

additional nucleoproteins of the calf thymus, and the nucleoprotein of the hog thyroid have been characterized as substances uniform in their electrophoretic behavior.

For this class of proteins, the isoelectric point is near pH 4. Exact determinations are impossible because of their limited solubility.

These proteins have much greater mobilities

in the intervals studied, pH 2 to 3.5 and pH 5 to 9 than do the usual non-conjugated proteins.

The corresponding thymonucleic acid and histone have been prepared, and each is found to be electrophoretically homogeneous. The histone is insoluble at its isoelectric point which is in the vicinity of pH 12.

RECEIVED OCTOBER 22, 1940

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Polymeric Methyl Silicon Oxides¹

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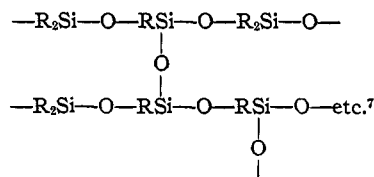
While the hydrides and alkyls of tetravalent silicon are monomeric and volatile, their oxygen derivatives usually exist in the form of polymeric structures of alternate silicon and oxygen atoms.² Thus prosiloxane³ has liquid and solid forms, and the silicones⁴ are usually polymeric. Since these organic silicon-oxygen chains resemble those of silica and the inorganic silicates, we may properly speak of the compounds generally as organo-silicon oxides.

This paper is concerned with some new polymeric methyl silicon oxides which attain their polymeric structure by a process of condensation of the corresponding methyl silicols. Our interest in this field was aroused by Dr. J. F. Hyde of the Corning Glass Company, who showed Dr. A. L. Marshall of this Laboratory some samples of phenyl silicone which he considered promising as impregnants for glass fiber tape.

Kipping⁵ first recognized that the silicanediols $R_2Si(OH)_2$ condense intermolecularly to yield polymeric anhydrides and silicones. The silicanetriols $RSi(OH)_3$ likewise were known to condense to white, powdery "siliconic acids" $(RSiOOH)_x$.⁶

During the course of an investigation of the phenyl and alkyl silicones in this Laboratory, it was found that the silicanediols may be made to

condense intermolecularly with the silicanetriols to yield solid polymers, probably of a cross-linked siloxane structure:



Within a certain range of R/Si ratios, characteristic for each R group and decreasing as the size of the R group was increased, the polymers were found to be resinous solids of high thermal stability.

Since the interesting properties of such resins probably derive from the siloxane linkage, the greatest advantage of such a linkage was sought in a polymer having a minimum organic content and a maximum of silicon and oxygen. While methyl silicon oxide was the logical choice, the methyl silicon chlorides and methyl silicols to be used as starting materials were heretofore unknown. Preliminary attempts to isolate the methyl silicon chlorides were unsuccessful, but it was discovered that a methyl silicon oxide could be prepared by direct hydrolysis of the reaction products resulting from the action of methylmagnesium bromide on silicon tetrachloride in ether. When such a reaction mixture was poured on ice, hydrolysis of the chlorides and condensation of the resulting silicols occurred simultaneously, giving liquid products which could be condensed further to resinous solids. The subsequent iso-

(7) A similar structure has been proposed by Andrianov and his co-workers for the film-forming products obtained by hydrolyzing alkyl-substituted silicon esters; see *Org. Chem. Ind. U. S. S. R.*, **6**, 203 (1939); *J. Gen. Chem. U. S. S. R.*, **8**, 552, 558, 1255 (1938); also Kalinin, *Compt. rend. Acad. Sci. U. S. S. R.*, **18**, 433 (1938). Andrianov does not report any work on the methyl-substituted esters.

(1) This paper was read on September 10, 1940, at the 100th Meeting of the American Chemical Society at Detroit, Michigan.

(2) Sidgwick, "The Electronic Theory of Valency," Oxford Univ. Press, New York, N. Y., 1932, p. 159.

(3) Stock, *Ber.*, **50**, 1769 (1917); **49**, 108 (1916).

(4) Kipping, *J. Chem. Soc.*, **101**, 2106 (1912); Krause and von Grosse, "Die Chemie der metallorganischen Verbindungen," Berlin, 1937, pp. 278-286.

(5) Kipping, *ibid.*, **91**, 218 (1907); **93**, 439 (1908); **95**, 302 (1909); **101**, 2106 (1912); **101**, 2142 (1912).

(6) Kipping, *ibid.*, **105**, 679 (1914); **107**, 459 (1915); Ladenburg, *Ann.*, **164**, 300 (1872); **173**, 147 (1874).

lation of methyl silicon trichloride and dimethyl silicon dichloride⁸ later allowed preparation of the resins from these pure materials, and it will be shown that the products obtained were identical with those resulting from the first procedure.

Experimental

1. Preparation by Direct Hydrolysis.—Methylmagnesium bromide, prepared in approximately 2 *N* solution, was analyzed by collecting the methane evolved upon reaction with water. Silicon tetrachloride was dissolved in twice its volume of absolute ether, cooled to -30° , and sufficient methylmagnesium bromide to give the desired CH_3/Si ratio was added slowly with rapid stirring. The cold reaction mixture was then hydrolyzed by pouring on cracked ice, and the ether layer separated and washed with water. Evaporation of the ether at 30° left initial condensation products of the methyl silicols, and these were heated further in air until they condensed to the desired hardness.

2. Analysis.—The solid methyl silicon oxides were analyzed by slow oxidation in a stream of oxygen. The oxygen was purified by passing over hot copper oxide and through ascarite and dehydrite; it was then passed into a quartz-glass combustion tube 1.5×18 cm. containing a roll of fine platinum gauze followed by a plug of glass wool. A sample of 0.1 to 0.2 g. was weighed in a small porcelain boat, which was inserted in the combustion tube ahead of the platinum gauze. After connecting the tube to the system, the sample was heated by a small electric furnace, and the platinum was kept at 850° by means of another furnace. The sample was oxidized at a moderate temperature (300 to 500°) to avoid ignition, for slow oxidation resulted in a coherent mass of silica whereas a flame produced a fine smoke of silica, which was difficult to trap.⁹ The hot platinum oxidized any vapors that may have been driven out of the sample, and the glass wool plug stopped particles of silica that were carried by the gases. Water vapor was absorbed by dehydrite, and carbon dioxide by ascarite and dehydrite, in glass-stoppered absorption tubes. A protective tube of ascarite and dehydrite prevented back-diffusion of carbon dioxide or moisture.

The combustion tube, filled with oxygen, was weighed before a run, and again after oxidation of the sample. The difference between the latter weight and that of the tube (plus boat) before the run represented silica formed by oxidation of the sample. From the weights of silicon dioxide, water, and carbon dioxide obtained, the percentages of Si, H, and C were calculated, and oxygen was obtained by difference. The analytical method thus gives a direct determination of three of the four constituents on a single sample. That the remainder was oxygen was shown in some cases by a negative test for halogens and by a spectrographic analysis that revealed silicon as the only metal present.

(8) See following paper by Gilliam, Liebhaufsky and Winslow, *THIS JOURNAL*, 63, 801 (1941).

(9) Heating of the sample at a low temperature, combined with complete oxidation of the evolved materials at a much higher temperature, is essential for satisfactory analytical results. Direct ignition of these resins in platinum over an open flame, for example, gives a product that remains black even after hours of heating.

The method was checked against the standard micro-combustion method for carbon and hydrogen on several occasions, and the agreement was found to be good. Typical data for two resins appear below:

	Resin no. 16		Resin no. 32	
	Method described	Micro	Method described	Micro
% C	23.1	23.05	17.7	17.76
% H	6.05	6.02	4.84	4.74
% Si	40.4		38.6	
% O by diff.	30.45		38.86	

3. Preparation from Methyl Silicon Chlorides.— CH_3SiCl_3 and $(\text{CH}_3)_2\text{SiCl}_2$ were prepared and purified as described in the following paper. Mixtures of the two were prepared volumetrically from the known liquid densities to provide C/Si ratios of 1.2, 1.3, 1.4 and 1.5. In each case, 6 g. of the mixture was dissolved in 50 cc. of ether and poured on 100 g. of ice. The ether layer was separated, washed free of chlorides in a separatory funnel, and the ether evaporated at 30° . The condensed silicols were then heated to temperatures sufficient to give a hardness of about 70 Rockwell by the superficial hardness test, using a $1/16$ in. ball under 15 kg. load.

The analyses were done by the method outlined above, using samples of approximately 0.1 g. The densities were determined by displacement of water from a pycnometer, and the refractive indices by means of an Abbe refractometer.

Results

An extended series of preparations by the first method outlined above, in which the ratio of methyl groups to silicon atoms was varied, gave a series of products with the following general properties: (a) with an average of 1.0 to 1.3 methyl groups per silicon atom (by analysis) in the polymer, the condensation proceeded at room temperature through a sticky, sirupy stage to a hard, transparent resin. Upon being warmed, this resin became a brittle, glassy mass. (b) With an average of 1.3 to 1.5 methyl groups per silicon atom, condensation at room temperature gave a colorless, oily liquid. Upon being heated to 100° , the viscosity of this liquid rose and the volatility decreased. Further heating in the range 150 – 200° caused gelation in a few hours, and the gel gradually hardened to a colorless, transparent, horny resin (Fig. 1). Continued heating in this temperature range made the product more brittle but caused no other change. (c) With an average of 1.5 to 1.9 methyl groups per silicon atom, the products were quite volatile at the temperature required for condensation. Heating to 200° for several hours produced a soft, rubbery gel; continued heating for several weeks at 200° made the gel brittle.

The transparent resins within the range CH_3/Si

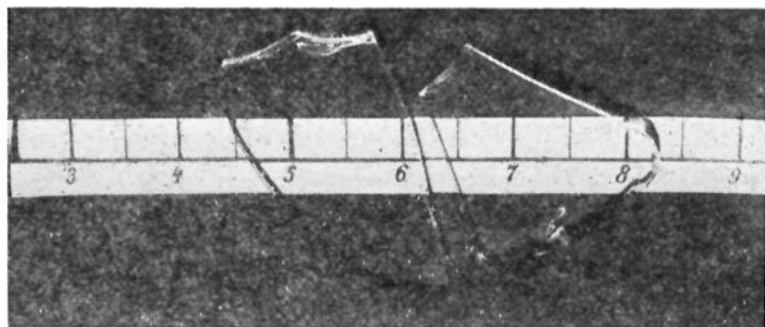


Fig. 1.—Polymeric methyl silicon oxide, before and after heating to 200° for one year.

= 1.3 to 1.5 were investigated more fully, and were found to possess interesting properties. The liquid initial condensation products were soluble in hydrocarbons and alcohols, and were converted to gels by dehydrating agents or by heat. After gelation, the mass was no longer completely soluble and did not melt; further heating made it entirely insoluble and infusible. Perhaps the most remarkable property of these methyl silicon oxides is their thermal stability; samples heated to 550° for sixteen hours in vacuum and to 450° for one hour in hydrogen were not changed beyond discoloration. Heating to 200° in air for a year produced no perceptible change in the resin, as is shown in Fig. 1. At 300° in air, the resin disintegrated on the surface through oxidation of the methyl groups, leaving a residue of silica. At 400° the oxidation was rapid, which suggested the analytical scheme described above.

The properties of resins prepared by the second method described above are summarized in Table I.

That the polymers prepared by both methods were identical was demonstrated by comparing the compositions, densities, and refractive indices of the samples. Such comparison is given in Table II.

Resin no.	R1	R2	R3	R4
Intended C/Si ratio	1.2	1.3	1.4	1.5
Temp. to harden	100°	120°	141°	100°
Time to harden	2 hr.	1½ hr.	4 hr.	24 hr.
% C found	20.28	22.30	23.45	25.0
% H found	6.11	7.70	7.60	6.55
% Si found	40.59	39.0	38.85	39.0
% O by dif.	33.02	31.0	31.1	29.45
C/Si ratio found	1.17	1.34	1.41	1.50
Density	1.20	1.15	1.08	1.06
Refractive index	1.425	1.422	1.421	1.418

	Prepared by Grignard reaction	Prepared by hydrolysis of mixed chlorides
C/Si ratio	1.34	1.34
Empirical formula by anal.	(CH ₃) _{1.34} SiO _{1.37}	(CH ₃) _{1.34} SiO _{1.40}
Appearance	Colorless horny resin	
Density	1.19	1.15
Refractive index	1.423	1.422

It seems evident from these experiments that the mechanism of formation of these methyl silicon oxides is one of condensation. Dimethyl silicanediol and methyl silicanetriol condense with themselves and with each other to produce what is believed to be a cross-linked structure of siloxane chains. When this condensation has advanced sufficiently, the result is a resinous solid.

Summary

1. Polymeric methyl silicon oxides, new organosilicon compounds obtained by intermolecular condensation of methyl silicols, are described.
2. Two methods of preparation are given: the action of CH₃MgBr on SiCl₄ followed by direct hydrolysis; and the hydrolysis of known mixtures of CH₃SiCl₃ and (CH₃)₂SiCl₂.
3. The structure of these resinous polymeric substances consists essentially of a siloxane network in which the methyl groups are attached directly to silicon.

SCHENECTADY, NEW YORK RECEIVED OCTOBER 24, 1940