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**ELASTOMERIC AND MECHANICAL PROPERTIES OF POLY-
m-CARBORANYLENESILOXANES. V. THERMAL STABILITY
OF SILOXANE ELASTOMERS**

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Princeton, New Jersey**

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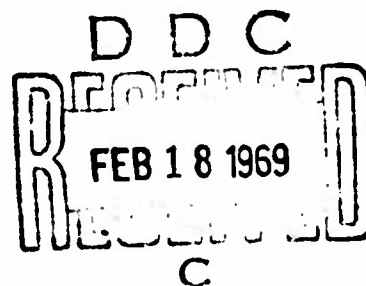
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ABSTRACT and INTRODUCTION

Previous reports^{1,2} on poly-m-carboranylenesiloxane, or SiB, have emphasized the superior oxidative stability of these systems in comparison with other high temperature elastomers such as silicone rubber. The extreme thermal stability of SiB-2 was illustrated, but not thoroughly explored. Since many applications of high temperature elastomers could conceivably be in oxygen free environments, the desirability of comparative data was evident. This paper reports on a careful comparative study of the thermal stabilities of SiB-2, poly(dimethylsiloxane) and poly(trifluoropropyl methyl siloxane), using the technique of chemical stress relaxation in highly purified nitrogen. The thermal stability of SiB-2 is quite outstanding in this test.

EXPERIMENTAL

Materials:

The silicone rubber and SiB-2 elastomers were identical to those described in Part III.² The poly(trifluoropropyl methyl siloxane), or Silastic, was kindly supplied by T. D. Talcott of the Dow Corning Co., Midland, Michigan. The filled and unfilled Silastics were cured for 15 minutes at 260°F using 2% benzoyl peroxide. All samples were extracted with benzene and vacuum dried before use.

Instrumental:

The relaxometers used to measure thermal stability are described elsewhere.³ An effort was made to expose all samples to the same conditions before and during the relaxation experiments. Thus all samples were exposed to 99.996% nitrogen at 100°C for at least 16 hours in the relaxometer, after which the temperature of the sample was increased to the temperature of the experiment, and held for one hour. The sample was then extended less than 10%, and the resulting force was measured as a function of time.

RESULTS AND DISCUSSION

The rate of force decay during a high temperature relaxation experiment in an inert atmosphere is a highly sensitive measure of the thermal stability of the network chains which must carry the load. The parameter used to characterize the rate of relaxation is the chemical relaxation time, τ_{ch} , which is the time required for the relative stress in the sample to fall to $1/e = 36.8\%$. Values for τ_{ch} taken from Figures 1-5 are listed in Table 1 for the temperatures at which the various elastomers were tested. It is significant that SiB-2 outperforms the Silastic and silicone rubbers by about two orders of magnitude, dramatically confirming the high stability conferred to the siloxane linkage by the carborane units present in the main chains. The trifluoropropyl side groups of the Silastic elastomer do not enhance the thermal stability of the siloxane linkage (their purpose is mainly to increase solvent resistance.) The presence of filler (mostly silica) gives added thermal stability to these elastomeric systems with the exception of SiB-2 where there is no effect. There is good evidence that this may be due, in part, to an increased rate of crosslinking at high temperatures in the presence of filler.²

The apparent activation energies of relaxation, obtained from plots of $\ln \tau_{ch}$ vs $1/T$ are also listed in Table 1. A high apparent activation energy does not imply a stable elastomer.

TABLE I

Chemical Relaxation Times and Apparent Activation Energies for
Siloxane Elastomers in Nitrogen

<u>Polymer</u>	<u>Figure</u>	$(\tau_{ch} \text{ seconds}) \times 10^{-4}$			<u>E*, kcal/mole</u>
		<u>300°C</u>	<u>325°C</u>	<u>350°C</u>	
Silicone Rubber	1	0.36	0.23	0.15	12
Silastic 420	2				
unfilled		0.15	0.035	- - -	40
Silastic L5-53	3				
filled		0.40	0.15	0.034	40
SiB-2, unfilled	4	> 14	8.3	5.2	15
SiB-2, filled	5	> 12	6.3	2.5	22

Figure 1

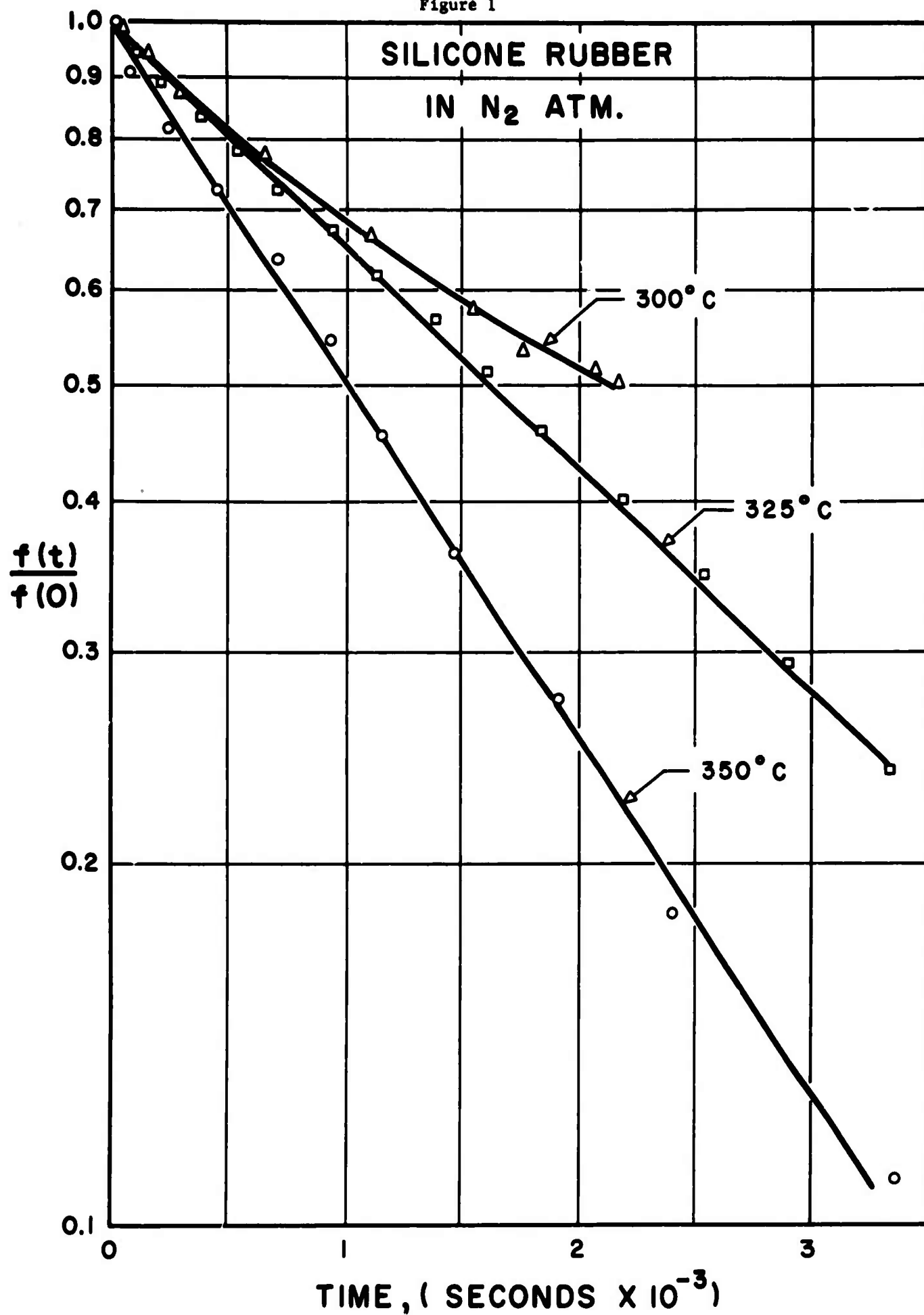


Figure 2

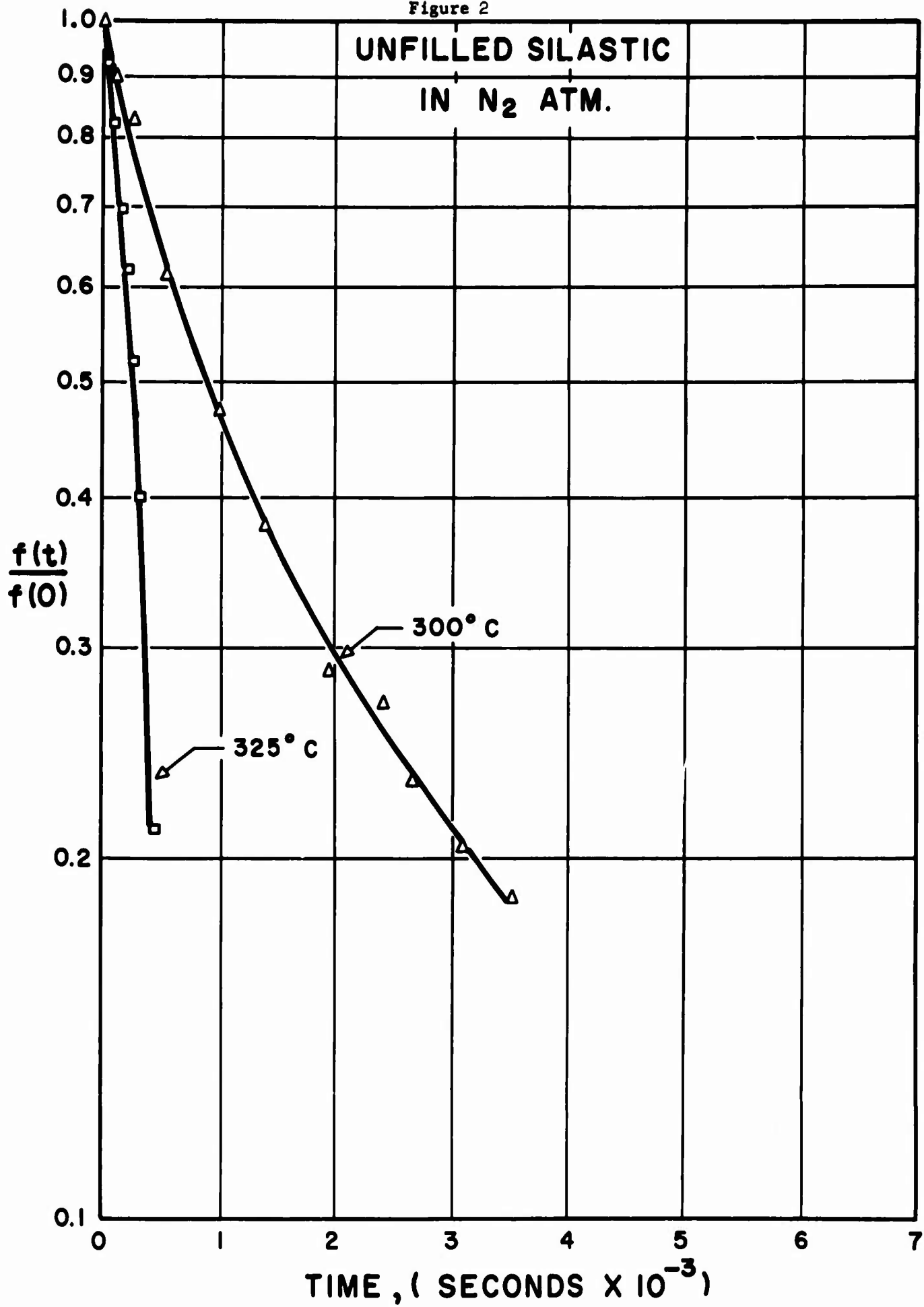


Figure 5

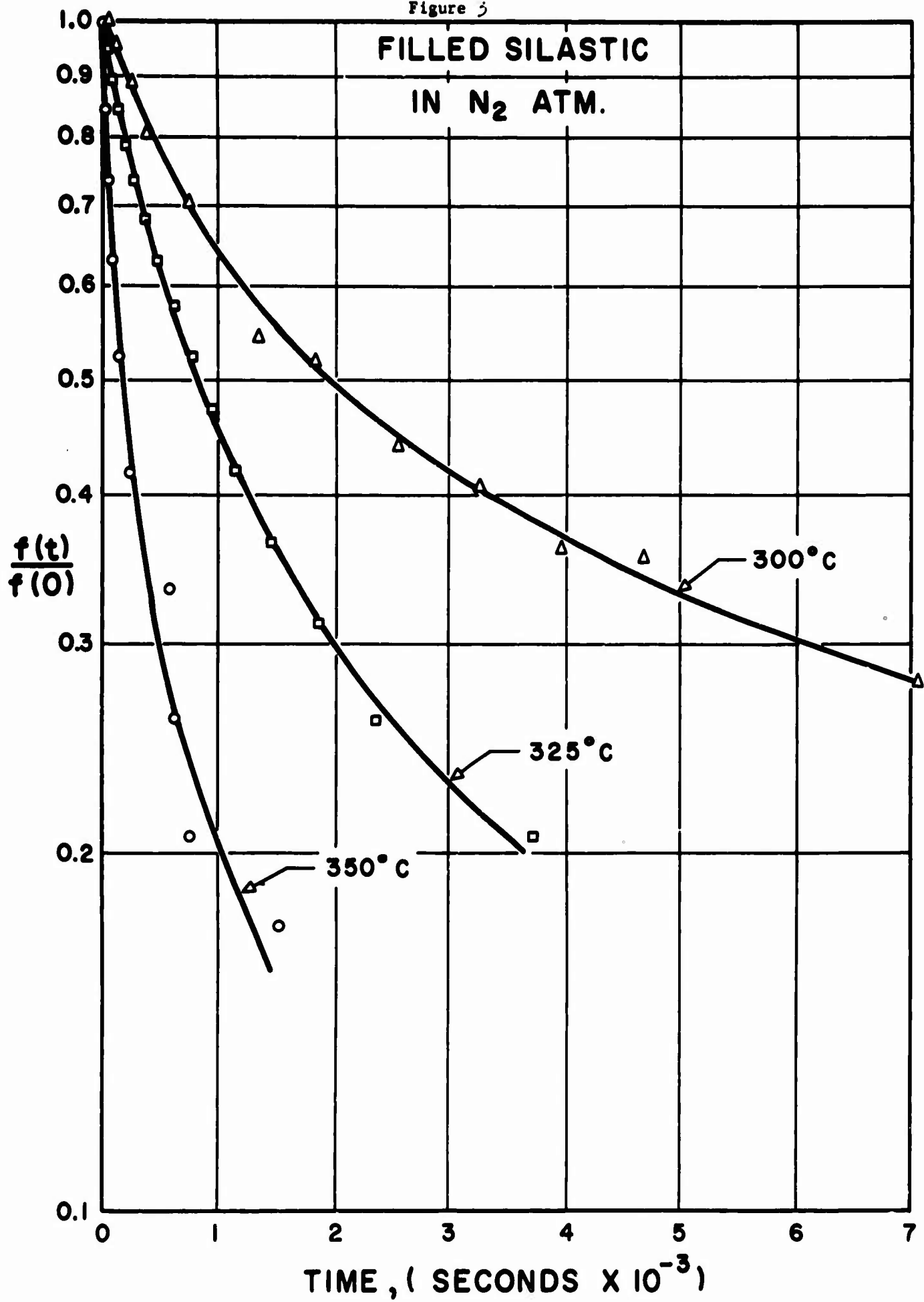


Figure 4

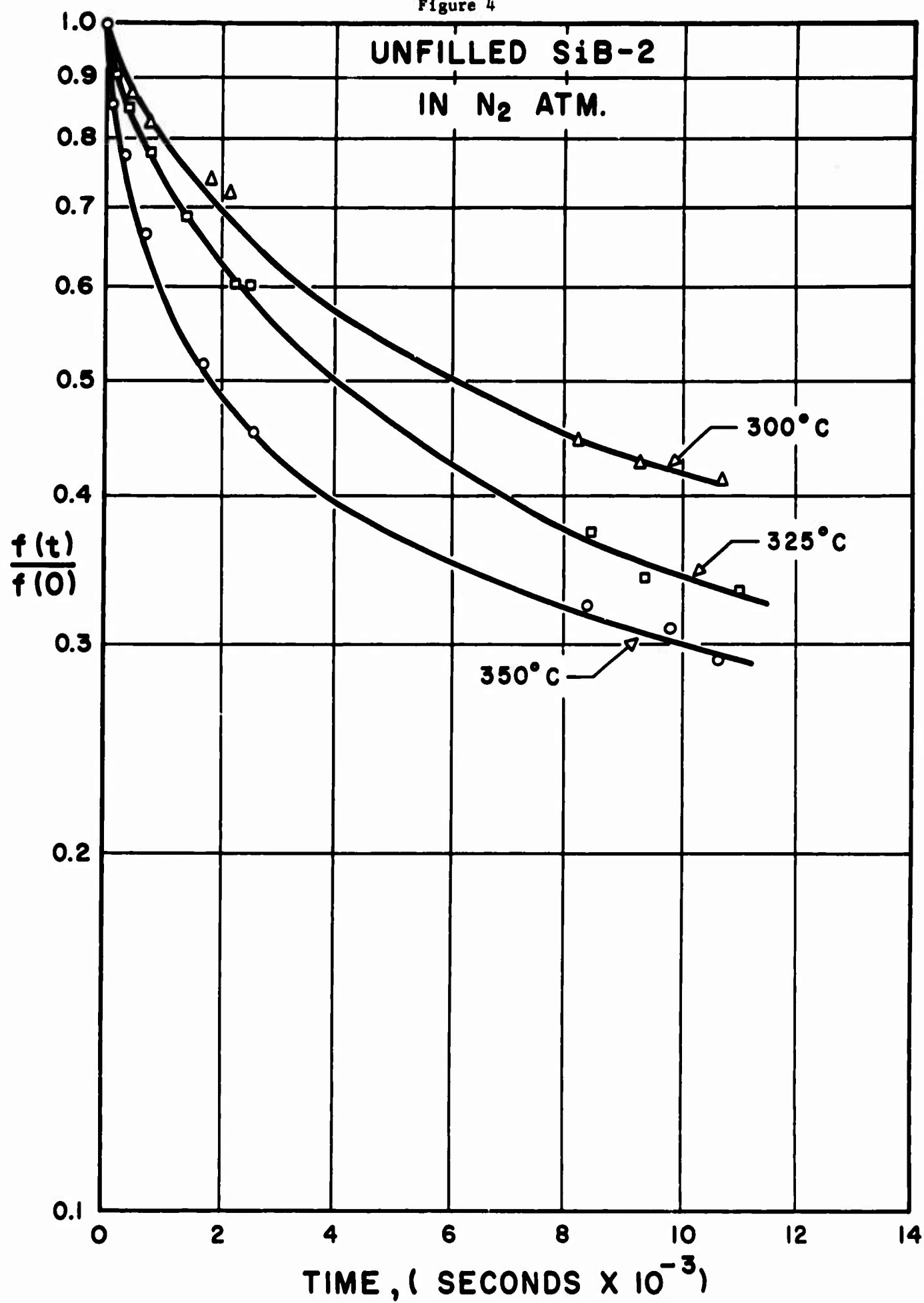
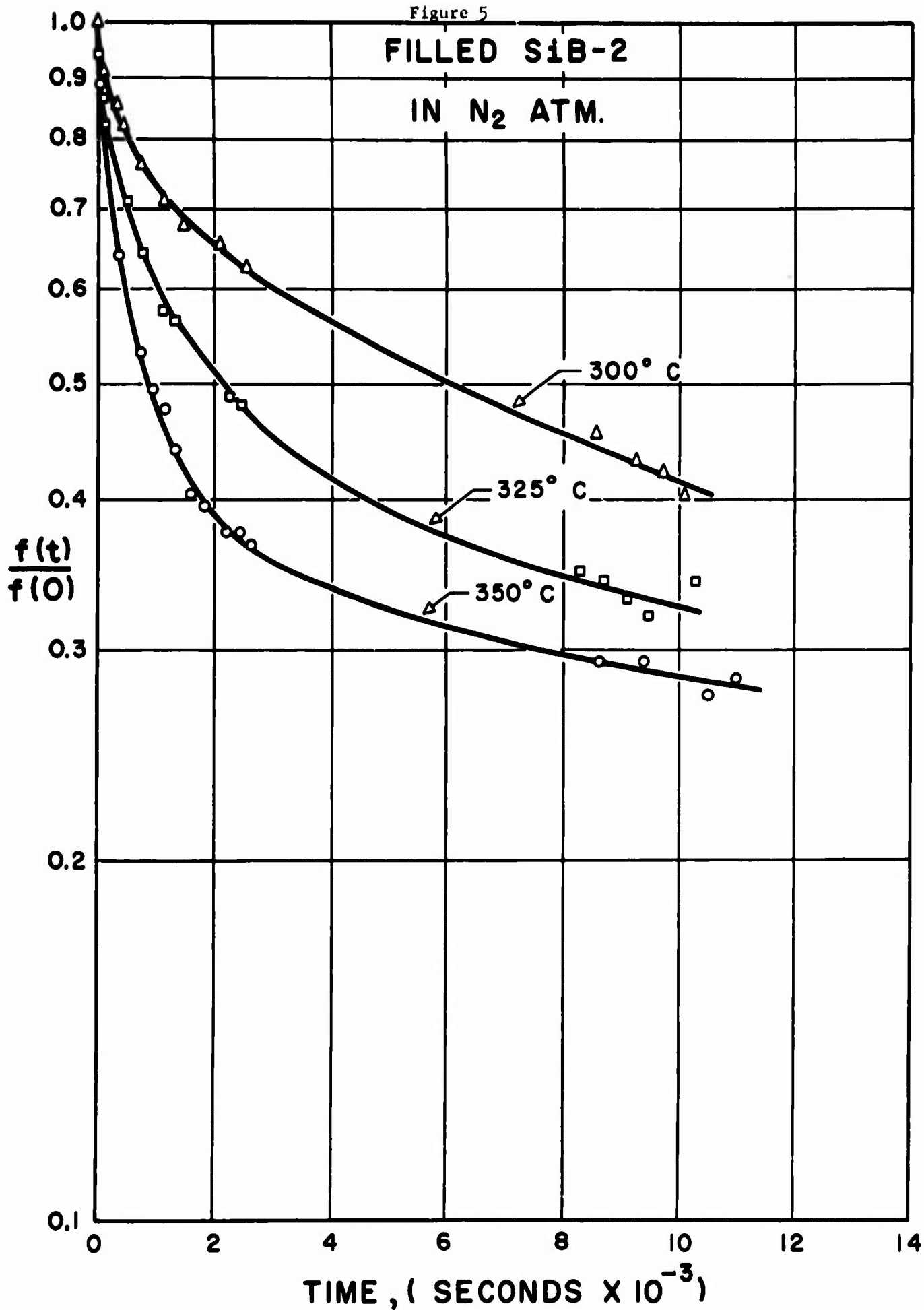


Figure 5



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2. E.J. Zaganlaris, L.H. Sperling, and A.V. Tobolsky, J. Macromol. Sci.-Chem., A1(6), 1111 (1967).
3. M.T. Shaw and A.V. Tobolsky, Technical Report No. 111, Office of Naval Research.

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13 ABSTRACT

The thermal stabilities of elastomers based on poly(dimethyl silozane), poly (trifluoropropyl methyl silozane) and poly-m-carboranyl siloxane, represented by SiB-2, were compared by the technique of chemical stress relaxation in nitrogen. Filled and unfilled elastomers were tested in the temperature range of 300-350°C. The SiB-2 elastomers showed chemical relaxation times which were 50-100 times greater than the other elastomers, illustrating their outstanding thermal stability.

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