

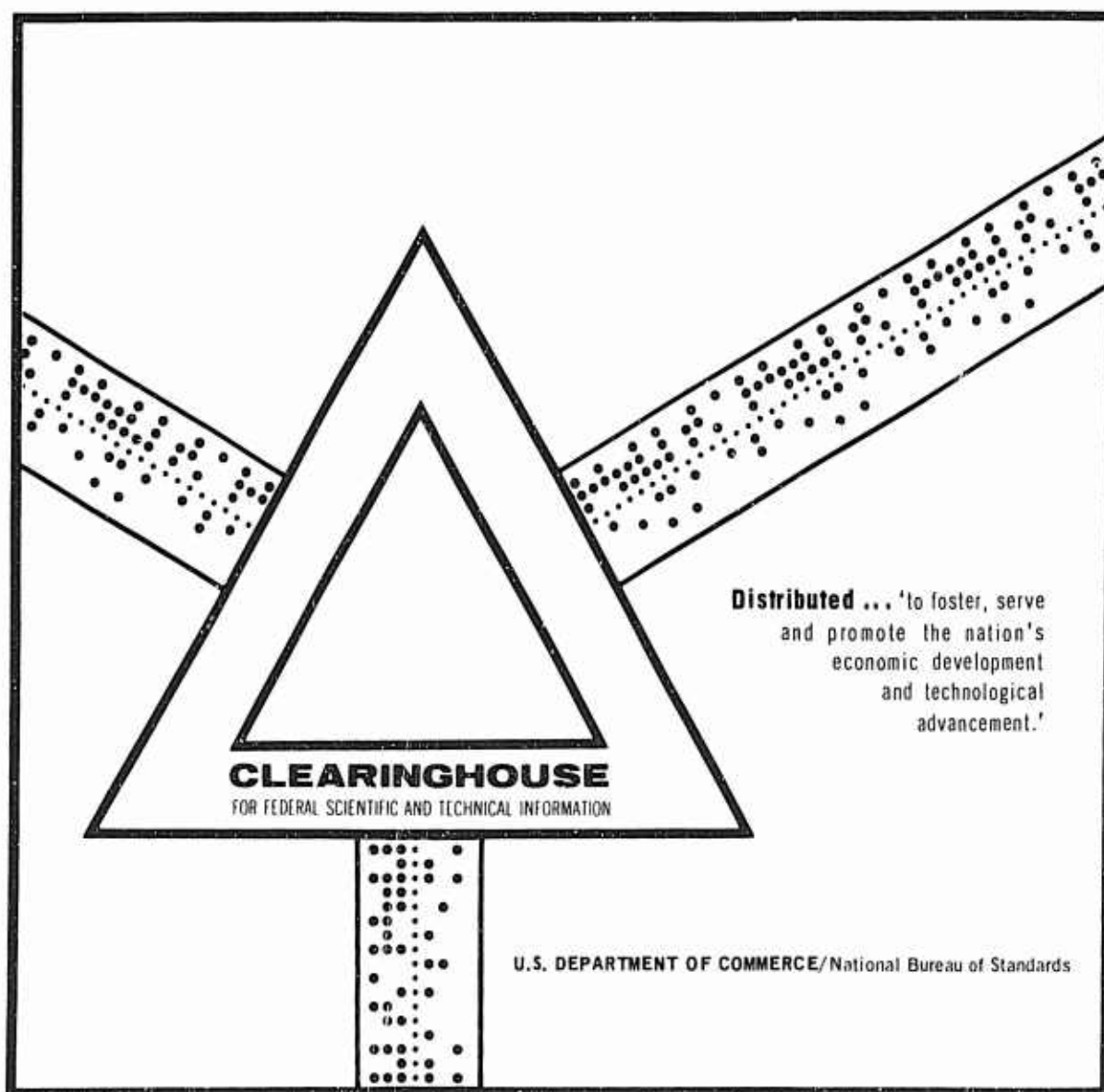
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THERMAL STABILITY OF NETWORKS CONTAINING
SILOXANE LINKAGES

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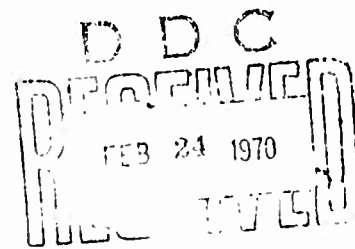
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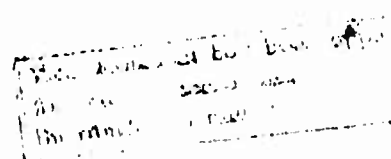
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Introduction:

Elastomers based on the siloxane linkage include some of the most thermally resistant known since the silicon - oxygen bond has an energy of dissociation about 30% greater than the carbon-carbon bond upon which most conventional polymeric materials are based⁴. However, the siloxane linkage appears to have available low energy dissociation routes involving exchange with hydroxyl-containing impurities or even with other siloxane units^{1-3,6}. These reactions are reversible, lead to identical products (except where cyclicization is involved) and generally the crosslinked sample shows little weight loss or deterioration of properties². The technique of chemical stress relaxation, where the elastomer is given a constant elongation and the force decay is measured, reveals these reactions, and has been used extensively to study the effect of impurities (including chain ends) on the thermal stability of dimethyl siloxane elastomers¹⁻⁴. There has been little attempt to apply this method in a unified manner to determine the relative thermal stabilities of the various modifications of the basic dimethylsiloxane elastomer, which have recently been synthesized in an effort to improve stability.

The modifications we report on here include a pendent trifluoropropyl substitution for a methyl group on each unit (Silastic LS-53), a random replacement of 1/3 of the oxygen atoms with m-carborane units

(Dexsil-201), a regular replacement of $\frac{1}{4}$ of the oxygen atoms with m-carborane groups (Dexsil-300) and a random replacement of $\frac{1}{5}$ of the oxygen atoms with m-carborane units plus replacement of $\frac{1}{5}$ of the methyl groups with phenyl groups (Dexsil-402) ⁵. The stability of these materials in nitrogen or vacuum was compared to assess the protection given by the various substituents against the facile degradation reactions suffered by silicone rubber.

Experimental:

The silicone rubber, supplied through the courtesy of Dr. A. C. Martellock of the General Electric Company, Waterford, New York, was crosslinked with t-butyl peroxide via pendant vinyl groups (0.2 mole %), extracted with benzene and vacuum dried. The filled silicone rubber contained fume silica to produce a Shore A hardness of 40. It was cured with benzoyl peroxide.

The Silastic LS-53 samples were donated by Dr. T.D. Talcott of the Dow Corning Company, Midland, Michigan. They were cured with 2pph benzoyl peroxide at 200°F for 15 minutes, extracted with benzene and vacuum dried. The Dexsil samples were supplied by the Olin Corporation, New Haven, Connecticut. The Dexsil 300 was received as a gum and cured with 200 mrad of gamma radiation. The Dexsil-201 samples were press-molded both with and without peroxide (1pph dichlorobenzoyl) and air post cured. The Dexsil-402 was compounded with 20pph Cab-O-Sil and 1pph dichlorobenzoyl peroxide and pressmolded at 110°C for 10 minutes. A Dexsil-201 sample with the same composition was fabricated for a direct

comparison. The latter samples were air postcured, extracted with acetone and vacuum dried.

The conditions for the stress relaxation experiments are listed in the Table. The runs in nitrogen (20ppm O₂, 20ppm H₂O) were performed using a standard relaxation balance⁷ with an attached nitrogen chamber, while the runs in vacuum (0.5 microns) employed a spring balance of recent design⁸. The samples were held in vacuum or nitrogen at an elevated temperature for 16 hours and at the test temperature for 1/2 hour before the runs were started.

Results and Discussion:

The chemical stress relaxation times (time required for the force to reach 1/e of its initial value) and half times (time to reach 1/2 of the initial value) are listed in the Table along with the conditions for the run. Some of the more pertinent runs at 350°C are illustrated in the Figure.

Of the unfilled materials, the Dexsil-201 with no peroxide shows clearly the best stability. The crosslinking in this material is believed to result from water and residual polymerization catalyst which generate (during pressing) reactive sites by displacing methyl groups⁵. The network contains no C-C or Si-C-Si linkages and the m-carborane units along the chain give extraordinary stability to the siloxane linkages. Adding peroxide (to give additional crosslinks via vinyl groups attached to the carborane groups) has a detrimental effect, lowering the stability to that of filled silicone rubber at 300°C in

nitrogen. At higher temperatures, the effect is less noticeable, perhaps because the weak linkages introduced by the peroxide have all disappeared before the run is started.

Reducing the number of carborane groups by 50% to give Dexsil-300 results in a loss of stability, even though the carborane groups are evenly spaced, leaving no long sequences of siloxane linkages unprotected. At fault may be the relatively weak C-C and Si-C-Si bonds introduced during the radiation crosslinking process⁹. Radiation is also known to lead to Si-O-Si bonds⁹ which may be responsible for a decrease in the rate of stress relaxation noted at longer times analogous to sulfur-cured ethylene-propylene terpolymer with weak polysulfide and stronger disulfide and monosulfide crosslinkages¹⁰.

A comparison of the relaxation times for the filled Dexsil-201 and 402 samples shows that pendant phenyl groups cannot provide the same protection as main chain carborane groups against facile thermal reactions.

Placing pendant trifluoropropyl groups along the chain is not a route to thermal stability, as evidenced by the short relaxation times of the Silastic LS-53 samples. Iron oxide filler is necessary to give a material suitable for high temperature use.

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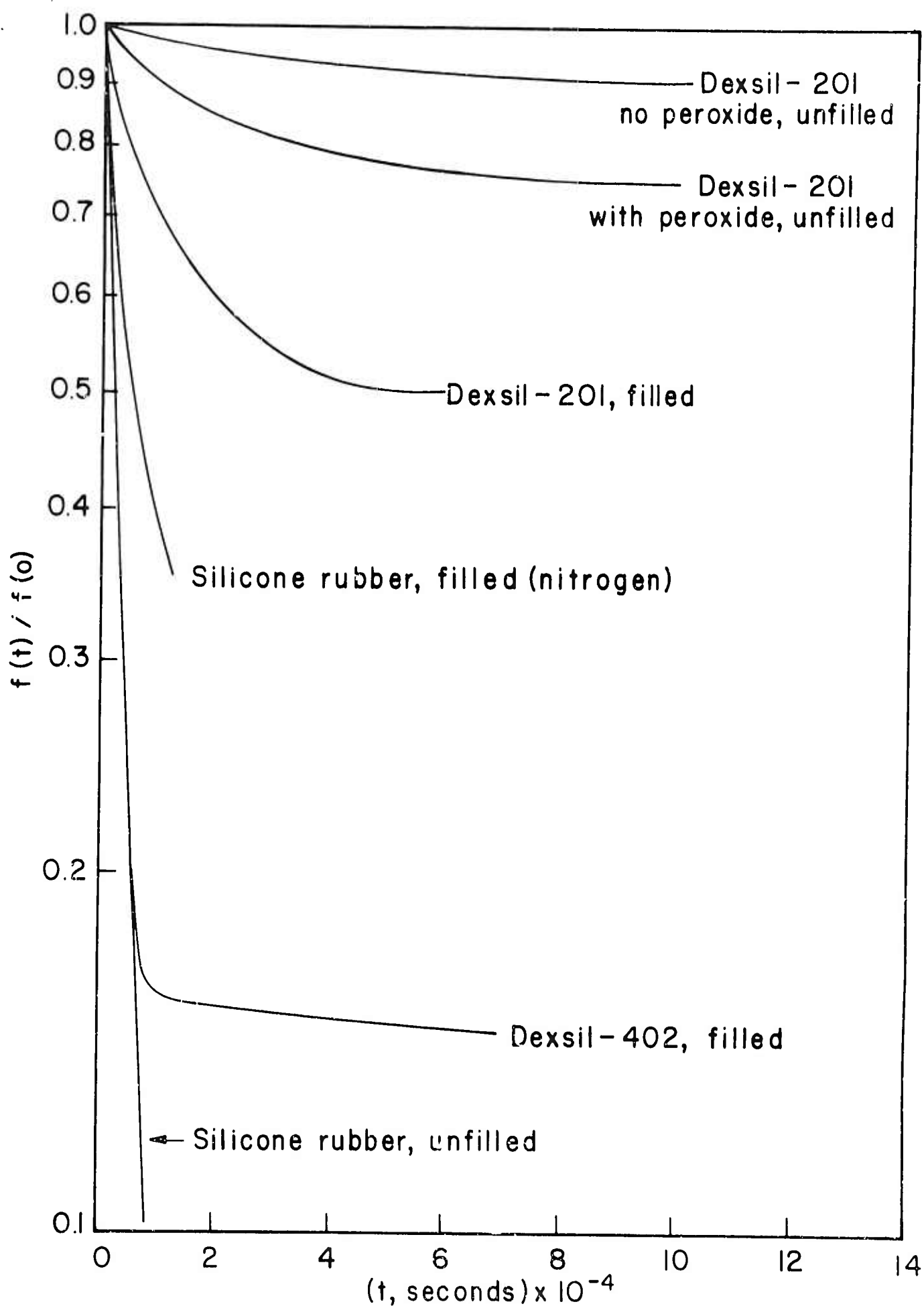
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Chemical Relaxation Times and Half Times of Siloxane-Containing Elastomers.

Polymer	Filler	Cure and Post-Cure Treatment	Test atmosphere & Temperature, °C.	$\left[t\left(\frac{1}{2}\right), \right] \times 10^{-4}$ seconds	$\left[t(1/e), \right] 10^{-4}$ seconds
Silicone Rubber	none	TBP through vinyl. Extracted with benzene & vacuum dried.	Nitrogen, 300 325 350 Vacuum, 350	0.21 0.16 0.10 0.13	0.36 0.23 0.14 0.24
"	Fume silica to Hardness 40	Benzoyl peroxide, Extracted with Benzene and vacuum dried.	Nitrogen, 300 315 330 350	6.4 4.1 2.3 0.55	>14 8.6 5.3 1.25
Silastic LS-53, poly(trifluoropropyl-methyl siloxane)	1pph silica	2pph benzoyl peroxide. Extracted with benzene and vacuum dried.	Nitrogen, 300 325 350	0.085 0.025 -	0.15 0.035 -
"	1pph silica 10pph iron oxide	"	Nitrogen, 300 325 350	0.20 0.085 0.015	0.40 0.14 0.035
Dexsil-201	none	Press molded, air post cure.	Vacuum, 350 400 450	>>14 >>14 1.7	- - 2.8
"	none	1pph DCBP, air post cure, extr. acetone vacuum dried.	Nitrogen, 300 325 350 Vacuum, 350	6.0 4.0 1.8 >14	>14 8.3 5.1 >14
Dexsil-300	none	200 mrad γ -cure	Vacuum, 400	0.35	>2.0
Dexsil 402	20pph Cab-O-Sil	2pph DCBP, air post cure, extr. acetone vacuum dried.	Vacuum, 350	0.25	0.35
Dexsil 201			Vacuum, 350	4.8	>7

Caption for Figure

Stress Relaxation of Siloxane-Containing Elastomers at 50°C
in Vacuum



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12. ABSTRACT The thermal stability of elastomers containing siloxane linkages has been compared using the technique of chemical stress relaxation in an inert environment. Enhancement of the already high stability of the basic poly(dimethylsiloxane) silicone rubber by the substitution of hetero groups in and on the main chain was proved. Particularly dramatic was the effect of the m-carborane moiety in SiB-2 elastomers which enhanced the thermal stability of the siloxane chain by more than 100°C.		

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Chemical Stress Relaxation						
SiB-2 Elastomers						
Siloxane Elastomers						
Silicone Rubber						