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Quarterly Report

for

June 1, 1962 to September 1, 1962

on

ELASTOMERIC SEALS AND MATERIALS AT CRYOGENIC TEMPERATURES

by

D. H. Weitzel, P. R. Ludtke, Y. Ohori, R. F. Robbins, and
F. B. Peterson

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
BOULDER LABORATORIES
Boulder, Colorado

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FOREWORD

This report was prepared by the National Bureau of Standards under USAF Contract No. 33(616)-61-04. This contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 73405. "Elastomeric and Compliant Materials". The work was administered under the direction of Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Mr. Roger Headrick acting as Project Engineer.

Abstract

Additional data from the experiments on force decay, sealability, thermal expansion, and T_g are presented, together with brief discussions of the new results. The high speed rotating seal effort has been reactivated (with partial funding from another source) and machining of parts for the tester has begun. A simple method for automatic recording of rebound resilience has been developed. Two papers presented at the 1962 Cryogenic Engineering Conference are included.

1.0 Force and Seal Evaluation (P. R. L.)

1.1 New Results

Work has continued on the force evaluation experiment. Results obtained since our last report are shown in Table 1.

Only two compounds of Group III have been tested to date. These are butyl 325-1 (III-18D) and butyl 325 (III-18E), resin cured. The resin cured butyl, Figure 1, had considerable force decay, but low "compression set"[*]. Leaks occurred at approximately 204°K. This compound shows little promise for a good cryogenic seal.

The sulfur cured butyl (III-18D), Figure 2, had much better seal properties. There was less force decay at room temperature and during cooldown.

Although the O-ring was given slightly less initial force and compression than the resin cured sample, the leak occurred at a lower temperature (≈ 166°K). The "compression set" was high (52%) compared to 28% for the resin cured compound.

Excluding the slight difference in monomer ratio, the sulfur cure seems far superior to the resin cure for force decay and sealing ability in this particular co-polymer. The reverse seems to be true of "compression set", a result which should be investigated more carefully. There is too little data to say anything conclusive about Group III. Further testing of the remaining compounds will

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[*] Here defined as $\frac{\text{original thickness - final thickness}}{\text{original thickness - compressed thickness}}$
The tests were conducted over a three day period during which there were three temperature cycles from room temperature to 76°K.

Polymer	A. S. D. Compound Number	Shore A Hardness	Initial Force (lbs.)	Percent Force Lost During Initial Relaxation	Compressed O-ring Thickness	Percent Compression	Compression Set ††	Material Failure	Force at Start of Cooldown			Leak Occurred				
									#1	#2	#3	Temp. (°K)	Force (lbs.)	He. Pres (p. s. i g.)	Off Scale Time ***	L. R at 76°K x10^6 (atm cm^3/sec)
Group III																
Butyl 325	III-18E	75	14,600	37%	.027"	81%	28%	None	9200	----	----	200	6200	100	16 min.	
										3800	----	204	2100	100	13 min.	
											3600	204	1500	100	16 min.	
Butyl 325-1	III-18D	80	13,800	25%	.029"	79%	52%	None	10,000	----	----	169	5200	100	16 min.	
										7300	----	166	4000	100	12 min.	
											6800	155	3100	100	9 min.	
Group IV †																
Cis-4 Polybutadiene	IV-29B	70	19,000†	11%	.026"	81%	28%	None	19,000	----	----	104	11,300	100		65
										16,000	----	——	——	500	No Leak Occurred	
											15,800	104	10,800	1,000	1 sec.	
EPR "Nordel" (Du Pont)	IV-A-9B	70	13,400	42%	.026"	81%	16%	None	7800	----	----	160	2000	100	10 min.	
										5100	----	156	1100	100	6 min.	
											3900	160	<500	100	5 min.	
Group VII																
"Genthane"S (Gen. Tire & Rubber)	VII-28E	60	13,400	42%	.028"	80%	25%	None	7800	----	----	190	6000	100	1 sec.	
										4100	----	200	2000	100	1 sec.	
											3600	192	1300	100	1 sec.	
"Adiprene"C (Du Pont)	VII-21F	70	13,600	28%	.036"	74%	17%	None	9800	----	----	134	5000	100	26 min.	
										6500	----	139	2800	100	13 min.	
											6000	139	1800	100	20 min.	
Group IX																
Epoxy Rubber (Narmco)	IX-L-51	100+	10,600*	47%	.059"	58%	42%	None	5600	----	----	177	2600	100	48 min.	
										2500	----	170	----	100	22 min.	
											2200	170	----	100	11 min.	
Epoxy Rubber (Narmco)	IX-ET-9	90	11,200*	59%	.054"	61%	5.7%	None	4600	----	----	164	1400	100	15 min.	
										3000	----	165	----	100	39 min.	
											1300	150	----	100	44 min.	
"Viton" (DuPont) (Parker Comp. 77-545)	----	72	14,000	69%	.028"	80%	36%	None	4400	----	----	224	1200	100	41 min.	
										2500	----	225	----	100	27 min.	
											1900	230	----	100	44 min.	

* This is the maximum initial force the epoxy rubbers would support without material failure.

† 19,000 lbs. initial force instead of the usual 14,000.

*** Time required for leak rate to increase from zero to $3 \times 10^{-4} \frac{\text{atm cc}}{\text{sec}}$

†† Defined as $\frac{\text{Original thickness - Final thickness}}{\text{Original thickness - Compressed thickness}}$

TABLE 1. Force and Seal Evaluation Test Data

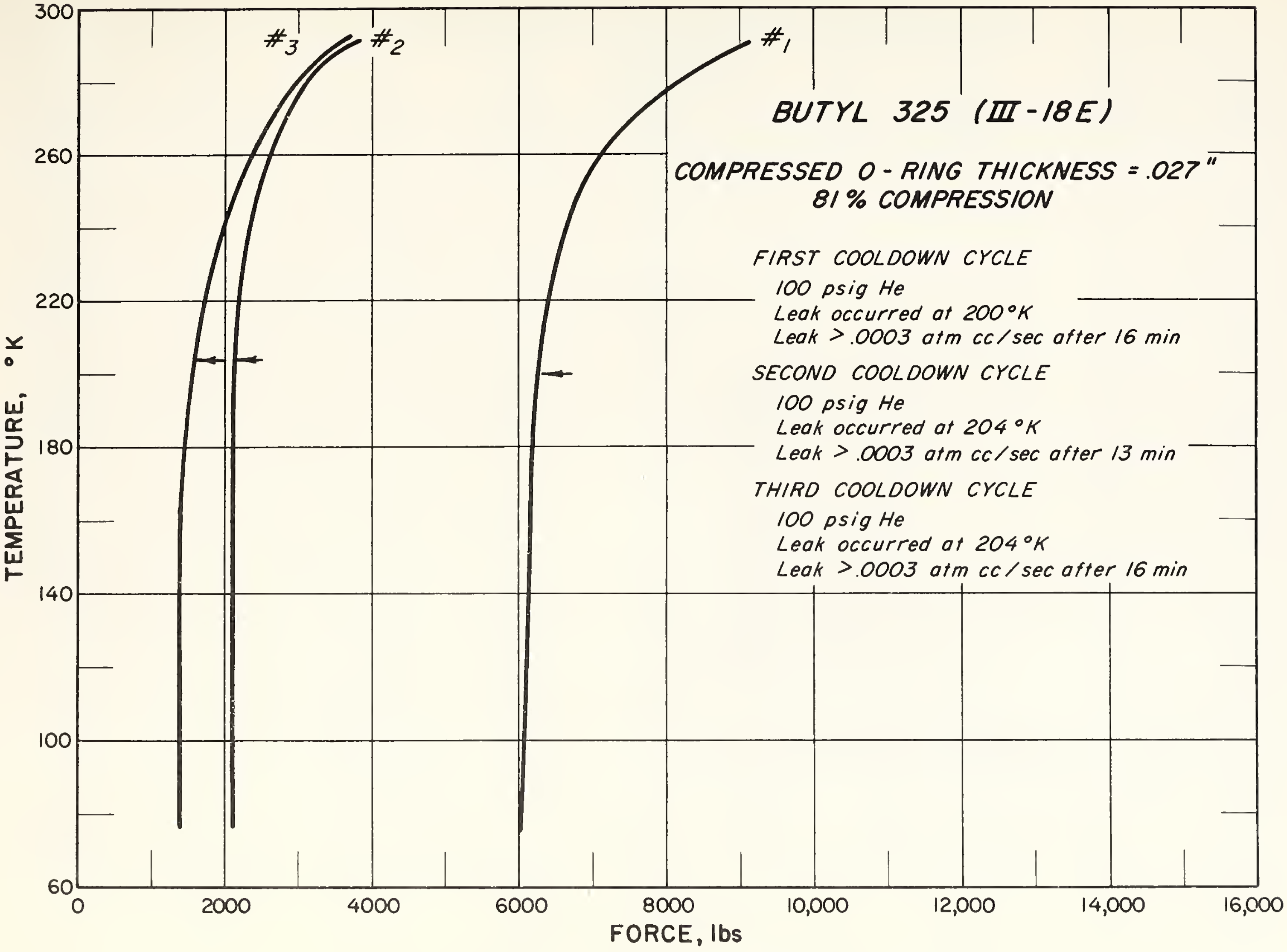

Figure 1. Force-Temperature Curve Butyl 325

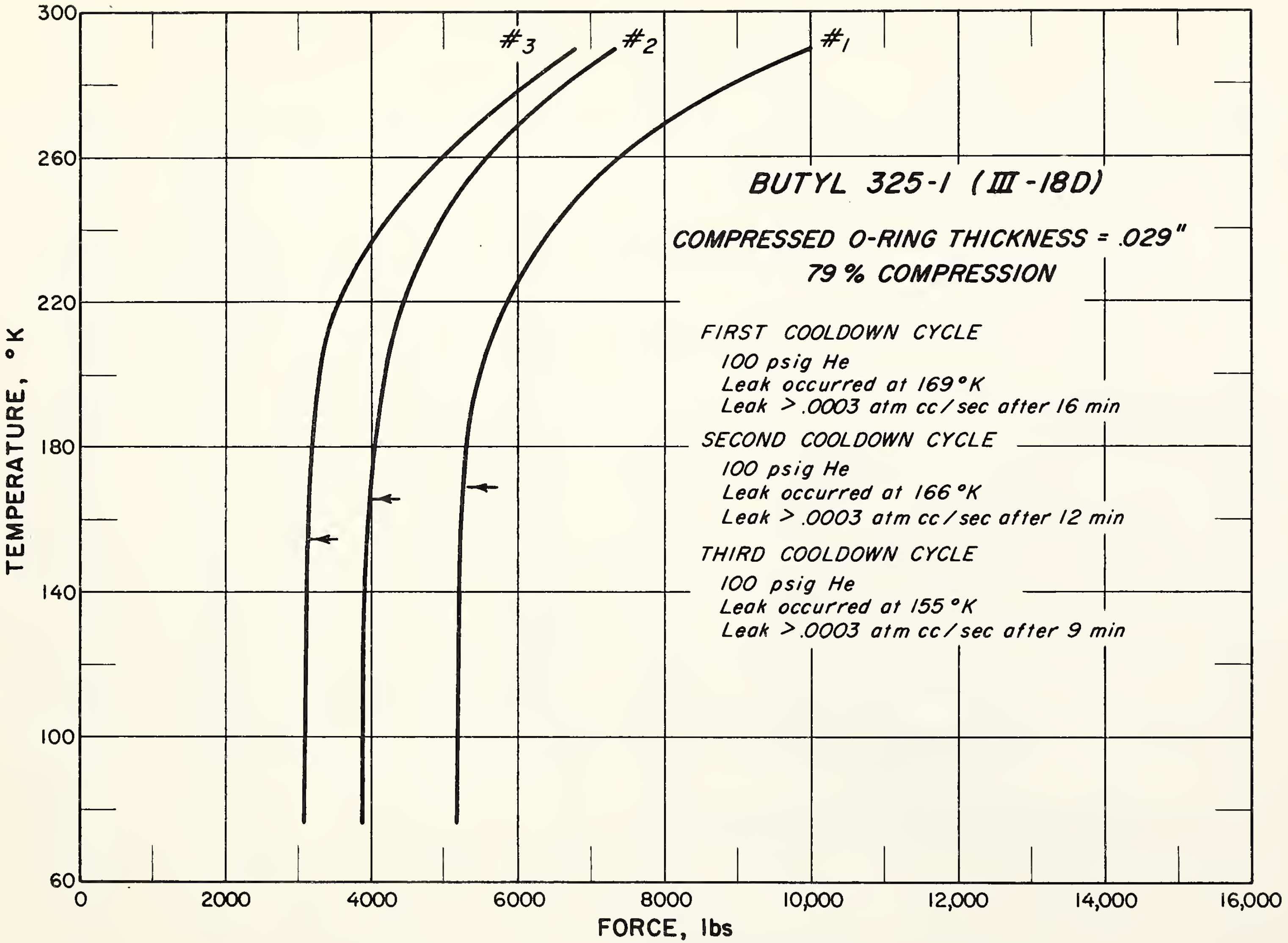

Figure 2. Force-Temperature Curve, Butyl 325-1

provide data for comparative results.

"Nordel"[*] (one percent unsaturated EPR)(IV-A-9B), Figure 3, was tested. There was considerable force decay and little compression set. It appears that "Nordel" has more force decay than EPR 40. (See attached paper H-8). However, the EPR 40 O-ring was compressed to .018" and "Nordel" to .026" thickness. "Nordel" supported 14,000 lbs of force when compressed to .026" and did not tend to ooze out from under the disc like EPR 40. The "compression set" of "Nordel" after these tests was only 16%.

A cis-4 polybutadiene (IV-29B), Figure 4, O-ring was given 19,000 pounds of initial force instead of the usual 14,000 pounds. There was little force decay at room temperature, as with previous tests with this compound. The curves indicate considerable loss of force during cooldown but the force returns again upon warming. This elastomer gave a medium "compression set" value after the tests (28%).

The O-ring developed small leaks at 104°K during the first and third cooldown cycles. No leak occurred during the second cooldown cycle. Here is an O-ring which developed a small leak with 100 psig helium pressure but did not leak during the following cooldown cycle at 500 psig helium pressure. During the subsequent cooldown at 1000 psig there was again a small leak.

Cis-4 polybutadiene (IV-29B) gave better seal performance than natural rubber (IV-8A)(see paper H-8) in the range of 14,000 pounds initial force, but the reverse is true in the 18,000 pound initial force range.

The two polyurethane elastomers of Group VII were tested. "Genthane" S (VII-28E), Figure 5, had considerable force decay before cooldown (42%). The O-ring leaked at relatively high temperatures (≈ 195°K) and the leak rate was very high.

"Adiprene" C (VII-21F), Figure 6, performed much better than "Genthane" S. Only 28% of the initial force was lost, the "compression set" was relatively low, the O-ring leaked at a much lower temperature (≈ 136°K) and the leak rate was considerably less. Moreover, this better performance occurred with only 74% compression. This compound would probably hold a seal at 80% compression

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[*] Trademark credits are given in Table 1.

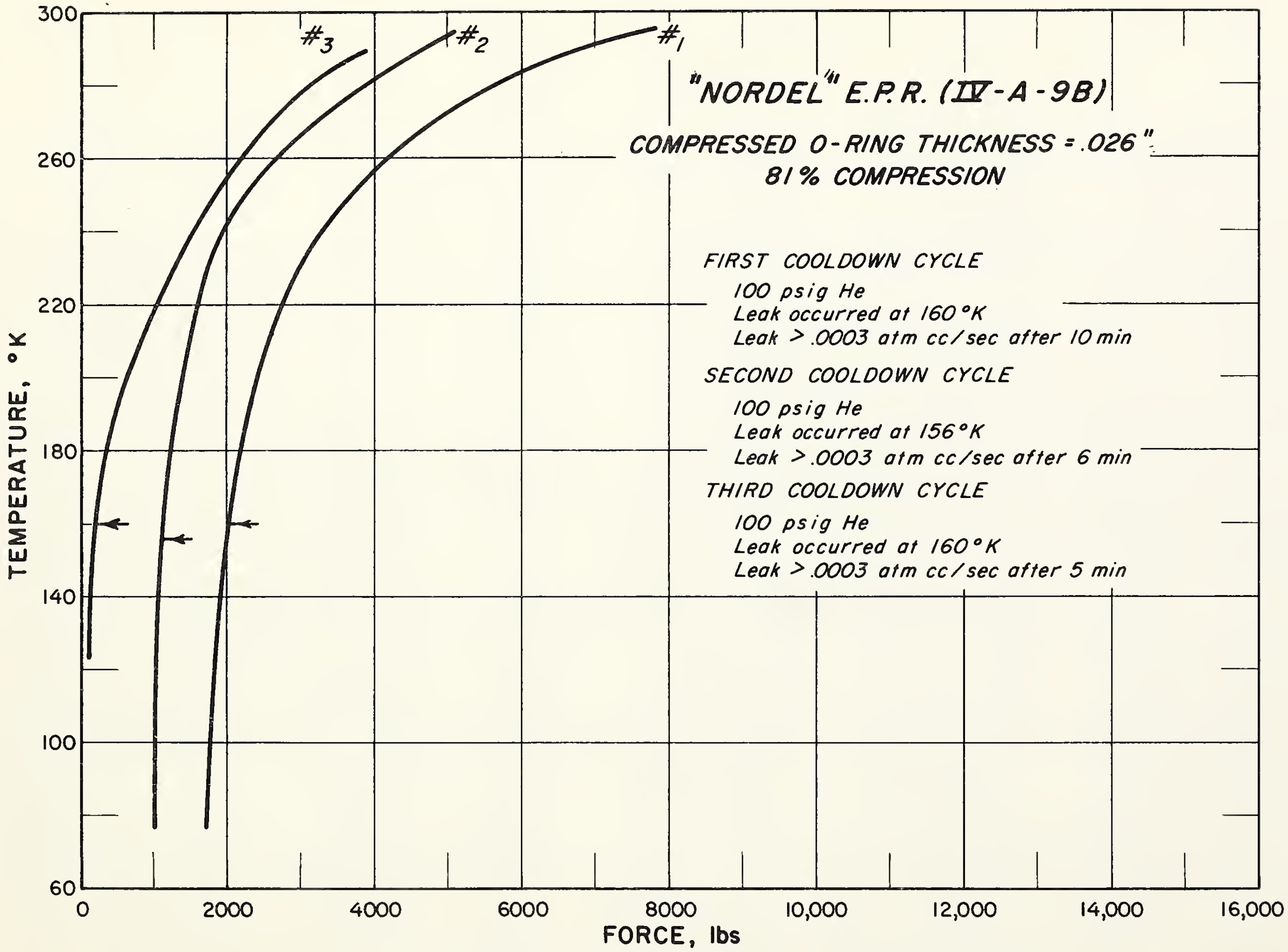


Figure 3. Force-Temperature Curve, "Nordel" E. P. R.

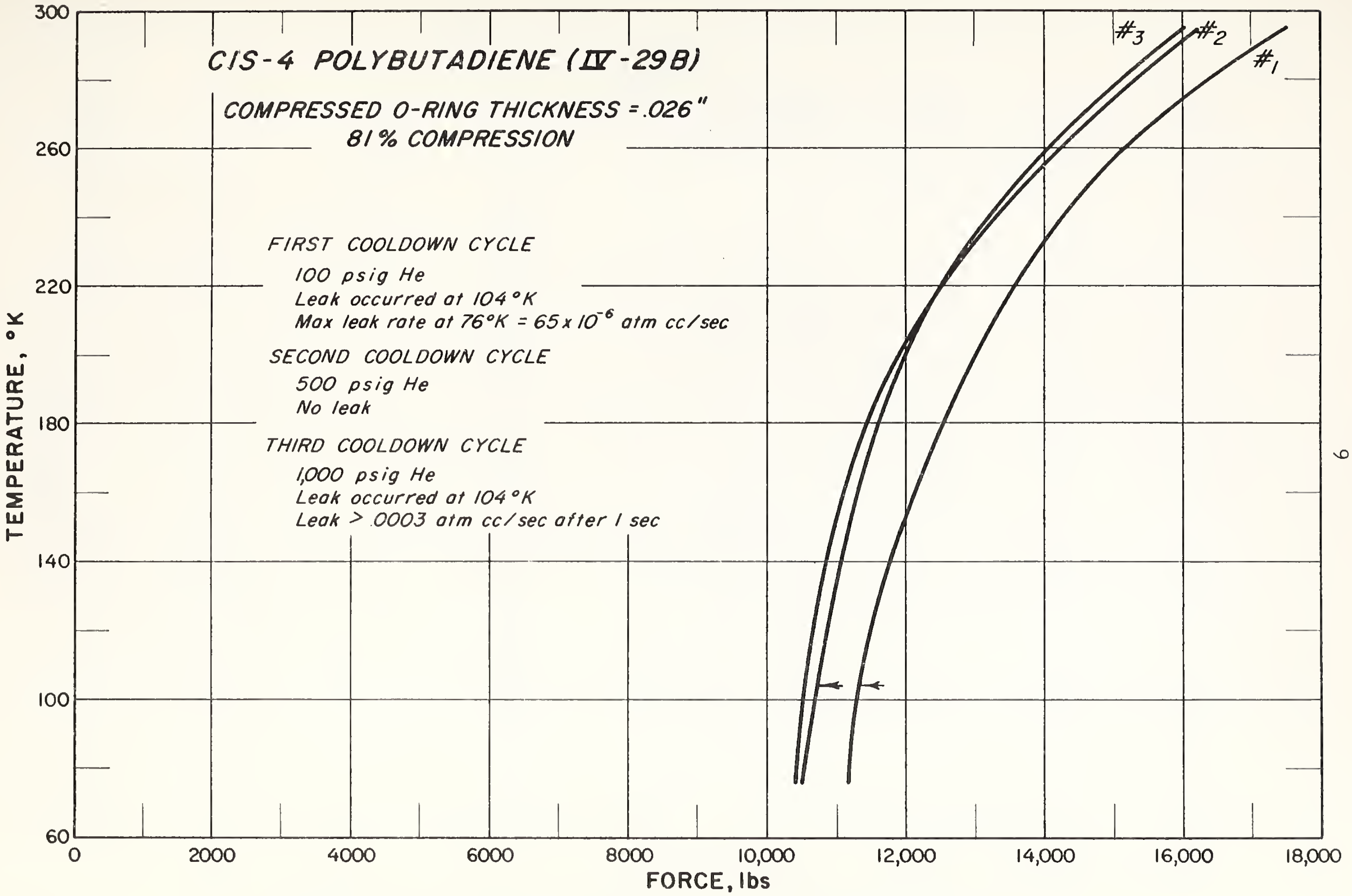


Figure 4. Force-Temperature Curve, Cis-4 Polybutadiene

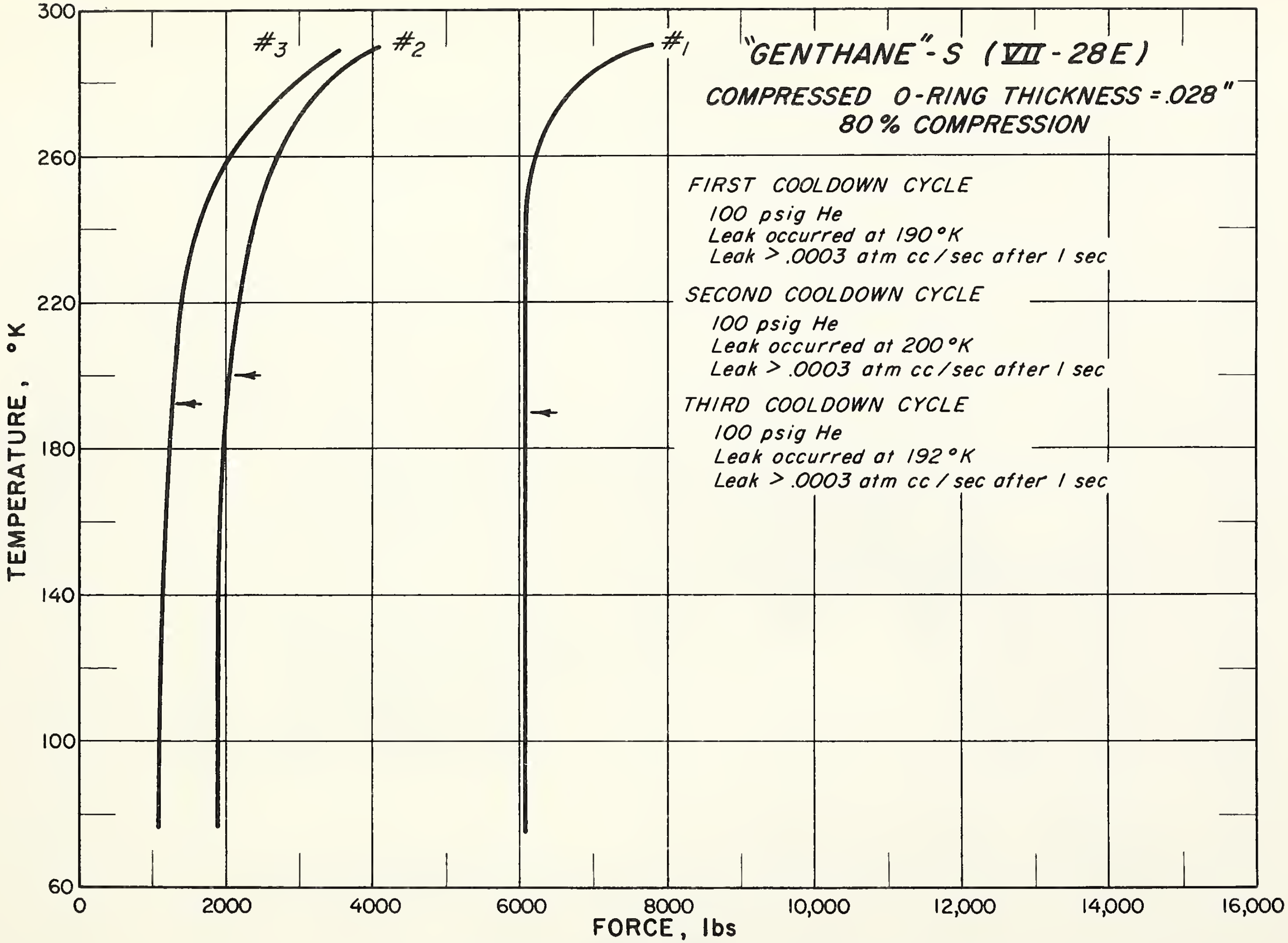


Figure 5. Force-Temperature Curve, "Genthane"-S

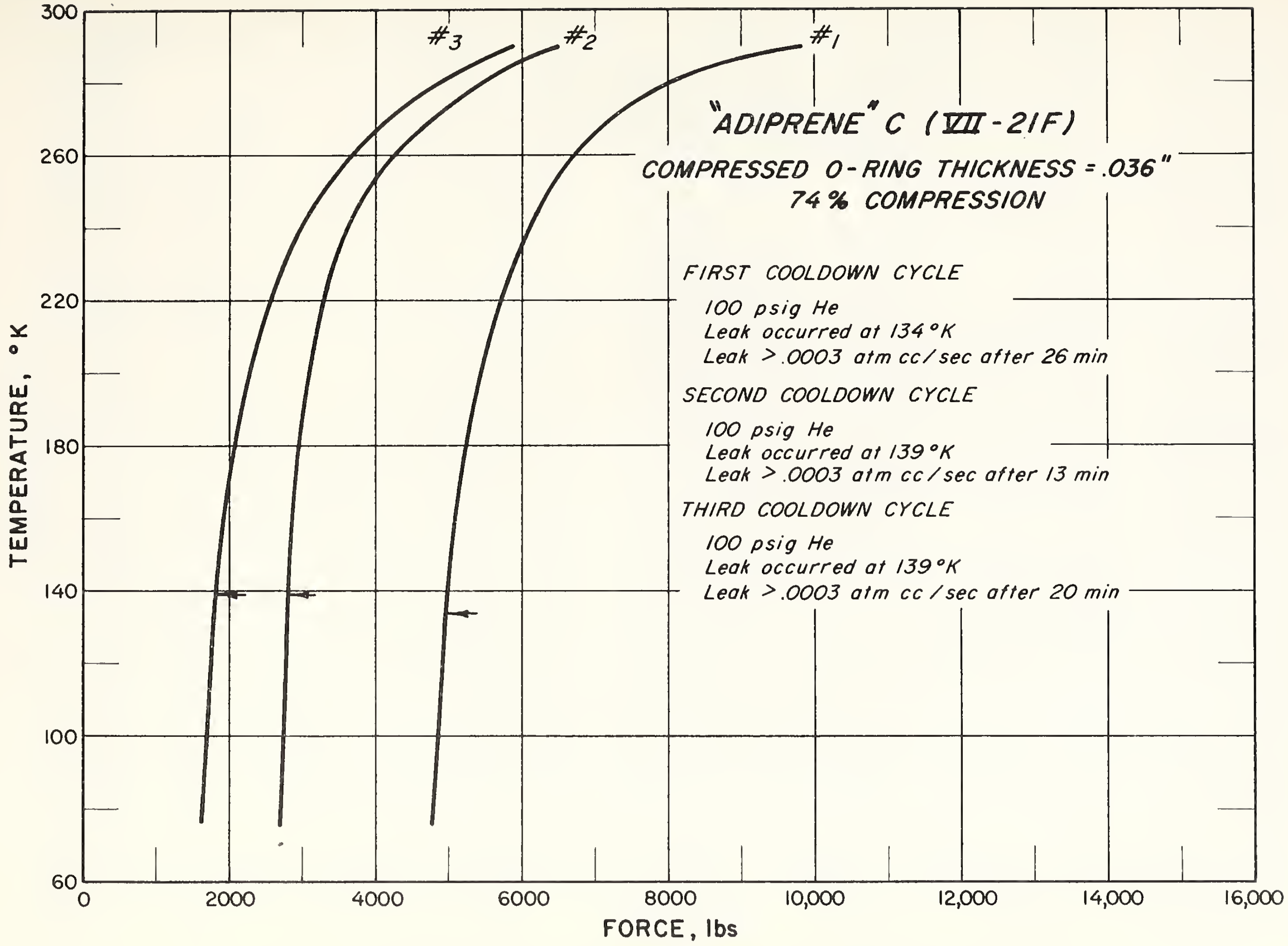


Figure 6. Force-Temperature Curve, "Adiprene" C

and should be tested further.

The two epoxy rubbers, IX-ET-9 , Figure 7, and IX-L-51, Figure 8, were tested extensively. Severe material failure occurred when these O-rings were given too much compression. They were tested with an initial force just below that which caused the material to fail at room temperature.

If an O-ring of compound IX-L-51 is compressed to less than .059", material failure occurs. When the compound was compressed to .059", which required 10,600 pounds, the force decay was excessive and the "compression set" was 42%.

The IX-ET-9 compound could be compressed to .054" without suffering material failure. The force required for this compression was 11,200 pounds. The force decay was excessive (59%) and the "compression set" extremely small (5.7%).

These two epoxy rubbers will not support a high compressive force without suffering material failure, but they will maintain a seal to a comparatively low temperature with the lower compression. An epoxy rubber specifically compounded for this application might maintain a seal at cryogenic temperature with less than the usual amount of compression.

An O-ring of "Viton" (Parker Co. Compound 77-545), Figure 9, was tested for comparison with the ASD compounds. This compound performed very similar to the ASD "Vitons". 54% of the initial force was lost within 90 minutes after loading at room temperature and 69% of the initial force was lost before the O-ring was cooled down. The O-ring leaked at a relatively high temperature (227°K).

1.2 Room Temperature Force Decay

1.2.1 Introduction

A test of room temperature force decay was performed on some of the ASD compounds.

This test was conducted primarily as a check on the ambient force decay measurements obtained with the washer type strain gages. The thickness one-half hour after removal from the press, and the extent of material failure were also observed.

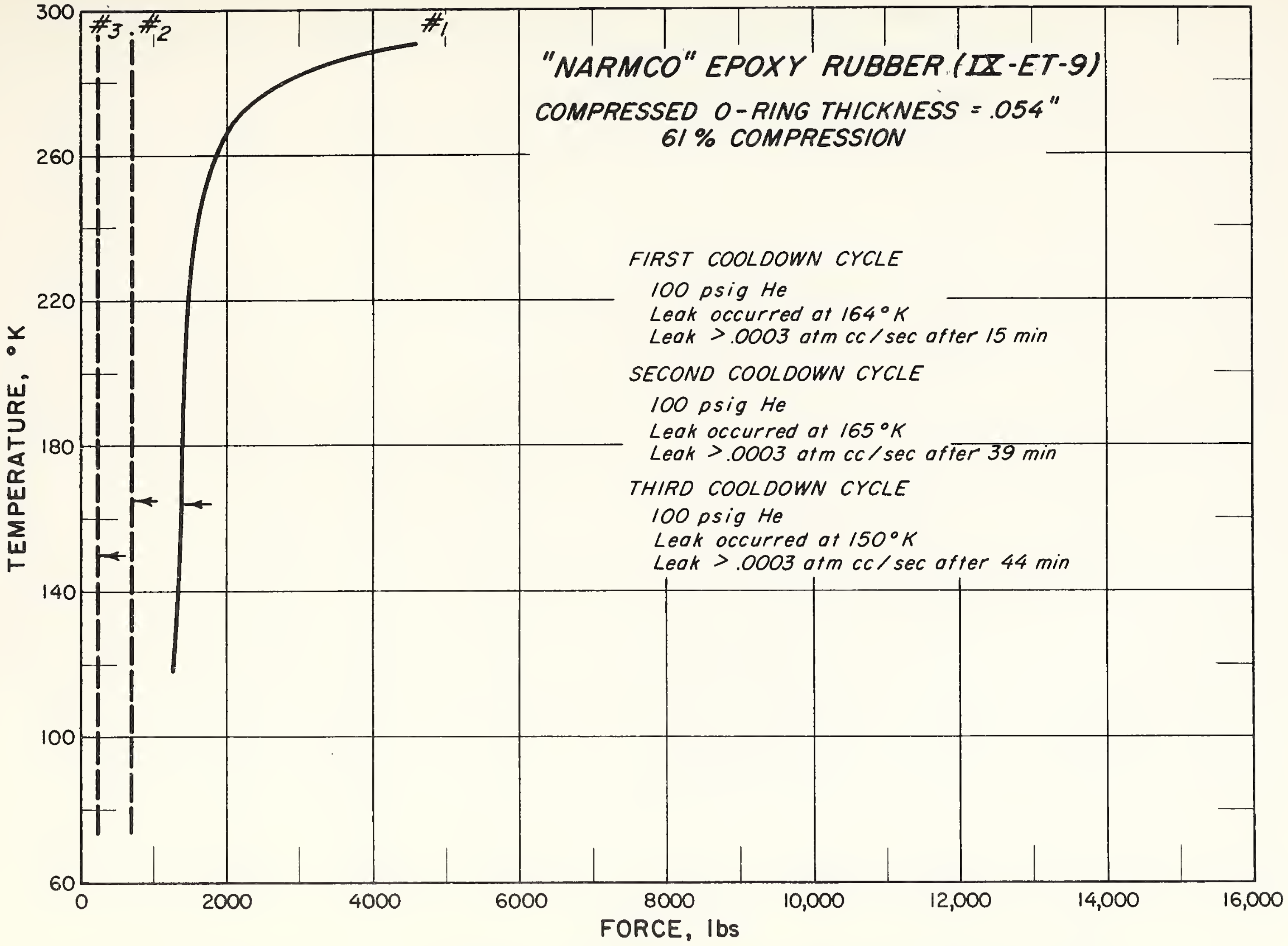


Figure 7. Force-Temperature Curve, "Narmco" Epoxy Rubber (IX-ET-9)

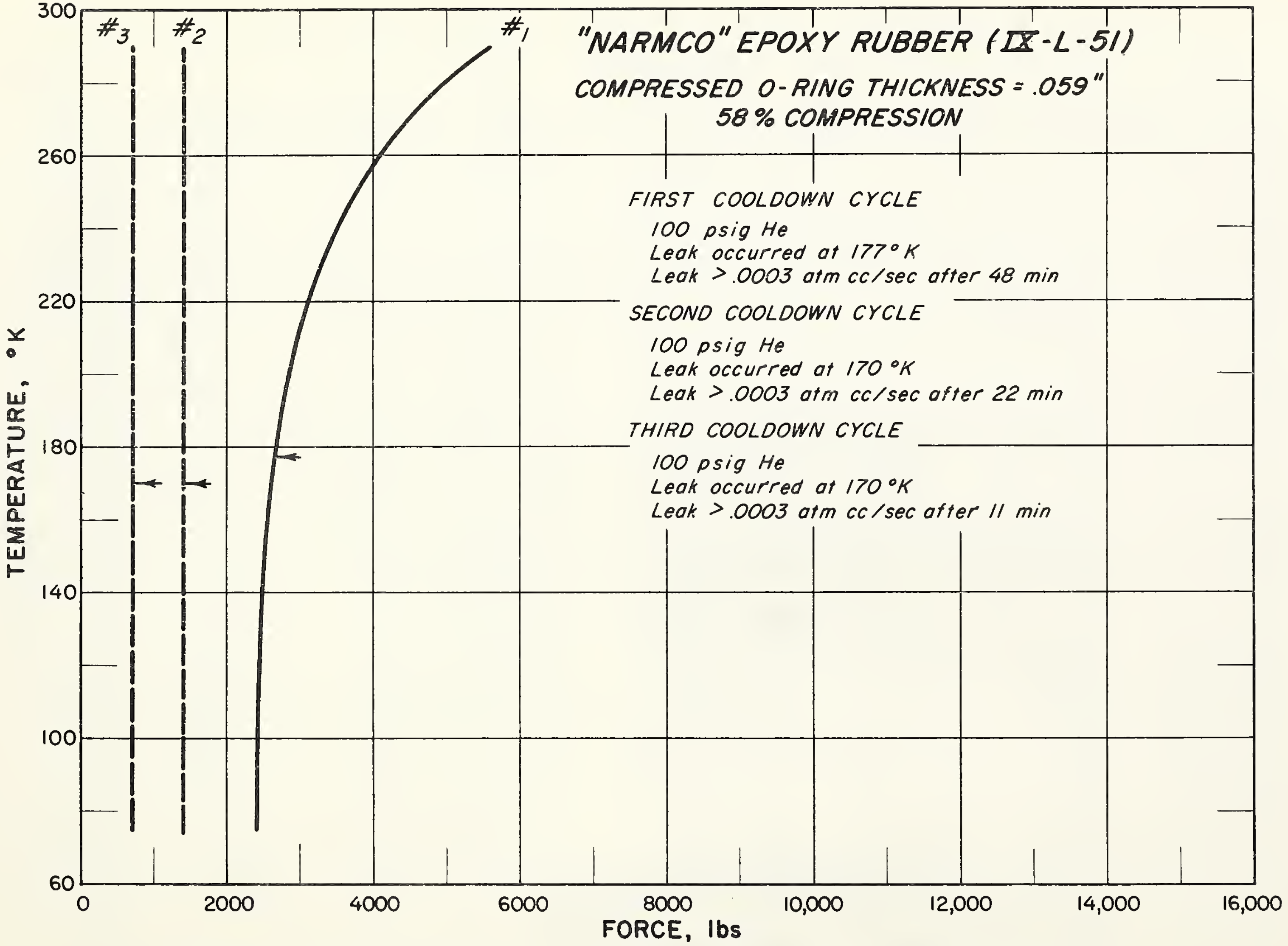


Figure 8. Force-Temperature Curve, "Narmco" Epoxy Rubber (IX-L-51)

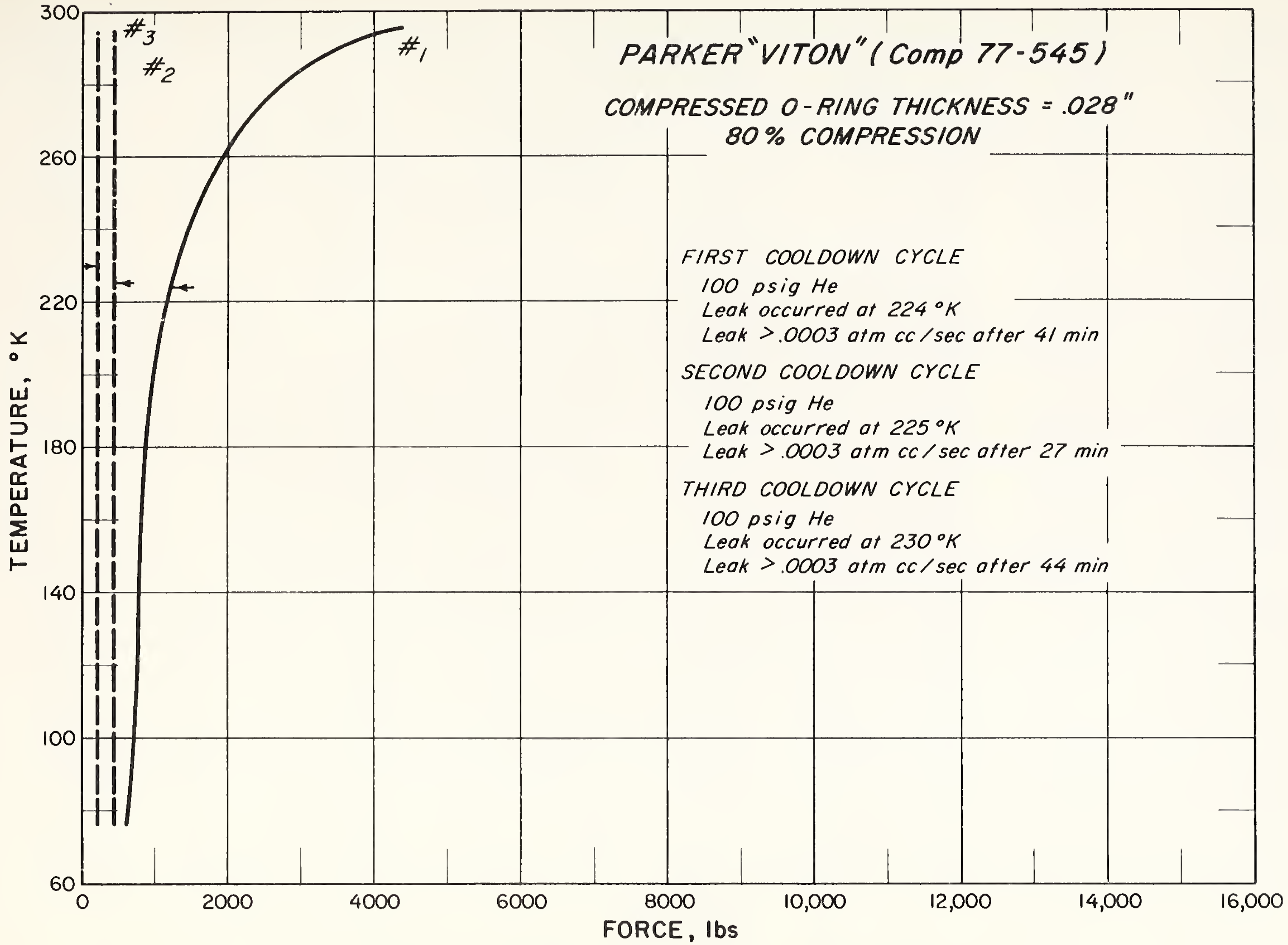


Figure 9. Force-Temperature Curve, Parker "Viton"

1.2.2 Procedure and Results

The 1 inch x .140 inch cross-section O-rings were compressed with an initial force of 18,000 pounds in a hydraulic press. The O-ring was allowed to relax and creep for one hour at room temperature. The force was then measured after this 60 minute relaxation period. The results are shown in Table 2.

To check for leakage in the hydraulic system, the compression plates with no O-ring were compressed to 18,000 pounds and left for the test period of one hour. Approximately 10% of the initial force was lost due to leakage.

The force decay results of this test are in fair agreement with the force washer measurements. Cis-4 polybutadiene is again the best elastomer for force decay performance, and the fluorocarbons had the largest force decay of the group. Table 2 lists the materials in order of performance for this particular test.

Possibly the most interesting result of this test is the permanent set characteristics of the fluorocarbons and Group IV. The average thickness of the fluorocarbons one-half hour after removal from the press was 120", or 85% or the original thickness.

Neoprene, natural rubber and polyisoprene, on the other hand, had an average thickness of only .085", or 61% of the original, when measured after one-half hour. These elastomers suffer high permanent set but they consistently give good cryogenic seal performance. This leads one to conclude that "compression set" is not necessarily a good criteria for cryogenic seal performance. It should be noted, of course, that this permanent set resulted from a compression of 80 to 90%, while the usual "compression set" method (such as ASTM No. 395-55B) calls for an initial compression of only about 50%. The results obtained by the two methods are quite different. The high initial compression was adopted here to conform with treatment given the O-ring when used as a cryogenic seal.

1.3 Practical Test Apparatus

1.3.1 Introduction

Much emphasis has been placed upon the importance of spring-

Polymer	A. S. D. Compound Number	Initial Force (lbs)	Final Force (lbs)	Thickness 1/2 hour after removal (% of original)	Percent of Force Lost
Cis-4 Polybutadiene	IV-29B	18,000	16,000	89%	11%
"Adiprene" C (Dupont)	VII-21F		15,300	94%	15%
Polyisoprene	IV-29A		15,200	57%	16%
"Paracril" 18/80 (Naugtuck Chem.)	II-21A		14,900	84%	17%
Natural Rubber	IV-8A		14,800	61%	18%
EPR-40 (75 durom)	IV-29C		14,800	76%	18%
"Genthane" S (Gen. Tire & Rubber)	VII-28E		14,800	95%	18%
"Neoprene" (Dupont)	IV-8B		14,200	64%	21%
"Nordel" EPR (Dupont)	A9B		14,300	91%	21%
EPR-40	IV-29C		14,300	86%	21%
"Hycar" 1002 (B. F. Goodrich)	II-21B		14,100	74%	22%
"Synpol" 1013 (U. S. Chem. Co.)	II-21E		14,000	74%	22%
"Viton" A-HV (Dupont)	I-12B		14,000	85%	22%
"Fluorel" (Minn. Min. &Mfg.)	I-12C		14,100	88%	22%
"Viton" (Dupont) (Parker Comp. 77-545)	----		14,000	91%	22%
"Synpol" 1000 (U. S. Chem. Co.)	II-21D		13,700	80%	24%
"Paracril" D (Naugtuck Chem.)	II-21C		13,100	77%	27%
"Viton" B (Dupont)	I-12A		13,200	93%	27%
"Teflon" (Dupont)	----		11,900	34%	34%
"Viton" A (Dupont)	I-8D		11,700	73%	35%
Compression Plates Only	----		16,300	----	9%

TABLE 2 Room Temperature Force Decay

loading in maintaining a seal at cryogenic temperature. Since even the better compounds are developing small leaks in the force evaluation apparatus, it was decided to test these better compounds in a practical test apparatus which had considerable springloading. Moreover, to determine the least amount of force and compression necessary to maintain a cryogenic seal in a springloaded test jig. This apparatus is shown in Figure 10.

1.3.2 Procedure

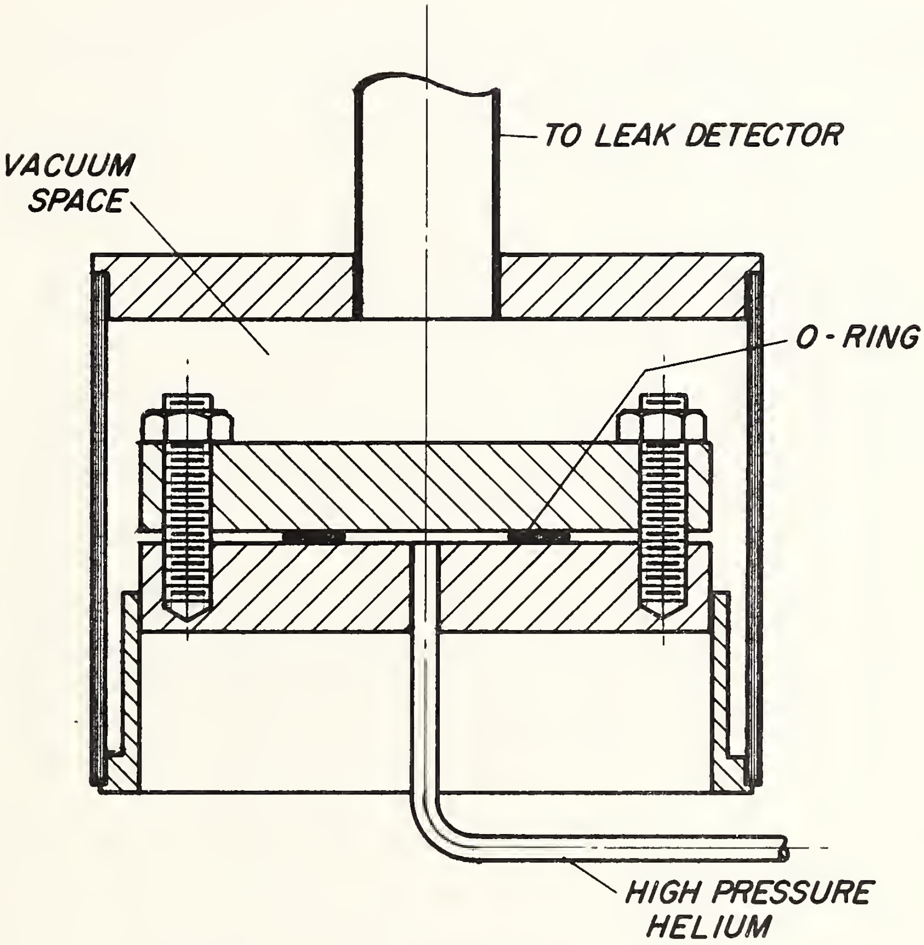
The O-ring was compressed with a given amount of torque on each of the 3/8" x 24 bolts. The separation between the top plate and base was measured at the edge. However, this separation is not the compressed thickness of the elastomer because the top plate tends to bow. The cover was then soldered on and the entire jig immersed in LN_2 for cooling.

The standard test procedure in all of the tests was as follows: The jig was cooled by immersion in LN_2 for 90 minutes with 100 psig helium pressure inside the O-ring. After 90 minutes the pressure was increased to 1200 psig. Cooling continued at this higher pressure for 30 minutes. After two hours the jig was taken out of the LN_2 and struck sharply with an 11-ounce hardwood hammer for one minute as a vibration test. The jig was then allowed to warm up overnight. The following day the test jig was immersed in LN_2 for two hours with 1200 psig helium pressure inside the O-ring. After two hours the jig was removed from the LN_2 and struck sharply with the 11-ounce hardwood hammer for approximately one minute. This completed the two temperature cycle tests. The results are listed in Table 3.

1.3.3 Results

Results indicate that approximately 150 in. lb. on each of the six bolts was necessary to insure a good cryogenic seal with one of the better seal compounds. From torque tables, 150 in. lb. corresponds to about 12,000 pounds total compressive force on the O-ring. This figure could vary as much as 3000 pounds due to friction.

Four of the tests were made with 275 in. lb. on the bolts, but this much force is not necessary for the better compounds. It is interesting to note that ASD "Viton" A(I-8D) would not maintain a seal with this higher torque and springloading. The top plate had a permanent concave set of .009" after these four tests.



O - RING SEAL TEST JIG

FIGURE 10

Polymer	ASD Compound Number	Initial Torque (in. lb)	Separation at edge of Plates	Thickness upon removal (% of original thickness)	Cycle	Leak	
						Temp. (°K)	He Pressure (psig)
"Viton" A (Dupont)	I-8D	275	.022"	48%	1	82°K	100
					2	123°K	1200
"Viton" Parker (77-545)	——	150	.033"	74%	1	78°K	800[**]
					2	80°K	1200
"Viton" Parker (77-545)	——	275	.025"	74%	1	---No Leak---	
					2	---No Leak---	
Natural Rubber	IV-8A	125	.029"	64%	1	78°K	750[**]
Natural Rubber	IV-8A	150	.027"	61%	1	---No Leak---	
					2	---No Leak---	
Natural Rubber	IV-8A	275	.021"	49%	1	---No Leak---	
					2	---No Leak---	
Cis 4 Polybutadiene	IV-29B	150	.029"	89%	1	---No Leak---	
					2	---No Leak---	
Cis 4 Polybutadiene	IV-29B	275	.022"	84%	1	---No Leak---	
					2	---No Leak---	
"Neoprene" (Dupont)	IV-8B	150	.030"	52%	1	---No Leak---	
					2	76°K	1200[*]
"Neoprene" (Dupont)	IV-8B	150	.030"	56%	1	76°K	1200[*]
					2	---No Leak---	
Polyisoprene	IV-29A	150	.025"	57%	1	---No Leak---	
					2	---No Leak---	
EPR-40	IV-29C	150	.023"	73%	1	---No Leak---	
					2	---No Leak---	
"Hycar" 1002 (B. F. Goodrich)	II-21B	150	.026"	74%	1	---No Leak---	
					2	---No Leak---	

[*] These leaks were caused by striking the test apparatus sharply with a wooden hammer.

[**] These leaks occurred when the pressure was being increased from 100 to 1200 psig helium pressure.

TABLE 3. Results of Practical Flange Seal Tests

The above tests should be conclusive evidence for the importance of springloading in a flange assembly. Moreover, although the better compounds are leaking with 14,000 and 18,000 pounds of force in the force evaluation test jig, this much force is not necessary for a reliable seal in a springloaded test jig.

From the above tests, one should note the good compressive set properties of Cis 4 polybutadiene. This compound is outstanding in this physical property.

1.4 Seal Endurance Test

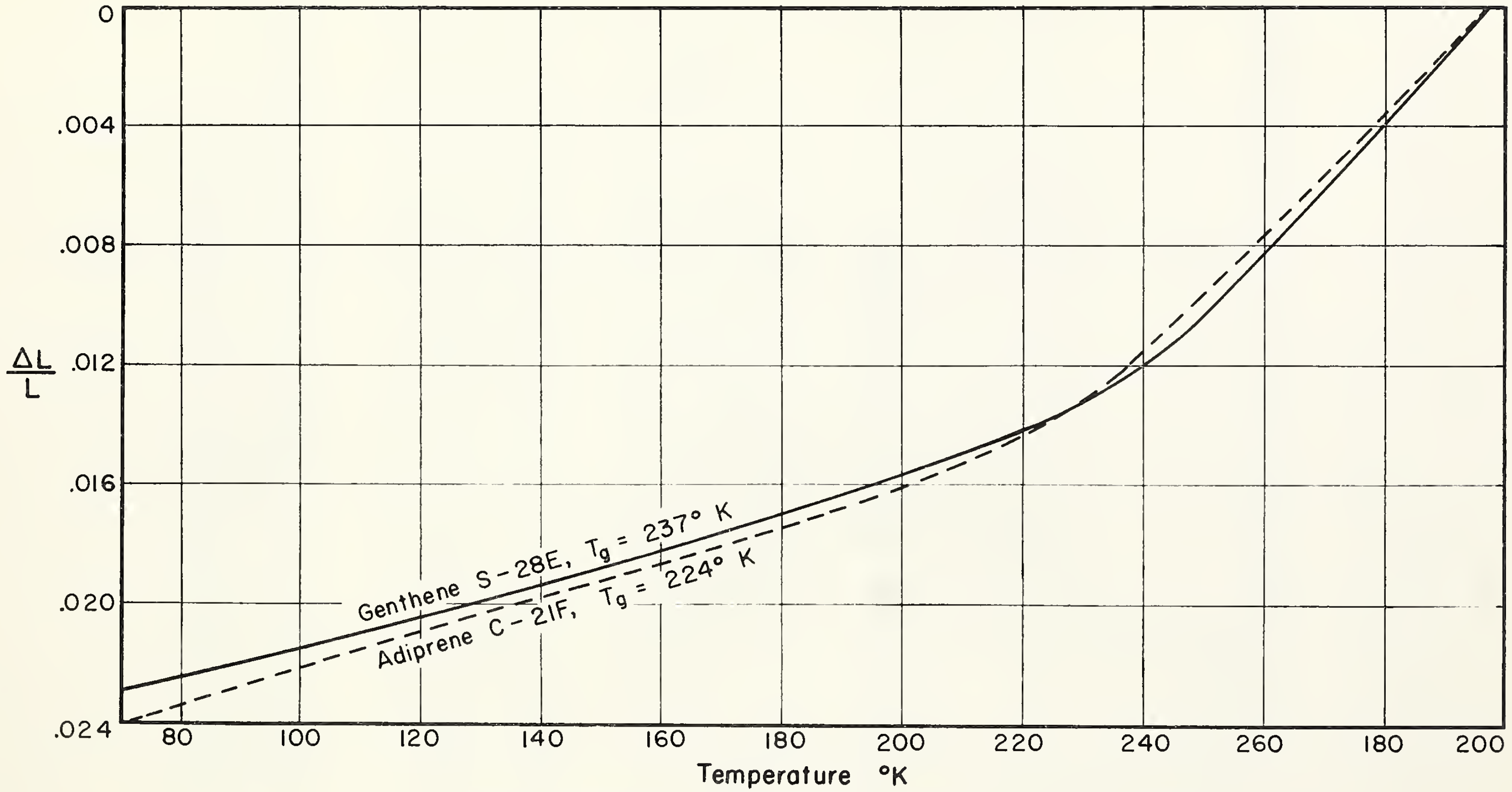
The small test jig shown in Figure 10 is presently being used for an endurance test for the better compounds at 80% compression. This test should reveal the effects of long term creep and relaxation on an O-ring seal. To date, natural rubber at 80% compression has maintained a seal for 25 days with a cooldown to 76°K every working day, with 1200 psig helium pressure and no vibration. This testing requires little time and the series is just beginning.

2.0 Linear Thermal Contraction and T_g (Y. O.)

During this reporting period samples of silicone, acrylate, polyurethane, and epoxy rubbers were measured for thermal contraction, and the respective values of T_g were obtained. Results for the silicones are given in the attached copy of paper H-9, while the other results are given in Figures 11, 12, and 13, and Table IV.

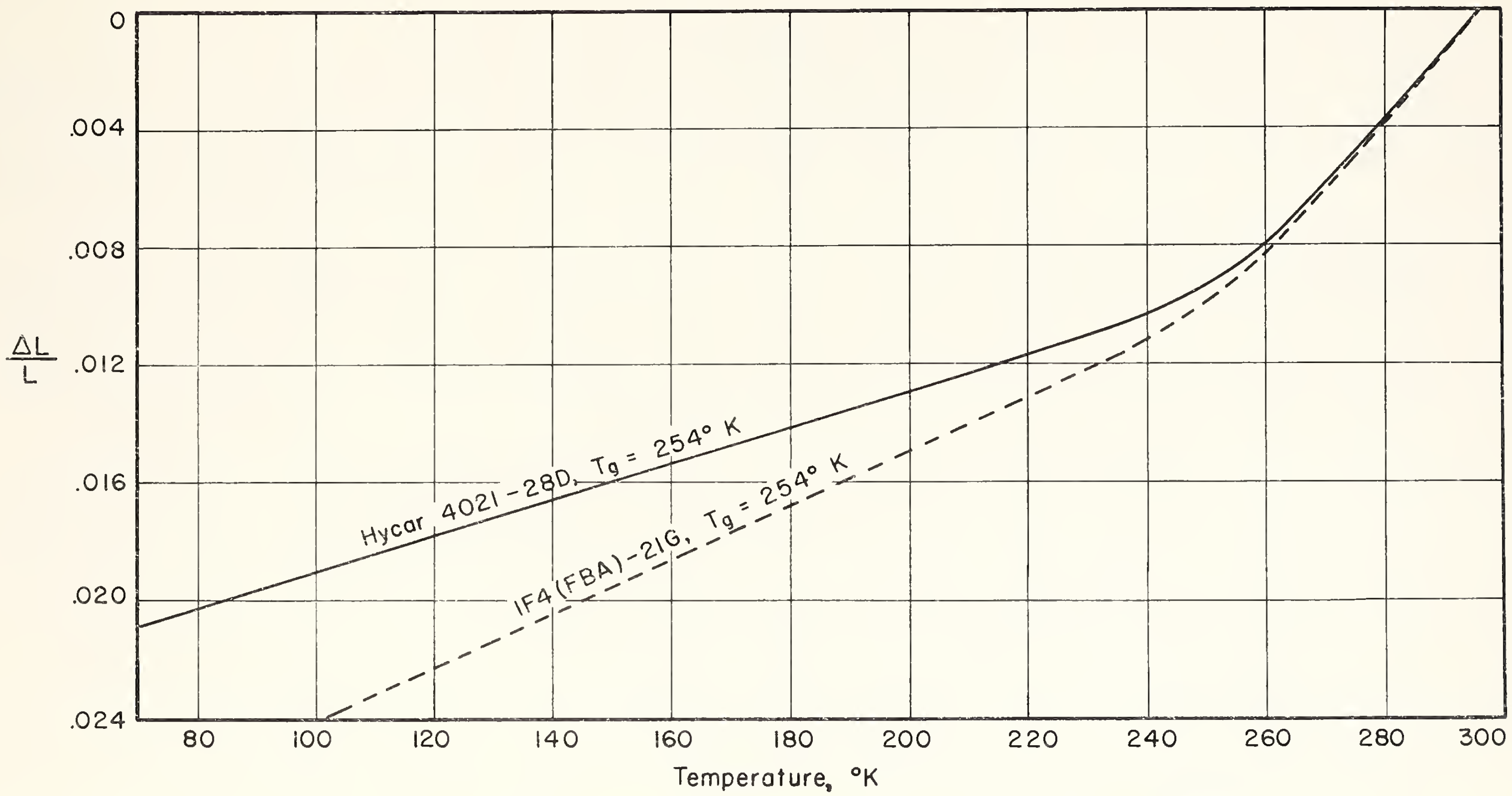
The polyurethane rubbers have results similar to the butadiene-acrylonitrile rubbers, the $\Delta L/L$ of the former being slightly larger. The polyacrylates and epoxy rubbers have similar values of T_g (254 and 264°K), which are in the upper range for this property. Results will be compared and analysed more completely in the summary report.

Yet to be reported are the rest of the hydrocarbon rubbers, the experimental cyano silicone, the polysulfides, the rest of Group VIII, and seven new additions which include variations of neoprene, silicone, ethylene/propylene, and a Dupont plastic known as HT-1.



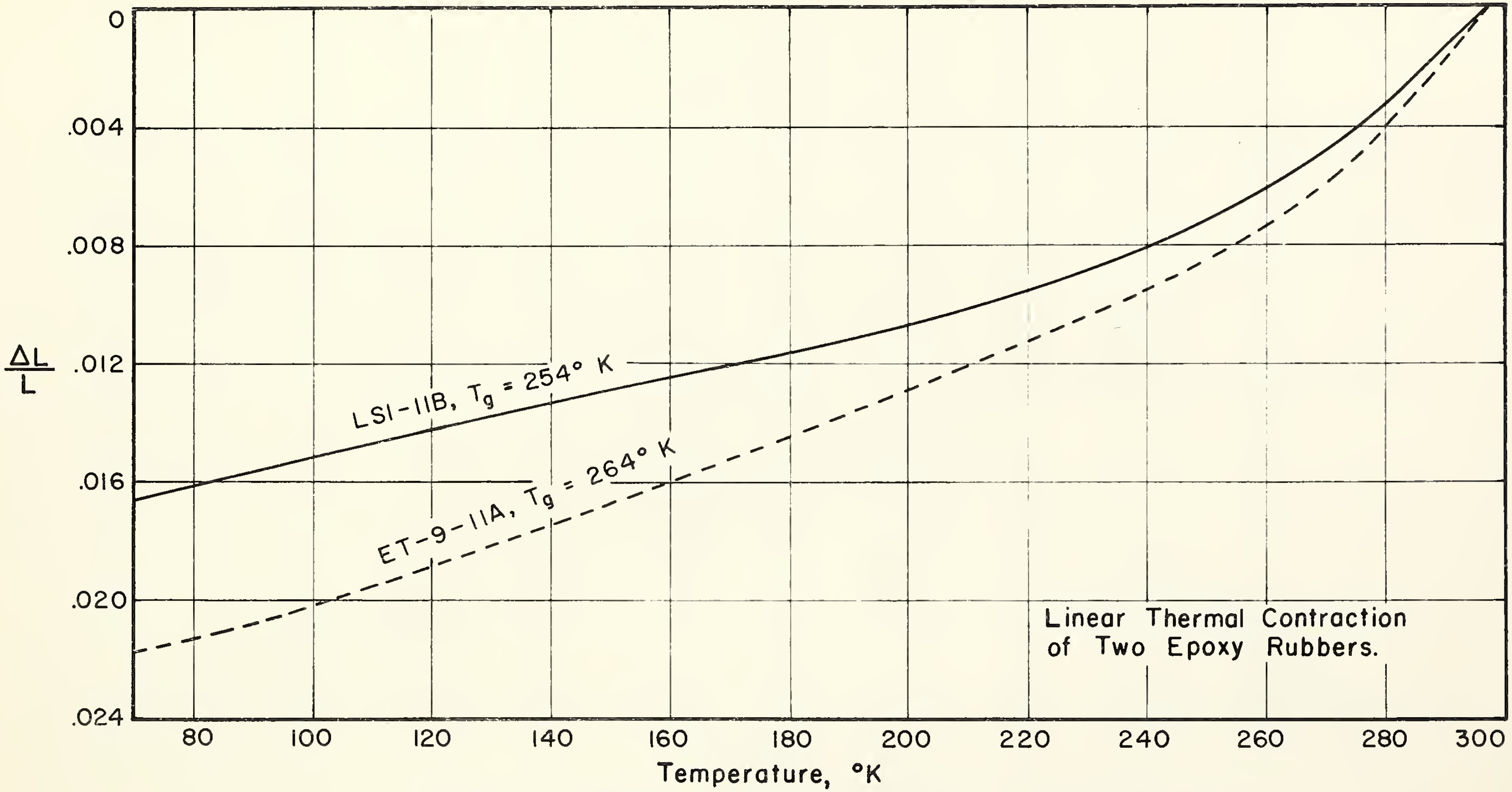
Linear Thermal Contraction and T_G Group VII

Fig. 11



Linear Thermal Contraction and T_G, Group VIII

Fig. 12



Linear Thermal Contraction and T_g, Group IX
Fig. 13

Sample number	Compound name	T_g °K	α_r $10^4/°K$	α_g $10^4/°K$	a_2 $10^4/°K$	$\Delta L/L$ from 297°K to 76°K in x 10^2
VII-28E	"Genthene"[1] S	237	2. 2	. 55	4. 8	2. 25
VII-21F	"Adiprene"[2] C	224	2. 0	. 60	4. 2	2. 36
VIII-21G	IFA(FBA)	254	2. 3	. 94	4. 2	2. 58
VIII-28D	"Hycar"[3]	254	2. 2	. 63	4. 8	2. 05
IX-11A	ET-9	264	2. 6	. 71	5. 7	2. 15
IX-11B	L51	254	1. 9	. 46	4. 2	1. 63

1) Trademark, General Tire and Rubber Co.

2) Trademark, E. I. Dupont de Nemours and Co.

3) Trademark, B. F. Goodrich Chemical Co.

TABLE 4 Thermal Expansion and T_g

3.0 Rotating Seals (D. H. W. and F. B. P.)

Funding for a limited rotating seal effort has been obtained from another source. By combining this support with a small amount from contract 33(616)-61-04, we have been able to reactivate the rotating seals study.

3.1 Introduction

Mechanical seals have been used for many years in non-cryogenic temperature applications. They are commonly used for sealing high speed rotating shafts where very little leakage can be tolerated and where shaft wear is not permitted.

This type of seal is formed at the interface of two flat-faced rings, the faces being perpendicular (usually) to the axis of the rotating shaft. Each ring is lapped to a flatness of several light bands. One ring (called the sealing ring) is fastened to the shaft and revolves with it, while the other (called the mating ring) is held stationary within the seal housing. The ring faces are held together by three basic methods or a combination of these: fluid pressure, spring-loading, or magnetically.

The design of a mechanical seal is further classified as to whether it is balanced or unbalanced. For our purposes the seal will be considered balanced when the sum of the unit hydraulic and spring (or magnetic) loads on the seal interface is less than the pressure of the fluid sealed. If this sum is greater than the pressure of the fluid, the seal is unbalanced. This definition of the balance of a seal allows a description of various operating parameters without reference to the unknown variable of fluid pressure distribution across the seal interface.

There are many factors which influence ring wear and fluid leakage. Surface material and finish, interface pressure, lubrication, relative face velocity, interface temperature, and centrifugal force are the major factors which determine seal operation.

3.2 Experimental Program

The performance of mechanical seals at cryogenic temperature is to be investigated. The seals will be operating in an atmosphere of helium gas or liquid hydrogen or nitrogen. Cooling will be to a liquid nitrogen or hydrogen bath around the seal housing; the bath and the heat generated at the interfaces will determine the temperature of the tests.

Initially, the seals will be of the unbalanced type with sealed fluid pressure in the range 25 to 50 psig. The sealing rings will be made of chromium-plated stainless steel; the mating rings will initially be of carbon. The general design will be that of a standard bellows-type mechanical seal as manufactured by several of the leading seal companies. The first seals to be tested have been ordered from Chicago Rawhide Manufacturing Company. All commercial components of the tester have been ordered, final design drawings have been completed, and machining of the parts has begun.

Figure 14 gives a general view of the tester. Two rotating seals will be tested simultaneously, with the shaft rotation in the neighborhood of 10, 000 rpm. The rubbing surfaces have an average diameter of about 1-1/8 inches around a 3/4 inch diameter shaft, giving a surface velocity of about 3000 ft/min at 10, 000 rpm. Instrumentation will be provided to measure the leak rate across each seal, the wear rates of the mating rings, the temperature of the mating rings, and the frictional torque developed at the seal faces.

4. 0 Rebound Resilience

(D. H. W. and Y. O.)

4. 1 Apparatus

Modifications of the rebound resilience apparatus have been completed for automatic recording of results. The modifications consist of an ejector which drops steel balls on the sample at 3 minute intervals and a method for recording both rebound heights and temperatures during cooldown or warmup. A semi-schematic representation of the apparatus is given in Figure 15.

The timer and ejector consists of a slowly rotating disc with a hole at one point in its circumference. A supply of steel balls on an inclined trough provides "ammunition" for the ejector, which picks up and drops a ball during each revolution. Accuracy of the drop is maintained by solid support of the ejector and sample, and by causing the ball to roll over a v-shaped notch in a thin metal dam as it leaves the hole in the disc.

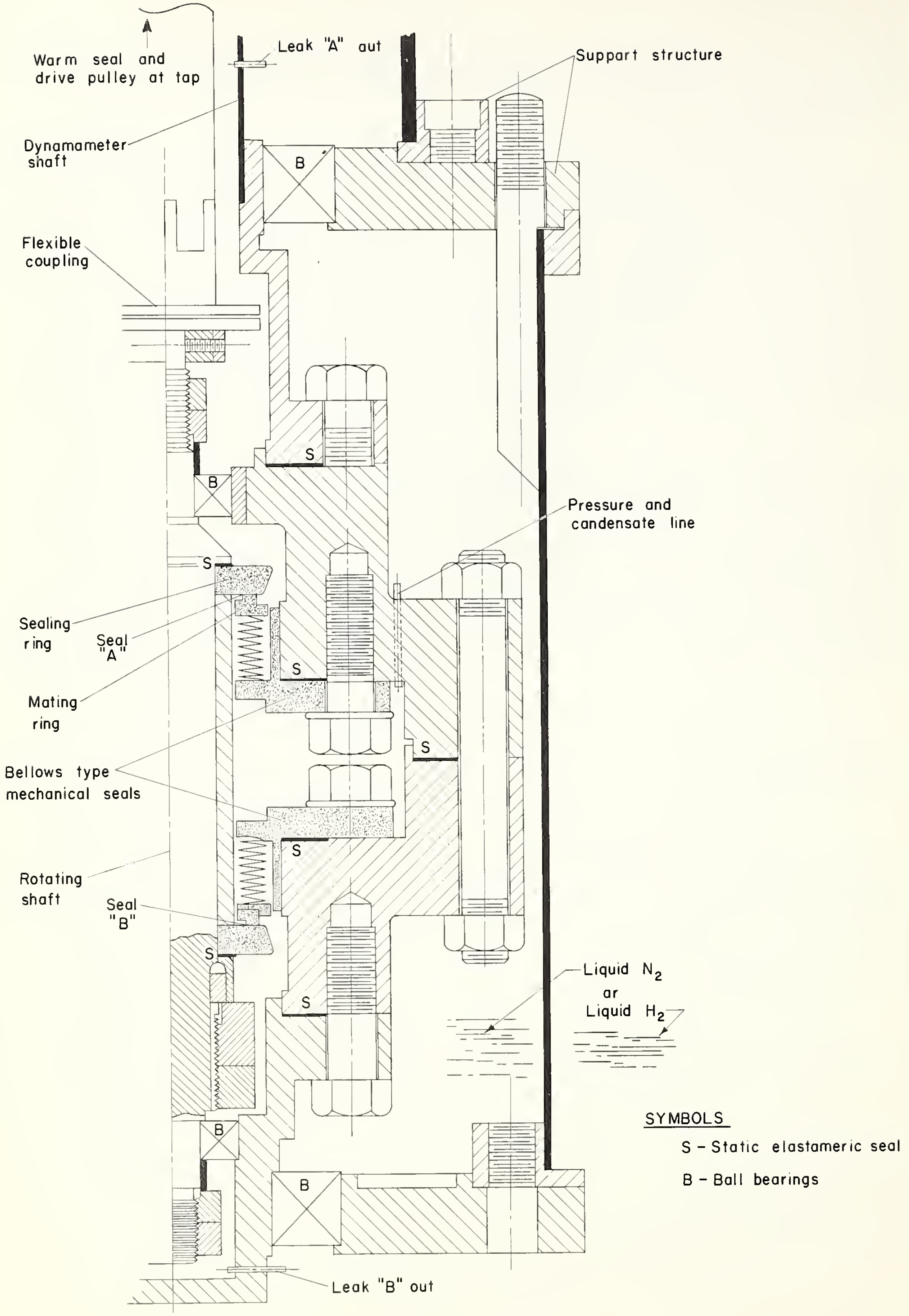


Fig. 14 High Speed, Rotating Seal Tester

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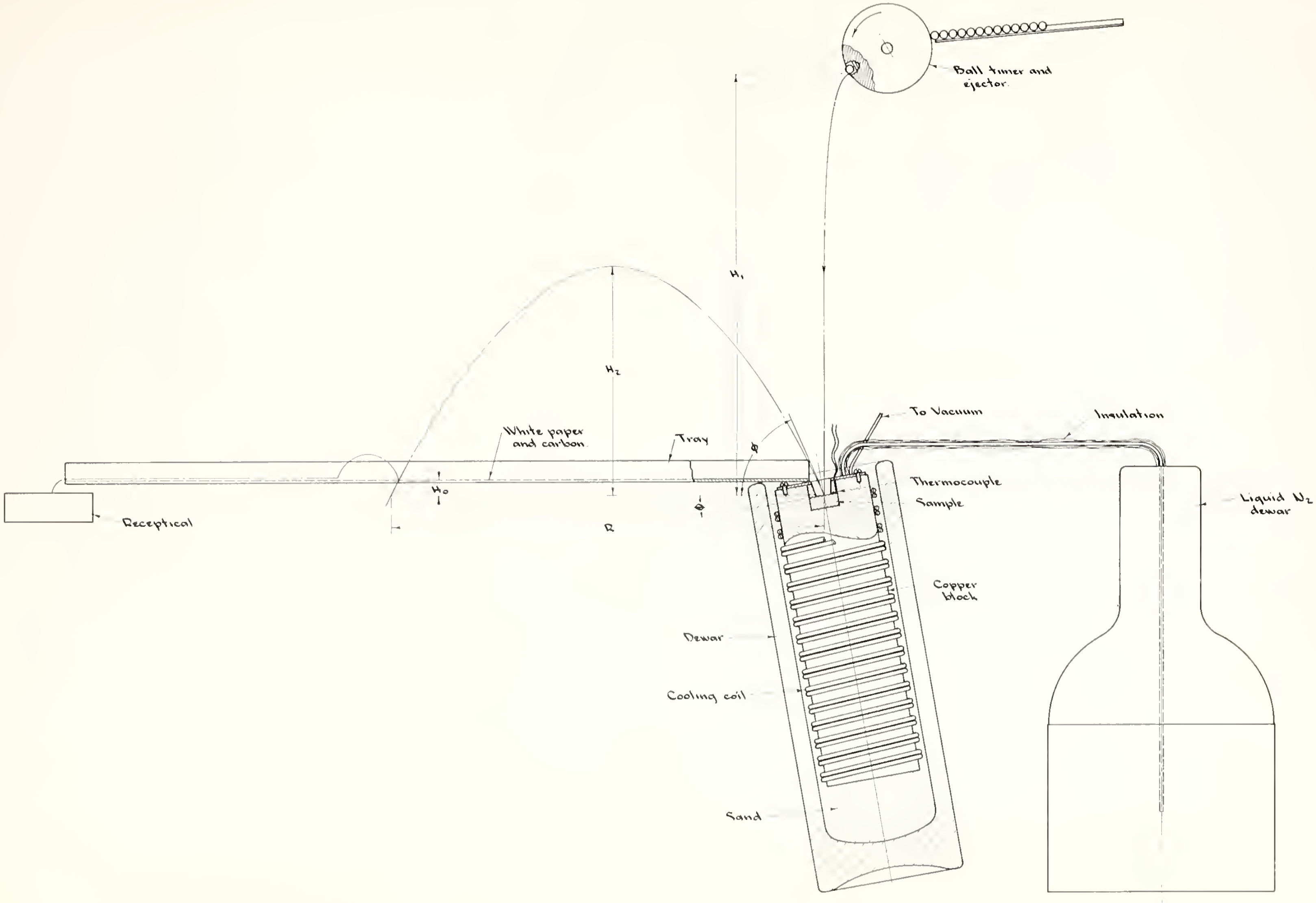

FIGURE 15: REBOUND RESILIENCE APPARATUS

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Height of rebound is obtained by positioning the sample surface at a known angle with the horizontal and measuring the horizontal range of the trajectory. From the horizontal range and the angle of launch the maximum vertical height of the trajectory (neglecting air resistance) is easily calculated. An automatic record of the horizontal range of each rebound is obtained by allowing the balls to fall on a strip of white paper covered by carbon paper.

Slow cooling is accomplished by drawing liquid nitrogen through copper coils soldered to a heavy copper cylinder which is supported in a stainless steel dewar by filling the intervening space with sand. The sample is held under light spring tension in a recess in the top of the copper cylinder. A thermocouple held firmly against the top surface of the sample provides a continuous record, through a strip chart recorder, of sample temperature. By noting the time at the start of a run this record can be coordinated with the record of horizontal ranges.

4.2 Calculation

Using the notation given on Figure 15, it is necessary to find a relation between the rebound height H_2 and the horizontal range R, making use of the angle ϕ at which the rebounding ball leaves the sample.

If V_o is the initial velocity of the rebound, the vertical height above the sample surface at any time t will be $(V_o \sin \phi)t - 1/2\ gt^2$, where g is the gravitational acceleration constant. Differentiation with respect to time and equation to zero gives $\frac{V_o \sin \phi}{g}$ as the time of maximum height, and $\frac{V_o^2 \sin^2 \phi}{2g}$ as the value of H_2. Thus

$$H_2 = \frac{V_o^2 \sin^2 \phi}{2g} \quad \text{or}$$

$$V_o = \frac{(2gH_2)^{1/2}}{\sin \phi} \tag{1}$$

When $H = H_o$, that is when the ball has reached the level of the paper, the time of flight will be

$$t_R = \frac{V_o \sin\phi + (V_o^2 \sin^2\phi - 2gH_o)^{1/2}}{g} \tag{2}$$

from which

$$R = \frac{V_o}{g} \cos\phi \left[V_o \sin\phi + (V_o^2 \sin^2\phi - 2gH_o)^{1/2} \right] \tag{3}$$

The elimination of V_o through use of (1) gives

$$R = 2 \cot\phi \left[H_2 + (H_2^2 - H_2H_o)^{1/2} \right] \tag{4}$$

which is the desired relation.

The value of H_o is not difficult to measure. The value of ϕ is 90° - 2θ, where θ is the angle which the sample surface makes with the horizontal. Another way to determine ϕ is to measure both R and H_2 for a few rebounds and use equation (4). After the constants ϕ and H_o have been determined, a plot of equation (4) can be used to read off H_2 as a function of R.

Force and Seal Evaluation of Elastomeric O-Rings

by

P. R. Ludtke and D. H. Weitzel
Cryogenic Engineering Laboratory
National Bureau of Standards
Boulder, Colorado

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FORCE AND SEAL EVALUATION OF ELASTOMERIC O-RINGS*

P. R. Ludtke and D. H. Weitzel
Cryogenic Engineering Laboratory
National Bureau of Standards
Boulder, Colorado

1. Introduction

The purpose of this experiment is to observe the force variation and sealing ability of various compressed elastomeric O-rings as they are cooled from room temperature to 76°K. We particularly want to investigate what happens to the force at the second-order transition point (T_g), where the elastomer becomes brittle, and how the force varies below T_g, where the elastomer remains brittle like glass; to decide if there is a correlation between the force on a compressed O-ring and its seal performance; to determine the extent of this correlation and what mechanism is involved which permits some elastomeric O-rings to leak at high compressive forces and others to leak at relatively low compressive forces; and to determine from force loss, leak detection results, and other physical and mechanical properties, which elastomer or group of elastomers appears to be most promising for cryogenic seal applications.

This is done by compressing an elastomeric O-ring with a given initial force and observing the reduction in force due to relaxation, creep, and thermal contraction as it is cooled to 76°K. The O-ring functions as a seal and the leakage is monitored by a helium leak detector. The force-temperature curve is continuously recorded and the point at which a leak begins is noted.

The test apparatus is shown in Figure 1. The plates and bolts are overdesigned to minimize flexing and stretching. Flexing of flanges and stretching of bolts causes springloading in most practical seal applications.

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Springloading helps maintain a seal, but more meaningful comparisons of the various elastomers can be obtained if springloading is minimized.

The stressed parts of the jig are made of invar. This includes force washers, loading sleeves, top plate, studs, pillars, and compression disc. The pillars are placed adjacent to the studs between the base and top plate to maintain a nearly constant separation between these surfaces and keep them accurately parallel at all times. This insures uniform compression of the O-ring. The surfaces compressing the O-ring are given a normal machine finish of approximately 32 microinches.

The bellows assembly contains three washer type strain gages. Liquid nitrogen is circulated through the bellows to maintain the force washers at 76°K and to slowly cool the entire apparatus. A thermocouple placed beside the O-ring provides a record of the O-ring temperature. The force washers and three external fixed resistors constitute a bridge circuit which provides a signal proportional to the force on the O-ring. The force and temperature signals are continuously recorded during a cooldown cycle.

2. Procedure

The 0. 140 inch thick x 1 inch I. D. O-ring is given an initial force of approximately 14, 000 pounds. The force is brought to 14, 000 pounds by varying the number of mica shims between the compression disc and the bellows. Although the initial force is standard in these tests, the compressed O-rings vary in thickness (0. 013 to 0. 034 inches), depending on the hardness of the compound. After the O-ring is compressed, the outer cover is soldered to the base of the test jig with Rose's fusible metal. The soldering process warms the O-ring slightly and accelerates relaxation of the elastomer, but probably does not affect the total relaxation.

After the test jig cools to room temperature the force is measured again to determine the reduction in force during this initial relaxation period. This is the force at the start of the first cooldown cycle. The O-ring is then cooled to 76°K over a period of about two hours. During the first cooldown cycle the helium pressure inside the compressed O-ring is 100 psig. If the O-ring does not leak, the helium pressure is increased to 500 psig for the second cooldown cycle. If the seal is still tight, the helium pressure is increased to 1000 psig for the third and last cooldown cycle. If a leak occurs which exceeds the maximum leak rate of the leak detector (0. 0003 atm cc/sec), the helium pressure is not increased for the following cooldown cycles.

When a leak occurs, the temperature and force are noted and the time required for the leak rate to increase from the minimum detectable value to 0. 0003 atm cc/sec is measured. This time is indicated on the cooldown Figures 2 through 6. The points at which leaks began are denoted by arrows on the figures.

If the force at start of cooldown is less than 3000 pounds, no reliable measure of force decay can be obtained. In these cases, vertical dashed lines are shown on the temperature-force figures. The initial force measurements at ambient temperature are within 10 to 15% of their true values.

3. Results and Discussion

Three groups of elastomer samples compounded by the Elastomers Section of Aeronautical Systems Division have been tested to date. These samples are grouped according to the compounding monomers. Vinylidene fluoride is common to all the compounds of group I, and butadiene is the main monomer in the compounds of group II. Group IV contains natural rubber and the polymers with similar structure. Results are given in Figures 2 through 6 and summarized in Table 1.

Force-temperature curves for "Viton" *A (ASD Compound I-8D) are shown in Figure 2. These curves are typical of the fluorocarbon elastomers in group I. The compounds in this group all have the characteristic of losing

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* Trade names are placed in quotation marks, and credited in the table of compounding recipes given in the appendix at the end of this paper.

most of their compressive force during the initial relaxation period. This is the period when the outer cover is soldered to the base of the jig and the entire jig is then allowed to cool back to room temperature.

The "Viton" O-rings lost 70-90% of their initial force before cooldown was begun, and they leaked at relatively high temperatures, around 230°K. However, the leak rate was small and there was no material failure. "Fluorel" (ASD Compound I-12C) performed almost the same as the "Vitons", but maintained its force at a slightly higher value.

In some previous tests(1) the vinylidene fluoride-perfluoropropylene O-rings have maintained a seal at cryogenic temperatures. These successful tests utilized one or more of the following advantages: the seal was spring-loaded due to flexing of the flanges; there was radial confinement of the elastomer; or a thinner (0. 070 inch cross section) O-ring was used. For the present series of tests the O-ring is compressed between heavy rigid plates. There is no springloading except that due to compression of the loading sleeves, there is no radial confinement other than radial friction, and the O-ring has a 0. 140 inch cross section diameter. The seal performance of vinylidene fluoride-perfluoropropylene O-rings under these conditions was relatively poor.

Elastomers of "Kel F"-3700 (ASD Compound I-12E), and "Kel F"-5500 (ASD Compound I-12D) performed similar to the "Viton" compounds, but there was a higher percentage of initial force lost (80-93%) and this was accompanied by severe material failure. "Kel F"-3700 held together better than "Kel F"-5500. The latter was completely shredded.

The compounds of group I will support a high initial force but cannot maintain this force. The O-rings tend to flow or relax and lose most of the initial force before cooldown. The immediate force decay of the compounds in this group is probably due to the less rigid cross linking bonds. These compounds all leaked at approximately the same temperature (230°K) and none of the O-rings held 100 psig helium at 76°K.

Group II consists of butadiene copolymers. These are the "Synpols" of butadiene and styrene, and "Hycar"-1002 and "Paracril", which are copolymers of butadiene and acrylonitrile.

There was no characteristic pattern of behavior for the elastomer samples of group II. "Synpol" 1000 (ASD Compound II-21D) maintained a considerable amount of force but the leak temperature was relatively high (200°K). "Synpol" 1013 (ASD Compound II-21E), Figure 3 maintained less force than "Synpol" 1000 but the leak temperature was much lower. The seal began leaking at 104°K. At 76°K the leak rate was constant at 5×10^{-6} atm cc/sec. The helium pressure inside the O-ring was increased to 500 psig for the second cooldown and the O-ring began leaking at 147°K. After eleven more minutes of cooling the leak rate was greater than 0.0003 atm cc/sec., the maximum reading on the leak detector. Comparing these two butadiene-styrene polymers, one can conclude that "Synpol" 1000 maintains the initial force better but "Synpol" 1013 leaks at a much lower temperature and should give better performance in a seal application.

"Paracril" D (ASD Compound II-21C) lost 53% of the initial force before cooldown and maintained only 2000 pounds of force after the first cooldown. The leak temperatures were high (≈ 260°K). "Paracril" 18-80, (ASD Compound II-21A) performed much better. Only 31% of the initial force was lost and the O-ring maintained 8100 pounds of force after the first cooldown. The leak temperatures were approximately 190°K. "Hycar" 1002 (ASD Compound II-21B), Figure 4, performed best of the butadiene-acrylonitrile polymers. Only 27% of the initial force was lost before cooldown and the O-ring maintained 7500 pounds of force after the first cooldown. The O-ring began leaking at 104°K during the first cooldown. After being cooled to 76°K, the leak rate was constant at 165×10^{-6} atm cc/sec. The second cooldown pressure was also 100 psig helium. The leak rate at 76°K was 260×10^{-6} atm cc/sec. The helium pressure was increased to 500 psig for the third cooldown. The O-ring began to leak at 104°K and the leak exceeded 0.0003 atm cc/sec before the O-ring temperature reached 76°K. The compression set defined as $\frac{\text{original thickness - final unstressed thickness}}{\text{original thickness - compressed thickness}}$ was relatively low (32%).

The above three polymers of butadiene-acrylonitrile all have the same compounding recipe and cure treatment. This leaves one to conclude that 70/30, the monomer ratio used in "Hycar"-1002, is the best of the three ratios tested for seal performance of these copolymers.

Group IV consists of ethylene/propylene, cis-4 polybutadiene, natural rubber, isoprene, and chloroprene. These performed comparatively well, with the exception of the sample of ethylene/propylene (ASD Compound IV-29C), which extruded and could not be confined between the compression disc and base. A harder compound of this polymer, and one crosslinked with sulfur, will be tested later.

Cis-4 polybutadiene (ASD Compound IV-29B), Figure 5, performed the best of all the elastomer samples tested at 14,000 pounds initial force. Only 29% of the initial force was lost before cooldown and there was still 8000 pounds of force at the start of the second cooldown cycle. The compression set was only 23%. No leak occurred during the first cooldown cycle at 100 psig helium pressure, nor during the second cycle at 500 psig. A leak did occur during the third cooldown cycle at a temperature of 123°K and 1000 psig pressure.

When the leak occurred, the force had decayed to approximately 500 pounds. Since the gas pressure on the compression disc inside the compressed O-ring would account for most of this force, it appears that the compression force on the O-ring when it leaked was almost zero.

It was expected that an O-ring would maintain a seal if the minimum pressure on the sealing surface was greater than the gas pressure inside the O-ring. However, these tests indicate that most of the O-rings begin to leak while the compression force on the O-ring is still quite high. It appears likely that small leak passages between the sealing surface and O-ring can occur with some of the elastomers even though most of the sealing surface is under high compressive force. This may indicate some irregularity or nonuniformity in the way these highly compressed elastomers contract when they are cooled.

Cis-4 polybutadiene has another virtue. From recent tests of thermal expansion, it has been determined that the second-order glassy transition temperature (T_g) for this compound is approximately 168°K. The transition temperature for most of the other elastomer samples is in the range from 202°K to 262°K. At T_g random thermal motion of the molecular chains is inhibited by the fact that free rotation of chain elements about single bonds will not take place at an appreciable rate, and the elastomer becomes brittle like glass. The lower brittle point temperature of cis-4 polybutadiene may be a contributing factor to its excellent seal performance.

Two separate tests were made using natural rubber (ASD Compound IV-8A) one with 14, 000 pounds initial force, and the other with 18, 000 pounds initial force. The O-ring that was given 14, 000 pounds initial force lost only 17% before cooldown. After the first cooldown cycle the O-ring still maintained a force of 9200 pounds. However, in spite of the high force maintained by the O-ring, the seal leaked at 154°K during the first cooldown, and at 169°K for the second and third cooldown cycles.

The natural rubber O-ring which was given 18, 000 pounds initial force (Figure 6) lost only 27% before cooldown. After the first cooldown cycle the O-ring still maintained a force of 12, 000 pounds. No leak occurred during cooldown cycles at 100, 500, and 1000 psig. However, after the test jig was removed from the dewar and jarred lightly on the concrete floor, a leak occurred at 76°K and 1250 psig helium pressure. The O-ring compression was 83% and there was no material failure. Results from this and previous tests(1) indicate that natural rubber will make a reliable seal at 76°K if given an adequate amount of compression (83-90%).

Polyisoprene, (ASD Compound IV-29A) lost only 18% of the initial force before cooldown and the O-ring maintained a force of 7200 pounds after the first cooldown. A small leak occurred at 88°K during the first cooldown with 100 psig helium pressure. At 76°K the leak rate became constant at 8×10^{-6} atm cc/sec. The helium pressure inside the O-ring was increased to 500 psig for the second and third cooldown. A leak began at 122°K during each of these cycles and exceeded 0. 0003 atm cc/sec. immediately. Examination of the O-ring after testing revealed small pock marks or pits in the compressed surfaces of the O-ring. This pitting was not observed in the other elastomer samples of this group and may be due to the milling procedure.

"Neoprene" (ASD Compound IV-8B) lost 48% of its initial force before cooldown. This compound maintained less of the initial force than the others in group IV. The compression set was also high (85%). However, in previous tests(1) "Neoprene" has made excellent seals at slightly higher compression.

The compounds in group IV show low force decay and good sealing ability. In previous tests(1) "Neoprene" and natural rubber have made good cryogenic seals and the present tests indicate that polyisoprene and cis-4 polybutadiene have even better properties for O-ring applications. It is felt that all of the elastomers in group IV except the ASD sample of ethylene-propylene rubber would maintain a leak-tight seal at 76°K if given an initial force of 18, 000 pounds in the present test jig.

4. Conclusions

Several observations have been made in the testing to date. If an O-ring leaks, there is very little difference in the leak temperature for the second and third cooldown, and the leak temperature is usually lower for the first cooldown cycle. The lower leak temperature for the first cycle is probably due to the higher force present at the start of the first cooldown. But, after the soldering procedure and one cooldown cycle, the O-rings tend to come to equilibrium and maintain a fairly constant force for the second and third cooldown cycles. Hence, the constant leak temperature for these last two cooldown cycles. This is encouraging from the standpoint of seals for continuous use.

Another observation made during the testing is the apparent unimportance of the cooldown pressure. It seems that if an O-ring will hold a seal at 76°K with 100 psig helium pressure, it has an excellent chance of maintaining this seal at 76°K and 500 psig helium pressure. There has been no test made to date where a seal leaked at 500 psig and not 100 psig.

Observations of the force on a compressed O-ring during cooldown have been revealing. There is more force loss above the brittle point than below. It was hoped that it would be possible to accurately determine the brittle point of the compressed elastomer from a characteristic change in force at T_g. This was not possible and may be because of springloading in the force gages and sleeves. A modulus calculation shows that the sleeves and force gages are compressed or springloaded 0.002 inches at 76°K by 14,000 pounds of force. In the design of the test apparatus, every precaution was taken to minimize springloading. However, the force gages and sleeve assemblies operate on the principle of elasticity within the elastic limit and it is therefore impossible to eliminate all springloading. It is probably this springloading which prevents any characteristic change of force as the

O-ring passes through the brittle point.

There was little change in force below T_g for the highly compressed elastomers (80% and above). Some of the thicker O-rings that were given less compression showed more force loss below T_g. This was expected from thermal expansion measurements.

Most enlightning is the amount of force lost by the various elastomers through various phases of the testing process. Some of these compounds have strong internal bonds which do not break down under high compressive forces and temperature cycling, while others tend to flow or relax and lose most of the compressive force.

The belief that the force on the sealing surface should be near zero when a leak occurs was not supported. Some of the O-rings developed leaks with 6000 pounds of force on the sealing surface. Results indicate that the sealing ability of an elastomer O-ring is dependent upon the force maintained on the sealing surfaces, but the amount of force required varies considerably among the elastomeric compounds.

The elastomers in group IV have shown the best seal performance to date, and have also maintained more force through the testing cycles than the other elastomers. Cis-4 polybutadiene was the best elastomer in group IV. The good performance of this group is probably due to the high internal cohesive forces which prevent the O-ring from flowing and creeping, and thus maintain the force on the sealing surfaces of the O-ring.

A force of 18,000 pounds to maintain a seal of this size amounts to approximately 6000 pounds per linear inch of O-ring, which is too high for many practical applications. However, it should be emphasized that one purpose of this program is a critical examination of the elastomer behavior in order to isolate the most promising material for seal applications. It has been previously shown(1) that a number of these compounds will make satisfactory cryogenic seals with flange loads of around 2000 pounds per linear inch of seal. This was with thinner O-rings and a flange which is sufficiently stressed to result in significant springloading. In the present program these advantages are deliberately minimized in order to bring out differences in the performance of the elastomer compounds.

The work will continue with further modifications of both polymer and compounding. It is our belief that considerable progress in the development of elastomeric compounds for cryogenic seals can be made through this program.

Reference

(1) Elastomeric Seals and Materials at Cryogenic Temperatures, Aeronautical Systems Division Technical Data Report 62-31 (Available from ASTIA or from Cryogenic Engineering Laboratory, National Bureau of Standards).

Polymer	A.S.D. Compound Number	Shore A. Hardness	Initial Force (lbs.)	Percent Force Lost During Initial Relaxation	Compressed O-ring Thickness	Percent Compression	Compression Set	Material Failure	Force at Start of Cooldown			Leak Occurred				
									#1	#2	#3	Temp. (°K)	Force (lbs.)	He. Pres. (p.s.i.g.)	Off Scale Time***	L. R. at 76°K $\times 10^6$ (atm cm^3/sec)
Group #1																
"Viton" A (Du Pont)	1-8D	80	14,000	80%	.037"	74%	46%	None	2800			209	1500	100	26 min.	
										<500		250	<500	100	30 min.	
											<500	252	<500	100	38 min.	
"Viton" A-HV (Du Pont)	1-12B	80	14,000	79%	.033"	76%	71%	None	3000			233	1800	100	32 min.	
										<500		250	<500	100	36 min.	
											<500	256	<500	100	37 min.	
"Viton" B (Du Pont)	1-12A	75	14,600	90%	.028"	80%	56%	None	1500			233	<500	100	32 min.	
										700		238	<500	100	33 min.	
											700	240	<500	100	37 min.	
"Kel F" 5500 (Minnesota Mining & Mfg.)	1-12D	80	13,800	93%	.020"	86%	88%	Severe	1000			241	<500	100	22 min.	
										<500		241	<500	100	17 min.	
											<500	244	<500	100	15 min.	
"Kel F" 3700 (Minnesota Mining & Mfg.)	1-12E	75	14,700	80%	.013"	93%	83%	Severe	3000			233	<500	100	1 min.	
										<500		236	<500	100	1 sec.	
											<500	237	<500	100	1 sec.	
"Fluorel" (Minnesota Mining & Mfg.)	I-12C	80	14,000	67%	.033"	76%	52%	None	4600			232	3000	100	6 min.	
										2300		235	----	100	6 min.	
											2200	236	----	100	4 min.	
Group #II																
"Synpol" 1013 (U.S. Chem. Co.)	II-21E	70	12,600	63%	.027"	81%	34%	None	4600			104	1700	100		5
										4100		147	800	500	11 min.	
											3200	146	----	500	5 min.	
"Paracril" 18/80 (Naugatuck Chem. Division)	II-21A	75	14,000	31%	.024"	83%	39%	None	9600			185	5500	100	12 min.	
										8100		192	5000	100	9 min.	
											7400	195	4800	100	13 min.	
"Hycar" 1002 (B. F. Goodrich Chem. Company)	II-21B	75	14,200	27%	.034"	76%	32%	None	10,300			104	5700	100		165
										7500		125	5000	100		260
											6700	104	4200	500	18 min.	
"Paracril" D (Naugatuck Chem. Division)	II-21C	85	14,300	53%	.034"	76%	47%	None	6700			241	4400	100	36 min.	
										2000		274	----	100	40 min.	
											2000	277	----	100	42 min.	
"Synpol" 1000 (U.S. Chem. Co.)	II-21D	65	13,400	30%	.026"	81%	30%	None	10,000			200	7200	100	15 min.	
										6100		204	3100	100	23 min.	
											5800	202	2900	100	22 min.	
Group #IV																
EPR-40	IV-29C	60	14,000	21%	.018"	87%	33%	None	11,000			196	5800	100	1 min.	
										9000		208	5300	100	11 min.	
											8800	---	----	---	-------	
Cis-4 Polybutadiene	IV-29B	70	14,000	19%	.032"	77%	23%	None	11,500			No Leak Occurred				
										8000		No Leak Occurred				
											7500	123	400	1000	1 sec.	
Natural Rubber	IV-8A	65	14,200	17%	.023"	84%	64%	None	11,800			154	7500	100	26 min.	
										9200		169	6500	100	21 min.	
											9200	167	6300	100	16 min.	
Polyisoprene	IV-29A	70	14,000	18%	.026"	81%	70%	None	10,000			88	4100	100		8
										7200		122	2300	500	1 sec.	
											7200	122	2600	500	1 sec.	
"Neoprene" (Du Pont)	IV-8B	75	13,500	48%	.030"	79%	85%	None	7100			179	2700	100	13 min.	
										5100		200	2500	100	18 min.	
											4800	207	2300	100	19 min.	
Natural Rubber *	IV-8A	65	18,000	27%	.024"	83%	58%	None	13,000			No Leak Occurred				
										12,000		No Leak Occurred				
											12,000	76°K**	7400	1250	1 sec.	

* 18,000# initial force instead of usual 14,000#.

** A leak occurred when the test jig was removed from the liquid nitrogen bath and set down on the concrete floor.

*** Time required for leak rate to increase from zero to 3×10^{-4} atm cc/sec.

TABLE I - FORCE EVALUATION TEST DATA

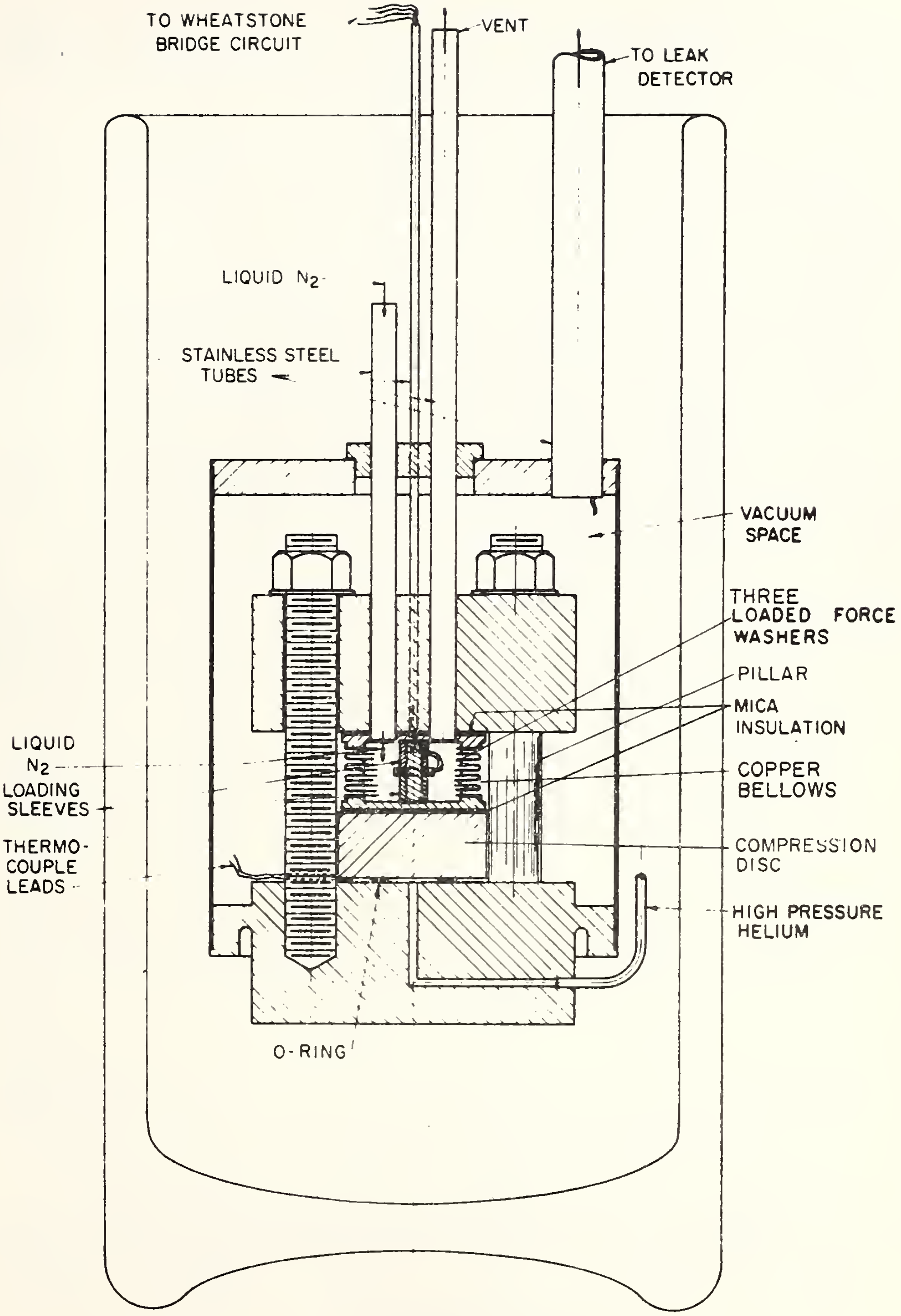

Figure 1. Force - Temperature Test Apparatus

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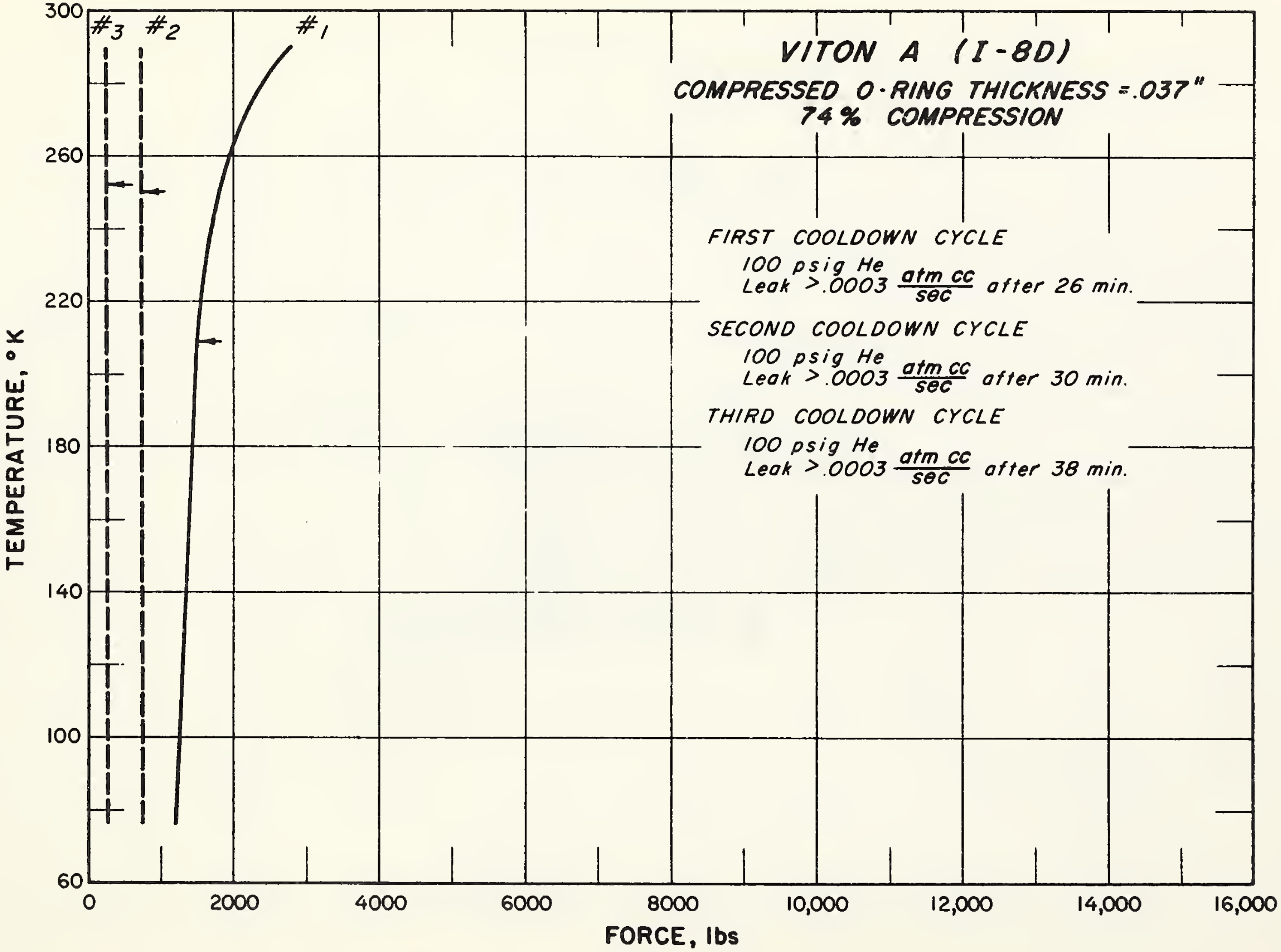

Figure 2. Force-Temperature Curve, "Viton" A

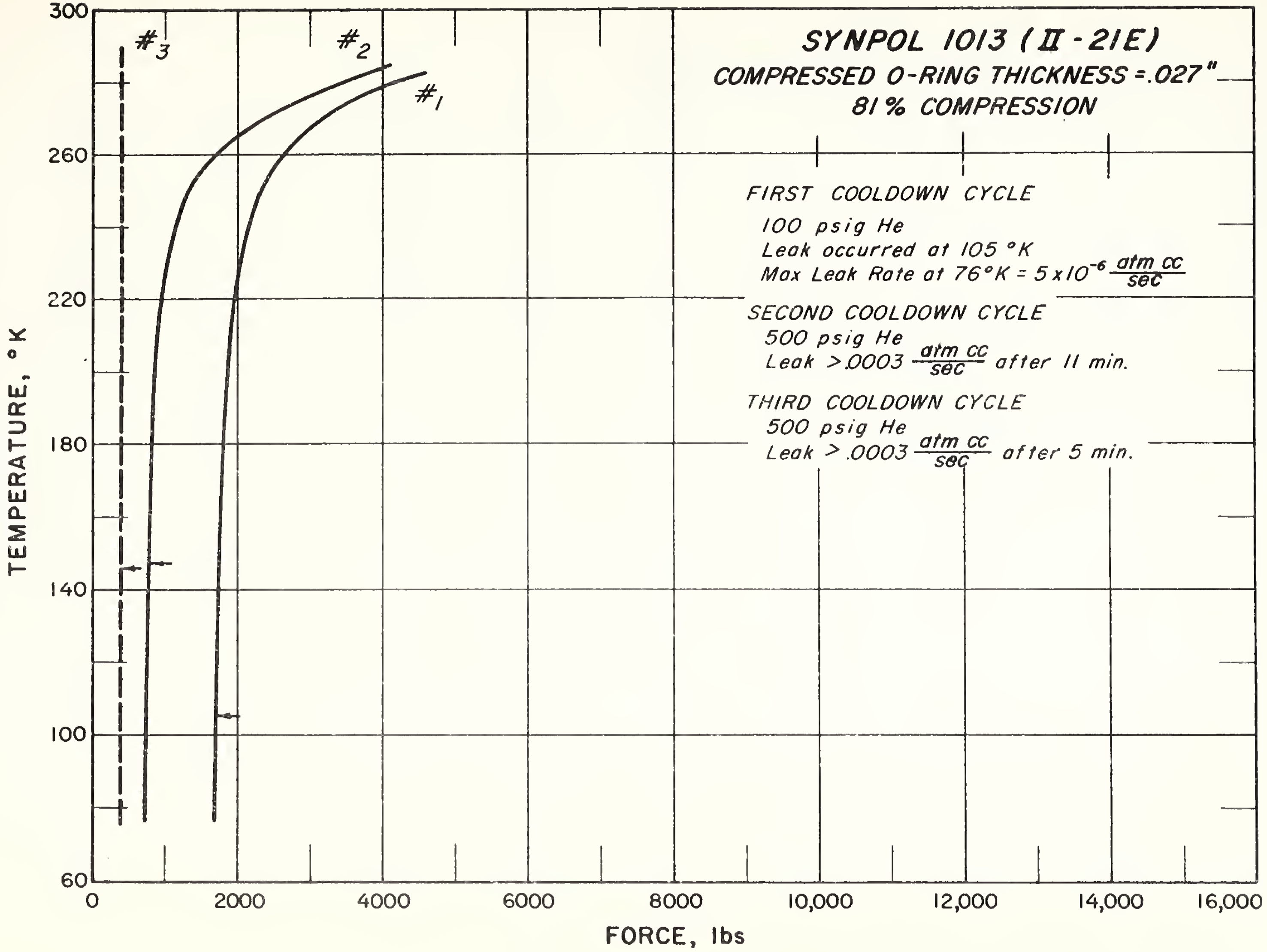

Figure 3. Force-Temperature Curve, "Synpol" 1013

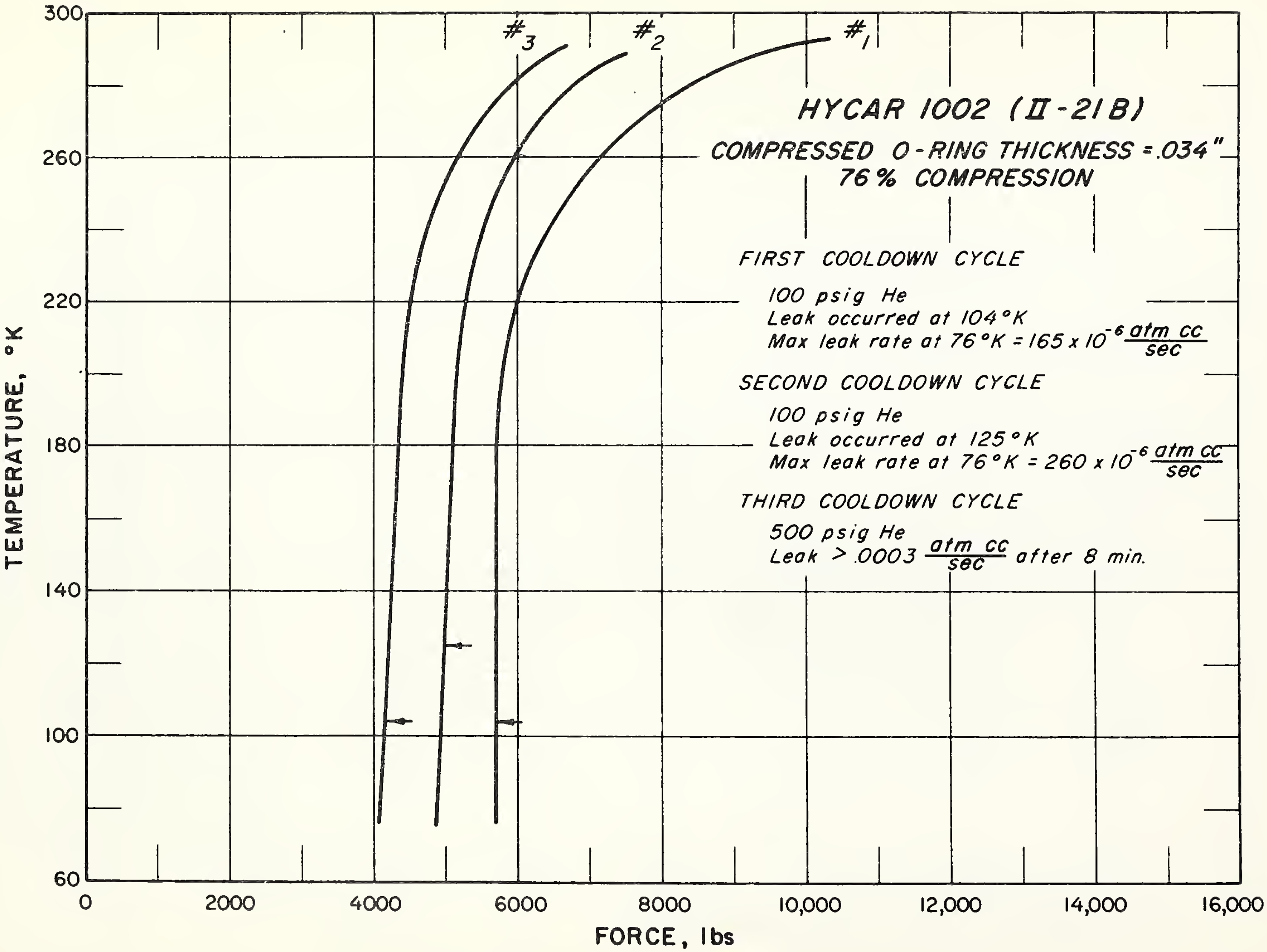

Figure 4. Force-Temperature Curve, "Hycar" 1002

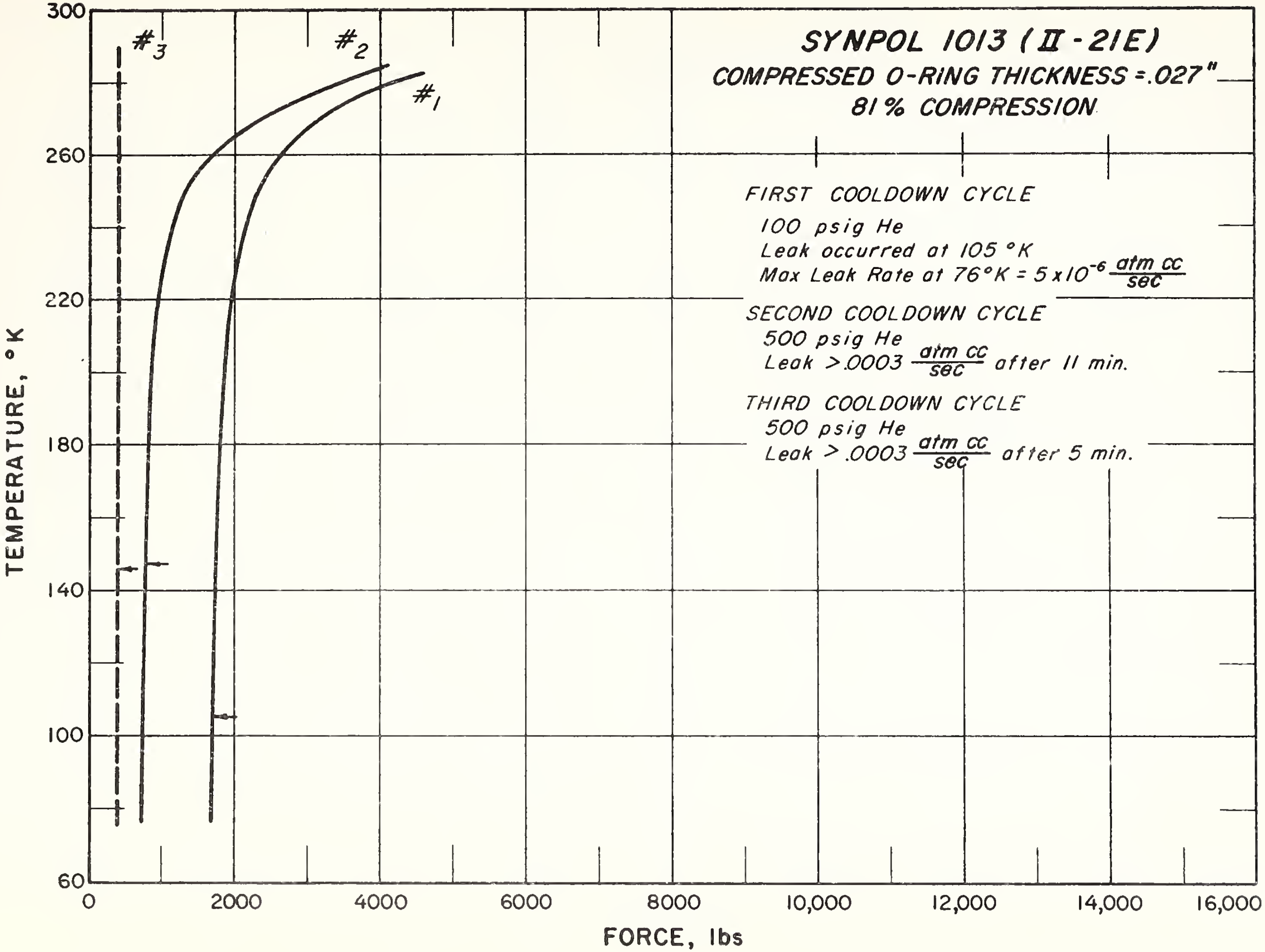

Figure 3. Force-Temperature Curve, "Synpol" 1013

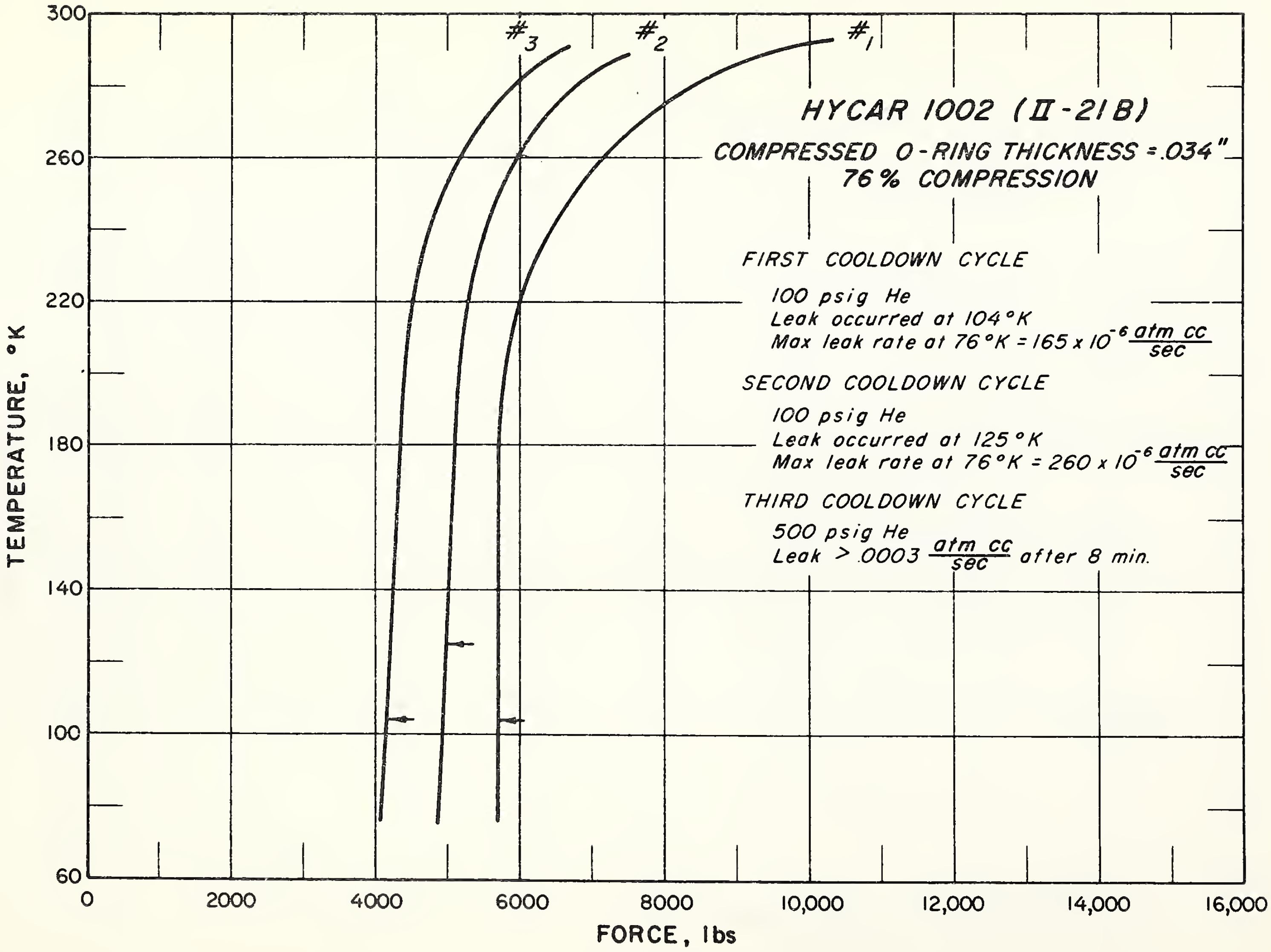

Figure 4. Force-Temperature Curve, "Hycar" 1002

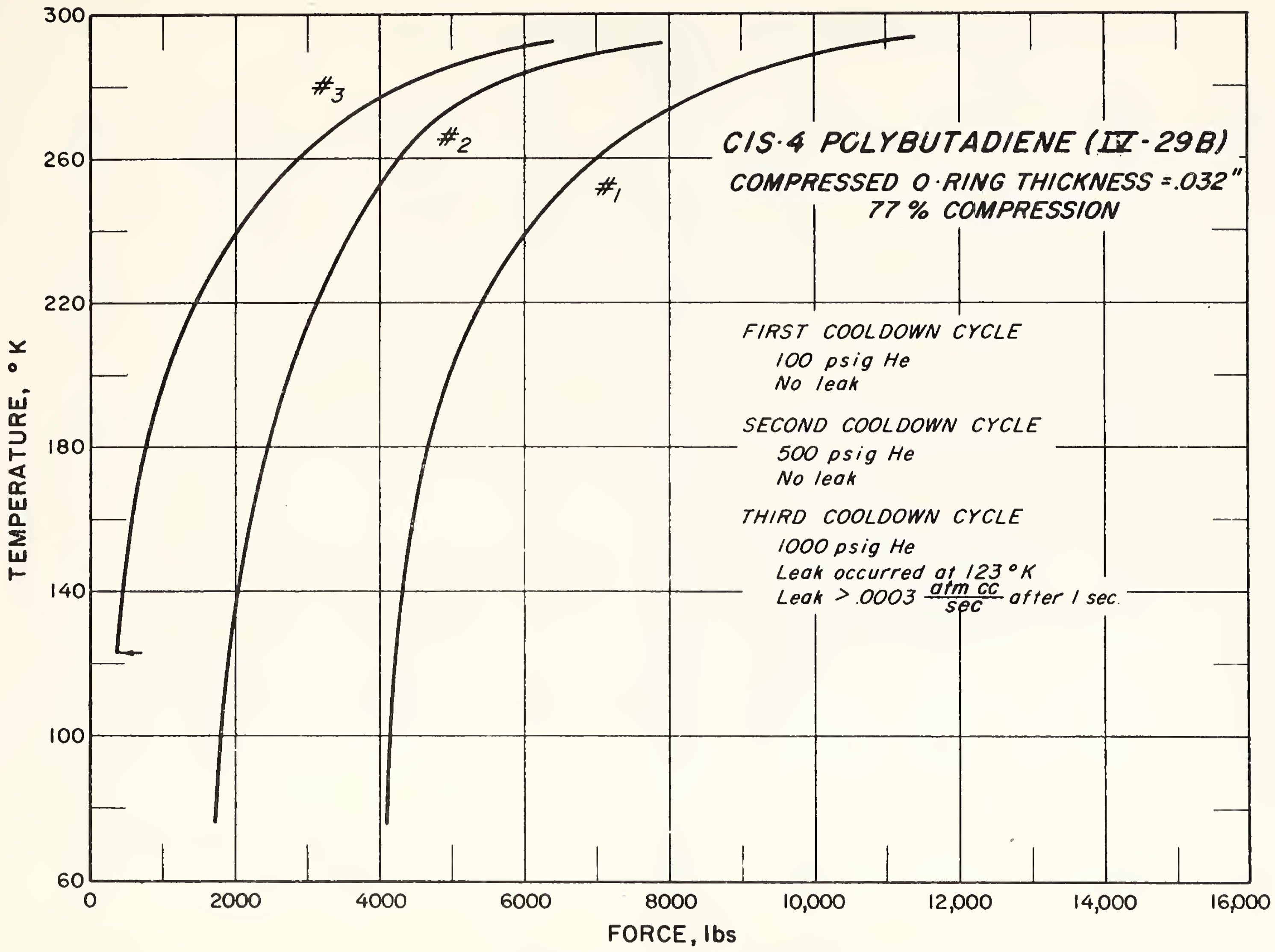

Figure 5. Force-Temperature Curve, Polybutadiene

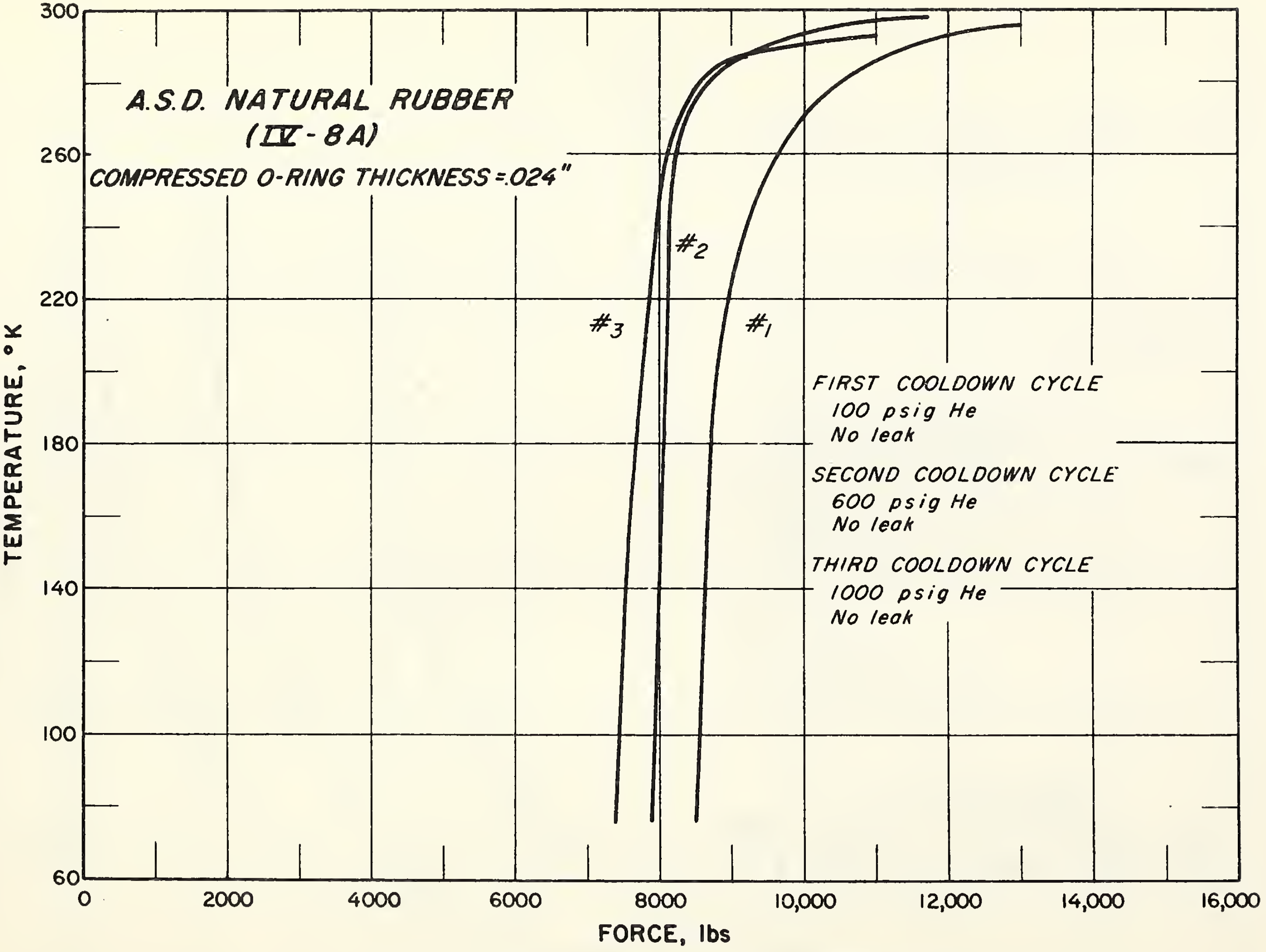

Figure 6. Force-Temperature Curve, Natural Rubber

Appendix. Compounding Recipes of ASD Materials

ASD No.	Polymer	Estimated Monomer Ratio	Recipe		Hardness (Shore A)
Group I					
I-8D	Vinylidene Fluoride & Perfluoropropylene ("Viton" A, Du Pont)	70/30	Polymer	100	80
			Magnesium Oxide	20	
			Hexamethylene Diamine Carbamate	1.3	
			M T Carbon Black	25	
			Cure 20 min at 280 F		
			Post cure 16 hr at 400 F		
I-12A	Vinylidene Fluoride & Perfluoropropylene (Third Monomer Unknown) ("Viton" B, Du Pont)	Terpolymer	Additives ditto 8D		75
			Cure 20 min at 310 F		
			Post cure 16 hr at 400 F		
I-12B	Vinylidene Fluoride & Perfluoropropylene ("Viton" A-HV, Du Pont)	70/30	Same as I-12A		80
I-12C	Vinylidene Fluoride & Perfluoropropylene ("Fluorel", Minnesota Mining & Mfg.)	70/30	Same as I-12A		80
I-12D	Vinylidene Fluoride & Monochlorotrifluoroethylene ("Kel F" 5500, Minnesota Mining & Mfg.)	50/50	Polymer	100	75
			Zinc Oxide	5	
			"Hi Sil"	15	
			Dibasic Lead Phosphite	5	
			Benzoyl Peroxide	3	
			Cure 20 min at 280 F		
			Post cure 16 hr at 300 F		
I-12E	Vinylidene Fluoride & Monochlorotrifluoroethylene ("Kel F" 3700, Minnesota Mining & Mfg.)	70/30	Polymer	100	80
			Zinc Oxide	5	
			E P Carbon Black	10	
			Dibasic Lead Phosphite	5	
			Hexamethylene Diamine Carbamate	1.3	
			Cure 30 min at 310 F		
			Post cure 13 hr at 300 F		

ASD No.	Polymer	Estimated Monomer Ratio	Recipe		Hardness (Shore A)
Group II					
II-21A	Butadiene & Acrylonitrile ("Paracril" 18-80 Naugatuck Chem. Co.)	80/18	Polymer	100	75
			Zinc Oxide	5	
			Altax (MBTS)	1.5	
			Stearic Acid	1.5	
			Sulfur	1.5	
			FEF Black	50	
			Cure 20 min at 310 F		
II-21B	Butadiene & Acrylonitrile ("Hycar" 1002, B. F. Goodrich Chem. Co.)	70/30	Same as II-21A		75
II-21C	Butadiene & Acrylonitrile ("Paracril" D, Naugatuck Chem. Co.)	45/55	Same as II-21A		85
II-21D	Butadiene & Styrene ("Synpol" 1000, Texas-U.S. Chem. Co.)	77/23	Polymer	100	65
			Zinc Oxide	5	
			Altax (MBTS)	1.75	
			Stearic Acid	1.5	
			Sulfur	2	
			EPC Black	40	
			Cure 50 min at 320 F		
II-21E	Butadiene & Styrene ("Synpol" 1013, Texas-U.S. Chem. Co.)	57/43	Same as II-21D		70
II-29D	Butadiene & Styrene ("Paracril" 18/80, Naugatuck Chem. Co.)	80/18	Polymer	100	40
			Zinc Oxide	5	
			Stearic Acid	1.75	
			Sulfur	1.5	
			Altax	1.5	
			Cure 30 min at 310 F		
II-29E	Butadiene & Styrene ("Synpol" 1000, Texas-U.S. Chem. Co.)	77/23	Same as II-29E		40

ASD No.	Polymer	Estimated Monomer Ratio	Recipe		Hardness (Shore A)
Group III					
III-18C	Isobutylene & Isoprene (Butyl 035)	99/1	Polymer	100	70
			Zinc Oxide	5	
			Stearic Acid	1	
			Altax (MBTS)	0.5	
			TMTDS	1	
			Sulfur	2	
			HAF Black	50	
			Cure 30 min at 310 F		
Group IV					
IV-8A	Natural Rubber (Smoked Sheet)		Polymer	100	65
			Stearic Acid	3	
			Zinc Oxide	5	
			N-Cyclohexyl-2-Benzothiazole Sulfenamide	6	
			Sulfur	2.75	
			High Abrasive Furnace Black	50	
			Polymerized trimethyldihydroquinoline (Resin D)	1	
			Cure 15 min at 310 F		
IV-8B	Chloroprene ("Neoprene," Du Pont)		Polymer	100	85
			Stearic Acid	5	
			Zinc Oxide	5	
			Magnesium Oxide	4	
			High Modulus Furnace Black	50	
			Na 22	.5	
			Cure 20 min at 310 F		
IV-29A	Polyisoprene (Coral)		Polymer	100	
			Zinc Oxide	5	
			Stearic Acid	3	
			Sulfur	2.5	
			Santocure	0.5	
			HAF Black	60	
			Cure 20 min at 310 F		

ASD No.	Polymer	Estimated Monomer Ratio	Recipe		Hardness (Shore A)
IV-29B	Cis 4 Polybutadiene		Polymer	100	70
			Zinc Oxide	5	
			Stearic Acid	.5	
			Sulfur	2.5	
			High Abrasive Furnace Black	50	
			Cure 30 min at 310 F		
IV-29C	Ethylene and Propylene (EPR-40)		Polymer	100	60
			Stearic Acid	1	
			Sulfur	.8	
			High Abrasive Furnace Black	50	
			Dicumyl Peroxide	4	
			Cure 20 min at 310 F		

Linear Thermal Expansion of Elastomers in the Range 300°K to 76°K

by

R. F. Robbins, Y. Ohori and D. H. Weitzel
Cryogenic Engineering Laboratory
National Bureau of Standards
Boulder, Colorado

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Linear Thermal Expansion of Elastomers in the Range 300°K to 76°K*

By

R. F. Robbins, Y. Ohori and D. H. Weitzel

1. Introduction

In the search for reliable, simple low temperature static seals, O-rings made from elastomers have received little acclaim, since rubber-like materials become glassy at temperatures above 140°K, and no longer exhibit the properties ordinarily associated with O-ring seals. However, it has been demonstrated that with proper design the rubbery properties of the materials are necessary only during assembly of the seal [1]. During cooldown the sealing force is maintained at a safe level if the initial force is large enough.

If a material is to be chosen from the ever increasing list of elastomers commercially obtainable, thermal expansion information at cryogenic temperatures must be available. This paper will present continuous linear thermal expansion data for representative compounds of most elastomers, over the temperature range 76°K to 300°K. The dilatometer developed for this series of tests will be described. The results will be analyzed with regard to comparisons between similar compounds, and similar groups of compounds. The characteristic temperature at which the glassy state transition occurs will be discussed.

2. Thermal Expansion Mechanisms

It is widely accepted that there are two distinct mechanisms responsible for the contraction of an elastomer while the temperature is being reduced, and that the effect of one of these mechanisms becomes negligible as the material cools to its glassy state transition temperature (T_g). Present throughout the temperature range is the effect of changes in amplitude of atomic vibrations.

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This contribution to thermal contraction is the usual one which is responsible for dimensional changes in all types of solids. Much has been written concerning the second cause for contraction of elastomers [2, 3, 4, 5, for example]; two of the most popular interpretations will be introduced at this time.

First, consider the "diffusion of holes" theory advanced by Alfrey, et al, [3] and others. The elasticity of rubber-like materials is made possible by the random orientation of long molecular chains which are tangled with one another, and joined occasionally by chemical bonds. Such an imperfect packing requires that there be certain gaps or "holes" in the structure [6]. When these materials cool, the structure becomes more packed and tends toward a more ordered state, causing the equilibrium volume of the holes, and hence the free volume, to decrease. However, this volume contraction cannot take place instantaneously since the molecules must move to a new position. The molecular re-orientation cannot affect the "true" volume of the sample; it can only redistribute the holes, which will combine or divide in a random fashion. A consequence of this diffusion of holes is that if the material is to contract, some of the holes must diffuse to the surface of the sample and disappear [4].

At temperatures above the T_g range the time necessary to attain an equilibrium free volume is much less than normal experimental times. Near T_g the equilibrium time required approaches the experimental time, and below T_g the holes are essentially "frozen in" and the material is unable to reach its equilibrium structure within a reasonable length of time. Hence the sharp change of slope of thermal expansion curves around T_g. Some contraction still takes place below T_g due to the change in the amplitude of atomic vibrations with temperature. This vibrational effect, previously mentioned, is predominant only below T_g for elastomeric materials.

Next, consider the concept of free rotation about carbon-carbon bonds, to be compared with the considerations of hole diffusion. T_g was inferentially defined above as the temperature where the time required to attain the equilibrium free volume was equal to the time of the experimental observation. T_g can also be defined as the temperature where the rotations about C-C bonds ceases [3, 7]. The viscous flow mechanism for polymer transitions advanced by Boyer and Spencer [4] is in accord with the concept of free rotation, and will be discussed briefly.

The behavior of an elastomer around T_g can be visualized more clearly if all the molecules in the test sample are assumed to be oriented either parallel or perpendicular to the direction of length measurement. Considering those chains that are perpendicular, contraction with cooling can be caused by decreased vibration of the molecules. This contraction is not affected by T_g, since the vibrations continue to decrease as the temperature is reduced. Contraction in the chains parallel to the measurement, however, cannot be explained in the same manner, because the primary bond distance along the chains is fixed [7]. The mechanism of Boyer and Spencer suggests that contraction in the parallel direction is caused by gross movement of the chains, which slide past one another and orient in a position which results in a net contraction of the sample. This viscous flow does not appear below T_g.

In samples randomly oriented, such as the polymers tested in this program, the length changes parallel and perpendicular to the chains would be superimposed on one another, and entanglements would inhibit the movements. However, since length-wise movement is zero below T_g, this theory predicts a change in slope of the expansion curve at T_g in agreement with known results. This theory also predicts differences in the expansivities of oriented samples measured in different directions, a result which has been verified experimentally [4]. Another obvious prediction is that if a rubber-like material at room temperature could be oriented so that the chains were mostly parallel to the direction of compressive force, contraction below T_g could be reduced to near zero in an O-ring seal application.

3. Apparatus and Procedure

The relatively large changes in length with temperature associated with most high polymers allows use of a simple dilatometer for linear thermal expansion measurements. The apparatus shown in Figure 1 yields data reproducible within 4%, with the exception of errors near room temperature. A check of the accuracy of the length measurements was made by measuring the contraction of an aluminum sample of known thermal expansion; the results agreed to within 2% over the entire temperature range. Thus, the errors inherent in the apparatus are 2% or less, and errors due to the nature of the polymer samples are also around 2%.

A 2-inch long by 1/2-inch diameter sample is surrounded by a heavy-wall copper tube or shield which helps maintain uniform sample temperature. The sample and tube are supported by three invar rods connected to a brass top plate. On top of the sample rests an invar rod with brass ends, which applies a constant force of 98 grams to the sample. The top plate and sample support assembly can be easily lifted out of the cooling system in order to change samples. Analysis of the possible error due to the effect of the 98 gram applied force indicated that the effect is negligible.

Around the sample support assembly is a second copper shield which has soldered around it a coil of copper tubing which carries a small flow of nitrogen gas. This gas is discharged inside the shield near the bottom, and serves as the heat transfer medium which cools the sample. The shield is supported and surrounded by expanded polystyrene which serves as insulation to slow down the cooling rate.

The polystyrene is enclosed by a flanged metal can which is immersed in a bath of liquid nitrogen. Thus, the major part of the cooldown is by slow conduction through the N_2 gas and expanded polystyrene surrounding the sample. The final part of the cooldown is achieved by introducing liquid nitrogen directly into the space around the sample. Average cooldown rate is about 40 Kelvin degrees per hour.

Both length and temperature are measured electrically, and continuously recorded by a 6-point millivolt recorder. One thermocouple (introduced with the aid of a sewing needle) is located inside the sample and a second thermocouple is taped to the sample surface. When these temperatures are not exactly

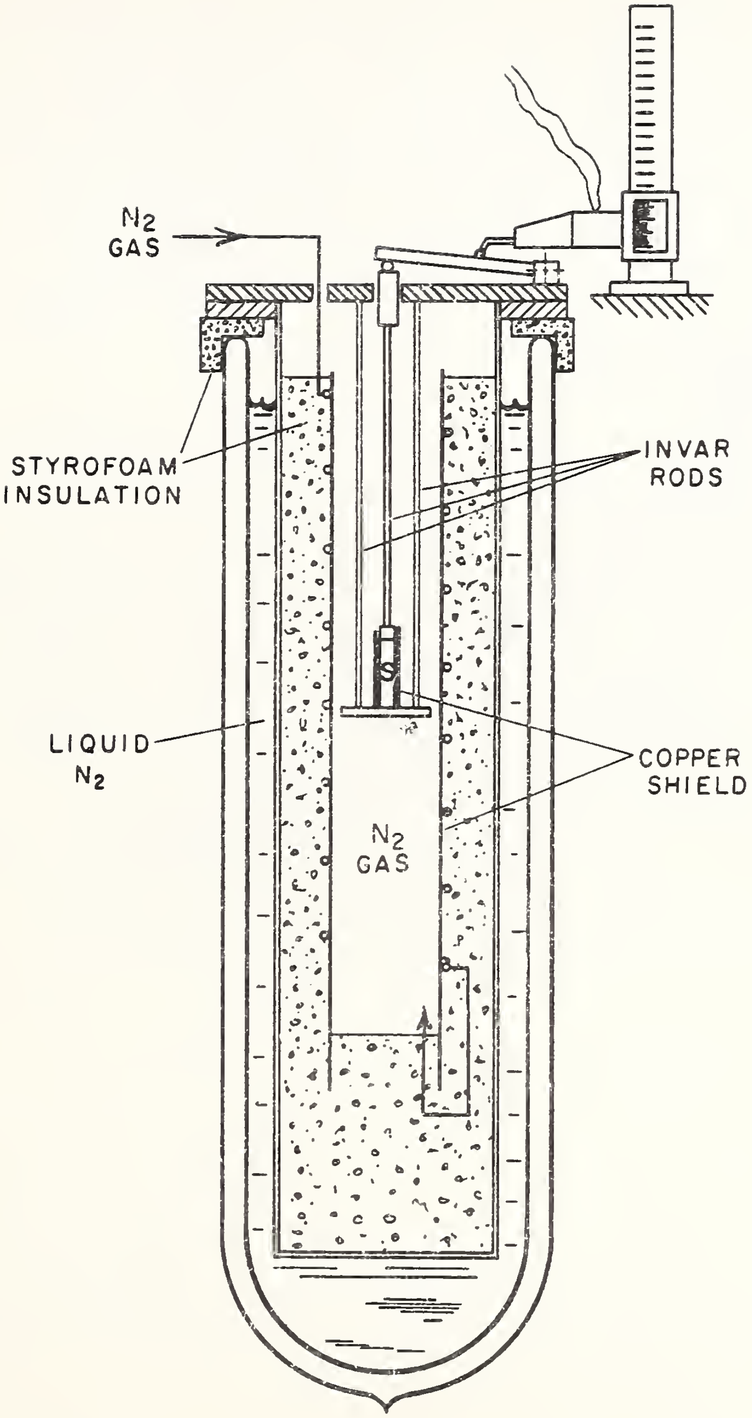

Figure 1. Cryogenic Dilatometer

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the same, an average of the two is used. Length measurement is achieved by means of a sensitive differential transformer which is activated by a hinged finger. The free end of the finger rests on a lever which moves up and down as the length of the sample changes with temperature. Sensitivity can be adjusted by moving the transformer to different positions along the length of the lever. Calibration is performed after each test by slipping the leaves of a thickness gauge between the lever and the top of the rod which rests on the sample.

4. Experimental Results

Figures 2, 3, 4, 5, and 6 show results which have thus far been obtained in our program. Each curve has been repeated at least once; in cases where the tests on a given material were not in good agreement, more runs were required to insure the reporting of reliable data. Useful numbers derived from the curves are presented in Table 1. The coefficients of expansion, α_r and α_g, were calculated by taking the slopes of the straight portions of the $\Delta L/L$ vs. temperature curves above and below T_g, respectively. The temperature at the intersection of these lines was selected for "T_g experimental" in Table 1.

Examination of the results will be attempted as follows. The samples within each group will be compared, then if there are sub-groups, the subgroups within the group will be discussed. Finally, groups will be compared with each other.

4.1 Group I - The Fluorocarbons

Members of the fluorocarbon group have in recent years demonstrated superiority to other groups in high temperature stability and resistance to chemical reaction with many fluids now in use in fuel-oxidizer combustion systems. The continuous thermal expansions of representative samples of several "Vitons"(A), three "Kel-F"(B) compounds and "Fluorel"(B) are shown in Figure

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A Trademark, E. I. duPont de Nemours and Co., Inc.

B Trademarks, Minnesota Mining and Mfg. Co.

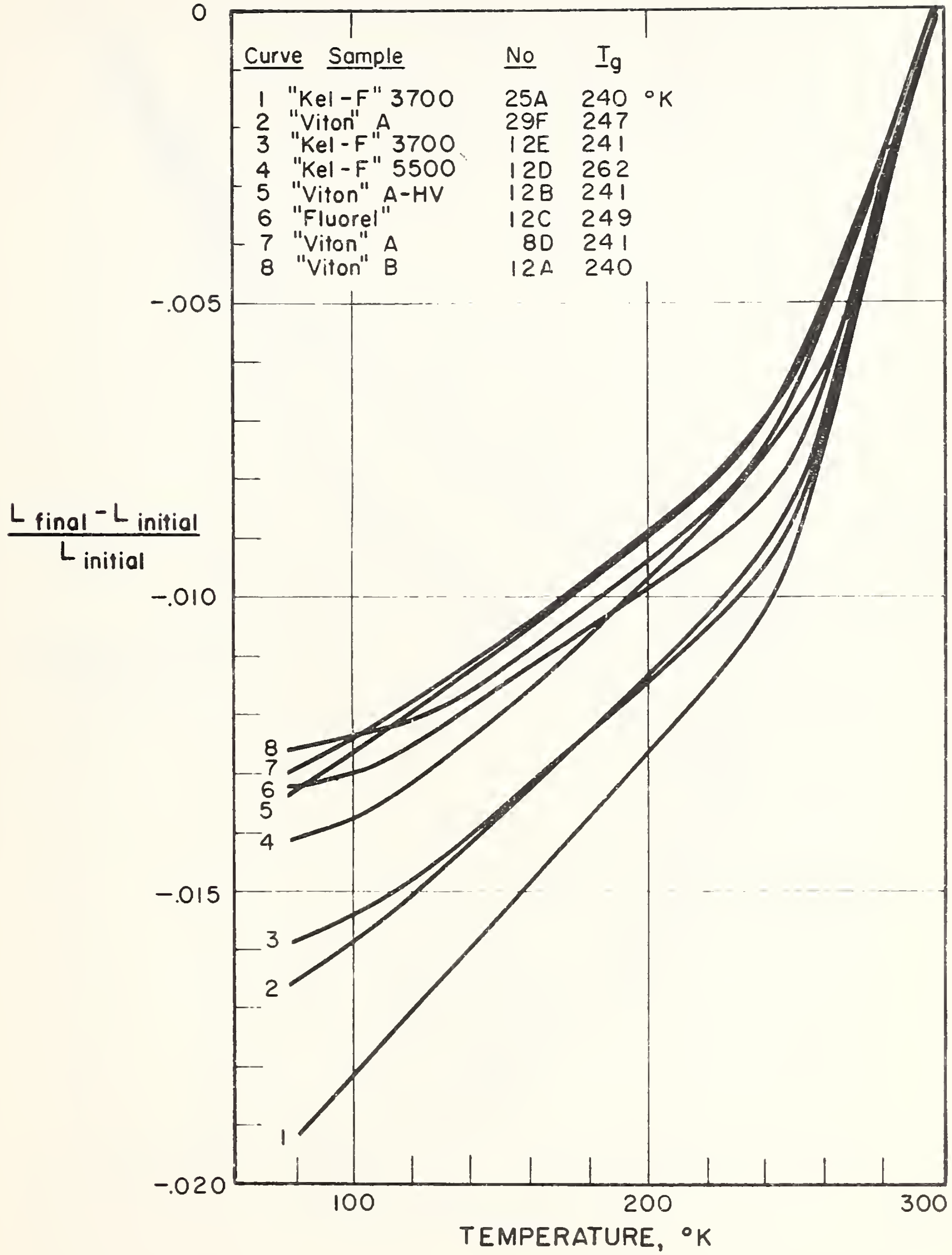


Figure 2. Thermal Expansion and T_G, Group I

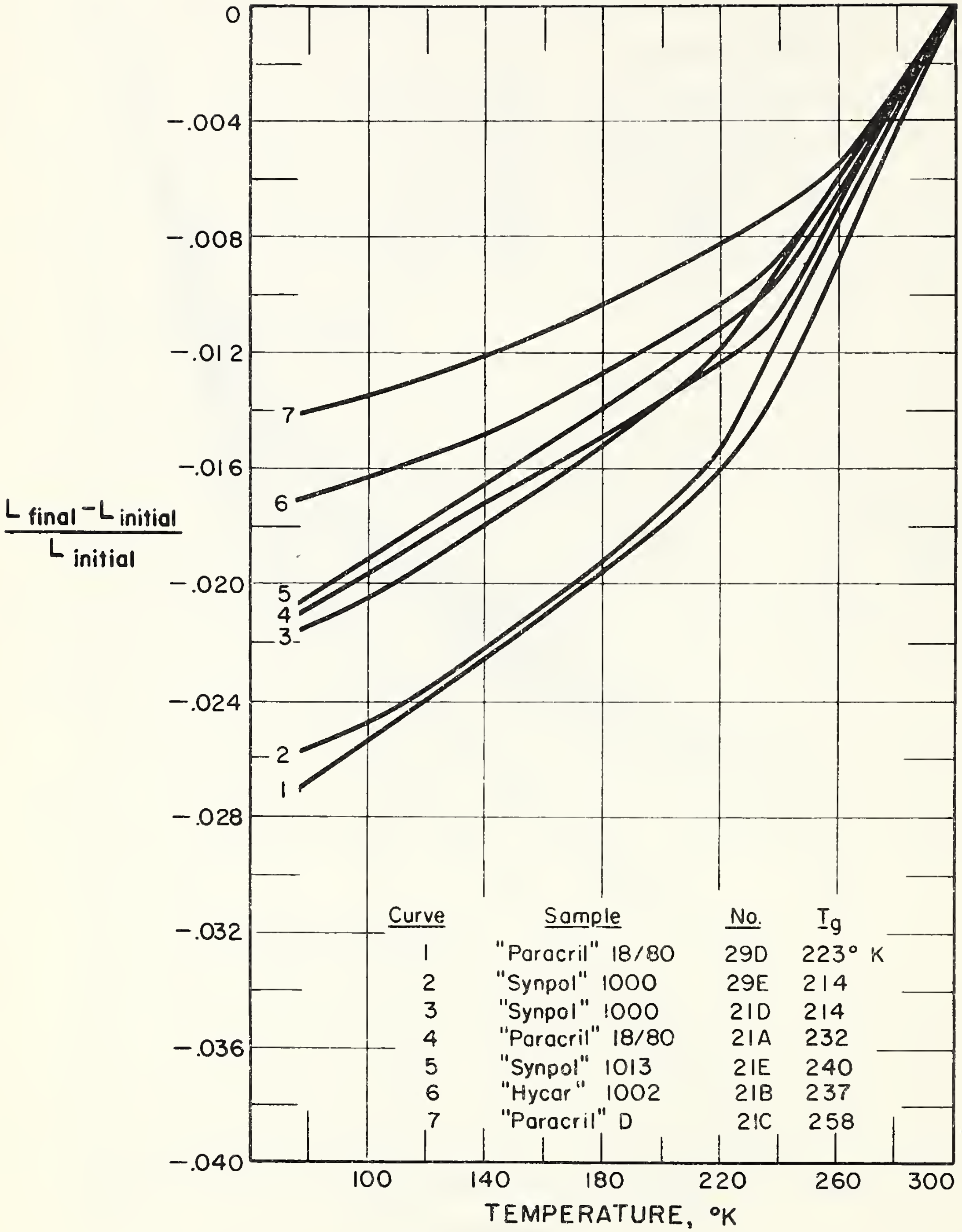
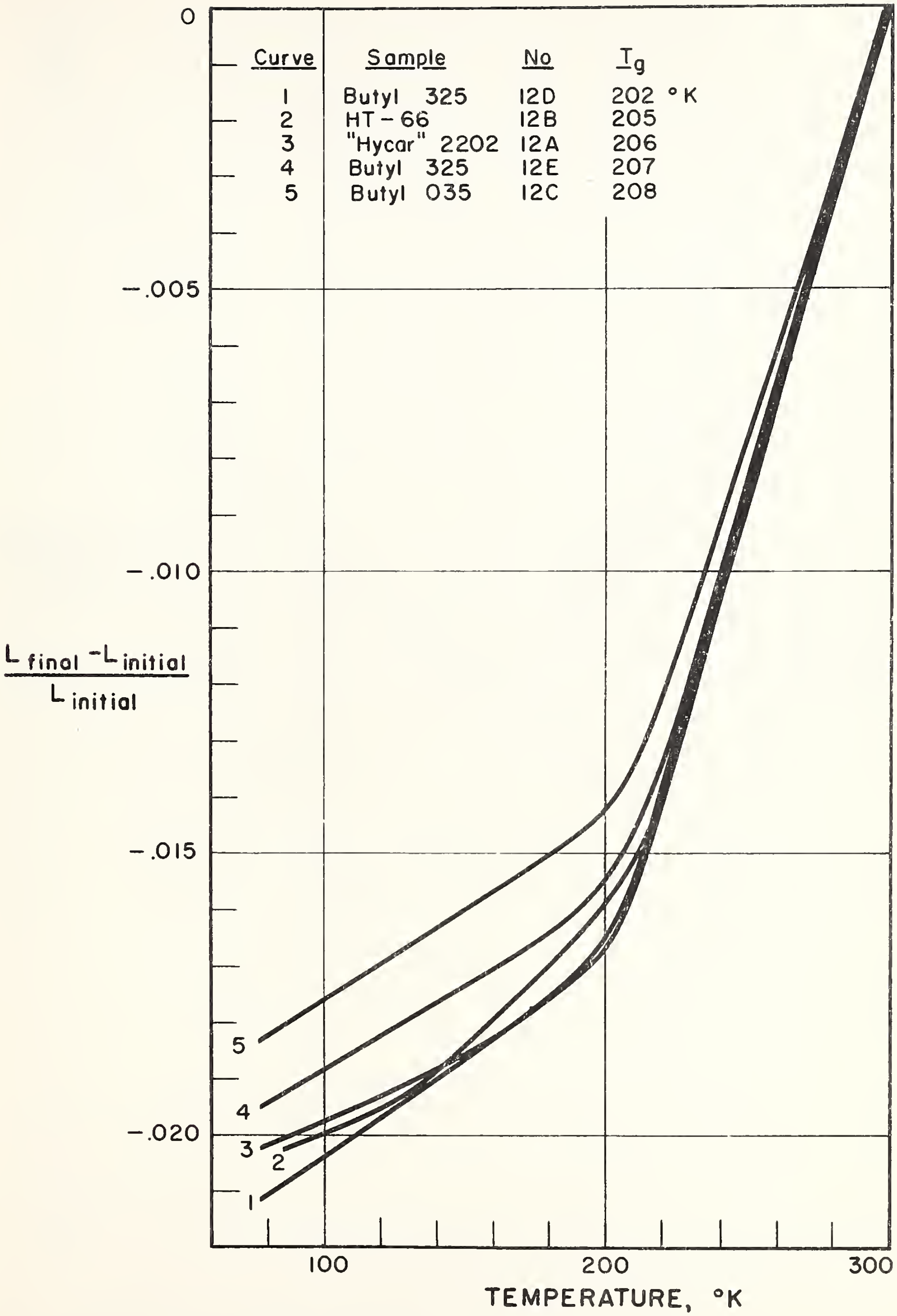


Figure 3. Thermal Expansion and T_G, Group II



Curve	Sample	No	T_g
1	Butyl 325	12D	202 °K
2	HT-66	12B	205
3	"Hycar" 2202	12A	206
4	Butyl 325	12E	207
5	Butyl 035	12C	208

Figure 4. Thermal Expansion and T_G, Group III

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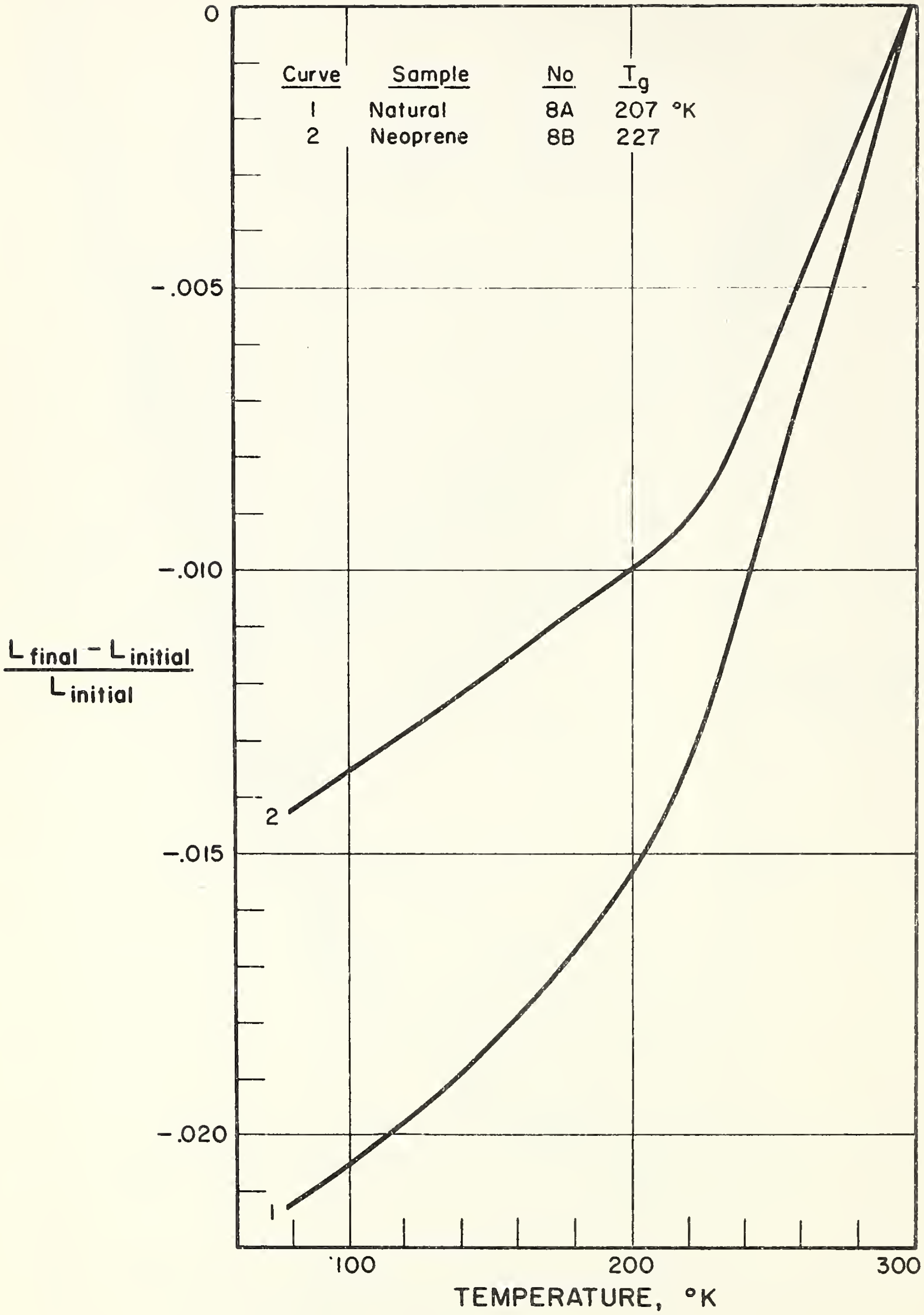

Figure 5. Thermal Expansion and T_G, Group IV

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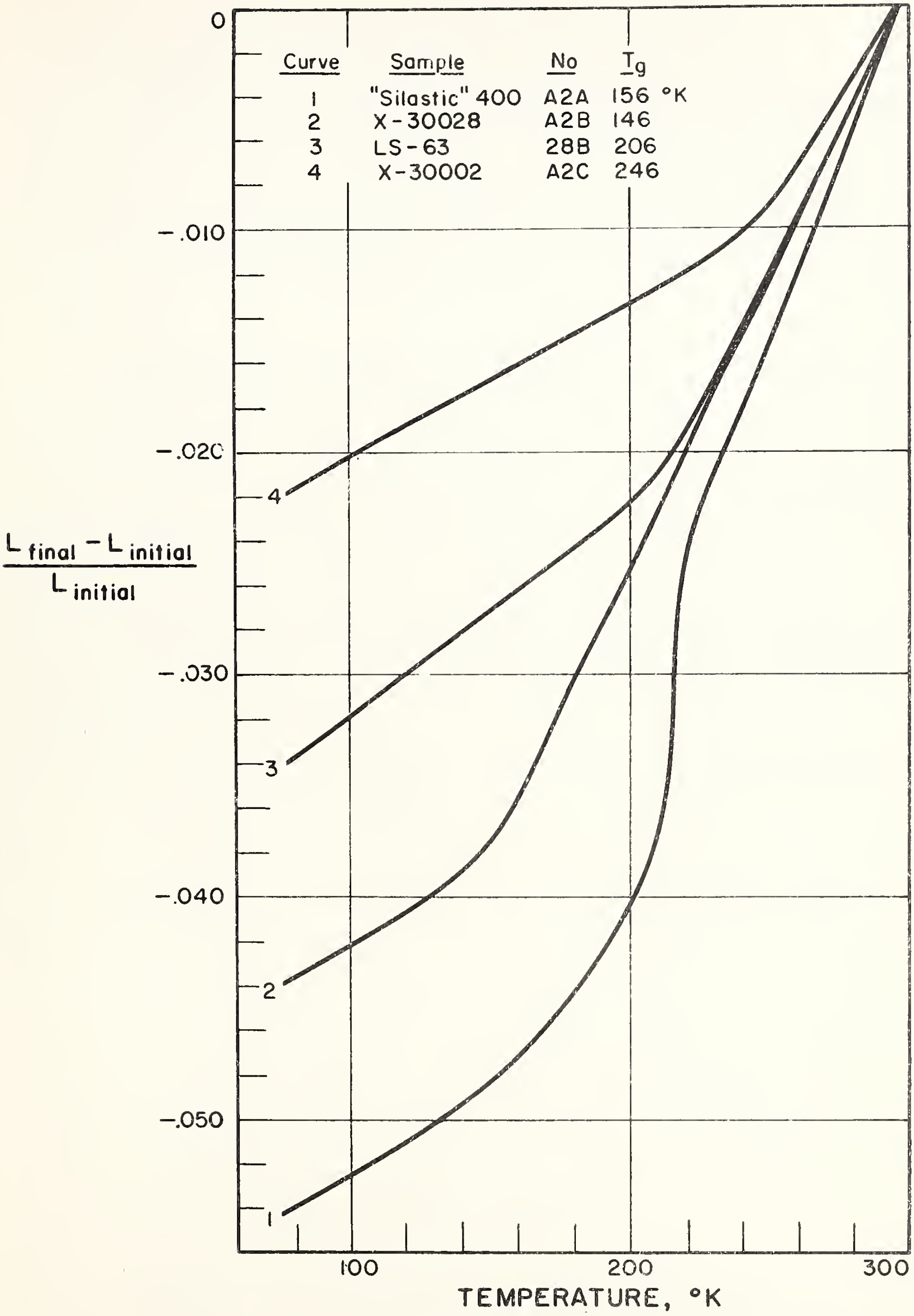

Figure 6. Thermal Expansion and T_G, Group V

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Sample number	Compound name	T_g Eq. (5) ^oK	T_g Eq. (4) ^oK	T_g Experimental ^oK	α_r $10^4/^oK$	α_g $10^4/^oK$	α_2 $10^4/^oK$	$\Delta L/L$ from 297^oK to 76^oK in x 10^2
I- 8D	"Viton" A	242	247	241	1.3	0.36	3.3	1.29
I-29F	"Viton" A	242	247	247	1.8	0.48	4.0	1.65
I-12B	"Viton" A-HV	242	247	241	1.3	0.36	2.7	1.35
I-12A	"Viton" B	---	---	240	1.4	0.36	3.0	1.26
I-12D	"Kel-F" 5500	264	270	262	1.9	0.45	4.5	1.41
I-12E	"Kel-F" 3700	250	254	248	1.9	0.45	4.5	1.58
I-25A	"Kel-F" 3700	250	254	240	1.9	0.55	3.9	1.94
I-12C	"Fluorel"	242	247	249	1.8	0.33	4.5	1.32
II-21D	"Synpol" 1000	213	212	214	1.5	0.68	2.4	2.15
II-29E	"Synpol" 1000	213	212	214	2.0	0.76	3.6	2.59
II-21E	"Synpol" 1013	240	239	240	1.6	0.69	2.7	2.05
II-21A	"Paracril" 18/80	---	---	232	1.8	0.58	3.6	2.09
II-29D	"Paracril" 18/80	---	---	223	2.2	0.72	4.5	2.70
II-21B	"Hycar" 1002	---	---	237	1.5	0.56	2.7	1.71
II-21C	"Paracril" D	---	---	258	1.5	0.56	2.7	1.41
III-12C	Butyl 035	203	203	208	1.6	0.54	3.2	1.84
III-12E	Butyl 325	203	203	207	1.8	0.29	4.5	1.94
III-12D	Butyl 325	203	203	202	1.7	0.36	3.9	2.11
III-12A	"Hycar" 2202	---	---	206	1.9	0.28	4.8	2.02
III-12B	HT - 66	203	203	205	1.7	0.38	3.9	2.02
IV- 8A	Natural	---	---	207	1.7	0.49	3.6	2.14
IV- 8B	Neoprene	---	---	227	1.3	0.35	3.0	1.44
V-A2A	"Silastic" 400	---	---	156	3.3	0.82	2.7	5.43
V-A2C	X-30002	---	---	246	2.0	0.70	4.2	2.21
V-28A	LS - 63	---	---	208	2.47	0.95	4.5	3.40
V-A2B	X-30028	---	---	146	2.59	0.74	2.7	4.40

Table I

Summary of Thermal Expansion and T_g Results

2. Compounding recipes for all samples are given in Appendix 1.

Members of the Viton family tested have identical compounding recipes, and the main difference in the base polymers is polymerization time, resulting in differences in molecular weight. There is no correlation between molecular weight and T_g, which brings the first general conclusion found true throughout: in the range of molecular weights normally necessary for the synthesis of an elastomer, there is no clear-cut dependence of T_g or expansivity on molecular weight.

"Kel-F" 5500 and "Kel-F" 3700 are both copolymers, differing mainly in the monomer ratios. Gum 3700 contains 70 weight % vinylidene fluoride and 30% monochlorotrifluoroethylene, and 5500 contains equal parts of the same monomers. The much higher T_g of 5500 can be partially explained by its higher ratio of monochlorotrifluoroethylene, a highly polar compound which tends to hinder movement of the chains past one another.

When "Kel-F" 3700 is filled with silica instead of carbon black, T_g is lowered by 8°K and the overall contraction from 300°K to 76°K is increased by 20%. Therefore, if a lower T_g is desired, a silica filler could be substituted for carbon black with success. The higher contraction tends to discount this advantage in cryogenic seal applications.

4.2 Group II - Butadiene Copolymers

Elastomers made by copolymerization of butadiene with both styrene and acrylonitrile were tested, and the results are graphically shown in Figure 3. The "Synpol"(A) elastomers have 77/23 and 57/43 monomer ratios of butadiene and styrene, this being the only difference between "Synpol" 1000 and "Synpol" 1013. One sees that T_g is higher and overall contractions smaller for 1013, which contains more styrene with its bulky phenyl group. The test using an unfilled sample of "Synpol" 1000 (II-29E) resulted in 17% more contraction than the filled compound, although T_g was not affected.

(A) Trademark, Texas - U. S. Chemical Co.

The butadiene-acrylonitrile copolymers tested were "Hycar"(B) 1002, "Paracril"(C) 18/80, and "Paracril" D. The weight fractions of acrylonitrile for these three are 30%, 18%, and 55%, respectively, the balance being butadiene in each case. Since acrylonitrile is highly polar, T_g increases with increasing percent acrylonitrile. It should be noted that T_g for the unfilled 18/80 compound was lower by 9°K than the filled compound.

4.3 Group III - Isobutylene-Isoprenes

Figure 4 shows the results obtained using several different isobutylene isoprene copolymers with only small percentages of isoprene present. Conclusions to be drawn here are as follows: slight monomer ratio changes, the use of resin cure, bromination, and chlorination do not alter T_g appreciably. However, contraction is increased by 14% if the isoprene content is increased from 1 to 2.5%.

4.4 Group IV - Natural Rubber and Neoprene

In Figure 5 we present curves for natural rubber and neoprene. Assuming the structural positions of the corresponding atoms and groups are the same for these two common elastomers, we see that the only difference is that in neoprene the methyl group has been replaced by a chlorine atom. As a result, neoprene has strong polar points which change conditions such that T_g is 227°K, as compared with 207°K for natural rubber. This change in T_g in part accounts for the large difference between the overall contractions of the two materials; however, the larger coefficient of expansion for natural rubber is hard to explain. We see from the compounding recipes that identical amounts of filler were present in both samples.

B Trademark, B. F. Goodrich Chemical Co.

C Trademark, Nanyatuck Chemical Co.

4.5 Group V - Silicone Rubbers

The results for some experimental silicones are shown in Figure 6. Silastic 400, which is a straight dimethyl silicone rubber, crystallizes at about 215°K, accompanied by an almost discontinuous change in length. It then contracts along a different slope than previous to crystallization and finally goes through T_g at about 156°K. Because of this crystallization the overall $\Delta L/L$ from room temperature (297°K) to 76°K is very large -0.0543.

Crystallization does not take place in the modified versions. When the dimethyl silicone rubber is modified with 30 mole % vinyl, the overall $\Delta L/L$ is decreased by an amount similar to the contraction due to crystallization in the straight dimethyl rubber. Moreover, the T_g is decreased from 156°K to 146°K. The $\Delta L/L$ is lowered to .034 by fluorinating (LS-63); however T_g increases to 208°K. Finally, $\Delta L/L$ is reduced to .022 when modified with 50 mole % phenyl, as T_g goes up to 246°K.

The vinyl modified silicone rubber has the lowest T_g found to date (146°K); however, $\Delta L/L$ is .044, which is rather large. Additional vinyl modification might result in enhanced overall properties. On the other hand, less phenyl modification in X-3 0002 may lower T_g without too drastic an increase in $\Delta L/L$.

The above results with the silicones demonstrate the effect of a variation of T_g on the contraction to 76°K. In cryogenics one is interested in elastomers with low T_g, in addition to low contraction. Perhaps the silicones are the most promising group for future investigations.

4.6 Effect of Fillers on $\Delta L/L$

Addition of carbon black filler of some 20% volume resulted in a reduction of $\Delta L/L$ by roughly 20% for the three compounds with gum samples available. When carbon black filler was used instead of silica, the $\Delta L/L$ of "Kel F" 3700 was lowered by 20%.

The first result suggests an approach in estimating the overall $\Delta L/L$ of an elastomer when the $\Delta L/L$ of the unfilled sample and the percent by volume of the gum in the filled elastomer is known. The product of the $\Delta L/L$ unfilled and percent gum should give a close estimate. Applying this to our three groups of samples for which we had filled and unfilled samples, the largest deviation was 3%.

5. Correlation of the Results With Existing Theory

The phenomena associated with the "freezing" of elastomeric polymers during cooldown has been discussed by countless authors; some popular opinions on these matters were presented in section 2. As a result of the interpretation of the glassy transition many empirical relations have been postulated. To conclude this paper, some relations which lend themselves to experimental verification will be discussed.

5.1 A Relation Between Linear Expansion Coefficients α_g and α_r

In section 2 it was suggested that viscous flow plays an important part in thermal expansion, and that below T_g the free volume of a sample is constant. It has also been postulated that T_g for various polymers is a state of constant fractional free volume. The dependence of free volume on temperature is taken to be the difference between the volume expansion coefficients a_r and a_g, where the subscripts refer to the "rubbery" and "glassy" states. Then

$$f = f_g + (a_r - a_g)\ (T - T_g) = f_g + a_2\ (T - T_g),\quad \text{for } T \geq T_g \tag{1}$$

where

f is the fractional free volume at T

f_g is the fractional free volume at T_g

$$a_2 = a_r - a_g \tag{2}$$

Other workers [9, 10] have combined equation (1) with both theoretical and experimental viscosity considerations, and have found that a_2 and f_g are about constant for many elastomers. The values they derived [10] were

f_g = 0.025 (dimensionless)

$a_2 = 4.8 \times 10^{-4}\ \text{deg}^{-1}$

In Table 1 values of a_2 are calculated from the linear coefficients α_r and α_g, by assuming

$$a_2 = 3\,(\alpha_r - \alpha_g) \tag{3}$$

to be in the range of 2.7 to $4.8 \times 10^{-4}\ \text{deg}^{-1}$, in general agreement with the above values by others.

5.2 Two Relations Between Monomer Ratios and T_g

The value of T_g for an amorphous copolymer can be estimated if the values of T_g of both homopolymers are known. One of the more widely used empirical formulas relating these is [12, 13]

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \tag{4}$$

where T_{g_1} and T_{g_2} apply to the homopolymers and W_1 and W_2 are their respective weight fractions. In some cases, the following formula has been found to be more accurate [14]:

$$T_g = x_1 T_{g_1} + x_2 T_{g_2} \tag{5}$$

Here x_1 and x_2 are the mole fractions of the homopolymers.

Table 1 shows the values of T_g calculated by equations 4 and 5, and the experimental T_g obtained by extrapolating straight line portions of the expansions below and above T_g, using the intersection as T_g. Values of T_g for the homopolymers were obtained from published data [15]. The experimental and calculated results are in good agreement, indicating that either equation 4 or 5 can be applied to predict values of T_g for new materials which might have applications at low temperature.

6. Conclusions

From the relations between T_g's of the component homopolymers with that of the resulting copolymer, one sees that the limit of the T_g of copolymers is that of the homopolymers.

To obtain a low T_g one must avoid polymers with polar groups and/or bulky groups. Polar groups afford opportunities for intermolecular links which hinder rotation necessary for "rubberyness". Bulky groups cause stiffness, and also serve as obstructions to contractions. On the other hand, the same reasons that polar and bulky groups raise T_g serve to lower overall thermal contraction, since α_r is always less than α_g.

Fillers can be used to lower contraction, and new ceramic fillers with negative coefficients of expansion might be combined with specific polymers to obtain a material with a desired contraction.

The authors feel that the data presented here, together with design data available from commercial sources, should enable the design engineer to find many new uses for elastomers at cryogenic temperatures.

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Appendix. Compounding Recipes of ASD Materials

ASD No.	Polymer	Estimated Monomer Ratio	Recipe		Hardness (Shore A)
Group I					
I-8D	Vinylidene Fluoride & Perfluoropropylene ("Viton" A, Du Pont)	70/30	Polymer Magnesium Oxide Hexamethylene Diamine Carbamate M T Carbon Black Cure 20 min at 280 F Post cure 16 hr at 400 F	100 20 1.3 25	80
I-12A	Vinylidene Fluoride & Perfluoropropylene (Third Monomer Unknown) ("Viton" B, Du Pont)	Terpolymer	Additives ditto 8D Cure 20 min at 310 F Post cure 16 hr at 400 F		75
I-12B	Vinylidene Fluoride & Perfluoropropylene ("Viton" A-HV, Du Pont)	70/30	Same as I-12A		80
I-12C	Vinylidene Fluoride & Perfluoropropylene ("Fluorel", Minnesota Mining & Mfg.)	70/30	Same as I-12A		80
I-12D	Vinylidene Fluoride & Monochlorotrifluoroethylene ("Kel F" 5500, Minnesota Mining & Mfg.)	50/50	Polymer Zinc Oxide "Hi Sil" Dibasic Lead Phosphite Benzoyl Peroxide Cure 20 min at 280 F Post cure 16 hr at 300 F	100 5 15 5 3	75
I-12E	Vinlyidene Fluoride & Monochlorotrifluoroethylene ("Kel F" 3700, Minnesota Mining & Mfg.)	70/30	Polymer Zinc Oxide E P Carbon Black Dibasic Lead Phosphite Hexamethylene Diamine Carbamate Cure 30 min at 310 F Post cure 13 hr at 300 F	100 5 10 5 1.3	80

ASD No.	Polymer	Estimated Monomer Ratio	Recipe		Hardness (Shore A)
Group II					
II-21A	Butadiene & Acrylonitrile ("Paracril"18-80, Naugatuck Chem. Co.)	80/18	Polymer	100	75
			Zinc Oxide	5	
			Altax (MBTS)	1.5	
			Stearic Acid	1.5	
			Sulfur	1.5	
			FEF Black	50	
			Cure 20 min at 310 F		
II-21B	Butadiene & Acrylonitrile ("Hycar"1002, B. F. Goodrich Chem. Co.)	70/30	Same as II-21A		75
II-21C	Butadiene & Acrylonitrile ("Paracril"D, Naugatuck Chem. Co.)	45/55	Same as II-21A		85
II-21D	Butadiene & Styrene ("Synpol"1000, Texas-U. S. Chem. Co.)	77/23	Polymer	100	65
			Zinc Oxide	5	
			Altax (MBTS)	1.75	
			Stearic Acid	1.5	
			Sulfur	2	
			EPC Black	40	
			Cure 50 min at 320 F		
II-21E	Butadiene & Styrene ("Synpol"1013, Texas-U. S. Chem. Co.)	57/43	Same as II-21D		70
II-29D	Butadiene & Styrene ("Paracril"18/80, Naugatuck Chem. Co.)	80/18	Polymer	100	40
			Zinc Oxide	5	
			Stearic Acid	1.75	
			Sulfur	1.5	
			Altax	1.5	
			Cure 30 min at 310 F		
II-29E	Butadiene & Styrene ("Synpol"1000, Texas-U. S. Chem. Co.)	77/23	Same as II-29D		40

ASD No.	Polymer	Estimated Monomer Ratio	Recipe		Hardness (Shore A)
Group III					
III-18C	Isobutylene & Isoprene (Butyl 035)	99/1	Polymer	100	70
			Zinc Oxide	5	
			Stearic Oxide	1	
			Altax (MBTS)	0.5	
			TMTDS	1	
			Sulfur	2	
			HAF Black	50	
			Cure 30 min at 310 F		
III-12D	Isobutylene & Isoprene (Butyl 325)	97.5/2.5	Polymer	100	75
			Zinc Oxide	5	
			Stearic Acid	1	
			Benzothiazyl Disulfide	.5	
			Tetra Methyl Thiuram Disulfide	1	
			Sulfur	2	
			High Abrasive Furnace Black	50	
			Cure 30 min at 310 F		
III-12E	ditto (Resin Cure)	97.5/2.5	Polymer	100	75
			Zinc Oxide	5	
			Stearic Acid	1	
			High Abrasive Furnace Black	50	
			Chlorinated Phenolic Resin	12	
			Cure 30 min at 310 F		
III-12A	Isobutylene & Isoprene (Brominated) ("Hycar" 2202, B. F. Goodrich Chem. Co.)	---	Polymer	100	80
			Zinc Oxide	5	
			Stearic Acid	3	
			Benzothiazyl Disulfide	.4	
			Tetra Methyl Thiuram Disulfide	.8	
			Sulfur	2	
			Easy Process Channel Black	50	
			Cure 30 min at 310 F		

ASD No.	Polymer	Estimated Monomer Ratio	Recipe		Hardness (Shore A)
III-12B	Isobutylene & Isoprene (Chlorinated, 1%) (HT-66, Enjay Chem. Co.)	97/2/1	Polymer	100	70
			Zinc Oxide	5	
			Stearic Acid	1	
			Benzothiazyl Disulfide	.5	
			Tetra Methyl Thiuram Disulfide	1	
			Sulfur	2	
			High Abrasive Furnace Black	50	
			Cure 30 min at 310 F		
<u>Group IV</u>					
IV-8A	Natural Rubber (Smoked Sheet)		Polymer	100	65
			Stearic Acid	3	
			Zinc Oxide	5	
			N-Cyclohexyl-2-Benzothiazole Sulfenamide	.6	
			Sulfur	2.75	
			High Abrasive Furnace Black	50	
			Polymerized trimethyldihydroquinoline (Resin D)	1	
			Cure 15 min at 310 F		
IV-8B	Chloroprene ("Neoprene", Du Pont)		Polymer	100	85
			Stearic Acid	5	
			Zinc Oxide	5	
			Magnesium Oxide	4	
			High Modulus Furnace Black	50	
			Na 22	.5	
			Cure 20 min at 310 F		
IV-29A	Polyisoprene (Coral)		Polymer	100	
			Zinc Oxide	5	
			Stearic Acid	3	
			Sulfur	2.5	
			Santocure	0.5	
			HAF Black	60	
			Cure 20 min at 310 F		

ASD No.	Polymer	Estimated Monomer Ratio	Recipe		Hardness (Shore A)
IV-29B	Cis 4 Polybutadiene		Polymer	100	70
			Zinc Oxide	5	
			Stearic Acid	.5	
			Sulfur	2.5	
			High Abrasive Furnace Black	50	
			Cure 30 min at 310 F		
IV-29C	Ethylene and Propylene (EPR-40)		Polymer	100	60
			Stearic Acid	1	
			Sulfur	.8	
			High Abrasive Furnace Black	50	
			Dicumyl Peroxide	4	
			Cure 20 min at 310 F		
<u>Group V</u>					
V-A2B	Methyl Silicone Modified with 30 mole % Vinyl ("Silastic" X30028, Dow Corning Corp.)		Polymer	100	
			Hi Sil X303	30	
			Benzoyl Peroxide	3	
			Cure 10 min at 260 F		
V-A2A	Methyl Silicone Modified with 50 mole % Vinyl ("Silastic" X30002, Dow Corning Corp.)		Polymer	100	
			Hi Sil X303	30	
			Benzoyl Peroxide	3	
			Cure 10 min at 260 F		
V-A2C	Straight Methyl Silicone ("Silastic" 400, Dow Corning Corp.)		Polymer	100	
			Hi Sil X303	30	
			Benzoyl Peroxide	3	
			Cure 10 min at 260 F		
V-28A	Fluorinated Silicone		Polymer	100	
			(No Additives)		
			Cure 20 min at 240 F		
			Post Cure 24 min at 300 F		

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