ML-TDR-64-50
Part II

ELASTOMERIC SEALS AND MATERIALS AT CRYOGENIC TEMPERATURES

D. H. Weitzel, R. F. Robbins and P. R. Ludtke
National Bureau of Standards

TECHNICAL REPORT ML-TDR-64-50, Part II
March 1965

Air Force Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specification, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

DDC release to OTS not authorized.

Qualified requesters may obtain copies of this report from the Defense Documentation Center, (DDC), Cameron Station, Alexandria, Virginia, 22314.

Dissemination outside the Department of Defense or to recipients other than Government defense contractors is prohibited.

Copies of RTD Technical Reports and Technical Notes should not be returned to the Research and Technology Division unless return is required by security considerations, contractural obligations, or notice on a specific document.

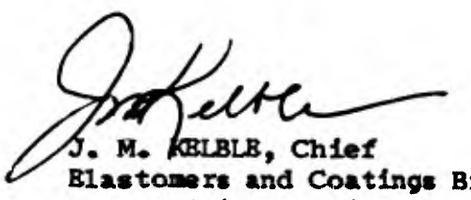
FOREWORD

This report was prepared by the National Bureau of Standards under USAF Delivery Order No. 33(615)-64-1002. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734005, "Elastomeric and Compliant Materials." The contract was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Mr. Roger E. Headrick and Mr. Kermon Murray acting as Project Engineers.

Many of the items compared in this report were commercial items that were not developed or manufactured to meet any Government specification, to withstand the tests to which they were subjected, or to operate as applied during this study. Any failure to meet the objectives of this study is no reflection on any of the commercial items discussed herein or on any manufacturer.

This report covers work conducted from December 1963 to January 1965. Personnel who performed the work and wrote the report were D. H. Weitzel, R. F. Robbins, and P. R. Ludtke. The manuscript was released by the authors for publication as an Air Force Materials Laboratory Technical Data Report on February 15, 1965.

This report has been reviewed and is approved.



J. M. KELBLE, Chief
Elastomers and Coatings Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

This research deals with low temperature investigations of elastomeric polymers, with particular emphasis on their use as seals at cryogenic temperatures. The present report starts with a brief review of elastomer O-rings used as crush gaskets, followed by new work on elastomer-indium combination seals and various O-ring coatings. Pressure actuated seals are then examined in some detail, both analytically and experimentally. Several new designs which combine pressure actuating metal bodies with elastomeric (or other) sealing surfaces are described, and experimental results are given.

A brief study of the behavior of thin elastomeric membranes at cryogenic temperatures was made with a view to their possible use for expulsion bladder construction.

Studies of elastomer properties include a look at creep of highly compressed O-rings over 15-day periods, the effects of fillers and chain orientation on thermal expansion rates, and differential thermal analysis as a tool for study of low temperature transitions. The automatic ball rebound apparatus has been further refined, and will be used for a detailed study of damping at high frequencies and at temperatures from approximately 100 K to 100 C.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (Continued)

1. ELASTOMER O-RINGS AS CRUSH GASKETS

Since elastomeric O-rings do not maintain their rubbery properties at cryogenic temperatures, they cannot function here as they do at ordinary temperatures. That is to say rubber O-rings will not exhibit their automatic pressure energizing feature after they have been cooled below their brittle transition temperature. Certain elastomeric O-rings of small cross section can, however, be very effectively used as crush gaskets for cryogenic seal applications.

1.1 Review and Application Examples

A very brief review of previously reported work[1-11] shows the best elastomeric materials for cryogenic static seal applications include medium hard compounds of natural rubber, neoprene, polybutadiene, polyisoprene, vinyl pyridine-acrylonitrile, vinylidene fluoride and perfluoropropylene, and butadiene-acrylonitrile, with several others performing well under some conditions. The cross section should be kept as small as is compatible with reasonable flange machining tolerances; in most cases a cross section diameter of .070 in. is satisfactory. Successful flange designs for this type of seal are illustrated in figures 1, 2, and 3.

Figures 4 and 5 show modifications of the stepped flange and highly compressed O-ring design which have recently been used for a cavitation study apparatus at this laboratory. One seal (figure 4) connects lucite to aluminum; the apparatus will use two of these. The other seal (figure 5) connects stainless steel weld neck flanges. Commercial flanges were modified by machining mating steps on the flange faces as shown in figure 5. At least 12 of these modified weld neck flanges will be used in the apparatus for cryogenic liquid lines having inside diameters of one to four inches. Liquid hydrogen and liquid oxygen are the fluids to be studied.

Seal test sections were assembled as shown. One end was blanked off, the other end was necked down and passed through a seal in the top plate of a vacuum jacket which was continuously pumped by a helium leak detector. The seals were tested at room temperature, at 76 K, and during warmup. Cooling was accomplished by transferring liquid nitrogen into the section. Helium gas pressure was introduced after the liquid level had dropped below the joint.

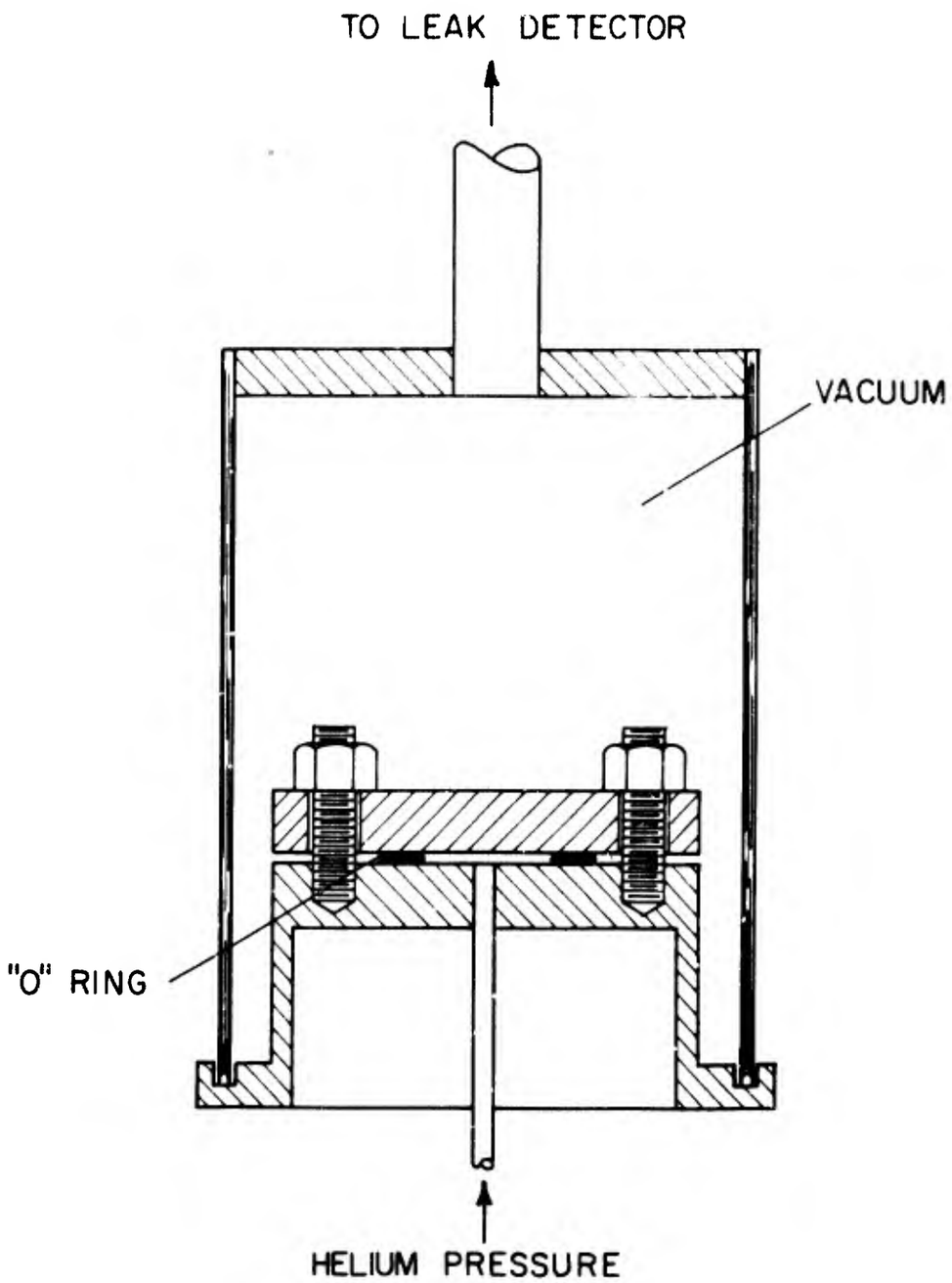


Figure 1 Three-eighths inch Flat Flange

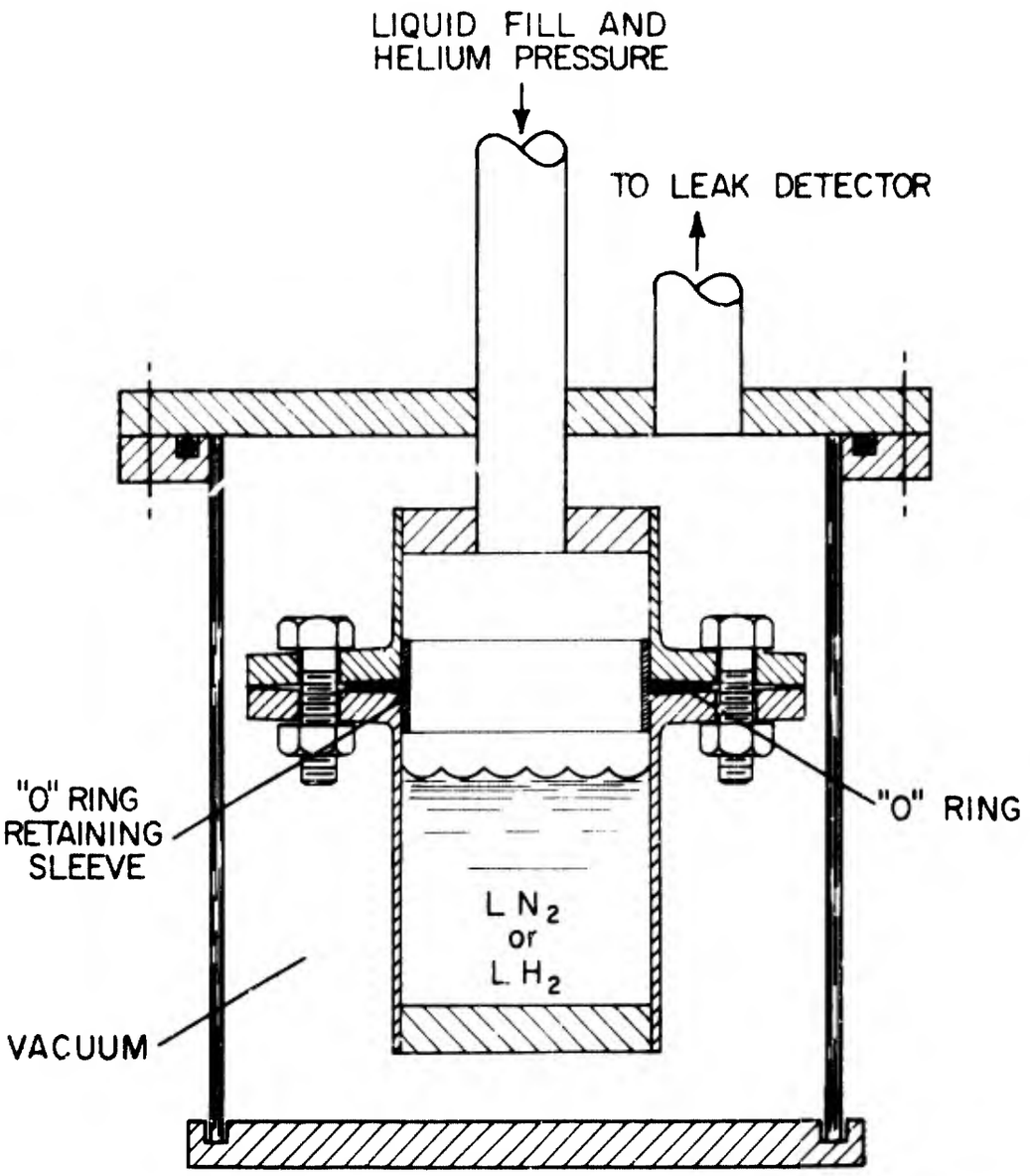


Figure 2 Flat Flange and Retaining Sleeve

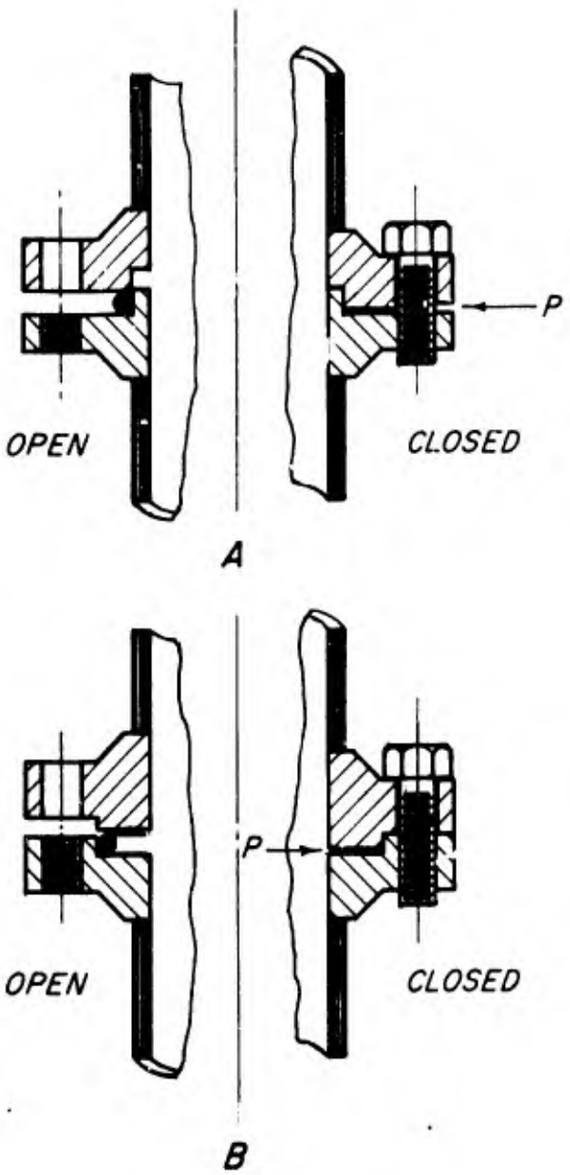


Figure 3 Stepped Flanges

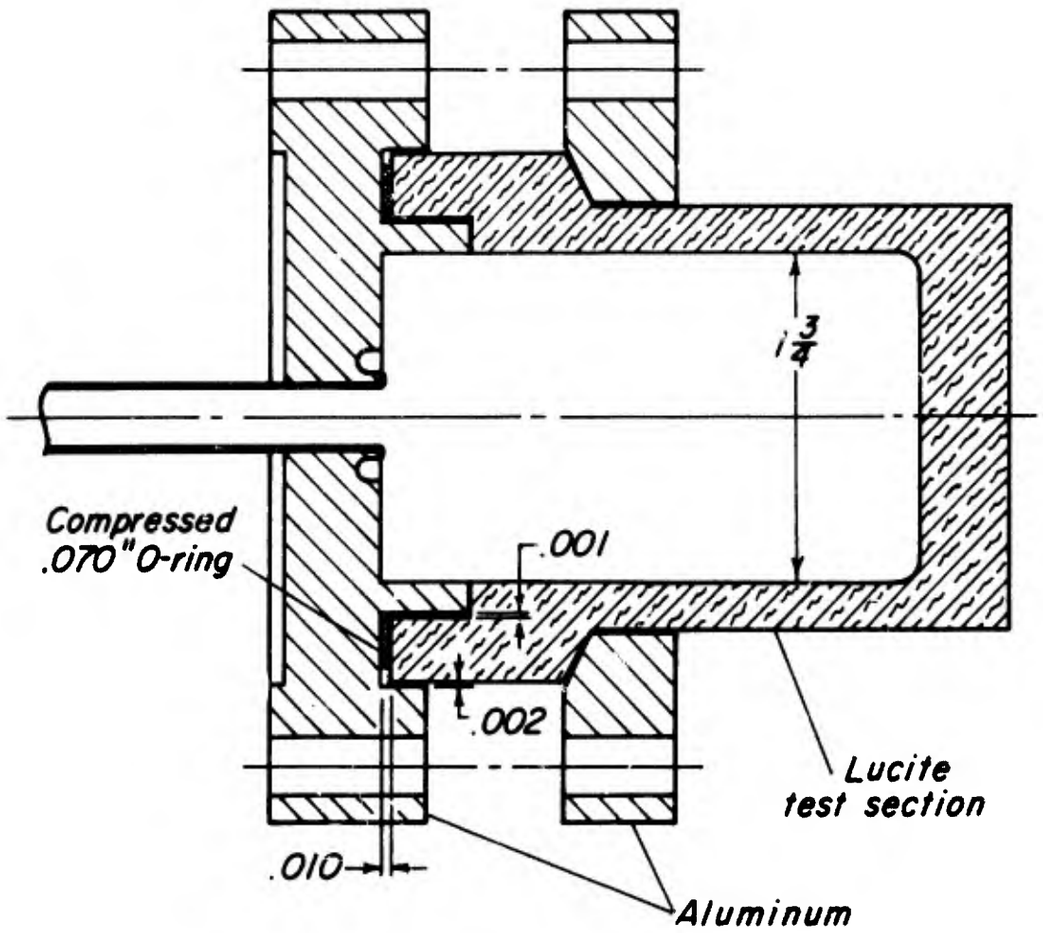


Figure 4 Lucite to Aluminum Seal

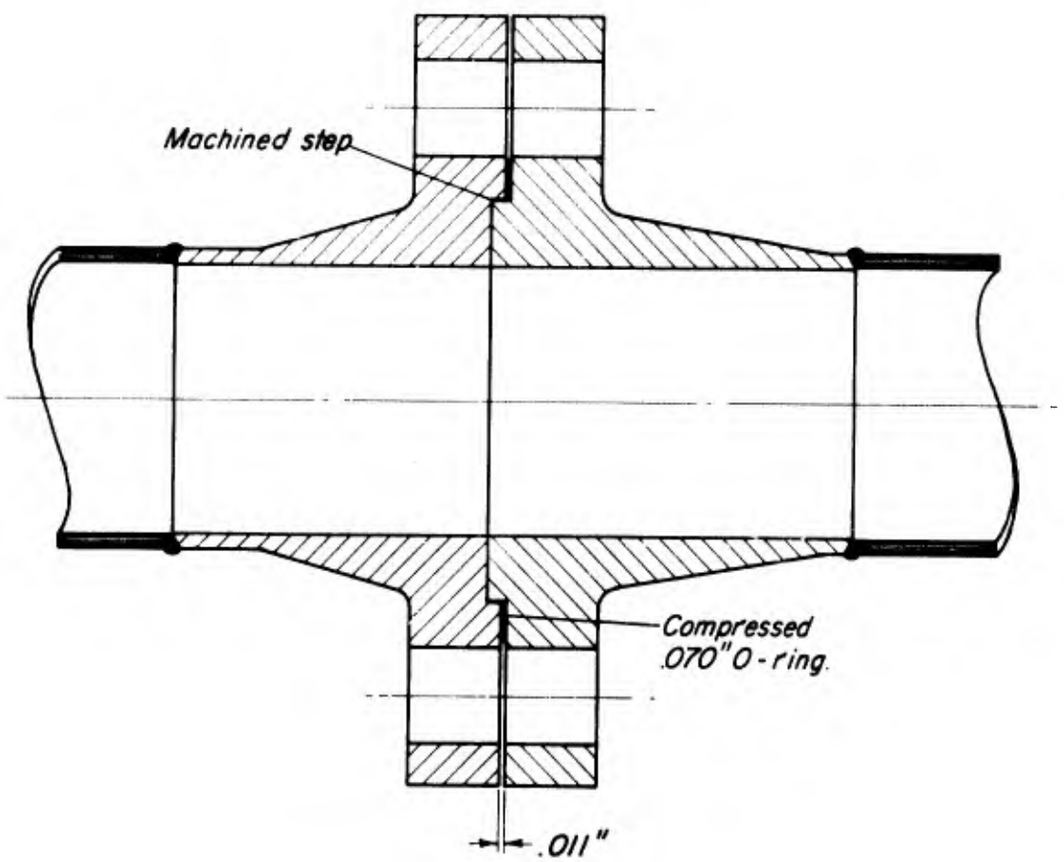


Figure 5 Modified Weld Neck Flanges

The lucite to aluminum seal was tested with a .070 in. cross section diameter Buna N* O-ring compressed to .010 in. Hardness was approximately 80 durometer. Final torque on eight aluminum bolts, 3/8 in. diameter, 16 threads/in., was 50 in-lb. Sequence of pressure and temperature cycles was as follows:

	Pressure	Temperature
(1)	1 atm	room
(2)	1 atm	76 K
(3)	300 psig	76 K
(4)	cycled between (2) and (3)	several times
(5)	300 psig	warmup
(6)	1 atm	room
(7)	1 atm	76 K
(8)	300 psig	76 K
(9)	500 psig	76 K
(10)	500 psig	warmup

There was no indication of leakage during any of the above testing. Sensitivity of the instrument was 10^{-6} atm cc/sec or better.

The modified weld neck flange (1-1/2 in. I.D.) was assembled with a .070 in. cross section diameter Viton O-ring with a hardness of about 77 durometer. When the mating steps "bottomed out" the O-ring had a compressed thickness of .011 in. Clearance at the outside edges of the flanges was .008 to .009 in., showing a small amount of flange flexure. The eight flange bolts (1/2 in. diameter, stainless steel, 13 threads/in.) were pulled down hard, using 40 to 50 ft-lb of torque.

Sequence of pressure and temperature cycles was as follows:

Pressure	Temperature
500 psig	room
1 atm	76 K
500 psig	76 K
1 atm	76 K
500 psig	room
1 atm	76 K
500 psig	76 K
1 atm	76 K
650 psig	warmup

* A LOX compatible Viton® O-ring will be used in the actual apparatus. Buna N (less reliable in past tests) was substituted for this test because of immediate availability.

® DuPont Trademark

For this seal, also, there was no indication of any leakage during the test cycling.

Although figures 4 and 5 may at first glance appear to be different designs, it should be recognized that both are examples of simple stepped flanges with .070 in. cross section elastomer O-rings placed around the O. D. of the male part of the step. The lucite to aluminum seal shown in figure 4 is not a tongue and groove design which fully confines the O-ring, inasmuch as the final width of the compressed O-ring is less than the width of the groove.

1.2 Elastomer-Indium "Sandwich" Seals

Previously reported work[3, 11, 12] has analyzed the likelihood that leakage past a compressed O-ring below the brittle transition temperature is due to unseating of the initial seal as a result of differential contraction at the interface between the brittle elastomer and the metal flange surface. Polytetrafluoroethylene, aluminum, lead, gold, and indium films were tested as interface "lubricants" to prevent these leak passages from forming. Indium performed best, and an elastomer-indium "sandwich seal" (figure 6) was developed. Only about one-third of the flange load required for a plain elastomer O-ring was necessary, and the seal was less sensitive to vibrations and mechanical shock. The tests were performed with a constant force apparatus which has been adequately described in previous reports[3, 11].

The amount of initial force required for a reliable cryogenic seal in an ordinary flanged joint is useful information for design purposes. Early in the program, the rule of thumb for a reliable seal was to give the O-ring 80 to 90 percent linear compression. There are, however, so many parameters to be considered that a general rule of this kind can be quite misleading. Elastomer hardness and flange design are the two most important parameters which can vary the amount of initial compression required. Loading curves for three 1 in. I. D. x 1/8 in. cross section O-rings of varying hardness are shown in figure 7. Force vs. percent compression data were obtained for a soft (50 durometer), an average (66 durometer), and a hard (80 durometer) O-ring. From the loading curves of figure 7 one can immediately see the wide range of initial force required to obtain 70 or 80 percent compression. For a 50 durometer neoprene O-ring, 70% compression requires about 2000 pounds of force while an 80 durometer neoprene O-ring requires about 38,000 pounds for the same compression. A better recommendation for a reliable seal might be given in terms of force per linear inch for an elastomer of given cross section and hardness.

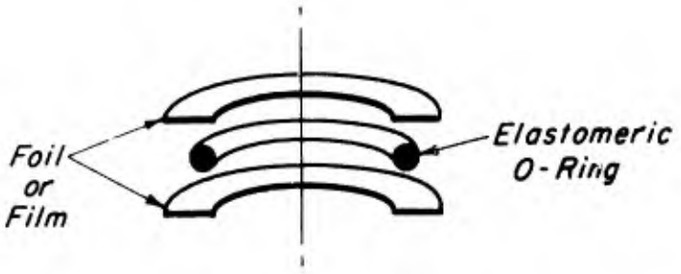


Figure 6 Sandwich Seal Configuration

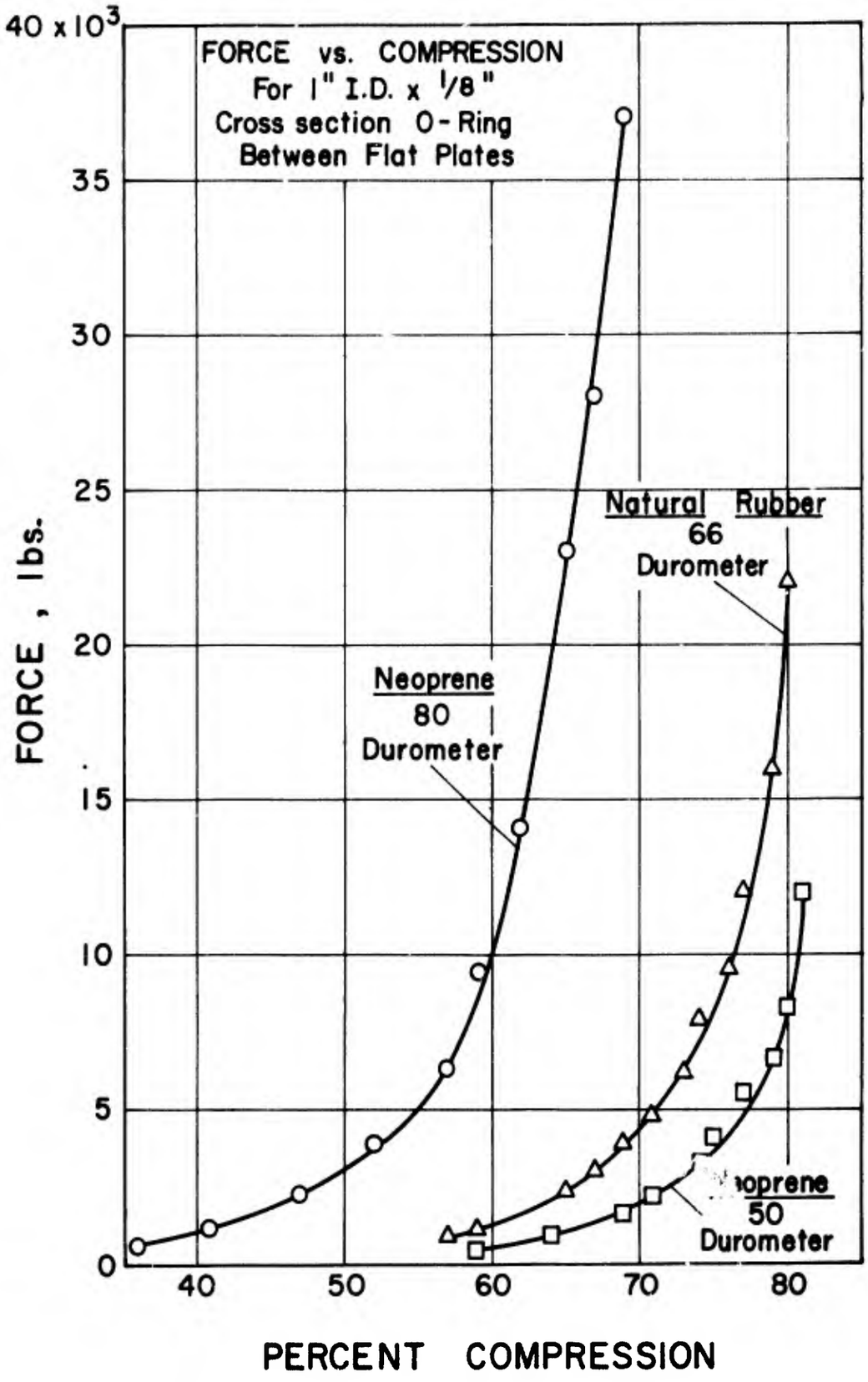


Figure 7 Force vs Compression for Elastomer O-Rings

In order to determine the initial force required for the elastomer-indium sandwich seal when used between simple flat flanges, the apparatus shown in figure 8 (used for much of our early testing) was again employed. It consists of a pair of 3/8 in. thick flat plates, bolts for compression, high pressure helium inlet, and a vacuum cover.

1.2.1 Test Procedure

A sandwich seal of three mil indium foil and 66 durometer natural rubber were compressed between the flat flanges and initial force determined by measuring the flange separation and referring to figure 7.

Indium ribbon was used in this series of tests. Five or six small lengths of 3/8 in. wide indium ribbon were lapped over one another without too much care to form a circle of indium ribbon on each plate of the test jig, as shown in figure 8.

After soldering on the vacuum cover and connecting to the helium leak detector, the seal was pressurized to 1000 psig and the test jig was cooled to 76 K by immersion in liquid nitrogen for approximately two hours. Leakage greater than 10^{-7} atm. cc/sec, was considered a seal failure. If the O-ring did not leak during cooldown, the test jig was struck sharply 10 to 15 times with an 11 oz. hardwood hammer while at 76 K for an additional shock or vibration test.

1.2.2 Test Results

Four tests were made using an average hardness (66 durometer) O-ring of natural rubber with overlapping segments of three mil thick indium for the washers. The results are shown in table 1.

One test was made at both 60 and 65 percent compression and two tests were made at 70 percent compression. The initial force on the 1 in. I. D. x 1/8 in. cross section O-ring was obtained from the loading curve of figure 7. The force exerted by the gas pressure inside the O-ring was considered negligible, since the area inside the compressed O-ring was only about 0. 2 square inches.

None of the seals leaked during cooldown to 76 K. The seals given 60 and 65 percent compression did leak when struck sharply with the hardwood hammer. The O-rings given 70 percent compression did not leak when struck with the hammer.

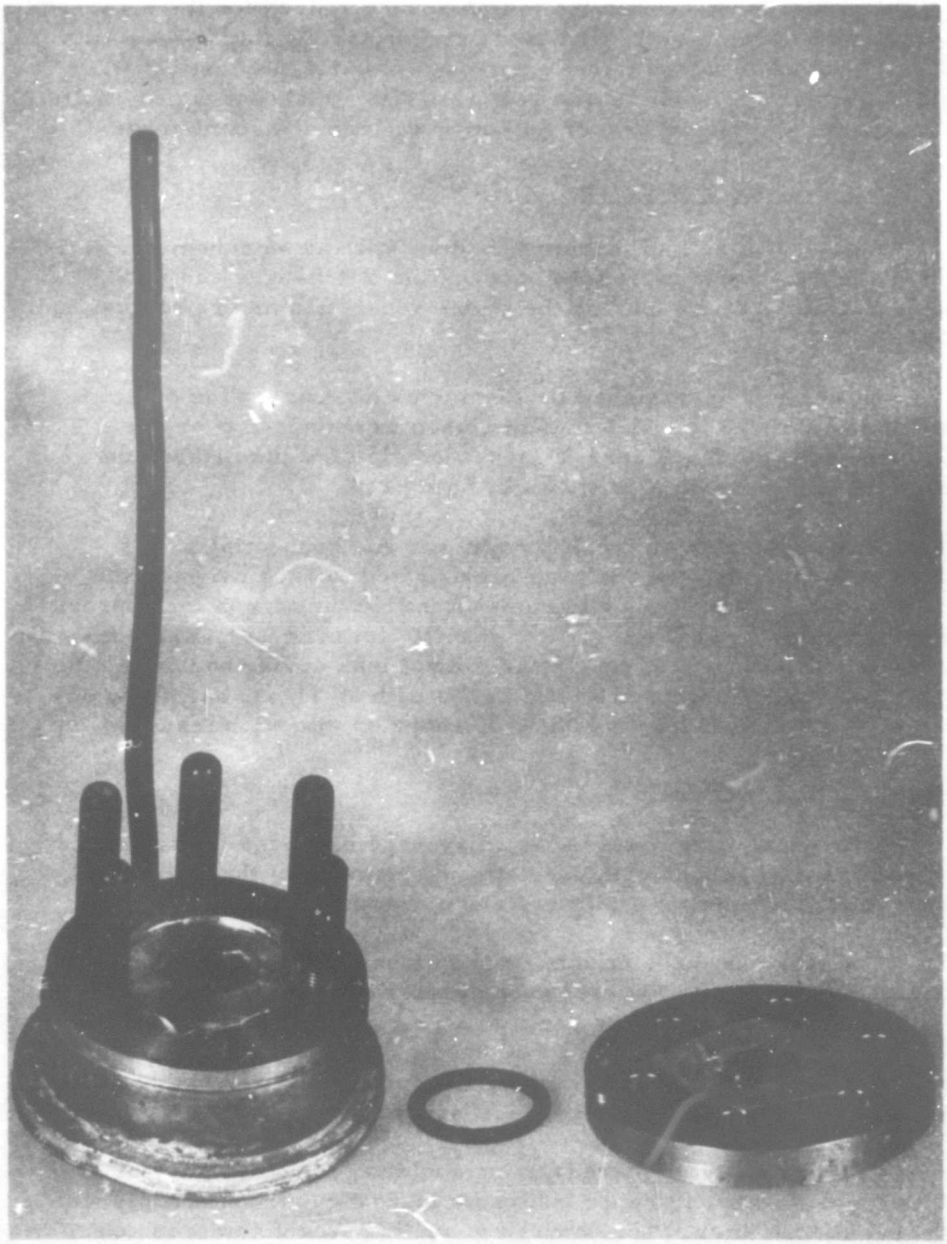


Figure 8 Flat Flanges With Indium-Elastomer Seal

Compound	Percent Compression	Initial Force (lbs.)	Initial Force Per Linear Inch of O-Ring (*/lin. in.)	Leaked* During Cooldown to 76°K	Leaked* During Shock Test	Hardness
Natural Rubber (IV-8A)	60	1200	340	No	Yes	66
"	65	2500	700	No	Yes	66
"	70	4500	1250	No	No	66
"	70	4500	1250	No	No	66

* 1000 psig Helium to Vacuum Leak Greater Than 10^{-7} Atm. cc/sec.

Table 1. Indium-Elastomer Sandwich Seal Tests

These tests indicate that 340 pounds initial force per linear inch is sufficient to maintain a seal to 76 K, but this would not be considered a reliable seal for applications involving severe vibration or mechanical shock. Approximately 1250 pounds initial force per linear inch were required to make a shock proof seal which leaked less than 10^{-7} atm cc/sec. when separating 1000 psig helium from high vacuum at 76 K. The tests were conducted with 3/8 in. thick stainless steel flat flanges and seals consisting of a 66 durometer natural rubber O-ring, 1 in. I. D. x 1/8 in. cross section, with overlapping pieces of three mil thick indium foil between elastomer and flange.

Overlapping segments of indium ribbon apparently seal as well as a continuous washer so there should be no need to cut large washers from sheets of foil.

1.3 Coated Elastomer O-rings

Since indium film effectively seals an elastomer-flange interface, the possibility of coating or plating indium (or other material) directly on the O-ring was investigated. An indium coated O-ring would make a one piece seal and eliminate handling and cutting of indium washers or ribbon. Two types of plating processes were tried and a third type is under consideration.

1.3.1 Electro-Plated Indium

An indium electro-plated neoprene O-ring was tested first. The elastomer O-ring was first coated with copper and then the indium was electro-plated on the copper base. The indium plating was cracked and blistered before testing (see figure 9), and did not look promising for this application.

The O-ring was tested in the constant force test apparatus with 3000 pounds compressive force and 1000 psig helium pressure. The O-ring leaked during cooldown to 76 K and was immediately removed and inspected. About 60 percent of the indium plating had flaked off due to compression and/or cooldown, leaving the harder copper base exposed as shown in figure 10.

This plating process was considered unsatisfactory because of the hard copper base between the elastomer and indium which resulted in cracking and flaking. The seal performance was no better than a plain elastomer O-ring and no further testing was done on O-rings with this type of plating.

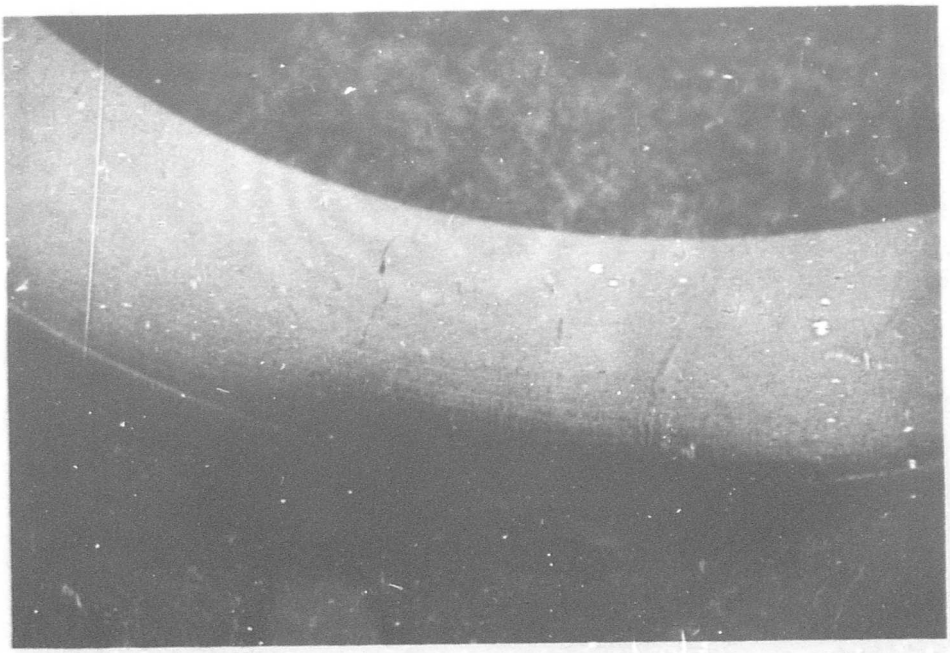


Figure 9 Electro-Plated Indium on Neoprene Before Test

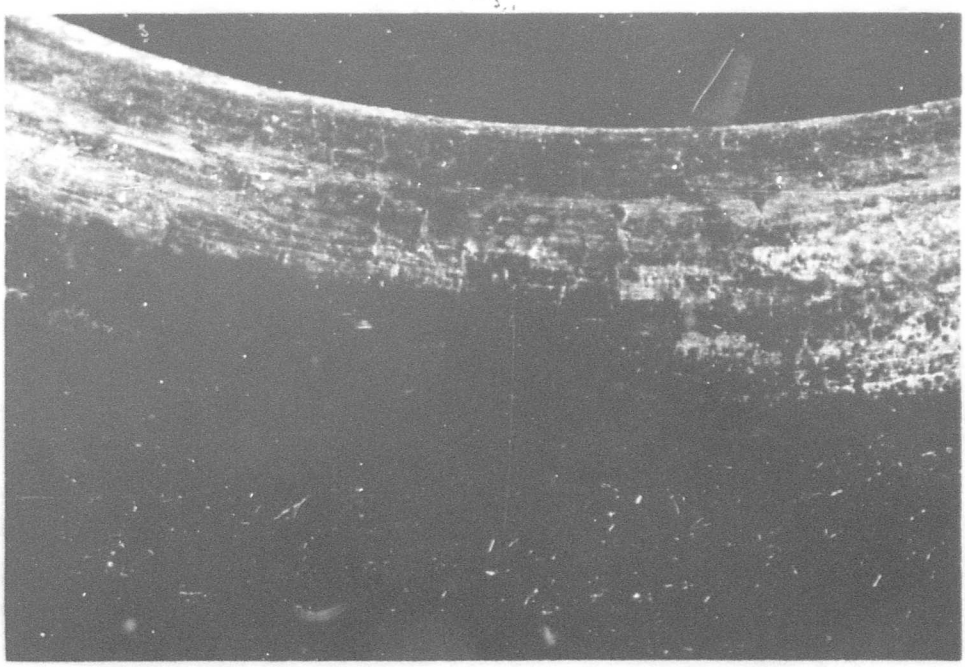


Figure 10 Electro-Plated Indium on Neoprene After Test

1.3.2 Vacuum Deposited Indium

Indium was vacuum deposited directly on the O-ring. This coating was not as thick as the electro-plated indium and had a powdery appearance, as shown in figure 11. The coating was continuous and there were no cracks, blisters or flaking. However, it appeared that the coating could be rubbed off rather easily.

Only one test was made on a vacuum deposited indium coated O-ring. The O-ring sealed 1000 psig helium pressure to 76 K with only 3000 pounds compressive force. Previous tests have shown that plain O-rings of this size require approximately 5500 pounds force to maintain this type seal[3]. Thus there was a significant improvement in seal perfromance.

1.3.3 Electro-Plated Gold

A gold plated O-ring was also tested for interface seal performance. Gold is another popular cryogenic sealing metal. It is LOX compatible but does not flow as easily as indium. The gold plating showed cracks and flaking near the cracks before being tested. This is shown in figure 12.

The O-ring was tested in the constant force apparatus. At room temperature five thousand pounds of force was required to seal 100 psig helium and 6000 pounds of force was required to seal 1000 psig. This is extremely poor seal performance compared to a plain elastomer O-ring and no cooldown was made. The gold plating flaked off in chunks and had many cracks after being compressed.

1.3.4 Teflon® Coatings

Teflon coated O-rings were tested for two reasons. It is possible that an elastomer O-ring totally encapsulated in Teflon might be acceptable in a LOX application. However, no totally encapsulated O-rings appear to be available at the present time. Five different Teflon coating processes have been examined and each had a seam or seams in the Teflon, or the coating was porous or of poor quality.

The second reason for looking at Teflon coatings was to determine if a coating of this material would improve the interface sealing ability of a plain elastomer even though the Teflon film used in the sandwich seal testing did not[3].

® "Teflon" is a DuPont Trademark

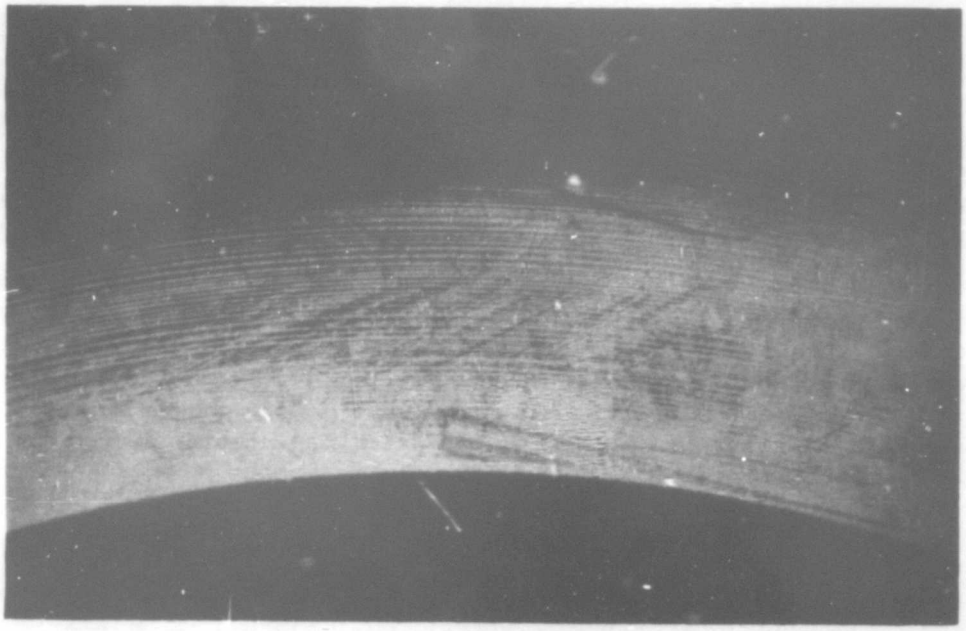


Figure 11 Vacuum Deposited Indium on Neoprene Before Test

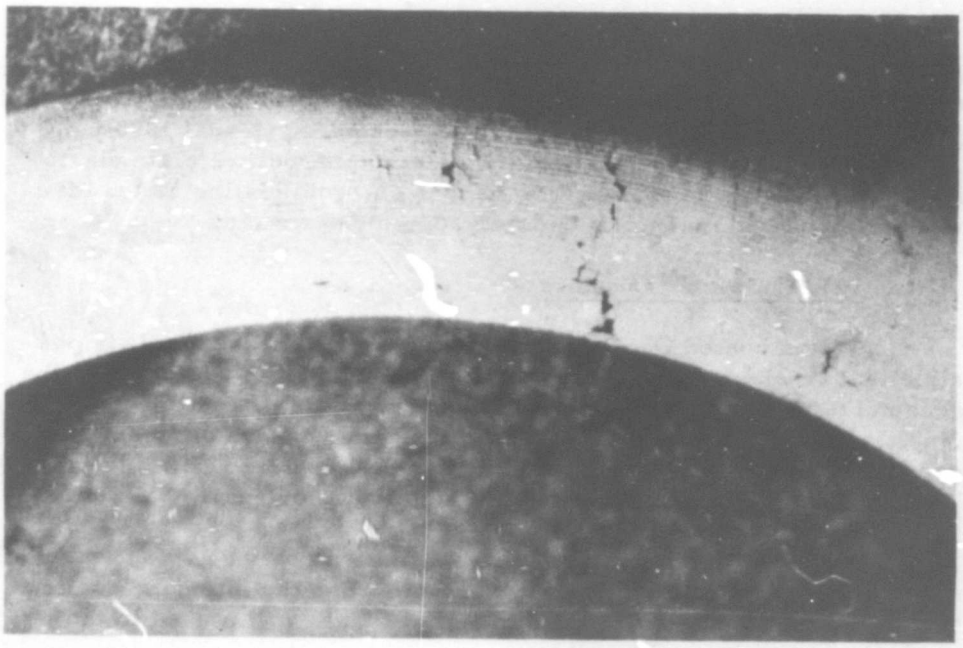


Figure 12 Electro-Plated Gold on Neoprene Before Test

O-rings coated with Teflon film had very good appearance: a nice smooth film with seams on the I. D. and O. D. of the O-ring. There was a very good bond between elastomer and Teflon; the coating was five to eight mils thick. An enlarged photo of TFE coated O-ring with seams on I. D. and O. D. is shown in figure 13.

One of these O-rings was tested in the constant force test apparatus. Seven thousand pounds of force would not seal 1000 psig helium at room temperature. This is extremely poor seal performance and probably results from the fact that the base material (elastomer) is softer than the Teflon surface coating. For effective sealing, the softer material should be on the surface. The test was repeated with a different O-ring. Again 7000 pounds force would not seal 1000 psig helium pressure at ambient temperature. In spite of the fine appearance and superior bonding process, these coated O-rings cannot approach the high vacuum sealing performance of a plain elastomer O-ring. A photo of the O-ring after being compressed is shown in figure 14. The good bond between the rubber and Teflon coating is evident from the wrinkling of the surface of the O-ring.

1.3.5 TFE Dispersion Type Coating

This coating was one to two mils thick and seemed to have a fairly good bond with the elastomer. It was possible to stretch these O-rings without damage to the coating, which was not possible with the more rigid film type coating. The coating was examined carefully under 30X magnification to verify that stretching did not harm the coating or cause it to flake off.

An O-ring was tested in the constant force test apparatus. It would not seal 1000 psig helium with 3000 pounds of compressive force at room temperature, so the force was increased to 4000 pounds, which resulted in a seal. The O-ring was cooled but leaked during cooldown. Another O-ring was tested with 5000 pounds of force and 1000 psig helium pressure; it also leaked during cooldown. This type of Teflon coating is better than Teflon film coating but does not improve the seal performance of a plain elastomer O-ring.

1.3.6 Summary of Coating Tests

The vacuum deposited indium coating is the most promising of the coatings tested to date. This coating does help seal the interface, but it is powdery and delicate and further testing should be done.

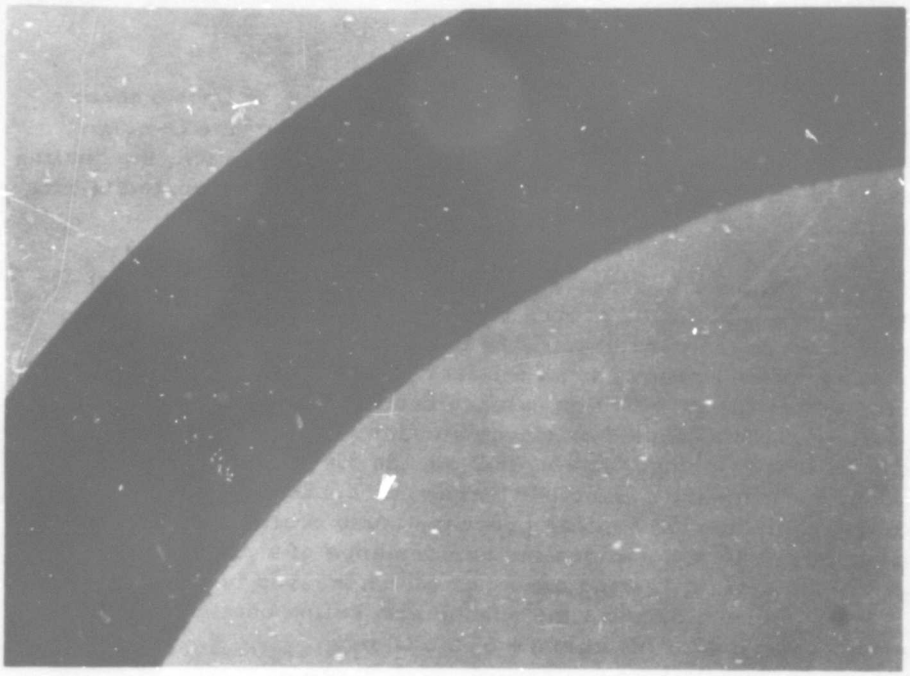


Figure 13 Teflon Film Coated O-Ring Before Test

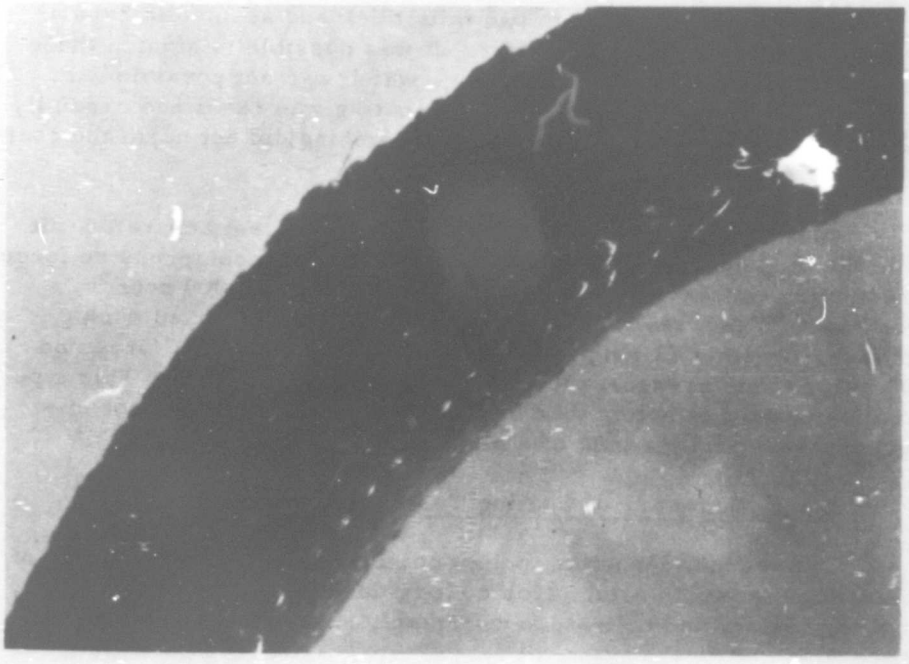


Figure 14 Teflon Film Coated O-Ring After Test

Indium electro-plating on conductive rubber sounds promising and should not be powdery like the vacuum deposited indium.

The "slippery rubber" treatment[3] and the Teflon coatings tested to date offer no seal improvement over a plain elastomer. Several Teflon coating processes have been examined. The first was very inferior quality while the others were close fitting TFE film covers with unbonded seams. None of the Teflon film coatings completely encapsulated the elastomer O-ring and none of the Teflon coatings improve the seal performance of a plain elastomer. There is no apparent advantage in using Teflon coatings on elastomers for cryogenic static seals.

2. IMPROVED SEAL DESIGNS

2.1 Elastomers and Advanced Design Criteria

Demands imposed on leak tight fluid connectors in cryogenic as well as other systems are steadily becoming more stringent. For aerospace vehicles in particular the importance of reliable and light weight seals and connectors is receiving urgent emphasis[13, 14]. Only the most efficient and best engineered seals and connectors can be considered for these advancing requirements.

The elastomeric O-ring and groove is at once the simplest, cheapest, and most soundly engineered design available. The O-ring has an extremely low modulus and deforms elastically on a microscopic as well as on a macroscopic scale, which enables it to make an initial seal with minimum sealing pressure. After this its fluid-like properties enable it to automatically function as a force multiplying (pressure actuating) device. This ideal behavior depends, however, on elastomeric properties -- properties which are highly temperature dependent and which no longer exist at cryogenic temperatures. Note, however, that the elastomeric O-ring functions in a uniquely effective way to do two things:

(1) make the seal, and
(2) maintain the seal.

For cryogenic applications we must forego the second of these unique behaviors because the sealing material is no longer elastomeric. But the first advantage, easy and effective sealing at room temperature, can still be counted on.

When considering elastomers for cryogenic applications, then, we must look for a new mechanism to maintain the seal but we should not overlook the advantage which elastomers have for initially making the seal at room temperature. It has been found, for example[13], that elastomers require a seating stress 2-1/2 to 3 orders of magnitude less than metals and an order of magnitude less than nonelastomeric polymers such as Teflon. Simple crush type gaskets attempt to overwhelm rather than make use of fluid pressure. This alone makes them too crude for consideration as optimum designs in light weight flight hardware. At the very least one should avoid designs in which the fluid pressure subtracts from the sealing pressure. In a good design the sealing pressure will be independent of the fluid pressure, and a better design will use the fluid pressure to increase the sealing pressure

Additional mechanisms which can be used to maintain the seal are spring loading and temperature actuation. Temperature actuation has been successfully used in certain applications[15, 16], but this principle would appear to have one serious limitation: it is unidirectional in a temperature sense. By this we mean that a seal which gets tighter when the temperature goes down must loosen when the temperature goes up. The optimum seal should be reliable during complete temperature cycles between assembly and cryogenic as well as during temperature excusions which may be well above the temperature at which the seal is initiated. It seems to us, therefore, that pressure actuation backed up by a temperature independent spring loading constitutes the only really sound approach to static seal design.

If, then, a seal which utilizes spring loading and pressure actuation (or pressure balancing as it is called in rotating seal technology) is basically the best, we see that elastomers should be compared with plastics, soft metals, etc., as sealing materials to be used in conjunction with a metal seal body or skeleton. For cryogenic service the elastomer O-ring and groove cannot function as a complete sealing system. Highly compressed elastomer O-rings between flat or stepped flanges can be used and are better than most crush type gaskets, as has been shown, but they are crush type gaskets and make no use of pressure actuation.

Having thus narrowed our discussion, we state the problem of optimum cryogenic seal design in two parts:

(1) What is the best spring loading and pressure actuating seal body and flange design?
(2) What is the best sealing material to use with the chosen seal design?

2.2 Seal Body and Flange Designs

Spring loading and pressure actuating seal designs have been classified in various ways and discussed in various categories[3, 11, 17]. A distinction which has perhaps been neglected concerns the orientation of the sealing surfaces with respect to the central axis of the pipe line or vessel. The most usual arrangements have the sealing surfaces perpendicular to the axis, as in ordinary flanged joints. The usual C, V, or K shaped pressure actuated designs also seal against flat surfaces which are perpendicular to the axis of the seal and pipeline.

In all of these the sealing forces are axial, i.e., parallel to the axis of the pipeline, and the applied force (bolt tension, etc.) is also axial. In an axial seal the fastener which holds the joint together and gives it strength must also provide the sealing force, and it serves this additional function without the aid of any force multiplying mechanical advantage.

It is possible to design seals which have sealing surfaces parallel to the axis of the pipe; these utilize sealing forces which are perpendicular to the axis, i.e., they require radial sealing forces. An elastomeric O-ring in a groove experiences radial sealing forces derived from the fluid pressure. The Logan temperature actuated seal depends primarily on radial sealing forces[15]. Several all metal seal designs force a deformable metal into a corner[18,19]; these use sealing forces which lie between axial and radial, and sealing surfaces which are both parallel and perpendicular to the axis.

Characteristics of axial seals (surfaces perpendicular and sealing forces parallel to axis) include the following:

(1) Advantage

The principal advantage is the fact that the seal can be inserted or removed with minimum axial movement of the flanges or pipeline.

(2) Disadvantages

(a) Bolt circle must be relatively far from the pipe wall to make room for the seal "legs." This increases flange weight not only because of greater flange diameter, but also because fluid pressure acting through the long moment arm between pipe wall and bolt circle results in high flange deflections which reduce the stress in the seal. A seal which will follow large axial flange movements is therefore required.

(b) Sealing forces are parallel to the applied force of the mechanical fastener (bolts, etc.) which hold the joint together. This requires additional fastener strength and weight.

Characteristics of radial seals (surfaces parallel and sealing forces perpendicular to axis) include the following:

(1) Advantages

(a) Since the seal can be designed to occupy very little radial space (sometimes no more than the thickness of the pipe wall) the bolt circle or other connector can be placed immediately adjacent to the pipe wall for maximum strength to weight ratio.

(b) A radial (or almost radial) sealing force is achieved from the axial fastener acting through an inclined plane or wedge with high mechanical advantage. Fastener strength can approach the theoretical minimum, which is only that required to make the joint as strong as the pipe.

(c) Sealing surfaces are on the inner wall of the flange, where they are protected from mechanical damage during handling and assembly.

(2) Disadvantages

(a) A feature which is sometimes a disadvantage of radial seals is the fact that axial movement equal to the length of the seal is required for assembly or disassembly of the joint.

Seals with conical sealing surfaces represent a compromise between axial and radial sealing forces. The angle which the sealing surface makes with the seal axis is a powerful and easily varied design parameter. As shown above, a radial sealing action has significant advantages. For small diameters, however, a purely radial seal may be impractical because of strength limitations of the seal body material. A seal body which provides purely radial spring loading is stressed by hoop compression. A safe compressive deflection for a high strength material such as Inconel X is about 0.3 percent. For a one inch diameter radial seal, then, an inward diametral deflection of three mils (1.5 mil springback all around) is available, and this ratio of deflection to diameter will hold for all diameters. Thus a four inch radial seal can safely provide a six mil springback between the sealing surfaces.

If the maximum elastic deflection of a purely radial seal does not provide sufficient springback to follow anticipated dimensional changes, the hoop can be modified to a double cone configuration which begins to trade some of the hoop stressing for beam bending. Figure 15 shows three steps in the change from an essentially radial seal to the more common axial seal. The desired degree of flexing and elastic springback can always be obtained in this way by simply varying the angle of the cone as dictated by the diameter of the seal.

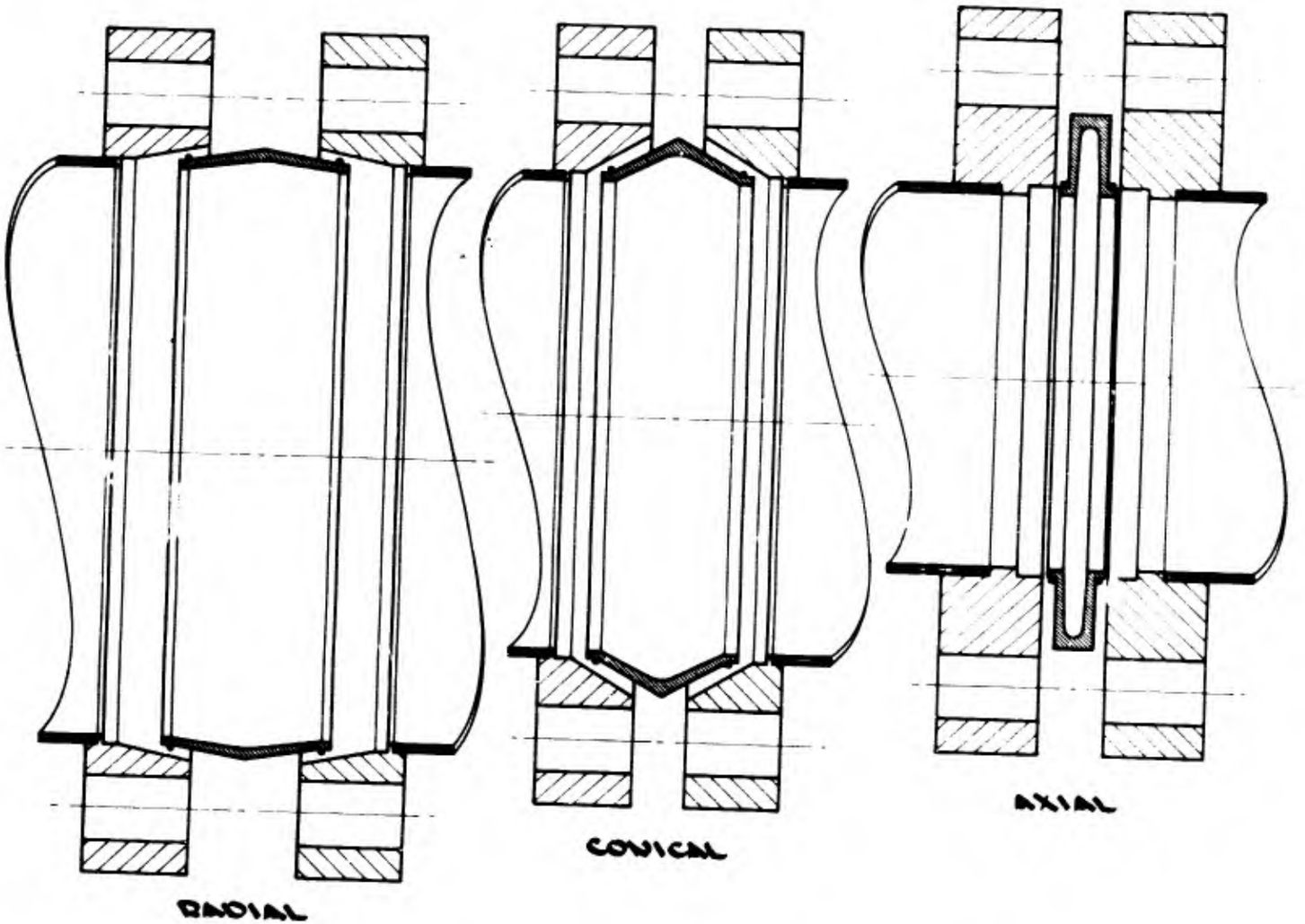


Figure 15 Radial, Conical and Axial Seal Configurations

Important points to be noted are:

1. This is a truly pressure actuated seal which makes effective use of the fluid pressure regardless of the angle which the seal beams make with the axis of the pipe.

2. A variety of sealing materials, including but not limited to elastomers, can be used with the seal.

3. The sealing material can be placed around the seal body in the form of snug fitting O-rings of elastomer, plastic, or soft metal.

4. If a plated or coated sealing surface is preferred the angle which the machined cone in the flange makes with the axis of the pipe should be slightly greater than the corresponding angle of the seal body. This insures a narrow sealing area and preserves the pressure actuation principle.

2.3 Sealing Materials

These are the materials which deform or flow to fill in the asperities between the flange surfaces, or between the flange and seal body surfaces in the case of a two-part seal. The variety of materials which is used (or whose use is attempted) to fulfill this roll is little short of amazing. One might assume that the most easily deformed material would unquestionably be best. If we limit our choice to solids, the softest metal is indium and the softest non-metal is rubber. Both of these are used, but so is aluminum, lead, copper, nickel, gold, silver, and even steel, as well as many plastics.

This multiplicity of sealing materials comes about partly because of environmental requirements such as temperature extremes and fluid compatibility, and partly because of the great variety of seal designs which are in use. In some cases a basic seal design is "tried out" with many different sealing materials, a prime example being the scores of gasket materials which are used with simple bolted flanges. A reluctance to depart from conventional sealing concepts (such as axially loaded crush gaskets) often leads to great expenditures of energy in attempts to make basically poor designs work under less than ideal conditions.

If we have a basically good seal design which incorporates pressure actuation and elastic springback, the softest and most resilient sealing material which is available should be used with it. This is rubber. Environmental conditions such as high temperature or fluid

compatibility may rule out the use of rubber, but it has been repeatably shown that a thin layer of compressed rubber will maintain a seal at cryogenic temperatures[11]. The statement is often made that a sealing material must yield and flow plastically in order to make an effective seal. Rubber neither yields nor flows plastically and it makes the best seal known. The high temperature and fluid compatibility limitations of elastomers cannot be denied, however, even though the boundaries of these limitations are being slowly pushed back. Relatively new fluoroelastomers are now acceptable for use with oxygen if tested on a batch to batch basis[20], and this same class of materials is being developed for use at higher and higher temperatures.

If environmental or operational conditions rule out the use of elastomeric sealing material, a soft metal or plastic can be used. These materials yield and deform plastically, so the spring loading characteristics of the seal body become particularly important. Indium deforms easiest (10% strain at compressive stress of 310 psi) and readily flows under pressure even at cryogenic temperatures. Swenson[21] has published data which indicates that (before work hardening) the compressive yield of indium at -423F is no more than twice its value at room temperature. This tendency to cold flow is a disadvantage in a rigid seal, but if a sufficiently thin layer of indium is backed up by an elastic member one has a very effective seal combination. Disadvantages of indium are its low melting point (313 F) and the fact that it is not acceptable for use in oxygen systems.

The fluoroethylene polymers are often used as seal coatings on metal body seals. They are compatible with oxygen and some can be used at temperatures approaching 500 F. They have fairly low yield strength at room temperature (3000 psi for Teflon FEP) with sharp rise in strength as the temperature is decreased (23,000 psi for Teflon FEP at -423 F)[22]. Because of the high yield strength at cryogenic temperatures they are not likely to reseat if the seal is broken by transient conditions.

Metals having intermediate hardness and higher melting points are useful sealing materials in ultra high vacuum systems which must be bakeable, and in systems which involve high operating temperatures. Copper and gold are most popular for these applications, having yield strengths of 8000 to 10,000 psi and melting points approaching 2000 F. The yield strength of annealed copper is quite insensitive to temperature, making it a good candidate for cryogenic as well as high temperature applications.

2.4 Axial Seals

Two examples of pressure actuated seal designs using elastomeric sealing media and axial sealing forces have been developed and tested. Photographs of one seal body are shown in figure 16; this seal was made at NBS. Figure 17 is a dimensioned cross section of the seal and flanges. Drawings of the second seal are shown in figure 18; this seal combined the experience of NBS and Del Mfg. Co., and was made by Del.

2.4.1 Del-NBS Pressure Actuated Axial Seal

After some discussion with Del Mfg. Co., it was decided that an Inconel X U-shaped body could be incorporated with tabs of some of the better O-ring materials in the design shown in figure 18. The upper drawing shows the seal proper with some dimensions to indicate size. Inside diameter of the body is 1.0 inch. The seal reflects design characteristics consistent with both NBS and Del experience.

Load-deflection curves for the body with and without tabs were measured on the Instron tensile testing machine. The results are shown in figures 19 and 20. Note that it only takes 400 lb, or 128 lb/in, to compress the body and tabs .054 inch, or to within .048 inch of the maximum. No yielding of the seal body was produced by this compression. Many people have studied deflection characteristics of the U-shaped seal body from a theoretical viewpoint[17, 19, 23]. The use of either plate or beam theory results in error, but beam theory as described by Wallach[17] agrees quite well with the experimental results. If we consider each leg of the body of figure 18 to undergo an initial deformation y_ℓ at the sealing point due to bolt tightening, the sealing force R_s per inch of circumference is described by beam theory as

$$R_s = -y_\ell \, E/(1-\nu^2)\left(\frac{\ell}{h}\right)^3, \qquad (1)$$

where

E = Youngs modulus

ν = poisson's ratio

ℓ = leg length

h = leg thickness.

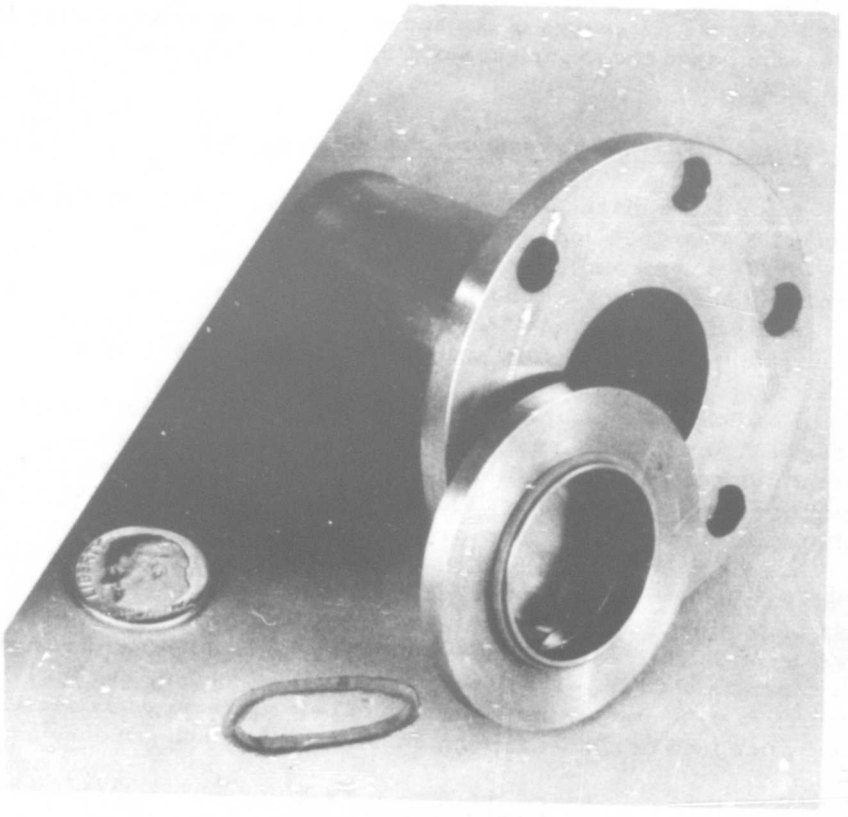


Figure 16 NBS Pressure Actuated Axial Seal

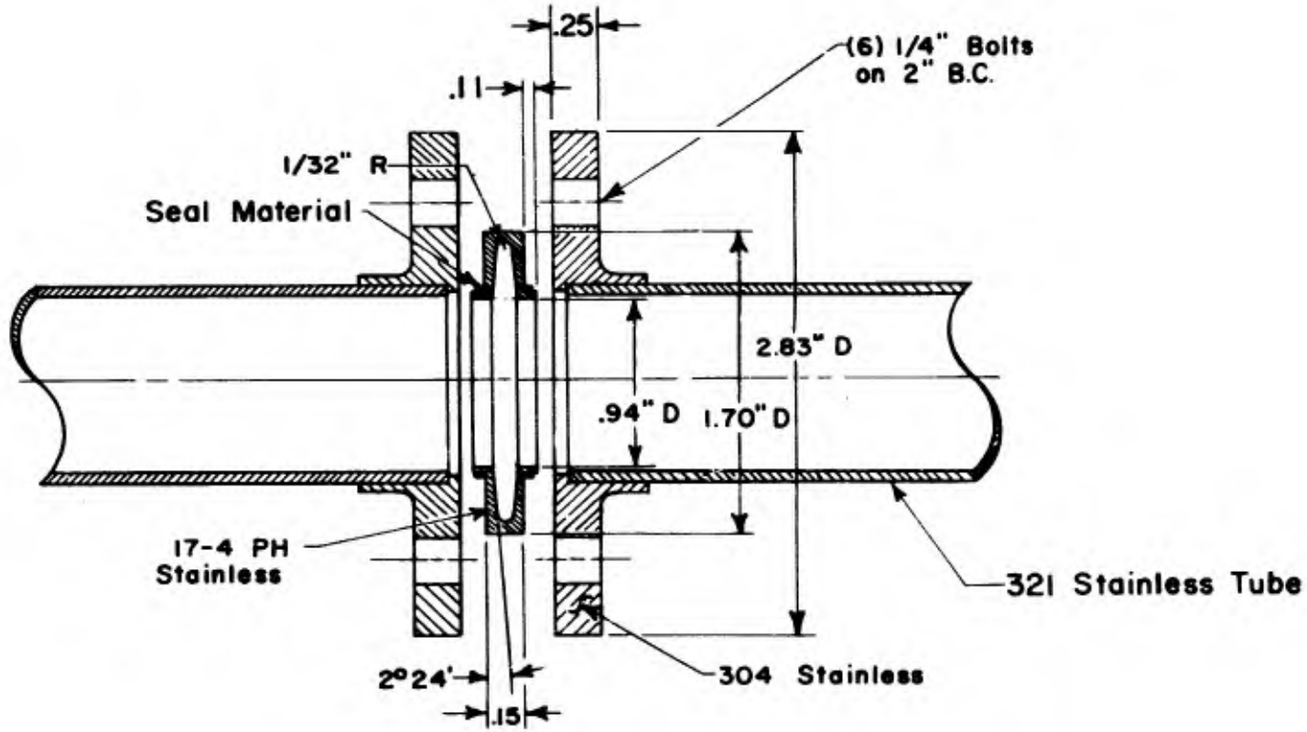
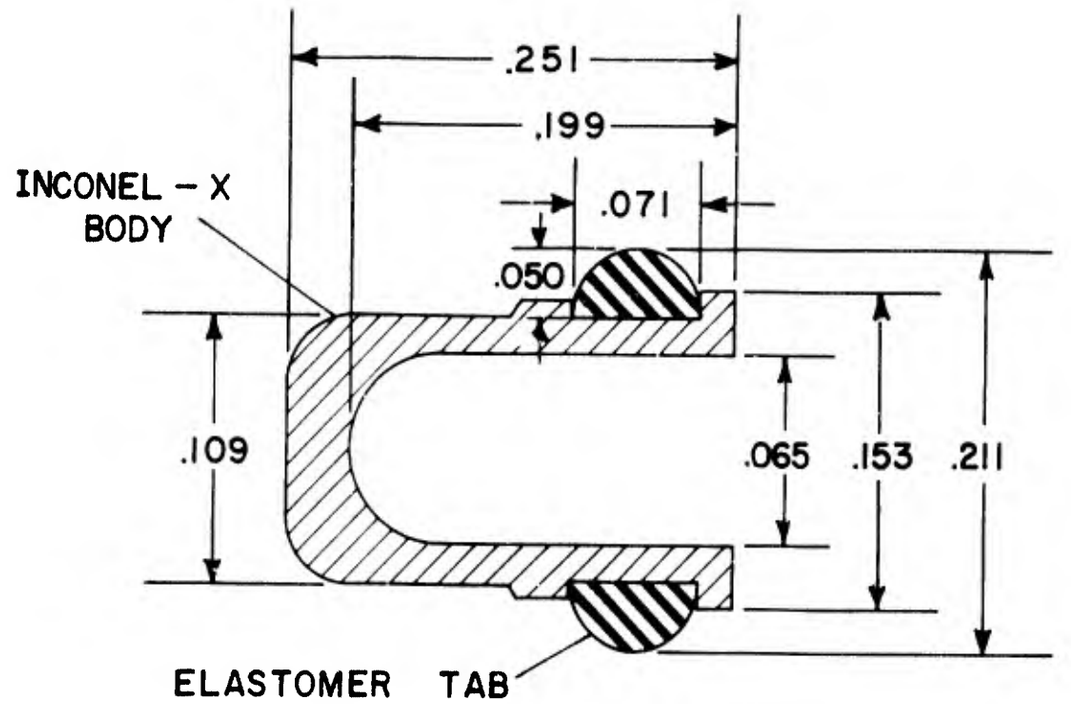


Figure 17 NBS Pressure Actuated Axial Seal and Flanges



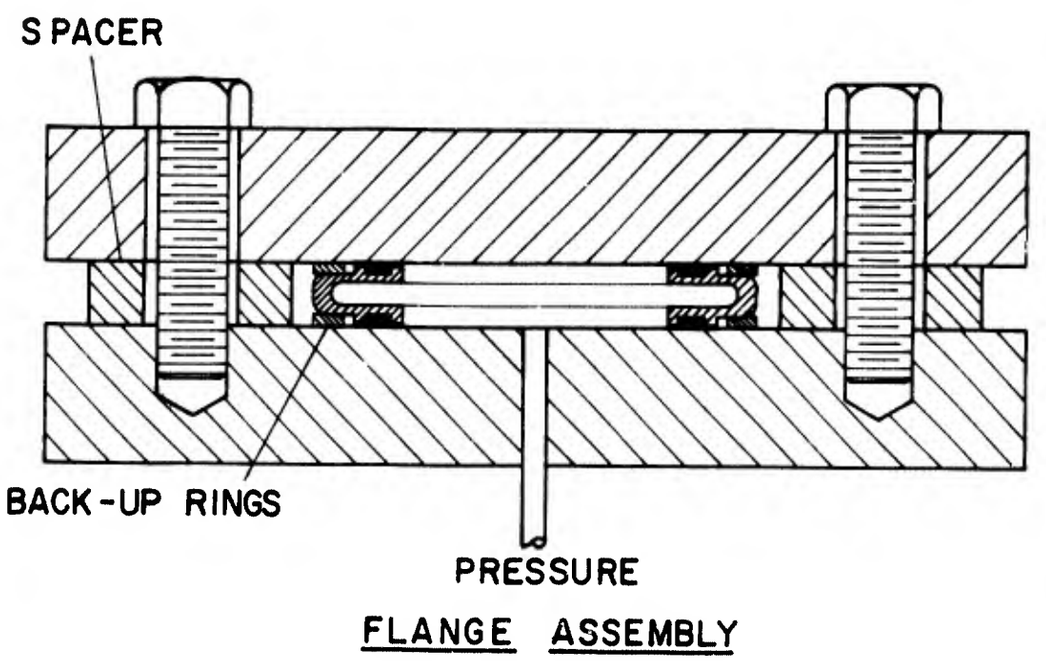


Figure 18 Del-NBS Pressure Actuated Axial Seal and Flanges

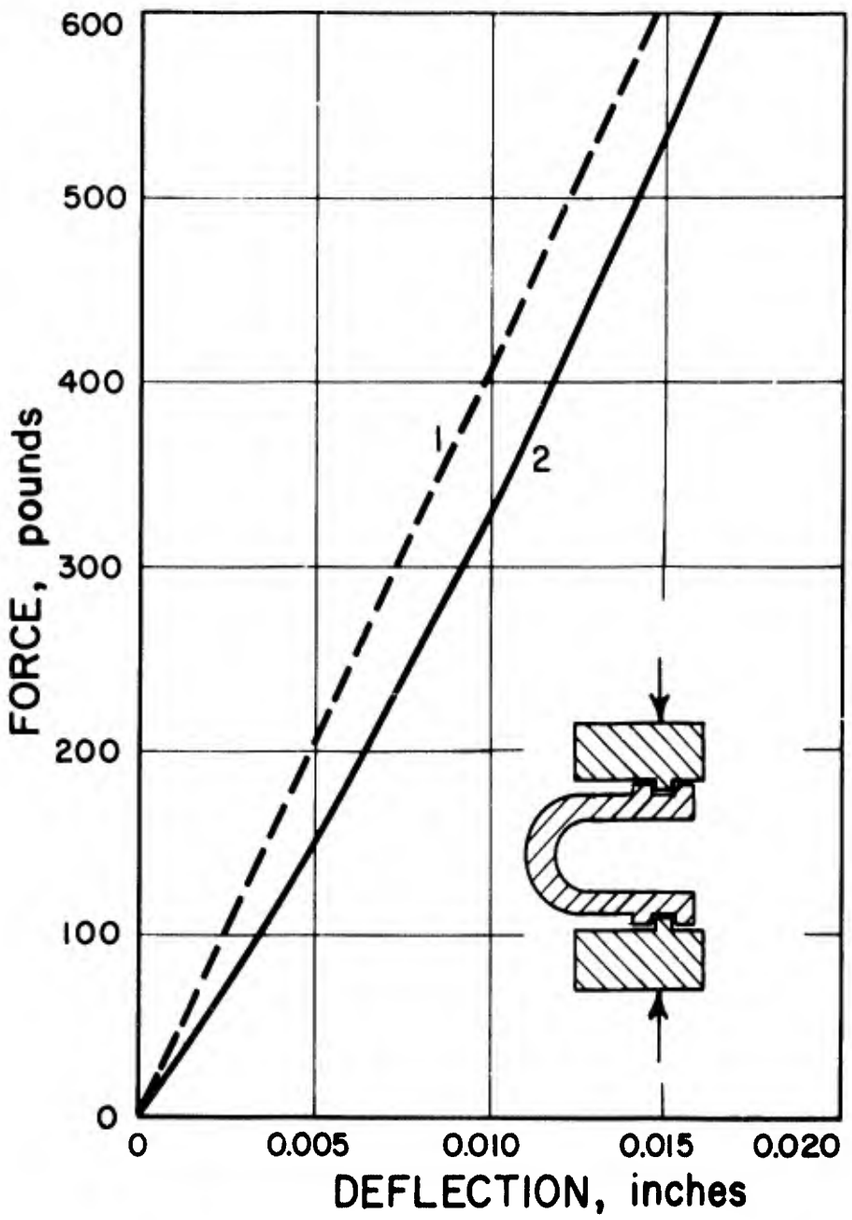


Figure 19 Force vs Deflection for the Seal Body

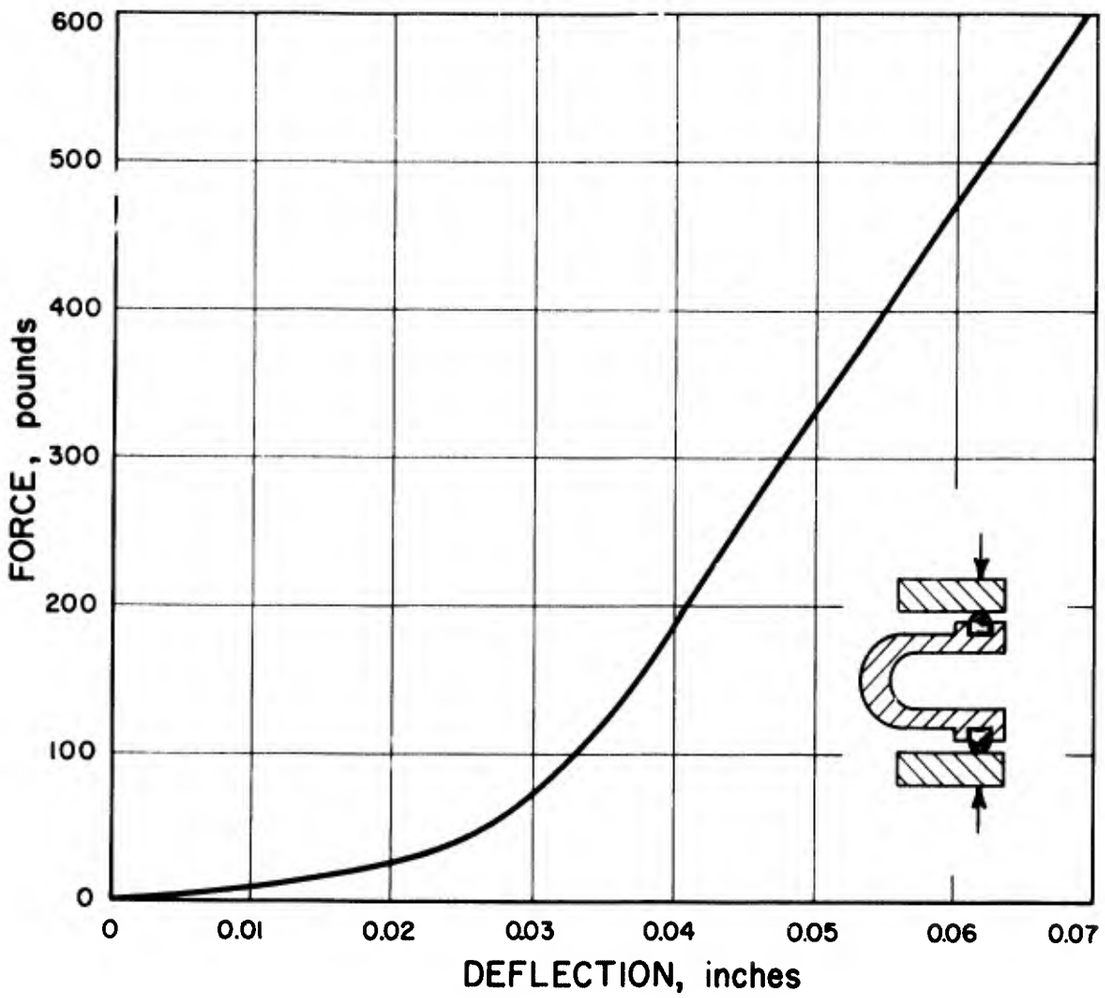


Figure 20 Force vs Deflection for the Seal Assembly

Equation (1) holds when the leg thickness is constant and the leg is initially on a plane parallel to the flange surface. Curve 1 of figure 19 shows the body deflection calculated by equation (1) for the Del body. Considering the difficulty in measuring leg thickness and length, both of which enter the equation as cubic expressions, the agreement is quite good.

The increase in R_s due to internal pressure can be calculated from:

$$R_s = 3p\ell/8 - y_\ell \, Eh^3/4\ell^3(1-\nu^2) \qquad (2)$$

where

p = internal pressure, psi, and the other symbols are the same as equation (1).

Note that y_ℓ must be known before the pressure actuation can be calculated. Figure 21 shows R_s as a function of pressure for several leg deflections. This knowledge of the deflection characteristics of the design may enable better designs to be proposed after experimental results are obtained.

2.4.1.1 Experimental Results

The four bodies purchased from Del Mfg. Co., all supposedly identical and with the dimensions shown in figure 18, were used in seal tests designed to cover a range of initial compressions and connector assembly techniques. In all cases the test jig was enclosed in a vacuum jacket and cooled to 76 K, and the seal was compressed between two flanges in a manner similar to that shown in figure 18. The usual mass spectrometer leak detection method was used; leaks of helium gas of the order of 10^{-6} atm cc/sec could be easily detected.

Table 2 summarizes the pertinent results of nine seal tests.. The following comments supplement the column titles. Natural Rubber (NR) tabs were used in all tests except 3 and 4, when Viton® (V) were used. The natural rubber apparently gave better results, but the tests with Viton were not sufficient to eliminate its consideration. Certainly LOX compatibility information encourages further investigation of Viton tabs. In some cases the tabs and/or bodies had been used for previous tests, and this information is given on lines 3 and 4. The spacers and back-up rings were not used until the later tests (lines 5 and 6) and the success of tests 8 and 9 is largely credited to these accessories, which promote uniform leg deflection. These stops

® "Viton" is a DuPont Trademark

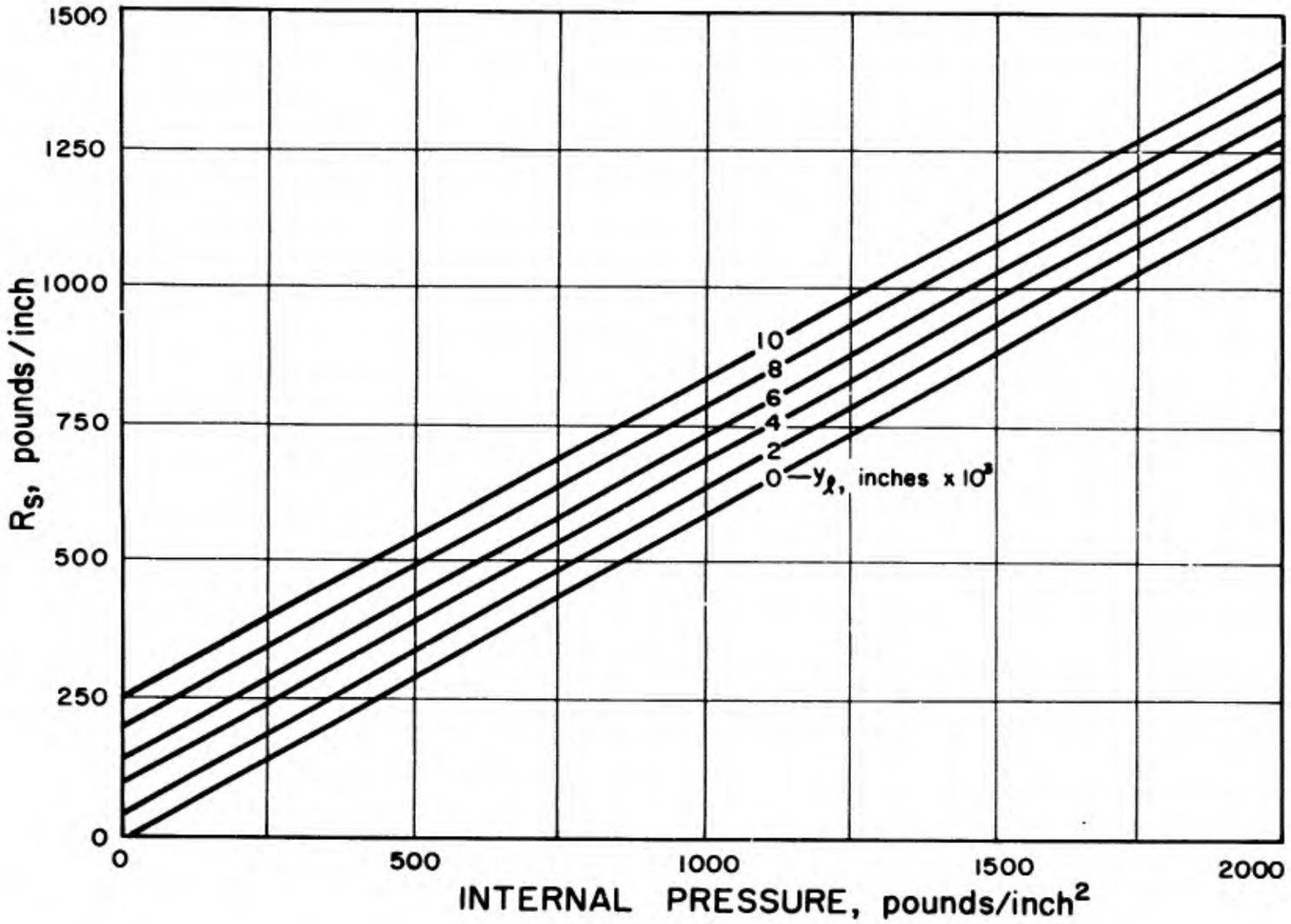


Figure 21 Pressure Dependence of the Sealing Force

should be incorporated in future seal body designs. The seal force is determined from figure 21, with y_ℓ determined from t_c (the back-up ring thickness) and figures 19 and 20. Internal pressure was kept constant during cooldown, but varied from test to test. The highly successful seal of test 9 was pulsed from 0 psig to 600 psig several times at 76 K, after cooldown at 600 psig, with no ill effect. "Zero leak" was defined as less than 2×10^{-7} atm cc/sec of helium gas. The maximum leak rate measurable on the leak detector scale was 3×10^{-4} atm cc/sec. After each successful cooldown the test jig was removed from the liquid nitrogen bath and jarred by striking it with a hardwood hammer. This "vibration test" caused leakage only in test 2, which did not incorporate a flange spacer or back-up rings.

Table 2. Pressure Actuated Seal Test Results

Test PA No.	1	2	3	4	5	7	8	9
Tab Matl	NR	NR	V	V	NR	NR	NR	NR
Used Tabs	No	No	No	No	No	No	Yes	Yes
Used body	No	Yes	No	Yes	Yes	Yes	Yes	Yes
Spacer	No	No	No	No	.130	.150	.130	.130
Back-up Rings	No	No	No	No	No	Yes	Yes	Yes
t_c, mils	25	15	16/29	0/0	~10	20	10	10
Seal force, lb/in	200	260	205	350	680	500	290	250-560
Internal Pressure, psi	125	125	10	150	750	600	125	0-600
Temp at Initial Leak, °K	150	None	152	185	178	297	None	None
Temp at Leak Off Scale, °K	106	None	115	(a)	178	99	None	None
Leaked upon Jarring		Yes					No	No

(a) stopped test at 150°K before off scale leak

It was mentioned earlier that the seal body used for the room temperature deflection tests on the Instron tensile machine did not yield. Unfortunately the design did not hold up as well in the seal tests. At the conclusion of the tests shown in table 2 all four of the seal bodies purchased from Del were yielded considerably. In some cases the bodies seemed to yield at deflections less than the maximum deflection of the tensile tests. This result indicates that the bodies were

not uniformly fabricated, since there is no reason to believe that thermal shock would cause permanent set or yielding of Inconel X. In every case it appears that the yielding occurred near the sealing end of the leg, instead of at the junctions with the web, even though beam theory predicts that the web junction should be the point of highest stress. This indicates that the ends of the beam should be thickened to eliminate this possibility.

2.4.1.2 Conclusions

The tests to date indicate that an elastomer sealing material can be combined with a conventional pressure actuated seal body for use in a cryogenic connector with simple, flat, lightweight flanges. If properly designed, this seal will withstand high deflections caused by pressure surges in the cryogenic temperature range. When the seal is initially assembled the soft elastomeric surface will fill small imperfections in the flanges, and therefore eliminate small leak paths which are present in conventional designs using a harder seal material[14].

An improved body design, incorporating the spacer and back-up rings and eliminating yielding of the body, will be necessary before the important factor of reliability can be established. In the testing to date the desired results were obtained only after several failures indicated the need for back-up rings and high deflections. It is expected that future testing will establish design parameters for reliable, lightweight, pressure actuated connectors using elastomer seal materials.

2.4.2 NBS Pressure Actuated Axial Seal

Figure 22 is the measured load vs. deflection curve for the NBS axial seal body of figures 16 and 17, which was made of 17-4 PH stainless steel. The curve is for the complete seal body consisting of two connected beams or "legs"; for one beam the deflection values should be divided by two. The load is given in pounds per inch of beam length, where the total beam length is taken to be the average circumference of the seal "leg."

The photographs of figure 16 show the seal body with a size 8 unfilled natural rubber band (cross section .030 x .060 in.) stretched around it, and an unstressed band in the foreground. A linear stretch of 67 percent was required to position the rubber band.

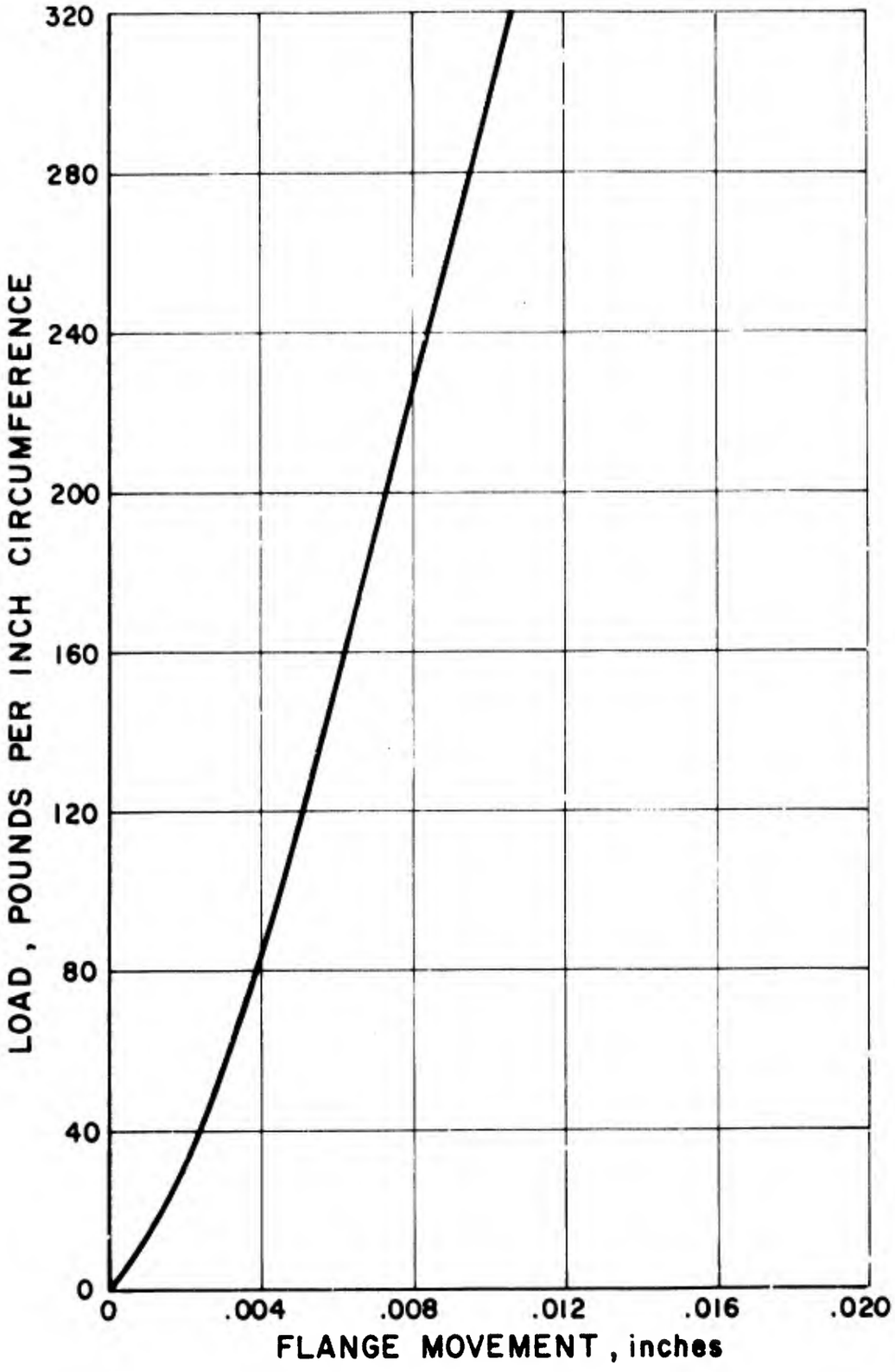


Figure 22 Loading of NBS Axial Seal Body

The flanges were silver soldered to sections of stainless steel tubing which were long enough to duplicate structural characteristics of joints in actual pipe lines. The ends were plugged, one plug drilled, and a smaller tube was soldered to the hole. This tube passed through the top plate of a vacuum chamber which was continuously pumped by the leak detector. The small tube provided means for alternately pressurizing the joint with helium gas or introducing cryogenic liquid for cool down.

The seal was first assembled with size 8 rubber bands and given a simple bubble and pressure decay test. These tests indicated no detectable leak at room temperature or at 76 K at all pressures from one atmosphere to 1000 psig. Repeated cycles between these pressure extremes while keeping the joint immersed in quietly boiling liquid nitrogen showed no leaks large enough to be observed as bubbles of escaping helium.

The joint was then placed in the vacuum tight container and tested with the helium leak detector at room temperature. At 1000 psig the leak rate slowly climbed to 44 scale units (each equivalent to 1×10^{-6} atm cc/sec), reaching this value after about one hour. When the helium pressure was dropped to one atmosphere, the leak rate dropped to six units after five minutes. The vacuum container was pumped overnight, after which the leak rate of the test joint was below 0.05 units (background reading) at one atmosphere, but climbed to 30 units after half an hour at 1000 psig. The joint was then disassembled and reassembled with a larger (size 10) rubber band. This required a "pre-stretch" of only 20 percent, leaving a larger cross section to be compressed during assembly of the joint. A thermocouple was also installed on the flange near the elastomer.

Characteristic of this assembly was a fairly reproducible pressure-dependent leak rate at room temperature, as shown in figure 23. This may have been due to permeability of the gum elastomer. The advantage of pressure actuation at the 1000 psig maximum was not apparent.

After the room temperature test the helium pressure line was removed and the seal was cooled by introducing liquid nitrogen through a slender stainless steel tube which reached to the blanked off pipe section below the joint. After cooling to about 170 K, the helium pressure line was again connected and leak rates were observed during warm up of the joint.

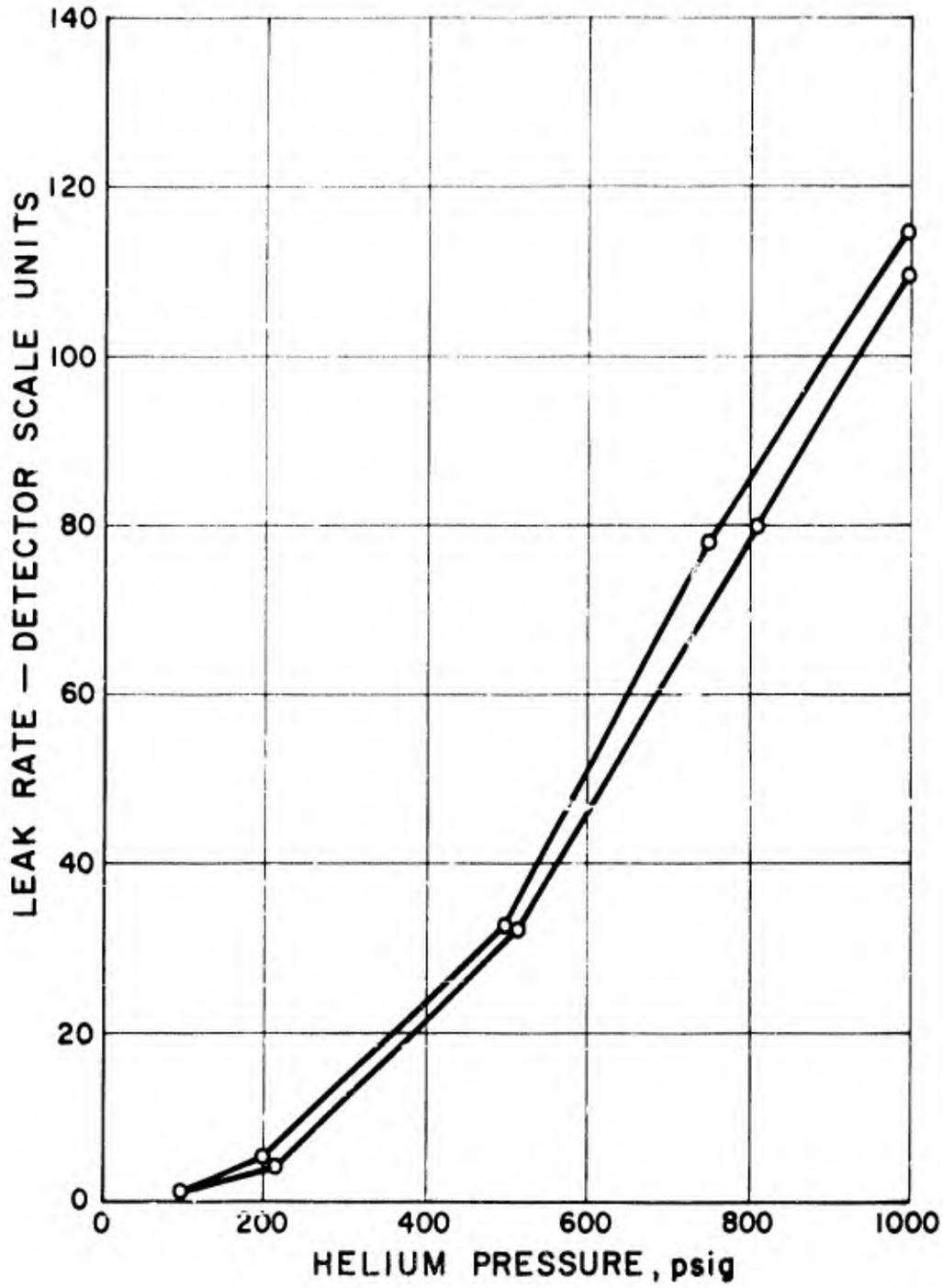


Figure 23 Leak Rate vs Pressure at Room Temperature

Figure 24 gives the temperature, pressure, and leak rate history during 120 minutes required for the seal to warm from 170 to 270 K. From 170 to 190 K there was essentially zero leak, even though the helium pressure was raised to 1000 psig. When the leak rate meter began to move slightly the pressure was dropped to around 200 psig, but the leak rate continued to increase slowly. After an hour the temperature had reached 225 K and the leak rate peaked at 0.65 scale units. The leak rate then dropped off, indicating an improvement in the seal, probably as the elastomer passed through the brittle to rubbery transition. At 240 K the leak rate was again down to the background level, so the pressure was again raised to 1000 psig. There was no further increase in leak rate. This was unexpected behavior, indicating that the low temperatur cycle had a beneficial effect on the seal. Whatever the explanation may be, the seal at 270 K was now much better than that which had been observed at room temperature before cool down, as shown in figure 23.

After this test the seal was left with 125 psig helium inside the joint and checked again at room temperature on the following day. At 525 psig the leak rate stabilized at 50 to 60 units; at 1000 psig the rate was 200 to 250 units. These rates are somewhat higher than those of the original test before cool down. The seal was disassembled and the thickness measured. It was found that the legs had not been flexed beyond their elastic limit.

An additional test was carried out, using .070 in. cross section O-rings of 60 durometer polybutadiene as the sealing material. As before, the seal showed no detectable leak at 1000 psig and 76 K, but some erratic low level leakage at intermediate and room temperatures.

Upon disassembly it was found that one or both of the metal seal body legs had yielded in bending so that the relaxed "height" or thickness of the body had gone from 0.37 in. to 0.29 in. This shows that the .070 in. 60 durometer O-rings are too "fat", or too hard, or both.

Additional testing of this type of seal body at higher pressures and lower temperatures and with different elastomer O-rings and bands would doubtless prove valuable, but the necessary time has not been available.

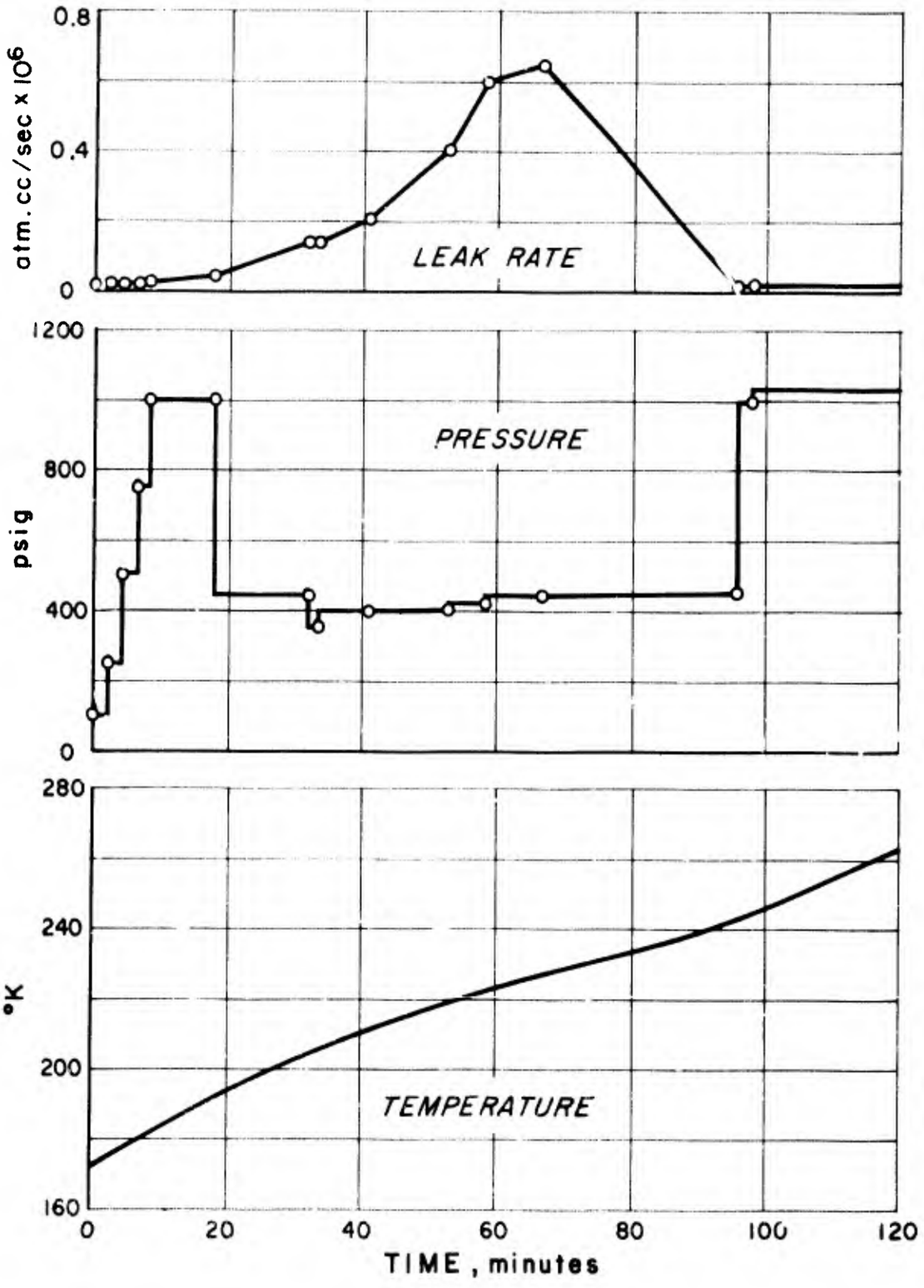


Figure 24 Performance of NBS Axial Seal

2.5 Conical or "Y" Seal

Figure 25 shows shop drawings of a conical or "Y" seal which is pressure actuated and suitable for use with elastomeric O-rings or bands. The seal legs have the same cross section dimensions as those of the axial seal discussed in section 2.4.2, but this seal differs in two important respects: (1) The seal legs make an angle of 45° with the seal axis; thus the sealing force is midway between radial and axial. (2) The seal body is an integral part of a thin flange which clamps between the pipe flanges; this gives the seal a "Y" shape when viewed in cross section.

This is a spring loading pressure energized design. Its advantage over axial seals is the "half radial" configuration which allows lower clamping forces and flanges of smaller diameter for a given seal leg length. At the same time the sealing material is not subjected to the extreme shearing or "smearing" forces which accompany the assembly of a purely radial ring-shaped seal. Soft metal sealing surfaces can flow under strong shearing forces, but elastomers are likely to be shredded or torn.

A difficulty sometimes experienced with ring or hoop-shaped seals is cocking during assembly. The "Y" seal eliminates this problem because of the aligning action of the integral flange.

A "Y" seal having the material and dimensions shown in figure 25 was machined in the NBS shop. Assembly and testing were the same as described for the axial seal in section 2.4.2, i.e., the flanges were silver soldered to short sections of tubing, placed in a vacuum chamber, cooled internally with liquid nitrogen, and tested to 1000 psig with helium gas.

2.5.1 "Y" Seal With Rubber Bands

The first test of this seal was made with sealing rings consisting of size 10 (.030 in. x .060 in. x 2.75 in. circum.) unfilled natural rubber bands. These required approximately 50 percent extension to stretch around the 1.3 in. diameter seal body. If constant volume is assumed, the "stretched" cross section would be approximately .025 in. x .050 in. The width after compression was observed by cooling

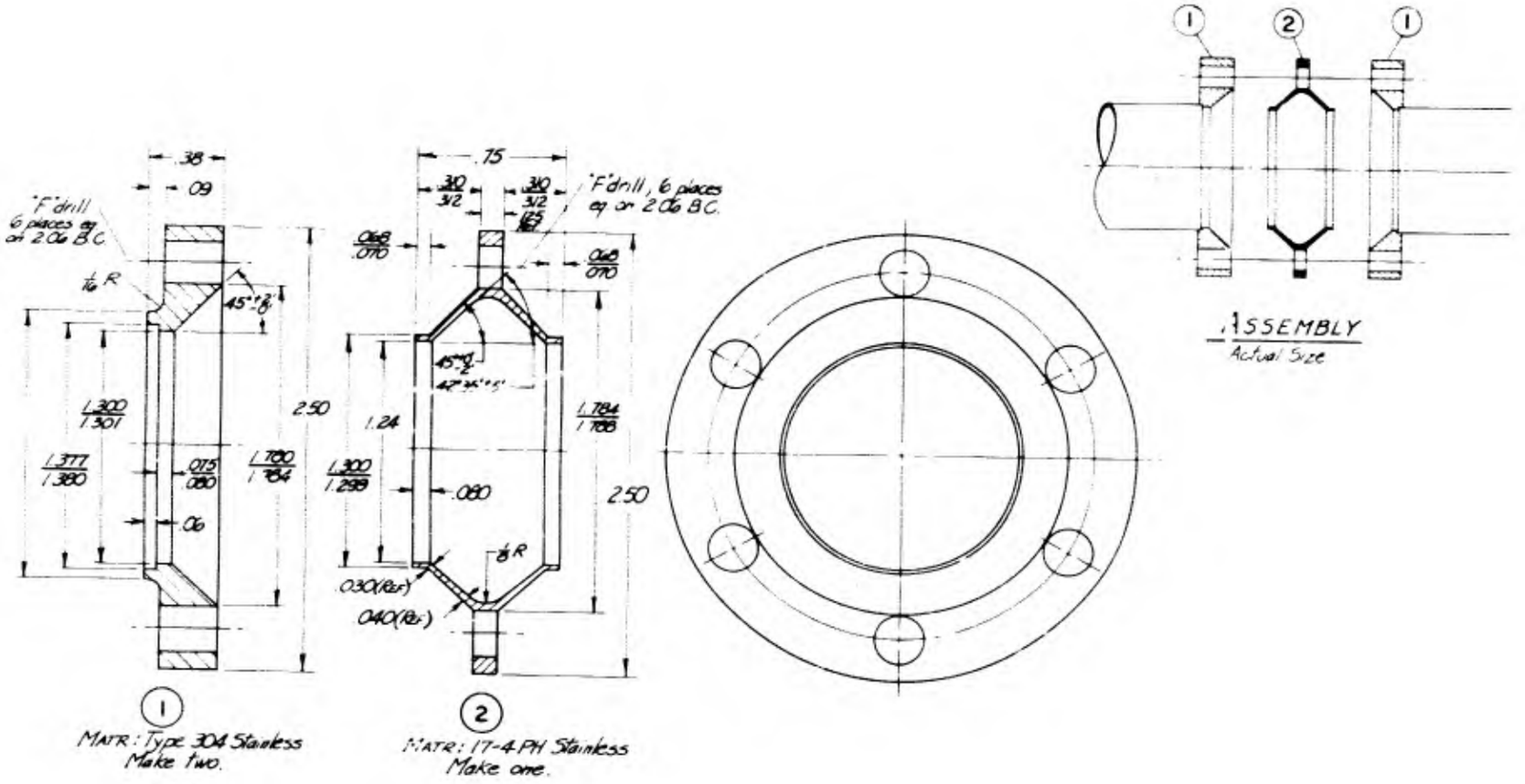


Figure 25· Conical or "Y" Seal.

the assembled seal in liquid nitrogen and disassembling while the rubber was still frozen. The compressed width determined in this way was about 0.11 in., giving a compressed thickness of about .016 in., or approximately 50 percent compression when compared with the original thickness of .030 in. This also indicates that the seal legs deflected approximately .016 in.

During the first room temperature test a slight leak began at 100 psig and slowly built up to 0.2 scale units (0.2×10^{-6} atm cc/sec) after half an hour. The helium pressure line was then removed, and the blanked off section below the seal was filled with liquid nitrogen for testing at 76 K. The pressure was raised by increments over a period of about an hour and a half when, at 940 psig, there was a sudden high leak rate (above 3×10^{-4} atm cc/sec). After 3 or 4 minutes the pressure was dropped to 500 psig; the seal reseated and remained completely tight at all pressures through 1040 psig.

The seal was then allowed to warm up overnight, with the pressure on it, and next day was leak checked again at room temperature and at 76 K. Figure 26 gives the leak rate and pressure history of the room temperature test and also shows that the seal remained completely tight at all pressures and pressure cycles from 0 to 1030 psig after this second cool down to 76 K. After three hours the seal was still tight; by this time the temperature was estimated to be around 150 to 200 K.

The somewhat erratic behavior of the seal at room temperature is similar to that observed for the axial seal with rubber bands, as discussed in section 2.4.2. Improved seal performance after the first cooldown and pressure cycle was also observed with both of these designs. The unfilled gum rubber bands are very soft in comparison with usual elastomer O-ring materials, posing the possibility of "blow-by" due to distortion of the sealing material when exposed to high pressure. A final freezing before disassembly and examination at the end of the above tests, however, revealed smooth uniform compression of both rubber bands with no evidence of distortion. When the bands warmed to room temperature they regained their original dimensions and showed no sign of mater al failure.

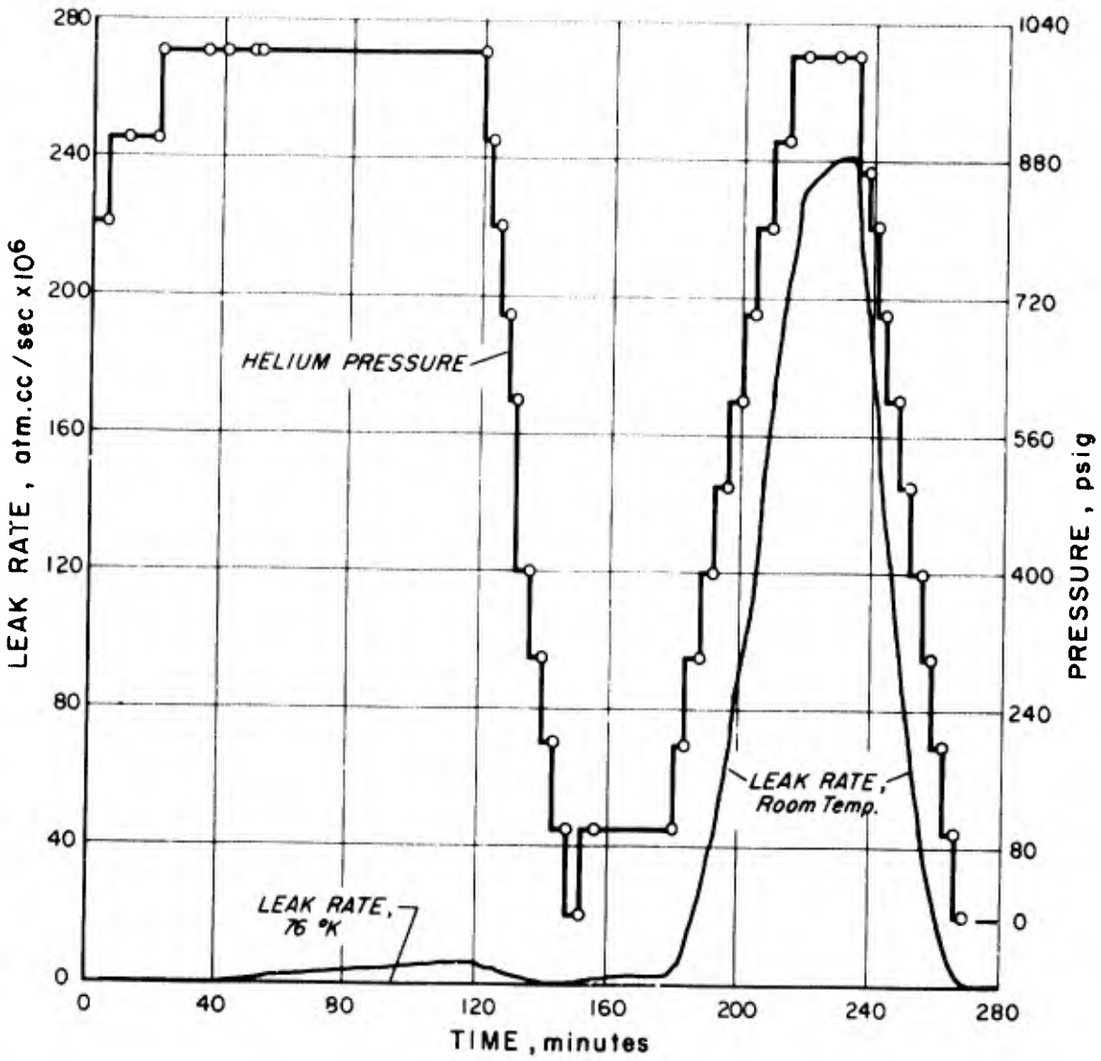


Figure 26 Performance of "Y" Seal With Rubber Band Sealing Rings

2.5.2 "Y" Seal With Indium Coating

Most metal body pressure actuated seals use soft metals or plastics for the sealing surfaces. Since our own experience with indium as a sealing material with various seal designs has been quite good, it seemed worthwhile to make a direct comparison between indium and rubber bands on the "Y" seal body. A fillet of indium was accordingly "tinned" on the seal body and trimmed on a lathe to a band approximately 3/32 in. wide which bridged the corner where the seal is made. The thickness of the indium at the point of compression was about .030 in. before the seal was assembled.

Figure 27 shows the performance of this seal at room temperature and after cooling to 76 K. Comparison with figure 26 shows that indium as a sealing medium on this seal body is somewhat less reliable than soft rubber bands. At room temperature the indium coating leaked more than 3×10^{-4} atm cc/sec at 800 psig; the rubber bands leaked only 2.4×10^{-4} atm cc/sec at 1000 psig. At 76 K both seals were tight but the indium began to leak during warmup after reaching a temperature of about 200 K. The rubber bands showed no detectable leak during a similar warmup period.

Of course neither of these sealing media has been explored in depth, but the design concept of the "Y" seal body appears to be sound. The next test will be made with standard .070 in. cross section diameter elastomer O-rings on the "Y" body.

2.6 Radial Seals

A diagram of a purely radial seal of extremely simple design is shown in figure 28. The seal body is simple a squarely cut section of tubing, its length depending on the diameter of the fitting and its wall thickness depending on the material used and the pressure to be confined. The inner circumference of the flanges are machined with a straight section followed by a slight taper and a stop. The straight section makes a snug fit with the O. D. of the sealing ring and holds the ring in axial alignment before compression begins. Further tightening of the flange bolts exerts strong compressive forces at the ends of the cylinder as it slides along the taper. This shearing and compression makes the seal, and the stops at the ends of the taper assure an accurate final alignment of the flexed seal body. The length of the tube is slightly less than the final distance between the stops.

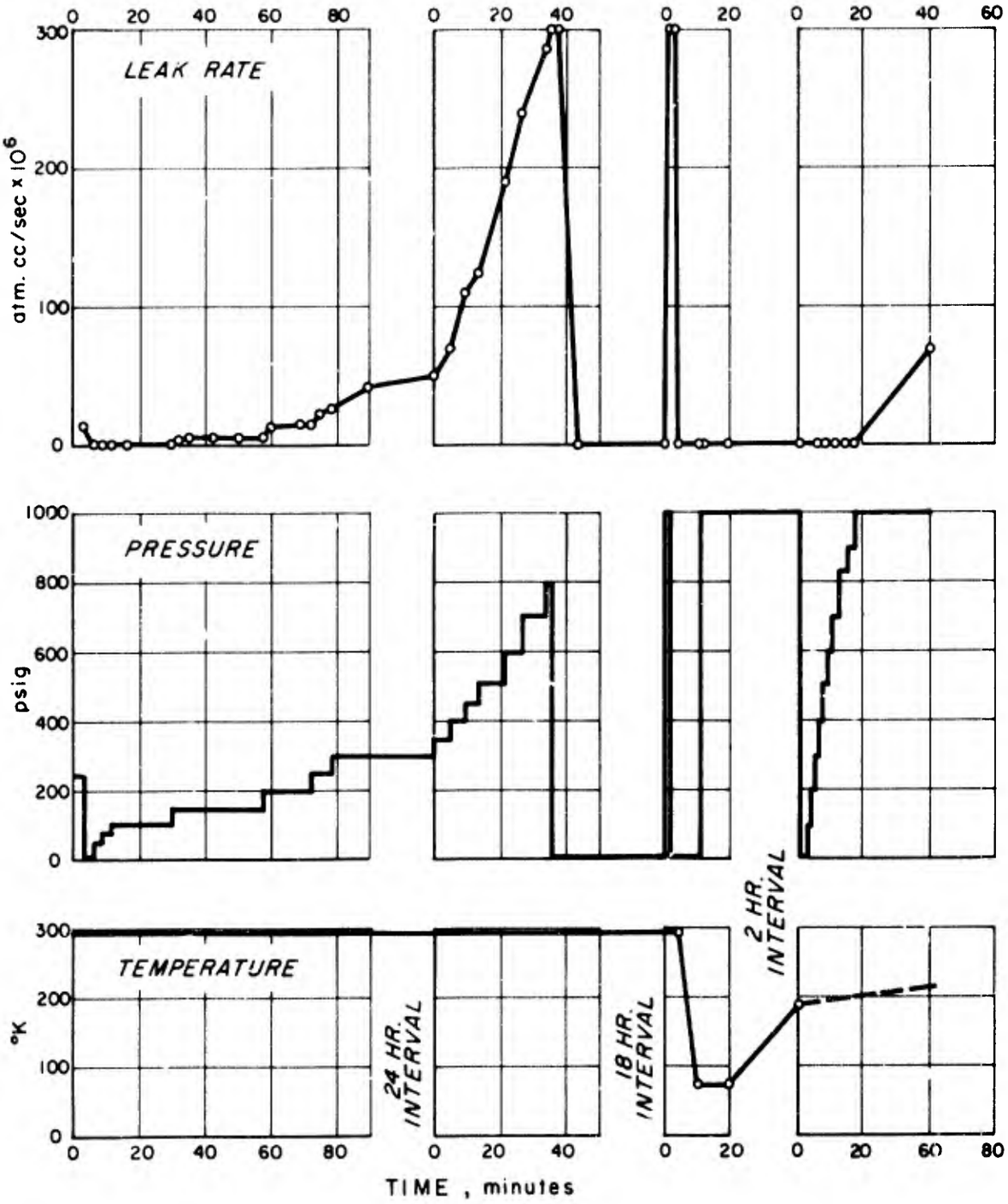


Figure 27 Performance of "Y" Seal With Indium Sealing Surfaces

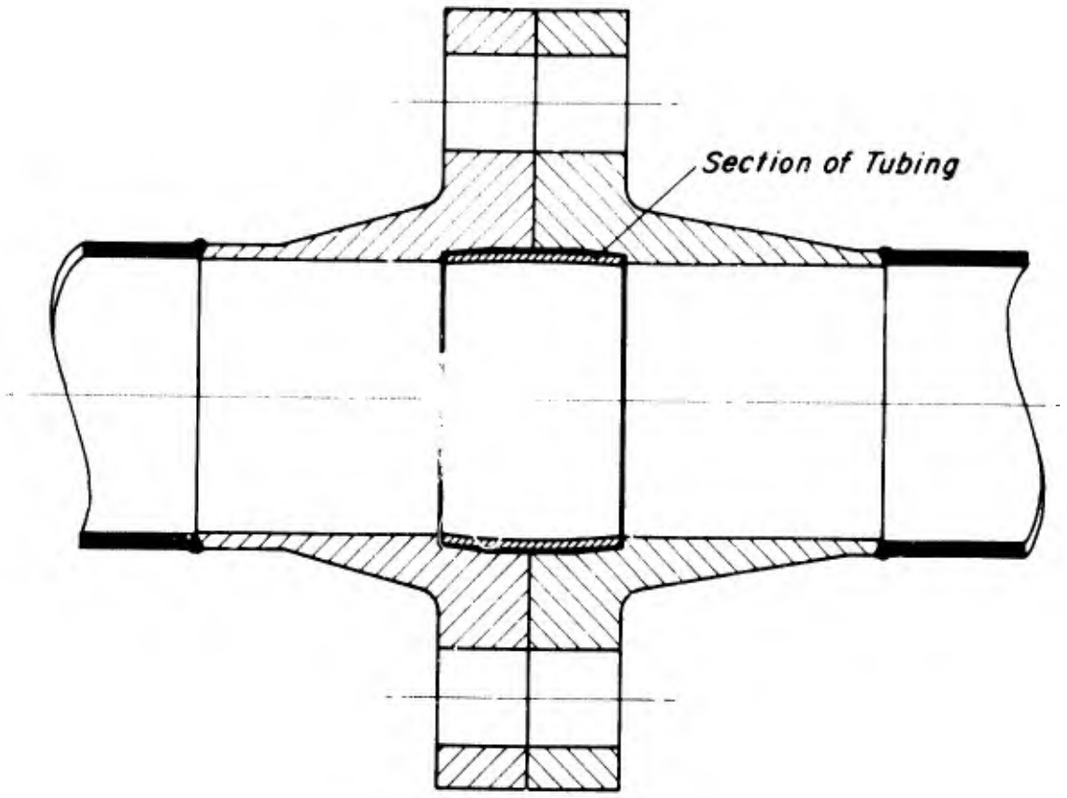


Figure 28 Simple Radial Seal

This allows complete flange closure without restricting radial motion at the ends of the seal body. Clamping forces are very small because of the high mechanical advantage of the taper (about 6°). The final configuration is spring loaded to the elastic limit of the tube material, and pressure energized with a large multiplication factor. Flange diameter (and weight) can be held to an absolute minimum because sealing forces are radial and the seal body requires about the same annular space as the walls of the pipeline.

If such a radial seal body is made of copper, it is possible that no plating or coating of softer material will be required at the sealing surfaces. There should be some yielding of the copper at the ends of the compressed tube; this will be backed up by unyielded copper which is progressively stressed from its elastic limit near the ends of the tube to well within its elastic limit at the center. Copper, indium, or gold plating on a stiffer ring material such as steel or beryllium copper are other simple and attractive possibilities. In a similar manner the seal ring could be coated with tetrafluoroethylene or an elastomer. For soft coatings the outside corners at the ends of the seal body should be rounded to spread the load and to prevent cutting through the coating.

A more serious problem with an elastomer coating has been mentioned before: the elastomer may tear or peel under the strong shearing stresses which accompany assembly of the seal. A suitable lubricant, either dry or in the form of grease, may be effective for solving this problem.

If the radial seal body can be made of the same material as the confining flanges, the problem of different thermal expansion rates during cooldown and warmup should be largely eliminated. For a coated ring the sealing material will have its own expansion rate, but since it is very thin and in intimate contact with the parent metal, it probably will not slip and unseat after the initial seal is made.

A slight variation of this simple radial seal idea is shown in the dimensioned drawing of figure 29, which has been machined in the NBS shop and is presently being assembled for testing. A thin flange has been added to the cylindrical seal body, giving the seal a "T" shape when viewed in cross section. The central flange helps hold the seal in alignment during assembly and insures accurate centering between the mating pipe flanges at final closure. It also allows easy disassembly of the joint, accomplished by jacking against the central flange through threaded holes in the main flanges.

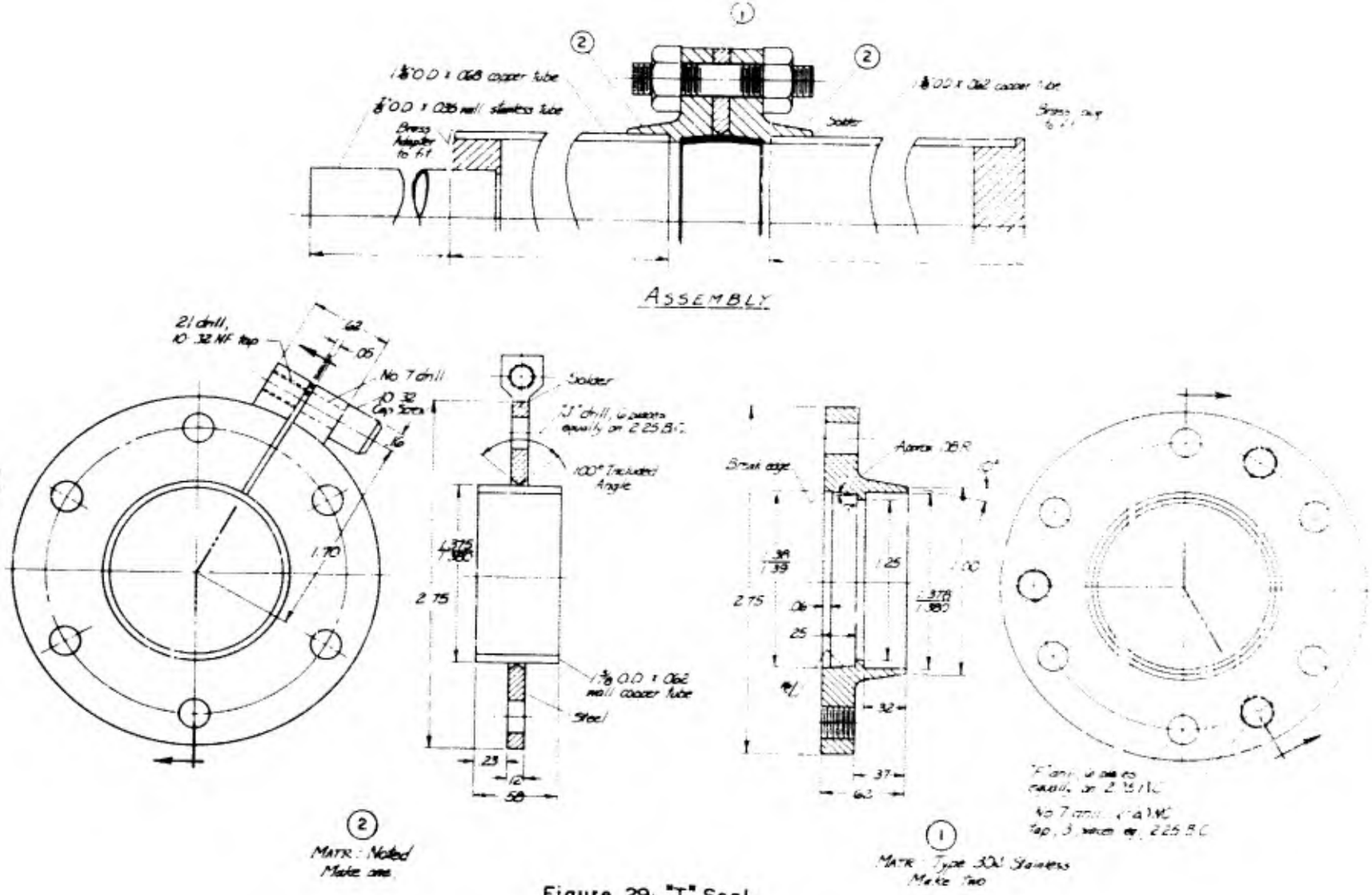


Figure 29. "T" Seal

As shown in figure 29, the central flange is fastened to the sealing ring by mechanical force through a blunt knife edge rather than by soldering. This is a convenience which allows easy variation of sealing rings, and makes it easy to center the flange on the rings before assembly. Also, there is no danger of changing the temper of the sealing rings since there is no heating. Another advantage is the possibility of releasing the grip on the ring just before final closure of the flanges in order to allow full use of the pressure of the confined fluid to actuate the seal.

3. FILMS AND BLADDERS

3.1 Introduction

The transfer of cryogenic fluids from storage to the combustion chamber is a major problem of space propulsion systems. This problem does not exist in ground support systems since heavy pumps or pressurization systems are allowed. The weightless condition in space further complicates the problem. A simple scheme for performing transfer is to expel the fluid by pressurizing a flexible bladder which either surrounds the fluid or is collapsed in the storage vessel. In either case pressurization will cause expulsion of the fluid even in the weightless condition.

The search for suitable materials for bladders that will collapse and expand at cryogenic temperatures has been restricted to thin films of plastics. Various laminated structures have been investigated[24], but a completely satisfactory solution to the problem has not yet been found. We have conducted a limited feasibility study on thin film elastomers for possible use as expulsion bladders.

3.2 Low Temperature Flexibility of Thin Films

Below the glass transition temperature elastomers are quite brittle, and lack the toughness of many plastics such as tetrafluoroethylene. However, brittleness does not preclude use of elastomers as expulsion bladders per se. Considerable flexibility can be achieved in thin films below the glass transition, as will be readily seen by the following analysis[25]. Consider the stresses in the following cross sections of a material bent to radius r, as shown in figure 30. Bending of the film causes tension of the outer surface and compression of the inner surface, while the circle of mean radius r remains unstressed. The radius over which the film can bend without failure depends upon the ultimate tensile strength σ_u and Young's modulus E_y in the following manner:

$$E_y = \sigma/\epsilon = \sigma_m \Big/ \left[\left(\left(r + \frac{t}{2} \right) \phi - r\phi \right) / r\phi \right] \qquad (1)$$

which reduces to:

$$r_m = \frac{E_y t}{2\sigma_u} \qquad (2)$$

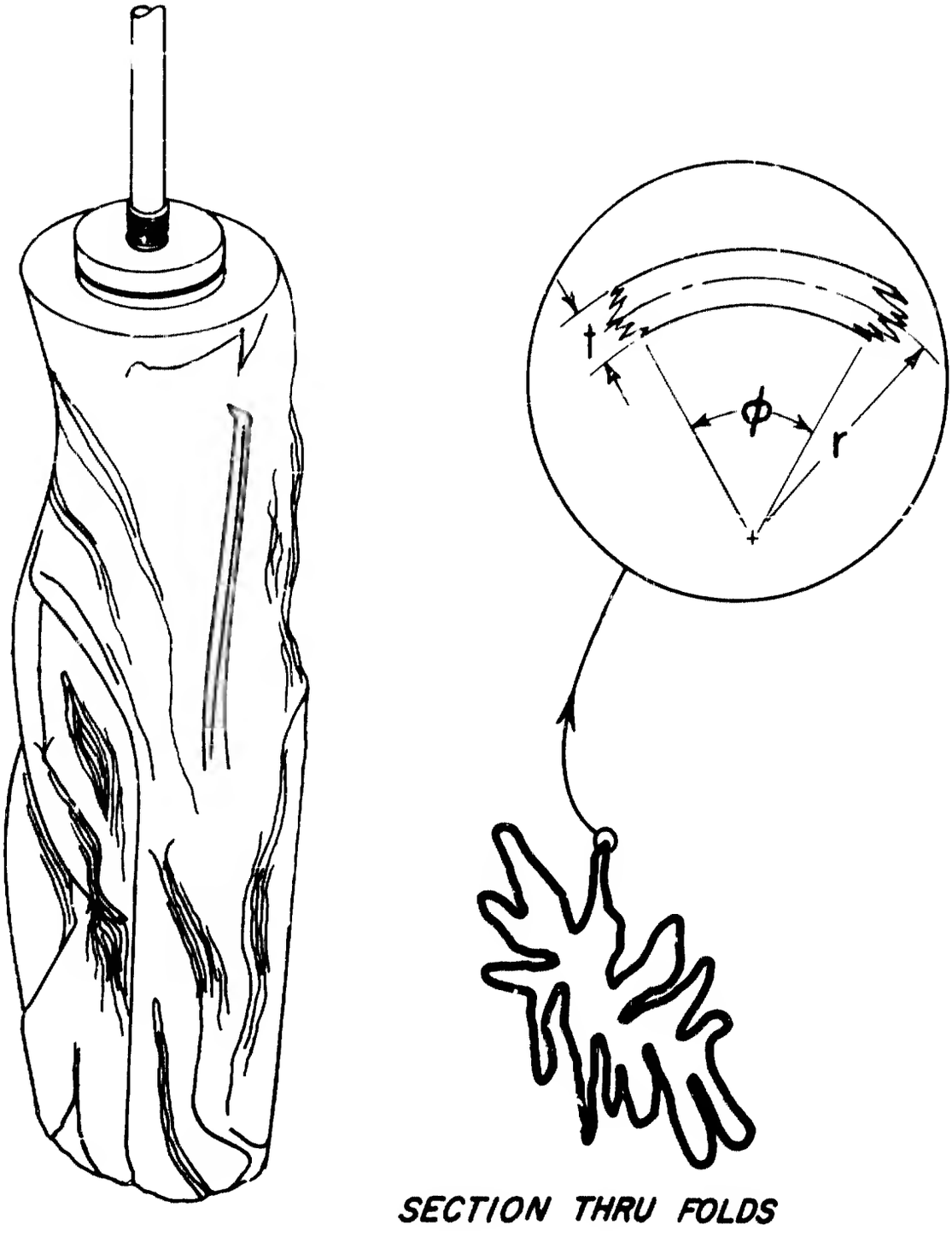


Figure 30 Expulsion Bladder Representation

The minimum bending radius r_m is seen to be proportional to the film thickness t. At 76 K estimates of E_y and 0_u for neoprene are 1×10^6 and 1×10^4, respectively. Therefore a .001 in. film should not fail if the minimum radius of curvature is above 0.05 in.

Thus elastomers may theoretically be used for expulsion of cryogenic liquid if film thickness and bending radius are kept within limits which do not appear to be unreasonable.

3.3 Film Evaluation

A preliminary evaluation consisted of three increasingly severe mechanical tests while the sample was immersed in liquid nitrogen. These were:

(1) Simple folding 180°
(2) Folding 180° and creasing the fold
(3) Folding 180° and creasing, then folding 180° and creasing the second time perpendicular to the first fold.

The above tests were tried on an eight to twelve mil sample of compression molded natural rubber film. The sample was immersed in liquid nitrogen and could be folded 180° without breaking, but would break in two when an attempt was made to crease the fold.

The same samples were then stretched about 200% and frozen in this thinner configuration. In this thinner form it was possible to perform all three of the above tests but the sample would always crack during test number three (double creasing).

These samples were much thicker than the desired one to two mils, and the tests were not very discriminating. A more discriminating test approximating an actual bladder application was devised. An apparatus was constructed wherein the elastomer film could be inflated to a hemispheric shape, frozen in this configuration, and then alternately collapsed and pressurized while immersed in liquid nitrogen. This test apparatus is shown in figure 31.

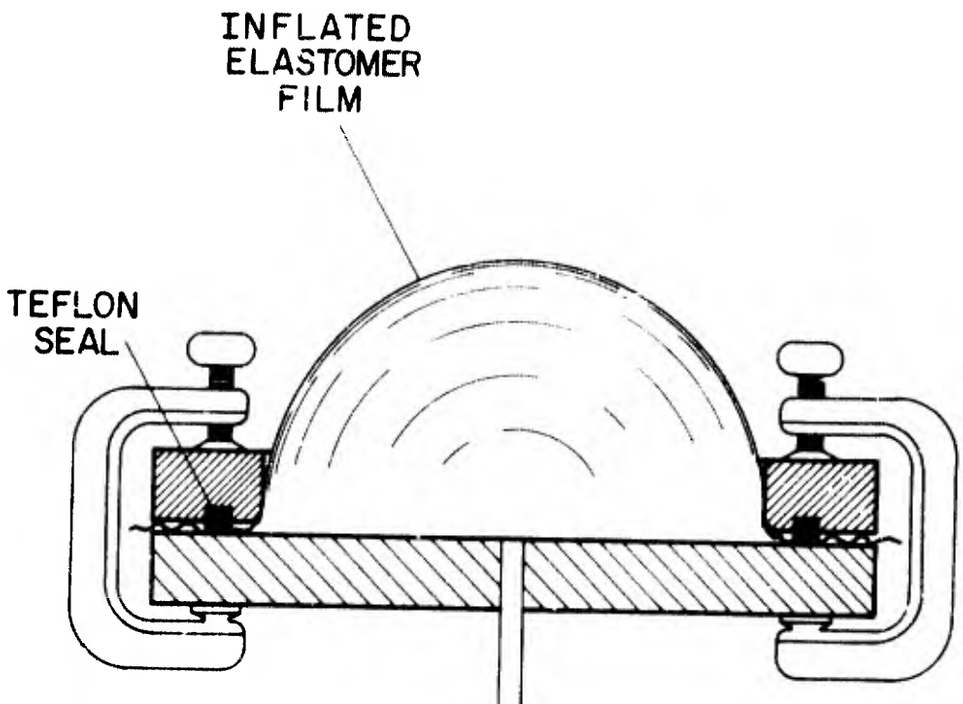


Figure 31 Elastomer Film Test Apparatus

An elastomer film was clamped between a brass plate and a brass ring with the aid of a Teflon seal ring and small "C" clamps, as shown in figure 31. A copper tube through the plate could be connected either to vacuum or to a helium gas supply. The film was inflated to a hemispheric shape, then cooled below T_g in this shape with cold nitrogen gas, and finally immersed completely in liquid nitrogen.

After immersion, the sample was cycled by evacuating the helium gas and collapsing the hemisphere, then pressurizing with helium to inflate the sample back to the hemispheric shape.

Two tests were made using eight to twelve mil compression molded natural rubber film. Small pin holes in the film were sealed with RTV silicone. Each sample developed cracks during the collapsing phase of the first cycle. This depleted the eight to twelve mil sample material and no more tests were made with film of this thickness.

A thicker (16 to 19 mil) cast film sample was tested but this sample developed a large crack as it was being immersed in liquid nitrogen.

Additional samples of neoprene and Viton gum stock were obtained from the Air Force Materials Laboratory. The samples varied in thickness from six to eighteen mils, and the thickness of a given sheet was constant within ± two mils. No pin holes were visible in these films.

All of these samples were successfully cooled in the hemispherical shape without failure, but none survived evacuation at 76 K. For films with a thickness greater than ten mils failure was immediate, and no flexibility was observed. The thinner films would form several dents in the hemisphere without failure, but as soon as a three surface corner developed the critical radius of curvature would be reached and a crack would occur. The Viton molded films seemed to be somewhat more resistant to brittle failure than the neoprene films, which were cast, indicating that the molding procedure is perhaps superior to solution casting in terms of film strength.

It can be concluded from these tests that films greater than five mil thickness fabricated from neoprene or Viton cannot be used for expulsion bladders. Other materials would be expected to behave in a similar manner. The only promise for elastomers in this application would be in laminating several very thin films to provide the needed strength with maximum flexibility. Future work should be restricted to testing of films less than three mil thickness, with a goal of several laminated layers each less than one mil in thickness.

Viton is probably a good choice of base polymer, but it would also be interesting to test a silicone film made from gum stock, which might facilitate thin film fabrication due to the gum silicones viscous consistency at room temperature. If films less than three mils thick cannot be fabricated, the evaluation of elastomers for use as expulsion bladders should be terminated.

4. SOME STUDIES OF ELASTOMER PROPERTIES

This section summarizes brief studies which have been conducted during the past year in four areas of elastomer properties. The first area is creep, or the change in linear dimension which takes place when an elastomer is held in a stressed condition for an extended time interval. Creep is clearly related to the use of highly compressed O-ring seals.

A second property of interest is thermal expansion, which also can be related to elastomer seal applications, but the concern here is with large temperature changes rather than time intervals. The effects of fillers and chain orientation are examined as possible parameters for control of thermal expansion rates.

A third property for continued study is the important brittle transition which occurs in all elastomers at some characteristic temperature between normal ambient and cryogenic. A brief study of this and other transitions was carried out, using differential thermal analysis as the technique of observation.

The last property studied during the past year was ball rebound resilience, and in particular the variation of resilience with temperature. This effort has resulted in the development of an apparatus which automatically generates and records data for the construction of temperature vs. resilience plots.

4.1 Creep of Elastomer O-Rings

What is the storage life of a highly compressed elastomer seal? For how long can the better compounds be considered reliable? Creep and stress relaxation are properties directly related to the sealing pressure a highly compressed O-ring can maintain over a period of time.

Previous stress relaxation tests have indicated that compounds with a high cis 1-4 structure consistently show low rates of stress relaxation[3]. These compounds are cis 1-4 polybutadiene, natural rubber, polyisoprene and neoprene. A creep test would give added information to compare with the stress relaxation results and give some indication of the storage life of the better elastomer compounds. With this goal in mind, a test program was initiated.

4.1.1 Procedure and Results

The test apparatus consisted of a high pressure bellows (1000 psig) with a heavy plate on the movable end, as shown in figure 32. An O-ring was compressed between the movable plate and a stationary plate by pressurizing the bellows with helium gas. 1000 psig gas pressure exerts 4400 pounds of force on the compressed O-ring and this force was maintained throughout a 15 day test period. The stem of a rigidly mounted dial indicator extended through a hold in the stationary plate to measure the change in thickness of the O-ring during the test period.

The surfaces of the compressing plates and the O-ring were degreased with trichloroethane solvent prior to the test. The top plate was then bolted down to a precise setting, compressing the 1 in. I.D. x 1/8 in. cross section O-ring slightly. The gas pressure was then slowly applied over a three minute period to 1000 psig. Zero time was at the instant the pressure reached 1000 psig, and thickness measurements were taken at intervals during the next 15 days.

The final compressed thickness was measured at the end of the 15 day period. The O-ring was then removed and one hour after removal the final no-load thickness was measured for a compression set determination. Compression set was defined as

$$\frac{\text{Original thickness - final unstressed thickness}}{\text{Original thickness - compressed thickness}}$$

The test results are shown in figure 33 and table 3, and are not inconsistent with stress relaxation data obtained earlier. Cis 1-4 polybutadiene had the least creep of all the compounds tested and this elastomer also has the highest cis 1-4 backbone structure (~ 98%). The ASD polybutadiene compound 61-20-A was tested over the full 15 day period; creep and compression set were very low. A Parco® polybutadiene compound was tested (Parco compound No. 162-60) for comparison with the ASD compound. Since the creep for the first six hours was almost identical, the test was terminated so other compounds could be tested.

® "Parco" is a Plastic and Rubber Products Company Trademark

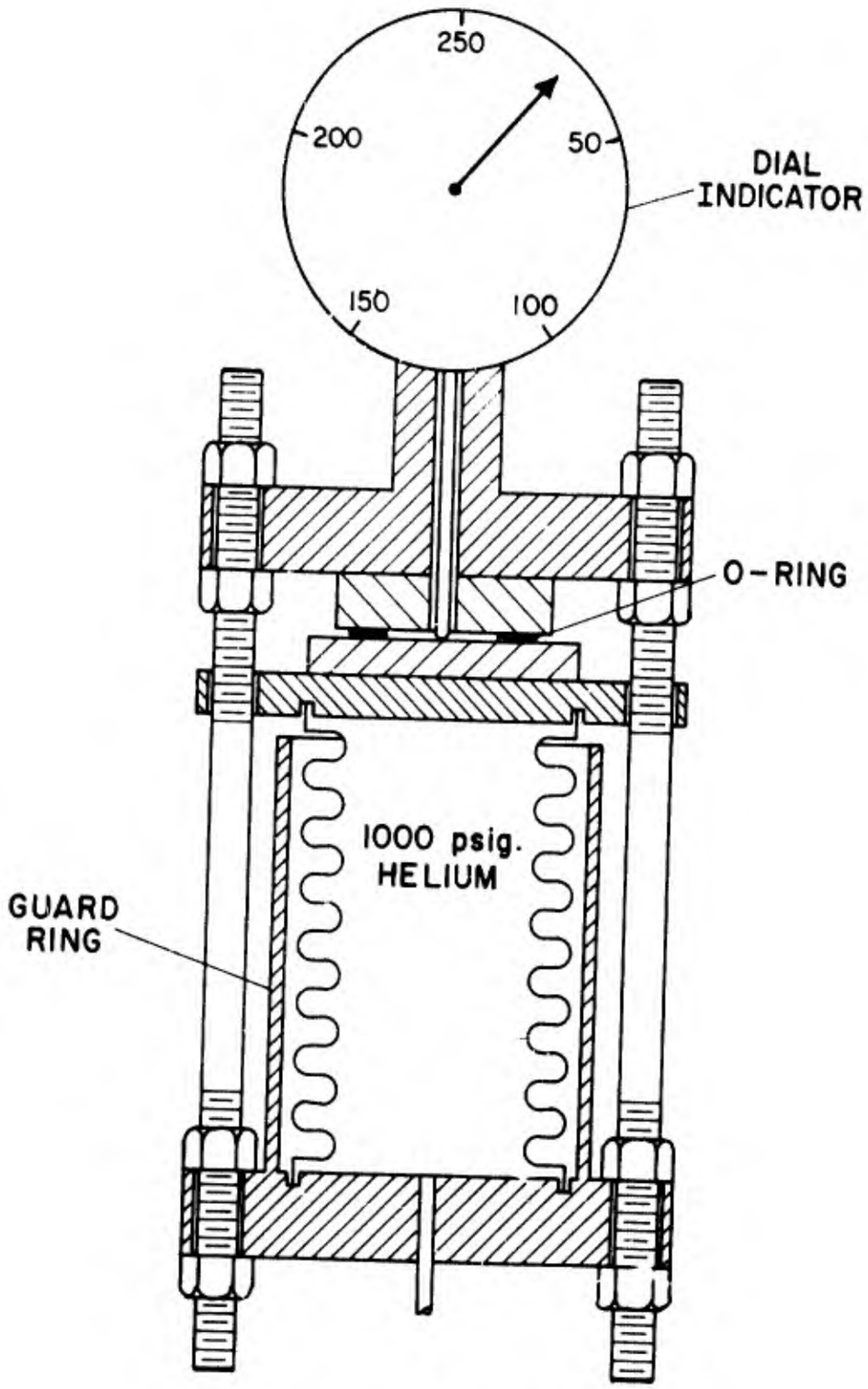


Figure 32 Creep Test Apparatus

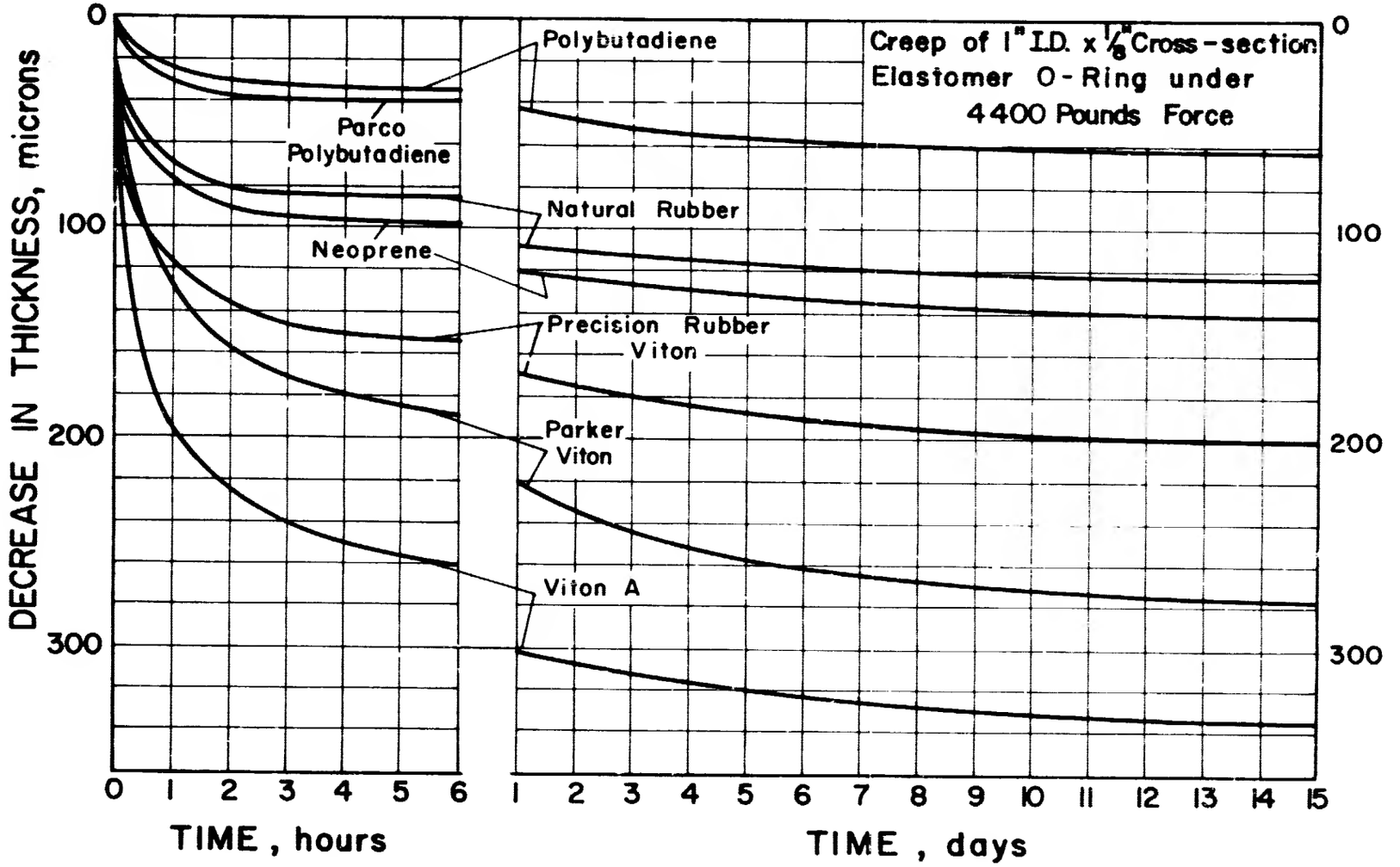


Figure 33 Elastomer O-Ring Creep Test Data

Compound	Hardness	Compression Set *	Final Compressed Thickness	Compound Number
Natural Rubber	66	40%	.035"	ASD(IV-8A)
Neoprene	80	39%	.034"	ASD(IV-8B)
"Viton" A	80	55%	.034"	ASD(IV-8D)
Parker "Viton"	72	27%	.041"	Parker (77-545)
Precision Rubber "Viton"	80	41%	.043"	Precision (ECD-487-X7)
Polybutadiene	67	16%	.035"	ASD(61-20-A)
Parco Polybutadiene	60	Test Terminated After Six Hours		Parco(162-60)

* Compressed with 4400 lbs. force for 15 days at ambient temperature and the final non-compressed thickness measured one hour after removal from test apparatus.

Table 3. Creep Test Data

Natural rubber and neoprene show a little more creep than polybutadiene. Three compounds of Viton were also tested. The ASD compound (IV-8D) had extremely high creep and considerable compression set. This same compound showed high stress relaxation in previous tests[3]. The Parker*Viton recipe is not available, but this compound has somewhat better creep characteristics and considerably better compression set properties than the ASD compound. A Precision Rubber**"Low Temperature" Viton was also tested. Again the compounding recipe is not available, but our test showed less creep than was found for the other two Viton samples.

4.1.2 Summary

Polybutadiene has less creep than any of the elastomers tested to date and most of this creep occurs during the first two hours of compression. Natural rubber and neoprene have slightly more creep and slightly less cis 1-4 structure. High cis 1-4 molecular chain configuration apparently results in low creep as well as low force relaxation under compressive load.

The fluorocarbon elastomers have high creep characteristics and because of this are not recommended for applications which require high stresses (such as cryogenic seals) unless fully confined. If closely confined (as in a tongue and groove flange design) a high rate of creep should have little effect on the sealing ability of the elastomer.

Most of the creep takes place the first two hours after compression and the creep rate of the better elastomers is very low after about two days. This 15 day test tends to indicate that creep and relaxation will not be a serious problem with elastomers having high cis 1-4 chain structure. Longer tests and a more thorough investigation would have to be made in order to determine the maximum storage life of the low creep elastomers.

---

* Parker Seal Company

** Precision Rubber Products Corporation

4.2 Reductions in Thermal Expansion

4.2.1 Low Expansivit, Filler

In the reporting period the continuous linear thermal expansions of two compounds containing the filler Lithafrax® were measured. This filler has negative expansivity at room temperature and, although no information is available, the expansivity is probably negative in the low temperature range as well. Measurements were also conducted on identical compounds not containing Lithafrax, and an analysis of the reduction in expansion was made.

The goal of these efforts is to reduce the expansivity below T_g to the range of metals commonly used for bolt and flange connectors, such as the 300 series stainless steels. If this goal could be achieved and applied to the fabrication of elastomeric O-rings, the shrinkage in the glassy state would no longer cause force decay and radial movement at the seal interface, and much lower initial bolt loading would be required to obtain leak-free cryogenic connectors. Low expansivity elastomers might also find wide use in tank linings, potting systems, and other applications where the high contraction, rather than the brittle nature of the material, precludes its use today.

4.2.1.1 Sample Preparation

Base polymers for the two elastomers tested were Fluorel®, a fluoroelastomer similar to the Viton family, and Hycar®, a butadiene-acrylonitrile copolymer. The compounding recipes are given in table 4. It can be seen that the only difference between the two recipes for each compound is 50 parts by weight of Lithafrax. Some carbon black filler is present in all samples, 25 parts MT black in the Fluorel and 50 parts FEF in the Hycar. The combination of fillers had no noticeable effect on the room temperature rubbery properties of the samples. Curing procedures complied with standard practice in obtaining good rubbery properties, and were identical for samples with the same base polymer. The samples were molded as 2 inch long by 1/2 inch diameter rods to accommodate the existing apparatus, which has been described previously[3].

® "Lithafrax" is a Carborundum Company Trademark

® "Fluorel" is a Minnesota Mining and Manufacturing Co., Trademark

® "Hycar" is a B. F. Goodrich Company Trademark

4.2.1.2 Testing and Results

Since the object of the tests was to determine the effects of Lithafrax filler on expansion, rather than to provide engineering data for the designer, only two tests were performed on each sample and the accuracy of the values is about ±8 percent, not within the limits obtained in previously reported work[3]. All tests were performed during warming after a cooling period of about 2 hours, and for the Fluorel the data were extrapolated from 100 K to 76 K due to some difficulty in obtaining accurate data in this range.

Figure 34 shows the results with the Fluorel samples, with data for 304 s. s.[22] included for comparison. The expansion coefficients obtained from the slopes of the straight lines above and below T_g are shown in the table on the graph. Above T_g the expansivity is reduced 22 percent by the addition of Lithafrax. Below T_g the reduction is 45 percent, and the resulting coefficient approaches that of 304 s. s. This is quite encouraging; how much Lithafrax can be added before the room temperature properties of the material are compromised is not known, but Fluorel should be investigated further.

Table 4. Compounding Recipes

Fluorel

	A	B
Fluorel	100	100
MgO	20	20
MT Black	25	25
HMDA	1.3	1.3
Lithafrax		50

Hycar 1002

	A	B
Hycar 1002	100	100
Zinc OX	5	5
Stearic Acid	1.5	1.5
Sulfur	1.5	1.5
Altax	1.5	1.5
FEF Black	50	50
Lithafrax		50

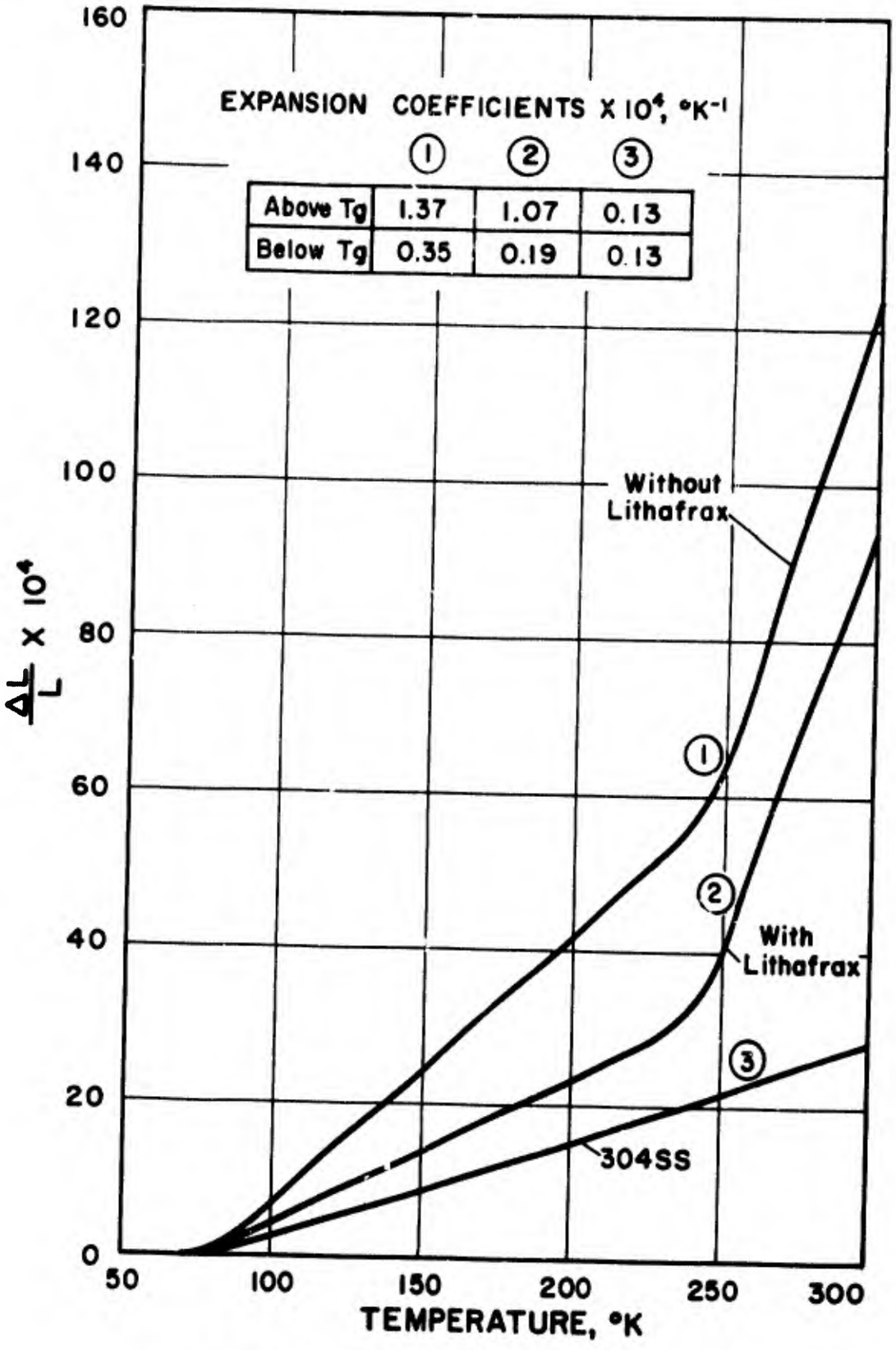


Figure 34 Thermal Expansion of Fluorel

Figure 35 shows results obtained with Hycar 1002. Both above and below T_g the expansivity was reduced by about 38 percent in contrast to the widely different reductions observed for Fluorel. This may indicate that for Hycar the Lithafrax restricts chain movements above T_g and therefore inhibits high elasticity, an undesirable result which could lead to high stress relaxation at room temperature.

4.2.1.3 Analysis of Results

Keeping the above results in mind, it is well to consider the causes for the reduction in expansivity. Lithafrax is a fired, ground lithium-aluminum-silicate powder with a particle size smaller than 325 mesh and a true density of about 2.40 g/ml. In the bulk form, the powder density is about 0.95 g/ml. When this powder is mixed with the elastomer it does not bond to the long chain molecules, but takes up space around which the chains must move. An approximate method of calculating the effect of the filler on the thermal expansion is to separate the parts and consider the sample as a rod with two segments, whose equivalent lengths are determined by the respective volumes of the filler and polymer.

Figure 36-A shows a model of the true samples with the filler particles intermixed among the long chain molecules. In figure 36-B the model used to calculate the effect of the filler is shown, with the filler separated from the polymer. The total linear contraction in the lengthwise direction is assumed equal for the two models, that is:

$$L_T = L_R + L_F, \quad (1)$$

and

$$\Delta L_T = \Delta L_R + \Delta L_F, \quad (2)$$

$$\frac{\Delta L_T}{L_T} = \frac{\Delta L_R + \Delta L_F}{L_T}, \quad (3)$$

$$L_R = 2 - L_F, \quad (4)$$

where L_R = the length of the unfilled part

L_F = the length of the filler

L_T = the filled sample length

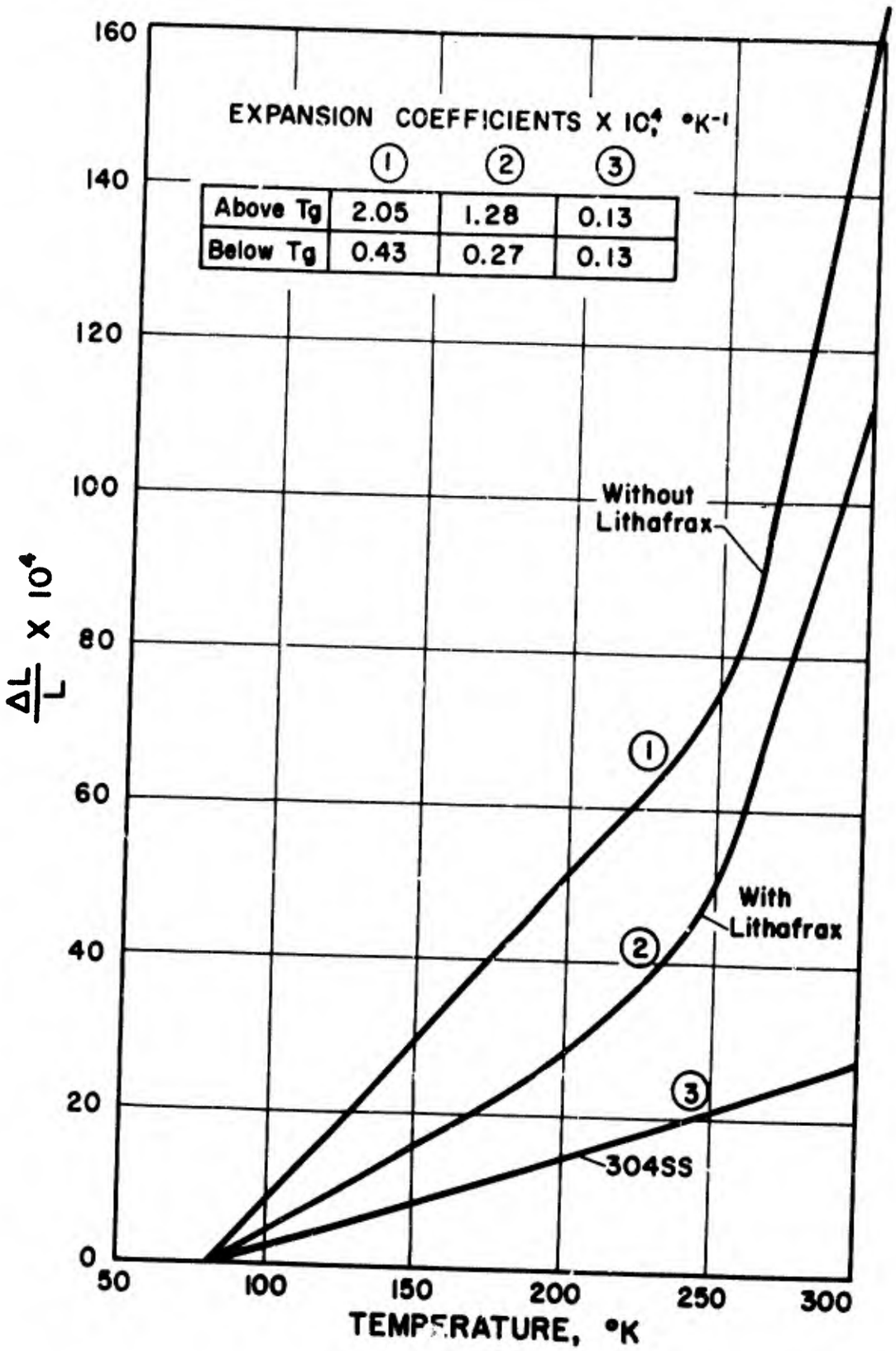


Figure 35 Thermal Expansion of Hycar

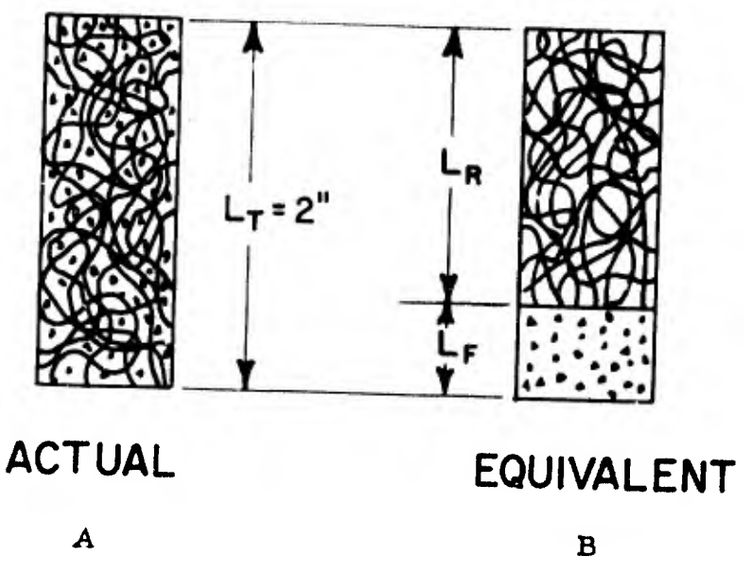


Figure 36 Models for Expansion Representation

since $$\alpha_F = \frac{1}{L_F} \frac{dL_F}{dT} \quad (5)$$

and $$\alpha_R = \frac{1}{L_R} \frac{dL_R}{dT}$$

it can be shown that the expansivity (α) of the filled sample depends on the expansivities of the filler and the unfilled sample in the following manner:

$$\alpha_T \text{calc} = \alpha_R - \frac{V_F}{V_T} (\alpha_R - \alpha_F) \quad (6)$$

where $\frac{V_F}{V_T}$ is the volume fraction filler in the sample

V_F is calculated from $V_F = (W_T)\left(\frac{W_F}{W_T}\right)\left(\frac{1}{\rho_F}\right)$ (7)

where $\frac{W_F}{W_T}$ is the weight fraction filler and ρ is the filler density.

Therefore the calculated expansivity depends on the density chosen to represent the filler. If the filler particles are completely "wetted" the true density of the particles should be representative of the volume occupied. However, the particle size is large enough to expect some void space around the particles, and the bulk density of the filler may accordingly represent the occupied volume more accurately.

Table 5 compares experimental results of expansivities of filled samples above and below T_g with values calculated from equation 6, using both true and bulk densities in equation 7. It can be seen that the bulk density values are in closer agreement in all but one case, and this indicates that the particle size should be reduced to promote more intimate contact between filler and polymer. This could allow more Lithafrax to be used, to lower the expansivity further, without loss of the desirable room temperature rubbery properties of the polymer.

Table 5. Experimental vs Calculated Expansion Coefficients

	Fluorel		Hycar	
	above T_g	below T_g	above T_g	below T_g
α exp, unfilled	1.37×10^{-4}	0.35×10^{-4}	2.05×10^{-4}	0.43×10^{-4}
α exp, filled	1.07×10^{-4}	0.19×10^{-4}	1.28×10^{-4}	0.27×10^{-4}
α calc, filled[(a)]	1.06×10^{-4}	0.27×10^{-4}	1.78×10^{-4}	0.37×10^{-4}
α calc, filled[(b)]	0.64×10^{-4}	0.16×10^{-4}	1.38×10^{-4}	0.29×10^{-4}

(a) using true filler density of 2.4 g/ml
(b) using bulk filler density of 0.95 g/ml

4.2.1.4 Conclusions

It has been shown that addition of Lithafrax filler reduces the expansivity of Fluorel and Hycar significantly. Analysis of the results in terms of a simple model indicates that the Lithafrax particles are somewhat larger than optimum, and therefore a smaller particle size combined with larger weight fractions of Lithafrax could reduce the expansivity below T_g to values approaching that of the 300 series stainless steels. It is recommended that this approach be included in future thermal expansion testing, together with the chain orientation work currently in progress.

4.2.2 Linear Thermal Expansion of Oriented Polymers

In the reporting period a study of length changes with temperature of neoprene WRT was carried out. Six compounds of this base polymer were prepared by Gates Rubber Company of Denver, under the supervision of Mr. H. Tramutt, acting on suggestions of NBS personnel. The parameters varied in the samples were filler content and chain orientation.

Thermal expansion curves for the temperature range 76 K to 300 K are presented here, and a discussion of the changes in expansivity due to chain orientation and filler variation is given.

4.2.2.1 Sample Preparation

Previous efforts to determine the effect of chain orientation on thermal expansion were restricted to measurements on a single sample provided by AFML. The results of these tests were discussed in the 1963 summary report,[3] and prompted further efforts to obtain oriented samples for test. The Gates Rubber Company realized the possible potential for an elastomer of very low expansivity, and contributed samples of neoprene WRT, each with different combinations of chain orientation and filler content.

The three unoriented samples were compression molded in 1 inch by 5/8 inch diameter molds, and cured 3 hours at 300 F. The oriented samples were partially cured at 160 F without stress, then stretched 100%, and cured to completion at 300 F in the oriented position. Comparisons of filler effect were achieved by compounding samples with no filler, samples loaded with 100 parts carbon black, and samples with 100 parts Lithafrax, each cured in both the oriented and the unoriented condition.

Figures 37, 38, and 39 show cross sections of the oriented samples cut parallel to the direction of length measurement. The photographs indicate that the most successful orientation was achieved with the sample filled with carbon black, although no estimate of the degree of orientation can be made since the visual indication is a result of elongated bubbles rather than chain alignment. Since no indication is noticed in the unfilled sample, it may be that the carbon black helps achieve the desired orientation. Figure 40 shows cross sections of the unoriented samples; the only feature worth noting here is the absence of bubble formation, which shows that the curing procedure was superior for these samples.

4.2.2.2 Experimental Results

The results are shown in figures 41 and 42. which are plots of unit expansion versus temperature from 76 K to 300 K. Curves 1 and 2 of figure 41 show expansion of the unfilled samples, curve 1 unoriented and curve 2 oriented. It can be seen that chain orientation reduced the expansivity below T_g as expected. Curves 3 and 4 are samples loaded with carbon black, the oriented compound (curve 4) again having lower expansivity.

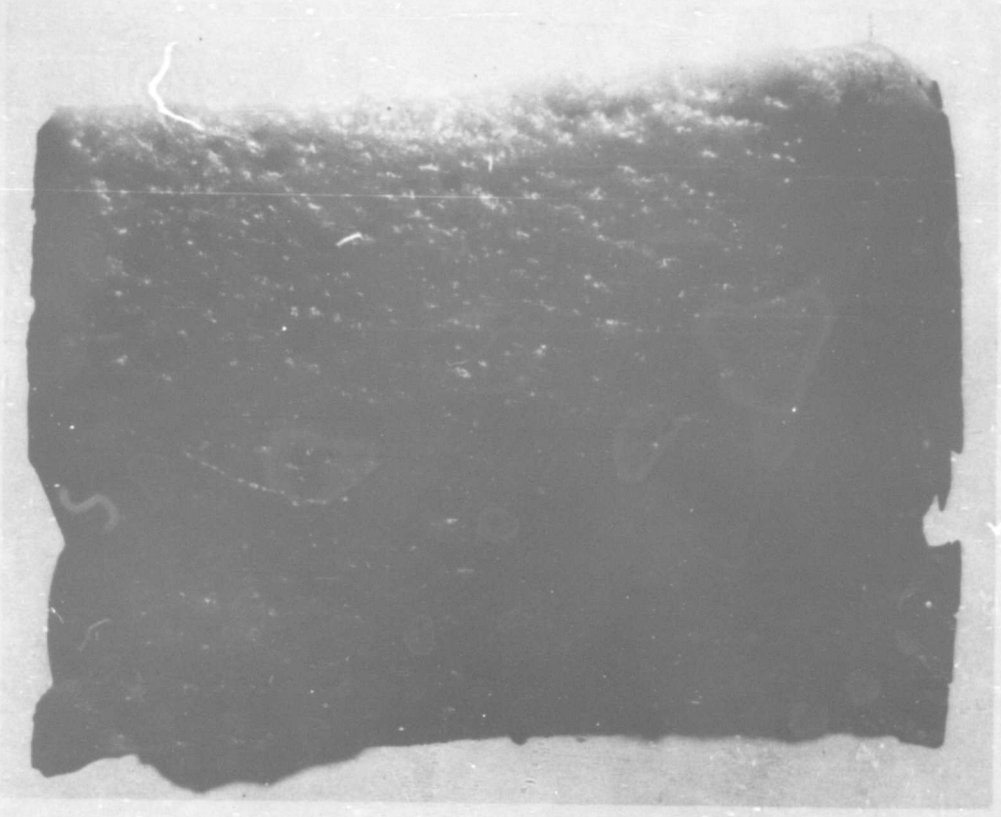


Figure 37 Oriented Gum Neoprene WRT - 11X

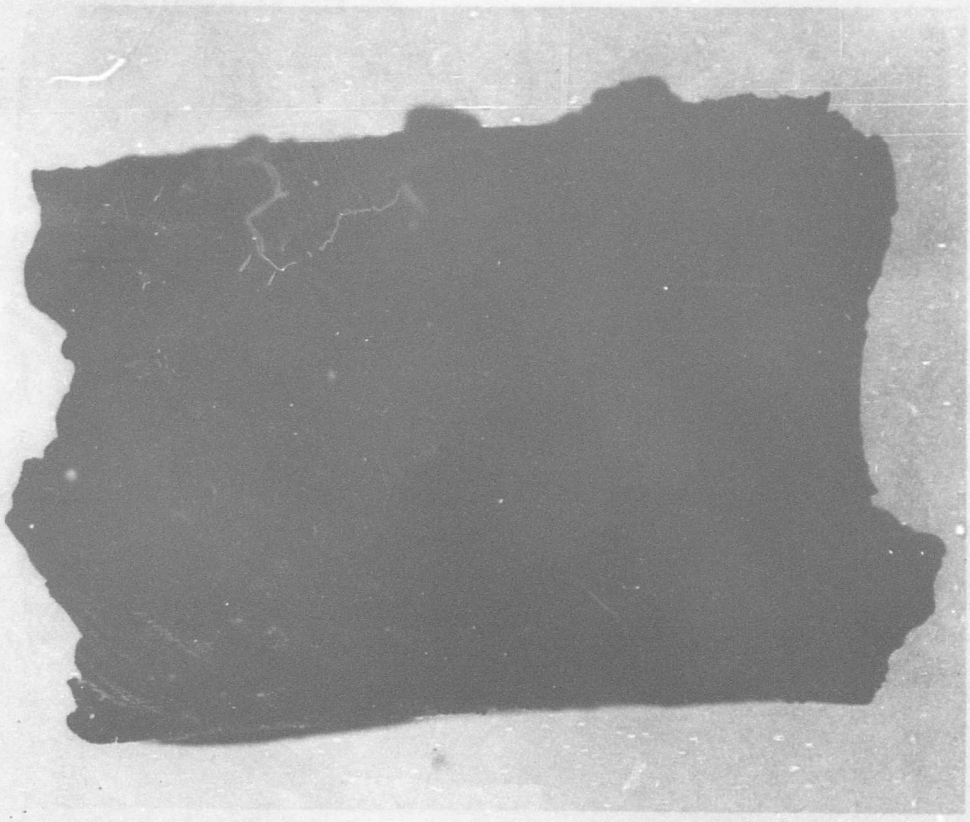


Figure 38 Oriented Neoprene WRT With Lithafrax Filler - 11X

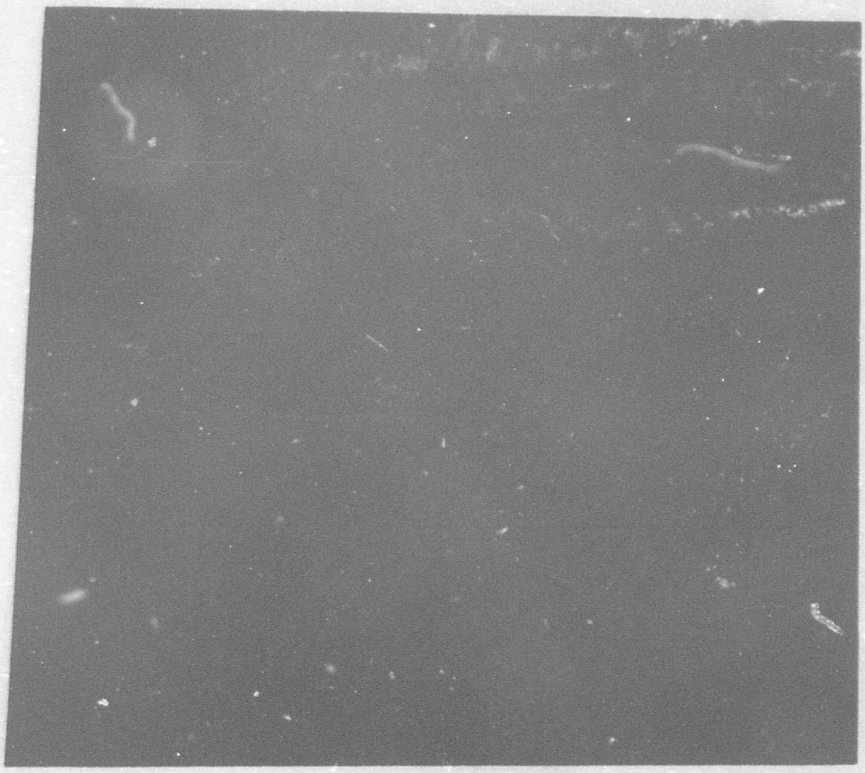
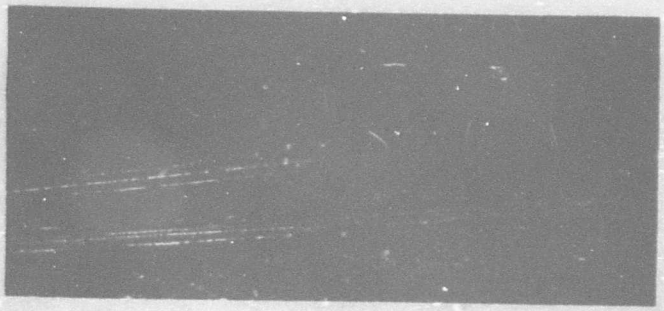
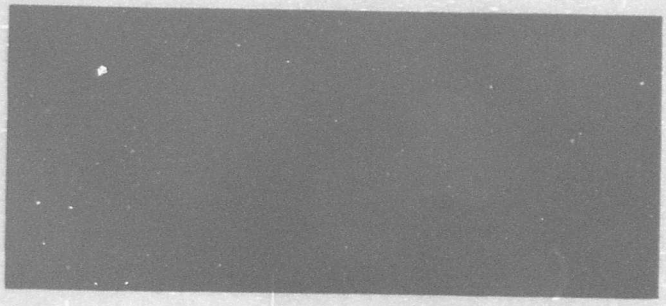


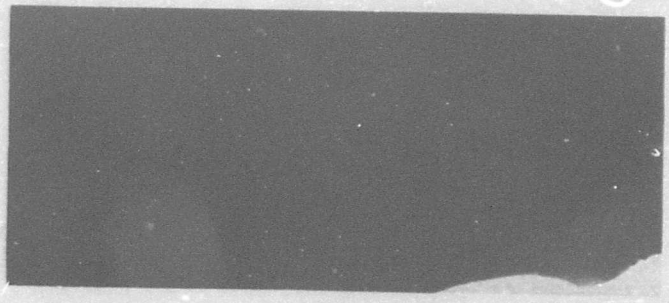
Figure 39 Oriented Neoprene WRT With Carbon Black Filler - 11X



A. Carbon Black Filled



B. Lithafrax Filled



C. No Filler

Figure 40 Unoriented Neoprene WRT Samples - 11X

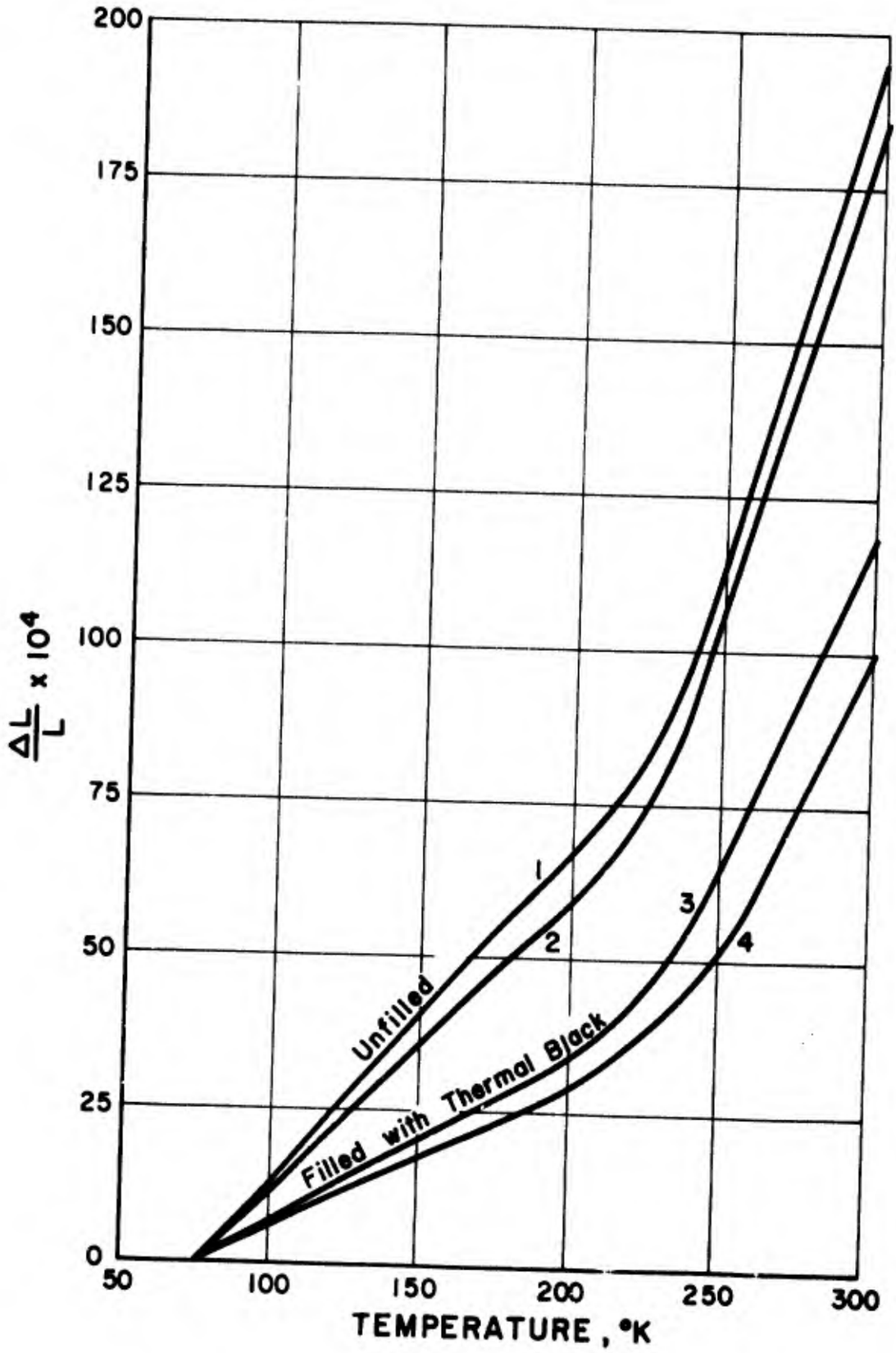


Figure 41 Linear Thermal Expansion of Neoprene WRT - Gum and Carbon Black Filler

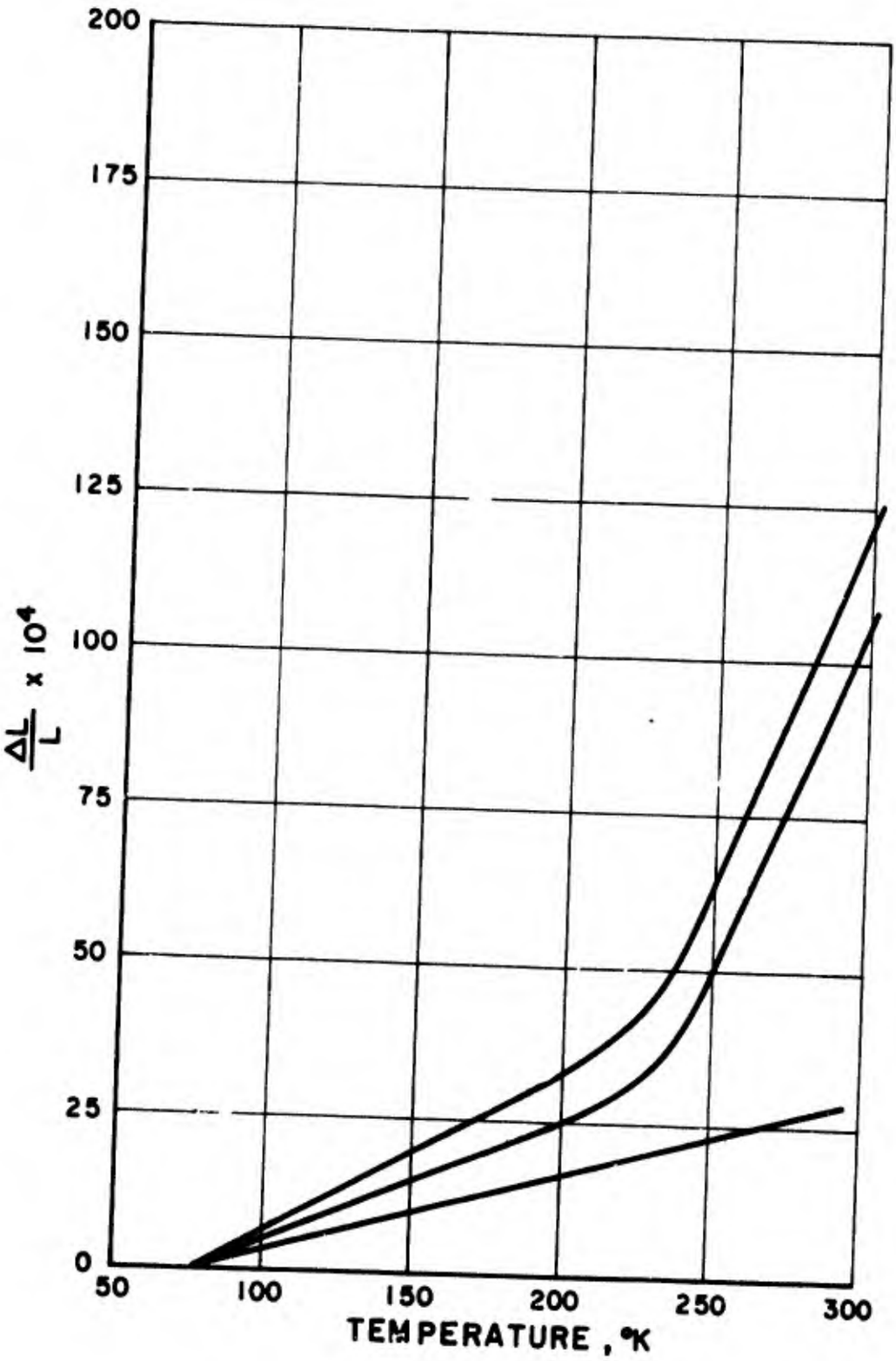


Figure 42 Linear Thermal Expansion of Neoprene WRT - Lithafrax Filled

It was expected that the samples loaded with Lithafrax a filler with a negative expansion coefficient at room temperature, would experience the smallest dimension changes with temperature change. However, the results (figure 42) indicate little improvement over the curves for carbon black.

Table 6 summarizes the results by presenting coefficients of linear thermal expansion of the six samples above and below the glass transition temperature. The lowest value achieved, $.19 \times 10^{-4}/°K$ for the oriented Lithafrax filled sample below T_g, is still considerably more than the expansion of stainless steel. However progress has been made, and the goal is in sight.

Table 6. Coefficients of Linear Thermal Expansion of Neoprene WRT

	Unfilled	Lithafrax Filled	Carbon Black Filled
unoriented, above T_g	1.63×10^{-4}	1.15×10^{-4}	1.26×10^{-4}
unoriented, below T_g	0.53×10^{-4}	0.26×10^{-4}	0.26×10^{-4}
oriented, above T_g	1.57×10^{-4}	1.12×10^{-4}	0.97×10^{-4}
oriented, below T_g	0.47×10^{-4}	0.19×10^{-4}	0.23×10^{-4}

4.3 Studies of Transitions

Study of the glass transition (T_g) continues to be an important part of the effort described in this report. The most valuable result achieved in the reporting period is the refinement of an apparatus to measure T_g with controlled pressure environments. The apparatus will be described, and results in the pressure range from 10^{-4} mm Hg to 350 psi will be presented.

4.3.1 Apparatus and Operation

The technique used to measure the transitions in question is called differential thermal analysis (DTA). Many other methods are employed by research workers in this field, since changes in elastic modulus, expansion coefficient, damping factor, and other properties also occur at T_g. DTA was chosen for this study since the only link

required between the sample and the outside world is two pair of thermocouple wires, a consideration most important in high vacuum (or high pressure) low temperature measurements.

Figure 43 can be employed to explain the operating principle. The sample (1/2 in. diam. x 1/2 in. long) is suspended in a cavity by means of thermocouple wires. The temperature of the sample wall is measured by a copper-constantan thermocouple. The temperature difference between the wall and a point in the interior of the sample, preferably the exact center, is measured by a differential copper-constantan couple. As the sample is cooled or warmed, changes in T_1 will lag behind changes in T_2 due to the low thermal conductivity (k) of elastomers. At constant heat flow $(T_2 - T_1)$ should remain essentially constant if k does not change. However, when a transition occurs $(T_2 - T_1)$ changes radically due to changes in both heat capacity (c_p) and k. Thus by observing $(T_2 - T_1)$ and measuring T_3 one can locate and characterize any transitions that alter k or c_p.

The sample chamber is presently designed to withstand up to 2000 psi pressure. In order to eliminate unnecessary junctions the differential thermocouple wires must leave the chamber intact. This is accomplished by passing the wires through a 1/32 in. hole in the chamber cap B (figure 43), after which the wires are sealed in place with a room temperature vulcanizing silicone elastomer sealant D. The sealant is forced into the hole in the uncured state, and after curing will not extrude through the small opening at the pressure levels tested to date. The sealant can be easily removed after curing, and has solved the thermocouple problem satisfactorily.

The seal between the cap B and the chamber body A is a bead of indium E tinned to the surface of A. This demountable seal has also proved satisfactory in both the high vacuum and the pressure tests. The thermocouples are attached to the sample with a cement F to insure intimate contact.

Cooling of the apparatus is achieved by conduction through a copper tube C soldered to the sample chamber. The arrangement is shown more clearly in figure 44. The heater H can be employed to control the heat leaving or entering the chamber, but has not been used for the warming tests described later in the report. Expanded foam disks D and E serve to inhibit the entrance of air into the dewar F.

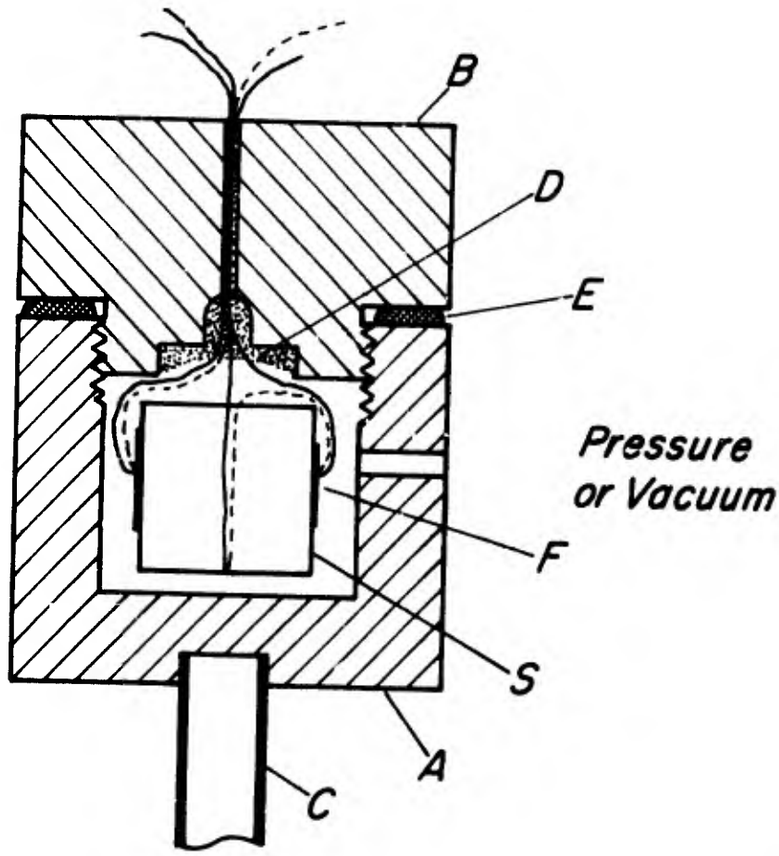


Figure 43 DTA Sample Chamber

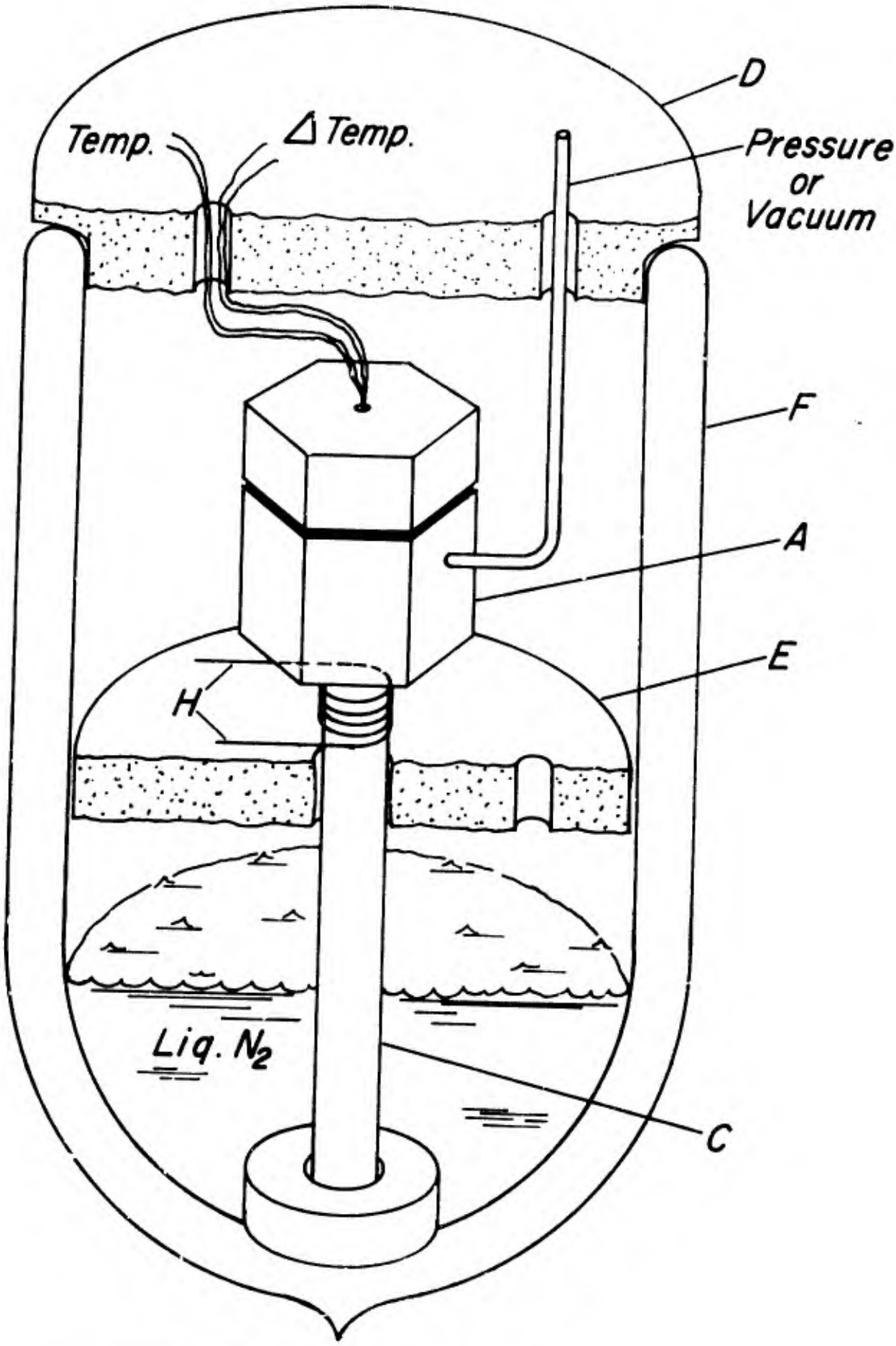


Figure 44 DTA Dewar System

The pressure line can be directly connected to either a gas pressure cylinder or a vacuum pumping system capable of achieving 10^{-6} mm Hg at the system inlet. The chamber A is made from 1-1/4 in. hexagonal stock to facilitate assembly.

The test results presented in the following section were conducted during warming after slow cooldown to 76 K. Typical warming rates of the order of 30 K/hour caused temperature differentials of around 0.2 to 0.6 K in the transition region, and minor transitions causing less than 0.02 K change in ΔT were easily observed using a chopper amplifier, a 10 mv recorder, and a voltage regulator.

4.3.2 Results and Discussion

Figure 45 shows typical DTA results for polyisoprene. These were calculated from thermocouple potential vs. time curves traced continuously in the manner described above. If no transitions were present, one would expect ΔT to decrease with increasing temperature since the warming rate decreases as temperature increases. Therefore any rise of ΔT is indicative of a thermal distortion of the system, either due to changes in k or c_p of the sample or to a sudden heat liberation in the vicinity of the sample wall. The three curves, taken with 125 to 350 psi helium gas in the sample chamber, are quite similar in shape. Three major "transitions" are apparent although it was expected that only the glass transition at 214 K would be observed. The 156 K "transition" is mystifying, and no explanation can be offered at this time. Results obtained at atmospheric pressure did not show this transition.

The glass transition (T_g) is clearly shown at around 214 K. No clear-cut change in T_g can be correlated with pressure, but in this pressure range T_g was not expected to vary enough to be easily detectable at the fairly rapid warming rates used. The high sensitivity of the system allows the "bump" at 200 K to be recognized as a true effect which is perhaps a local initiation of relaxation of stressed molecules. This "bump" could also be interpreted as a very weak first order effect preparatory to the stronger second order effect at T_g.

The third transition in the 225 to 235 K range is interpreted as crystal melting, and is understandable since polyisoprene is the primary constituent of natural rubber, which is known to crystallize at temperatures between T_g and 290 K. The sharpness of the transition

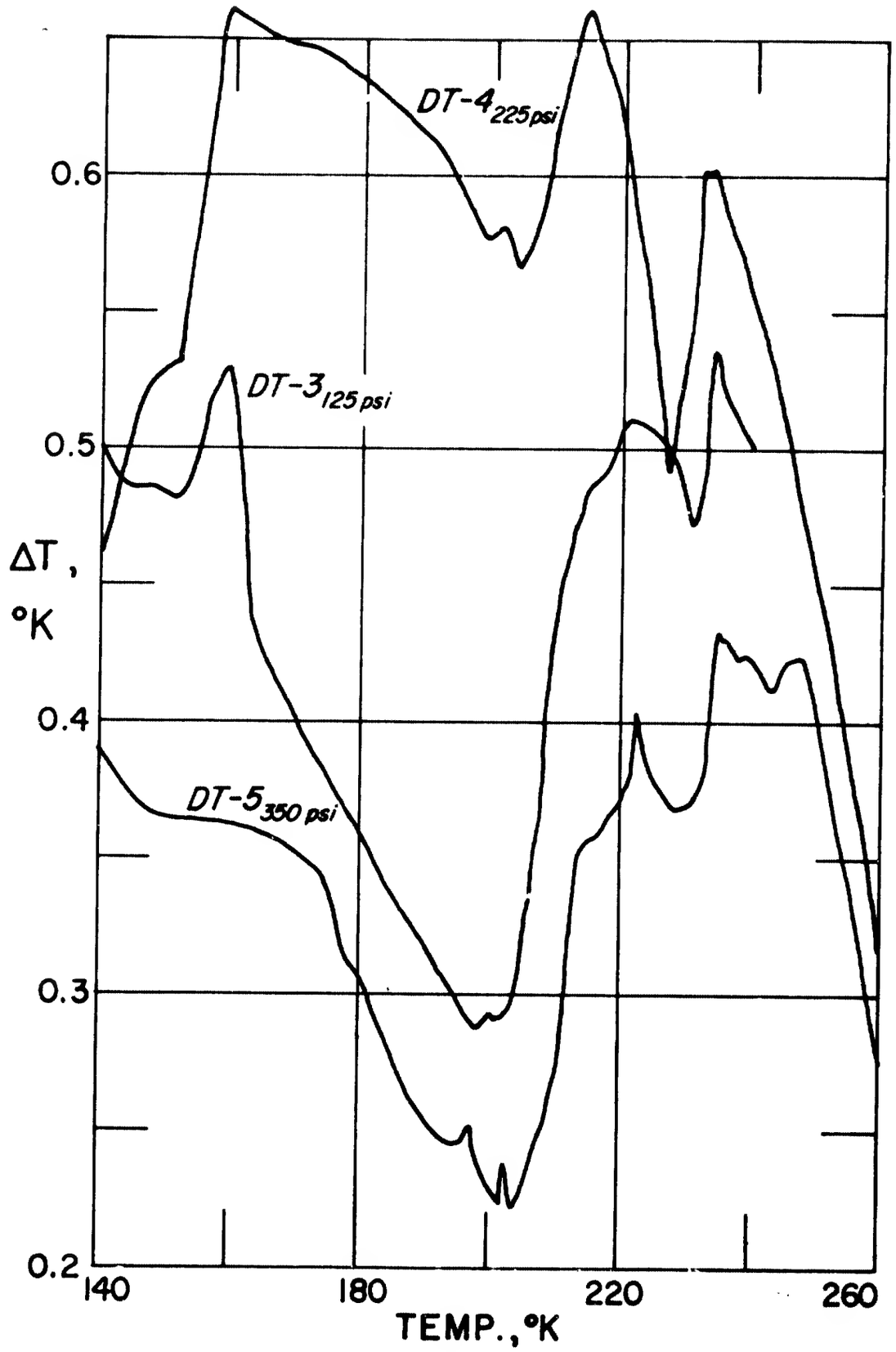


Figure 45 Polyisoprene DTA Curves With Helium Pressure Surrounding Sample

is not typical of crystal melting, and the temperature is somewhat lower than we would expect. Further study of crystal melting in polyisoprene is indicated by this preliminary observation.

Figure 46 shows the DTA curve for the same polyisoprene sample with a vacuum of about 10^{-4} torr in the sample chamber. Unfortunately the low temperature region of the curve was not steady enough to indicate the 145 K transition. Slower warming rates would solve this problem. The "bump" at 200 K is clearly shown here to be separate from the glass transition at 215 K, and the crystal melting region is sharply defined at 232 K. The temperature region above 240 K was distorted due to ice formation on the exterior of the sample chamber.

It can be concluded that the existing differential thermal analysis apparatus can be used to study in detail transitions which occur at low temperatures in elastomeric materials. More careful temperature control in both warming and cooling will be utilized with this apparatus to study the observed transitions in more detail. The pressure range will be extended to the limit of the chamber, consistent with the pressure capability of the support equipment.

4.4 Ball Rebound Resilience

The relationship between rebound resilience and temperature of polymers has fascinated investigators for at least two decades. In 1946 L. Mullins presented a classic paper entitled "Effect of Temperature on Resilience"[26]. Mullins used a pendulum instrument described by Lüpke in 1933[27]. A more recent work, "Studies on Resilience of High Polymers" published in 1961 (in Japan) by K. Fujimoto[28] contains many resilience vs. temperature plots, and the section on butadiene type synthetic rubbers alone contains 26 references to related work.

Pendulums of various kinds, dropping balls or weights, and continuous forced oscillations are the most common methods used for studying the dynamic behavior of polymers. The extreme sensitivity of viscoelasticity and mechanical properties of polymers to temperature and rate of loading makes measurements of this kind an essential part of polymer characterization. Considerable progress is being made in attempts to correlate resilience-temperature profiles with structure and molecular configuration. Examples are work of Natta, et al, in Italy[29] and recent work by Armeniades, Raphael, and Howarth of Arthur D. Little, Inc.[30, 31, 32, 33].

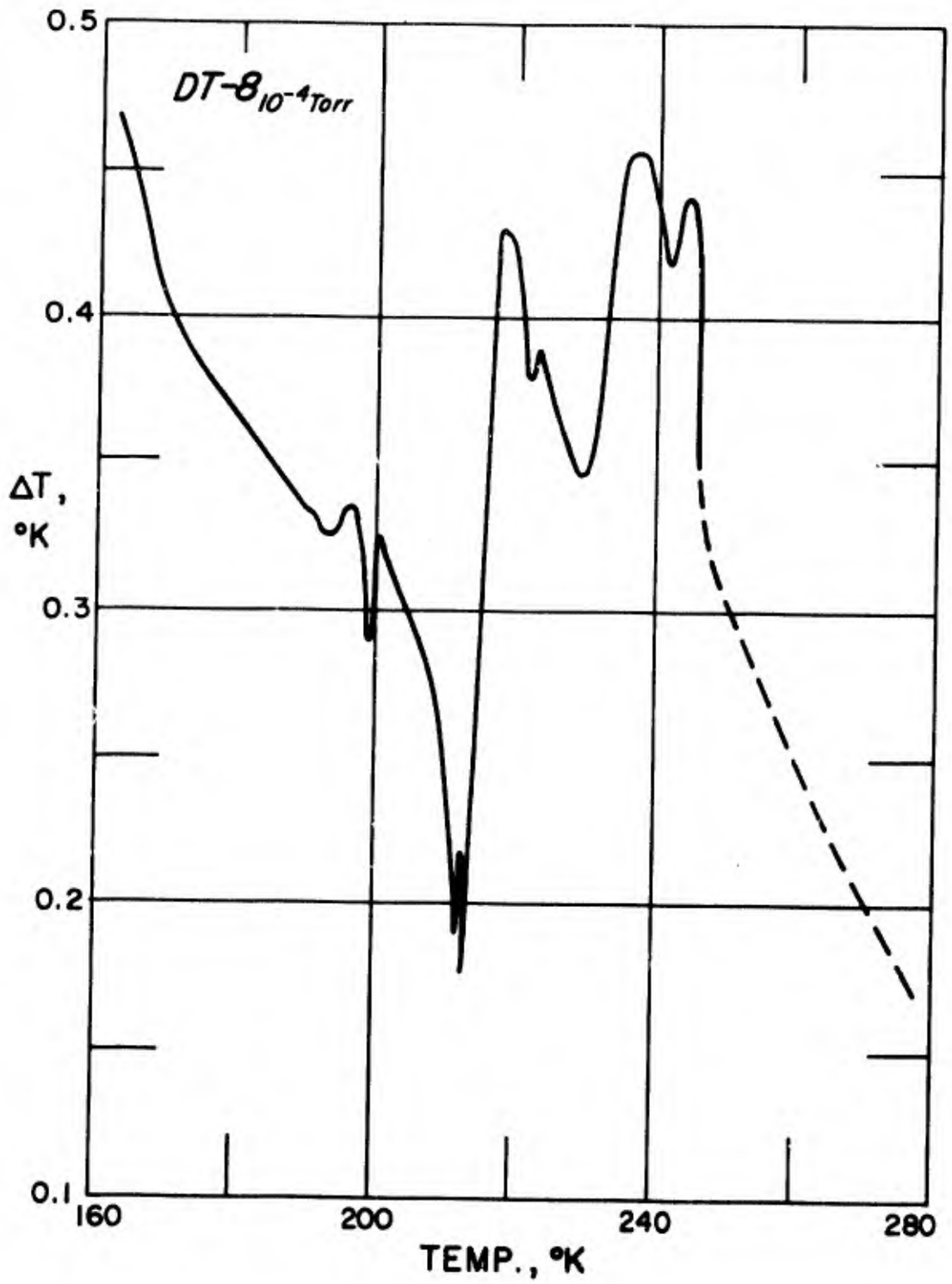


Figure 46 Polyisoprene DTA Curves With Vacuum Surrounding Sample

The instrument developed at Arthur D. Little, Inc.[34] has been widely advertized as a "new method" for obtaining "thermophysical profiles." Since resilience vs. temperature plots obtained by the ball rebound method are by no means new, this is somewhat exaggerated terminology. The "thermophysical profiles" presented in the ADL literature are nevertheless very impressive and have no doubt stimulated considerable new interest in the ball rebound method. The most significant advantage of ball rebound as opposed to pendulum rebound is the fact that a steel ball does not experience energy-robbing oscillations when it rebounds from a relatively soft sample.

In our own case, these studies have encouraged us to reactivate the NBS ball rebound apparatus which was developed under the present contract early in 1962[2]. This instrumentation in its present form is shown in figure 47. It is fully automatic, requiring only occasional checks to adjust heating or cooling rates, etc., and periodic reloading of the ball magazine. It provides a continuous record of both temperature and rebound on a strip chart recorder.

The apparatus comprises a ball timer and dropper, a sample holder in a cryostat with provision for heating and cooling, a narrow horizontal platform supported at the level of the top sample surface, three plexiglass shields, and a 10 mv strip chart recorder. A copper-constantan thermocouple with 76 K reference junction provides a continuous sample temperature signal for the recorder. The chart from the recorder is brought out through the recorder door (glass removed) and passed under a narrow strip of carbon paper which covers the platform and is secured with tape to the outside of the plastic shield nearest the recorder. The chart paper is kept taut by utilizing a spring clip and a small weight. The ball strikes the sample surface and rebounds with a horizontal as well as a vertical velocity component because of the non-horizontal position of the sample surface. The horizontal range of the rebound is thus recorded on the carbon covered chart paper at a fixed interval below the corresponding temperature record.

The resilience of the sample is defined as the ratio of the energy of the ball after impact to its energy before impact. It was shown in our previous report[2] that

$$r = \left(\frac{1}{2\,H \sin 2\phi}\right) R$$

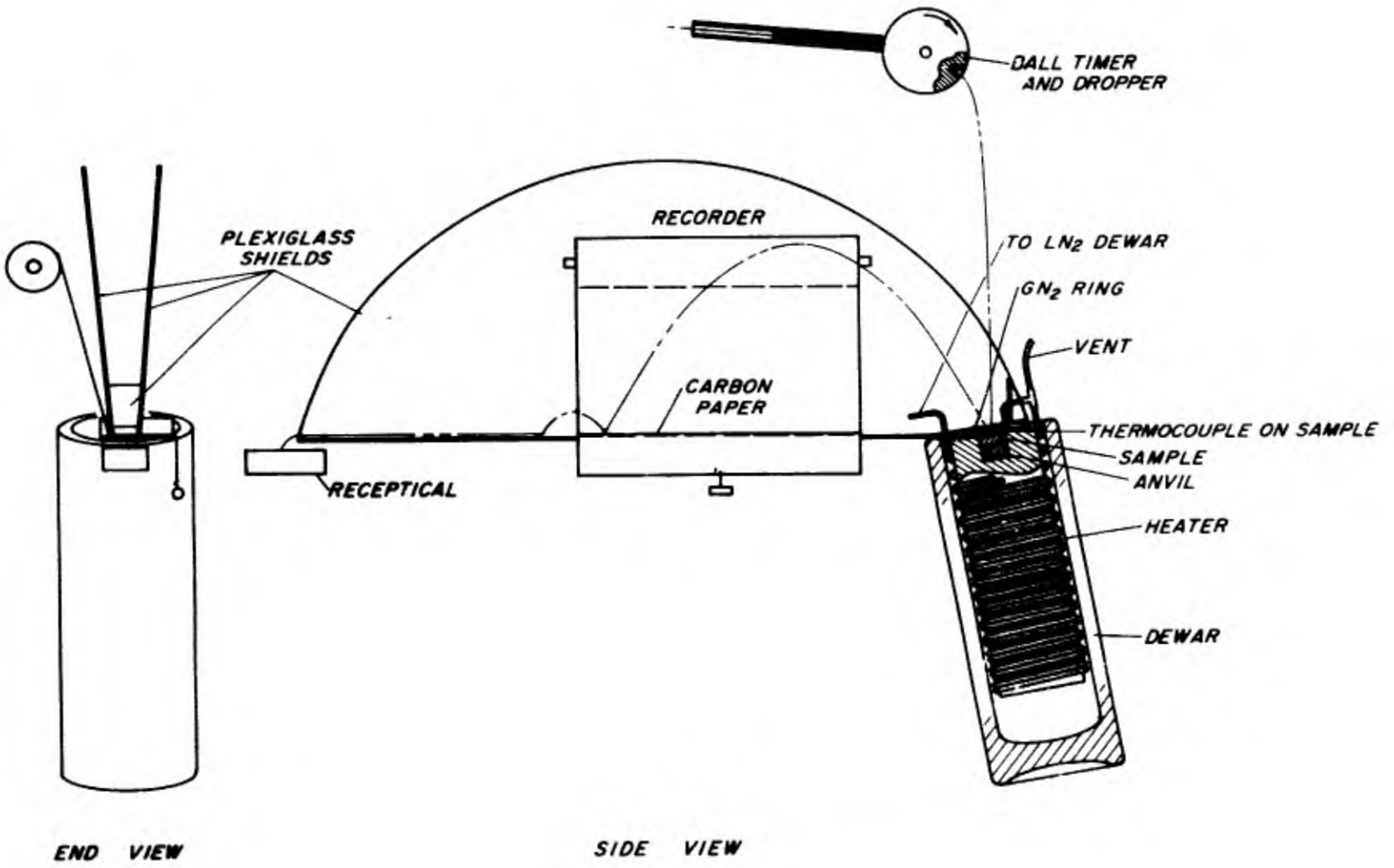


Figure 47 Automatic Ball Rebound Apparatus

where r is resilience, R is the horizontal range of the rebound at the level of the sample surface, and the quality in parenthesis is a proportionality constant determined by the dimensions of the apparatus. (H is the height of the drop and ϕ is the angle which the trajectory of the rebounding ball makes with a horizontal plane as it leaves the sample surface. ϕ is accurately determined from the equations of the trajectory by measuring both height and horizontal range for a few rebounds.)

The cylindrical copper block which contains the sample and anvil is wound with cooling coils and an electric heater. The heater is variac controlled, and controlled cooling is accomplished by forcing liquid nitrogen through the coils at any desired rate. The sample is held firmly in position on top of the anvil by means of a flexible plate screwed to the top of the block. A hole in the plate allows the falling ball to strike the sample and rebound. Around the hole in the plate is soldered a ring of copper tubing with perforations spaced around its inside circumference. The purpose of this perforated ring is to simultaneously purge and temper the top surface of the sample. This is accomplished by short circuiting to the perforated ring some of the venting gas which has come to temperature equilibrium with the copper block. This exhausting nitrogen stream continuously sweeps across the top of the sample in order to (a) prevent frost formation on the sample and (b) reduce thermal gradients by exposing the top of the sample to the same temperature as that contacting its bottom and sides. When the temperature of the sample is above ambient a small stream of N_2 gas is kept flowing through the coils and over the sample. This allows the use of fairly thick samples without danger of serious temperature gradients and greatly reduces the danger of the anvil "showing through", as may be the case when very thin samples are used. In general the sample should be thick enough so that the time required for an elastic wave to be reflected from its bottom and return to the surface is longer than the time of contact. When this condition exists the measured resilience should be essentially independent of sample thickness.

The time of contact of the ball with the sample is an important variable which would be well worth measuring. This could readily be done with (for example) high speed motion picture photography, or with a photocell, collimated light beam, and an electronic counter with printer. From the period of contact (equal to half a deformation cycle) one would know the frequency of the vibration impressed on the sample,

and from the variation of frequency with temperature would come knowledge of the temperature dependence of the dynamic modulus of the material. If, in addition, one has some data on the relation between modulus and frequency at various temperatures, some very basic studies and extrapolations of dynamic properties can be made[35].

The frequency of the impressed vibration at constant temperature will (for a given material) depend on the height of the drop (velocity of impact) and the weight of the ball. The timer and dropper shows in figure 47 is carried on a movable platform, so height of drop is an easily varied parameter. Balls of various sizes can also be used without modification of the apparatus. We have available from this apparatus, then, the damping factor as a function of temperature, the frequency of impressed vibration as a function of temperature, and possibly the frequency of vibration as a function of impressed energy.

Most of our effort to date has been devoted to development and automation of the ball rebound apparatus, with only a small amount of time spent on accumulation of data or interpretation of results. The system as it now stands is simple, inexpensive, and thoroughly reliable. The timer drops a ball every three minutes, and as many balls as desired can be loaded into the "magazine", which is simply a length of glass tubing having an I. D. slightly greater than the diameter of the balls. We are currently using 5/16 in. diameter steel balls. Our elastomer samples are standard compression test buttons 1/2 in. thick with a circular cross section area of one square inch. Most of the top sample surface is covered with aluminum foil; a 1/2 in. diameter circle in the center is exposed for the balls to fall upon. The balls can be dropped from a height of two or three feet without any difficulty, and consistently strike the center of the sample.

Continued work with this apparatus will be directed toward three primary objectives:

(1) Collection of sufficient data to plot a fair number of "thermophysical profiles."

(2) Determination of the cause of considerable scattering of data (now experienced) at temperatures below T_g.

(3) Possible addition of frequency measurement feature, as mentioned above.

5. SUMMARY AND RECOMMENDATIONS

5.1 Elastomers for Cryogenic Seals

Elastomeric O-rings in grooves of conventional design cannot be used for seals at cryogenic temperatures. Certain standard O-rings of small cross section can, however, be very successfully used as seals of the crush gasket type, and give completely satisfactory service for cryogenic applications. Elastomers can also be used as sealing materials on metal body seals which utilize the pressure of the confined fluid to enhance the seal efficiency. These designs are particularly attractive where minimum connector weight is an important consideration. Future work should be directed toward perfection of these concepts, which combine the easy sealing qualities of elastomers with the seal-maintaining features of properly designed seal bodies and flanges.

5.2 Elastomer Properties

Low creep and stress relaxation rates are desirable properties for elastomers which are maintained under high compressive loading for extended periods. O rings which are used as crush gaskets or as sealing materials on metal bodies are subjected to this type of service. Elastomers having high cis 1-4 chain structure show up best in creep and relaxation tests of up to 15 days duration. Longer tests would be necessary to determine maximum storage life of assembled seals.

Thermal expansion rates, particularly below the brittle transition temperature, and the transition temperatures themselves, are significant properties which relate to cryogenic applications of elastomers. Our studies show that expansion rates are subject to some control through use of low expansivity fillers and chain orientation techniques. A method for study of transitions by means of differential thermal analysis is under development. Some progress has been made but much work remains to be done in these areas.

Ball rebound resilience shows much promise as a useful analytical tool for characterization of polymers. An automatic self-recording apparatus has been developed for this work and can be used for study of damping characteristics as a function of temperature, frequency, and impact energy.

5.3 Films and Bladders

A brief study of the behavior of thin elastomeric films at cryogenic temperatures was carried out to see if elastomers are worth considering as materials for construction of expulsion bladders for cryogenic fluids. Films thicker than five mils show no promise, but an investigation of laminated structures made up of much thinner films (one mil or less) would be well worth some further investigation.

6. REFERENCES

1. D. H. Weitzel, R. F. Robbins, P. R. Ludtke, Y. Ohori, and R. N. Herring, "Elastomeric Seals and Materials at Cryogenic Temperatures", Aeronautical Systems Division Technical Data Report 62-31, Dec., 1961.

2. D. H. Weitzel, R. F. Robbins, P. R. Ludtke, and Y. Ohori, "Elastomeric Seals and Materials at Cryogenic Temperatures", Aeronautical Systems Division Technical Data Report 62-31, Part II, May, 1963.

3. D. H. Weitzel, R. F. Robbins, P. R. Ludtke, and Y. Ohori, "Elastomeric Seals and Materials at Cryogenic Temperatures", Air Force Materials Laboratory Technical Data Report 64-50, March, 1964.

4. D. H. Weitzel, R. F. Robbins, G. R. Bopp, and W. R. Bjorklund, "Elastomers for Static Seals at Cryogenic Temperatures", in Advances in Cryogenic Engineering, 6, 219 (K. D. Timmerhaus, Editor, Plenum Press, 1960).

5. R. F. Robbins, D. H. Weitzel, and R. N. Herring, "The Application and Behavior of Elastomers at Cryogenic Temperatures", in Advances in Cryogenic Engineering, 7, 343 (K. D. Timmerhaus, Editor, Plenum Press, 1961).

6. F. W. Tipton,* G. E. Trepus,* R. S. Roper,* D. H. Weitzel, and R. F. Robbins, "Elastomers for Cryogenic Sealing", Proceedings of the Sixth J. A. N. A. Conference on Elastomer Research and Development, 2, 397-419, U. S. Army Quartermaster Research and Engineering Command (Oct. 1960).
   * Employed by Boeing Airplane Company.

7. D. H. Weitzel, R. F. Robbins, G. R. Bopp, and W. R. Bjorklund, "Low Temperature Static Seals Using Elastomers and Plastics", Rev. Sci. Instr. 31, 1350-1351 (Dec. 1960).

8. D. H. Weitzel, R. F. Robbins, G. R. Bopp, and W. R. Bjorklund, "Elastomers for Static Seals at Cryogenic Temperatures", Advances in Cryogenic Engineering, 6, 219-227 (1961).

9. R. F. Robbins, D. H. Weitzel, and R. N. Herring, "The Application and Behavior of Elastomers at Cryogenic Temperatures", Advances in Cryogenic Engineering 7, 343-352 (1962).

10. P. R. Ludtke and D. H. Weitzel, "Force and Seal Evaluation of Elastomeric O-Rings", Advances in Cryogenic Engineering, 8, 467-477 (1963).

11. D. H. Weitzel, P. R. Ludtke, and R. F. Robbins, "Design of Static Elastomeric Seals for Cryogenic Temperatures", Proceedings of the Conference on Design of Leak-Tight Separable Fluid Connectors, Vol. 2, 139-165, NASA, Huntsville, Ala. (March 1964).

12. P. R. Ludtke, "Recent Developments in Using Elastomers for Static Cryogenic Seals", Proceedings of Seventh National Symposium, Society of Aerospace Materials and Process Engineers, Los Angeles, California (May 1964).

13. O. F. Trout, Jr., "Sealing Manned Spacecraft", Aeronautics and Aerospace Engineering (Aug. 1963).

14. H. Bergeler, "Zero Leak Effort for Saturn Vehicles", Geo. C. Marshall SFC Conference on Leak Tight Separable Fluid Connector Design (March 1964).

15. S. E. Logan, "Static Seal for Low-Temperature Fluids", Jet Propulsion, pp 334-340 (July 1955).

16. W. A. Prince, "Bimetallic Seal for Advanced Aerospace Fluid Systems", Geo. C. Marshall SFC Conference on Leak Tight Separable Fluid Connector Design (March 1964).

17. J. Wallach, "Analysis of Pressure Energized Seals", Geo. C. Marshall SFC Conference on Leak Tight Separable Fluid Connector Design (March 1964).

18. H. Dyhstra, "Design and Test of Marman 'Conoseal'", Geo. C. Marshall SFC Conference on Leak Tight Separable Fluid Connector Design (March 1964).

19. B. Goobich, "Helium Leak-Tight Seal - - Functional Analysis and Development", Geo. C. Marshall SFC Conference on Leak Tight Separable Fluid Connector Design (March 1964).

20. C. F. Key, and W. A. Riehl, "Compatibility of Materials with Liquid Oxygen", NASA Internal Report MTP-P&VE-M-63-14 (1963).

21. C. A. Swenson, "Properties of Indium and Thallium at Low Temperatures", Phys. Rev. 100, 6, 1607-1614 (Dec. 1955).

22. T. F. Durham, R. M. McClintock, R. P. Reed, C. J. Guntner, and K. A. Warren, Cryogenic Materials Data Handbook, OTS Report PB 171 809.

23. W. E. Field, "Criteria for the Selection of Optimum Seal Properties for Space Vehicles", Third National Meeting of ASTM Technical Committee O on Aerospace (Oct. 1963).

24. O. H. Pope, and V. E. Isakson, "Positive Expulsion of Cryogenic Liquids", Beech Aircraft Engineering Report No. 14252, Contract NAS 9-513 (March 1964).

25. R. M. McClintock, Private correspondence.

26. L. Mullins, "Effect of Temperature on Resilience", Transactions of the Institution of the Rubber Industry, XXI, 235 (1945-46).

27. Lupke, Vanderbilt News 3, 10 (1933).

28. K. Fujimoto, "Studies on Resilience of High Polymers, IV, Studies of Butadiene Type Synthetic Rubbers", Nippon Gomu Kyokaiski 34, 246-53 (1961).

29. G. Natta, G. Sartori, A. Valvassori, G. Mazzanti, and G. Crespi, "New Ethylene-Propylene Elastomers", Hydrocarbon Processing and Petroleum Refiner 41, 9,261 (1962).

30. J. T. Howarth, C. D. Armeniades, and T. Raphael, "Thermophysical Profiles of Elastomers by the ADL Ball Rebound Tester", 145th Meeting Am. Chem. Soc. (Sept. 1963).

31. T. Raphael, and C. D. Armeniades, "Significance and Interpretation of the Thermophysical Profiles Obtained by the ADL Ball Rebound Tester", 145th Meeting Am. Chem. Soc. (Sept. 1963).

32. T. Raphael,and C. D. Armeniades, "Thermophysical Characterization of Plastics by the ADL Ball Rebound Tester", 20th Ann. Tech. Conf., Soc. Plastic Engrs., Inc. (Jan. 1964).

33. T. Raphael, and C. D. Armeniades, "Thermophysical Properties of Polymers," Plastics Technology (March 1964).

34. C. D. Armeniades, and T. Raphael, "The ADL Ball Rebound Tester", A New Instrument for the Thermophysical Characterization of Polymers", 145th Meeting Am. Chem. Soc. (Sept. 1963).

35. A. R. Payne, and J. R. Scott, "Engineering Design With Rubber", Chap. 2, Interscience, New York (1960).

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
National Bureau of Standards
Cryogenic Engineering Laboratory
Boulder, Colorado

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. REPORT TITLE

ELASTOMERIC SEALS AND MATERIALS AT CRYOGENIC TEMPERATURES

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Summary Report - December 1963-January 1965

5. AUTHOR(S) (Last name, first name, initial)

Weitzel, D. H., Robbins, R. F., and Ludtke, P. R.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
March 1965	98	35

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
D.O. No. 33(615)-64-1002 b. PROJECT NO 7340 c Task No. 734005 d.	ML-TDR-64-50, Part II 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. AVAILABILITY/LIMITATION NOTICES DDC release to CFSTI not authorized. Qualified requestors may obtain copies of this report from the Defense Documentation Center (DDC), Cameron Station, Alexandria, Virginia 22314. Dissemination outside the Department of Defense or to recipients other than Government Defense contractors is prohibited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Air Force Materials Laboratory Research and Technology Division Wright-Patterson AFB, Ohio 45433

13. ABSTRACT

This research deals with low temperature investigations of elastomeric polymers, with particular emphasis on their use as seals at cryogenic temperatures. The present report starts with a brief review of elastomeric O-rings used as crush gaskets, followed by new work on elastomer-indium combination seals and various O-ring coatings. Pressure actuated seals are then examined in some detail, both analytically and experimentally. Several new designs which combine pressure actuating metal bodies with elastomeric (or other) sealing surfaces are described, and experimental results are given. (U)

A brief study of the behavior of thin elastomeric membranes at cryogenic temperatures was made with a view to their possible use for expulsion bladder construction. (U)

Studies of elastomer properties include a look at creep of highly compressed O-rings over 15-day periods, the effects of fillers and chain orientation on thermal expansion rates, and differential thermal analysis as a tool for study of low temperature transitions. The automatic ball rebound apparatus has been further refined, and will be used for a detailed study of damping at high frequencies and at temperatures from approximately 100 K to 100°C. (U)

DD FORM 1 JAN 64 1473

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Elastomers						
Polymers						
Seals						
Cryogenic						
Bladders						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS), (S), (C), or (U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

GPO 880-177