

# Effects of Catalyst on the Electrical Properties of Silicone Rubber\*

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## Synopsis

Electrical properties, such as dissipation factor and electric conductivity, were studied for silicone rubber sheets. The specimens were prepared by the reaction of  $\alpha,\omega$ -dihydroxypolysiloxane with ethoxysilane, using dibutyltin dilaurate as a catalyst, at a relative humidity of about 100% at various temperatures and for various reaction times. It was found that the electrical properties were a function of the vulcanizing conditions; i.e., the further the vulcanization proceeded, the higher the dissipation factor and the electric conductivity. A reaction describing deterioration in electrical properties was then considered. Infrared spectroscopic studies on dibutyltin dilaurate showed that the dibutyltin dilaurates were partly hydrolyzed to lauric acid and dibutyltin dihydroxide. It was concluded that electrical property deteriorations, which were caused by changes in the vulcanizing conditions, were due to dibutyltin dilaurate hydrolysis. However, since the decomposed products were finally oxidized at elevated temperatures in an oxygen atmosphere, with a subsequent change to electrically inactive compounds, the initial electrical properties were recovered.

## INTRODUCTION

There has been special interest in silicone rubbers because of their practical applications to semiconductor devices. Since these devices, in general, require very high reliability, the polymers used should possess excellent reliability characteristics such as heat and humidity resistance and low impurity levels. Silicone rubbers are widely used as junction-coating resins for thyristors and diodes and are also useful as coating resins which can protect semiconductor devices not only from  $\alpha$ -rays, but also sometimes from mechanical damage.<sup>1,2</sup>

Polmanteer has written an all-encompassing review of current developments in silicone elastomer technology.<sup>3</sup> Saam et al.<sup>4</sup> and Severnyi et al.<sup>5</sup> have suggested mechanisms for the curing process as it relates to silicone compounds.

When silicone rubbers are used as the encapsulation material for integrated circuits or other semiconductor devices, it is necessary to ensure that the device operations are not adversely affected by the rubbers. Therefore, an evaluation of the electrical properties of silicone rubber is necessary. Our group has previously observed the interesting phenomenon<sup>6</sup> that changes in an oven atmosphere during heat treatment affected the dissipation factor of rubber sheets vulcanized under the same conditions: in a nitrogen atmosphere, the dissipation factor did not change, while in oxygen it did.

Gupta et al.<sup>7</sup> have reported the effect of heat treatment under vacuum and in air on the dielectric relaxation of polyacrylonitrile.

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TABLE I  
 Composition of Liquid Silicone

Agent	Formula	Ratio (wt %)	Viscosity 25°C (Pa·s)	Density 25°C (g/cm <sup>3</sup> )
Prepolymer <sup>a</sup>	$\text{HO}-\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{O} \\   \\ \text{CH}_3 \end{array} \right]_n-\text{H}$	73		
Crosslinking	$\text{H}_3\text{C}_2\text{O}-\left[ \begin{array}{c} \text{OC}_2\text{H}_5 \\   \\ \text{Si}-\text{O} \\   \\ \text{OC}_2\text{H}_5 \end{array} \right]_{3-6}-\text{C}_2\text{H}_5$	2	11	1.2
Filler	CaCO <sub>3</sub>	25		

<sup>a</sup> The viscosity is 2 Pa·s at 25°C.

The purpose of the present paper was to elucidate the factors which caused a deterioration in electrical properties of silicone rubber sheets which were extensively vulcanized at various temperatures for various reaction times.

## EXPERIMENTAL

### Materials

The composition of liquid silicone used in this investigation is shown in Table I, together with its characteristics. In the preparation of rubber sheets, 6 μmol/g of dibutyltin dilaurate was employed as catalyst. Hydrolytic and pyrolytic products of dibutyltin dilaurate were added to the liquid silicone before vulcanizing in order to determine their effects on electrical properties of vulcanized products. Their chemical formulas are given in Table II.

The samples were vulcanized at a relative humidity of about 100% at temperatures between 20°C and 40°C for 3–24 h. Round, thick sheets 10 cm in diameter with a hardness of 40–45 Shore A at 25°C were obtained. Some samples were heated at 200°C for 10 h under controlled atmospheres at 1 atm pressure.

 TABLE II  
 Compounds Added to Liquid Silicone

Compounds	Formula	MW	mp (°C)
Dibutyltin dilaurate <sup>a,b</sup>	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn(OCOC <sub>11</sub> H <sub>23</sub> ) <sub>2</sub>	630.7	13
Lauric acid <sup>a</sup>	C <sub>11</sub> H <sub>23</sub> COOH	200.2	44
Dibutyltin dihydroxide <sup>b</sup>	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn(OH) <sub>2</sub>	266.9	115
Butylstannonic acid <sup>a,b</sup>	C <sub>4</sub> H <sub>9</sub> SnOOH	208.8	—
Tin(II) oxide <sup>a</sup>	SnO	134.7	—
Tin(IV) dioxide <sup>a</sup>	SnO <sub>2</sub>	150.7	—

<sup>a</sup> Commercial, high purity reagent.

<sup>b</sup> The compounds were recrystallized from butyl alcohol.

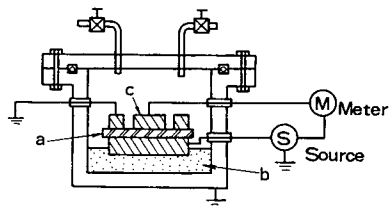


Fig. 1. A cross-sectional view of the autoclave used to measure the electrical properties of rubber sheets: (a) silicone rubber sheets; (b) polytetrafluoroethylene insulator; (c) stainless-steel main electrode (5 cm in diameter with an electropolished mirror finish surface).

### Measurement of Electrical Properties

The initial electrical properties of the rubber sheets were measured in a nitrogen-filled autoclave (Fig. 1) to avoid oxidation. The autoclave was then placed in an oven and heated to a constant temperature. The electrical properties of the rubber sheet were measured at various temperatures between 20°C and 200°C. The dissipation factor was measured at 50 Hz with a 1 kV source. Electrical conductance was measured at 1 kV after a direct current charge of 1-min duration.

### Infrared Spectra

The infrared spectra of the samples were recorded using a Hitachi Grating Spectrophotometer Model 215 with a KBr cell. The degree of hydrolysis under various conditions was determined for the decomposed products of dibutyltin dilaurate by using the standard curve described previously.<sup>6</sup>

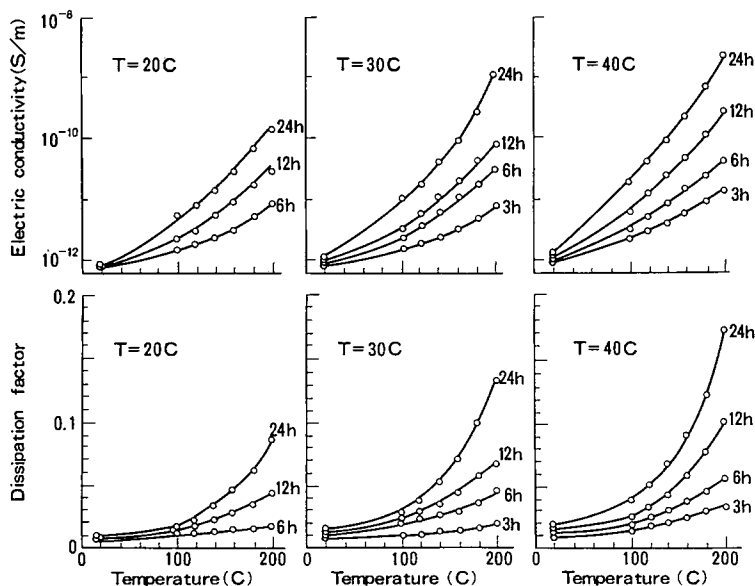


Fig. 2. Relationship between temperature and electrical properties of rubber sheets.  $T$  = vulcanization temperature;  $h$  = vulcanization time (h).

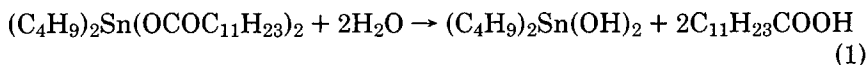
## RESULTS AND DISCUSSION

## Electrical Property Behavior

Figure 2 shows the temperature dependence of the dissipation factor and the electrical conductivity of rubber sheets vulcanized at various temperatures for various reaction times. As shown in the plots, the dissipation factor and electric conductivity increase with increasing temperature; and, the longer the reaction time, the higher the dissipation factor and the electric conductivity. Rubber sheets which were vulcanized at higher temperatures for longer times showed higher dissipation factor and higher electric conductivity. Such a phenomenon is rather unusual when compared to thermosetting resins such as epoxides,<sup>8</sup> polyimides,<sup>9</sup> etc., in which the dissipation factor becomes smaller as vulcanization proceeds. The reasons for this observed deterioration in electrical properties were then investigated.

## Hydrolysis of Catalyst

It was found from infrared spectroscopic studies that dibutyltin dilaurate itself is partly hydrolyzed to lauric acid and dibutyltin dihydroxide at a relative humidity of about 100% at room temperature. The hydrolysis of dibutyltin dilaurate is represented by



It was assumed that this reaction also occurred for the dibutyltin dilaurate used as a catalyst in the preparation of rubber sheets. The residual quantities of lauric acid and dibutyltin dihydroxide were then determined from the infrared spectroscopic data for a vulcanized rubber sheet and are shown in Figure 3. As shown in the figure, increasing the time and temperature tends to increase the residual quantities of both. A linear relationship was observed between the residual quantities and reaction time. The observations were limited to the initial stage of the dibutyltin dilaurate decomposition reaction. For example, the maximum quantities measured for lauric acid and dibutyltin dihydroxide in rubber sheets

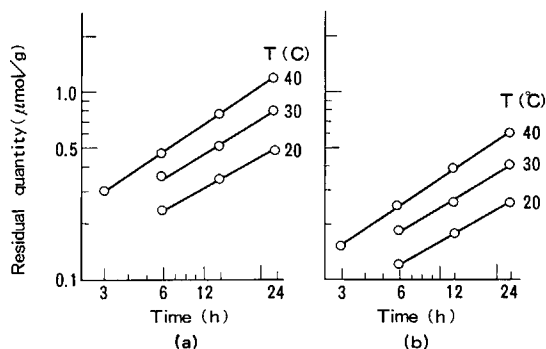


Fig. 3. Relationship between vulcanizing conditions and the residual quantities of lauric acid and dibutyltin dihydroxide in rubber sheets.  $T$  = vulcanization temperature.

(a) Lauric acid; (b) dibutyltin dihydroxide.

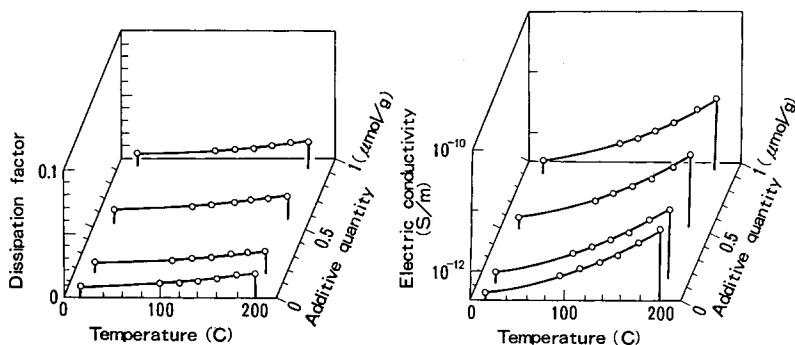


Fig. 4. Relationship between the amount of lauric acid ( $C_{11}H_{23}COOH$ ) added to liquid silicone and the temperature dependence of the electrical properties of rubber sheets vulcanized at  $20^{\circ}C$  for 6 h.

were  $1.2 \mu\text{mol/g}$  and  $0.6 \mu\text{mol/g}$ , respectively. Considering the added amount ( $6 \mu\text{mol/g}$ ) of dibutyltin dilaurate and the stoichiometry in eq. (1), the degree of decomposition should be below 10%. In any case, the results in Figure 3 suggest that the decomposition products of catalyst are present in the samples and that their quantities are functions of the vulcanizing conditions.

### Influence of Additive Compounds

Various quantities of lauric acid and  $6 \mu\text{mol/g}$  of dibutyltin dilaurate were added to liquid silicone having the composition shown in Table I. The mixtures were vulcanized at  $20^{\circ}C$  for 6 h. Figure 4 shows how the electrical property-temperature curves of rubber sheet differ depending on the quantity of added lauric acid. It is clear that the amount of lauric acid does not have a significant effect on the electrical properties of rubber sheets. However, there is some possibility that lauric acid might be vaporized at the elevated temperatures of the measurements, because the vapor pressure of lauric acid is 60 Pa at  $141^{\circ}C$ . The electrical properties of rubber sheets at a given elevated temperature stayed almost unchanged. Therefore, it can be concluded that the lauric acid produced from the catalyst by its decomposition during vulcanization had no pronounced effect on the electrical properties of the rubber sheets.

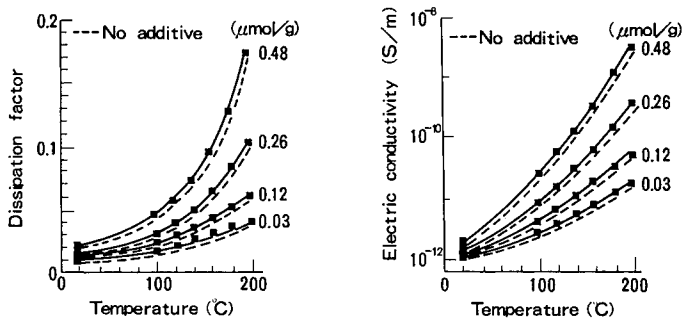


Fig. 5. Comparison of sheets to which dibutyltin dihydroxide was added ( $\mu\text{mol/g}$ ) and sheets to which no additive was used. (■) Additive ( $C_4H_9$ ) $_2$ Sn(OH) $_2$  used, with vulcanization at  $20^{\circ}C$  for 6 hours; (---) no additive used, with vulcanization at  $40^{\circ}C$  for 3, 6, 12, and 24 h, as shown in Figure 2.

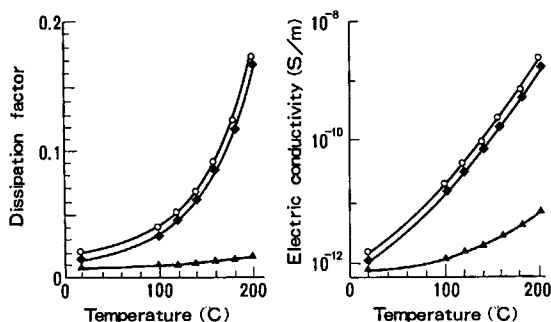


Fig. 6. Effect of atmospheric changes and heat treatment (200°C, for 10 h) on the electrical properties of rubber sheets vulcanized at 40°C for 24 h: (O) without heat treatment; (◆) in N<sub>2</sub>; (▲) in O<sub>2</sub>.

The temperature dependence of electrical properties of rubber sheets having different amounts of dibutyltin dihydroxide is shown in Figure 5. For comparison, results for rubber sheets having no additive are also given. Dibutyltin dihydroxide would be expected to remain in the rubber sheet without oxidizing or vaporizing, since the electrical properties were measured in the nitrogen-filled autoclave. Figure 5 shows clearly that the values of the dissipation factor and the electric conductivity obtained for the sheets having different amounts of dibutyltin dihydroxide increase with the amount of dibutyltin dihydroxide and that these values are very similar to those obtained for the sheets treated at 40°C for 3–24 h.

It can be concluded from the results shown in Figure 5 that dibutyltin dihydroxide has a pronounced effect on the dissipation factor and electric conductivity of the rubber sheet. Variations in the electrical properties of rubber sheets vulcanized at various temperatures for various lengths of time are partially due to the presence of dibutyltin dihydroxide produced from the catalyst during the vulcanization process.

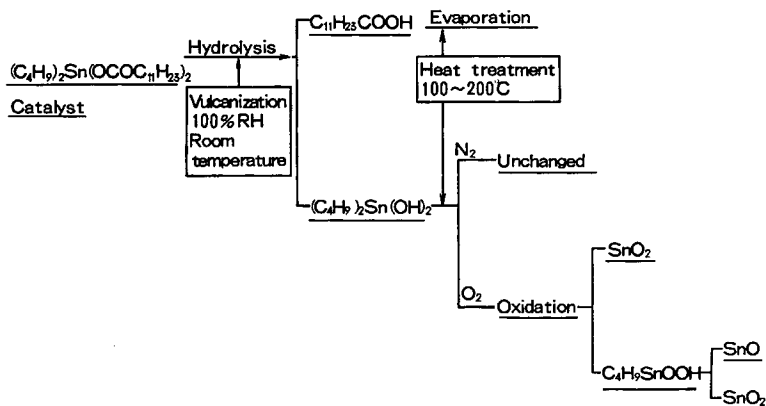


Fig. 7. Flow chart describing changes in the dibutyltin dilaurate catalyst.

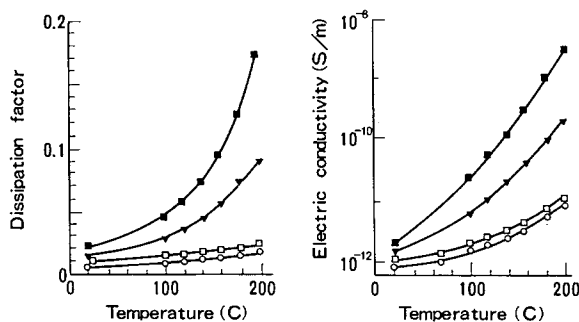


Fig. 8. Influence of the oxidation products of dibutyltin dihydroxide on the electrical properties of rubber sheets vulcanized at 20°C for 6 h. 0.48  $\mu\text{mol/g}$  of the compound was added to liquid silicone. Additive: (■)  $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{OH})_2$ ; (▼)  $\text{C}_4\text{H}_9\text{SnOOH}$ ; (□)  $\text{SnO}$ ; (○)  $\text{SnO}_2$ .

### Effect of Heating Atmosphere

In Figure 6, the electrical properties measured for rubber sheets that were heated at 200°C for 10 h in nitrogen or oxygen atmospheres are compared with those measured for an untreated one. These results suggest that oxidation brings about the reduction in the dissipation factor and electric conductivity.

As is well known, thermal degradation, including oxidation, of polymers causes the deterioration of electrical properties of polymers.<sup>10</sup> Consequently, dissipation factors and electric conductivity become larger and larger as the degree of degradation increases. Therefore, the results observed in Figure 6 should not be due to such degradation of polymer chains. The observed results make sense when two facts are taken into account. Dibutyltin dihydroxide, which is the hydrolyzed product of the catalyst, causes an enhancement in dissipation factor and electric conductivity (cf. Fig. 5). However, if dibutyltin dihydroxide in the rubber sheets is oxidized at 200°C in an oxygen atmosphere, electrically inactive compounds are produced.

Baum and Considine<sup>11</sup> have reported that dibutyltin dihydroxide was oxidized to tin(IV) dioxide with heat treatment in an oxygen atmosphere, but not with heat treatment in nitrogen.

### Mechanism

All the decomposition products obtained from the original catalyst during the various stages in forming the rubber sheets are summarized in Figure 7 as a flow chart. The catalyst dibutyltin dilaurate is partly hydrolyzed to lauric acid and dibutyltin dihydroxide at a relative humidity of about 100% at room temperature. The dihydroxide does not undergo pyrolysis in a nitrogen atmosphere during the heat treatment at 200°C, but it can be partially oxidized in an oxygen atmosphere. This oxidation is probably followed by two reactions, one of which directly produces tin(IV) dioxide, while the other produces an intermediate butylstannonic acid.<sup>12</sup>

The effect of these decomposition products on the electrical properties is presented in Figure 8. The effectiveness of these compounds on the electrical properties of silicone rubber sheets decreases in the order



That is, dibutyltin dihydroxide, which is the hydrolyzed product of dibutyltin dilaurate, is very effective, leading to an increase in the dissipation factor and electric conductivity, while tin(IV) dioxide, which is the final oxidation product of dibutyltin dihydroxide, is inactive, leading to no change in the electrical properties.

### CONCLUSION

Electrical properties of silicone rubber sheets that were prepared from liquid silicone composed of  $\alpha,\omega$ -dihydroxypolydimethylsiloxane, tetraethoxysilane, dibutyltin dilaurate, and calcium carbonate differ, depending on the vulcanizing conditions of the liquid silicone. Hydrolysis and pyrolysis of the catalyst dibutyltin dilaurate occurs during the vulcanization to give various products. Some of these products, such as dibutyltin dihydroxide, are found to be effective in enhancing the dissipation factor and electric conductivity of the silicone rubber, while others, such as tin(IV) dioxide, are inactive. Accordingly, the variations in electrical properties observed for the silicone rubber sheets are due to the decomposition of the catalyst.

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