	296·5
5	7·08	3300	370·6
6	8·05	3720	444·8
7	8·65	3960	518·9
8	13·87	4430	593·0
*cyclo*Pentane . . .	5·554	1878	70·1
*cyclo*Hexane . . .	15·21	2905	84·2

The gradual change of energy of activation for viscous flow with increase in molecular weight is to be contrasted with the rapid change shown by cyclic hydrocarbons. Similar conclusions are drawn by D. F. Wilcock,[49a] who has compared the energy of vaporisation with the activation energy for viscous flow and has deduced therefrom that the unit of flow in silicone fluids of high molecular weight is $[SiMeO]_7$. This is somewhat larger than the unit of flow for hydrocarbons which contains about twenty carbon atoms, but the energy of activation for viscous flow in the case of hydrocarbons is about 70% greater than that for the linear methylpolysiloxanes, and so the siloxane chains must move about more readily. In other words, the forces of attraction between siloxane chains are less than those between hydrocarbon chains of similar molecular weight.

Mention has already been made of the ionic character of the siloxane

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[48] C. B. Hurd, *ibid.*, p. 364; M. J. Hunter, E. L. Warwick, J. F. Hyde, and C. C. Currie, *ibid.*, p. 2284; M. J. Hunter, J. F. Hyde, E. L. Warwick, and H. J. Fletcher, *ibid.*, p. 667; D. F. Wilcock, *ibid.*, p. 691; W. I. Patnode and D. F. Wilcock, *ibid.*, p. 358; E. B. Baker, A. J. Barry, and M. J. Hunter, *Ind. Eng. Chem.*, 1946, **38**, 117; A. J. Barry, *J. Appl. Physics*, 1946, **17**, 1020; R. O. Sauer and D. J. Mead, *J. Amer. Chem. Soc.*, 1946, **68**, 1794.

[49] *J. Chem. Physics*, 1944, **12**, 24. [49a] *J. Amer. Chem. Soc.*, 1946, **68**, 691.

bond in connection with equilibration. W. L. Roth [50] has examined the crystal structure of octamethyl*spiro*[5 : 5]pentasiloxane (IX), and has deduced that methyl groups attached to silicon atoms are free to move with large amplitude at a fixed radius, that silicon atoms carrying two methyl groups are hindered sterically, and that the silicon atoms are free to move in polysiloxane rings as in a ball-and-socket joint. This is considered to be supporting evidence for the ionic character of siloxane bonds. From the dipole moment of hexamethyldisiloxane, R. O. Sauer and D. J. Mead [51] have deduced that the bond angle for Si–O is 160° ± 15°.

Silicones containing Other Radicals.—In the space of this review it is only possible to discuss in very general terms the silicones containing radicals other than methyl and phenyl. Many of these materials were prepared in the classical period of organosilicon chemistry and are described in previous reviews, but they have been subjected to a more critical examination in the search for useful materials. The importance of the radical in governing the properties of silicones need hardly be stressed. Diethylsilicone, one of the first silicones to be produced, has been re-examined by T. Alfrey, F. J. Honn, and H. Mark,[52] who noticed that it reacts with phosphoric oxide to give a hydrolysable cross-linked material. F. J. Hyde and R. C. DeLong [7] describe the preparation and hydrolysis of diethyl-,

TABLE VIII

Physical properties of silicone fluids

$\eta^{25°}$ (c.-stks.).	η temp. coeff.*	F.p.	B.p. at mm.		Flash point, °F.	$d^{25°}_{25°}$.	1000κ.†	$n^{25°}$.
0·65	0·31	− 68°	99·5°	760	30°	0·761	1·598	1·3748
1·0	0·37	− 86	152	760	100	0·818	1·451	1·3822
1·5	0·46	− 76	192	760	160	0·852	1·312	1·3872
2·0	0·48	− 84	230	760	195	0·871	1·247	1·3902
3·0	0·51	− 70	70—100	0·5	225	0·896	1·170	1·394
5·0	0·55	− 70	120—160	0·5	270	0·918	1·095	1·397
10	0·57	− 67	> 200	0·5	350	0·940	1·035	1·399
20	0·59	− 60	> 200	0·5	520	0·950	1·025	1·400
50	0·59	− 55	> 250	0·5	540	0·955	1·000	1·402
		A.S.T.M. pour-point.	Volatility (%) on heating for 48 hours at 200°.					
100	0·60	− 55°	< 2		600	0·968	0·969	1·4030
200	0·62	− 53	< 2		615	0·971	0·968	1·4031
350	0·62	− 50	< 2		625	0·972	0·966	1·4032
500	0·62	− 50	< 2		625	0·972	0·965	1·4033
1000	0·62	− 50	< 2		640	0·973	0·963	1·4035

* Temperature coefficient $= 1 - \eta^{210°F}/\eta^{100°F}$.
† κ = expansion coefficient per °c. (25—100°).

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[50] *J. Amer. Chem. Soc.*, 1947, **69**, 474.

[51] *Ibid.*, 1946, **68**, 1794.

[52] *J. Polym. Sci.*, 1946, **I**, 102.

phenylethyl-, and phenylmethyl-dichlorosilanes, and K. A. Andrianov [4, 53] has studied silicones containing ethyl, *iso*butyl, *iso*amyl, and *n*-hexyl radicals. By hydrolysing triethoxyalkylsilanes with an insufficiency of water he obtained glassy, resinous materials which were soluble in organic solvents. These belong to the series $(EtO)_2SiR{\cdot}[O{\cdot}SiR(OEt)]_n{\cdot}O{\cdot}SiR(OEt)_2$.[4] Diethoxydiethylsilanes, similarly treated, yield linear polymers of general formula $EtO{\cdot}SiR_2{\cdot}[O{\cdot}SiR_2]_n{\cdot}O{\cdot}SiR{\cdot}OEt$. Polymers containing up to 10 silicon atoms could be obtained by varying the amount of water.[53]

All these silicones have good dielectric properties, and are unusually stable when heated in air. The methyl- and phenyl-silicones are the most resistant to oxidation ; as might be expected, the alkyl silicones become more prone to oxidation as the carbon chain is lengthened and the material becomes more paraffinic. Of the silicones, those containing only methyl groups are unique in that all the carbon atoms are attached to silicon atoms : in the methyl silicones the silicon content is at a maximum.

Industrial Significance of Silicones

Because of their special properties, the silicones have found application in various technological fields. They are marketed in such forms as fluids, lubricants, greases, elastomers, and resins. Furthermore, certain silicones possess the interesting property of water-repellency, and some organosilicon compounds are able to impart this property to other materials. The various industrial silicone preparations and their uses are now reviewed.

Silicone Fluids.—The fluids consist of water-white, inert liquids having a wide range of viscosity and molecular complexity. As a class, they are characterised by high thermal stability and small change of viscosity with temperature. A summary of their physical properties is given in Table VIII.[54] Comparison of Tables V and VI with VIII indicates that these commercial fluids are almost certainly end-stoppered dimethylsiloxane polymers containing negligible amounts of cyclic compounds. Because of their small viscosity–temperature coefficient and wide fluid range, these liquids are advocated for use in hydraulic systems [55] and for damping instruments. Their stability at elevated temperatures renders them suitable for employment in thermally responsive devices and high-temperature baths,[56] and those of extremely low vapour pressure can be successfully used in diffusion pumps.[57] Other interesting applications are as mould-release agents, particularly in rubber technology, and for breaking emulsions.[58] Certain grades are remarkably effective in reducing the foaming tendency of hydrocarbon oils, even in concentrations as low as 1 in 10^6.[59] The silicone fluids are unusually compressible, and this fact is

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[53] *J. Gen. Chem.* (*U.S.S.R.*), 1946, **16,** (78), 487, 633, 639.

[54] S. L. Bass, *Chem. and Ind.*, 1947, **14** and **15,** 171 and 189.

[55] V. G. Fitzsimmons, D. L. Pickett, R. O. Militz, and W. A. Zisman, *Trans. Amer. Soc. Mech. Eng.*, 1946, **68,** 361.

[56] L. M. White, *Ind. Eng. Chem. Anal.*, 1947, **19,** 432.

[57] G. P. Brown, *Rev. Sci. Instr.*, 1945, **16,** 316.

[58] Anon., *Chem. and Eng. News*, 1946, **24,** 1260.

[59] R. G. Larsen and H. Diamond, U.S.P. 2,375,007.

likely to be of value in the design of shock-absorbing equipment,[60] particularly for aircraft. Small mechanisms that must operate at low temperatures can be lubricated with the lighter silicone oils, while at the other end of the temperature scale, lubrication can be successfully accomplished up to 250°. It is understood that the correct choice of metals for bearing and shaft is important, some combinations being unsuitable for lubrication with silicones.[61] The electrical properties of the less volatile fluids suggest their use as liquid dielectrics, particularly in the construction of condensers; for example, the dielectric constant at 20° and 1000 cycles is 2·7—2·8, falling linearly with temperature to 2·43—2·48 at 110°.[62] Power factors are of the order of 0·0001 at 1000 cycles with little change up to 10^7 cycles, and breakdown voltages are about 350 volts per mil.

Silicone Rubbers.—Mention has already been made of the rubbery gel consisting of high polymers of dimethylsiloxane which was prepared and examined by D. W. Scott.[42] This material can be obtained from lower polymers by heating with ferric or aluminium chloride,[63] and can be converted into rubber-like products by heating with suitable agents for producing cross-linkage. Unlike the vulcanising agents used for natural rubber, the agents for cross-linking silicone gum are powerful oxidising substances such as organic peroxides,[64] and it is presumed that some of the methyl groups are oxidised away, to enable siloxane bridges to be formed. The gum is compounded with inert fillers and the appropriate amount of an organic peroxide, and is then moulded or extruded at 150° to bring about dimensional stability. The full strength of the material is subsequently attained by a lengthy cure at 250°. Compounded silicone pastes can also be used for coating and laminating.

This interesting elastomer has excellent heat and oxygen resistance, and has been employed as a gasket material for joints exposed to temperatures of 200° or more. It is also used as insulation on heat-resistant electrical wiring. The comparatively low tensile strength (up to 750 lbs./sq. in.), combined with poor resistance to abrasion and tearing, have limited its application. It also suffers from a fairly high compression set at elevated temperature, but further development will doubtless lead to considerably improved properties.

Silicone Greases.—A number of silicone lubricants of grease-like consistency are produced, chiefly for lubricating ball-bearings exposed to unusually high temperatures. Like the fluids, these greases show high thermal stability and chemical inertness. Their low volatility is a striking and important feature; typical greases were heated at 175° for 40 hours and were still serviceable as lubricants after suffering weight losses of only 3·3—4·6%. Under the same conditions, petroleum-based lubricants had

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[60] B. E. O'Connor, *J. Soc. Auto. Eng.*, 1946, **54**, 46.

[61] V. G. Fitzsimmons, D. L. Pickett, R. O. Militz, and W. A. Zisman, *Trans. Amer. Soc. Mech. Eng.*, 1946, **68**, 361; J. E. Brophy, R. O. Militz, and W. A. Zisman, *ibid.*, p. 355.

[62] E. B. Baker, A. J. Barry, and M. J. Hunter, *Ind. Eng. Chem.*, 1946, **38**, 1117.

[63] D. V. N. Hardy, *Endeavour*, 1947, **6** (21), 34.

[64] British Thomson Houston Co., B.P. 592,018.

lost 35—58% of their weight.[54] Some of these greases are compounded with materials like graphite and lithium soaps and are claimed to be suitable for ball-bearings at speeds up to 10,000 r.p.m. and over a temperature range of – 75° to 200°.[65]

Pride of place among silicone greases must be given to the so-called ignition sealing compound [66] which is produced on a very large scale. It is one of the most easily made of the silicones, being produced by hydrolysis of a mixture of silicon tetrachloride, dimethyldichlorosilane, and methyltrichlorosilane, or their corresponding ethoxy-compounds. It is a colourless translucent grease which suffers practically no change of consistency between – 40° and 200°. Applied to the spark-plug wells and the disconnectable junctions of aircraft ignition harnesses, it has proved effective in preventing short circuits arising from the deposition of water films and in eliminating engine failure due to corona discharge at high altitudes. It will be appreciated that this compound breaks down largely into silica, and it is therefore not liable to tracking, a serious disadvantage of purely organic insulations. The extensive use of ignition-sealing compound has been an important factor in ensuring safe flying at high altitudes. It proved to have other useful properties ; for example, it is an excellent lubricant and preservative for rubber, and is an effective lubricant for the moving parts of rotating antennæ.

Yet other forms of silicone grease are produced for lubricating stopcocks, plug-cocks, and other sliding surfaces. Because of their low volatility, ability to wet a wide variety of surfaces, and high film strength they are particularly useful in high-vacuum systems.

Silicone Resins.—Hydrolysis of trifunctional organosilicon compounds leads ultimately to intractable cross-linked materials ; so far as is known, these are unsuitable for industrial application. It is necessary to control the amount of cross-linkage in order to develop the desired properties for specific uses. It will be apparent that the requisite amount of cross-linkage can only be found by trial, and that it will vary according to the nature of the organic radicals present. Such resins are usually produced by one of three methods : (*a*) pure bi- and poly-functional intermediates are admixed, hydrolysed, and condensed to a stage short of the gel point in order to retain solubility in organic solvents ; [67] (*b*) mixtures of intermediates are prepared by synthesis, and are hydrolysed and condensed as above ; (*c*) the hydrolysis product of a bifunctional intermediate is partly oxidised at a suitable temperature by blowing air through it either in presence [7] or in absence of a catalyst.

Method (*b*) cannot provide the same measure of control as (*a*), and must yield somewhat different products owing to the inevitable inclusion of minor amounts of mono- and tetra-functional intermediates. The scope of method (*a*) can be widened by the inclusion of monofunctional material,[68]

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[65] T. A. Kauppi and W. W. Pedersen, *Lubrication Eng.*, 1947, **3**, 17 ; *Nat. Petr. News*, 1945, 5th Dec.

[66] S. L. Bass and T. A. Kauppi, *Proc. Inst. Radio Eng.*, 1945, **33**, 441.

[67] E. G. Rochow, U.S.P. 2,258,218.

[68] *Idem*, U.S.P. 2,258,220.

and simple consideration of the principles involved makes it apparent that resins can theoretically be produced from mono- and tri-functional compounds alone, or even from mono- and tetra-functional intermediates. The judicious inclusion of end-stopping material controls the ability of the poly-functional groups to cross-link.

The various types of resin, the methods used in their production, and their uses are covered by a continually growing patent literature which it is impossible to summarise within the scope of this review. It must suffice to indicate what appear to be the most useful types of resins and to state their known applications.

Methylsilicone resins were first described by E. G. Rochow and W. F. Gilliam,[6] who found that useful products were obtainable by methods (*a*) and (*b*) with Me : Si ratios between 1·3 and 1·5 (see Table IX). The initial hydrolysis products were colourless oily liquids which became more viscous on heating to 100°. Further heating caused gelation to colourless horny resins.

TABLE IX

Methylsilicone resins

Me : Si ratio:	1·2.	1·3.	1·4.	1·5.
Temp. to harden . . .	100°	120°	141°	100°
Time to harden (hrs.) . .	2	1·5	4	24
Density of resin . . .	1·2	1·15	1·08	1·06
Refractive index . . .	1·425	1·422	1·421	1·418

These resins are infusible, and remarkably stable at elevated temperature ; when they were heated in a vacuum at 550° for 16 hours, no change beyond discoloration was observed. Heating at 200° in air for 1 year produced no perceptible change, but at 300° the surface methyl groups are oxidised and silica produced. This decomposition is unaccompanied by carbon formation and so the resins are highly suited for use as electrical insulation, particularly when account is taken of their behaviour under electrical stress. The dielectric constant (60$\sim$) of one sample was 3·7/26° and 3·6/56°, and the power factor (60$\sim$) was 0·008/26° and 0·0045/56°.

Ethylsilicone resins [7, 68] are softer, more soluble, and slower to cure than those containing methyl groups. A preferred range of composition is 0·5—1·5 Et groups per Si atom, and resins having Et : Si $\simeq$ 1 form adhesive films of fair flexibility.

Resins derived from the simpler aromatic siloxanes do not appear to be useful, but their properties can be modified by introducing halogen atoms into the aromatic nuclei.[69] Silicones containing the trichlorophenyl group are thermally stable at 450°, and very resistant to oxidation at elevated temperature. They have good electrical properties and they are flameproof. The fluorophenyl silicones are also thermally stable and flame-proof.

[69] E. G. Rochow, U.S.P. 2,258,219.

Particularly valuable resins are those containing both alkyl and aryl substituents. These can be obtained either from intermediates having an alkyl and an aryl group attached to the same silicon atom or from mixtures of alkyl- and aryl-substituted intermediates. A phenylmethylsilicone resin having Me : Ph : Si = 1 : 0·8 : 1 had a power factor (60~) of 0·001 and a dielectric strength of 800 volts per mil at 100°.[70] Its electric properties, thermal stability, and abrasion resistance are superior to those of the methylsilicone resins. Phenylethylsilicone resins also have good dielectric and mechanical properties but, being more prone to oxidation than phenylmethylsilicone resins, they are unsuitable for continuous operation above 175°.[7, 71]

Commercial silicone resins have been mainly developed in the direction of new insulating materials for electrical machines. The electrical industries have made much use of organic varnishes and drying oils in conjunction with paper and cotton, but these materials deteriorate fairly rapidly at temperatures in excess of 100°. Hence heavy-duty machines, subjected as they are to frequent periods of overload, are likely to be short-lived. The superior thermal stability of silicone resins, together with the replacement of paper and cotton by glass fabric, enable the permissible temperature limit to be raised at least to 160°, with normal expectation of life.[72, 72a] This means that the insulation is no longer the limiting factor in the design of electrical machines, and it becomes possible to produce smaller machines for a given output, a matter of importance, *e.g.*, in aircraft. Alternatively, the life of heavy-duty machines can be prolonged. Conservative estimates of service life have been made from the results of accelerated tests.[72a]

TABLE X

Comparison of rigid laminates for electrical applications

Nature of fabric :	Cotton.	Glass.	Glass.
Nature of resin :	Phenolic.	Melamine.	Silicone.
Flexural strength, p.s.i. :			
⅛″ panel, longitudinally	18,000	48,500	22,000
⅛″ panel, transversally	17,500	62,300	28,000
Tensile strength, p.s.i.	9,000	30,000	15,000
Water absorption, % :			
⅛″ panel, 24 hours	1·25	1·45	0·21
Dielectric strength, volts/mil.	200	260	250
Power factor, % at 1000~	10·0	2·7	0·51
Loss factor, % at 1000~	60·0	19·5	1·95
Insulation resistance, wet (megohms)	2·5	60	120,000

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[70] *Idem*, U.S.P. 2,258,222.

[71] J. F. Hyde, U.S.P. 2,371,050.

[72] G. L. Moses, *Westinghouse Eng.*, Sept. 1944, 138 ; T. A. Kauppi and G. L. Moses, *Trans. Amer. Inst. Elect. Eng.*, 1945, **64,** 90 ; J. Dekiep, L. R. Hill, and G. L. Moses, *ibid.*, p. 94 ; R. F. Horrell, *Plastics* (U.S.), 1946, **4,** 50.

[72a] T. A. Kauppi, G. Grant, G. L. Moses, and R. F. Horrell, *Westinghouse Eng.*, Sept. 1945, 135.

Silicone resins dissolved in toluene or similar solvent can be applied as varnishes to insulate wires, or the varnishes can be employed to impregnate glass fabric so as to produce a flexible insulation. Several layers of the resin-impregnated fabric can be bonded to yield laminates [73] suitable for making small rigid insulators or for large panel boards (see Table X). Other useful insulations are obtained from combinations of silicone resins with asbestos, mica, etc. It is to be emphasised that the curing of these silicone resins requires higher temperatures than are normally used in the electrical industries.

Silicone resins are also suitable for the preparation of heat-resistant paints and enamels. Such protective coatings are also resistant to excessive moisture, oxidation, and ultra-violet rays. White enamels based on silicone resins do not yellow with age.

Most silicone resins appear to be suitable for use in comparatively thin layers. Attempts to use them in thick layers usually lead to cracking, and this must be associated with the fact that silicones can only cure by elimination of water. Cure always proceeds more rapidly on the surface and therefore tends to obstruct the escape of moisture from the interior. The strains so set up lead to embrittlement and cracking. Efforts are being made to overcome this difficulty by using silicones with unsaturated radicals so that high-polymeric materials may be obtained, at least partially, by polymerisation.[74]

Water-repellent Surfaces.—During the preparation of methylchlorosilanes it was observed that all glassware coming into contact with these substances became water-repellent. It was found that brief exposure to the vapours [75] was sufficient to cause the effect, and that other surfaces such as ceramics, paper, and textiles could also be treated to render them water-repellent. Subsequently it transpired that silicone fluids could produce similar results, but in this case it is necessary to subject the impregnated material to a heat treatment.[76]

In the case of the methylchlorosilanes, the mechanism appears to involve chemical reaction with the surface, for example with superficial hydroxyl groups, whereby a molecular barrier is formed. This should prove more stable than a mechanically applied coating of paraffin wax. F. J. Norton [77] has estimated the thickness of such water-repellent films on ceramics as being of the order of $1{\cdot}9 \times 10^{-5}$ cm., which corresponds to a layer of about 300 molecules in depth. The mechanism with the silicone fluids is not so clear, but it probably involves absorption or adsorption according to the nature of the surface involved. So far the most important practical application has been in the electrical field, where the property has been utilized for the protection of steatite insulators in radio and radar equipment.[76]

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[73] L. V. Larsen, J. J. Whelton, and J. J. Pyle, *Modern Plastics*, 1946, **23,** 160.

[74] K. A. Andrianov, *J. Gen. Chem.* (*U.S.S.R.*), 1946, **16** (78), 639; Y. N. Volnov and A. Reutt, *ibid.*, 1940, **10,** 1600.

[75] W. I. Patnode, U.S.P. 2,306,222.

[76] O. K. Johannson and J. J. Torok, *Proc. Inst. Radio Eng.*, 1946, **34,** 296.

[77] *General Electric Review*, Aug., 1944.

Under certain conditions, notably in humid tropical areas, films of conducting water are deposited on these insulators, with consequent failure of the apparatus. The water-repellent film causes the water to form minute droplets which, being discontinuous, maintain the electrical resistance at a suitably high value to permit the operation of the equipment.

Conclusion.—Although not exhaustive, this account will demonstrate that silicones have interesting and unusual properties not possessed by other high polymers. Because of their brief commercial history, production is still on a relatively small scale, and furthermore, such amounts as are available are manufactured exclusively in the United States. Partly because of the small output and the inherent difficulties of preparation, production costs are high. It follows that, for the present, applications are likely to be confined to comparatively small but essential uses, where it can be shown that no other material is as satisfactory. Nevertheless it is to be anticipated, as with other polymers, that increasing production will lead to lower costs and therefore wider application.

The development of silicones from chemical curiosities to new materials of technological importance provides a stimulating new chapter in the annals of chemistry. It is apparent that further developments cannot long be delayed and that interesting theoretical results must accrue from the scientific study of these novel materials.

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