INCREASE IN WATER REPELLENCY AND THERMAL STABILITY OF CERAMIC INSULATING MATERIALS

By

E. ADY, P. HENCSEI, T. GÁBOR and K. BECKER-PÁLOSSY

Department for Inorganic Chemistry, Technical University, Budapest

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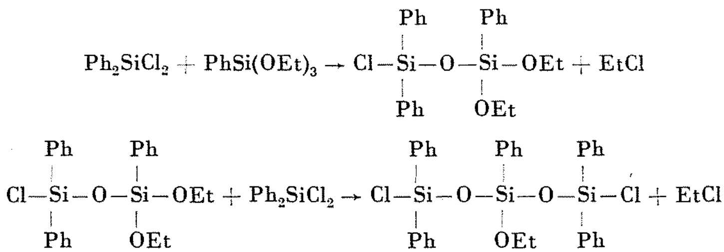
Introduction

The electrical industry makes wide use of various ceramic insulating materials of which good thermal stability and water repellency are expected. Our present paper has been dealt with the improvement of these properties by using various silicone resins i.e. oil coatings.

Production and testing of silicone resins

1. *Polydiphenyl-phenyl silicone resin*

The synthesis of polydiphenyl-phenyl-siloxanes was made after the method of ANDRIANOV and BREJTMANN [1] starting from phenyl-triethoxy-silane and diphenyl-dichloro-silane. During the synthesis a gradual poly-condensation takes place first and polyorganosiloxanes containing ethoxy and chloride groups result, while ethyl chloride leaves according to the reaction scheme:



$$Ph = C_6H_5-, \quad Et = C_2H_5- .$$

Later these products condensate with each other and with the monomers, giving oligomers containing linear and cyclic units. The oligomers are hydrolyzed in hydrochloric medium and the polycondensation of the hydrolysate results in the polydiphenyl-phenyl silicone resin to be used.

The infrared spectrum of the produced silicone resin was determined on UR-20 infrared spectrophotometer. For the record the viscous resin free of solvents was warmed and dropped between KBr plates warmed to 80 °C. The recording was done by using KBr, NaCl and LiF prisms in the ranges of 400 to 850 cm^{-1}, 670—2100 cm^{-1} 1900—5000 cm^{-1} wave number, respectively. The infrared spectrum is shown in Fig. 1.

In the 2100 to 2800 cm^{-1} wave number range and above 4100 cm^{-1} wave number no absorption bands were observed. The Si—Cl vibration band of low intensity at 810 cm^{-1} proved that hydrolysis took place and only a small quantity of Si—Cl group remained in the resin.

The 3200 to 3560 cm^{-1} absorption band for Si—OH, too, proved the favourable properties of the resin and the efficiency of the synthesis. The intensive bands in the 1000 to 1140 cm^{-1} range corresponded to the siloxane bond. The increase in the intensity of the bands in direction of the higher wave numbers showed, that the siloxane chain was not evenly long and the equilibrium of the chain lengths was shifted towards the big chain lengths.

The thermal stability of the resin was tested on Perkin-Elmer apparatus. The thermal diagram is shown in Fig. 2.

2. *Methyl-silicon resin*

According to literature data [2, 3] the hydrolysis is the most favourable in the mixtures of methyl-trichloro-silane and dimethyl-dichloro-silane with a CH_3 to Si ratio between 1.0 and 1.6. Resins of this type are condensed at relatively low temperatures and have a good thermal stability. The methyl-chloro-silanes hydrolyse with water under usual circumstances very rapidly in solvent media e.g. toluene into the corresponding silanoles, which are immediately condensed to siloxanes. In the hydrolysis of methyl-trichloro-silane cross linking poly-siloxanes form, they are stable and do not solve in organic compounds. If the CH_3 to Si ratio is increased over 1 i.e. dimethyl-dichloro-silane, is hydrolysed in addition to methyl-trichloro-silane, the cross linking polymers gradually transform into linear or cyclic methyl-polysiloxanes soluble in liquid and organic solvents. The methods of hydrolysis and synthesis are very important, because the methyl resins are rather inclined to gelification. To avoid this and to diminish the rate of hydrolysis, the butylester of the silanes was produced first, and there after hydrolysed. The applied CH_3 to Si ratio was 1.28.

The thermal diagram of the produced methyl-silicone resin is shown in Fig. 3.

It appears that but a slight decomposition occurred over 560 °C, the percentage of the decomposed material did not exceed 35% at 560 to 680 °C.

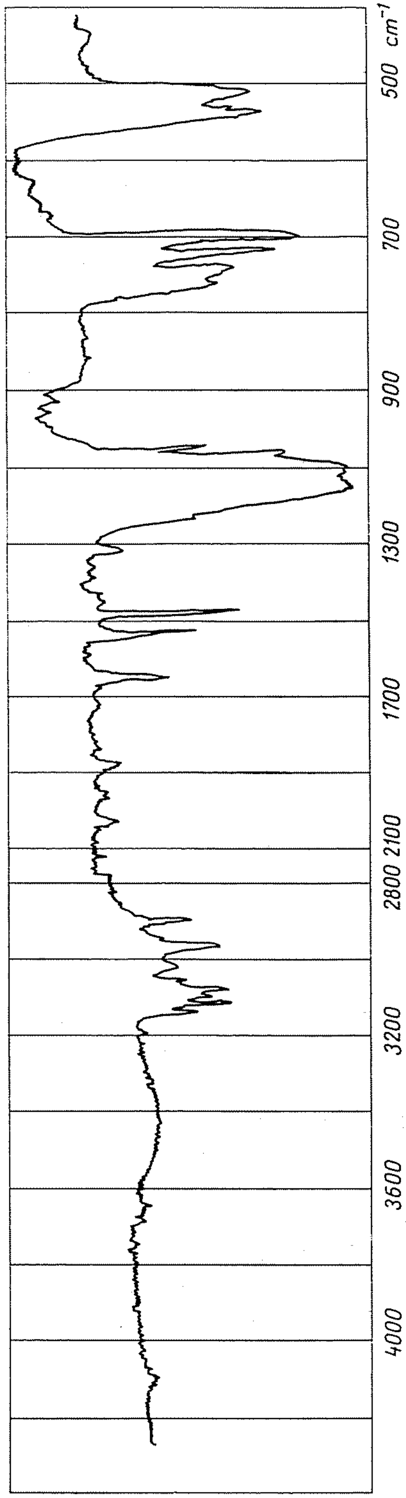


Fig. 1. Infrared spectrum of poly-diphenyl-phenyl-silicone resin

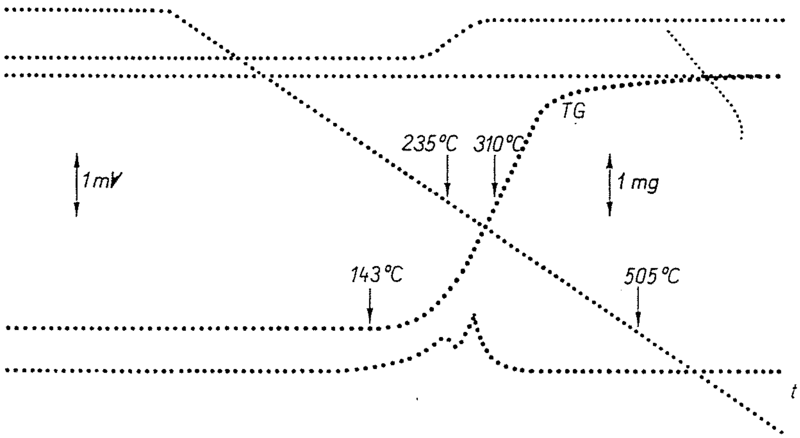


Fig. 2. Thermal diagram of poly-diphenyl-phenyl-silicone resin

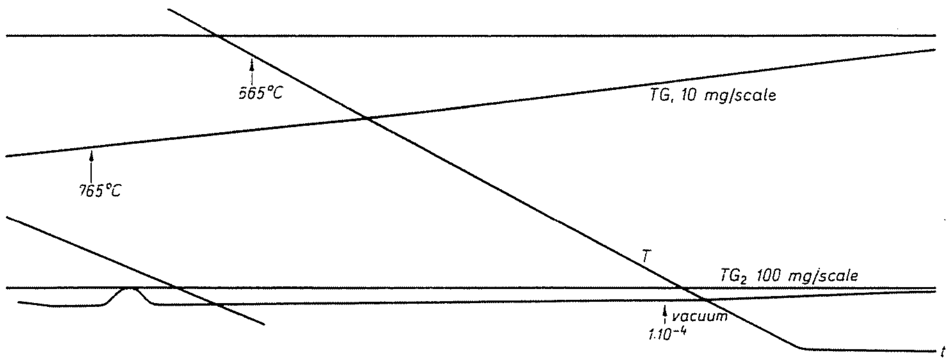


Fig. 3. Thermal diagram of methyl-silicone resin

Not only the thermal diagrams but the long-term thermal stabilities of the two prepared resins were determined on the basis of ANDRIANOV's investigations [4]. In tests at 250, 300, 350 and 400 °C the losses of weight of the solid resins vs. time have been determined as shown in Figs 4 and 5.

Exposed to long-term heating of 25 hours at 400 °C, the methyl-silicone resin is seen to exhibit a loss of weight as low as 13.3%. The long-term thermal stability of the polydiphenyl-phenyl-silicone resin is seen to be poorer its loss of weight being 15.2% at 350 °C already after 15 hours of heat treatment, while at 400 °C it begins to decompose at a high rate after a treatment of 2 hours and after 25 hours its loss of weight is 35%.

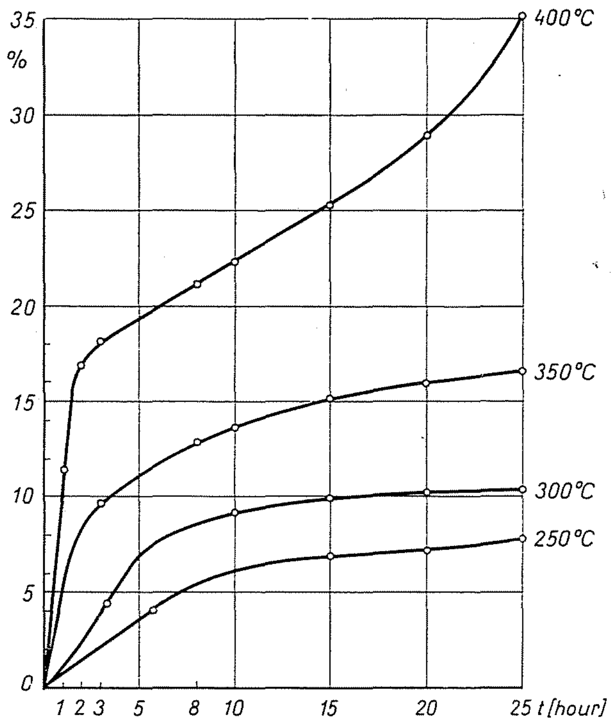


Fig. 4. Diagram of the longterm thermal stability of polydiphenyl-phenyl-silicone resin

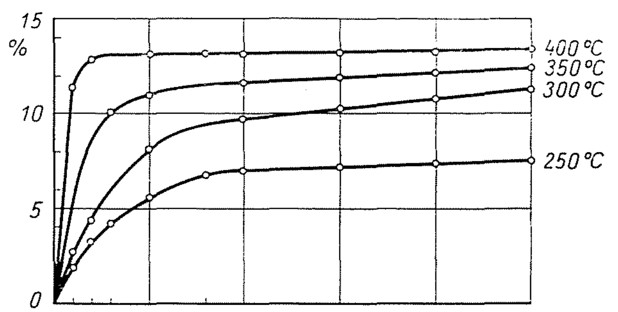


Fig. 5. Diagram of the longterm thermal stability of methyl-silicone resin

3. *Methyl-silicon oils*

Our research covered water realing by NM-I-200, NM-I-5000 and NM-I-100 000 methyl-silicone oils produced by the Nünchritz factory of VEB Chemiewerk. Among these the first one is a product containing low viscosity and low molecular weight, the second and third ones are materials with higher viscosity consisting of components of 50 000 and 100 000 molecular weight. Experiments were made to determine the solvents with best water-repellent properties. It could be stated that among alcohol, benzene and toluene solvents the last one was the most suitable. Among the three different methyl-silicone oils the best results were obtained with NM-I-200 silicone oil. It was necessary to determine the optimal concentration, too. The results of our experiments showed good water repellency at concentrations between 5 to 30%.

Another method was used in sealing with methyl-silicone oil. The ceramic units were pretreated with sodium-methyl-siliconate. The test sample was soaked in 20% sodium-methyl-siliconate solution for 2 hours, kept in CO_2 atmosphere at room temperature for 30 minutes and burnt in. After these the burning in and sealing with methyl-silicone oil was accomplished.

Sealing and testing ceramic forms

Sealing of ceramic units was done by degreasing and then soaking in toluene solutions made of silicone resins and oils, in these the ceramic forms were soaked after a previous. At last the burning in was accomplished at a predetermined temperature and for a given time. Test data are summarized in Table 1.

Table 1

	Concentration %	Time of wetting	Temperature of penetration °C	Time of penetration
Polydiphenyl-phenyl silicone resin	50	10 min	250	3 hour
Methyl silicone resin	20	10 min	150	3 hour
Methyl silicone oil (NM-I-200)	25	24 hour	200	1 hour
Sodium-methyl siliconate and methyl silicone oil	25	24 hour	200	1 hour

The water-repellency of the samples was quantitatively evaluated by comparing the rim angles of the water-drops dripped on the examined pieces. The temperature of heat treatment varied in the range of 500 to 740 °C, the time of treatment from 2 to 30 min. The results are summarized in Table 2.

The thermal stability of the sealed ceramics was evaluated from surface resistance measurements. The results are shown in Table 3.

Our investigations show the produced poly-diphenyl-phenyl and methyl-silicone resins to endure thermal shocks in the range of 500 to 740 °C their water repellency to be good and to have excellent electrical properties. Sealing with methyl-silicone oils is convenient in the range of 500 to 750 °C but with

Table 2

	Temperature of heat treating °C	Time of heat treating minutes	Evaluation of the drop test
Polydiphenyl-phenyl silicone resin	520	5	good
	520	10	good
	520	15	good
	520	17	good
	520	20	good
	560	2	good
	640	2	good
	640	15	bad
	740	2	good
	740	4	good
	740	5	bad
Methyl-silicone resin	540	6	good
	540	12	good
	540	30	good
	600	2	good
	600	5	good
	680	2	good
	740	2	good
	740	5	good
	740	10	bad
Methyl silicone oil	500	2	good
	500	5	good
	500	10	good
	550	2	good
	740	2	good
	740	4	bad
Sodium-methyl-siliconate and methyl-silicone oil	500	2	good
	500	5	good
	550	2	good
	740	2	bad

Table 3

	Temperature of heat treating °C	Time of heat treating minute	Surface resistance Ω
Polydiphenyl-phenyl silicone resin	500	5	$2 \cdot 10^{15}$
	550	2	$1 \cdot 10^{15}$
	550	5	$6 \cdot 10^{14}$
Methyl silicone resin	550	5	$1.4 \cdot 10^{15}$
	600	2	$7.2 \cdot 10^{14}$
	600	5	$2 \cdot 10^{15}$
	680	2	$1.1 \cdot 10^{15}$
Methyl-silicone oil	500	5	$1.3 \cdot 10^{15}$
Sodium-methyl-siliconate and methyl-silicone-oil	500	2	$1 \cdot 10^{11}$

the disadvantage that about 500 °C the coat reacts with the ceramic and discolouration takes place, while the water repellency is good in the given interval.

Summary

Thermal stability and water repellency of ceramic insulating materials can be increased by coating with polydiphenyl-phenyl silicone resins and methyl-silicone resins by using the toluene solution of these resins and of methyl-silicone oils. Thermal stability and sealing properties were determined from surface resistivity and the rim angles. The applied silicone coat proved to be convenient both in respect of thermal stability and water-repellency.

Experimental

Production of polydiphenyl-phenyl silicone resin

166 g of phenyl-triethoxy-silane and 169 g of diphenyl-dichloro-silane is made to react in the presence of 5 g $FeCl_3$ anhydride at 130 °C till no more ethylchloride is formed. The ethylchloride is taken up in a cooled Marcusson-head.

The quantity of the ethyl-chloride is 82 ml (85%). The yield of the oligomer is 81%. The hydrolysis of the oligomer is done by solving 120 g in 1500 ml benzene and the mixture of 300 ml water and 20 ml ccHCl is added unter continuous boiling and stirring. The mixture is boiled for 20 hours, after it will be washed to neutral with the saturated aqueous solution of $NaHCO_3$. After drying with $CaCl_2$ the benzene is distilled. The quantity of the hydrolyzate is 85 g (92%). The polycondensation of the hydrolyzate is done by heating 100 g hydrolizate, 20 ml methylalcohol and 0.5 g NaOH to 200 °C and kept at this temperature for 16 to 20 hours. The product will be solved in an equal quantity of toluene and this solution will be used for van-van sealing.

Production of methyl silicone resins

To the solution of 80 g methyl-trichloro-silane and 30 g dimethyl-dichloro-silane in 250 ml toluene, 120 buthylalcohol is added at 30 to 40 °C under continuous stirring. The mixture is boiled for 1 hour, after cooling 100 ml water is added under ice-cooling. It is boiled for another hour under stirring. After cooling the mixture is washed to neutral, water extracted and the solvent in excess distilled.

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Dr. Endre Ady
Dr. Pál Hencsei
Dr. Tamás Gábor
Dr. Katalin Becker-Pálossy
Budapest XI, Gellért tér 4, Hungary