

## Properties of DEXSIL 300 Rubbers

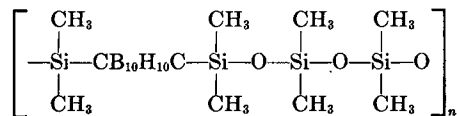
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### Synopsis

The physical and elastomeric properties of several DEXSIL 300 (10-SiB-3) samples were investigated. Modulus-temperature studies were used to determine the glass transition temperature  $T_g$ , the melting temperature  $T_m$ , and the oxidative crosslinking temperature  $T_{ox}$ . Stress relaxation in air at elevated temperatures was used to compare the oxidative stability of the various formulations. It was found that the  $T_g$  of DEXSIL 300 is some 30°C lower than that of DEXSIL 200 (10-SiB-2) polymers, extending the elastomeric properties of DEXSIL 300 to lower temperatures. At high temperatures, both silica filler and ferric oxide are found to increase  $T_{ox}$  to an ultimate value of 320°C. The effects of cure were also investigated, and  $\gamma$ -radiation-cured samples exhibit a slight degree of crystallinity with a melting temperature  $T_m = +40^\circ\text{C}$ . No crystallinity was detected in similar peroxide-cured samples. Stress relaxation results are presented in support of the modulus-temperature studies. Formulations with a low  $T_{ox}$  show oxidative effects earlier than those with a higher oxidation temperature. Silica- and ferric oxide-filled samples exhibit improved oxidative stability, as do samples filled with diphenylsilanediol.

### INTRODUCTION

A number of techniques have been used to characterize the elastomeric and mechanical properties of SiB rubbers. Some of these are the Gehman modulus test,<sup>1,2</sup> thermoelasticity,<sup>2</sup> stress relaxation,<sup>1,5</sup> and torsional braid analysis.<sup>6</sup> Previous studies have largely centered on SiB-1, SiB-2, and their copolymers. The present investigation is concerned with a study of SiB-3 (DEXSIL 300) which can be represented by



Particular attention is paid to the high-temperature oxidative properties of this polymer which were studied by the Gehman modulus determination and stress relaxation in air at elevated temperatures.

### EXPERIMENTAL

Several types of DEXSIL 300 samples were kindly supplied by Dr. J. Sieckhaus of the Olin Corporation, New Haven, Connecticut. The formulations are given in Table I. Along with these crosslinked specimens, a

TABLE I  
Formulations of Samples<sup>a</sup>

Sample	DEXSIL 300	Min-U- Sil	Cab-O-Sil	Fe <sub>2</sub> O <sub>3</sub>	Cure	Other additives	T <sub>i</sub> , °C	T <sub>ox</sub> , °C
A	100	—	—	—	2.5 VAROX	—	-65	275
B	100	—	—	—	100 mrad γ-radiation	—	-63	270
C	100	80	15	—	2.5 VAROX	—	-55	300
D	100	80	15	10	2.5 VAROX	—	-55	320
E	100	80	15	15	2.5 VAROX	—	—	320
F	100	—	—	10	2.5 VAROX	—	—	305
G	100	80	15	—	2.5 VAROX	3 IONOX	-60	290
H	100	80	15	10	2.5 VAROX	3 φ <sub>2</sub> Si(OH) <sub>2</sub>	-56	345
I	100	80	15	10	ABIN	—	—	307
J	100 DEXSIL 200	30	—	10	2 Lupercio CST peroxide	—	—	—

<sup>a</sup> The numbers in the table refer to the relative parts of each component in the formulations.

few gums of various formulations were supplied for radiation crosslinking studies which are now in progress. One of these  $\gamma$ -ray-crosslinked samples, an unfilled DEXSIL 300, was studied for the presence of crystallinity.

The 10-sec modulus  $G(10)$  was measured on a standard Gehman<sup>7</sup> and a high-temperature modification of this instrument.<sup>8</sup> The results from these two tests were combined to give modulus-temperature curves from  $-70^\circ\text{C}$  to  $+400^\circ\text{C}$ . A standard heating rate of  $1^\circ\text{C}/\text{min}$  was used. Stress relaxation studies were made on a spring relaxometer previously described.<sup>9</sup> All the runs to be reported here were made in an air atmosphere at elevated temperatures.

## RESULTS AND DISCUSSION

Gehman test results for the unfilled DEXSIL 300 samples A and B are shown in Figure 1. The general shape of the curves is typical of a crosslinked rubber sample. The modulus in the glassy region is above  $10^{10}$  dynes/cm<sup>2</sup>, as was found for all the DEXSIL samples. The inflection temperature  $T_i$ , defined as the temperature at which  $3G(10) = 1 \times 10^9$  dynes/cm<sup>2</sup> is  $-63^\circ$  to  $-65^\circ\text{C}$  for unfilled samples. The decrease in the glass temperature from SiB-2 ( $T_g = -30^\circ\text{C}$ ) is expected since the addition of more siloxyl units per carborane makes the structure more like polydimethylsiloxane with  $T_g = -123^\circ\text{C}$ . This effect is shown in Figure 2, which represents the copolymer equation for  $\text{-(CH}_3\text{)}_2\text{SiC}_2\text{B}_{10}\text{H}_{10}\text{-}$  and  $\text{-(CH}_3\text{)}_2\text{SiO-}$  groups. The data points between SiB-1.0 and SiB-2.0 were taken from Zaganarias, Sperling, and Tobolsky.<sup>2</sup>

Sample A, which was peroxide cured, shows the normal rubbery plateau at  $3G(10) = 2 \times 10^6$  dynes/cm<sup>2</sup>. Sample B, which was  $\gamma$ -radiation cured, shows two distinct rubbery plateaus. The first, extending from  $-50^\circ\text{C}$  to  $+40^\circ\text{C}$ , exhibits a modulus  $3G(10) = 5.5 \times 10^6$  and a melting point  $T_m = 40^\circ\text{C}$ . The second plateau, which starts at  $+40^\circ\text{C}$  and extends to the oxidation temperature, is at  $3G(10) = 4 \times 10^6$  dynes/cm<sup>2</sup>. Similar results, with a higher melting temperature, have been reported for DEXSIL 200.<sup>1</sup> No plateau associated with crystallinity is observed in peroxide-cured samples, probably because the crosslinking temperature is above  $T_m$ ; while in the case of  $\gamma$ -radiation crosslinking, the temperature is probably below  $T_m$  although some sample heating does take place. Above  $250^\circ\text{C}$ , these unfilled DEXSIL rubbers show an abrupt rise in the modulus attributed to oxidative crosslinking. As the temperature is raised, the samples become stiffer and eventually break. The termination of the modulus-temperature curve marks this breaking point. An oxidation temperature,  $T_{ox}$ , has been defined as the temperature at which extrapolations of the rubbery plateau and the steep rise in modulus cross. Both of these unfilled samples showed the same oxidation temperature  $T_{ox} = 270^\circ\text{-}275^\circ\text{C}$ . This is considerably lower than  $T_{ox} = 340^\circ\text{C}$  reported for an unfilled DEXSIL 200.<sup>1</sup>

The effects of fillers on the modulus-temperature curves of DEXSIL 300 are shown in Figure 3. Curve A, representing the unfilled polymer, has

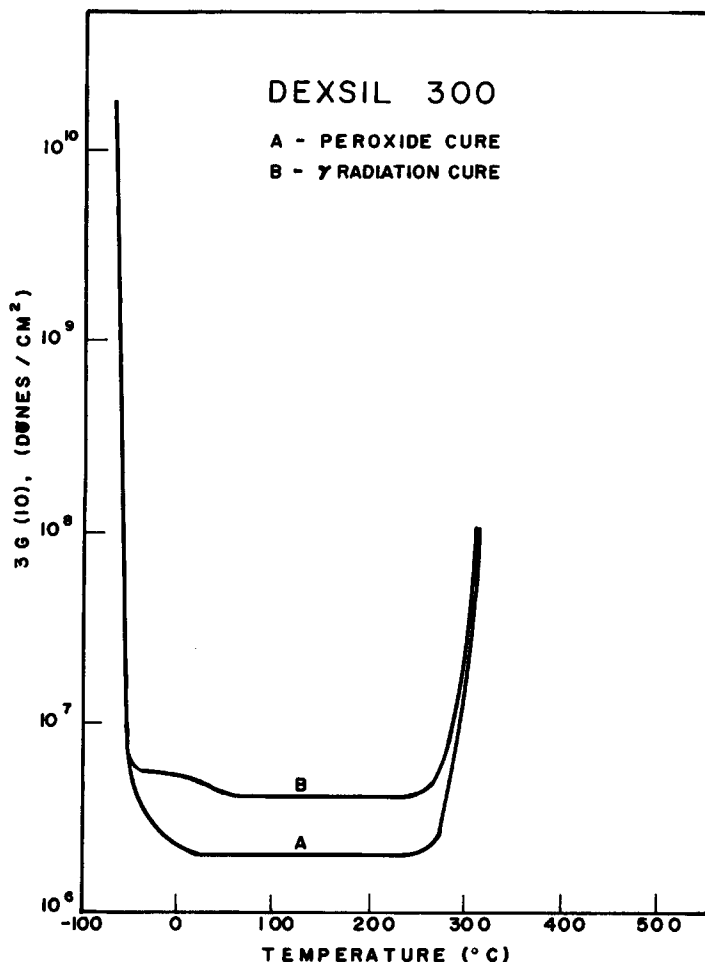


Fig. 1. Log modulus-vs.-temperature plots for samples A and B, showing differences due to type of cure.

been included for comparison. Three important points are to be noted. First, there is an increase of about 5–10°C in the inflection temperature  $T_i$  which is associated with the glass transition. Secondly, the rubber plateau modulus has been increased to about  $10^7$  dynes/cm<sup>2</sup>. Thirdly, the oxidation temperature  $T_{ox}$  has been increased in all cases to 300°C and above. Looking at the  $T_{ox}$  results in Table I, one notices that the addition of silica filler raises the oxidation temperature some 25°C to  $T_{ox} = 300^\circ\text{C}$  (sample C). Ferric oxide,  $\text{Fe}_2\text{O}_3$ , has been used for some time to increase the oxidative stability of silicones, and it is also being used in DEXSIL formulations. From the table, it is seen that addition of 10%  $\text{Fe}_2\text{O}_3$  to a silica-filled sample increases the oxidation temperature to 320°C (sample D), while addition of another 5%  $\text{Fe}_2\text{O}_3$  has no further effect on  $T_{ox}$  (sample E). The addition of ferric oxide alone, without silica filler, also raises the oxidation temperature

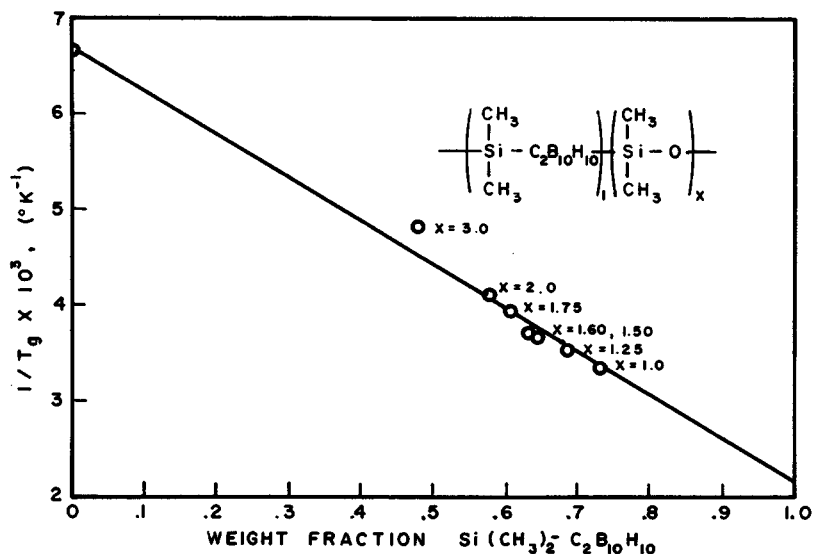


Fig. 2. Glass temperature vs. weight fraction  $\text{Si}(\text{CH}_3)_2\text{-C}_2\text{B}_{10}\text{H}_{10}$  in DEXSIL polymers.

compared to unfilled polymer. The resulting  $T_{ox}$  for a sample containing 10%  $\text{Fe}_2\text{O}_3$  and no silica filler is  $305^\circ\text{C}$  (sample F), which is an increase of  $30^\circ\text{C}$ . The combined enhancement of silica filler and ferric oxide is seen to be slightly less than the sum of the separate effects.

Another antioxidant which is frequently used in polymers is IONOX [1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene]. Sample G was formulated with the regular silica filler content and peroxide, but it contained 3 parts IONOX instead of the ferric oxide. The processed samples turned out poorer than those with the regular formulations, and the Gehman results indicate a decrease in oxidative stability.

In order to counteract oxidative crosslinking and the resulting sample stiffening at high temperatures, a monomeric unit capable of undergoing interchange reactions with siloxyl groups was added to one sample. This compound is diphenylsilanediol  $[(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2]$ , and the polymer sample formulation is given in Table I under sample H. As expected,  $T_{ox}$  increased some  $25^\circ\text{C}$  over a comparably filled DEXSIL 300 without the diol compound.

All of the previous samples were cured with peroxide (i.e., VAROX). Another sample, which was cured with azobisisobutyronitrile (ABIN), was tested on the Gehman apparatus. It also contained silica and  $\text{Fe}_2\text{O}_3$  and showed an oxidation temperature  $T_{ox} = 307^\circ\text{C}$  (sample I). It had been hoped that this cure would produce a more stable rubber at high temperatures; however, the Gehman results indicate that the oxidative stability of ABIN cured DEXSIL 300 is worse than that of peroxide cured samples.

The various DEXSIL 300 samples were also studied by stress relaxation in air at elevated temperatures. The results for a typical filled DEXSIL

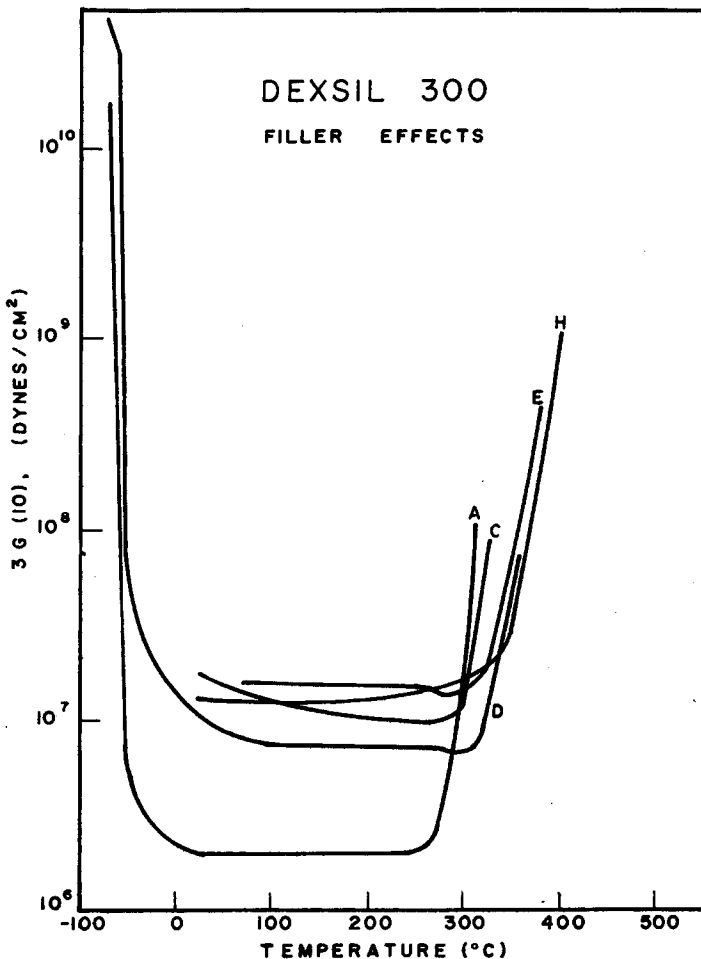


Fig. 3. Log modulus-vs.-temperature plots for samples A, C, D, E, and H, showing effects of filler.

300 polymer (sample D) are shown in Figure 4. The quantity  $f(t)/f(0)$  represents the ratio of the force at time  $t$  to that initially. At short times ( $<20,000$  sec), the sample shows relaxation behavior typical of rubbery materials, with the force steadily decreasing with time. Also it is seen that the rate of this relaxation increases with increasing temperature. The samples run at  $200^\circ$  and  $240^\circ\text{C}$  continue to show normal relaxation behavior for time periods extending over 30 hr. On the other hand, samples studied at about  $260^\circ\text{C}$  and above start to show oxidative effects within the same time period. This is evidenced by an upswing of the relaxation curve due to sample shrinkage accompanying oxidative crosslinking. Figure 4 shows that this oxidative effect occurs at shorter times and is more pronounced as the temperature is raised.

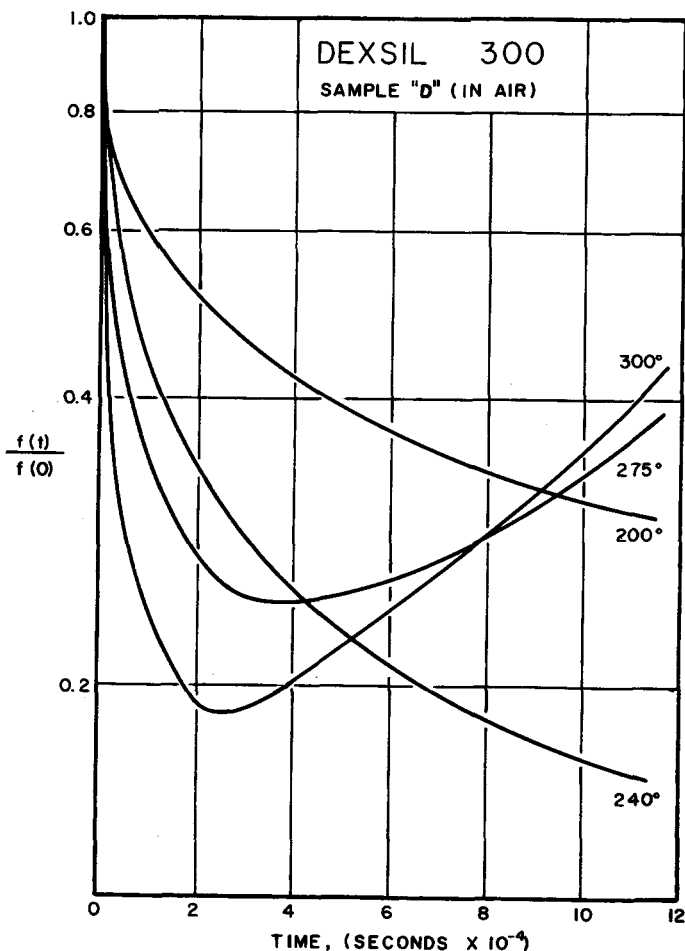


Fig. 4. Stress relaxation curves for sample D at various temperatures.

It is interesting to compare the relaxation behavior of DEXSIL 300 with that of DEXSIL 200, a similar polymer which contains fewer siloxyl groups per carborane unit. As can be seen from Figure 5, the oxidative stability of DEXSIL 300 at 300°C is considerably poorer than that of a less well-filled DEXSIL 200 (sample J). The DEXSIL 300 shows a more rapid initial stress relaxation followed by oxidation, while the 200 sample shows no oxidation effects at 300°C, even for more than 30 hr.

As was shown in the previous section on Gehman results, ferric oxide is quite effective in retarding oxidation. The stress relaxation experiment shows a pronounced difference between comparable DEXSIL 300 samples with and without ferric oxide (samples D and C, respectively). Figure 6 shows that the initial relaxation of both samples is identical. However, sample C, which contains no ferric oxide, starts to show oxidation effects

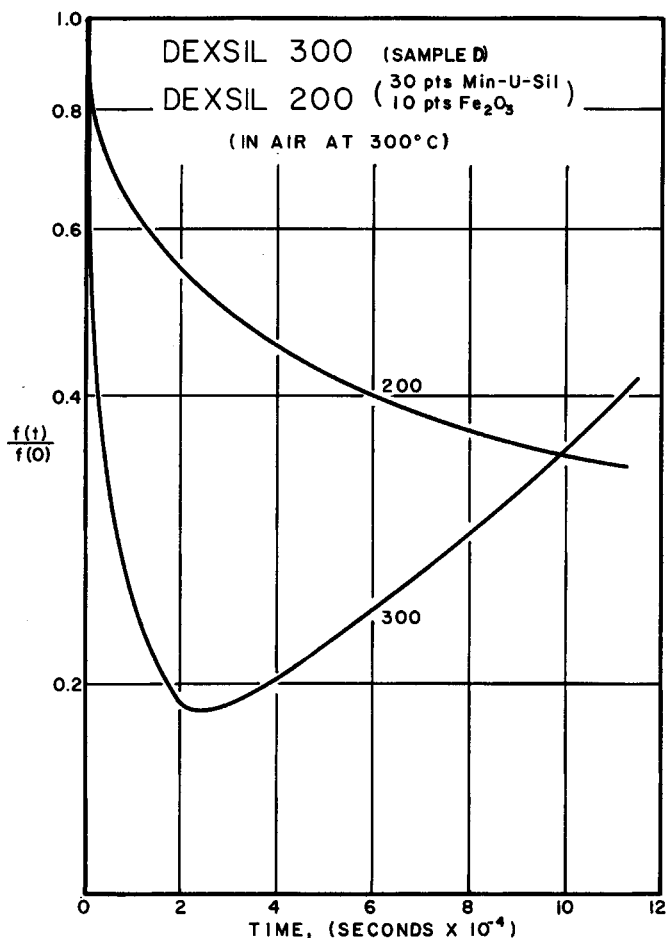
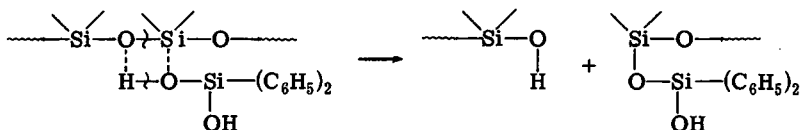


Fig. 5. Stress relaxation comparison of DEXSIL 200 and DEXSIL 300.

in about 2½ hr at 300°C. Sample D, with 10 parts Fe<sub>2</sub>O<sub>3</sub>, shows a delay in oxidative crosslinking of about 4 hr more than the unprotected sample. At the end of this experiment, comparison of the two samples showed that the one without ferric oxide was much more brittle and less elastic than the ferric oxide-containing specimen.

Another sample described earlier as showing improved oxidative properties is sample H, which contains diphenylsilanediol. This material is thought to participate in interchange reactions:



One sees from the above equation that the number of chain ends is increased by two for each reaction, and hence the number of network chains capable



of supporting a given stress will be decreased. Since this process reduces the number of effective chains and hence causes a decrease in the force measured in a stress relaxation experiment, it should counteract to some extent the additional crosslinking resulting from oxidation. This is in fact observed in Figure 7, where samples D and H are identical except that the latter contains 3 parts  $(C_6H_5)_2Si(OH)_2$ . While sample D shows oxida-

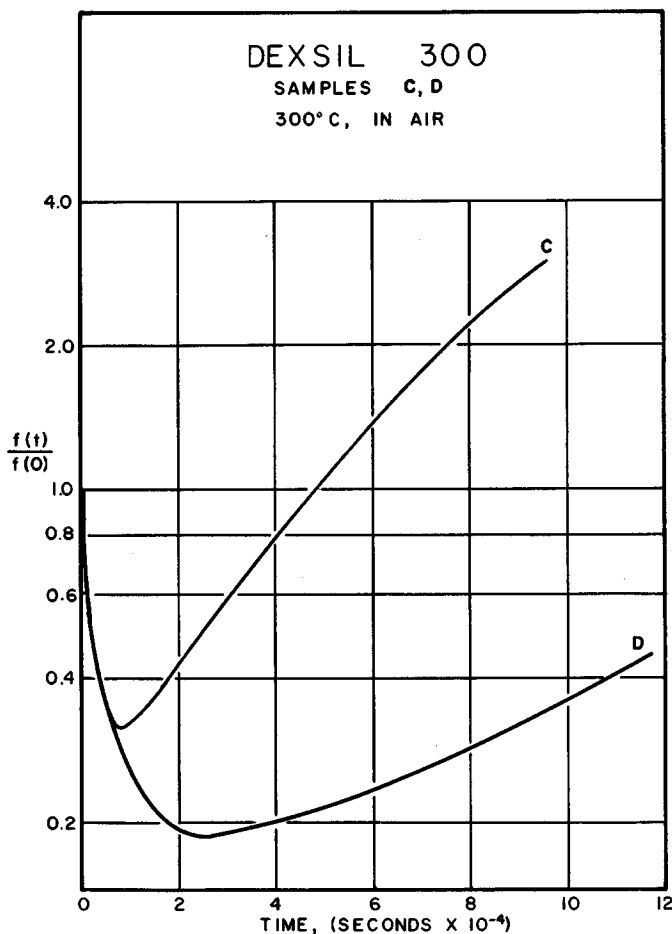


Fig. 6. Stress relaxation comparison of samples C and D, showing effects of ferric oxide on the relaxation curve.

tion effects in a matter of a few hours, sample H shows no upswing in its relaxation curve, even after more than a day. This is not to say, however, that sample H is more resistant oxidatively. Although the diphenylsilanediol does inhibit the upswing of the stress relaxation curve, it does so by a chain scission process and it does not prevent oxidation which is occurring simultaneously.

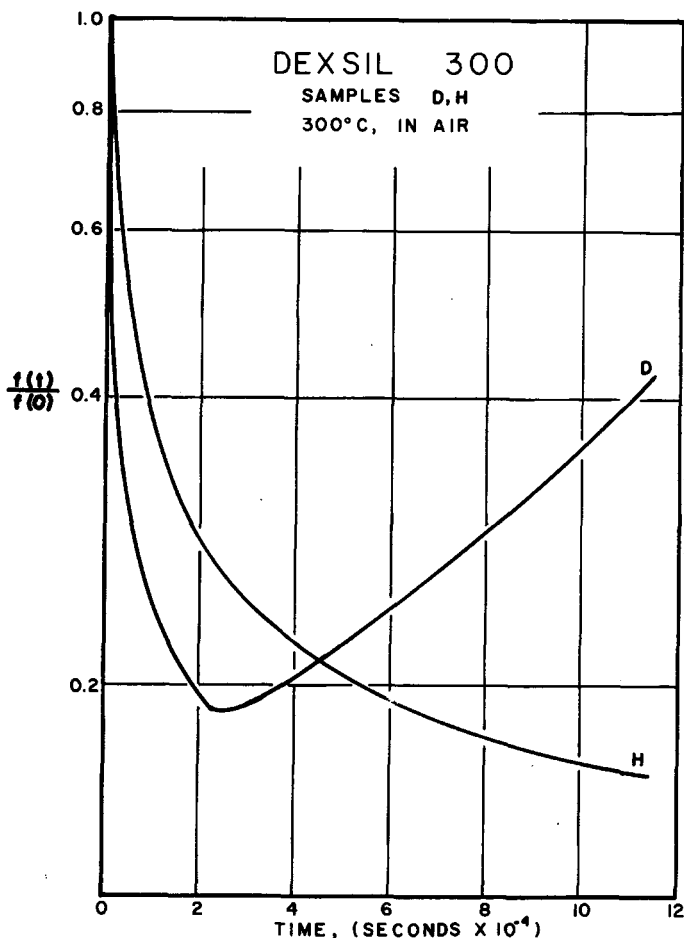


Fig. 7. Stress relaxation comparison of samples D and H, showing the effects of diphenylsilanediol.

### SUMMARY AND CONCLUSIONS

Summarizing the Gehman and stress relaxation results, it was found that:

1. DEXSIL 300 exhibits a glass transition at around  $-60^{\circ}$  to  $-65^{\circ}\text{C}$  for unfilled and  $-55^{\circ}\text{C}$  for filled samples, as compared to  $-30^{\circ}\text{C}$  for unfilled DEXSIL 200.
2. The rubbery modulus is around  $3G(10) = 2 \times 10^6$  dynes/cm<sup>2</sup> for unfilled and around  $1 \times 10^7$  dynes/cm<sup>2</sup> for filled samples.
3. The oxidative temperature  $T_{ox}$  occurs at around  $275^{\circ}\text{C}$  for unfilled samples of DEXSIL 300 and is increased to about  $300^{\circ}\text{C}$  by addition of either silica filler or ferric oxide. Addition of both of these materials raises  $T_{ox}$  to  $320^{\circ}\text{C}$ .  $T_{ox}$  for an unfilled DEXSIL 200 has previously been reported at  $340^{\circ}\text{C}$ .<sup>1</sup>

4. IONOX does not appear at this time to be a good antioxidant for SiB rubbers.

5. Diphenylsilanediol promotes chain interchange and apparently counteracts the stiffening due to oxidative crosslinking at high temperatures. It is questionable as to whether this is really an improvement, however.

6. Azobisisobutyronitrile has been shown to be a poorer crosslinking agent than peroxide in terms of high-temperature oxidative stability.

7. A  $\gamma$ -radiation-cured sample showed some crystallinity with  $T_m = +40^\circ\text{C}$ . No evidence of crystallinity was found in similar peroxide-cured samples.

8. The high-temperature oxidative properties are about the same for both  $\gamma$ -ray- and peroxide-cured samples which contain no filler.

At the present time, further work is being carried out on radiation crosslinking of filled DEXSIL 300 samples in an attempt to produce a more thermally and oxidatively stable system. A new vacuum relaxometer is being completed to characterize the thermal stability of these SiB polymers, and a linear temperature programmer has been built to aid in thermoelastic studies. Stress-strain work on ring-shaped specimens is also planned in an attempt to obtain more information on the ultimate properties of these rubbers.

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