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Long-Term Stiffening of Neoprene Pads for the Poseidon Missile Launch System

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Synopsis

In a previous paper[1] the development of neoprene formulations and mechanical designs to meet operational requirements for the Poseidon launch tube liner pads were presented. Subsequently, it was found that early development pads aged for three months at room temperature were ~10% stiffer than the vendor's qualification compression–deflection (C–D) test values. The increase was attributed to a combination of normal elastomer recovery and continued crosslinking due to the original low state of cure of the pads. A program was designed to study the effect of postcure time and temperature on C–D recovery, the effect of carbon black loading on the C–D recovery, and room temperature and accelerated aging at elevated temperature on these effects. Values of the molecular weight between crosslinks ($\bar{M}_c$) were determined experimentally to establish the state of cure. The results of these experiments are presented and discussed. Recommendations are given for reducing C–D variation by modifying carbon black loading and/or postcure conditions.

INTRODUCTION

It is known that the stress coordinate of a stress–strain curve is reduced with each successive deformation of the rubber specimen and that the recovery mechanism alone will not completely restore the rubber to the initial state in a reasonable time.[2] The stress difference between successive compression or extension cycles is associated with the normal "Mullins softening" of a filled vulcanizate. On aging at room temperature, the near-complete recovery from the second cycle to initial or virgin values for a well-cured vulcanizate is associated with "Mullins recovery" and should require a very long time. In 1947, Mullins showed that for black-filled natural rubber vulcanizates (~35% volume fraction carbon black), only about 15% recovery of load was attained between the first and second extensions of rubber strips after more than 100 hr of aging at room temperature. After 100 hr at 100°C, the recovery was about 90%. Although not specifically mentioned, it is assumed that Mullins worked with well-cured vulcanizates since no increase above initial or virgin load values was recorded.

The stiffening of the neoprene pads discussed in this paper was discovered during the early development phase of manufacturing after Westinghouse had accepted several pads that met the C–D specifications. At that time, virgin pads were precrushed 1.0 to 1.1 in. in a modified punch press, and no load–deflection record was taken. One to three days later, the pads were given the test-for-record (TFR) in the vendor's testing machine at a rate of 2.0 in./min. The TFR was the test that had to be within specified limits. Approximately three months later, randomly selected pads were retested and found to be about 10% stiffer than the vendor's TFR. It was suspected that the increase was due to a combination of elastomer recovery and additional crosslinking. Figure 1 shows typical static precrush and TFR C–D curves and illustrates that the difference is in the vicinity of 10%. Crystallization is not believed to be a significant process in the stiffening mechanism, as x-ray diffraction patterns of aged and unaged control specimens exhibited similar patterns.[3]

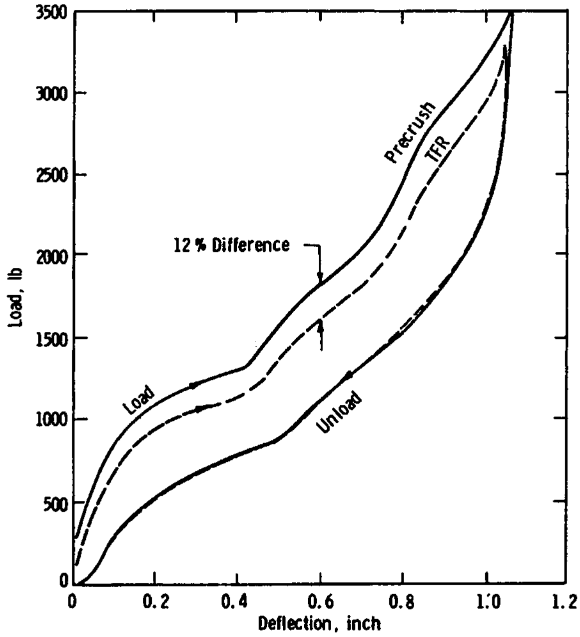

Fig. 1. Typical precrush and TFR compression–deflection records.

At this point, it is appropriate to define recovery and growth as used in the paper:

Recovery—Any increase in stress from a second or subsequent loading cycle, regardless of the mechanism, providing the absolute value is less than precrush or virgin stress level.

Growth—Any increase in stress from a second or subsequent loading cycle, regardless of the mechanism, providing the absolute value is greater than precrush.

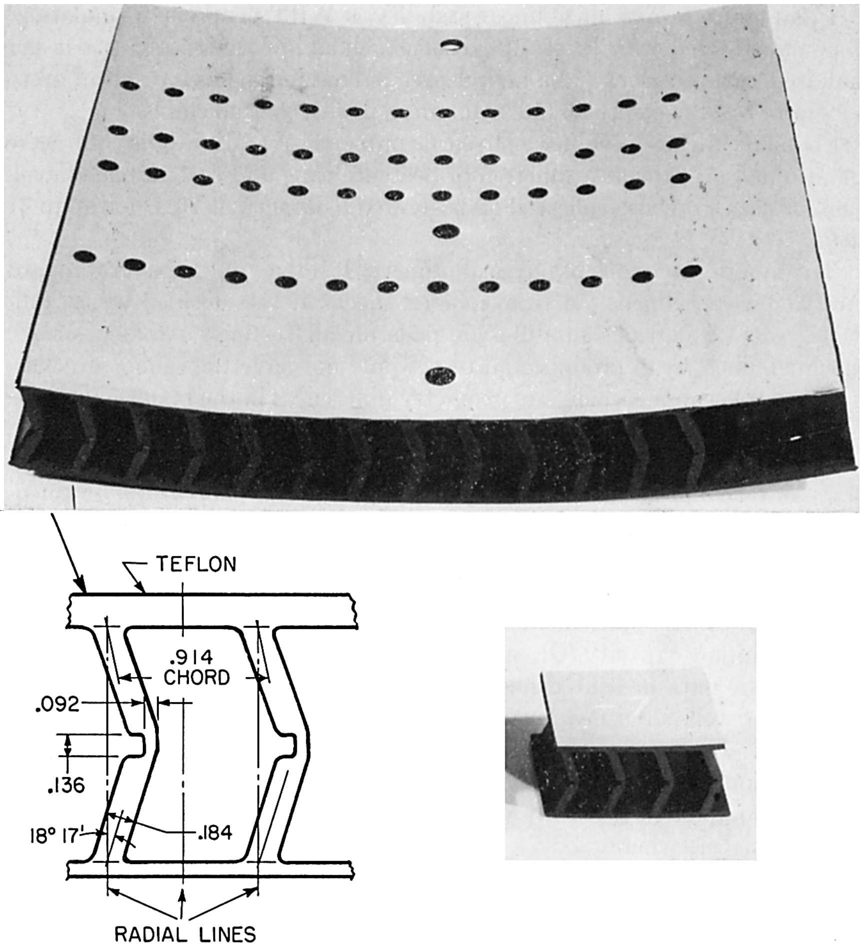

Fig. 2. Full-scale noeprene pad and specimen made by sectioning a pad.

These definitions are consistent with the term "% change" used in this paper. Negative values denote stresses or loads less than precrush, and positive numbers indicate values exceeding precrush.

The contribution of additional crosslinking was suspected because the state of cure of the subject pads was found to be quite low initially due to the short and variable postcure cycles employed by the vendor. Up to this time, postcuring conditions had not been studied in detail. Two hours of postcure in a laboratory oven at 150°C had been arbitrarily selected based on early successful experiments and was found satisfactory to meet all desired requirements. However, due to the slower temperature recovery inherent to the production postcure oven, pad temperatures seldom reach 150°C in 3 hr even though the nominal oven preheat temperature was about 155°C.[4] Hence, the state of cure of the subject pads was not considered adequate for maximum long-term stability under use conditions.

In an effort to maximize linear stability, a WRT neoprene formulation[1] was investigated with levels of carbon black as low as 116 phr (parts per hundred parts rubber) and a high degree of crosslinking as a result of up to $7^1/_2$ hr of oven postcure at 150°C monitored with thermocouples.

Crosslink density values, physical properties, and fatigue life were determined on pads as a function of postcure time and carbon black level. Similar data were also collected on postcured pads aged at 70°C for up to 31 days.

To obviate objections to physical property test data obtained on standard ASTM test specimens cut from molded sheets, it was decided to use full-scale pads or portions of full-scale pads for all testing. Molded sheets, although cheaper to produce and test, would not have the same cure characteristics because of mass and geometry differences in the material and the molds. Most crosslink density values and tensile data were obtained from samples die-cut from the bonding surface of full-scale pads to obtain data representative of actual pad material. Figure 2 is a photograph of a neoprene rubber pad. The bonding surface is the lower side of the pad.

The following is a chronologic presentation of the experiments conducted to attain neoprene liner pads with stable C–D characteristics with no sacrifice in other requirements such as rate sensitivity (dynamic-to-static ratio), damping capacity (Q), and fatigue life.

From the data presented herein, it is possible to determine the limit of growth for well-cured neoprene liner pads as a function of long-term 70°C air aging. Predictions as to the time duration that pads conform to C–D specification at service temperature have been determined as the result of a recently completed, tactically useful Arrhenius study.[5] These results will be published elsewhere.

EXPERIMENTAL

C–D Testing. Compression–deflection testing of full-sized pads is accomplished in a Baldwin Model FGT testing machine at 2 in./min free-running cross-head speed. Figure 3 shows a full-sized pad installed in the test apparatus. Specimens made by sectioning full-sized pads as shown in Figure 2 are tested in an Instron Universal Testing Machine at the same rate.

Fatigue Testing. Full-sized pads are cycled using the Baldwin apparatus described above and at the same rate. Thus, it is possible to realize about 50 cycles/hr to 1.1 in. deflection. Initiation and propagation of cracks in the struts are determined by periodic visual inspection during cycling.

Rate Sensitivity. The rate sensitivity, or dynamic-to-static (D/S) ratio, is determined in a modified sand-drop shock-test machine. The drop height is varied to achieve an initial deflection rate of about 74 in./sec. The apparatus is described in detail in previous papers.[1,6]

Damping. The quality factor Q is determined from the load-unload hysteresis loop with a double amplitude of 0.04 in. at 10 Hz. The apparatus is described in the same papers.[1,6]

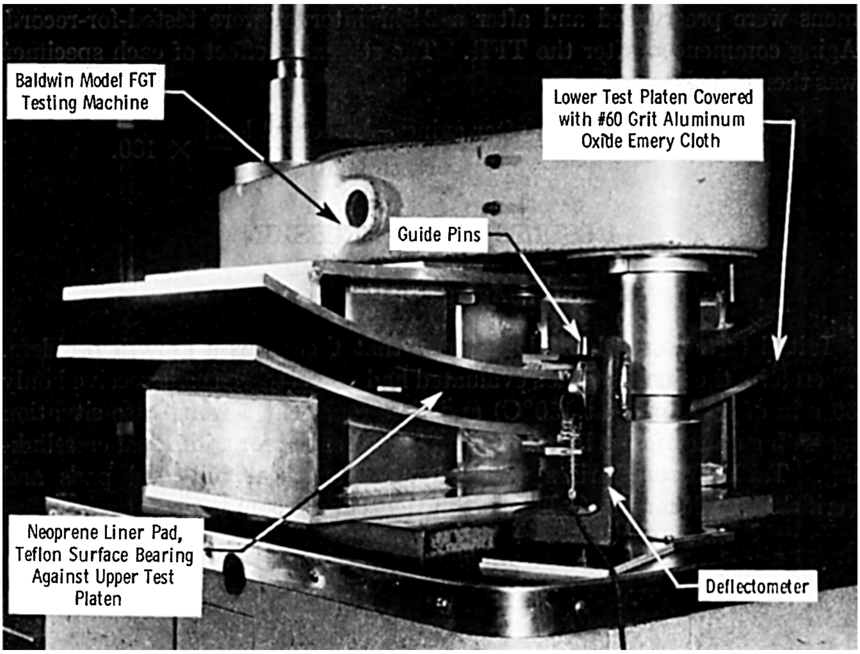

Fig. 3. Neoprene pad static C–D test apparatus.

Physical Properties. Physical properties such as elongation, tensile strength, and 100% modulus were determined in accordance with ASTM D412-66 at 20 in./min.

Acetone Extraction. Acetone extraction was accomplished in a manner similar to that described in ASTM D-1278 and ASTM D-297. Fully compounded and cured rubber was given six passes through a two-roll mill set with ~0.010 in. gap. The masticated specimen was weighed, placed in the thimble of a Soxhlet extraction unit, and extracted for 24 hr. The extracted sample was dried and reweighed, and the per cent weight loss was reported. The acetone extract was retained for infrared determination of antidegradants.

Crosslink Density and $\bar{M}_c$ Determinations. The technique described by Cluff, Gladding, and Pariser[7] was used for determination of crosslink density. Toluene solvent was used throughout. Molecular weight between crosslinks, $\bar{M}_c$, was computed from the crosslink density using the relationship

$$\bar{M}_c = \frac{d_1}{\nu_e/V}$$

where d_1 = density of rubber in g/cc, and ν_e/V = crosslink density in moles/cc.

Specimens for C–D Testing. Full-scale pads and specimens cut from full-scale pads as shown in Figure 2 were used for the aging studies. Specimens were precrushed and after a 24-hr interval were tested-for-record. Aging commenced after the TFR. The stiffening effect of each specimen was then calculated as

$$\% \text{ change} = \frac{\text{load after aging} - \text{precrush load}}{\text{precrush load}} \times 100.$$

RESULTS AND DISCUSSION

Aging Studies

Initial tests were planned to verify that there was a growth problem. Therefore, the first test pads evaluated had no postcure (pads received only 35 min of mold cure at 150°C) and thus represent a worst-case situation regarding state of cure by providing high potential for additional crosslinking. Table I summarizes the test data for these full-sized pads and verifies that ultimately C–D growth will occur at room temperature.

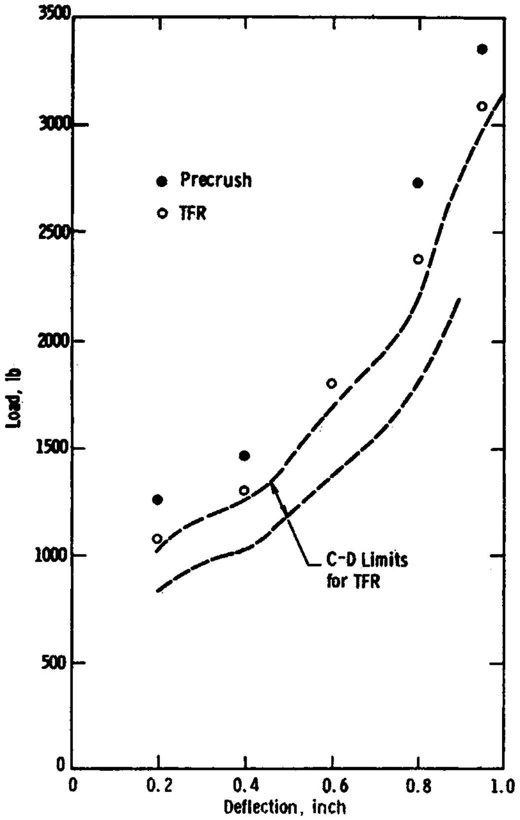

Fig. 4. Precrush and TFR values for pads molded from 140 phr carbon black compound and postcured $7^1/_2$ hr in the vendor's oven.

TABLE I

Summary of C–D Data after Aging at Room Temperature or 70°C[a]

Post-cure, hr at 150°C	70°C Aging						Room temperature aging					
	Aging time, days	Load change at indicated deflection, %					Aging time, days	Load change at indicated deflection, %				
		0.2″	0.4″	0.6″	0.8″	0.9″		0.2″	0.4″	0.6″	0.8″	0.9″
0	3[b]	16.3	16.4	17.3	17.8	15.9	93[c]	−0.5	0.9	1.1	4.9	4.6
	5[b]	16.7	17.2	18.6	19.4	—	275[c]	6.7	8.7	9.8	13.3	12.7
	7[b]	20.8	22.7	23.1	23.2	20.6						
	10[b]	18.7	23.0	20.5	20.1	13.7						
1	1[d]	0.7	1.3	1.4	2.7	—	39[d]	−5.8	−4.9	−3.8	−0.7	—
	3[d]	0.7	6.3	2.6	4.8	—	56[d]	−5.4	−4.3	−3.7	−0.8	—
	7[d]	9.9	15.0	12.8	12.9	—						
	14[d]	22.2	24.2	25.4	26.0	—						
2	1[d]	0.6	1.5	1.6	3.2	—	39[d]	−5.0	−4.2	−3.3	−0.3	—
	3[d]	−1.9	4.3	0.4	0.9	—	56[d]	−6.5	−5.6	−4.1	1.3	—
	7[d]	9.6	13.4	12.0	13.0	—						
	14[d]	17.6	20.6	21.0	22.6	—						

[a] Pads were molded from 140 phr carbon black compound and postcured as indicated in the vendor's oven.

[b] Average of three pads.

[c] Average of five pads.

[d] Average of two pads.

TABLE II

Selected Data on Pads of 808–79 with 128 phr FT Carbon Black

				Tensile Properties						
Sample code	Days at 70°C	$\bar{M}_c$, g/mole	Repeat of $\bar{M}_c$, g/mole	Tensile strength, psi	100% Modulus, psi	Elongation, %	24 hr acetone extraction in Soxhlet	Static cycling[a] of pads	Static cycling of pads after indicated aging at 70°C	Swelling index
Control, 0 hr postcure JM3-122A	0	3190	—	1330 1325	—	260, 265	5.7, 5.85	>1000 cycles, no cracks	—	1.68 1.68
Control, 6½ hr postcure JM3-122B	0	2270	—	1310 1275 1490	— 1360	170, 160 120	5.0, 5.1 5.3	415 cycles, no cracks	—	1.67 1.67
JM3-139A	5	2050	2170 2220	1525	1425	130	—	—	—	1.70 1.69
JM3-139B	10	2090	2200 2120	1590	1510	125	—	—	—	1.69 1.69
JM3-139C	17	1975	1860 1925	1600	1520	115	—	—	500 cycles, no cracks	1.68 1.68
JM3-139D	24	1890	2120 2220	1680	1615	115	—	—	—	1.69 1.68
JM3-139E	31	2090	2265 2265	1690	1665	105	—	—	173 cycles, crack in one short strut; after 230 cycles the crack grew to ¼ in.	1.68 1.68

Control, $7^{1}/_{2}$ hr postcure JMC-122D	0	2210	—	1260 1300 1630	— 1405	140, 140 135	5.2, 5.1	492 cycles, no cracks	—	1.67 1.66
JM3-139F	5	2140	2280 2300	1590	1470	120	5.2, 5.0	—	—	1.64 1.69
JM3-139G	10	1880	1995 2110	1690	1540	120	—	—	—	1.68 1.68
JM3-139H	17	2020	2060 2335	1640	1515	120	5.1, 5.1	—	500 cycles, no cracks	1.68
JM3-139I	24	1895	2095 2150	1700	1630	115	—	—	—	1.69 1.68
JM3-139J	31	2260	2480 2480	1720	1735	105	4.6, 4.4	—	145 cycles, crack in one shear strut; after ~400 cycles the strut broke completely	1.68 1.67

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[a] All cycles to 1.1 in. deflection at 2 in./min.

Since it was inconvenient to wait periods of months to obtain data, the recovery and growth effects were accelerated by heating specimens at 70°C for various periods of time. Pads containing 140 phr carbon black and given 0, 1, and 2 hr of postcure were aged at 70°C for periods of up to two weeks. Room-temperature aging of pads with 1 and 2 hr of postcure at 150°C was also conducted. The C–D data for these pads are also summarized in Table I.

Crosslink density measurements, presented in Table II, showed that pads with no postcure were less tightly crosslinked than those with either $6^{1}/_{2}$ or $7^{1}/_{2}$ hr of postcure at 150°C. However, Figure 4 shows that the additional postcure lead to a C–D response that was too stiff for the specification. It was therefore decided to examine longer postcures and compensate for the increased stiffness by reducing carbon black content. Thirty full-scale pads with 128 phr carbon black were obtained from the vendor. Samples were postcured in the vendor's oven for $6^{1}/_{2}$ or $7^{1}/_{2}$ hr at 150°C and then aged at 70°C or room temperature. Aging data are shown in Table III.

TABLE III
Summary of C–D Data after Aging at 70°C[a]

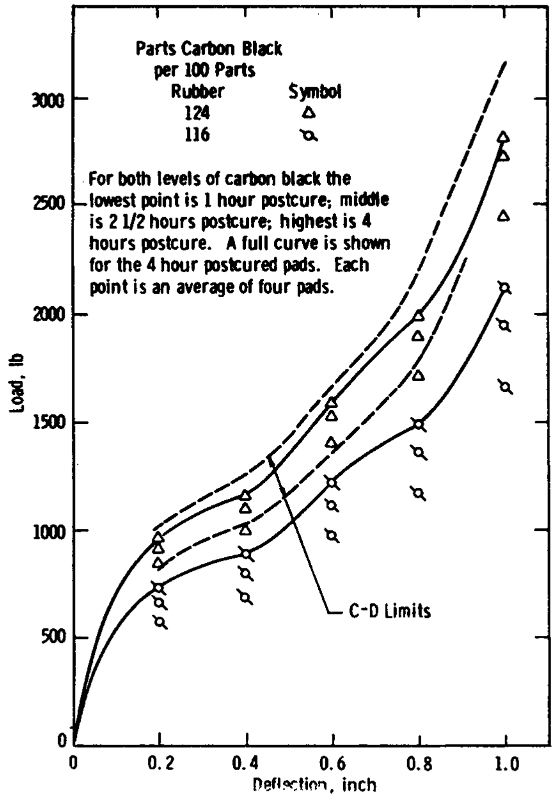
Postcure, hr	Aging time, days	Load change at indicated deflection,[b] %				
		0.2″	0.4″	0.6″	0.8″	1.0″
$6^{1}/_{2}$	5	−1.8	−0.5	−1.3	−4.1	−3.0
	10	5.9	6.5	5.7	3.1	5.3
	17	7.1	10.5	9.5	5.0	8.5
	24	11.9	15.5	14.1	8.6	12.3
	31	21.0	22.9	23.8	20.3	21.1
$7^{1}/_{2}$	5	−0.9	0.5	−0.2	−4.5	−1.2
	10	3.9	4.4	4.9	0.3	5.4
	17	6.1	9.2	8.7	3.0	8.9
	24	13.4	16.6	16.0	9.4	14.8
	31	20.1	22.8	23.7	17.3	22.6

[a] Pads were molded from 128 phr carbon black compound and postcured $6^{1}/_{2}$ or $7^{1}/_{2}$ hr in the vendor's oven.

[b] Average of three pads.

To give further credence to the hypothesis that long postcure produces C–D stability, two pads, previously not postcured, were given 5 hr of postcure at 150°C in the lab oven and aged at 70°C. Approximately ten days at 70°C were required to restore the pads to precrush level.

By now, it was quite apparent that longer postcures gave desired C–D stability but the absolute TFR loads exceeded specification limits even with the reduction in carbon black level to 128 phr. Therefore, further reduction was required, and pads with 124 and 116 phr carbon black were molded by the vendor. Postcuring was accomplished in the lab oven for periods of 1, $2^{1}/_{2}$, and 4 hr. All pads were precrushed, tested-for-record, and aged at room temperature for up to three months. Aging data are given in Table



For both levels of carbon black the lowest point is 1 hour postcure; middle is 2 1/2 hours postcure; highest is 4 hours postcure. A full curve is shown for the 4 hour postcured pads. Each point is an average of four pads.

Fig. 5. Test for record C–D data for two carbon black loadings and three postcure times at 150°C in a laboratory.

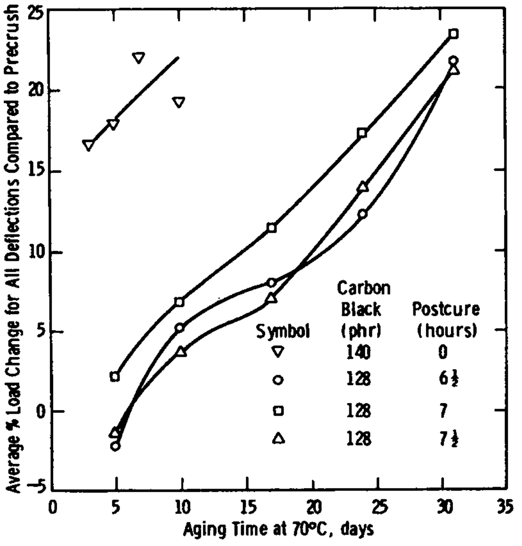


Fig. 6. Summary of 70°C aging results for pads postcured in the vendor's oven.

TABLE IV
Summary of C–D Data after Aging at Room Temperature[a]

Postcure, hr	Aging time, days	Load change at indicated deflection,[b] %				
		0.2″	0.4″	0.6″	0.8″	1.0″
		116 phr Carbon Black				
1	21	−11.3	−7.9	−7.5	−6.1	−1.1
	92	−5.4	−4.0	−3.3	−0.8	1.4
2¹/₂	21	−15.3	−9.5	−9.5	−8.1	−3.5
	92	−7.8	−5.1	−4.8	−2.0	−0.7
4	21	−13.7	−10.4	−10.7	−10.1	−3.6
	92	−9.6	−8.2	−7.1	−3.8	−1.0
		124 phr Carbon Black				
1	21	−10.1	−10.3	−8.1	−7.3	0.2
	92	−3.6	−3.5	−2.5	−0.7	1.3
2¹/₂	21	−11.2	−9.7	−9.7	−7.6	−0.8
	92	−7.8	−6.7	−6.2	−4.4	−1.7
4	21	−12.4	−10.7	−10.9	−9.1	−2.4
	92	−7.9	−6.5	−6.1	−3.1	−2.6

[a] Pads were molded from 116 or 124 phr carbon black compound and postcured 1, 2¹/₂, or 4 hr in a laboratory oven.

[b] Average of two pads.

IV. The optimum choice for desired TFR C–D level and stability was given by the 124-phr pads with 4 hr of postcure, as shown in Figure 5.

A series of pads containing 140 phr carbon black were also molded and postcured for 6¹/₂, 7, or 7¹/₂ hr at 150°C in the vendor's oven to determine whether longer postcure would reduce growth without significantly affecting dynamic/static ratio, Q value, and particularly fatigue life. No significant effect could be detected when comparing pads with short or long postcure history. C–D data for the aged pads with longer postcure are summarized in Figure 6. C–D data for pads with no postcure are also presented in the same figure for direct comparison. A significant reduction in growth is shown for the pads with long postcure compared to pads with short postcure aged at 70°C.

Crosslink density determinations on pads with the long postcures indicate that for practical purposes the state of cure is well fixed after 6¹/₂ hr of postcure at 150°C, and additional postcure is relatively ineffective. Excessive heating was thought to be detrimental from the standpoint of volatilizing antidegradants, but infrared examination of acetone extraction from the heated samples did not show significant reduction in the antioxidant concentration.

CONCLUSIONS

1. Well-cured neoprene pads, after aging, exhibit less increase in C–D stiffness above precrush values than do pads with a low degree of postcure.

2. Production pads with either 128 phr or 140 phr FT carbon black and postcured either $6^1/_2$, 7, or $7^1/_2$ hr at 150°C exhibit no crack formation after ~500 static cycles to 1.1-in. deflection. These same well-cured pads aged up to 17 days at 70°C do not crack after 500 static C–D cycles.

3. $\bar{M}_c$ values indicate a significant increase of state of cure as a function of postcure, being reduced almost 30% between no postcure and $6^1/_2$ hr of postcure at 150°C.

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