

Ferrosilicon 에서 Dimethyl Polysiloxane 의 合成

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Dimethyl Polysiloxane from Ferrosilicon

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요 약

Dimethyl polysiloxane 의 silicone 油를 70% Fe-Si 에서 合成하였다. 合成과정은 methyl alcohol 과 HCl 기체 의 반응에서 얻어지는 methyl chloride 의 제조, 銅분말을 촉매로 하여 methyl chloride 와 Fe-Si 의 반응에서 얻어지는 methyl chlorosilane 의 제조, 및 methylchlorosilane 의 加水分解와 重合으로 나누었다. 각合成과정 에서 반응온도, 반응시간, 촉매, 보조촉매등이 合成과정에 미치는 영향을 고려하여 반응조건을 조사하였다. 끝으로 粘度범위가 다른 몇가지 dimethyl polysiloxane 油를 얻었다.

Abstract

Silicone oil of dimethyl polysiloxane was synthesized from 70% ferrosilicon. The steps were divided into the preparation of methyl chloride from the reaction of methyl alcohol and hydrogen chloride gas, the preparation of methylchlorosilane by the reaction between methyl chloride and ferrosilicon using copper powder as a catalyst, the separation of methylchlorosilane, and the hydrolysis and polymerization of methylchlorosilane. Each step was discussed in detail in terms of the reaction conditions such as the effects of reaction temperature, reaction time, catalyst, and promotor on the synthesis processes. Finally, dimethyl polysiloxane oil of different viscosity range was obtained.

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Introduction

Silicone fluids, characterized by their low tempera-
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ture coefficient of viscosity, low vapor pressure, high electrical resistivity, and excellent thermal and chemical stabilities, are used as lubricants due to their flexible and linear molecular structure.

The silicon chemistry has been developed since 1900, and Rochow¹⁾ prepared organochlorosilane, which is an intermediate of silicone fluid, by a direct method, and Noll²⁾ by a reaction between Grignard reagent and silicon tetrachloride or silicic acid ester. The processes, however, were considered complicated and the production efficiency was so low that the production cost of silicone fluid was estimated high. A direct reaction between the metallic silicon and alkyl chloride, to promote the reaction rate, has been studied^{3,4)} in the production of dimethyl polysiloxane oil.

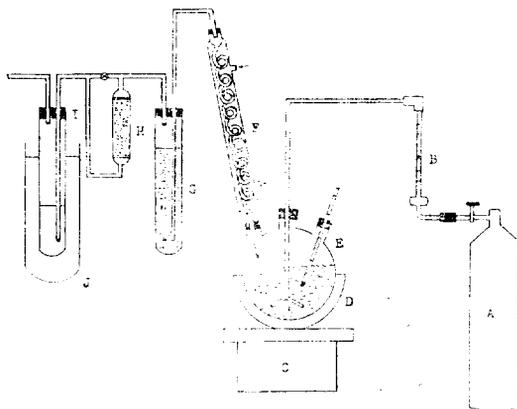
However, the work to be described in this paper is a study of reaction between ferrosilicon and methyl chloride, to form the same oil. Ferrosilicon, depending on a content of iron, has been known to have a lower reaction selectivity and forms less dimethyldichlorosilane, an intermediate^{5,6)}. Since the removal of iron from ferrosilicon is an awkward and costly process, 70% ferrosilicon was used in raw in this work, even if a low production efficiency was expected. The effects of reaction temperature, reaction time or contact time, flow rate of methyl chloride, particle size of ferrosilicon, catalyst, and promotor on the processes were tested, and few dimethyl polysiloxane oils of different viscosity range were synthesized.

Experimental

Methyl chloride: Methyl chloride was prepared by chlorinating methanol with hydrogen chloride gas using zinc chloride as a catalyst at 60–65°C. The hydrogen chloride gas was passed at a rate of 150 cc/min first, and then at a rate of 1,000–1,500 cc/min through a mixture of 400g of methanol and 100g of zinc chloride. The reaction product was first condensed at the reflux condenser, as shown in Fig. 1, and then the gas was flushed in water to remove unreacted methanol and excess hydrogen chloride gas. The gas product was dried on calcium chloride and was collected in a bottle

using a mixture of dry ice-acetone at –60°C.

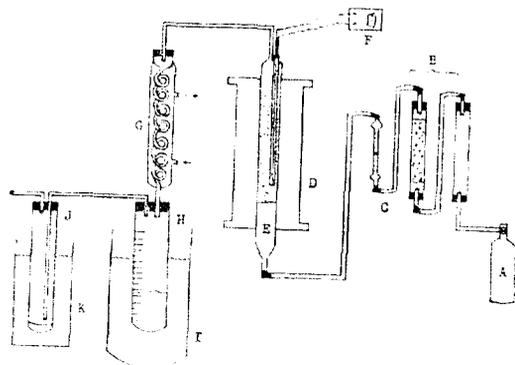
Methylchlorosilane: Methylchlorosilane was prepared by a reaction between 325 mesh 70% ferrosilicon and methyl chloride, previously made, in an ample, using 400 mesh copper powder as a catalyst. The glass tube reactor, shown in Fig. 2, was filled



- A : HCl bomb
- B : flowmeter
- C : magnetic agitator
- D : heating mantle
- E : reactor
- F : reflux condenser
- G : gas flushing bottle
- H : CaCl₂
- I : CH₃Cl Collector
- J : coolant bottle

Fig. 1. Apparatus for the synthesis of methyl chloride.

with ferrosilicon mixed with copper powder. The mixture was set on a glass wool and was inserted in a vertical furnace. The reaction tube was first flushed with nitrogen gas to expell air and moisture, for 2 hrs, and was heated up to 300–400°C for few more hrs, and finally methyl chloride was passed through for 24–30 or 40–45 hrs. The reaction product was condensed in the first cooler and the excess methyl chloride and uncondensed product were collected in the second cooler. The excess methyl chloride was evaporated slowly into air and the remaining product was added to the main product in the first cooler.



- A : CH_3Cl ample
 B : CaCl_2 dryer
 C : flowmeter
 D : furnace
 E : glass tube reactor
 F : pyrometer (thermocouple)
 G : condenser
 H : cooler (collector)
 I : dry ice+acetone
 J : cooler (collector)
 K : dry ice+acetone

Fig. 2. Apparatus for the synthesis of methylchlorosilane.

Separation of methylchlorosilanes: Since the methylchlorosilane, prepared above, contains monomethyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, and other impurities, those silanes were separated by a fractional distillation as shown in Fig. 3. The sample was refluxed for 2 hrs, and then the temperature at column was controlled at $5\text{--}10^\circ\text{C}$ lower than the temperature at head, and the temperature of flask at $5\text{--}10^\circ\text{C}$ higher than the temperature at head, thus controlling the distillates by the stopcock, J. The ratio of reflux to the overhead product was first controlled to 25-30 : 1 until 105 cc of overhead product was distilled out, and then maintained to 60-70 : 1 to prevent the mixing of dimethyldichlorosilane into methyltrichlorosilane.

Hydrolysis and polymerization of methylchlorosilane: Dimethyldichlorosilane, obtained from the separation of silanes, was mixed with small amounts of triethylchlorosilane in an ample using dry ice-acetone mixture as a coolant, and an adequate amount

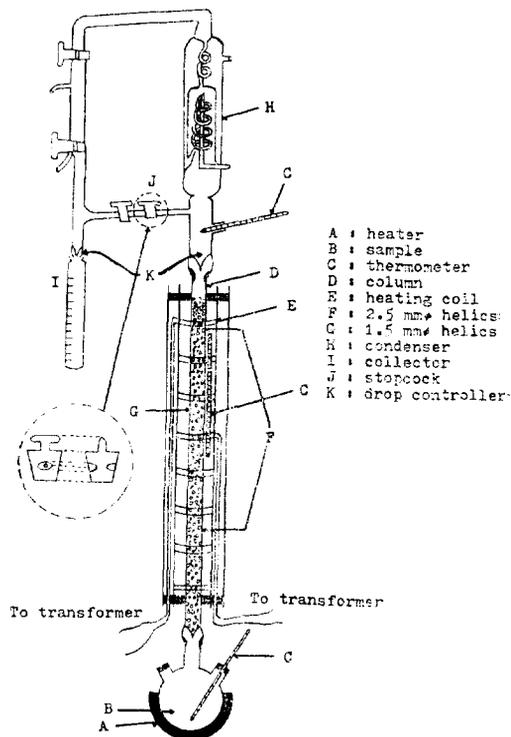


Fig. 3. Fractional distillation unit.

of water was added. The ample was sealed and was shaken for 24 hrs. The polymer layer was separated and washed. Then, 5% of conc. sulfuric acid was added to the polymer and was heated to 120°C and shaken for 6 hrs. The polymer was washed again with water and finally was treated by small amounts of anhydrous sodium carbonate.

Results and Discussion

Synthesis of methyl chloride

There are several ways of preparing methyl chloride. In this experiment, however, chlorination of methanol was used to obtain pure product and an easy separation of product, since the impurities in methyl chloride give some effects on silane preparation⁷). The average rate of formation was found to be 20-22 cc/hr, and the conversion rate of HCl to be 40-50% as

shown in *Fig. 4*. As the concentration of methanol decreased, the curve after 22 hrs of reaction time decreased rapidly. It was also found that the reaction product decreased when the temperature was maintained below 60°C.

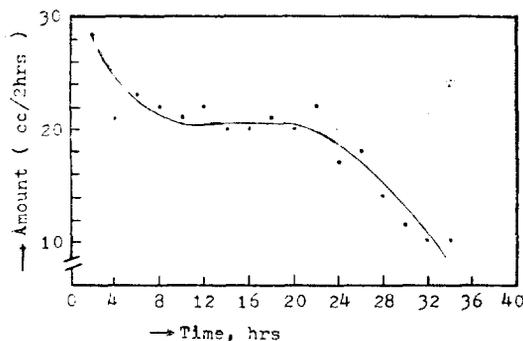


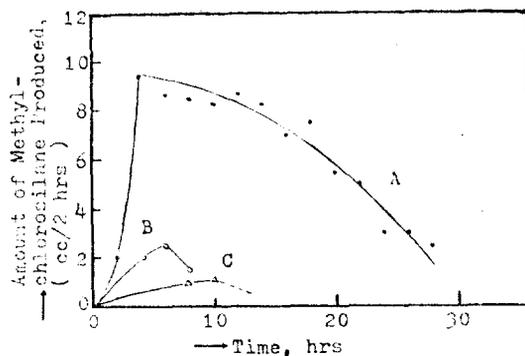
Fig. 4. Production of methyl chloride.

Synthesis of methylchlorosilane

In general, silicon surface forms an oxide at room temperature or is coated by decomposed products during the reaction with methyl chloride and a deactivation of surface can be observed, thus giving a slow reaction of silicon. Therefore, the reproducibility of the reaction was very difficult to control even if the contact mass was maintained uniformly. Since a difficulty was obtained at the cooling step, no diluent was used in this experiment.

A catalytic effect^{6,9)} was examined using copper powder. The reaction between ferrosilicon and methyl chloride was observed very slow when no catalyst was added, and only small amounts of silane was produced after 10 hrs of reaction. However, the reaction was catalyzed by 10% of copper powder at 325–335°C and less than 3 hrs of reaction time was observed to get the same amounts of silane at no catalyst, as shown in *Fig. 5*. Since the initial reaction temperature was raised by 20–30°C due to the exothermic reaction, the curve showed a maximum at the beginning.

There are several methods to raise the reactivity of methyl chloride and ferrosilicon using catalyst; namely, 1) heating ferrosilicon in the absence of



A : 350–360°C, 10% Cu, 30–32.5cc/min MeCl rate
 B : 325–330°C, " " "
 C : 350–360°C, no cat., " "

Fig. 5. Effect of catalyst on the production of methylchlorosilane

oxygen up to 1450°C, and adding 10–20% of catalyst to form an alloy of Si-catalyst, 2) simple mixing of ferrosilicon and catalyst homogeneously, 3) binding ferrosilicon and catalyst with NH_4HCO_3 , which can be easily decomposed, and making sintered pellet or bar at 900–1,200°C in the presence of hydrogen or nitrogen, 4) coprecipitation of ferrosilicon and catalyst which is coated on the ferrosilicon surface, and drying the coprecipitate in inert gas or vacuum, and 5) making molded pellet or bar of ferrosilicon and catalyst with glass powder or water glass.

A simple mixing and crushing of 60 mesh ferrosilicon and 10% of 325 mesh copper with a ball mill for 20 hrs and sieving to obtain 40 μ powder, was used in this experiment.

An effect of catalyst quantity on the production of silane is shown in *Fig. 6* and it was found that the methyl group was decomposed by the catalyst when 15% of copper was used, thus decreasing the production rate of silane.

An effect of flow rate of methyl chloride on the production of silane is shown in *Fig. 7*. The reaction was affected by the contact time of methyl chloride, ie, the flow rate of methyl chloride, and the contact mass. It was found that the reaction proceeded well enough when the contact time was long enough. However, the chance that product tends to decompose

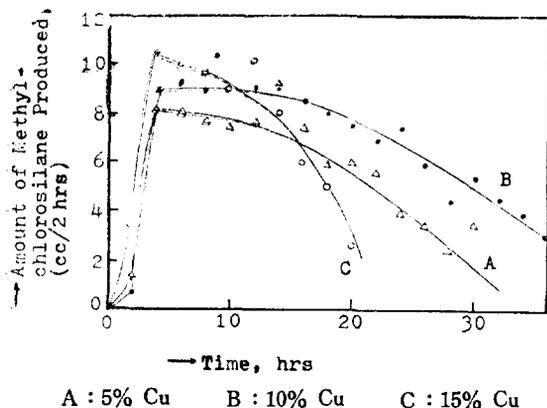


Fig. 6. Effect of catalyst quantity on the production of methylchlorosilane.

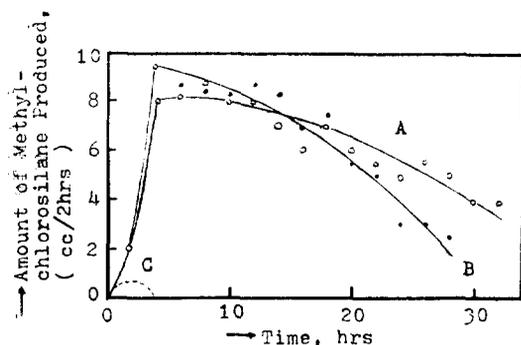


Fig. 7. Effect of flow rate of methyl chloride on the production of methylchlorosilane.

to methyltrichlorosilane was derived from the product that remained in the furnace too long. The best flow rate of methyl chloride was found to be 30-32.5 cc/min.

An effect of reaction temperature was also examined, as shown in Fig. 8. The flow rate of methyl chloride was maintained at 30-32.5 cc/min and the copper powder at 10%.

As the temperature went high, the rate of production increased. However, at a higher temperature of 455-465°C, the gas pressure in the furnace was accumulated, because the rate of outlet gas became slower than that of inlet gas. The best reaction temperature was found to be 370°C.

It is known that the contact mass was little covered

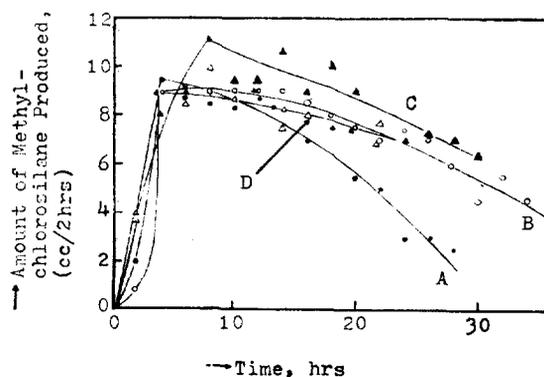
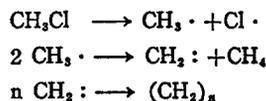


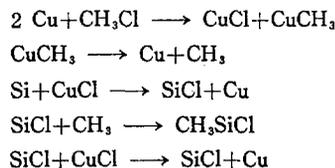
Fig. 8. Effect of reaction temperature on the production of methylchlorosilane.

by a non-volatile polyethylene, derived from the decomposition of methyl chloride, and curve D was observed lower than curve C in the figure.



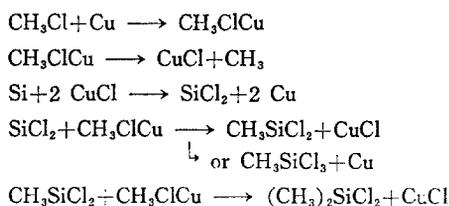
(To obtain a better condition of silane formation, effect of promotor^{9,10}) was observed besides the catalyst effect. The advantages of using promotor is known to promote the rate of reaction, to minimize catalyst quantity, and to minimize reaction temperature. Compounds such as zinc chloride, cadmium chloride, arsenic, antimony, magnesium, and a mixture of antimony and phosphorus are normally used as promotor. However, zinc powder was used in this experiment, and the optimum amounts of zinc was found to be 1.7%.)

To review the silane formation, Rochow¹¹) proposed the following mechanism:



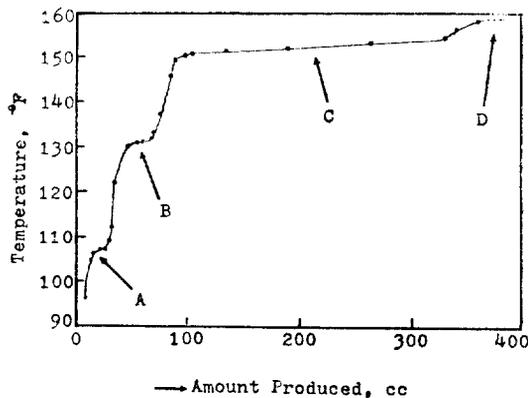
Even if the reaction on methyl radical is well known, the reason why the dimethyldichlorosilane is selectively formed is not yet known. Formation of

some of alkylchlorosilane and alkenylchlorosilane under 260°C cannot be explained, since the chlorination of silicon by cuprous chloride can be accomplished above 260°C, and there is no way as yet to confirm the presence of CuCH_3 . Other mechanisms are also proposed and one of them is as follows, but confirming the mechanism is not yet known.



Separation of silanes

Since the product obtained above contains several silanes, a fractional separation of the product was carried, and the result is shown in Fig. 9.



A : $\text{CH}_3\text{SiHCl}_2$ B : SiCl_4 & CH_3SiCl
C : CH_3SiCl_3 D : $(\text{CH}_3)_2\text{SiCl}_2$

Fig. 9. Fractional distillation of silanes.

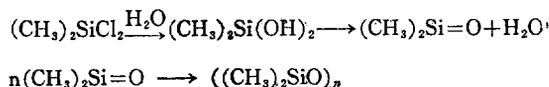
At the beginning, SiHCl_3 (b. p. = 31.8°C) and $(\text{CH}_3)_2\text{SiHCl}$ (b. p. = 35.4°C) were separated. A compound of $\text{CH}_3\text{SiHCl}_2$ (b. p. = 40.4 ± 0.1°C) was obtained next at 41.7°C (plateau A), and $(\text{CH}_3)_3\text{SiCl}$ (b. p. = 57.3 ± 1°C) and SiCl_4 (b. p. = 57.6°C) were distilled at a higher temperature (plateau B). The separation of these two compounds is very difficult, because they form an azeotrope at the temperature¹². These compounds are usually separated^{13,14} by using

phenol or alcohol, but it is known that the separation and purification method utilizing the difference in the rate of hydrolysis by water is more economical and convenient. The separation, however, was not attempted in this experiment, and the trimethylchlorosilane, used as a terminating agent for the polymerization step, was simply purchased.

At 66.5°C (plateau C), CH_3SiCl_3 (b. p. = 66.1 ± 0.1°C) was obtained and $(\text{CH}_3)_2\text{SiCH}_2$ (b. p. = 70.2 ± 0.01°C) on a further distillation at 70.2°C (plateau D). The $(\text{CH}_3)_2\text{SiCl}_2$ thus obtained was analyzed by a gas chromatography and its purity was found to be 99.6%.

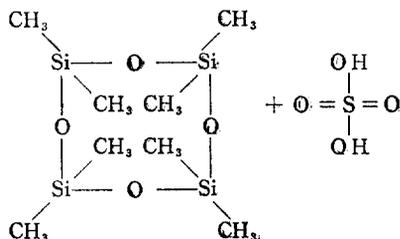
Hydrolysis and polymerization of dimethyldichlorosilane The rate of hydrolysis of silane increases as the polarity of Si-Cl bond increases, and as the number of chlorine increases, because polyorganosiloxane such as $\text{Cl}(\text{RR}'\text{SiO})_n\text{SiRR}'\text{Cl}$ normally forms in the mechanism. Since HCl, formed as a byproduct in the condensation reaction, acts like a catalyst, the composition of product largely depends on the concentration of hydrochloric acid, existence of solvent, and polarity of solvent.

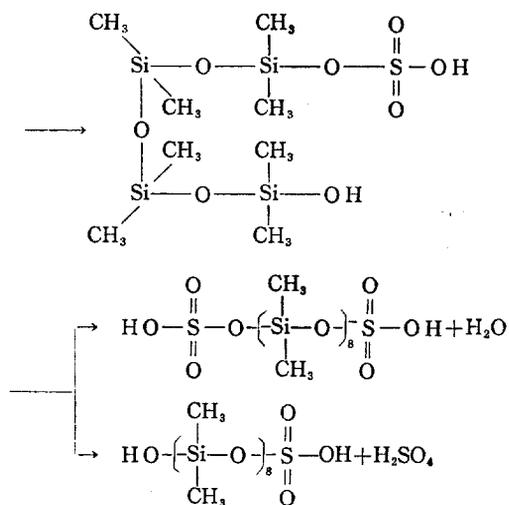
An excess water in the process will hydrolyze both chlorine into diol and a formation of cyclic compound such as trimer or tetramer is possible as shown in the following equations :



Therefore, the controlling of water quantity in the hydrolysis was an important factor.

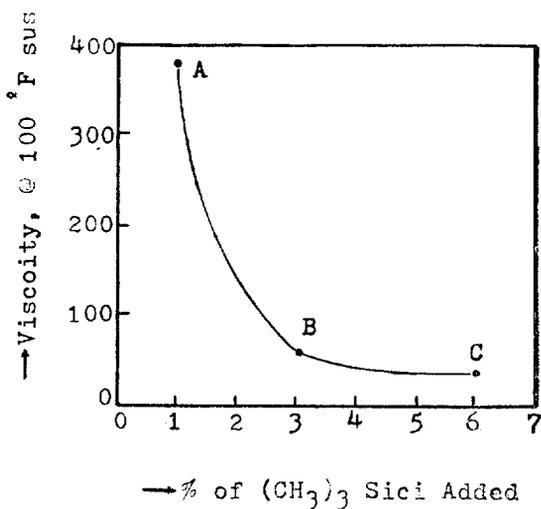
Polymerization, or so-called equilibration, process was attempted after the hydrolysis using sulfuric acid as a catalyst¹⁵, and a linear silicone oil was obtained.





Strong bases, such as hydroxides of alkali metals, can also be used as a catalyst^{16,17,18}, but the difficulty in washing out of hydroxides limits its usage. It is known that a transient catalyst^{19,20} is normally used in a continuous process, because the catalyst can easily be decomposed.

Silicone oil thus obtained is shown in Fig. 10 according to its viscosity range. The viscosity was dependent upon the amount of terminating agent added.



A : 375.8 sus @ 100°F
 B : 58.9 sus @ 00°F
 C : 36.7sus @100°F

Fig. 10. Viscosity of silicone oil produced.

Conclusions

Methyl chloride was formed at a rate of 10 cc/min when gaseous hydrogen chloride was reacted with methanol at a rate of 1,000-1,500cc/min for 2 hrs and then at a rate of 150 ± 5 cc/min, using zinc chloride as a catalyst. Since the reaction was carried in a liquid phase, the yield was found to be only 40-50%.

The optimum reaction conditions of preparing silane using 60 mesh ferrosilicon in a horizontal reaction tube were found to be; reaction temperature of $340 \pm 10^\circ\text{C}$, flow rate of methyl chloride at 30-32.5 cc/min, and 10% of 325 mesh copper powder as a catalyst. However the best reaction conditions using the same ferrosilicon in a vertical reaction tube were found to be; reaction temperature of $330 \pm 10^\circ\text{C}$, flow rate of methyl chloride at 40-42.5 cc/min, 10% of 325 mesh copper powder as a catalyst, and 1.7% of zinc as a promotor.

Fractional distillation of silane at a reflux ratio of 25-30 : 1 first and then at 60-70 : 1 led to the separation of dimethyldichlorosilane. Even the yield was low as 13%, the purity was found to be 99.6%.

The hydrolysis and polymerization of dimethyldichlorosilane then led to the final product of dimethyl polysiloxane oil of 40% yield. The viscosity range of the oil was found to be a function of the amount of trimethylchlorosilane, used as a terminating agent.

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