# THE DEVELOPMENT AND CHARACTERIZATION OF NEW STORABLE PROPELLANT BLADDER MATERIALS

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H. R. Lubowitz, J. F. Jones, R. A. Meyers and E. A. Burns

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**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION**
Contract NAS7-446

15 February 1968

Technical Management
Jet Propulsion Laboratory
Pasadena, California
John D. Ingham

This document constitutes the final report for the work accomplished during the periods 15 March - 25 November 1966 and 13 March 1967 - 15 January 1968 by TRW Systems for the National Aeronautics and Space Administration, Jet Propulsion Laboratory, under Contract NAS7-446 on the Development and Characterization of New Storable Propellant Bladder Materials.

The work was under the technical direction of Mr. John Ingham of the Jet Propulsion Laboratory, Pasadena, California and the NASA Headquarters Project Manager was Mr. Frank E. Compitello.

The Chemistry and Chemical Engineering Department of the Chemistry and Materials Laboratory, Power Systems Division was responsible for the work performed on this program. Mr. B. Dubrow, Manager, Chemistry and Chemical Engineering Department provided overall program supervision. Dr. E. A. Burns was Program Manager and Mr. H. R. Lubowitz was Principal Investigator. Acknowledgment is made of the technical assistance provided during this program by the following TRW Systems personnel:

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## ABSTRACT

This final report describes the work performed to advance the state-of-the-art of storable propellant expulsion bladder materials during the periods 15 March - 25 November 1966 and 13 March 1967 - 15 January 1968. This program consisted of a systematic material improvement study in which new materials were developed, prepared and characterized to determine their potential for service with storable propellants. The new materials were based on a polymeric chemical structure (CPBU), first identified under NASA sponsorship (Contract NAS3-4188), which had demonstrated excellent chemical compatibility and low propellant permeability.

This polymer, identified as poly(cyclized 1, 2 polybutadiene) tolyl urethane (CPBU) is a hard, stiff plastic whose mechanical properties are unsuited for bladder applications. The program was directed towards both chemical backbone modifications of CPBU and mechanical preparation of CPBU elastomeric composites as a means for introducing sufficient flexibility into the product for bladder use without significantly impairing the propellant compatibility and permeability. It was found that composite vulcanizates of CPBU, ethylene-propylene terpolymer (EPT), and carbon gave products which exhibited 1) greatly improved resistance to chemical permeation and 2) satisfactory mechanical properties. The nitrogen tetroxide compatibility of the CPBU/EPT/carbon composite vulcanizates is slightly better than that of "resistant" butyl and EPT elastomers used in TITAN, LEMDE and other liquid rocket engines employing nitrogen tetroxide. Studies were undertaken to prepare CPBU/elastomer composite vulcanizates with elastomers considered to be compatible with nitrogen tetroxide, namely, Kel-F and Viton B. In these studies it was necessary to modify the curing agent to effect chemical interaction between the CPBU and matrix material, which in turn had a deleterious

effect on the chemical resistance of the elastomeric matrix. Preliminary investigations of the underlying principles which control their further improvement in chemical and mechanical properties of advanced bladder materials have provided guidelines for future studies aimed at the development of qualified liquid propellant bladder systems.

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# 1. INTRODUCTION AND SUMMARY

This final report presents the work accomplished by TRW Systems for the National Aeronautics and Space Administration, Jet Propulsion Laboratory, under Contract NAS7-446 during the periods 15 March - 25 November 1966 and 15 March 1967 - 15 January 1968. This two phase program was comprised of laboratory studies aimed at developing, preparing and characterizing new materials which have potential for service as storable propellant bladders. The new materials investigated were based on a polymeric chemical structure first identified under NASA sponsorship (Contract NAS3-4188) which has demonstrated excellent chemical compatibility and very low permeability with standard storable propellants.

To satisfy the requirements for storable propellant bladder materials, polymeric formulations must be developed having the following combinations of characteristics:

- Resistant to chemical attack,
- Resistance to mass transfer of propellant, and
- Elastomeric properties.

Commonly used elastomeric materials are subject to chemical attack by strong oxidizing agents or swell and mechanically degrade by imbibition of low molecular weight compounds such as hydrazine and nitrogen tetroxide. Chemically resistant fluorocarbon polymers tend to provide physical paths for permeating by low molecular weight liquids. Consequently, new or modified elastomeric materials are needed for service with storable propellants.

TRW Systems under Contract NAS3-4188 synthesized for use as an ablative resin, a new composition of matter characterized by long chains of crosslinked, fused cyclohexane rings (Reference 1). This new polymer was investigated and found to be highly resistant and impermeable to nitrogen tetroxide. It also was not affected by hydrazine based fuels and commercial solvents. For example, nitrogen tetroxide permeability of poly(cyclized 1, 2-polybutadiene) tolyl urethane (CPBU), (the polymer developed as an ablative resin) showed at least a factor of 1300 improvement over the best fluorocarbon and 540, 000 over "resistant" butyl rubber. It was evident that if this hydrocarbon material could be made flexible it offered a highly attractive means for solving the problem of preparing bladder materials suitable for use with storable propellants.

NASA initiated support of this effort under Contract NAS7-466 as an initial step in preparing qualified liquid propellant bladder systems. This program investigated both chemical backbone modifications of CPBU as well as mechanical means for preparing CPBU elastomer composites. During the latter part of Phase I, it was found that the CPBU/elastomer formulations resulted in materials having greatly improved resistance to chemical permeation (over 150 times better than that exhibited by state-of-the-art fluorocarbon bladder materials). The elastomeric matrix briefly investigated duringthis period was an ethylene-propylene terpolymer (EPT) which contained active vinyl groups capable of reaction with the CPBU filler during vulcanization. These materials displayed an aging deterioration on exposure to nitrogen tetroxide which was related to the chemical behavior of the EPT matrix. The mechanical properties of the CPBU/EPT composite vulcanizates appeared to be adequate for application as storable propellant bladders.

As a direct consequence of the success achieved in Phase I, a second phase was initiated to investigate the use of other elastomeric matrices (which normally exhibit resistance to nitrogen tetroxide) in composite CPBU vulcanizates. A secondary objective of Phase II activities was to provide confirmatory evidence that CPBU uniquely inhibits permeation by interaction with matrix material.

It is believed from this exploratory research study that a technological advance was achieved in both the development of improved bladder materials as well as the processing of rubber composites. These composite vulcanizate formulations show promise of being further improved to provide materials for comprehensive bladder use evaluation in tank configurations.

The first phase effort is reported in four principle sections covering the following activities:

- Polymer structure-bladder consideration;
- Synthesis and preparation of candidate materials;
- Characterization of candidate materials; and
- Conclusions and recommendations.

The second phase effort is reported in three subsequent sections covering the following activities:

- Acquisition and characterization of $N_2O_4$ resistant elastomers;
- Chemistry and formulation of filled $N_2O_4$ resistant elastomers; and
- Preparation and evaluation of filled $N_2O_4$ resistant elastomers.

This report identifies in a separate section the new technology originating from the program. The information presented in the main body of the report is supplemented by appendices covering detailed synthesis procedures, permeability measurement techniques and nitrogen tetroxide permeability of related materials.

## 2. POLYMER STRUCTURE-BLADDER CONSIDERATIONS

Advanced concepts for storage of propellants in space and bipropellant positive expulsion bladders require a flexible material which is not degradable chemically nor permeable on direct exposure to storable propellants. Current propulsion systems for the Apollo Spacecraft employ fluorocarbon polymers for this purpose. However, these resins are permeated by nitrogen tetroxide and weakened in relatively short periods of time. To satisfy the requirement for storable propellant bladder materials, polymers must be prepared having the following combination of characteristics:

- Resistance to chemical attack,
- Resistance to mass transfer of propellant, and
- Elastomeric properties.

Commonly used elastomeric materials contain chemical groups and active sites which are subject to 1) chemical attack by strong oxidizing agents, such as nitrogen tetroxide, and 2) imbibition of low molecular weight compounds, such as hydrazine, and nitrogen tetroxide, which cause swelling and degrade chemical properties of the elastomer. Often, plastic materials which resist chemical attack are highly crosslinked, stiff polymers and do not have elastomeric properties (Reference 2).

Alternatively, polymer backbones that have been modified to contain strong chemical bonds, such as C-F, resist the chemical attack of nitrogen tetroxide. Polymer structures which contain a high number of C-F bonds are normally linear and hence, provide points whereby low molecular weight liquids can permeate and diffuse leading to substantial mass transfer. Other chemical structures which have demonstrated oxidative resistance are 1) polymers having redundant backbones (ladder polymers), and 2) backbone chains protected by pendant groups which hinder the migration of the oxidizer (to the vicinity of the backbone) for chemical attack. Plastic materials which have a high degree of crosslinking minimize the imbibition of low molecular weight liquids that cause swelling. However, the greater the crosslinking of a plastic, the poorer its elastic properties. Consequently, a compromise often must be established among elastic properties, chemical resistance, imbibition and permeability.

Under sponsorship of the National Aeronautics and Space Administration (Contract NAS3-4188) TRW Systems developed a new high carbon containing stiff resin, poly (cyclized 1,2-polybutadiene) tolyl urethane (CPBU) which was investigated for application as an ablative resin matrix suitable for use with advanced fluorine-containing propellants.

The idealized chemical structure of this polymer is characterized by long chains of linear fused cyclohexane rings and crosslinked backbones which are interconnected by tolyl urethane groups. The reaction steps during the formulation of this polymeric structure are shown in Figure 1. The polymerization occurs in two distinct steps:

- First, a long chain 1,2-polybutadiene diol is reacted with toluene diisocyanate to extend the linear molecular structure by forming a high molecular weight polyurethane. The polyurethane formed by this process exhibits elastomeric properties and is the B-stage form CPBU.
- Second, a free radical initiates cyclization and crosslinking of the pendant vinyl groups to form a hard stiff plastic. This plastic is the C-stage form of CPBU.

In the course of testing the oxidative stability of this new resin, it was observed to exhibit outstanding resistance to chemical attack by $N_2O_4$. In addition, poly (cyclized 1,2-polybutadiene) tolyl urethane (CPBU) was observed to exhibit resistance to absorption of hydrazine/unsymmetrical-dimethylhydrazine and common laboratory solvents and reagents. In Table I are listed the results of long term compatibility studies. The results of the compatibility tests clearly demonstrate the excellent chemical resistance of CPBU. The rate data are calculated as if a constant rate existed during the storage period. In general, this is not the case. The specimen normally has an initial weight increase followed by a leveling out. For example, the weight increase listed for nitrogen tetroxide absorption occurred in 21 days, and for the remaining storage time (42 days) the specimen gained no appreciable weight.

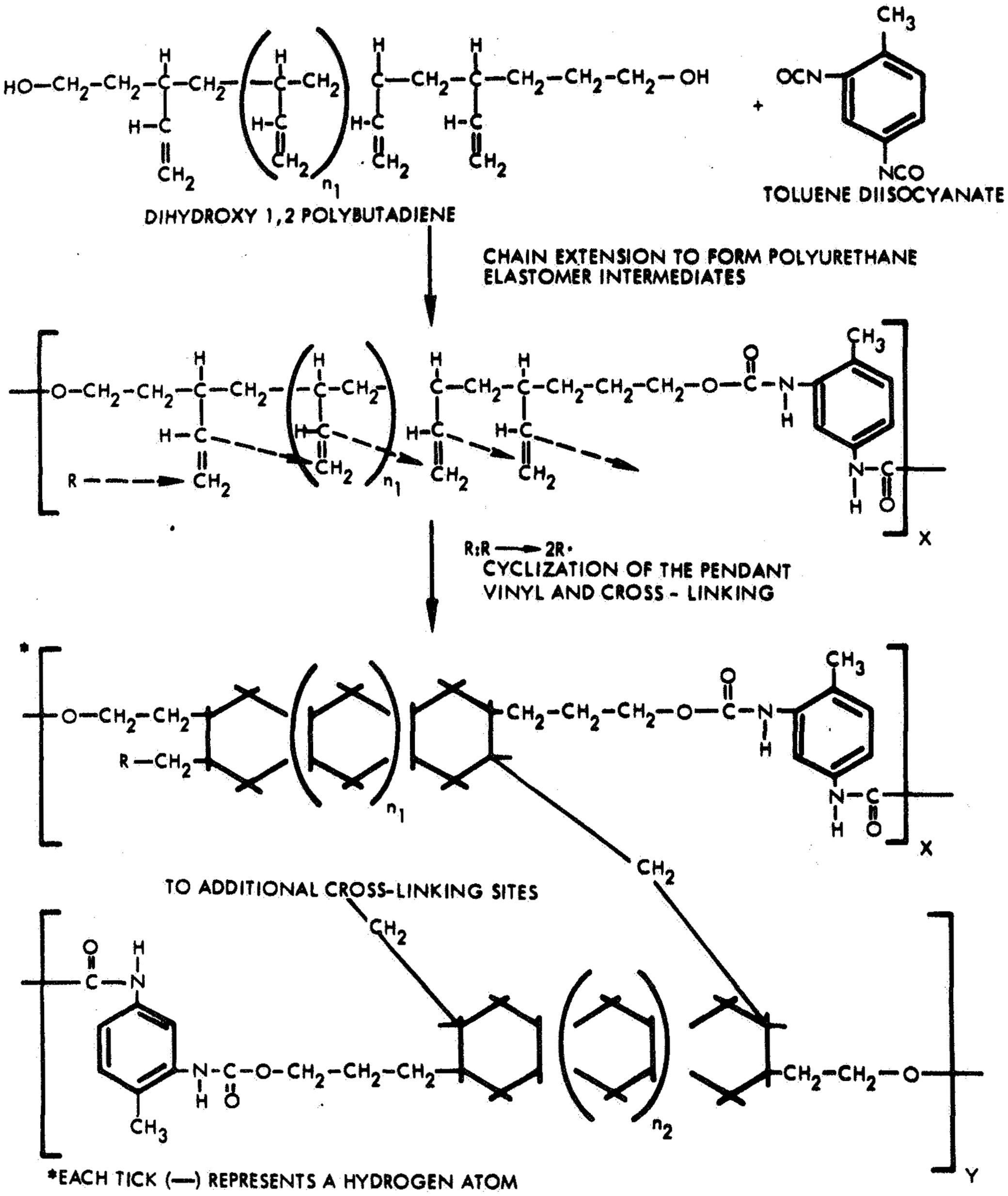


Figure 1. Idealized Reactions Occuring During Synthesis of Poly (Cyclized 1, 2-polybutadiene) Tolyl Urethane

## TABLE I

## LONG TERM COMPATIBILITY OF CPBU WITH VARIOUS CHEMICALS AT 24°C

| Chemical | Storage Period, Days | Absorption on Specimen | |
|---|---|---|---|
| | | Percent Weight Increase/Time, % $Day^{-1}$ | Weight Increase/Exposed Surface/Time, $mg/cm^2$-day |
| Hexane | 216 | 0.0062 | 0.0050 |
| Nitric Acid (17N) | 227 | 0.0155 | 0.0141 |
| Sulfuric Acid (36N) | 195 | 0.0006 | 0.0005 |
| Sulfuric Acid (12N) | 216 | 0.0020 | 0.0011 |
| Sodium Hydroxide (19M) | 216 | 0.0010 | 0.0006 |
| Sodium Hydroxide (3M) | 216 | 0.0031 | 0.0015 |
| Potassium Hydroxide (7M) | 108 | 0.0069 | 0.0030 |
| Hydrazine/Unsymmetrical-Dimethylhydrazine (50:50) | 58 | 0.0028 | 0.0044 |
| Nitrogen Tetroxide | 63 | 0.0018 | 0.0033 |

The superb resistance of the CPBU to degradation by nitrogen tetroxide and its potential as a component in a nitrogen tetroxide bladder material prompted studies to determine its permeability resistance. To provide a comparative basis for assessing the degree of permeability improvement, other materials often proposed for nitrogen tetroxide service namely, polytetrafluoroethylene (TFE), polytetrafluoroethylene (TFE)/tetrafluoroethylene-hexafluoropropene (FEP) laminates, polyvinylidene fluoride (Kynar), carboxy nitroso rubber (CNR), "resistant" butyl rubber and "resistant" ethylene propylene terpolymer rubber, were also examined using the identical laboratory procedures. The test evaluated the permeability rate of nitrogen tetroxide into water through a plastic film by monitoring the pH of the water. Details of this testing procedure are presented in Appendix B. The results of these tests are tabulated in Table II and selected permeability curves are shown in Figure 2. The data presented in Table II clearly demonstrate that CPBU offers a significant improvement over other commercially available materials which have been suggested for service with nitrogen tetroxide.

These results indicate that CPBU has at least a factor of 1300 improvement in permeability rate over the best fluorocarbon and 540,000 over "resistant" butyl rubber. From Table II it is seen that after 1200 hours exposure, CPBU is 4200 times better than TFE in absolute permeability expressed in $mg\text{-}mil/cm^2$. It is also seen that the permeability coefficients for TFE are not independent of membrane thickness. The ten-fold increase in "effective" permeability coefficient of 7.9 mil gauge over 32 mil gauge material is attributed to pinholes in the thinner material.

The superior chemical resistance of CPBU makes it a prime candidate for use in contact with earth storable spacecraft propellants. However, its high elastic modulus precludes its use as a propellant tank bladder material without molecular structural modification.

The inherent chemical stability of CPBU arises from its backbone "ladder" structure. The arrangement of $-CH_2-$ group in a crosslinked, redundant backbone "ladder" configuration produces polymers with high chemical stability. The "ladder" structure results in high modulus resins.

## TABLE II

## NITROGEN TETROXIDE PERMEABILITY

| Material | Thickness, mil | Permeability After Exposure Interval, $mg/cm^2$ | Permeability Rate | | "Effective" Permeability Coefficient, $mil\text{-}mg/cm^2\text{-}hr$ |
|---|---|---|---|---|---|
| | | | Interval, Hours | Rate $mg/cm^2\text{-}hr$ | |
| NT-5 Carboxynitroso Rubber | 38. | 272. | 0-94 | 3.33 | 125. |
| "Resistant" Butyl Rubber | 57. | 32.2 | 5-174 | 1.94 | 110.5 |
| Alcar 22C (CTFE) | 1.50 | 27. | 0-20 | 1.3 | 1.95 |
| Kynar (VF) | 2.0 | 82.2 | 20-138 | 0.65 | 1.30 |
| FEP/TFE | 9.8 | 55.0 | 0-360 | 0.16 | 1.57 |
| Teflon (TFE) | 7.9 | 104. | 0-360 | 0.31 | 2.41 |
| Teflon (TFE) | 32. | 0.99 | 20-1200 | 0.0085 | 0.272 |
| CPBU | 37. | 0.00274[a] | 0-200 | $1.86 \times 10^{-6}$ | $6.88 \times 10^{-5}$ |
| | | | 200-700 | $5.50 \times 10^{-6}$ | $2.04 \times 10^{-4}$ |
| | | | 700-2200 | $2.02 \times 10^{-7}$ | $7.47 \times 10^{-6}$ |

[a] This level was attained at approximately 800 hours exposure and remained there for the duration of the experiment.

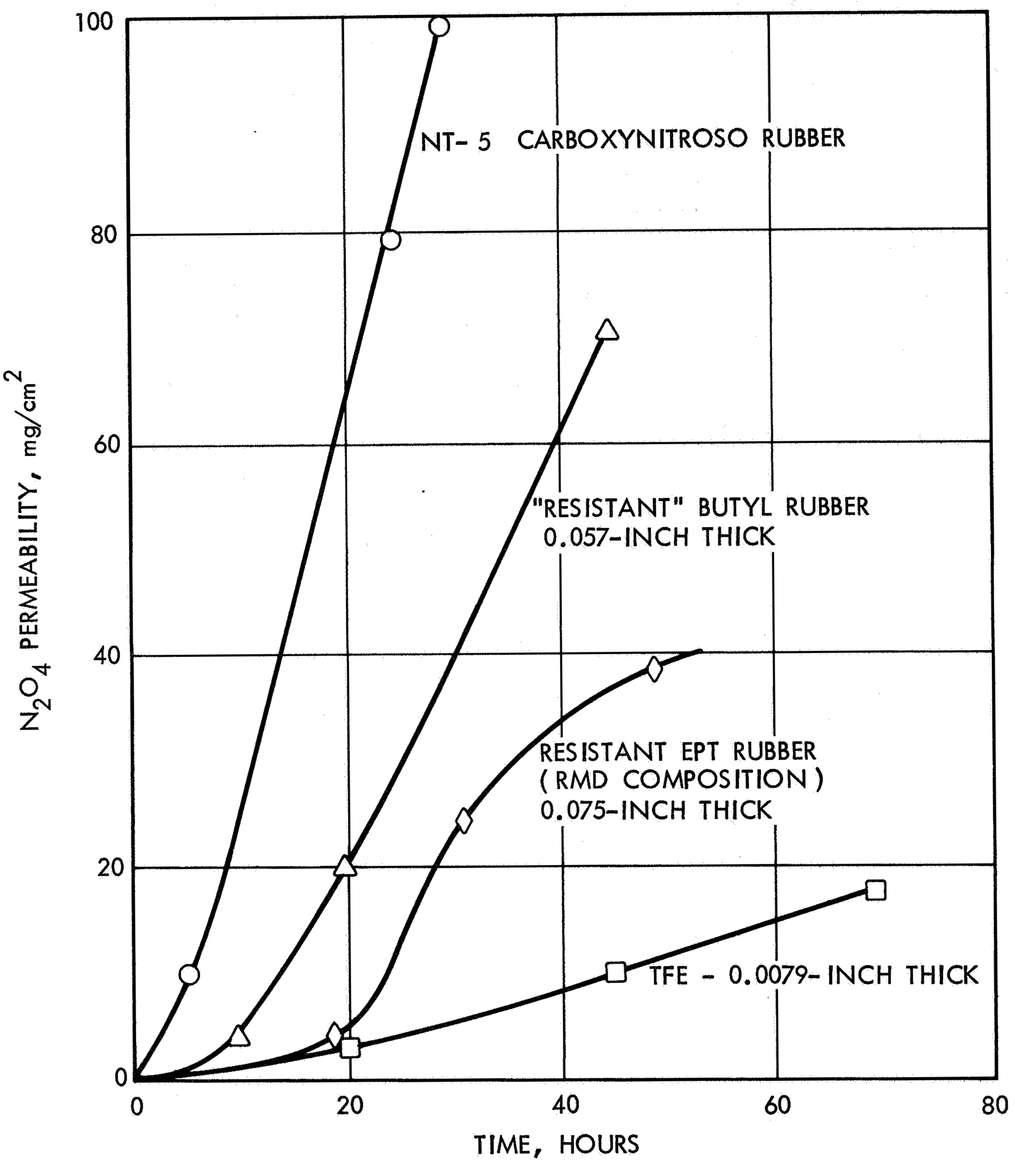


Figure 2. $N_2O_4$ Permeability of Selected Materials

In order to prepare materials which have a protective "ladder" structure similar to that of CPBU, and in addition, exhibit sufficient flexibility for use as a bladder, it is necessary to induce flexibility to the overall polymeric structure.

A systematic synthesis and testing program was established to determine the trade offs among chemical resistance, permeability and mechanical properties that could be realized by introducing points of flexibility into the CPBU polymer structure. During this program, a total of eight different approaches for modification of CPBU polymer and compositional assemblage were investigated. Descriptions of the synthesis approaches and methods for preparation of test specimens developed are presented in Section 3 and the results of characterization of the candidate materials are found in Section 4.

# 3. SYNTHESIS AND PREPARATION OF CANDIDATE MATERIALS

This section describes the technical approaches undertaken chronologically during this program to prepare flexible materials containing poly(cyclized 1, 2 polybutadiene)tolyl urethane (CPBU) having high chemical stability. The eight approaches explored were:

- Approach 1 - Internal Plasticization;
- Approach 2 - Variation in the Backbone Structure through Copolymerization;
- Approach 3 - Vulcanization of Butyl Rubber with Poly 1, 2-butadiene;
- Approach 4 - Introduction of Points of Flexibility in the Chain Extender;
- Approach 5 - Modification of the Fused Cyclohexane Ring Structure by Chain Transfer;
- Approach 6 - Preparation of CPBU-Rubber Composites;
- Approach 7 - External Plasticization; and
- Approach 8 - Non-Chain Extended CPBU.

The majority of the approaches consisted of tailoring of the chemical structure to introduce points and areas of flexibility in backbone and crosslinking segments, however Approaches 3 and 6 consisted of physically dispersing CPBU or its active ingredients into an elastomeric matrix as means to make the basic CPBU material flexible. Details of these technical approaches and a brief discussion of the experimental studies are presented below. Details of the laboratory synthesis and fabrication studies are presented in Appendix A.

## 3.1 INTERNAL PLASTICIZATION

### 3.1.1 Technical Approach

In recent studies, TRW Systems has prepared polymers based on the poly (cyclized 1, 2-polybutadiene) tolyl urethane structure which contain 1-octene or butyl 10-undecanoate internal plasticizing agents (Reference 3). These additives which react at crosslinking sites provide a method for enhancing the flexibility of the polymer. In general, long chain alkyl groups are desired for internal plasticization of polymers in order to improve their elastomeric qualities. An idealized molecular arrangement of 1-octene in the plasticized polymer is shown in Figure 3.

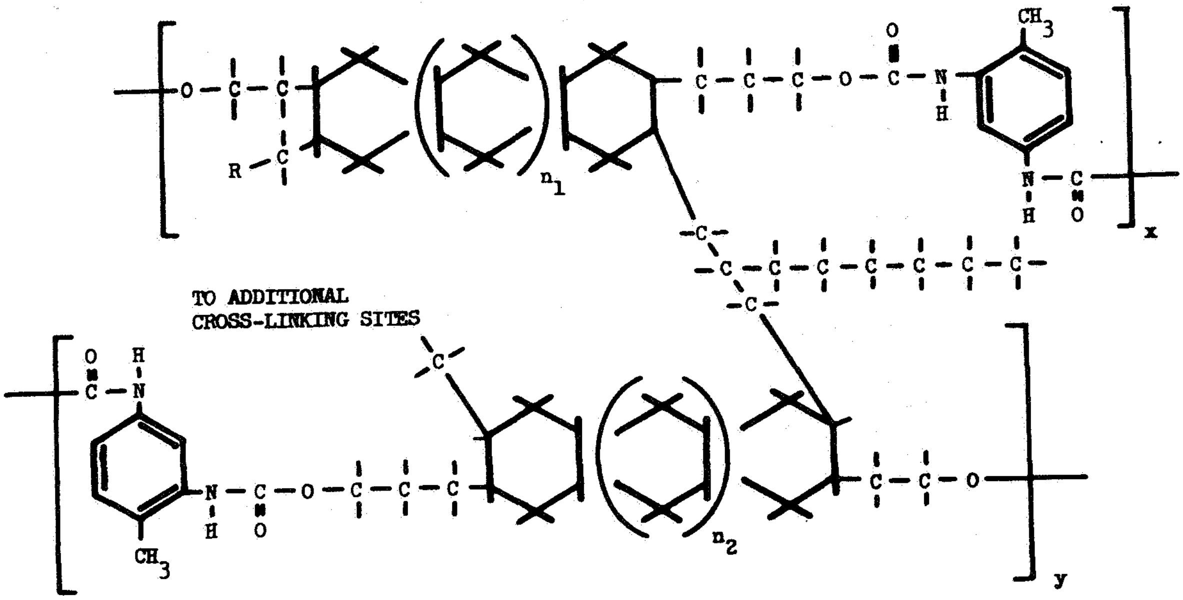


Figure 3. Poly (Cyclized 1, 2-Polybutadiene)Tolyl Urethane Internally Plasticized with Octene-1

### 3. 1. 2 Experimental

Modified formulations of CPBU were prepared containing the following internal plasticizers: 1-decene, 1-hexadecene, a mixture of 1-alkenes from six to ten carbon atoms in length, a mixture of 1-alkenes from fourteen to eighteen carbon atoms in length. Appropriate mixtures of internal plasticizer, 1, 2-polybutadiene diol, toluene diisocyanate, and di-tert-butyl peroxide were cast in plug or sheet form. Cure schedules were adjusted in order to maximize both $N_2O_4$ resistance and flexibility. It was found that more vigorous cures gave harder materials with more $N_2O_4$ resistance, while less vigorous cures gave softer materials with less $N_2O_4$ resistance. Experimental details of the formulations are presented in Appendix A.

The hardness of the cured specimens were determined using a Barcol tester. The cure schedule used and Barcol hardness found are given for each formulation in Table III. The 1-octene plasticized resins decreased in hardness as the amount of alkene was increased, as was

## TABLE III

## INTERNALLY PLASTICIZED CPBU[a] CONDITIONS AND CHARACTERISTICS

| Internal Plasticizer | Internal Plasticizer Context, phr[b] | Cure Time (days) | | | | | | Hardness |
|---|---|---|---|---|---|---|---|---|
| | | Room Temperature | 90°C | 110°C | 115°C | 120°C | 170°C | |
| 1-octene | 400 | 2 | 1 | 2 | 1 | - | - | o Barcol[c] |
| | 230 | 2 | 1 | 2 | 1 | - | - | 110 Shore A-2 |
| | 150 | 2 | 1 | 2 | 1 | - | - | 90 Shore A-2 |
| | 100 | 2 | 1 | 2 | 1 | - | - | 90 Shore A-2 |
| | 67 | - | 6 | - | - | 7 | 7 | 98 Shore A-2 |
| | 43 | - | 6 | - | - | 7 | 7 | 6 Barcol |
| | 25 | - | 6 | - | - | 7 | 7 | 15 Barcol |
| | 11 | - | 6 | - | - | 7 | 7 | 24 Barcol |
| 1-decene | 100 | 2 | 1 | 2 | 1 | - | - | 60 Shore A-2 |
| 1-hexadecene | 100 | 2 | 1 | 2 | 1 | - | - | 80 Shore A-2 |
| $C_6$-$C_{10}$ 1-alkene | 43 | - | 6 | - | - | 7 | 7 | 100+ Shore A-2 |
| | 25 | - | 6 | - | - | 7 | 7 | 19 Barcol |
| | 11 | - | 6 | - | - | 7 | 7 | 42 Barcol |
| $C_{14}$-$C_{16}$ 1-alkene | 67 | - | 6 | - | - | 7 | 7 | 93 Shore A-2 |
| | 43 | - | 6 | - | - | 7 | 7 | 98 Shore A-2 |
| | 25 | - | 6 | - | - | 7 | 7 | 100+ Shore A-2 |
| | 11 | - | 6 | - | - | 7 | 7 | 27 Barcol |
| $C_{14}$-$C_{18}$ 1-alkene | 67 | - | 6 | - | - | 7 | 7 | 94 Shore A-2 |
| | 43 | - | 6 | - | - | 7 | 7 | 97 Shore A-2 |
| | 25 | - | 6 | - | - | 7 | 7 | 99 Shore A-2 |
| | 11 | - | 6 | - | - | 7 | 7 | 99 Shore A-2 |

a. Di-t-butyl peroxide initiator is 2% w/w of total alkene monomer.

b. phr = parts per hundred 1, 2-polybutadiene diol.

c. Shore A hardness not determined.

predicted. This relationship was also true for the $C_6$-$C_{10}$, $C_{14}$-$C_{16}$, and $C_{14}$-$C_{18}$ formulations. It was also evident, as expected, that the hardness decreased as the molecular weight of the internal plasticizer increased.

## 3.2 VARIATIONS IN BACKBONE STRUCTURE THROUGH COPOLYMERIZATION

### 3.2.1 Technical Approach

A second approach for modifying the mechanical behavior or poly (cyclized 1,2-polybutadiene) tolyl urethane (CPBU) is based on varying the backbone structure by copolymerization (Reference 4). Copolymerizing diols with diisocyanates to produce copolymerized urethane was accomplished by TRW Systems prior to initiation of this program. The 1,2-polybutadiene diol was used together with a second diol which could not cyclized during the free radical reaction, but rather imparted flexibility to the final product. The relative amounts, types and molecular weights of the second diol significantly vary the mechanical properties of the resultant polymer as well as its usefulness in storable propellant service. Figure 4 schematically illustrates CPBU which is copolymerized with a flexible material.

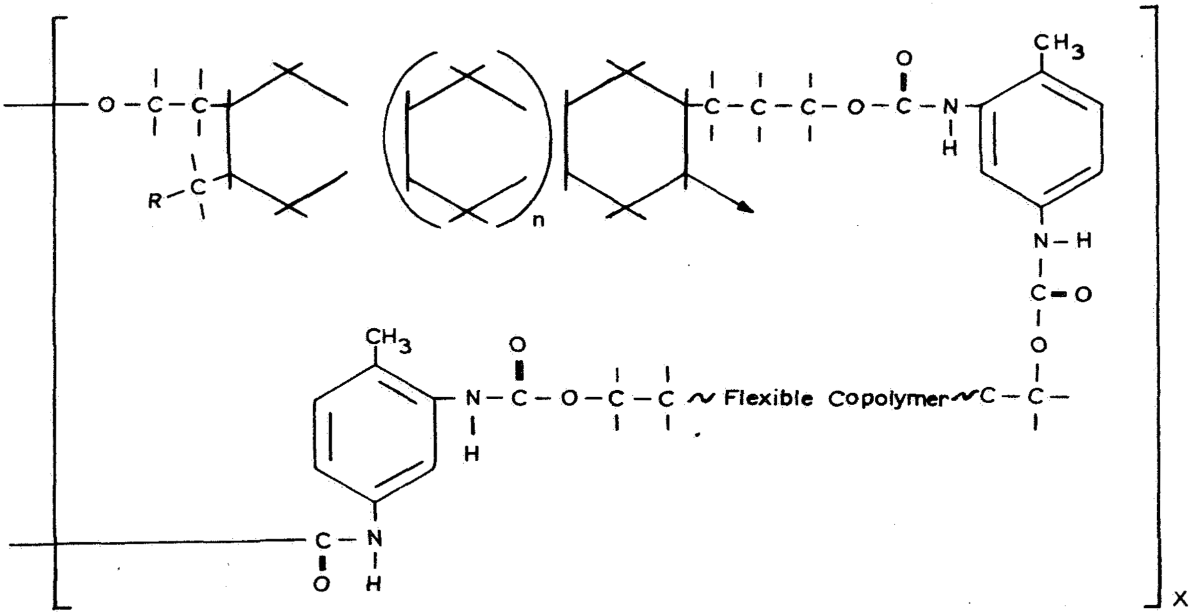


Figure 4. Poly (Cyclized 1,2-Polybutadiene) Tolyl Urethane Copolymerized with a Flexible Copolymer

### 3.2.2 Experimental

Three materials were investigated as copolymers with CPBU. These were 1) ricinoleic triglyceride, 2) 1,4-polybutadiene diol, and 3) Emery's Dimer Acid, a 36-carbon di-basic acid. Copolymerization with ricinoleic triglyceride and 1,4-polybutadiene diol went smoothly, but attempts to copolymerize Emery's Dimer Acid were unsuccessful because of immiscibility with the CPBU prepolymer. Cure schedule and hardness data are given for copolymerized CPBU in Table IV . Cure schedules were adjusted in order to maximize both $N_2O_4$ resistance and flexibility. It was found that more vigorous cures gave harder materials with more $N_2O_4$ resistance and less vigorous cures gave softer materials with less $N_2O_4$ resistance. Details of experimental procedures are presented in Appendix A.

Ricinoleic triglyceride copolymers decreased in hardness with increase in copolymer, for a given cure, as predicted. The effect of a more vigorous cure is evident, with the harder material being that with the longest cure. The 1,4-polybutadiene diol copolymers increased in hardness with increase in copolymer amount when a less vigorous cure cycle was used, while the reverse was true for the more vigorous cure cycle. However, none of the materials were significantly softened.

## 3.3 VULCANIZATION OF BUTYL RUBBER WITH POLY 1,2-BUTADIENE

Because of its chemical compatibility, butyl rubber is often suggested for nitrogen tetroxide service (Reference 5). However, it has sever permeability limitations. The approach described would provide a means for direct chemical introduction of the fused cyclohexane ring molecular structure into the butyl rubber matrix.

Butyl rubber consists mainly of polyisobutylene. The rubber, however, contains unsaturated segments, because in practice, polyisobutylene is prepared by copolymerizing isobutylene with isoprene. The unsaturated segments are employed subsequently in the vulcanization. It was proposed to blend butyl rubber with poly 1,2-butadiene together with free radical initiators. Upon vulcanization, the poly 1,2-butadiene would form the same crosslinked, cyclic structure in CPBU, and in addition, it would interact with the unsaturation present in the butyl rubber. In

## TABLE IV

## COPOLYMERIZED CPBU[a] CONDITIONS AND CHARACTERISTICS

| Copolymer | Copolymer Content, phr[b] | Cure Cycle (days) | | | Barcol Hardness |
|---|---|---|---|---|---|
| | | 90°C | 120°C | 170°C | |
| Ricinoleic Triglyceride | 5 | 3 | 4 | - | 42 |
| | 5 | 3 | 4 | 4 | 47 |
| | 10 | 3 | 4 | - | 38 |
| | 10 | 3 | 4 | 4 | 44 |
| | 20 | 3 | 4 | - | 35 |
| | 20 | 3 | 4 | 4 | 39 |
| | 30 | 3 | 4 | - | 32 |
| | 30 | 3 | 4 | 4 | 36 |
| 1,4-Polybutadiene Diol | 200 | 1 | 4 | - | 36 |
| | 100 | 1 | 4 | - | 34 |
| | 50 | 1 | 4 | - | 30 |
| | 25 | 1 | 4 | - | 22 |
| | 200 | 2 | 3 | 8 | 44 |
| | 100 | 2 | 3 | 8 | 47 |
| | 50 | 2 | 3 | 8 | 49 |

substance, the polymeric network would consist of crosslinked condensed cyclohexane rings separated by polyisobutylene segments. The latter segment would induce elasticity to the material.

During the course of this program, it became evident that modification of Approach 3 to utilize finely divided 1, 2-polybutadiene diol which had been chain extended with toluene diisocyanate (the elastomeric form of CPBU) in preference to 1, 2-polybutadiene would provide a vulcanized product which would maintain discrete particles of fully cured CPBU and be more likely to achieve the desired chemical and mechanical properties. In this approach, the vulcanizate is prepared as a two-phase system. As a result, the rubbery character of the continuous phase, the elastomeric portion is not reduced by the presence of the dispersed thermosetting resin. Nevertheless, the presence of the particulate phase, highly comminuted and chemically interacted with the elastomeric phase, is expected to advance the mechanical properties of the vulcanizate. This modification has been identified as Approach 6. Consequently, experimental effort was not undertaken on Approach 3 in preference to Approach 6. (Section 3. 6)

## 3.4 INTRODUCTION OF POINTS OF FLEXIBILITY IN THE CHAIN EXTENDER

### 3.4.1 Technical Approach

A logical location in the chemical structure of poly(cyclized 1, 2-polybutadiene) tolyl urethane (see Figure 5) for incorporation of points of flexibility in the structure lies in modification of the diisocyanate chain extender. Variations of the isocyanate which have been explored prior to this program by TRW Systems include using bitolyl diisocyanate, diphenyl methane diisocyanate, hexamethylene diisocyanate and General Mills-36 diisocyanate (Reference 4). These materials have demonstrated inertness to chemical attack by nitrogen tetroxide.

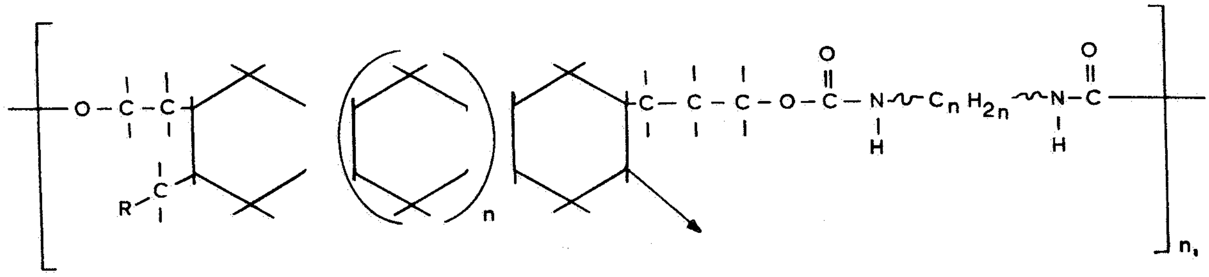


Figure 5. **Poly (Cyclized 1,2-Polybutadiene) Tolyl Urethane Chain Extended with a Long Chain Alkyl Diisocyanate**

### 3.4.2 Experimental

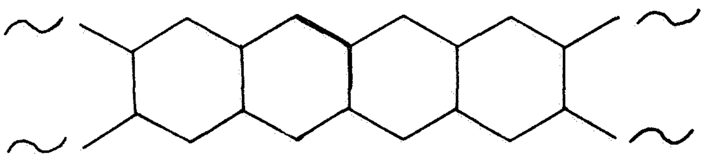
A candidate material was prepared in which the diisocyanate chain extender was modified by introduction of DDI (General Mills-36-carbon diisocyanate) which incorporates a long, flexible aliphatic chain between the isocyanate groups (Reference 6). The cure was 6 days at 90°C, 7 days at 120°C and 7 days at 180°C, with Barcol hardness of 20. Details of the experimental procedure used in preparation of this material are presented in Appendix A.

It was decided to explore the DDI diisocyanate initially to ascertain the value of this approach. The DDI material has two 18-carbon segments which are terminated by isocyanate groups. This long chain material provided the best opportunity to introduce flexibility in the backbone structure over other available diisocyanates, such as hexamethylene diisocyanate.

## 3.5 CHAIN TRANSFER MODIFICATION OF CPBU STRUCTURE

### 3.5.1 Technical Approach

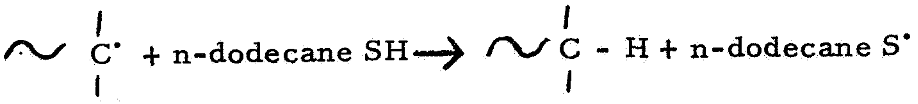
The fused cyclohexane ring structure which is thought to make up the backbone of CPBU



is not only a source of chemical and thermal resistance, but also a source of rigidity in the polymer molecule. Clearly, the modification of these rings to a cyclic form which is not rigid, but is still chemically resistant, would allow achievement of the two-fold goal of this project.

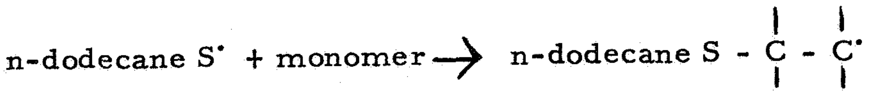
Chain transfer agents (in particular, 1-dodecane thiol) have long been used in rubber technology as chain length regulators (Reference 7). These are additives which terminate growing radical chains, and in turn, initiate new chains with the overall effect of shortening the average polymer chain length as outlined below.

Termination:



$$\sim\overset{|}{\underset{|}{C^{\bullet}}} + \text{n-dodecane SH} \rightarrow \sim\overset{|}{\underset{|}{C}} - H + \text{n-dodecane } S^{\bullet}$$

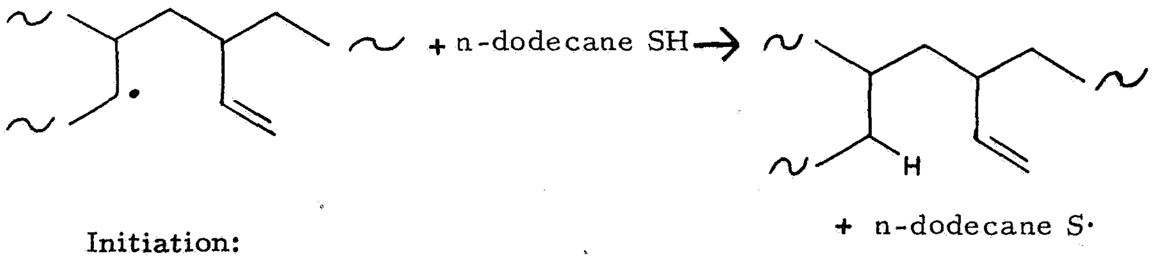
Initiation:



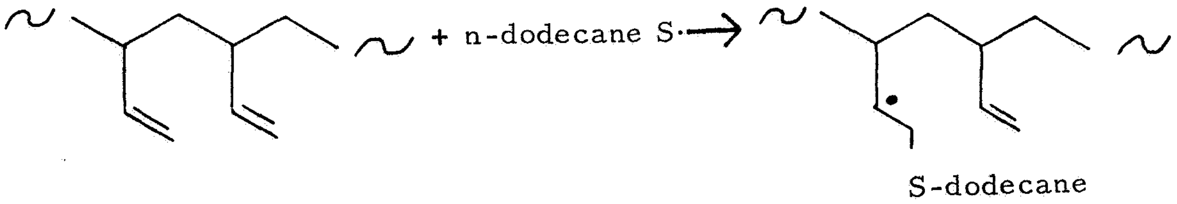
$$\text{n-dodecane } S^{\bullet} + \text{monomer} \rightarrow \text{n-dodecane } S - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C^{\bullet}}}$$

This process can be applied in the case of CPBU. A chain transfer agent, 1-dodecane thiol, will be included in CPBU formulations, for the purpose of interrupting the cyclization process through a mechanism of termination and initiation.

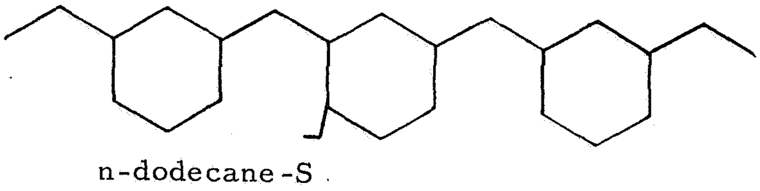
Termination:



Initiation:



This process should result in formation of an increased percentage of isolated cyclohexane rings with a concomitant decrease in number of fused cyclohexane rings.



In addition, the number of crosslinks between chains would be reduced. These two factors would increase the flexibility of CPBU. Further, the sulfide groups introduced into the structure are highly resistant to

$N_2O_4$. Thus, the overall effect should be an increase in flexibility of the resin with retention of chemical resistance.

### 3.5.2 Experimental

Several formulations containing small amounts of n-dodecane thiol chain transfer agent were prepared using the synthesis conditions outlined in Table V.

TABLE V

CHAIN TRANSFER MODIFIED CPBU CONDITIONS AND CHARACTERISTICS

| Chain Transfer Agent Content, phr[a] | Cure Cycle (Days) | | | Barcol Hardness |
|---|---|---|---|---|
| | 90°C | 120°C | 170°C | |
| 0.5 | 7 | 7 | 7 | 26 (Wide variance according to |
| 1. | 7 | 7 | 7 | 27 area of sample) |
| 5. | 7 | 7 | 7 | 28 |

a. phr = parts per hundred 1,2-polybutadiene diol.

As seen in Table V , the addition of n-dodecane thiol in the amounts indicated did not appreciably soften CPBU.

Details of the synthesis procedures used in preparation of this material are presented in Appendix A.

## 3.6 PREPARATION OF CPBU/ELASTOMER COMPOSITES

During the latter stages of the systematic preparation and characterization studies of this program, it became evident that introduction of points of flexibility in the backbone or crosslinks of the CPBU showed little promise to obtain the desired flexible, impermeable and chemical resistant product. Consequently, emphasis was changed to a new processing method which would permit preparation of CPBU in a particulate state homogenously dispersed in chemically resistant ethylene-propylene terpolymer (EPT) rubber. Because this method has yielded products with significantly enhanced bladder properties over state-of-the-art materials and provides the direction for even further improvement, the description of the technical approach and experimental studies will be presented in some detail here.

The last two approaches, which were conceived subsequent but investigated prior to the CPBU/elastomer composites are discussed in following sections.

### 3.6.1 Technical Approach

This approach consists of three principal steps:

- Preparation and comminution of elastomeric (B-stage) CPBU,
- Blending the CPBU with the EPT gum stock; and
- Vulcanization of the product.

Under vulcanization conditions chemically resistant, cured CPBU should be formed within the vulcanized rubber matrix. Consequently, CPBU composite vulcanizates containing finely divided CPBU interspersed within the crosslinked rubber matrix should exhibit enhanced $N_2O_4$ stability and permeability over EPT rubber. The elastomeric property of the vulcanizates should result from selected chemically-stable gum stocks which act as the elastomeric portion of the composition, while the reduced permeability should occur from the presence of CPBU. The resulting elastomeric vulcanizates would be expected to yield composite stocks which should be advanced over current "state-of-the-art" propellant bladder materials.

Underlying considerations in the selection of EPT gum stock were:

- Availability of unreacted vinyl groups which could participate in reaction with the pendant vinyl groups of the elastomer B-stage CPBU during vulcanization;
- Utilization of a curing process requiring free radicals available in the B-stage CPBU; and
- Exhibition of reasonable chemical stability to nitrogen tetroxide.

Preparation of the desired composite vulcanizate is possible only because of the elastomeric stage of CPBU and its free radical-initiated final cure reaction. The elastomeric state enhances the wetting and surface penetration of CPBU by the gum stock. On the other hand, dissolution of CPBU into the gum stock is minimized because the elastomeric CPBU is chemically crosslinked. As a consequence, interaction between the rubber gum stock and CPBU elastomer will be enhanced and the CPBU will retain its inherent chemical composition. The free radical-initiated chemical reaction of transforming CPBU from an elastomer to the hard stage is essentially the same reaction commonly employed in rubber vulcanization. Therefore, vulcanization of CPBU-rubber gum stock composites was expected to be accomplished with the formation of chemical bonds at the interface of CPBU and the vulcanized gum stock.

The features of the CPBU-rubber composites were expected to yield bladder materials which exhibit greater resistance to propellant permeability than that afforded by a simple additive contribution of the constituents. It is believed this synergistic result would arise because a significant portion of the rubber matrix will be affected by the CPBU surface. As a result of this interaction the mobility of the gum stock at the CPBU surface would be reduced. Thus, the resistance of the elastomeric portion was expected to be increased.

As a consequence of the interaction between the rubber matrix and the CPBU surface, the elastomeric properties of the composite vulcanizate might also be reduced, however, it was believed that the degree of reduction in flexibility would not significantly impair the application of the composite as a propellant bladder.

### 3.6.2 Experimental

#### 3.6.2.1 Preparation and Comminution of Elastomeric (B-Stage) CPBU

During this program a systematic study of the preparation and comminution of B-stage CPBU was not undertaken. The polyurethane rubber was prepared by simply reacting 1,2 polybutadiene diol and trimethyol propane with toluene diisocyanate. Dicumyl peroxide was added to the mixture in the normal manner (see Appendix A) for subsequent use as a peroxide free radical agent. The material was cast into a rod form and cured at 90°C in the absence of air.

Comminution of the CPBU was accomplished by first freezing the elastomeric form with liquid nitrogen and then grinding in a mill designed to operate at cryogenic temperatures. In the only comminution performed in this program, temperature control of the mill was defective and hence, a relatively large particle distribution resulted, with particles ranging from 175 to 500 microns in size.

### 3.6.2.2 Blending the CPBU with the EPT Gum Stock

#### 3.6.2.2.1 Initial Considerations

The process of the addition of a 'filler' to a rubber gum stock has been well defined by the rubber industry. Only two pieces of mixing equipment have gained permanent favor: the rubber mill, and the Banbury Mixer (Reference 8). The latter piece of equipment is mainly for use in production operations where labor costs are of great concern. The former, the two-roll rubber mill, is the standard piece of equipment used to study the mixing behavior of rubber stocks. It was on this type of equipment that the initial mixing method for CPBU/EPT composites was developed. A Pamco 7-1/2 horsepower rubber mill (incorporating a standard back roll to front roll friction ratio of 1.25 to 1) was obtained, installed and made operational. This apparatus is shown in Figure 6 together with identification of some of its key components.

First attempts in mixing were with a 50% w/w mixture of powdered CPBU elastomer in the EPT. Assuming a starting weight of 200 grams of EPT on the 6-inch by 12-inch mill, mixing was started on a tight (0.010-inch nip) mill and then slowly opened to about a 0.100-inch nip for final slabbing. In later studies, slight chilling was required on the back roll to keep the stock from splitting. Temperature of mixing necessarily must be kept below 250°F to prevent premature dissociation of the dicumyl peroxide free radical initiator present in both the CPBU powder and the EPT. Temperature control is provided by a hot/cold water system integral with the mixing rolls.

The initial formulation plan called for a series of mixing tests with varying CPBU/EPT mass ratios. After the 50% w/w loading of the initial attempt, the CPBU powder content was to raise to 80% w/w in 10% steps (if mixing will allow steps this large). An attempt was

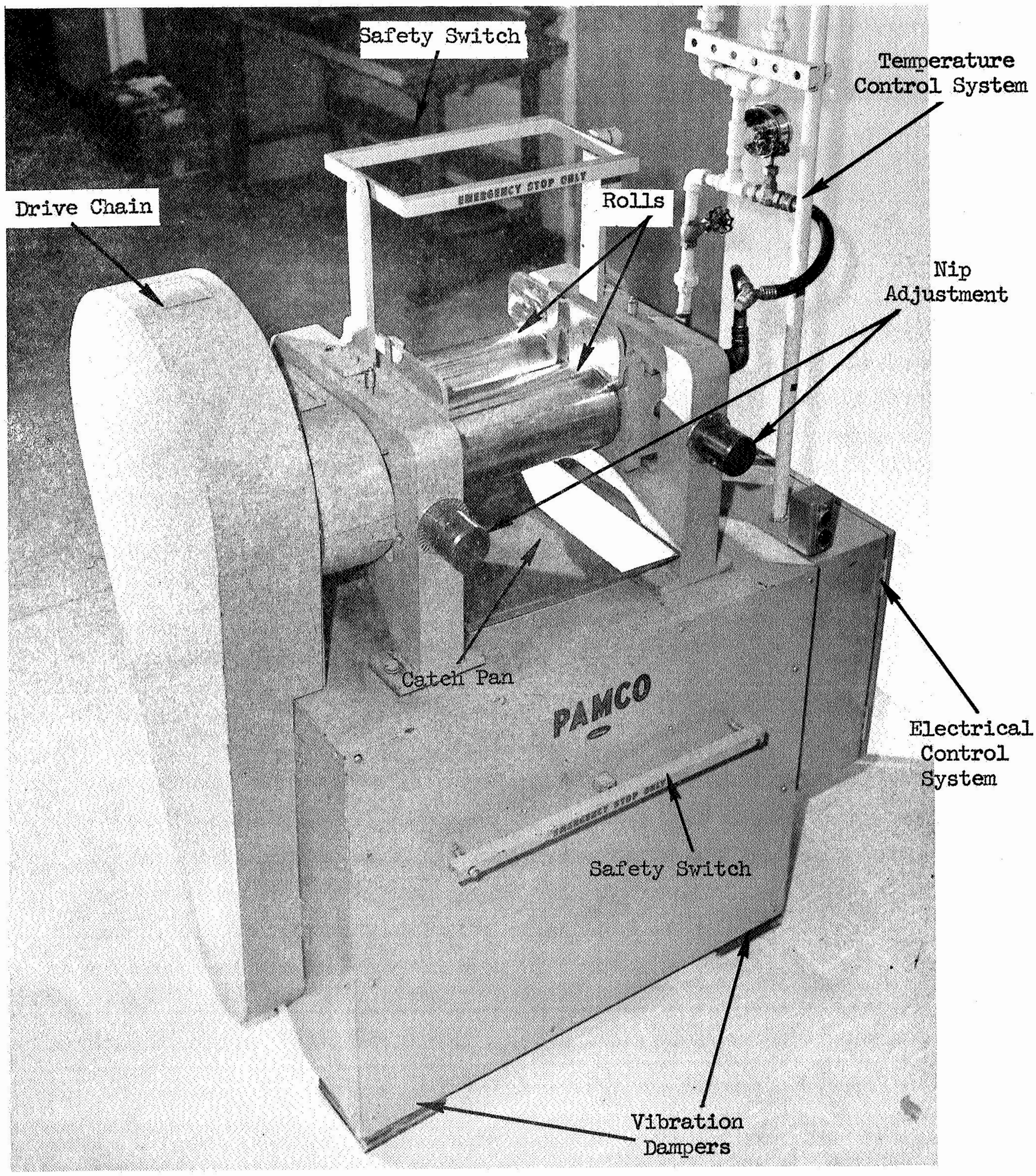


Figure 6. Pamco Rubber Mill

made to mix as much as 95% w/w CPBU into EPT. This study established the limits of mill mixing.

### 3. 6 2. 2. 2 CPBU/EPT Composites

EPT stocks (EPT 404, Enjay Chemical Company and NORDEL 1040, DuPont) were banded on the front roll of a rubber mill. Preweighed powdered elastomeric CPBU was fed slowly onto the top of the band. The CPBU was incorporated into the EPT with difficulty and required many cutting and folding operations to produce a homogeneous band. The curative was added and the band was again cut and folded many times to insure good mixing. The nip was opened to 0. 100 inch and the stock sheeted off. The compositional formulation of the CPBU/EPT blends are listed in Table VI together with a description of the green stock and the molded product.

It was noted that at concentrations of CPBU greater than 80 phr, the stock became quite "lacy" and dry. Above 80 phr CPBU, the stock powdered, fell off the roll and could not be prepared on the rubber mill. In this case, the mixture was mixed as a dry blend in a Baker Perkins Sigma Blade Mixer and moldings were made with the mixed powder. Dicumyl peroxide was selected as the curative for initial study because 1) TRW Systems experience with molding powders and laminates indicated that dicumyl peroxide offered certain processing advantages over di-t-butyl peroxide, and 2) "resistant" EPT rubber (used for comparison) is normally cured with dicumyl peroxide. It was evident from the early experiments that the green strength of the blend was important in determining the quality of the vulcanized product.

### 3. 6. 2. 2. 3 Preparation of EPT Standards for Comparison

"Resistant" EPT (Reference 9 ) rubber was selected as a standard for comparison to permit evaluation of candidate materials with respect to improved chemical and physical properties. Because this material contained carbon as an additive, a similar formulation without carbon was selected for comparison. Two other standards were prepared which contained di-t-butyl peroxide instead of dicumyl peroxide. The formulations prepared for reference standard purposes are listed in Table VII together with descriptions of the green stock and the vulcanized product.

## TABLE VI
## CPBU/EPT FORMULATION

| Constituents | Formulation, Parts by Weight | | | | | |
|---|---|---|---|---|---|---|
| | 4-3-1 | 4-3-2 | 4-3-3 | 4-3-4 | 4-3-5 | 4-3-6 |
| EPR 404 | 100 | 100 | - | - | - | - |
| NORDEL 1040 | - | - | 100 | 100 | 100 | 100 |
| CPBU Elastomer Powder[a] | 75 | 75 | 100 | 100 | 400 | 1900 |
| CPBU Prepolymer[b] | - | - | - | 80 | - | - |
| Diethylenetriamine[c] | - | 24 drops | - | - | - | - |
| Dicumyl Peroxide | 5 | 5 | 5 | 7 | 5 | 5 |
| **Properties** | | | | | | |
| Green Stock | d | d | e | f | e | e |
| Shore Hardness | 70A | 70A | 90A | 55D | 80D | 90D |
| Molded Appearance | g | h | g | g | j | j |
| Bend Test[k] | Fail | Fail | Fail | Fail | Fail | Fail |

a. Containing dicumyl peroxide.
b. Added to increase green strength; results negative.
c. Added for pH control to assure stock was basic pH.
d. Weak lacy gum.
e. Dry powder.
f. Sticky powder.
g. Cream colored, homogeneous elastomer.
h. Dark brown, homogeneous elastomer.
j. Transparent, with cloudy spots.
k. Survival of 180° bend on 0.075-inch thick specimen.

## TABLE VII
## EPT/CARBON BLACK/PEROXIDE CONTROL FORMULATIONS

| Constituents | Formulation, Parts by Weight | | | |
|---|---|---|---|---|
| | 1-1[a] | 1-2 | 1-3 | 1-4 |
| NORDEL 1040 | 100 | 100 | 100 | 100 |
| FEF Carbon Black | 50 | 50 | - | - |
| Dicumyl Peroxide | 5 | - | 5 | - |
| Di-t-Butyl Peroxide | - | 5 | - | 5 |
| Cure, Min/°F | 40/320 | 40/375 | 40/320 | 40/325 |
| **Properties** | | | | |
| Shore Hardness | 74A | 70A | 52A | 38A |
| Bend Test[b] | Pass | Pass | Pass | Pass |

[a] "Resistant" EPT reported by RMD Division, Thiokol Chemical Corporation.

[b] Survival of 180° bend on 0.075-inch thick specimen.

### 3.6.2.2.4 CPBU/EPT/Carbon Composites

In an effort to reduce or eliminate the "laciness" of the CPBU/EPT gum stocks during mixing, carbon black (FEF) was added as a processing aid to the blended gum and was found to produce unexpected good results. Not only did the "laciness" disappear, but also the green strength of the stock was considerably increased. It also appeared that the carbon black increased the tolerance of the EPT gum for CPBU powder, allowing greater amounts of CPBU to be added while maintaining a workable green stock.

The effect of carbon on the workability and green strength of the CPBU/EPT is readily seen by comparison of Figures 7 and 8. Figure 7 shows a typical CPBU/EPT blend on the rubber mill. The "laciness" and weak green strength is readily evident. In Figure 8 the same CPBU/EPT blend is shown with carbon black added. As is seen, a tight band resulted and the product has good green strength. Various attempts were made to maximize the amount of CPBU added to the EPT stock and still maintain a suitable green stock. First indications were that 50 phr carbon black was required up to 100 phr CPBU, and 100 phr carbon black was required above 100 phr CPBU. By varying processing conditions during mill mixing, it was found that a maximum of 400 phr CPBU could be incorporated with 50 phr of carbon black. Specifically, hot mixing and employing a tightly set nip provides the necessary wetting and mixing action; however, the stock was crumbly and fell in chunks into the mill pan. Subsequent cooling of the milled mass to room temperature followed by rapid sheeting-off at 0.100-inch nip setting (for 200-300 grams total on a 6 x 12 mill) provided green stocks with good strength. The di-tert-butyl peroxide curative (for the EPT) was added during the sheeting operation to minimize volatilization.

A series of formulations (See Table VIII) was made by this method employing a constant EPT/carbon black ratio of 100/50 parts by weight. The CPBU was varied from 40 phr to 400 phr (roughly 20-72% w/w). All formulations had good green strength, molded well, and produced uniform, flexible specimens after mold curing.

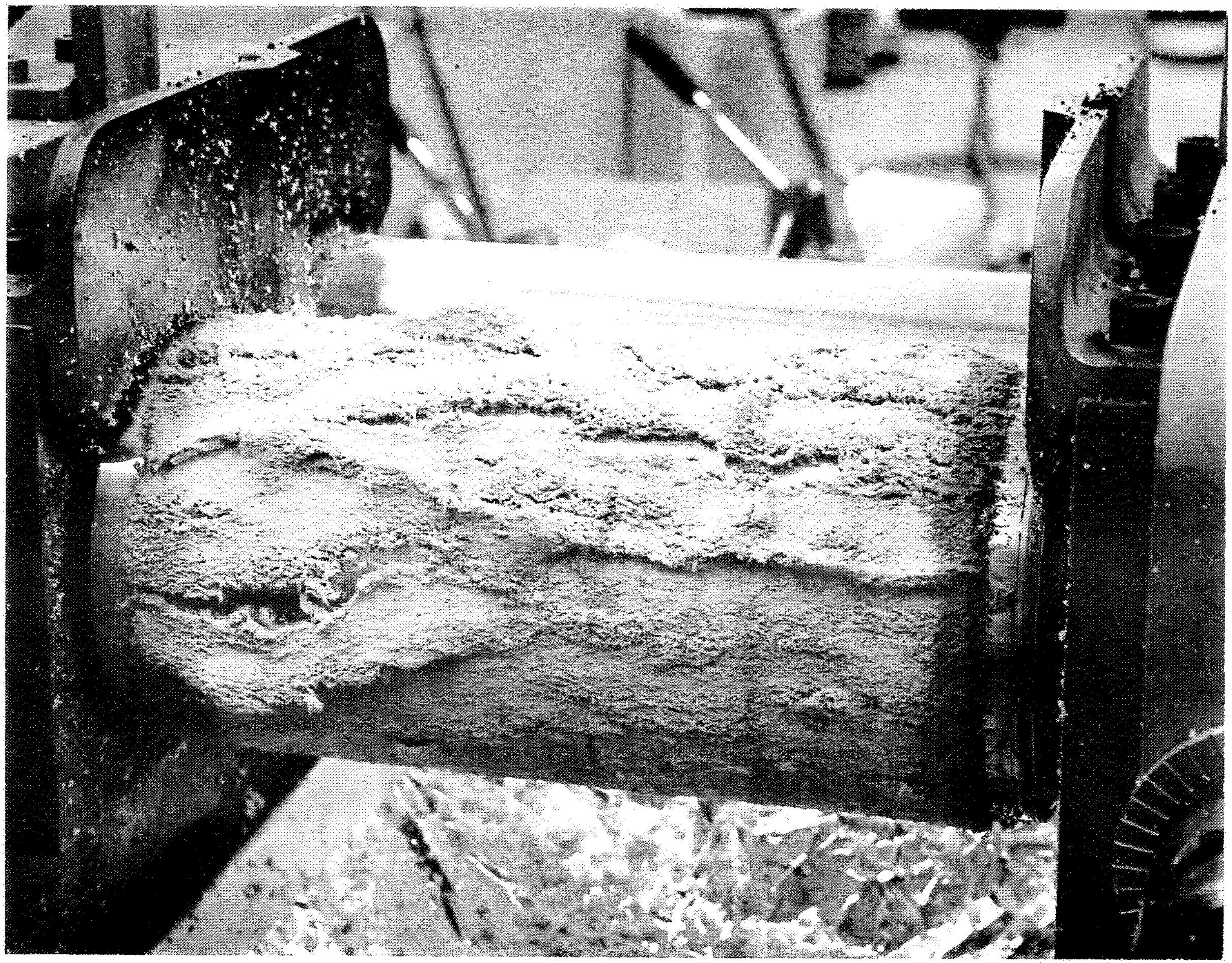


Figure 7. Typical CPBU/EPT Composite Formulation During Rubber Milling

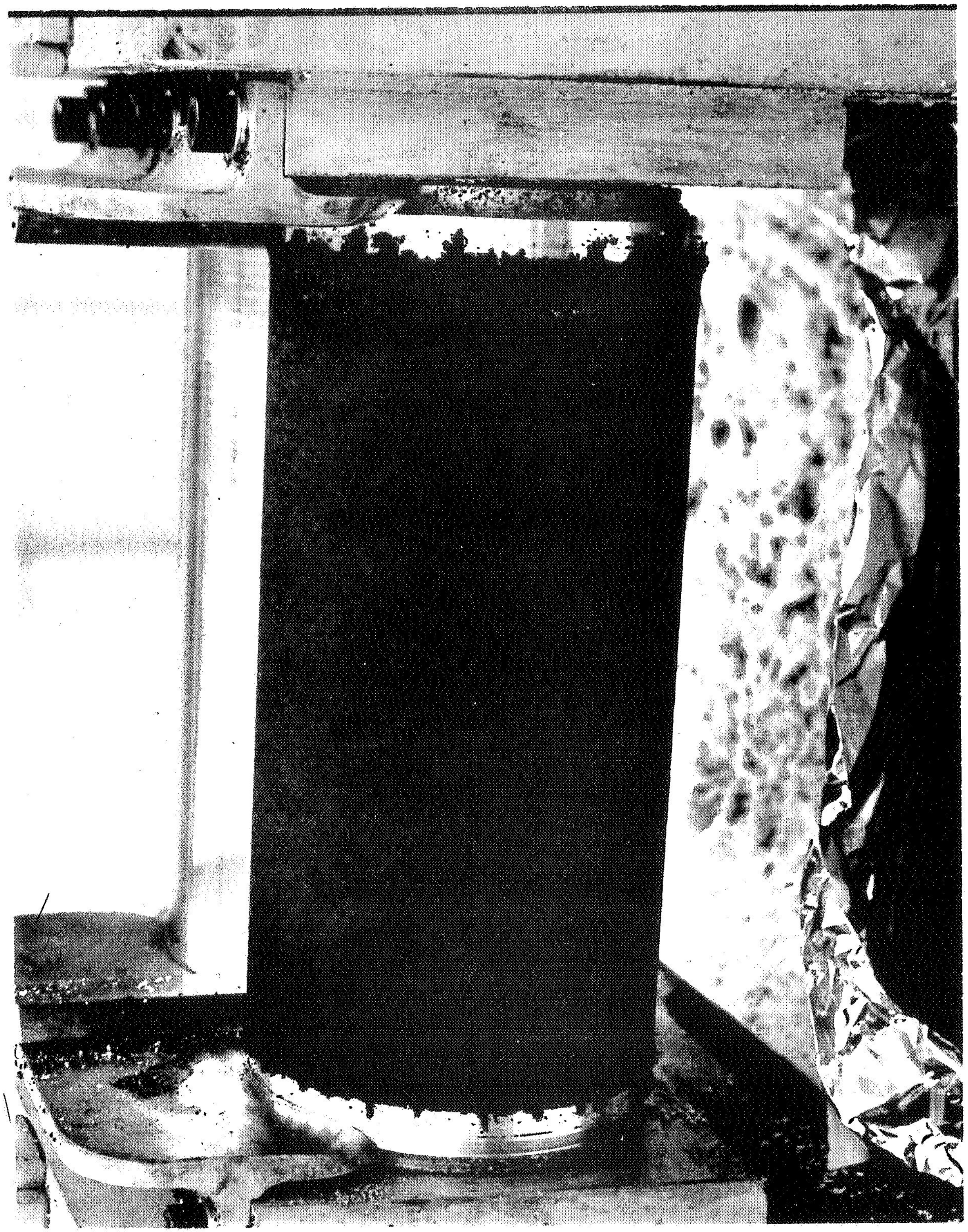


Figure 8. Typical CPBU/EPT/Carbon Composite Formulation During Rubber Milling

## TABLE VIII
## CPBU/EPT/CARBON COMPOSITE VULCANIZATE FORMULATION

| Constituents | Formulation, Parts by Weight | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1-1[a] | 9-1 | | 9-2 | | 9-3 | | 9-4 | |
| NORDEL 1040 | 100 | 100 | | 100 | | 100 | | 100 | |
| FEF Carbon Black | 50 | 50 | | 50 | | 50 | | 50 | |
| CPBU Powder[b] | -0- | 40 | | 100 | | 200 | | 400 | |
| Di-Tert-Butyl Peroxide | 5[d] | 5 | | 5 | | 5 | | 5 | |
| Cure, Min. at 375°F | 40 | 40 | 80 | 40 | 80 | 40 | 80 | 40 | 80 |
| Shore Hardness | A74 | A82 | A82 | A95 | A95 | D65 | D60 | D76 | D80 |
| Bend Test[c] | Pass | Pass | Pass | Pass | Pass | Fail | Fail | Fail | Fail |

a. Control, "Resistant" EPT reported by RMD Division, Thiokol Chemical Corporation.

b. Thermoset B-stage elastomer powder containing the appropriate amount of di-tert-butyl peroxide, particle size greater than 175 microns.

c. Survival of 180° bend on 0.075-inch thick specimen.

d. Dicumyl peroxide used in this one formula.

### 3.6.2.2.5 Preparation of CPBU/EPT/Carbon Standards for Comparison

It was speculated earlier (Section 3.6.1) that the CPBU filler would function in the cured composites as follows:

- A discrete particle not in solution with the elastomeric matrix;
- A particle with chemical functionality suitable for interaction with the elastomeric matrix; and
- A particle resistant to the chemical reaction and permeation of nitrogen tetroxide.

The form of CPBU selected for this study which meets all of the above criteria would necessarily be a comminuted form of the thermosetting version of the B-stage elastomer. It was speculated that a thermoplastic version of the B-stage (prepared by elimination of polyurethane crosslinking agents) would enter into solution with the EPT matrix either during mill mixing or during the cure. The resulting loss of the discrete particulate form, it was speculated, would thereby degrade the mechanical properties of the composite by embrittlement. It was also speculated that utilization of C-stage CPBU particles instead of the B-staged elastomer particles would not permit sufficient interaction with the matrix during vulcanization because of the relative absence of vinyl unsaturation on the particle surface, and hence the resistance to permeability would be lower.

Two control formulations were prepared which represent the two cases discussed above (utilization of B-stage thermoplastic and C-stage powder) to permit comparison with the candidate B-stage thermosetting powder formulations. This is a cursory comparison because the particle size of the C-stage material is significantly smaller (less than 10 microns) than that of the two B-stage materials. Consequently, it is not possible to separate completely the effect of particle size from the chemical interaction concept in the interpretation of the test data. During incorporation of the thermoplastic version material into the EPT gum stock, it was apparent that the B-stage particles dissolved into the matrix and did not remain as discrete particles. Table IX lists the chemical formulations used to prepare these comparison specimens.

## TABLE IX

## CONTROL FORMULATIONS FOR STUDY OF PERMEABILITY MECHANISM

| Constituents | Formulation, Parts by Weight | |
|---|---|---|
| | 9-8 | 7-3-3 |
| NORDEL 1040 | 100 | 100 |
| FEF Carbon Black | 50 | 50 |
| CPBU Powder Thermoplastic | 0 | 200 |
| CPBU Powder C-Stage | 100 | 0 |
| Di-Tert-Butyl Peroxide | 5 | 5 |
| Cure, Min/°F. | 40/375 | 40/375 |
| Shore Hardness | A-90 | D70 |
| Bend Test | Pass | Fail |

### 3.6.2.3 Vulcanization of the Product

Vulcanizing of the CPBU/EPT composites into test specimens was accomplished with standard rubber laboratory equipment. An ASTM D-15 Rubber Test Slab Mold (6-inch x 6-inch x 0.075-inch thick) was used to mold uniform specimens. In the studies conducted in this program, the time/temperature/pressure relationship of the vulcanizing conditions were not investigated in detail. In tests performed by other workers, an EPT stock (found useful for short exposures to $N_2O_4$) was press cured for 40 minutes at 320°F (Reference 9 ). These conditions also were very favorable for curing the CPBU powdered elastomer contained in the EPT. Initially it was assumed that this cure cycle was satisfactory for both materials, and the vulcanizations were performed under these conditions at a pressure sufficient to close the mold completely in 10 seconds. Studies of other cure schedules were investigated however on a limited scale; higher temperatures for shorter periods of time may be attractive, i. e., 375°F for 10 minutes. Shorter cure times with higher cure temperatures, compared with long time, lower temperature cures, would not tend to cause as much chemical breakdown in rubber stocks. Conversely, longer times at lower temperatures may be necessary to prevent excessive exotherms.

The vulcanization schedules used with the specific formulations studied are listed in Tables VI, VII, VIII, and IX.
In the only semi-systematic study, two cure times were used (40 minutes and 80 minutes both at 375°F) in the formulation series reported in Table VIII . There was no appreciable difference in appearance of the cured specimens between the 40 and 80 minute cures, although some hardness differences were noted.

The maximum value of one property of rubber stocks does not usually coincide with that of another property at the same degree of cure (Reference 10 ). That is to say, maximum tensile or tear strength will not necessarily coincide with maximum resistance to $N_2O_4$ attack and permeability. For this reason, it would be necessary to trade-off the mechanical and chemical properties to select the optimum cure cycle. Within a specified band of mechanical properties, end-use chemical testing (chemical resistance and permeability) would be used to guide this selection.

The molded specimens were evaluated by mechanical and chemical tests. Preliminary screening of the composites was the same as that utilized previously, e.g., 10-day resistance to $N_2O_4$ attack and a softness in the Shore D range or below. In addition to the above basic screening tests, a flexural test was instituted based on the ability of the molded CPBU-rubber composite to be bent $180^o$ (back on itself), without splitting or tearing. Because there is an interrelationship between flexibility and thickness, the standard 75-mil thick specimen was used for this test.

Detailed testing of formulations which passed the screening consisted of standard ASTM tensile and flexural mechanical property tests and $N_2O_4$ permeability measurements. Standard test slabs produced from an ASTM mold provided a sheet for punching out tensile and elongation specimens. The results obtained in characterizing the permeability and mechanical properties of these promising materials are presented in Section 4.

## 3.7 EXTERNAL PLASTICIZATION

### 3.7.1 Technical Approach

Another approach that was evaluated was based on external plasticization of CPBU with a halogenated wax. This material was selected as a plasticizer because it is chemically inert and it was believed that it could soften CPBU to an extent similar to that of poly vinyl chloride without impairing the overall $N_2O_4$ resistance of the plasticized material. Chlorowax 70, a halogenated wax of the Diamond Alkali Company, commonly used for external plasticization of non-crosslinked polymers, was selected for evaluation.

### 3.7.2 Experimental

CPBU which was plasticized with 5 phr Chlorowax 70 was prepared using the standard mixing techniques. A 0.500-inch diameter rod was cast and cured with the following CPBU time-temperature cure sequence:

| Temperature, °C | Time, Hours |
|---|---|
| 90 | 16 |
| 120 | 6 |
| 140 | 16 |
| 170 | 6 |

This cure cycle has recently been developed during TRW Company-supported studies and has been found to be as effective as those described above. The new cure cycle reduces the overall cure time from approximately 21 days and over to less than 2 days. Details of the experimental procedures are reported in Appendix A.

The 1/2-inch bar obtained using the Chlorowax 70 plasticizer was highly flexible and was able to withstand a 180° bend without tearing.

## 3.8 NON CHAIN EXTENDED CPBU

### 3.8.1 Technical Approach

The chain extension step using toluene diisocyanate, a difunctional diisocyanate, is a source of crosslinking in the elastomeric and fully cured CPBU product. This crosslinking is a necessary feature of the elastomeric material, but could be a source of rigidity in the final hard product. In view of this, an approach was investigated in which phenyl isocyanate was substituted for toluene diisocyanate in the usual CPBU formulation. In this manner a low molecular weight urethane precursor (non-chain extended) was produced for subsequent peroxide cure.

### 3.8.2 Experimental

The prepolymer diol and the phenyl urethane capped products were purified by recoagulation from toluene-methanol. The cure schedule described in Section 3.7.2 was used for this material. Experimental details are presented in Appendix A.

The product obtained from this synthesis was hard, having a Barcol hardness of 35 and resembled the standard chain extended CPBU product. Because the sample was not softened without chain extension, it is clear that the chain extension step plays only a secondary role, if any, in the final hardness of CPBU.

## 4. CHARACTERIZATION OF CANDIDATE MATERIALS

The candidate materials prepared in Task I of this program were evaluated in a step-wise testing program which called for preliminary screening, secondary screening and finally detailed testing of chemical resistance, permeability and mechanical properties. The preliminary screening consists of survival in 10-day immersion in $N_2O_4$ and improvement in flexibility as measured by 1) hardness in the Shore D, (or below) range, or 2) as in the later studies on CPBU/rubber composites, survival of a 180° bend on a 0.075-inch thick specimen. The secondary screening consisted of 1) measurement of $N_2O_4$ permeability of the candidate materials at ambient temperature, and 2) determination of the mechanical properties of the more outstanding materials. Measurements of 90-day aging characteristics after exposure to standard earth storable propellants was not conducted during this program as planned because the highly promising composite vulcanizates became available late in the program.

In this section are presented the results of the characterization of the materials prepared and described in Section 3. For clarity, these results are presented in the same sequence given in Section 3.

### 4.1 CHARACTERIZATION OF INTERNALLY PLASTICIZED CPBU

Nitrogen tetroxide resistance as a function of initial hardness and amount of plasticizer is presented in Table X. These results show that the formulations with the low ratios of 1-alkene to 1, 2-polybutadiene diol are softened while retaining a certain amount of $N_2O_4$ resistance. Although the 11 phr $C_{14}$-$C_{18}$ internally plasticized CPBU has the lowest hardness, it is still too high for use as a bladder material.

### 4.2 CHARACTERIZATION OF COPOLYMERIZED CPBU

Nitrogen tetroxide resistance as a function of initial hardness and amount of copolymer is presented in Table XI. Samples of the 1, 4-polybutadiene diol modified resins were pre-treated with nitric acid, sulfuric acid or bromine in order to remove residual unsaturation at the surface as a protection against reaction with nitrogen tetroxide. However,

## TABLE X
## INTERNAL PLASTICIZER CPBU PRELIMINARY SCREENING

| Internal Plasticizer | Internal Plasticizer Content, phr[a] | Weight Change,[b] $N_2O_4$ Resistance (10 day) | Hardness |
|---|---|---|---|
| None | | Excellent | 44 Barcol |
| 1-octane | 11 | Good | 24 Barcol |
| | 25 | Poor | 15 Barcol |
| | 43 | Poor | 6 Barcol |
| | 67 | Poor | 98 Shore A-2[d] |
| | 100 | Poor | 0 Barcol[e] |
| | 150 | Poor | 0 Barcol[e] |
| | 230 | Poor | 0 Barcol[e] |
| | 400 | Poor | 0 Barcol[e] |
| 1-decene | 100 | Poor | 0 Barcol[e] |
| 1-hexadecene | 100 | Poor | 0 Barcol |
| $C_6$-$C_{10}$ 1-alkene | 11 | Good | 42 Barcol |
| | 25 | Poor | 19 Barcol |
| | 43 | Poor | 100+ Shore A-2 |
| $C_{14}$-$C_{16}$ 1-alkene | 11 | Good | 27 Barcol |
| | 25 | Poor | 100+ Shore A-2 |
| | 43 | Poor | 98 Shore A-2 |
| | 67 | Poor | 93 Shore A-2 |
| $C_{14}$-$C_{18}$ 1-alkenes | 11 | Good | 99 Shore A-2 |
| | 25 | Poor | 99 Shore A-2 |
| | 43 | Poor | 97 Shore A-2 |
| | 67 | Poor | 94 Shore A-2 |

a. phr = parts per hundred 1, 2-polybutadiene diol.

b. Excellent = 0. 5 mg/cm$^2$ or less; Good = between 0. 5 and 6. 0 mg/cm$^2$; Poor = greater than 6. 0 mg/cm$^2$.

c. Neat CPBU.

d. The Shore A hardness test is for the range of materials which is softer than those in the Barcol range.

e. Shore A hardness not determined.

## TABLE XI

## COPOLYMERIZED CPBU PRELIMINARY SCREENING

| Copolymer | Copolymer Content, phr[a] | Weight Change,[b] $N_2O_4$ Resistance (10 day) | Hardness |
|---|---|---|---|
| Ricinoleic Triglyceride | 5 (Soft Cure) | Good | 42 Barcol |
| | 5 (Vigorous Cure | Good | 47 Barcol |
| | 10 (Soft Cure) | Good | 38 Barcol |
| | 10 (Vigorous Cure) | Good | 44 Barcol |
| | 20 (Soft Cure) | Good | 35 Barcol |
| | 20 (Vigorous Cure | Good | 39 Barcol |
| | 30 (Soft Cure) | Good | 32 Barcol |
| | 30 (Vigorous Cure) | Poor | 36 Barcol |
| 1, 4-Polybutadiene Diol | 200 (Soft Cure) | Good | 36 Barcol |
| | 200 (Vigorous Cure) | Excellent | 44 Barcol |
| | 100 (Soft Cure) | Good | 34 Barcol |
| | 100 (Vigorous Cure) | Excellent | 47 Barcol |
| | 50 (Soft Cure) | Good | 30 Barcol |
| | 50 (Vigorous Cure) | Excellent | 49 Barcol |
| | 25 (Soft Cure) | Good | 22 Barcol |

a. phr = part per hundred 1, 2-polybutadiene diol.

b. Excellent = 0. 5 $mg/cm^2$ or less; Good = between 0. 5 and 6. 0 $mg/cm^2$; Poor = greater than 6. 0 $mg/cm^2$.

it was found that pre-treatment gave no appreciably improved protection nor softening. Results of preliminary screening tests are reported only for the untreated state.

These results show that 1) 1,4-polybutadiene diol copolymer does not cause softening of CPBU, and 2) ricinoleic triglyceride softens CPBU to only a small extent, while materially decreasing $N_2O_4$ resistance. Therefore, no useful bladder materials have been obtained during the course of synthesis of these CPBU formulations.

## 4.3 CHARACTERIZATION OF CHAIN EXTENDER MODIFIED CPBU

Results of preliminary screening of the chain extender modified CPBU formulation is presented in Table XII.

TABLE XII

PRELIMINARY SCREENING OF CHAIN EXTENDER MODIFIED CPBU

| Weight Change,[a] $N_2O_4$ Resistance (10-day) | Barcol Hardness |
|---|---|
| Poor | 20 |

a. Excellent = 0.5 mg/cm$^2$ or less; Good = between 0.5 and 6.0 mg/cm$^2$; Poor = greater than 6.0 mg/cm$^2$.

Clearly, the modification in the chain extender, while only slightly softening CPBU, significantly lowered the $N_2O_4$ resistance. Because DDI, which is considered to be the most flexible of diisocyanate chain extenders, did not give the desired chemical and physical properties, further experimentation along these lines did not appear to be warranted.

## 4.4 CHARACTERIZATION OF CHAIN TRANSFER MODIFIED CPBU

Results of preliminary screening of the n-dodecane thiol chain transfer agent modified CPBU formulations showed that all three formulations were not appreciably softened (hardness of around 27 Barcol) and exhibited poor to good $N_2O_4$ resistance. Because of these unpromising results, further investigations using other chain transfer agents were not performed.

## 4.5 CHARACTERIZATION OF CPBU/RUBBER COMPOSITES

### 4.5.1 Resistance to Nitrogen Tetroxide Attack

The nitrogen tetroxide resistance of candidate CPBU/EPT and CPBU/EPT/carbon composites is summarized in Table XIII. It is seen that the early formulations of CPBU/EPT composites (Series 4-3-x) had relatively poor chemical resistance, however, the trend of increased resistance with increased CPBU content was generally evident. The chemical resistance of these specimens, although considered poor by the standards established in this program, was generally better than the control specimens of EPT (Series 1-x), which are currently used as elastomeric components in state-of-the-art rocket engines employing nitrogen tetroxide. The early CPBU/EPT/carbon composites (Series 2-x) and those produced later (Series 9-x) gave significantly improved chemical resistance over comparable state-of-the-art materials, with the improvement generally increasing as a function of CPBU content.

### 4.5.2 Nitrogen Tetroxide Permeability

The nitrogen tetroxide permeability-time cures of candidate CPBU/EPT/carbon composite materials (Series 9-x) are shown in Figure 9. Also shown in Figure 9 are permeability-time curves for the EPT control and the state-of-the-art 0.008-inch thick Teflon (TFE) obtained from Dielectrics, Inc. The CPBU/EPT/carbon vulcanizates and EPT/carbon control were 0.075-inch thick. In general, the 0.075-inch thick vulcanizates were sufficiently flexible for bladder service, whereas TFE must be less than 0.010-inch thick. (See Section 4.5.3). Consequently, Figure 9 compares materials at thicknesses which can be used for storable propellant expulsion bladders. Both the standard resistant EPT rubber and approximately 20% thermosetting B-stage CPBU have approximately the same permeability curve. However, when the content of CPBU is increased to at least 39% (Formulation 9-2), the significant improvement in permeability is observed. It is clear from these studies that increasing the CPBU content markedly decreases the permeability of the composite vulcanizate. It is also clear from comparisons of Figure 2 and Figure 9 that a significant improvement in permeability over common state-of-the-art bladder materials is afforded with CPBU/EPT/carbon composite vulcanizates.

## TABLE XIII

## $N_2O_4$ COMPATIBILITY OF CPBU/ELASTOMER FORMULATIONS

| Formulations | Weight Increase $N_2O_4$ Resistance (5 day) $mg/cm^2$ | Shore Hardness |
|---|---|---|
| EPT Controls | | |
| 1-1 | a | 74A |
| 1-2 | a | 70A |
| 1-3 | a | 52A |
| 1-4 | a | 38A |
| CPBU/EPT | | |
| 4-3-1 | 22.1 | 70A |
| 4-3-2 | a | 70A |
| 4-3-3 | 17.1 | 90A |
| 4-3-4 | 15.0 | 55D |
| 4-3-5 | 14.5 | 80D |
| 4-3-6 | 10.9 | 90D |
| CPBU/EPT/C | | |
| 9-1 | 10.5 | 82A |
| 9-2 | 5.3 | 95A |
| 9-3 | 3.9 | 65D |
| 9-4 | 2.1 | 76D |
| CPBU/EPT Controls | | |
| 9-8 | a | 90A |
| 7-3-3 | 12.4 | 70D |

a. Sample segregated into smaller chemically attacked sections which could not be weighed accurately.

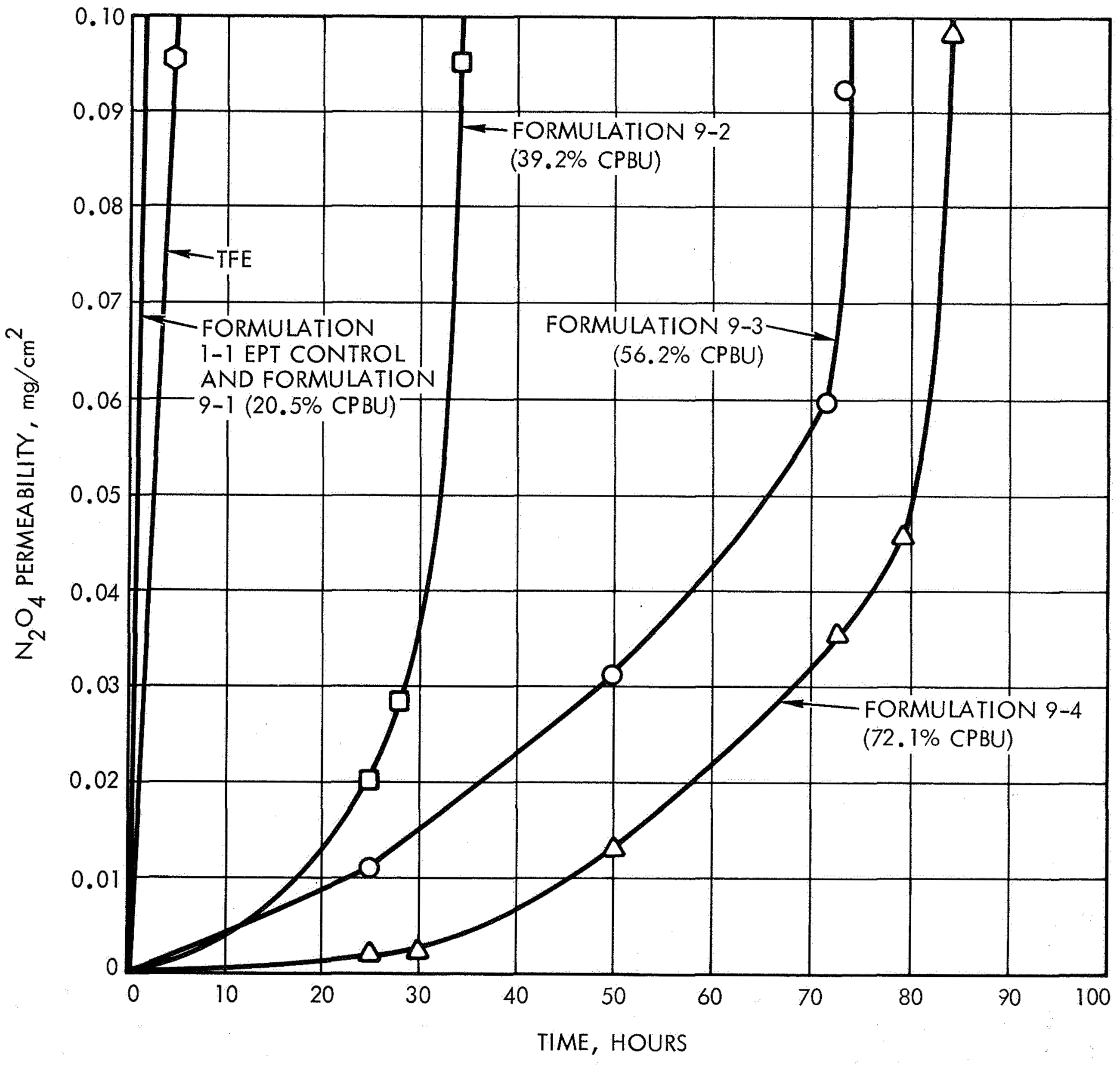


Figure 9. $N_2O_4$ Permeability of CPBU/EPT Composite Vulcanizates Compared with State-of-the-Art TFE Bladder Stock

Insight into the mechanism of permeability of nitrogen tetroxide is obtained through interpretation of the permeability curves of control of specimens containing the C-stage CPBU and the thermo-plastic B-stage CPBU shown in Figure 10. Comparably loaded thermoset CPBU specimens (Formulation 9-2 and 9-3) have been repeated in this curve to facilitate direct comparison of the candidate materials with the control specimens. The specimen filled with approximately 40% of C-stage CPBU (Formulation 9-8) shows low initial permeability; however, after 24 hours the permeability rate increases significantly. Comparison of this curve with that observed from Formulation 9-2 (40% thermosetting B-stage CPBU) shows that improved permeability is obtained when formation of C-stage CPBU occurs simultaneously with vulcanization of the EPT. This comparison infers that the improved permeability originates from interaction between the discrete particles and the elastomeric matrix. The permeability differences between specimens containing powdered thermosetting and thermoplastic CPBU ingredients (60% loaded) can be seen by inspection of Figure 10 curves for Formulation 9-3 (thermosetting B-stage) and Formulation 7-3-3 (thermoplastic B-stage). It is seen that improved permeability is obtained when the thermosetting B-stage CPBU is employed. The rapid loss of permeability resistance of the thermoplastic CPBU/EPT/carbon composite (Formulation 7-3-3) is attributed to the lack of discrete CPBU particles in the final composite.

### 4. 5. 3 Mechanical Properties

The tensile stress as a function of elongation was determined on Formulation 9-x candidate composite vulcanizates and a control using standard 0. 075-inch thick ASTM specimens and an Instron Testing Apparatus in conjunction with ASTM D-412 test method. The results of these tests are shown in Figure 11 together with a similar curve for 0. 008-inch thick Teflon (Reference 11 ). The standard 20 inch/min crosshead speed was used for the tests with the specimens prepared in this program. DuPont reported data at a crosshead speed of 1-inch/min for Teflon. The modulus at 30% elongation, and stress at failure of these specimens are listed in Table XIV.

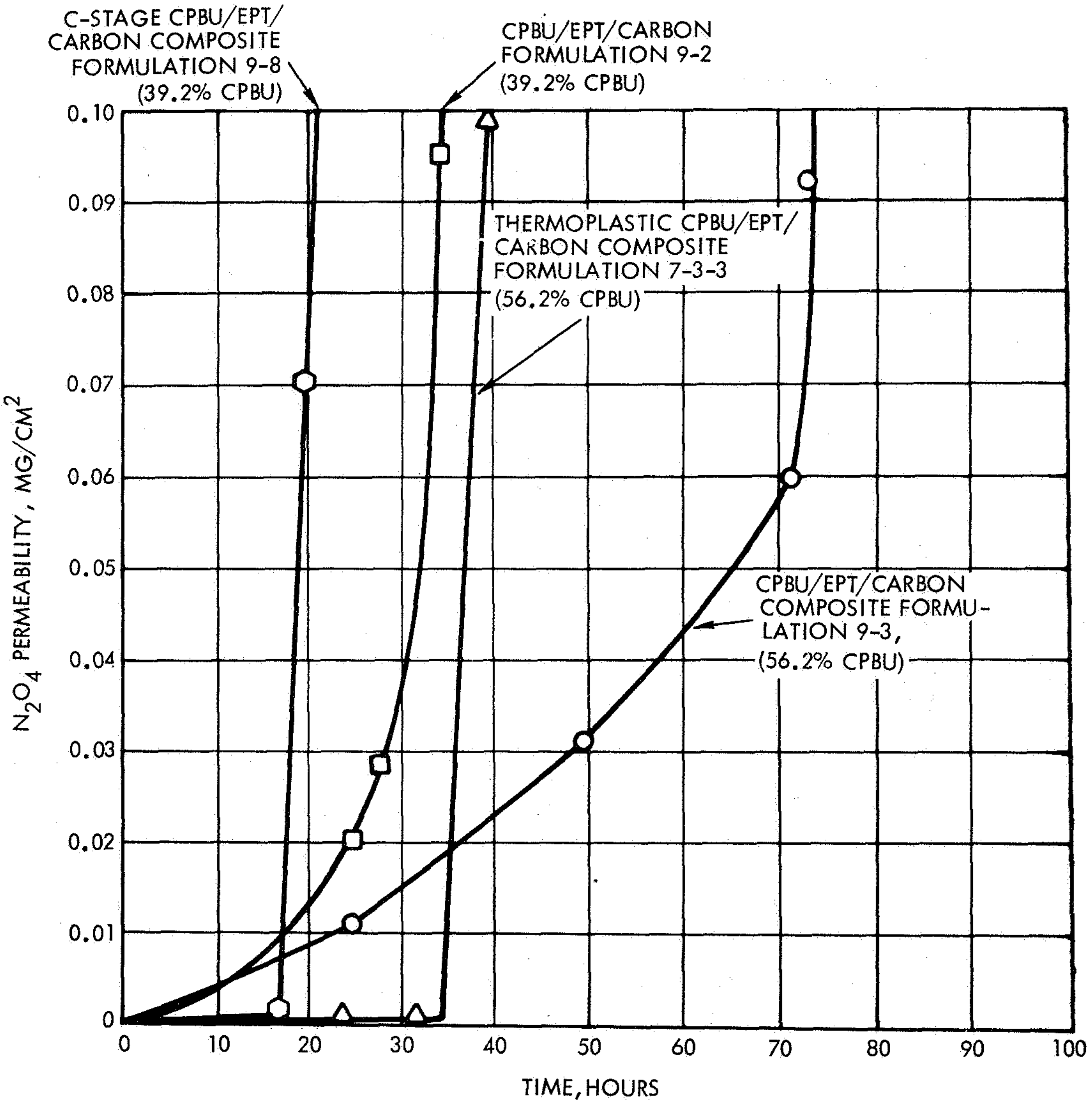


Figure 10. Comparison of $N_2O_4$ Permeability of Test and Control Specimens

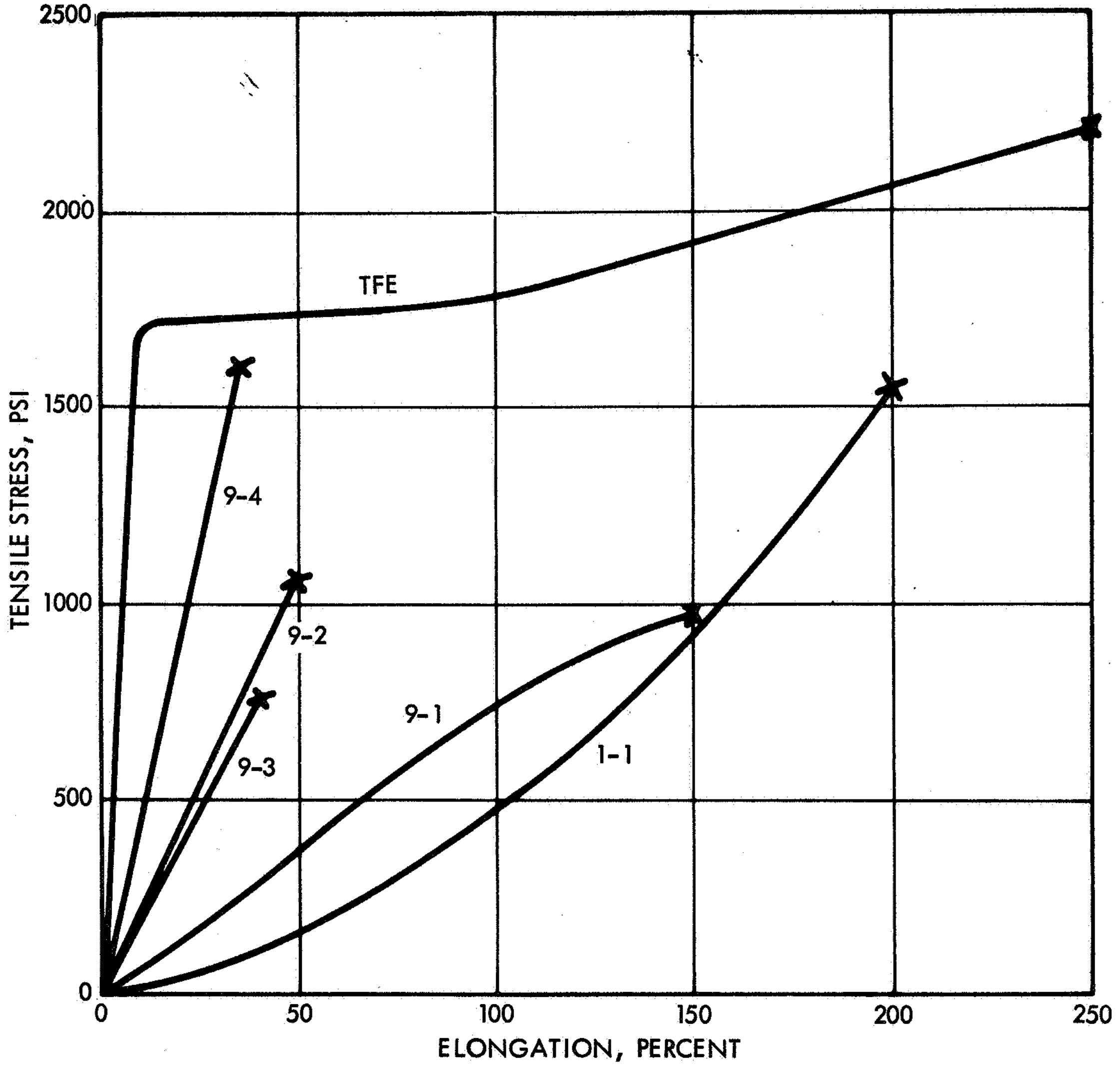


Figure 11. Stress-Elongation Curves of Candidate Composite Vulcanizates, Control and Comparison Materials

Testing Conditions:

1-1 thru 9-4 0.075-inch thick specimens
ASTM D-412, 20 - inches/min crosshead speed

TFE - 0.008-inch thick specimens 1 - inch/min crosshead speed (DuPont information)

X - break

## TABLE XIV

## MECHANICAL PROPERTIES OF COMPOSITE VULCANIZATES, CONTROL AND COMPARISON MATERIAL

| Sample | Modulus at 30% Elongation, psi | Elongation at Failure % | Stress at Failures psi |
|---|---|---|---|
| Control EPT | 330 | 200 | 1550 |
| CPBU/EPT/C | | | |
| 9-1, 20.5% CPBU | 500 | 150 | 970 |
| 9-2, 39.2% CPBU | 2160 | 50 | 760 |
| 9-3, 56.2% CPBU | 2000 | 40 | 1060 |
| 9-4, 72.1% CPBU | 4660 | 35 | 1600 |
| Teflon | 5660 | 300 | 2200 |

While the data shown in Table XIV and Figure 11 are only the results of single Instron test, rather than the average of a number, they do show that CPBU composite vulcanizates appear to have sufficiently promising mechanical properties for application as bladder materials. The higher loaded materials have marginal properties, however, it is expected that a development effort aimed at reducing the CPBU particle size will improve the mechanical properties as well as further enchancing the chemical resistance and permeability characteristics.

### 4.6 CHARACTERIZATION OF EXTERNALLY PLASTICIZED CPBU

Results of preliminary screening of the Chlorowax 70 externally plasticized CPBU formulation are presented in Table XV.

## TABLE XV

## PRELIMINARY SCREENING OF EXTERNALLY PLASTICIZED CPBU

| Weight Change, $N_2O_4$ Resistance (10-day) | Flexibility |
|---|---|
| Fell apart after four days | 1/2-inch bar could be bent 180° without tearing |

From these results it is seen that the desirable elastomeric properties were obtained, however, this was accomplished through loss of the $N_2O_4$ resistance. Chlorowax 70 was selected as a chemically resistant external plasticizer, however, the product did not retain the desired property. For this reason, further investigations with externally plasticized CPBU were not performed.

## 4.7 CHARACTERIZATION OF NON-CHAIN EXTENDED CPBU

Results of preliminary screening of the non-chain extended CPBU formulation are presented in Table XVI.

TABLE XVI

PRELIMINARY SCREENING OF NON-CHAIN EXTENDED CPBU

| Weight Change,[a] $N_2O_4$ Resistance (10-day) | Barcol Hardness |
|---|---|
| Excellent | 35 |

a. Excellent = 0.5 mg/cm$^2$ or less; Good = between 0.5 and 6.0 mg/cm$^2$; Poor = greater than 6.0 mg/cm$^2$.

These results indicate that the $N_2O_4$ resistance and hardness properties for the non-chain extended CPBU are approximately equivalent to those of the chain extended CPBU. Because the desired improvement in flexibility was not achieved, further investigation of non-chain extended CPBU was not performed.

## 5. PHASE I - CONCLUSIONS AND RECOMMENDATIONS

The laboratory synthesis, preparation and characterization of new candidate materials described in the preceding two sections have provided a sound technical basis for determining the potential of these materials as storable propellant bladder materials. These studies also provide guidance for continued studies towards the development of these new materials. It was ascertained that methods of preparing candidate materials based on direct modification of the chemical backbone of CPBU did not provide materials which were applicable for use as propellant bladders. However, the development of a processing means for preparing CPBU-elastomeric composites has resulted in materials which show exceedingly high promise for this use. This processing technique is considered to be a major breakthrough in the art of preparing compliant materials which resist chemical attack by storable propellants.

During this program processing techniques for preparing the composite vulcanizates were only briefly explored and it is believed by systematic variation of the critical fabrication parameters, additional significant improvements will be obtained. It is clear from results of this program that 1) a threshold for future improvement has been established and 2) guidelines for this improvement have been identified for continued effort aimed at the development of practical advanced storable propellant bladder materials.

Upon examination of the test specimens after the permeability measurements, it was clear that the long term compatibility with nitrogen tetroxide cannot be obtained with the present CPBU/EPT/carbon formulation. The material in contact with the nitrogen tetroxide shows definite chemical attack of the EPT matrix and, hence, is only suitable for short term (3 to 4 days) exposure. Interestingly enough, the materials prepared to date have chemical compatibility and permeability characteristics which are far better than those currently used in TITAN, LEMDE and other liquid propellant rocket engines employing nitrogen tetroxide (References 12 and 13). It is clear for long term nitrogen tetroxide service elastomeric matrices having better compatibility must be utilized.

The permeability curves of the candidate materials (Figure 9) show an indication of the degree of permeability improvement which can be attained through using a more chemically resistant matrix. If it is tacitly assumed that the rapid increase in slope as a function of time of the curves in Figure 9 is caused by chemical attack of the matrix, then one can utilize the initial slope (which is assumed to be independent of chemical attack) as a measure of the inherent permeability characteristics of CPBU/elastomeric composite prepared using a chemically inert matrix. Using this hypothesis, effective permeability coefficients were calculated and are listed in Table XVII. These theoretical calculations clearly show that the CPBU/elastomer composite vulcanizates are capable of providing even further improvements in nitrogen tetroxide permeability than that available from the experimental CPBU/EPT carbon composite vulcanizates.

TABLE XVII

THEORETICAL PERMEABILITY OF CPBU/EPT COMPOSITE VULCANIZATES ASSUMING NO CHEMICAL ATTACK OF MATRIX

| Material | Specimen Thickness mil | Permeability Rate[a] mg/cm$^2$-hr | "Effective"[b] Permeability Coefficients mil-mg/cm$^2$-hr |
|---|---|---|---|
| "Resistant" EPT | 75 | 0.21 | 15.8 |
| CPBU/EPT 39.2% loaded | 75 | $7.7 \times 10^{-4}$ | $5.8 \times 10^{-2}$ |
| CPBU/EPT 56.2% loaded | 75 | $4.5 \times 10^{-4}$ | $3.4 \times 10^{-2}$ |
| CPBU/EPT 72.1% loaded | 75 | $8.0 \times 10^{-5}$ | $6.0 \times 10^{-3}$ |
| CPBU | 37 | $1.9 \times 10^{-6}$[c] | $6.9 \times 10^{-5}$[c] |

a. Calculated from initial slope of permeability curve (See Figure 9)

b. Calculated as product of specimen thickness and permeability rate.

c. Average data over a 200-hour permeability test (See Table II)

In short term hydrazine permeability tests (64 hours) conducted by the Jet Propulsion Laboratory, a measurable quantity of hydrazine did not permeate the CPBU/EPT composite vulcanizates. Consequently, it appears that a usable material for hydrazine service offering outstanding permeability characteristics was developed during this program.

The effect of CPBU particle size and shape was not studied. The particle size of the B-staged CPBU employed was greater than 175 microns. It is believed that the experimental formulations would have exhibited better permeability resistance had the B-stage powder been significantly smaller. This belief follows from consideration of the exposed surface area - it is anticipated that the smaller the particle size the larger number of active sites would be available for reaction with the EPT matrix.

The interpretation of the results obtained in this program provide distinct guidelines for future exploratory research and development through study of chemical formulation and processing parameters to yield advanced propellant bladder materials. It is seen that CPBU filler concentration, size, shape and mechanical properties are critical experimental parameters in addition to the vital parameter of elastomeric matrix. Experimental parameters expected to have a second order effect are the CPBU peroxide type and concentration, and the vulcanization time, temperature and pressure.

Specific aspects of the critical experimental parameters recommended for further study are:

- Elastomeric Gum Stock - Four classes of gum stocks which have the capability for reaction with CPBU and which would extend the range of storable propellant utility include saturated hydrocarbons, fluorocarbons, silicones and fluoro nitroso elastomers.
- CPBU Filler Concentration - Studies of the trade-offs available among chemical permeability and resistance and mechanical properties as a function of filler content is required for engineering assessment.

- Filler Particle Size - Filler size must be optimized for the best balance of permeability and flexibility of the composite vulcanizate.
- Filler Particle Shape - The potential gain in varying particle size from spheroids to platelets must be determined experimentally.
- B-Stage CPBU Mechanical Properties - This parameter provides control of the degree of interpenetration of the filler with the matrix, and hence, requires evaluation to provide optimum engineering properties.

It is recommended that the exploratory research and development program outlined above be undertaken.

## 6. ACQUISITION AND CHARACTERIZATION OF $N_2O_4$ RESISTANT ELASTOMERS

In the work reported in Phase I of this program it was ascertained that elastomeric matrices which exhibit resistance to nitrogen tetroxide, but not necessarily permeability, were prime candidates for investigation using the composite vulcanizate concept. The following three candidate materials were considered for evaluation:

- Viton-B (terpolymer from perfluoropropene, vinylidene fluoride and a DuPont proprietary monomer)
- Kel-F 5500 elastomer (vinylidene fluoride-chlorotrifluoroethylene copolymer)
- Carboxy nitroso rubber

The Viton-B and Kel-F 5500 were selected for evaluation in this program because they offered the ability for chemical interaction of pendant vinyl groups during a peroxide cure.

### 6.1 ACQUISITION AND PREPARATION OF NEAT ELASTOMERS

Viton-B was acquired from E.I. duPont deNemours, Inc., and control formulations of neat molded gum stock were prepared using suggested manufacturer procedures. During this study, it was found that significantly improved mold test slabs (as determined by general appearance) were prepared by allowing the test slab to cool to ambient temperature under pressure prior to removal from the mold.

The Kel-F 5500 fluoroelastomer was acquired from the Minnesota Mining and Manufacturing Company and control formulations were molded using suggested manufacturer procedures. Both the formulation and curing conditions as given by the supplier were for carbon black filled or silica filled stocks and did not produce satisfactory cures on the filled formulations. An investigation of processing time, temperature, and pressure as well as concentration of both the benzoly peroxide curative and acid acceptor were investigated to provide suitable control specimens for $N_2O_4$ evaluation. It was found that magnesium oxide as an acid acceptor was not suitable for preparation of test specimens, however, zinc oxide provided a satisfactory alternate.

The composition and curing conditions of both the neat elastomeric matrices used in this program are given in Table XXVIII.

TABLE XVIII

COMPOSITION OF NEAT ELASTOMERIC MATRICES

| Ingredient | | Composition, phr<br>Viton-B Control | <br>Kel-F Control |
|---|---|---|---|
| Viton-B | | 100 | - |
| Maglite Y | | 15 | - |
| Kel-F 5500 | | - | 100 |
| Zinc Oxide | | - | 10 |
| Benzoyl Peroxide | | 5 | - |
| Mold Cure | Time, min | 30 | 30 |
| | Temperature, °F | 325 | 250 |
| Oven Post Cure | Time, hours | 24 | 16 |
| | Temperature, °F | 400 | 300 |

## 6.2 $N_2O_4$ PERMEABILITY CHARACTERIZATION

The nitrogen tetroxide permeability characterization of the neat Viton-B and Kel-F control specimens were determined using the screening method described in Appendix B. The raw data showing pH as a function of time is given in Figure 12. Analysis of the results, together with visual observation of the specimens following testing show that both rubber compounds were sufficiently compatible with the $N_2O_4$ to permit further study. Both compounds displayed rather high permeability rates, in the same range as that previously reported for the carboxy-nitroso rubber. Of the two compounds, the Viton-B appeared to have the better compatibility. Although slight bulging (away from the $N_2O_4$ side of the permeability cell) of the 0.105-inch thick stock was noted, no blisters or excessive swell were apparent. In the case of the Kel-F stock, however, some swell was obvious, accompanied by a more pronounced bulging as

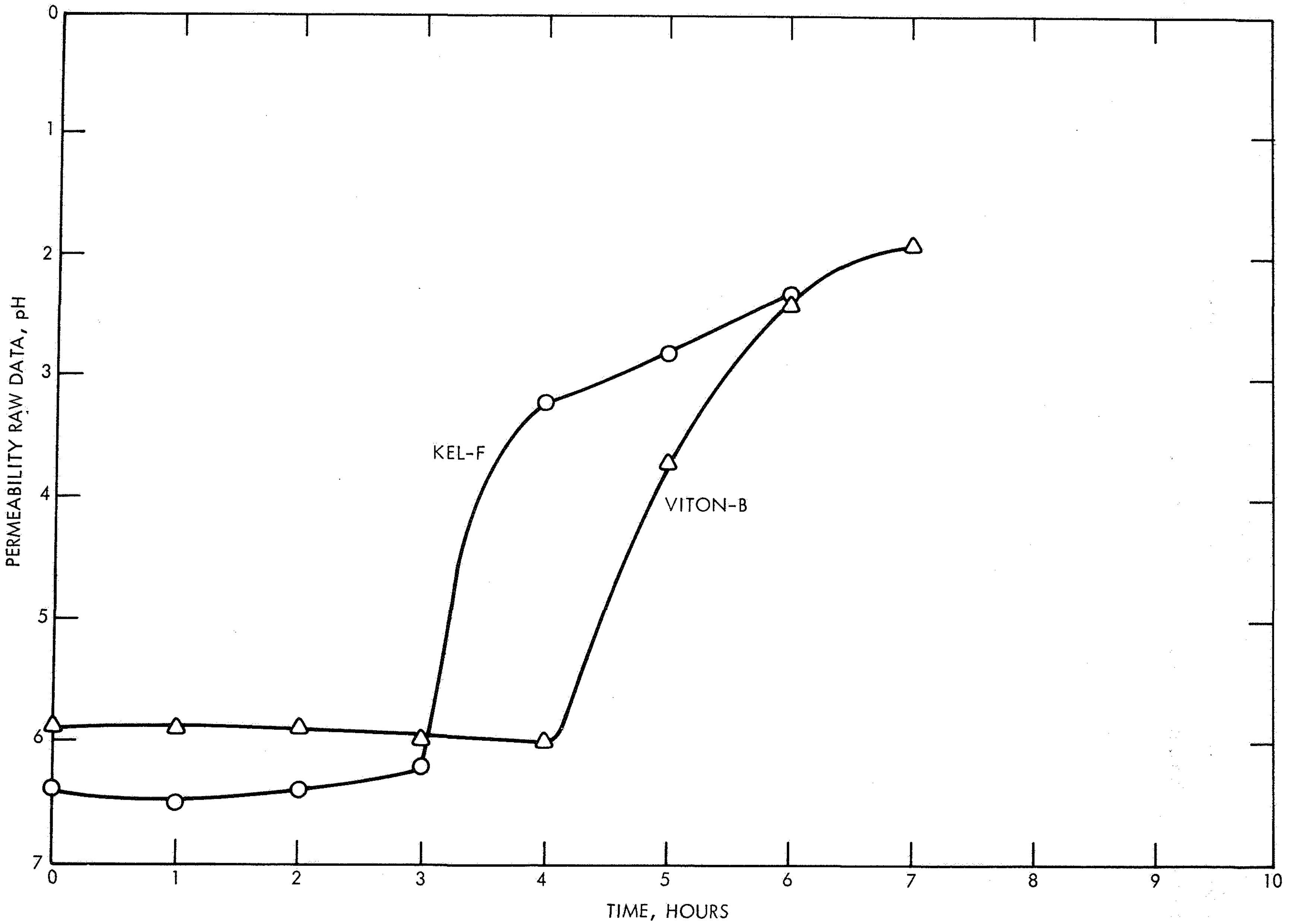


Figure 12. Nitrogen Tetroxide Permeability of Viton-B and Kel-F Control Specimens

well as blistering on the water ($HNO_3$) side of the permeability cell. In addition, the normally white Kel-F stock turned green where exposed to the $N_2O_4$ showing absorption of the oxidizer.

# 7. CHEMISTRY AND FORMULATION OF FILLED $N_2O_4$ RESISTANT ELASTOMERS

## 7.1 CHEMISTRY CONSIDERATIONS

During Phase I activities, it was found that the process of vulcanization of B-stage CPBU dispersed within the EPT gum stock offered significant improvement in permeability over that obtained from vulcanizing C-staged CPBU in the EPT matrix (Section 4.5.2) From this study it is apparent that interaction between the CPBU and the matrix occurred at least to an extent which improved the permeability characteristics.

For selection of candidate fillers and elastomeric matrices, the physical aspect of permeability of propellants through candidate bladder materials must be considered in relation to its chemical structure. There are four means by which propellants can permeate bladder materials. Flow processes for liquids and gases through membrane consist of:

- Streamline flow through macro and micro orifices,
- Knudsen gas flow through macro and micro orifices,
- Translation along pore surfaces, and
- Imbibition, establishment of a concentration gradient and then syneresis.

Macro orifices arise in bladder materials through methods of preparation and their number and size are inversely related to the bladder thickness. Micro orifices arise from the chemical constitution of the bladder materials and is related to the polymer free volume. Because of its high volatility and dissociation into low molecular weight species, nitrogen tetroxide, for example, is particularly suited to Knudsen diffusional flow. Translation of propellant along pore surfaces through membranes is related to the surface free energy and the wettability.

The important mode of mass transfer through current bladders, consists of imbibition into the bladder, establishment of a concentration gradient and then syneresis through the membrane. The ability for a penetrant to dissolve and diffuse through the membrane can be related to the characteristics of the membrane and penetrant. The presence of crystallites in an amorphous polymer results in a reduction of the polymer volume available for syneresis (sorption) of the penetrant. In addition, the diffusion of the penetrant through the polymer is restrained by the crystallites because there is:

- Reduction in the polymer volume available for diffusion, and
- Increased difficulty of permeation of the penetrant because of the necessity for detouring around the crystallites

As an approximation, the permeability is proportional to the product of the solubility constant and the diffusion coefficient. Because there is a reduction of both values by the presence of crystallites, the permeability of semi-crystalline materials is reduced to an extent dependent on the size and volume fraction of the crystallites.

A schematic drawing of the particulate CPBU in the cured elastomeric gum stock is shown in Figure 13. The vulcanizate of Figure 13 shows chain molecules of the gum stock chemically attached to particulate CPBU yet chemically unattached to each other. In other words, there is no chemical crosslinking in the elastomeric portion. This

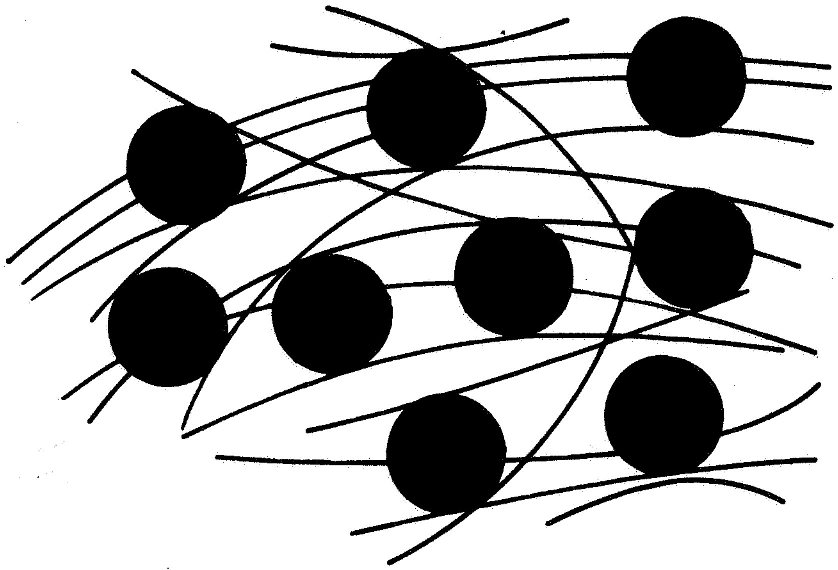


Figure 13. Schematic Drawing of CPBU Vulcanizate Structure

behavior is quite similar to that of semi-crystalline polymers. A schematic drawing of the fringed-micelle structure for semi-crystalline polymers is shown in Figure 14. It is seen in Figure 5 that the chain molecules pass successively through crystalline and amorphous regions. The permeability considerations described above for the CPBU vulcanizate are essentially the same as those exhibited by semi-crystalline polymers.

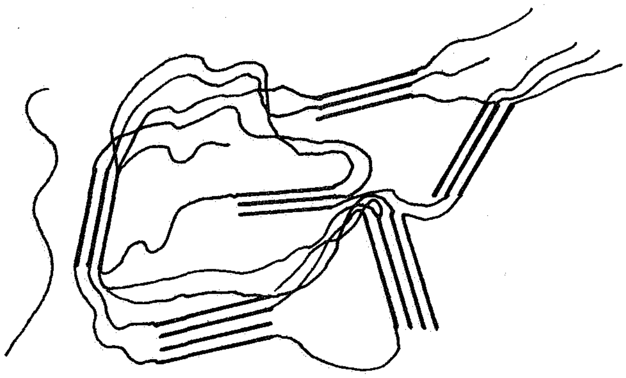


Figure 14. Fringed-Micelle Structure of Semi-Crystalline Polymers

Another view point consists of the permeant penetrating bladder materials by pore flow rather than diffusion caused by "flaws" in the bladder. Permeability by this mechanism as well as by diffusion can be lowered by increasing the concentration of CPBU filler because the probability of the flaw being generated through the vulcanizate will be diminished. The flaw is expected to occur in vulcanizates because of stress concentrations generated during processing. Where flaws do occur, however, the CPBU filler may be considered as checks to flaw growth thereby diminishing the probability of severe penetrations of the flaw into the bladder.

## 7.2 PREPARATION AND COMMINUTION OF CPBU

A key experimental parameter identified in Section 5 of this report is that of CPBU particle size. It is believed that considerably improved composite vulcanizate properties would be obtained if the particle size of the elastomeric form of CPBU were less than 100 microns. Consequently, considerable emphasis was placed on preparation of the finely divided B-stage CPBU powder.

Four formulations of CPBU B-stage were prepared (See Table XIX) using two different peroxides (dicumyl peroxide and Luperco 101XL) at two different concentrations each (2% and 5%). The Luperco 101XL, 2,5-bis(t-butyl peroxy) 2,5-dimethyl hexane, was selected because it has been found useful in curing Viton-B elastomers (Reference 15). The dicumyl peroxide formulations provide a second system for investigation as well as a material for comparative formulations using ethylene-propylene terpolymer (EPT) elastomer. Both peroxides provided C-stage CPBU cures as determined by hardness and $N_2O_4$ resistance. In earlier work t-butyl peroxide was employed in the B-staged CPBU, however, evaporative losses during mixing often caused poor cures and inconsistent results. The Luperco 101XL reacts by the same chemical mechanism at almost identical temperatures as does the t-butyl peroxide but provides a material with lower vapor pressure.

Comminution of the cast B-stage CPBU material through milling at liquid nitrogen temperatures into finely divided particles was investigated. Initial comminution yielded a product having a size of approximately 120-200 microns. Regrinding of these particles resulted in a product having a size of approximately less than 80 microns. Prime problems encountered were the "blow-back" of the particles on the grinder screen/feed system. The grinding vendor overcame this problem by modification of the liquid nitrogen feed/pressure control system.

Once CPBU B-stage particles were obtained in the desired size range, the CPBU filled composites were formulated and molded for nitrogen tetroxide permeability tests. Initial "thumb nail" test with an EPT matrix and evaluation of shore A hardness values showed that neither of the Luperco 101XL catalyzed CPBU powders, nor the 2% dicumyl peroxide catalyzed powder performed satisfactorily. The CPBU powder

## TABLE XIX
## B-STAGE CPBU FORMULATIONS FOR PREPARATION OF POWDERED FILLERS

| Ingredient | Formulation Composition, phr | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| CPBU Prepolymer | 100.0 | 100.0 | 100.0 | 100.0 |
| Trimethylolpropane | 2.0 | 2.0 | 2.0 | 2.0 |
| Toluene diisocyanate | 12.0 | 12.0 | 12.0 | 12.0 |
| Dicumyl peroxide | 2.0 | 5.0 | ----- | ----- |
| Luperco 101 XL (45% active) | ----- | ----- | 4.5 | 11.0 |

Cast in polyvinyl chloride bags to exclude air, and oven cured for 16 hrs at 180°F containing 5% dicumyl peroxide made excellent EPT composite vulcanizates and was the only version of the powder used in making subsequent test specimens.

## 7.3 SELECTION OF CANDIDATE FORMULATIONS

The key element postulated in Section 7.1 is that of elastomeric matrix-CPBU interaction during vulcanization yielding discrete particles of CPBU interlaced by the elastomeric matrix. The activities described below were undertaken to test this hypothesis further by preparing composite vulcanizates from the same matrix elastomer which were filled with powdered CPBU and other fillers which do not have a potential means for chemical bonding to the matrix other than by adhesive processes. It was the objective to use fillers such as silica, carbon, Teflon, ebonite etc. which had approximately the same particle size so that this factor would not play an overriding role in the permeability characteristics of the prepared composite vulcanizates. In the course of this program only three fillers were investigated and unfortunately it was not possible to obtain materials with identical particle sizes.

The composite vulcanizate formulations selected for evaluation were:

| Matrix | Filler | Approximate Filler Particle Size, μ |
|---|---|---|
| Viton-B | Carbon | 10 |
| | Silica | 44 |
| | CPBU | 80 |
| Kel-F 5500 | Carbon | 10 |
| | Silica | 44 |
| | CPBU | 80 |

Each formulation combination was prepared with at least four different concentrations of filler to permit evaluation of the effect of filler content on the $N_2O_4$ permeability characteristics of the composite vulcanizate. Because of the variation in particle size, the results presented in Section 8 must be considered in light of a possible second order effect caused by this variable.

# 8. PREPARATION AND EVALUATION OF FILLED $N_2O_4$ RESISTANT ELASTOMERS

## 8.1 VITON-B ELASTOMER INVESTIGATIONS

Viton-B base composite vulcanizates were prepared using the processing conditions established for the control specimens (Section 6.1). The specific formulations prepared into standard ASTM test slabs (6-inch x 6-inch x 0.075-inch) are shown in Table XX. With few exceptions, as noted, all formulations appeared to be useful elastomers and were subjected to nitrogen tetroxide permeability tests.

The nitrogen tetroxide permeability characteristics of 13 Viton-B base experimental rubbery composites were determined and the raw pH data are listed in Table XXI. These data show a sharp shift from higher pH to low pH within the period two to six hours. It is clear from these data that all the composites tested have relatively high $N_2O_4$ permeabilities. In some cases the composites were attacked so severly that light could be seen through the exposed area. In other cases, however, no catastrophic degradation was noted, although the results of pH vs time show the same "catastrophic failure" trend. Detailed inspection of these data show generally a slight increase in pH during the initial part of the test. It is believed that these results arise from water from the test cell leaching the MgO acid acceptor out of the composite as evidenced by a more basic pH. In nearly all cases, the "failure" of the compounds occurred very rapidly (pH measurements of 6-8 showing changes to 2-3 within a one-hour span).

As a result, composites were prepared that did not contain MgO. A series of compounds employing lead oxide (litharge) as the acid acceptor was investigated. The results of the $N_2O_4$ permeability testing of these composites are shown in Table XXII. As these data show, this approach did not appear to provide a satisfactory solution.

It was found that the presence of the B-stage CPBU particles as a filler, (containing its own active catalyst-dicumyl peroxide), when cured 30 minutes at 325°F with the Viton-B control formulation, caused the rubber to foam on molding and/or during post curing. To eliminate the

## TABLE XX

## COMPOSITION AND PROCESSING OF EXPLORATORY VITON B FORMULATIONS

| Ingredient | | Control | Silica Filler, phr | | | | Carbon Black Filler, phr | | | TFE Filler phr | | | CPBU Filler | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 20 | 40 | 60 | 80 | 20 | 40 | 60 | 20 | 40 | 60 | 40 | 60* |
| Viton B | | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Maglite Y (MgO) | | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | --- |
| Benzoyl Peroxide | | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| HAF Carbon Black | | --- | --- | --- | --- | --- | 20 | 40 | 60 | --- | --- | --- | --- | --- |
| 325-Mesh Silica | | --- | 20 | 40 | 60 | 80 | --- | --- | --- | --- | --- | --- | --- | --- |
| TFE Powder | | --- | --- | --- | --- | --- | --- | --- | --- | 20 | 40 | 60 | --- | --- |
| CPBU B-Stage Powder | | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | 40 | 60 |
| **Mold Cure** | Time, min | 30 | 30 | | | | 30 | | | 30 | | | 80 | [a] |
| | Temperature, °F | 325 | 325 | | | | 325 | | | 325 | | | 350 | |
| **Oven Post Cure** | Time, hrs | 24 | 24 | | | | 24 | | | 24 | | | 24 | 24[b] |
| | Temperature, °F | 400 | 400 | | | | 400 | | | 400 | | | 400 | 400 |

* Acid acceptor eliminated from formulation

[a] 30 minutes at 250°F followed by 30 minutes at 350°F

[b] Post cure under nitrogen

## TABLE XXI

## RAW DATA NITROGEN TETROXIDE PERMEABILITY TESTING OF FILLED AND UNFILLED VITON-B COMPOSITES

| Time hr | Acidity of Water Solution, pH | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control | Silica Filler, phr | | | | Carbon Black Filler, phr | | | TFE Filler, phr | | | CPBU Filler, phr | |
| | A | 20 | 40 | 60 | 80 | 20 | 40 | 60 | 20 | 40 | 60 | 40 | 60 |
| 0 | 5.90 | 6.20 | 6.70 | 8.20 | 7.20 | 6.55 | 6.15 | 6.10 | 5.90 | 6.00 | 6.90 | 7.30 | 5.55 |
| 1 | 5.90 | 5.95 | 6.10 | 8.40 | 7.05 | 6.35 | 6.20 | 6.90 | 6.00 | 6.15 | 6.85 | 7.35 | 5.55 |
| 2 | 5.90 | 5.80 | 6.90 | 8.60 | ---- | ---- | 6.25 | 7.10 | 6.10 | 6.20 | ---- | 7.10 | 5.72 |
| 3 | 6.00 | 6.00 | 6.80 | 8.75 | 7.00 | 1.80 | 6.30 | 7.30 | 3.70 | 6.05 | 6.85 | 7.70 | 5.68 |
| 4 | 6.00 | 6.15 | 3.30 | 3.25 | 6.90 | 1.15 | 2.85 | 7.75 | 3.10 | 2.85 | 6.85 | 3.60 | 5.65 |
| 5 | 3.65 | 4.20 | 2.20 | 2.20 | 2.65 | ---- | 1.60 | 8.20 | 2.75 | 2.10 | 6.80 | 2.50 | 5.65 |
| 6 | 2.40 | 2.83 | 1.75 | 1.85 | 2.10 | ---- | 1.35 | 2.50 | 2.25 | 1.90 | 6.85 | 2.15 | 5.55 |
| 7 | 1.90 | ---- | ---- | ---- | 1.60 | ---- | ---- | 2.00 | ---- | ---- | 3.65 | 1.80 | 5.45 |
| 11 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | 2.15 |
| 16 | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | ---- | 1.08 |

## TABLE XXII

## EFFECT OF ACID ACCEPTOR ON $N_2O_4$ PERMEABILITY OF VITON-B FORMULATIONS[a]

| Time<br>hr | Acidity of Water Solution, pH | | | |
|---|---|---|---|---|
| | MgO<br>15 phr | PbO<br>5 phr | PbO<br>10 phr | PbO<br>15 phr |
| 0 | 5.90 | 6.40 | 6.30 | 7.30 |
| 1 | 5.90 | 3.85 | 4.05 | 7.30 |
| 2 | 5.90 | | 2.90 | 2.95 |
| 3 | 6.00 | | 1.15 | 2.15 |
| 4 | 6.00 | | | 1.30 |
| 5 | 3.65 | | | |
| 6 | 2.40 | | | |
| 7 | 1.90 | | | |

[a] Base formula: Viton B = 100 phr; benzoyl peroxide = 5.0 phr; Acid acceptor = shown in Table

Cure: 30 min at 325°F in mold; 24 hr at 400°F in oven possibility of an undesirable interaction between two peroxides as the source of this problem, several composites containing dicumyl peroxide in place of the benzoyl peroxide in the Viton-B matrix were molded and subjected to post curing. No foaming was evidenced, however, none of these compounds were cured satisfactorily as evidenced by their thermoplastic nature during post curing at 400°F.

Additional development work showed that the only method suitable for producing solid CPBU filled test specimens was to use the formulations and processes described in Table XX. It was also found that cooling under pressure in the mold before post curing also provided less porosity.

Despite the high $N_2O_4$ permeability rate of the composite vulcanizates, compatibility tests run concurrently on sample strips of unfilled Viton-B composites formulated with MgO (control specimens) showed no significant amount of swell nor catastrophic decrease in physical properties. Analogously, carboxy nitroso rubbers (CNR) show very small changes in physical and mechanical properties in $N_2O_4$, but nevertheless are highly permeable.

## 8.2 KEL-F ELASTOMER BASE INVESTIGATION

A series of CPBU filled Kel-F elastomer base composite vulcanizates was prepared for $N_2O_4$ permeability characterization. The formulations, mold and post cures examined are listed in Table XXIII together with the raw pH permeability data. Because the CPBU-Kel-F composites did not show an appreciable improvement over the CPBU-Viton materials (which was attributed specifically to matrix material incompatibility) composites were not prepared with other fillers for test of $N_2O_4$ compatibility.

Inspection of the permeability data (Table XXIII) showed that the permeation of every compound increased rapidly after a short initiation period in a fashion similar to the Viton-B composite vulcanizates. In this case, however, the specimens did not have gross imperfections but rather appeared discolored and still intact. Previously it was determined that the neat cured Kel-F elastomer had superior chemical resistance compared to the Viton-B elastomer, however in the relatively short

## TABLE XXIII

## EFFECT OF FORMULATION AND CURE CONDITIONS ON CPBU FILLED KEL-F $N_2O_4$ PERMEABILITY

Formulation

| Ingredient | | Composition, phr | | | | |
|---|---|---|---|---|---|---|
| | | Control | 1 | 2 | 3 | 4 |
| Kel-F 5500 | | 100 | 100 | 100 | 100 | 100 |
| Benzoyl Peroxide | | 2 | 2 | 2 | 2 | 2 |
| Zinc Oxide | | 10 | 10 | 10 | - | - |
| CPBU B-Stage | | - | 60 | 60 | 60 | 60 |
| Mold Cure | Time, min. | 30 | 30 | 30 | 30 | 30 |
| | Temperature, °F | 250 | 250 | 250[a] | 250 | 250[a] |
| Oven Cure | Time, hrs. | 16 | 16 | 16 | 16 | 24 |
| | Temperature, °F | 300 | 300 | 400 | 300 | 400 |

Permeability Raw Data

| Time, hours | Aqueous Compartment pH | | | | |
|---|---|---|---|---|---|
| 0 | 6.40 | 6.15 | 8.05 | 7.70 | 8.65 |
| 1 | 6.50 | 6.15 | 8.20 | 4.65 | 9.00 |
| 2 | 6.40 | 6.00 | 7.70 | 3.80 | 9.10 |
| 3 | 6.15 | 4.00 | 7.25 | - | 10.20 |
| 4 | 3.10 | 3.80 | 7.25 | 2.20 | 9.20 |
| 5 | 2.75 | 3.70 | 7.10 | 1.70 | 9.30 |
| 6 | 2.25 | 3.60 | 6.60 | 1.50 | 9.20 |
| 7 | | 2.90 | 4.55 | 1.37 | 9.00 |
| 8 | | | | | 9.00 |
| 9 | | | | | - |
| 10 | | | | | - |
| 11 | | | | | 1.65 |

[a] Plus second step mold cure of 30 minutes at 350°F

period the Kel-F composites were exposed, $N_2O_4$ had a definite deleterious effect on the Kel-F matrix elastomer.

## 8.3 STUDIES WITH COMPATIBLE PERMEANTS

It is clear from the results presented in the two previous sections that it was not possible to determine whether elastomeric compositions containing CPBU uniquely prevent $N_2O_4$ permeation in comparison with other inert fillers. This difficulty was caused by incompatibility of the candidate elastomers, Viton B and Kel-F with nitrogen tetroxide. After coordination with the NASA JPL Project Manager, it was decided to investigate the permeation of nitrogen gas and hydrazine with Viton B and EPT-base composites respectively. These permeants are chemically compatible with the elastomeric matrices.

The formulation and processing conditions used to prepare these test materials are listed in Tables XXIV and XXV. The permeability of these permeates through the composites were determined by special procedures described in Appendices C and D. The permeability curve for these two tests are shown in Figures 15 and 16.

The permeability of hydrazine through the EPT series of compounds shows that the CPBU filled specimen displayed a definitely lower permeability rate than did the other unreactive fillers. It should be reiterated that the CPBU filler diameter was of the order of 80 microns, while the silica diameter was of 325 mesh (40 microns) and the carbon black 10 microns diameter. This difference in diameter, although apparently minor, has a large effect on the particle surface area available for wetting or interaction. It may be assumed that had the CPBU filler been of the smaller diameter the interaction with the matrix EPT stock would have been even greater and consequently the resistance to permeability may have been still greater.

The permeability of nitrogen gas through the Kel-F base materials shows that the carbon black filled stock (two specimens) would not take the moderate (15 psig) pressure and ruptured shortly after assembly in the permeability cell. The silica and CPBU filled Kel-F composites appeared to be approximately equal in permeability and it is not certain that either stock was sufficiently well cured to show differences as obvious as those noted in the hydrazine permeability through the EPT composites. The bubbly, foamy nature of both Viton-B and Kel-F may not be suitable, whatever the filler, for low permeability compliant propellant bladders.

## TABLE XXIV

## KEL-F ELASTOMER BASE COMPOSITES FORMULATIONS EMPLOYED IN $N_2$ PERMEABILITY STUDIES

| Ingredient | Specimen Composition, phr | | | |
|---|---|---|---|---|
| | Control | Carbon | Silica | CPBU |
| Kel-F 5500 | 100 | 100 | 100 | 100 |
| Zinc Oxide | 10 | 10 | 10 | 10 |
| Benzoyl Peroxide | 3 | 3 | 3 | 3 |
| Carbon Black (HAF) | --- | 40 | --- | --- |
| 325-Mesh Silica | --- | --- | 40 | --- |
| B-Stage CPBU Powder | --- | --- | --- | 40 |

Mold Cure: 30 min at 250°F

Post Cure: 16 hrs at 300°F in $N_2$
plus 4 hrs at 350°F in air

Thickness: 0.032 inches

## TABLE XXV

## EPT ELASTOMER BASE COMPOSITES FORMULATIONS EMPLOYED IN $N_2H_4$ PERMEABILITY STUDIES

| Ingredient | Specimen Composition, phr | | | |
|---|---|---|---|---|
| | Control | Silica | Carbon | CPBU |
| Nordel 1040 | 100 | 100 | 100 | 100 |
| HAF Carbon Black | 65 | 65 | 195 | 65 |
| 325-Mesh Silica | --- | 130 | --- | --- |
| B-stage CPBU Powder | --- | --- | --- | 130 |
| Dicup R (dicumyl peroxide) | 5 | 5 | 5 | 5 |

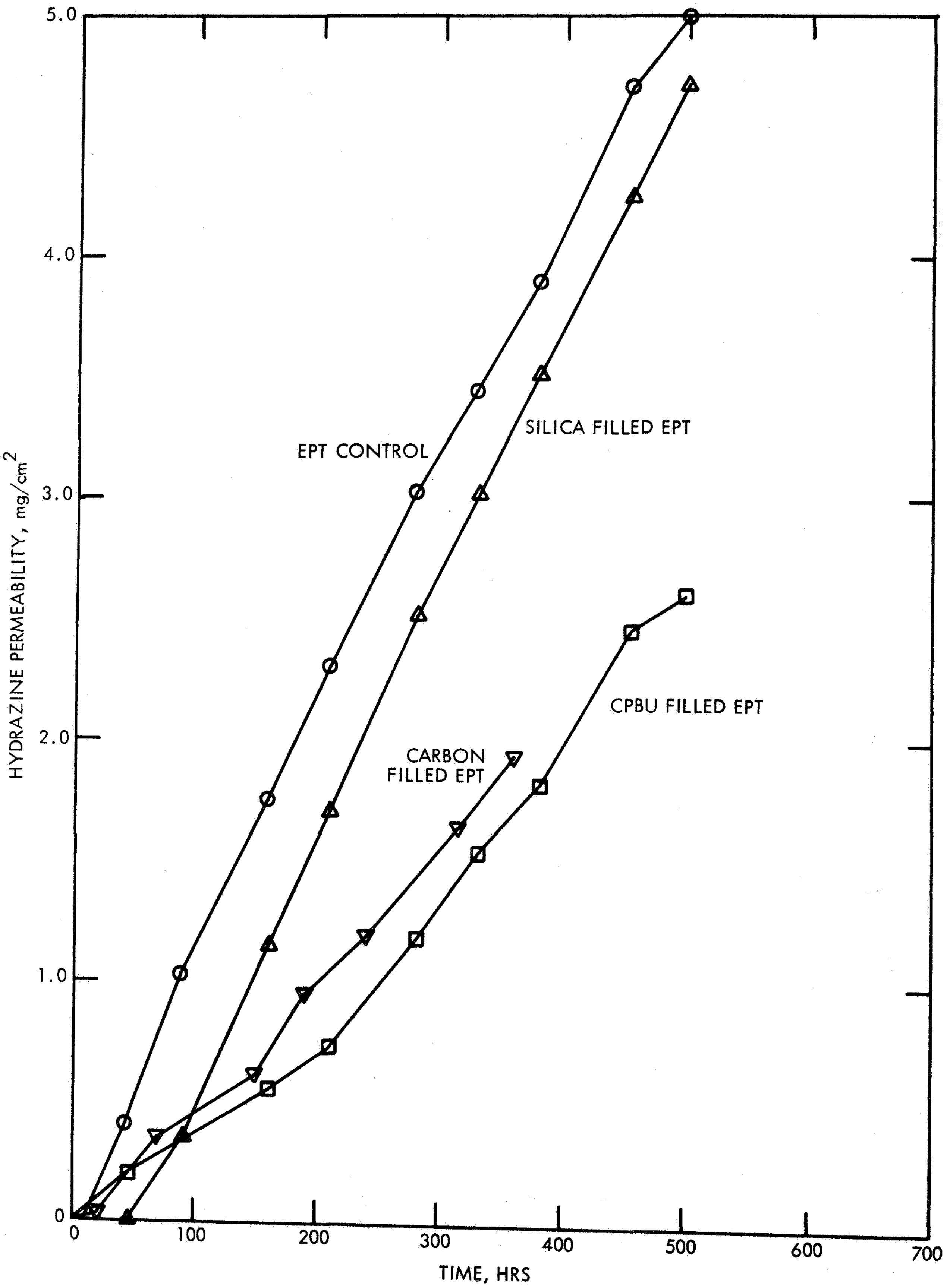


Figure 15. Hydrazine Permeability of Candidate Bladder Materials

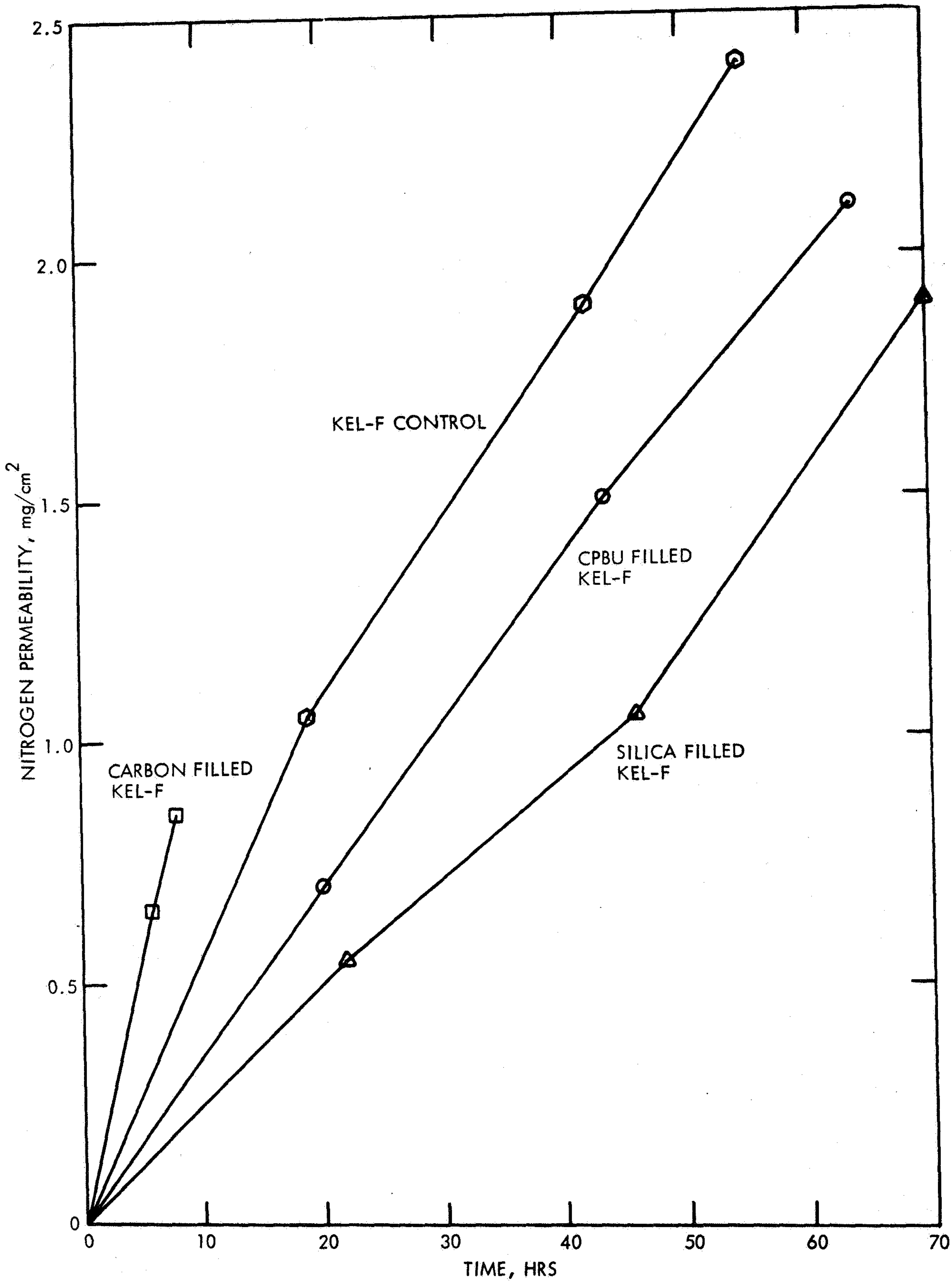


Figure 16. Permeability of Kel-F Elastomer Vulcanizates

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# 10. NEW TECHNOLOGY

During this program an invention disclosure (Docket No. 3679) was submitted to the TRW Systems Patent Department concerning vulcanized rubber gum stock reinforced by poly(cyclized 1, 2-polybutadiene) tolyl urethane (CPBU) filler. This composition of matter is characterized by organic filler that is hard and tough, dispersed in and chemically interacted with a rubbery matrix. In addition, this invention relates to methods and materials by which hard, tough filler dispersed in a rubber is fashioned in situ under rubber vulcanization conditions. The invention is directed to reducing the permeability of nitrogen tetroxide through chemically stable rubbers. However, there are wider implications which apply to products of rubber compounding technology. For example, CPBU as a filler for rubber gum stock may yield vulcanizates which have greater tear resistance than current vulcanizates. These improved vulcanizates may be emplyed as flooring materials, tires, tubes, gaskets, liners, etc.

The formation of tough, hard filler within a rubbery matrix under rubber vulcanization conditions and the delineation of materials whereby this phenomenon is accomplished is the novelty of the invention. The precursor of the hard filler, CPBU, is a polyurethane rubber material. This material, dispersed into rubber gum stock, usually by rubber milling techniques, cyclizes and crosslinks to form CPBU upon vulcanization or curing of the composite. Although current rubber technology employs tough, hard fillers for rubbers, e.g., phenolics, epoxides, carbon inorganic compounds, etc., the formation of hard filler in situ during vulcanization of rubber is new and novel.

Details of the processing considerations involved in this invention are presented in Section 3.6 and results of chemical resistance, permeability and mechanical property testing of initial formulations are presented in Section 4.5.

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# APPENDIX A

# SYNTHESIS OF MODIFIED CPBU FORMULATIONS

This Appendix describes the detailed procedures employed to synthesize six modified CPBU formulation classes. The experimental procedures are given for the following CPBU modifications as identified in Section 3 of this report:

- Internal Plasticization;
- Variation in the Backbone Structure through Copolymerization;
- Introduction of Points of Flexibility in the Chain Extender;
- Modification of the Fused Cyclohexane Ring Structure by Chain Transfer;
- External Plasticization; and
- Non-Chain Extended CPBU.

Individual formulations were obtained by substituting the appropriate ratios and cure times are listed in Section 3.

The experimental details for preparation of the CPBU/Rubber composites were presented in Section 3. 6. Also,a list of suppliers of ingredients is given.

## A. 1 Internal Plasticization

Modified formulations of CPBU containing internal plasticizers were prepared according to the following example.

### Eleven phr 1-Octene

Ninety parts 1, 2-polybutadiene diol having an average molecular weight of 2000 g/mol and 10 parts 1-alkene are placed in a glass vessel and mixed thoroughly. Di-t-butyl peroxide is added in the amount of 1. 8 parts and the solution is stirred. This is followed by the addition of nine parts toluene diisocyanate. The solution is stirred until it becomes homogeneous. The solution is degassed in a vacuum chamber ($<$ 1 torr) for approximately five minues or, until the air bubbles entrapped in the solution are removed. The solution is transferred into a mold to form a plug or cast between aluminum plates to form a sheet. The mold is placed in a vacuum chamber and evacuated to approximately one torr until entrapped air bubbles are removed (~2 min). Plug molds are capped prior to curing. No seal is provided for materials cast between aluminum sheets other than the seal provided by gelled resin. The cast material is now ready for curing and is cured as follows: Six hours at 90°C, seven hours at 170°C and seven hours at 170°C.

### A. 2 Variation in the Backbone Structure through Copolymerization

Two examples are given for modifying the CPBU backbone structure through copolymerization with a compound which cannot cyclize.

#### Five phr Ricinoleic Triglyceride

Twenty parts 1, 2-polybutadiene diol having an average molecular weight of 2000 g/mol and one part ricinoleic triglyceride having an equivalent weight of 342 are placed in a glass vessel and mixed thoroughly. Di-t-butyl peroxide is added in the amount of 0. 4 parts and the solution is stirred. This is followed by the addition of 2. 1 parts toluene diisocyanate. The solution is stirred until it becomes homogeneous. The material is degassed and cast into molds as described above. The resin is cured as follows: Three hours at 90°C, four hours at 120°C and four hours at 170°C.

#### One hundred phr 1, 2-polybutadiene diol

Ten parts 1, 2-polybutadiene diol having an average molecular weight of 2000 g/mol and ten parts 1, 4-polybutadiene diol having an average molecular weight of 2200 g/mol are placed in a glass vessel and mixed thoroughly. Di-t-butyl peroxide is added in the amount of 0. 4 parts and the solution is stirred. Toluene diisocyanate is then added (1. 84 parts) and the solution is stirred until it becomes homogeneous. The material is degassed and cast in the molds as described above. The resin is cured as follows: Two hours at 90°C, three hours at 120°C, and eight hours at 170°C.

### A. 3 Introduction of Points of Flexibility in the Chain Extenders

Ninety parts of 1, 2-polybutadiene diol having an average molecular weight of 2000 g/mol and 1. 8 parts of di-t-butyl peroxide are mixed thoroughly. This is followed by the addition of 32.4 parts of DDI (36-carbon diisocyanate). The solution is stirred until it becomes homogeneous. The solution is degassed in a vacuum chamber ($<$ 1 torr) for approximately five minutes or until the air bubbles entrapped in the solution are removed. The solution is transferred into a mold to form a plug. The mold is placed in a vacuum chamber and evacuated to approximately 1 torr until entrapped air bubbles are removed (~2 minutes), then then capped. The cast material is cured as follows: 7 days at 90°C, 7 days at 120°C and 7 days at 170°C.

### A. 4 Modification of Fused Cyclohexane Ring Structure by Chain Transfer

Chain transfer agent modified CPBU formulations were prepared according to the following example:

#### One phr 1-Dodecane Thiol

Ninety parts 1, 2-polybutadiene diol having an average molecular weight of 2000 g/mol, one part 1-dodecane thiol and 1.8 parts di-t-butyl peroxide is mixed thoroughly. This is followed by the addition of 9 parts toluene diisocyanate. The solution is stirred until it becomes homogeneous. The solution is degassed in a vacuum chamber ($<$ 1 torr) for approximately five minutes or until the air bubbles entrapped in the solution are removed. The solution is transferred into a mold to form a plug. The mold is placed in a vacuum chamber and evacuated to approximately 1 torr until entrapped air bubbles are removed (~ 2 minutes), then capped. The cast material is cured as follows: 7 days at 90°C, 7 days at 120°C, and 7 days at 170°C.

### A. 5 Externally Plasticized CPBU Modifications

One hundred parts of 1, 2-polybutadiene diol having an average molecular weight of 2000 g/mol, 2 parts of di-t-butyl peroxide and 10 parts of Chlorowax 70 are mixed thoroughly. Toluene diisocyanate is added in the amount of 10 parts and the solution is mixed until it becomes homogeneous. The solution is degassed in a vacuum chamber ($<$ 1 torr) for approximately five minutes or until the air bubbles entrapped in the solution are removed. The solution is transferred into a mold to form a plug. The mold is placed in a vacuum chamber and evacuated to approximately 1 torr until entrapped air bubbles are removed (~2 minutes), then capped. The cast material is cured as follows: 16 hours at 90°C, 6 hours at 120°C, 16 hours at 140°C and 6 hours at 170°C.

### A. 6 Non-Chain Extended CPBU

Twenty-one parts purified 1,2-polybutadiene diol and 2 parts of phenyl isocyanate are refluxed in 21 parts of benzene for five hours. The resulting polybutadiene phenyl urethane is purified by recoagulation from a 20:1 v/v methanol-toluene solution giving a liquid prepolymer having a number average molecular weight of 1560 g/mol. One gram of this prepolymer is mixed with 24 mg t-butyl peroxide (2.4 phr) and stirred until homogeneous. The mixture is degassed and sealed in a test tube. The sealed tube casting is cured as follows: 16 hours at 90°C, 6 hours at 120°C, 16 hours at 140°C and 6 hours at 170°C.

### A. 7 Suppliers of Ingredients for Modified CPBU Formulations

| Ingredient | Supplier |
|---|---|
| 1,2-Polybutadiene diol | U.S. Industrial Chemical Co.<br>Hydroxy No. 53.8 mgKOH/g<br>Acid No. 0.07 mgKOH/g<br>Average Molecular Wt. 2000g/mol<br>Vinyl content 82.7% of unsaturation |
| 1,4-Polybutadiene diol | Sinclair Petrochemicals Inc.<br>Sinclair Poly B-D R-45M |
| 1-Octene | J. T. Baker Chemical Co. |
| 1-Decene | J. T. Baker Chemical Co. |
| 1-Hexadecene | J. T. Baker Chemical Co. |
| n-Alpha olefins ($C_6$-$C_{10}$, $C_{14}$-$C_{16}$, $C_{14}$-$C_{18}$) | Gulf Oil Corporation |
| Ricinoleic triglyceride | The Baker Caster Oil Co., DB Oil |
| Toluene diisocyanate | Matheson, Coleman and Bell |
| Di-t-butyl peroxide | Wallace and Tiernan Inc. Lucidol Div. |
| 1-Dodecane thiol | Matheson, Coleman and Bell |
| Chlorowax 70 | Diamond Alkali Company |

| Ingredient | Supplier |
|---|---|
| Phenyl Isocyanate | Matheson, Coleman and Bell |
| Ethylene propylene terpolymer rubber (EPT) | E. I. DuPont de Nemours, Inc.<br>NORDEL 1040 |
| DDI diisocyanate | General Mills |
| Trimethylolpropane | Celanese Corporation |
| Dicumyl peroxide | Hercules Powder Co. |
| Viton-B elastomer gum | E. I. DuPont de Nemours, Inc. |
| Kel-F 5500 elastomer gum | Minnesota Mining and Manufacturing Co. |

# APPENDIX B

# NITROGEN TETROXIDE PERMEABILITY MEASUREMENTS

This appendix describes the design and use of special equipment employed in this program for the measurement of nitrogen tetroxide permeability through candidate and state-of-the-art bladder materials. The ambient temperature apparatus was used for all the measurements reported in the main body of this report. The high temperature apparatus was fabricated, calibrated and checked out with Teflon specimens alone; promising candidate materials were available too late in the program for long term testing.

## B. 1 AMBIENT TEMPERATURE APPARATUS

Measurement of the permeability of $N_2O_4$ through test specimens was accomplished by establishing a concentration gradient across a thin wafer of the specimen under study; nitrogen tetroxide on one side and deionized water on the other. The amount of nitrogen tetroxide that diffused through the specimen was determined by monitoring the hydrogen ion concentration in the compartment containing the water. For every mole of nitrogen tetroxide that diffuses through the specimen two moles of hydrogen ion are generated, e. g.,

$$N_2O_4 + H_2O \longrightarrow 2H^+ + NO_2^- + NO_3^-$$

The hydrogen ion concentration was measured electrometrically.

A photograph of the experimental arrangement of the diffusion apparatus is shown in Figure B-1. The following technical problems were overcome in the design and use of this apparatus:

- To insure that a $N_2O_4$ tight seal was effected at the glass-plastic interface without introduction of contaminants, the specimen was clamped snugly in place without the use of a sealant compound.
- The water tight glass-plastic seal was accomplished using a Neoprene O-ring.

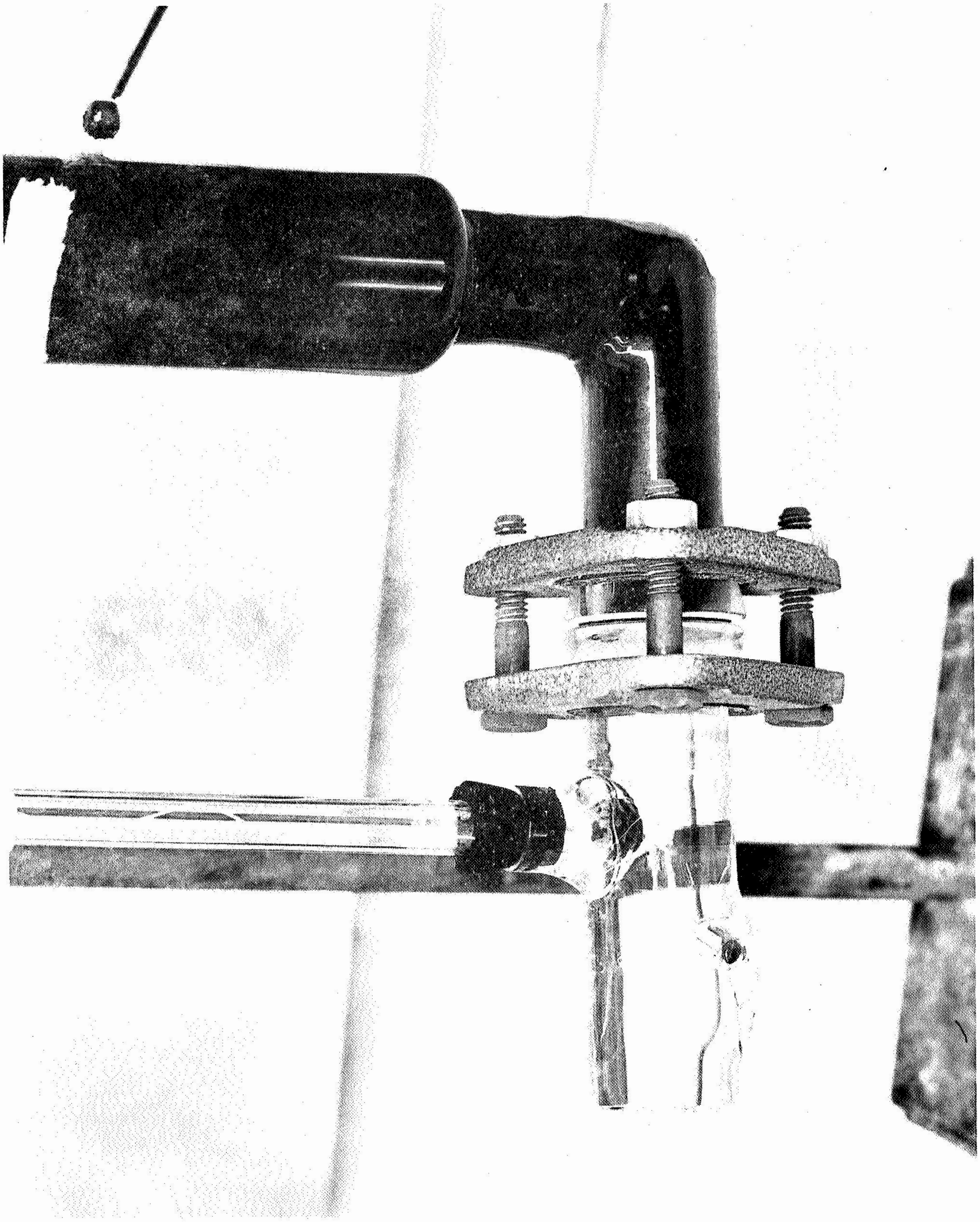

Figure B-1. Assembled Ambient Temperature Permeability Apparatus

- The interface was established in a vertical position for redundant protection against possible leaking during the experiment, e.g., the flow path for liquid would lead directly to the other side of the specimen.
- The water compartment was designed to have a small volume in order that a sensitive measure of hydrogen ion concentration variation could be measured.
- The water compartment containing a magnetic stirring bar and pH electrodes was sealed from the atmosphere to eliminate ingress of carbon dioxide which would interfere with the simple interpretation of the pH data. This requirement necessitated the use of an auxiliary pH electrode system for adjustment and calibration for the pH meter.

### B. 1. 1 Experimental

Apparatus. The pH measurements were performed using a Beckman combination silver-silver chloride/glass pH electrode pair with a Leeds and Northrup Model 7401 line operated pH meter. The diffusion apparatus compartments were fabricated from glass using 3/4-inch industrial glass pipe. An O-ring groove incorporated in the water compartment and a 3/4-inch pipe and a ground flat flange was employed in the $N_2O_4$ compartment. A 10-mm opening for the electrode was located in the water compartment and $N_2O_4$ compartment had a 12-inch length 1-1/2-inch diameter reservoir for long term storage of the $N_2O_4$. A magnetic stirring bar was placed in the water compartment to insure mixing of the diffused nitrogen tetroxide. The apparatus was held in place with an industrial glass pipe clamp.

Procedure. A known volume of deionized distilled water was transferred into the water compartment of the diffusion apparatus (after assembly) by means of a pipet. The electrode was sealed in place with a rubber seal and the magnetic stirrer was actuated. The pH of the water solution was determined and then monitored periodically during the experiment. The pH meter was calibrated and adjusted with a standard buffer solution using an auxiliary pH electrode pair. Nitrogen tetroxide was added to the other compartment and reservoir. The liquid was permitted to evaporate at room temperature, however, a new supply was added periodically to insure that the specimen was always in contact with the oxidizer.

### B. 1. 2 Results

Results showing the comparison of the pH in the water compartment for resistant butyl rubber, Teflon and CPBUare presented in Figure B-2. These data have been calculated in the form of a permeability measure,

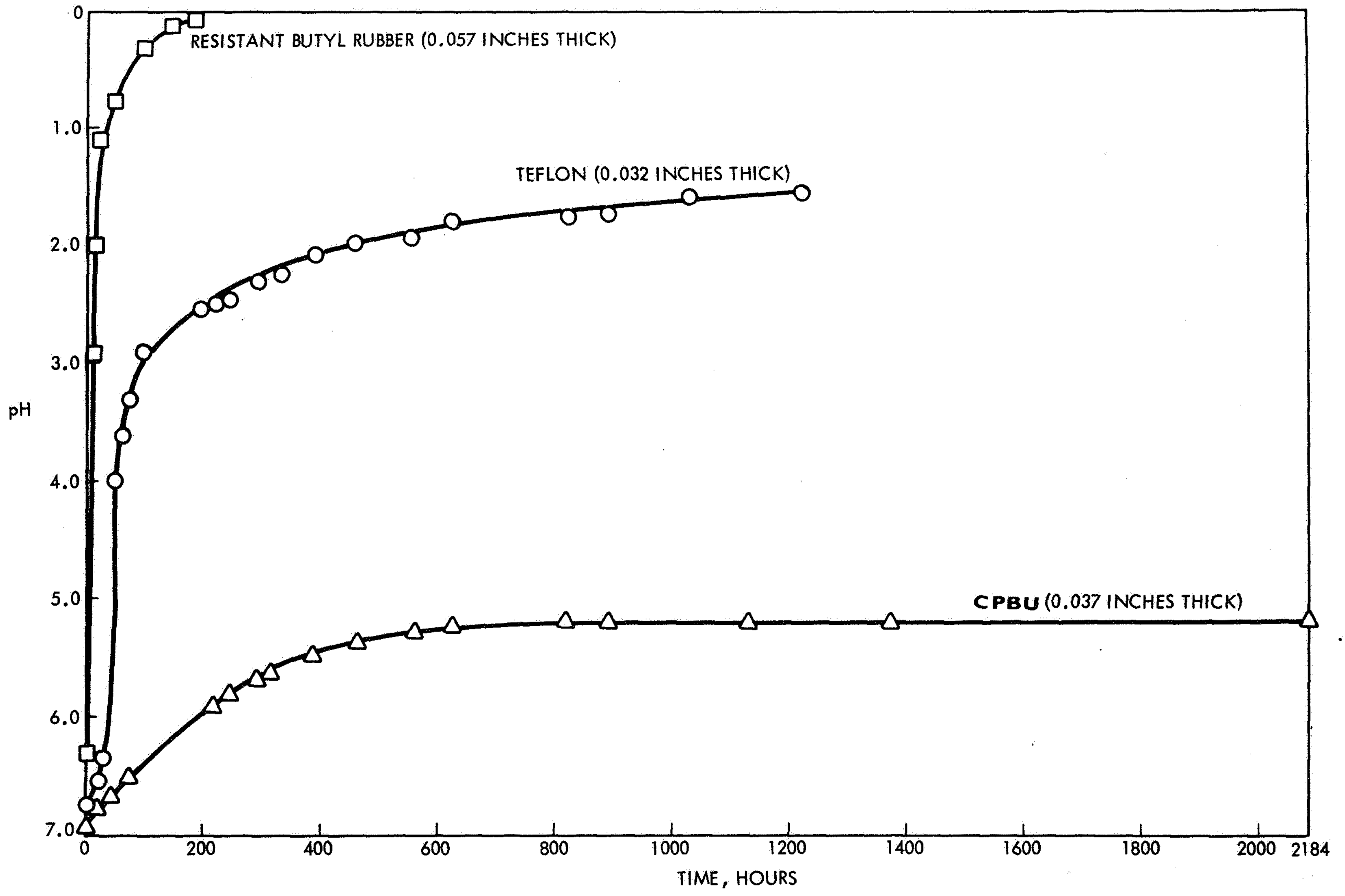

Figure B-2. Permeability Study Raw Data, pH as a Function of Time

$C_i$, the weight of nitrogen tetroxide per unit surface area. These data [calculated by use of Equation (15)] are shown in Figures B-3, B-4 and B-5 respectively.

$$C_i = \frac{\left[(H^+)_i - (H^+)_o\right] VM}{2A}$$

where

$(H^+)_i$ = hydrogen ion concentration at any time, i, mol/l

$(H^+)_o$ = initial hydrogen ion concentration, mol/l

V = volume of water in aqueous compartment, liters

M = molecular weight of $N_2O_4$, g/mol

A = effective surface area of specimen, $cm^2$

The results of similar $N_2O_4$ permeability measurements on NT-5 fluoronitroso rubber, Alcar 22c (CTFE), Kynar (VF), TFE/FEP laminates and TFE (10. 0079-inch thick) are shown in Figure B-6. The permeability data shown in Figure B-6 are summarized in Table II in the main body of the report.

## B. 2 HIGH TEMPERATURE APPARATUS

During this program an apparatus was constructed which permits the determination of nitrogen tetroxide permeability of candidate materials as a function of temperature. This apparatus uses the same principal as the ambient temperature apparatus but has been designed to overcome the constraints imposed at 130°F of both temperature and operation at 60. 0 psia (the vapor pressure of $N_2O_4$ at 130°F). The apparatus shown schematically in Figure B-7 consists of two chambers; one for $N_2O_4$, and the other for deionized water, which are separated by a thin wafer of the test specimen. The concentration gradient across the specimen is the driving force for the permeability measurements.

The apparatus is constructed of stainless steel and consists of 1) a Beckman Instrument Company Model 72500a High Pressure pH Electrode Pair Assembly (capable of operation 100 psig), (Reference 14), which serves as the water reservoir, and 2) the $N_2O_4$ reservoir. The diffusion

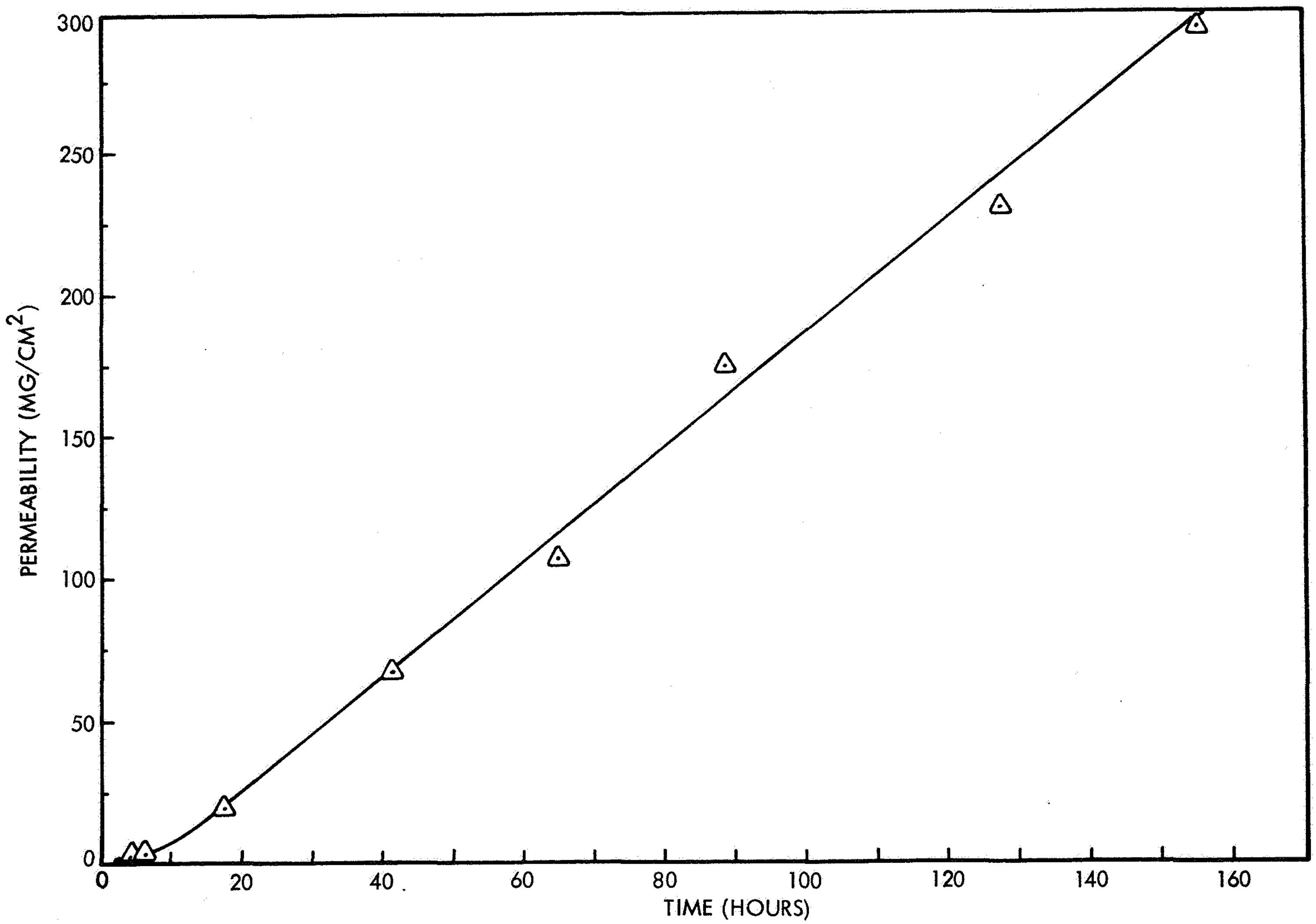

Figure B-3. Permeability of Nitrogen Tetroxide Through Resistant Butyl Rubber as a Function of Time

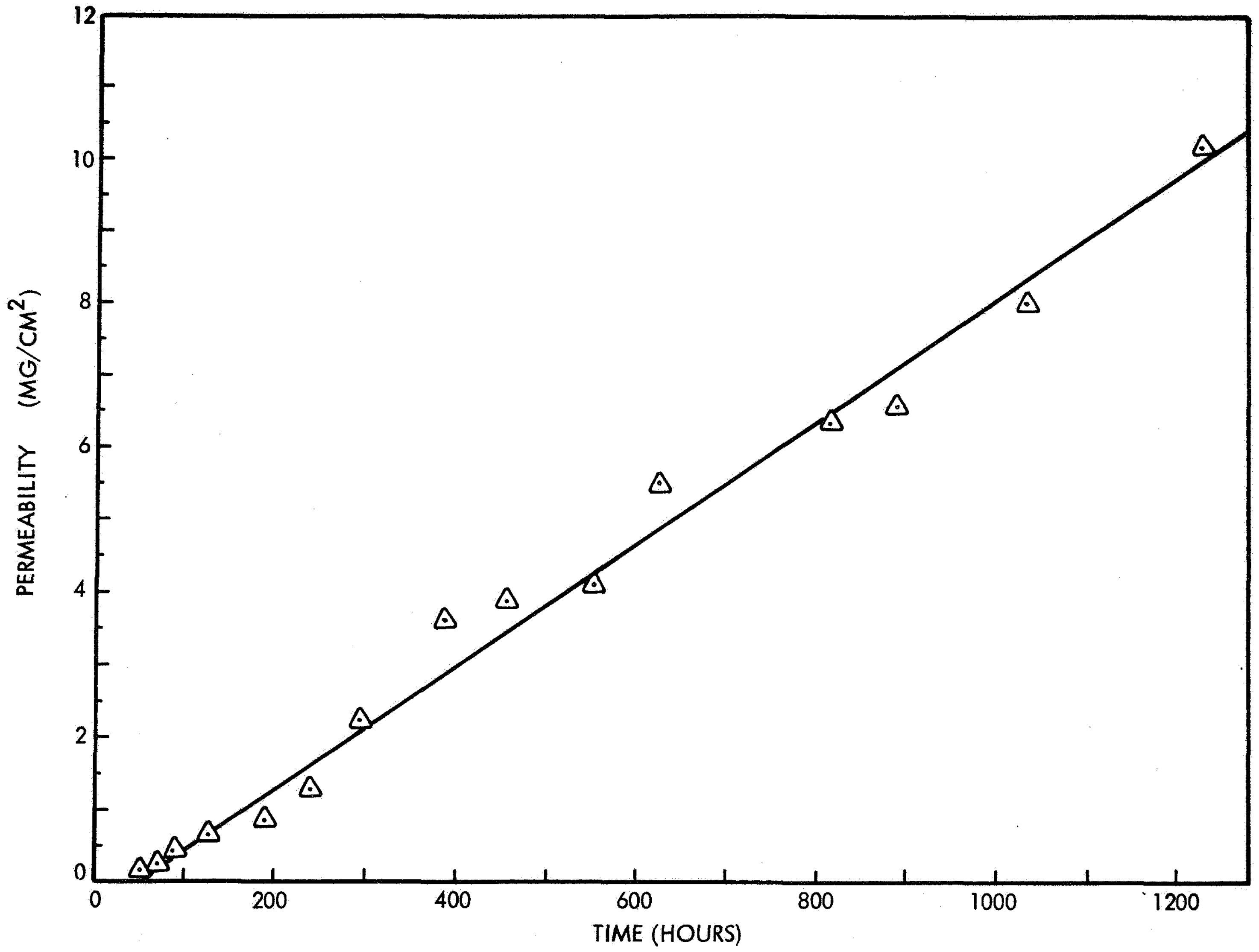

Figure B-4 Permeability of Nitrogen Tetroxide Through 0.032-inch Thick Teflon as a Function of Time

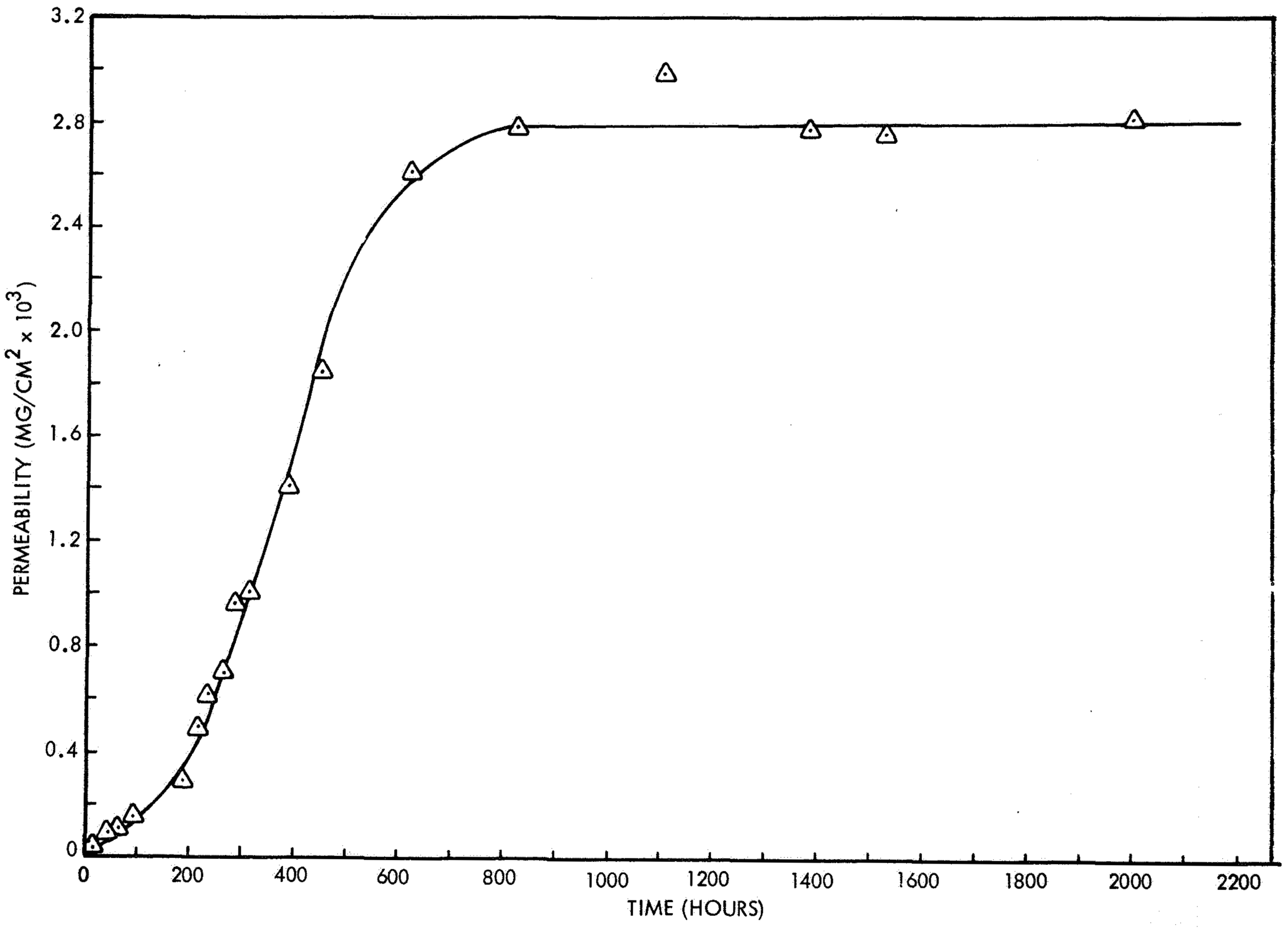

Figure B-5. Permeability of Nitrogen Tetroxide Through Poly (Cyclized 1,2-Polybutadiene) Tolyl Urethane as a Function of Time

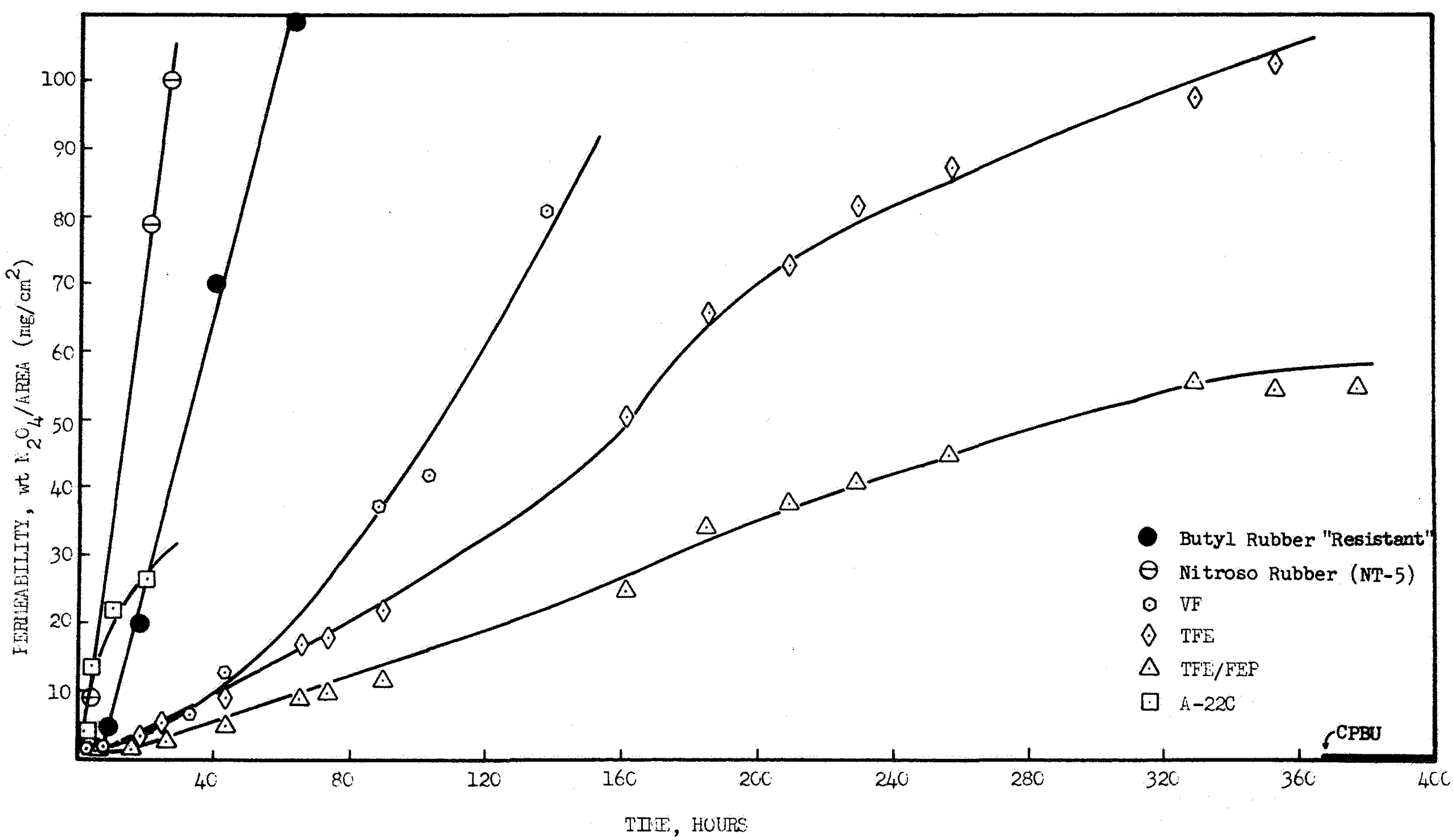

Figure B-6. Calculated Nitrogen Tetroxide Permeability as a Function of Time

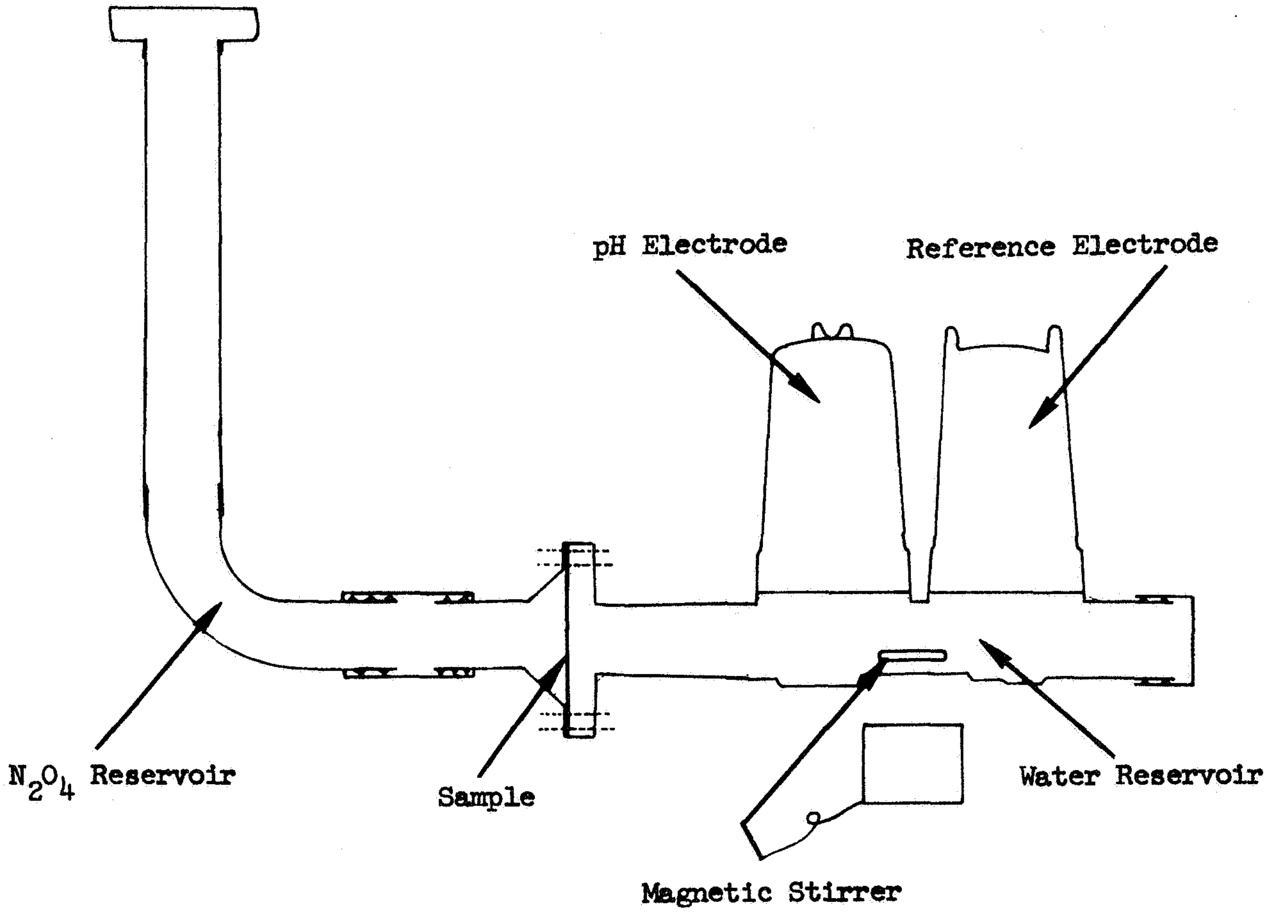

Figure B-7. Special High Temperature Permeability Apparatus

apparatus is filled by first assembling the test material in place, removing the threaded cap at the end of the $N_2O_4$ chamber, filling the reservoir with $N_2O_4$ and replacing the cap.

The water reservoir, containing the magnetic stirring bar, is filled through the electrode pair assembly to avoid entrappment of air. The diffusion apparatus is placed in the oven, the magnetic stirrer is started and the pH meter is attached to the electrodes. The temperature of the oven is controlled and maintained at a desired level.

The assembled components of the diffusion apparatus are shown in Figure B-8. The overall components of the high temperature permeability apparatus (shown in Figure B-9) consist of the diffusion apparatus, pH meter, and constant temperature oven.

Permeability measurements were conducted on 0. 032-inch Teflon sheet at $140^{o}F$. The permeability-time curve is shown in Figure B-10. Increase of temperature clearly increases the rate of permeability by an appreciable amount. At $140^{o}F$, Teflon had a total permeability of 3. 0 mg $N_2O_4/cm^2$ in 3. 5 hours whereas the same material required about 4. 0 hours to attain the same total permeability at $77^{o}F$.

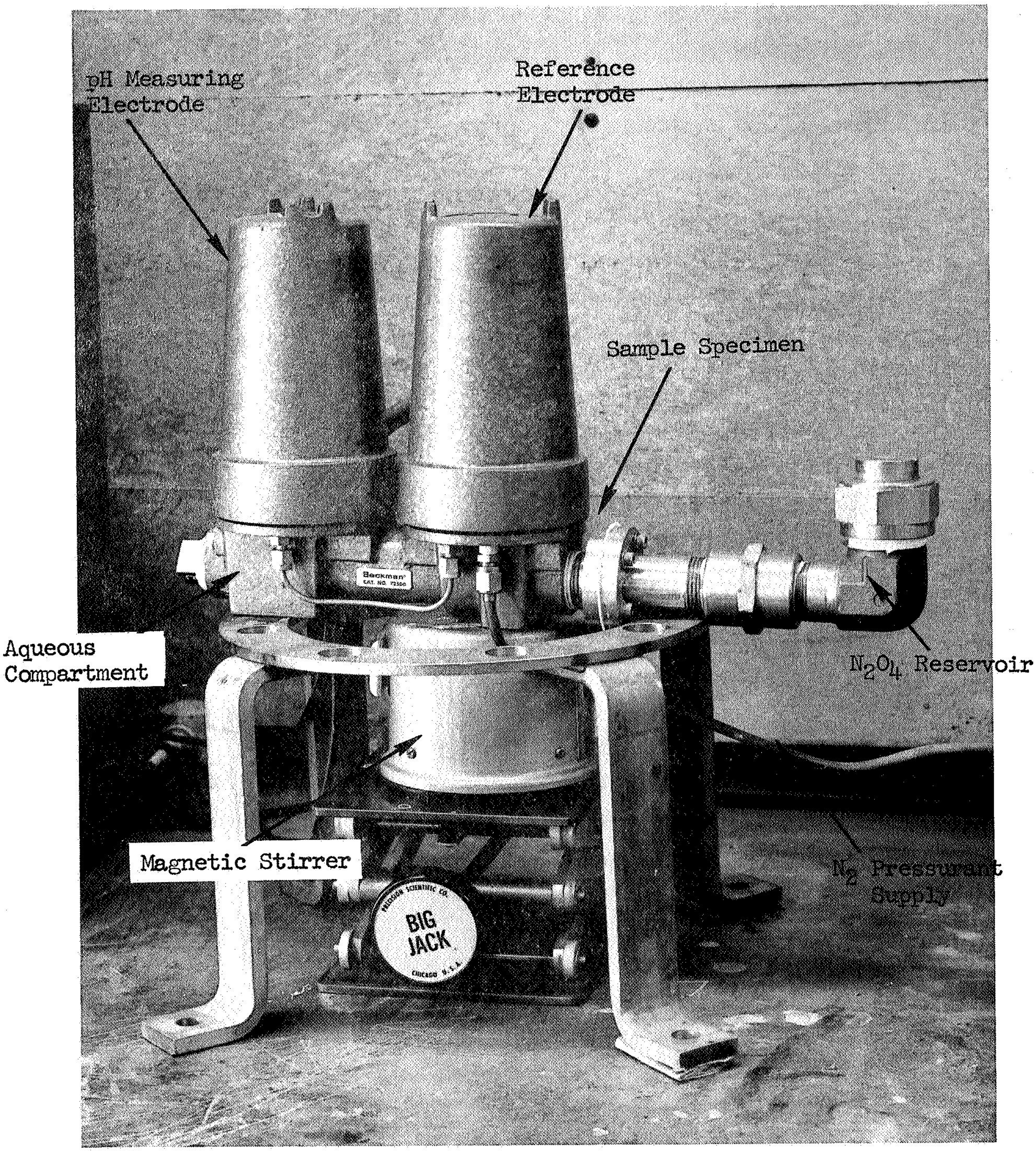

Figure B-8. Diffusion Apparatus

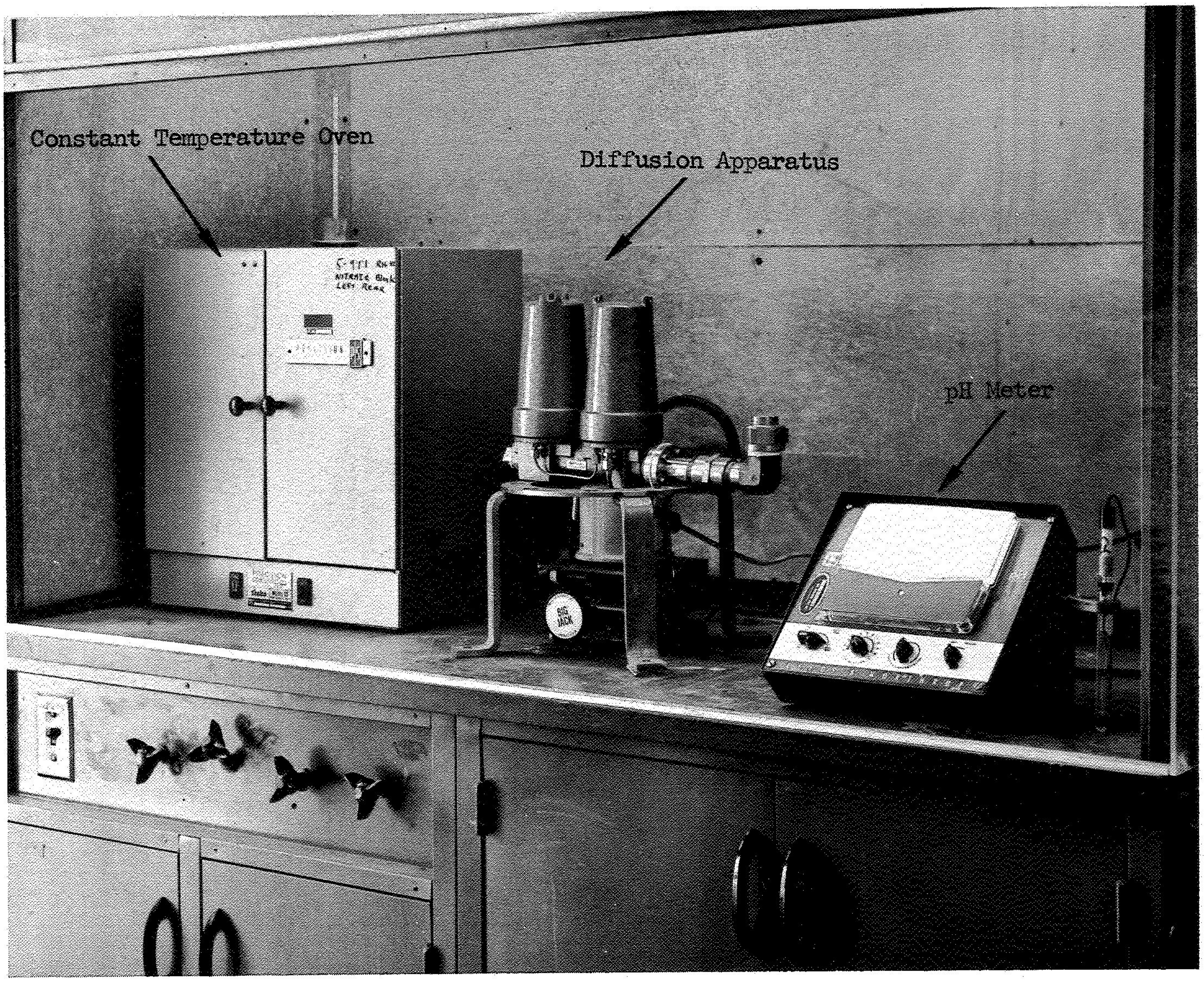

Figure B-2. Components of High Temperature Permeability Apparatus

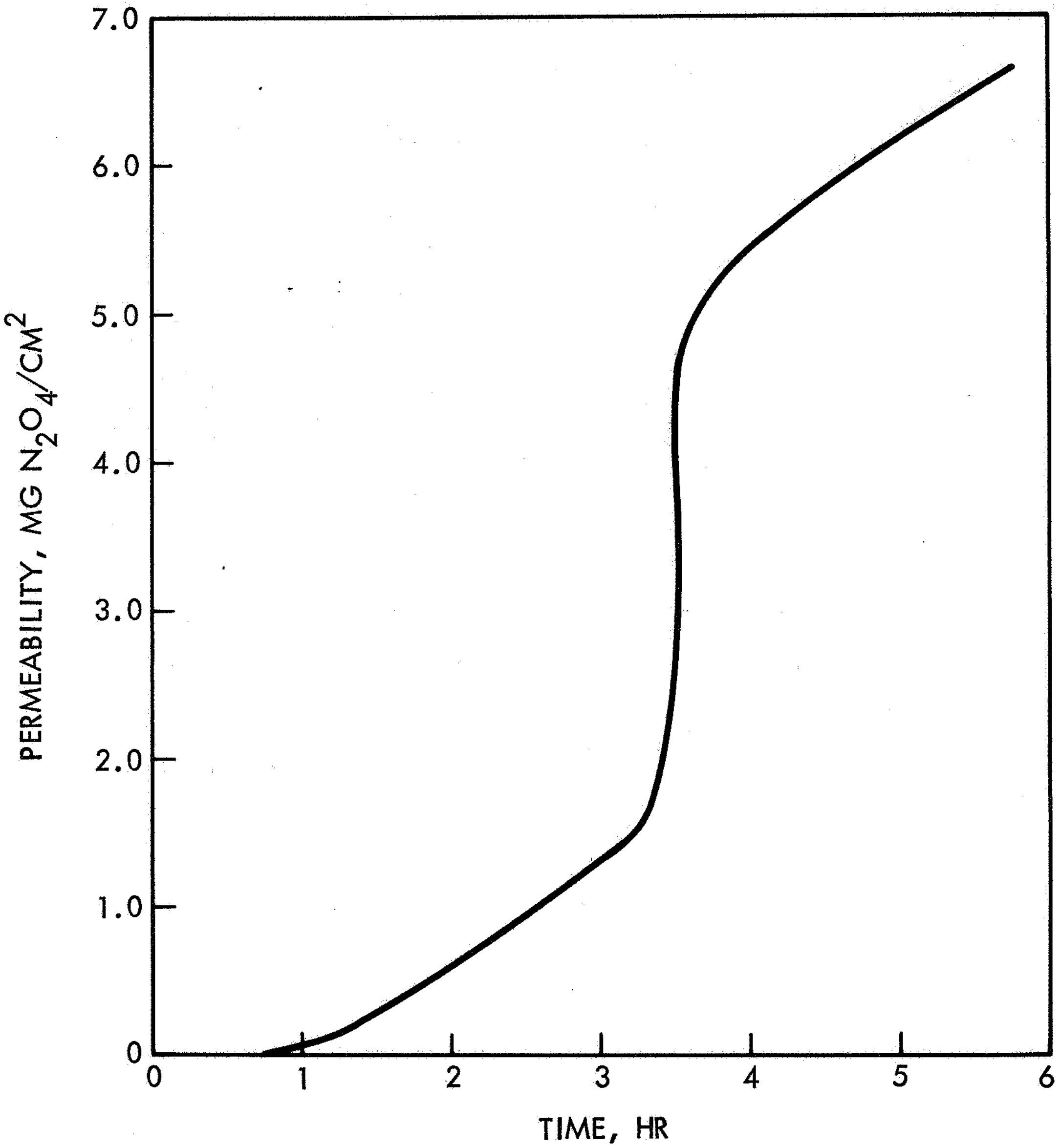

Figure B-10. Permeability of Nitrogen Tetroxide Through 0.032-inch Thick Teflon as a Function of Time at 140°F

# APPENDIX C

# HYDRAZINE PERMEABILITY MEASUREMENTS

This Appendix describes the design and use of a special apparatus employed in this program for the measurement of hydrazine permeability through candidate bladder materials. The technique employed consisted of establishing a concentration gradient across a specimen: hydrazine on one side and nitrogen gas on the other. By flowing the nitrogen gas from the back side of the test specimen through a glacial acetic acid trap, the hydrazine that diffused through was transported and absorbed in the glacial acetic acid. Periodic removal of the trap solution and titration with perchloric acid permitted quantitative determination of the hydrazine which diffused through the test specimen.

The apparatus employed in this measurement is shown schematically in Figure C-1. The apparatus consists of 1) an L-shaped tube for use as the hydrazine reservoir, 2) standard glass pipe joints, and 3) a straight flow-through tube fitted with gas inlet and outlet ports. The bladder material is placed between the tubes and the tubes joined using triangular glass pipe connectors. The gas inlet port is connected to a nitrogen supply and the gas outlet port is connected to two scrubber traps in series.

The hydrazine diffusion rate was determined by the following procedure:

> Hydrazine is added to the reservoir to insure, by means of a pressure head, continuous and intimate contact between the hydrazine and the bladder material. A measured quantity of glacial acetic acid was placed in each scrubber and the nitrogen purging gas supply was opened. The gas inlet port was constructed to permit direct flow of the nitrogen purging gas over the exposed bladder surface. Periodically the contents of the acetic acid scrubber were emptied into a 125-ml Erlenmeyer flask. The trapped material was titrated directly with a perchloric acid-glacial acetic acid solution to a quinaldine red end-point.

The hydrazine diffusion over any specific time interval was calculated as follows:

$$N_2H_4 \text{ diffused, mg/cm}^2 = \frac{(V_i - B)\,(N)\,(32.05)}{A}$$

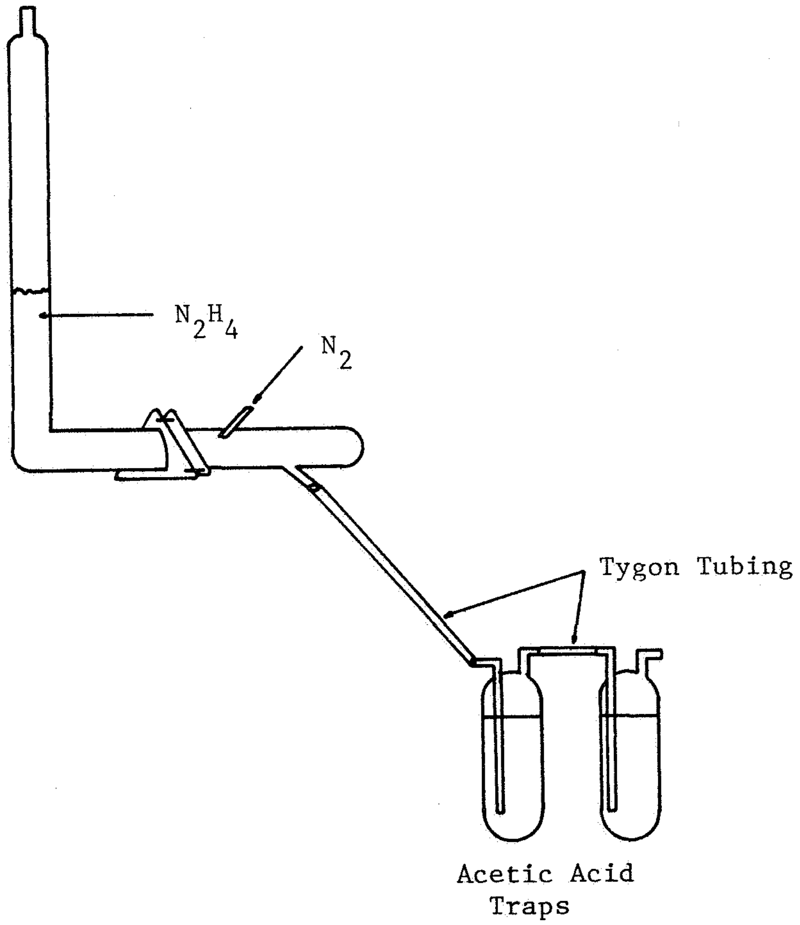

Figure C-1. Schematic Diagram of Hydrazine Permeability Measurement Apparatus

Where: $V_i$ = Volume of perchloric acid solution required to titrate the scrubber solution after any time period, $t_i$, ml

$B$ = Volume of perchloric acid solution for blank scrubber titration, ml

$N$ = Concentration of perchloric acid solution, normal

$A$ = Exposed bladder surface area, $cm^2$

# APPENDIX D

# GAS PERMEABILITY MEASUREMENTS

This Appendix describes the design and use of a special apparatus employed in this program for the measurement of inert gas permeability through candidate bladder materials. The technique employed consisted of establishing a pressure drop across a candidate bladder material: a fixed pressure level of inert gas on one side and low pressure on the other. The low pressure was monitored as a function of time and the quantity of gas which permeated through the bladder material was calculated assuming ideal gas laws.

The apparatus employed in this measurement is shown schematically in Figure D-1. The apparatus consisted of an L-shaped gas reservoir tube which was connected to the gas supply system. The high pressure part of the system consisted of a gas supply, vacuum outlet and pressure gauge. The low pressure side of the apparatus consisted of a straight tube fitted with ports for evacuation and constant pressure monitoring. Pressure monitoring was accomplished using a mercury manometer. The bladder material was inserted between the tubes and the tubes were joined using triangular pipe connectors.

The gas permeabilities were measured in the following manner:

> The entire apparatus was evacuated and the pressure monitored to insure that the system was leak-tight. The gas reservoir was then pressurized to 30 psi nitrogen. The gas supply system was regulated automatically during the test to insure that constant pressure was maintained in the reservoir. The pressure rise in the low pressure side of the apparatus caused by the permeation of the nitrogen gas was monitored periodically using a mercury manometer.

The nitrogen diffusion after a fixed period of time, $t_i$, was calculated as follows:

$$\text{Nitrogen diffusion, mg/cm}^2 = \frac{1.155\ PV}{A}$$

Where: P = Measured pressure change, atm.

V = Volume of low pressure side of apparatus, ml

A = Area of exposed bladder material, $cm^2$

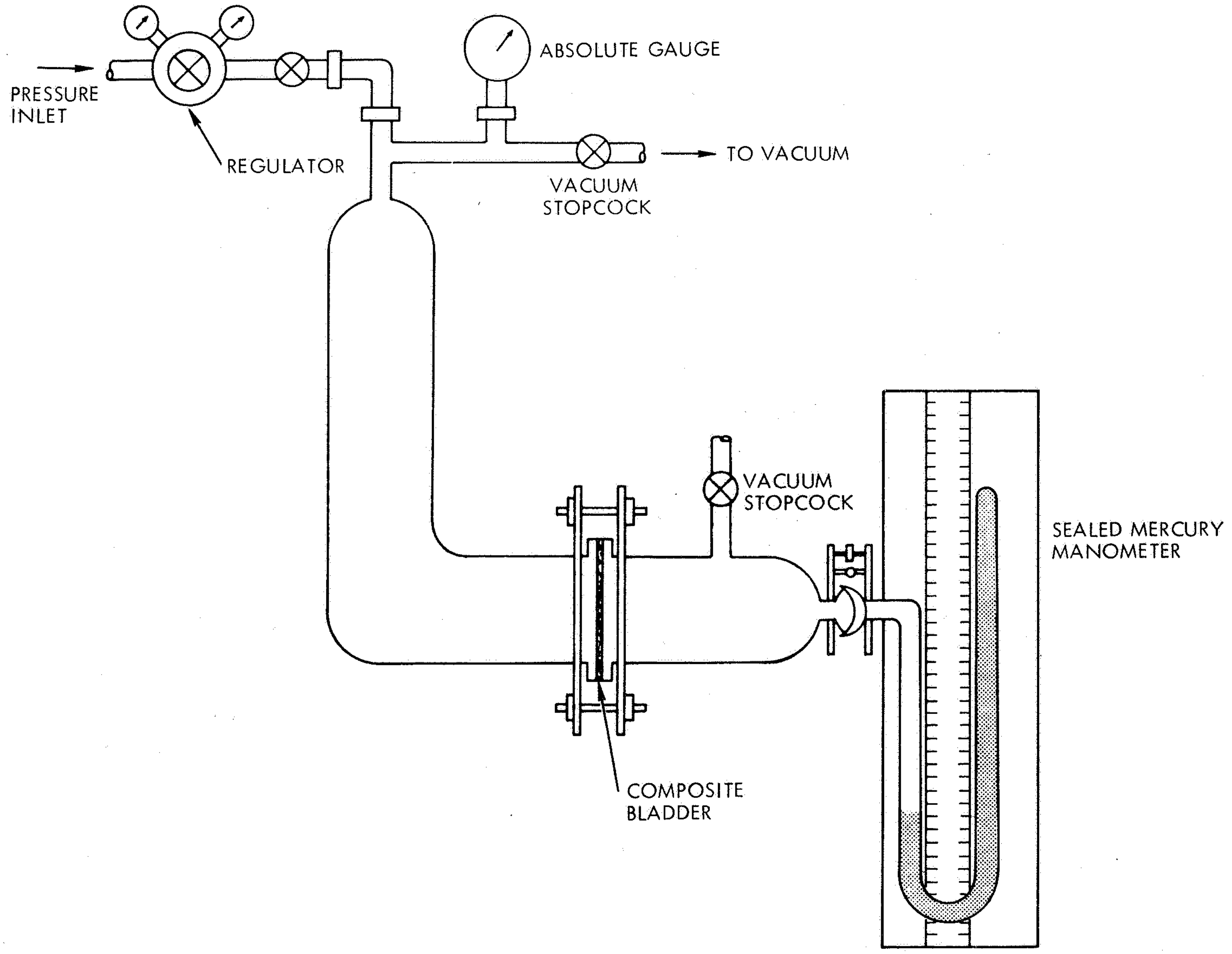

Figure D-1. Schematic Diagram of Gas Permeability Measurement Apparatus