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FINAL REPORT
STUDY OF ADVANCED BLADDER TECHNOLOGY, OF_2/DIBORANE

by

J. W. MARTIN, J. F. JONES AND J. A. NEFF

Prepared For:
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
CONTRACT NAS7-770
1 JULY 1970

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Jet Propulsion Laboratory
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TRW
SYSTEMS GROUP
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FOREWORD

This document constitutes the final report for the work accomplished between 2 September 1969 and 1 July 1970 by TRW Systems Group for the National Aeronautics and Space Administration, Jet Propulsion Laboratory, under Contract NAS7-770, "Study of Advanced Bladder Technology, OF_2/ Diborane".

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 Frank E. Compitello.

The Chemical Technology and Chemical Research and Services Departments of the Chemistry and Chemical Engineering Laboratory, Science and Technology Division were responsible for the work performed on this program. Mr. B. Dubrow, Manager, Chemistry and Chemical Engineering Laboratory, provided overall program supervision. Dr. E. A. Burns, Manager, Chemical Research and Services Department and Dr. J. L. Blumenthal, Manager, Chemical Technology Department provided technical coordination. Mr. J. F. Jones was Program Manager and Mr. J. W. Martin was Principal Investigator. Dr. J. A. Neff performed all of the propellant compatibility and permeability evaluations. Acknowledgment is made of the technical assistance provided during this program by the following TRW Systems Group personnel:

Members of the Technical Staff

Mr. A. Grunt	Chemical Research and Services Department

Technical Support

Mr. J. L. Bell	Chemical Technology Department
Mr. G. I. Fukumoto	Materials Engineering Laboratory
Mr. W. B. Turner	Chemical Research and Services Department

ABSTRACT

This final report describes the work performed by TRW Systems Group under Contract NAS7-770 to develop and characterize elastomeric materials suitable for use as positive expulsion bladders for the space storable propellants oxygen difluoride (OF_2) and diborane (B_2H_6). The work was based upon findings of a previous Contract (NAS7-702) in which short-term, static tests had identified cis 1,4-polybutadiene as compatible with OF_2 and acrylonitrile/butadiene copolymer (nitrile) as compatible with B_2H_6. The present work further investigated the previous findings in longer term tests, under dynamic conditions and at different temperatures.

A brief formulation study was conducted to optimize the mechanical properties (tensile strength and elongation at break) of compounds made from the polybutadiene and nitrile base polymers. Candidate compounds with the best mechanical properties were tested dynamically in the presence of propellant. In one procedure, specimens of the elastomers were strained in tension to failure while immersed in the respective propellants.

In a second dynamic test, a small-size diaphragm apparatus was built to "expel" the respective propellants. At -78.5°C, the prime candidate polybutadiene material (Compound 202-1) expelled OF_2 forty times at which point the test was stopped arbitrarily. At -45°C, the prime nitrile material (Compound 215-3) expelled B_2H_6 successfully 20 times prior to development of a leak, which was later analyzed to be induced by low temperature stress rather than by chemical attack.

Long-term compatibility tests showed that the relaxed and stressed polybutadiene (Compound 202-1) did not undergo significant degradation in OF_2 at -78.5°C. Similar tests with the nitrile (Compound 215-3) in B_2H_6 at -20°C showed that the propellant was reacting slowly with the base polymer.

Long-term permeability measurements showed the expected decreased permeability with lowered temperature for both candidates. The polybutadiene (Compound 202-1) had a very low permeability coefficient at -78.5°C and had an unmeasurably low coefficient at -95°C, a temperature at which the compound is semi-elastomeric (highly compliant). The nitrile (Compound 215-3) had higher, but manageable B_2H_6 permeability coefficients at the three temperatures tested. The lowest use temperatures identified for both materials appear to be within the system design requirements of no greater propellant vapor pressure than 300 psia.

1. INTRODUCTION AND SUMMARY

Elastomeric bladders and diaphragms make efficient use of tank volume and efficiently supply a high percentage of the propellant to the engine. However, elastomers generally are more permeable to propellants and pressurant gasses than alternative materials, and elastomers by their chemical nature frequently interact with the higher energy propellants, such as oxygen difloride (OF_2) and diborane (B_2H_6).

During Contract NAS7-446 (Reference 1) TRW Systems Group studied and sought to develop new elastomeric bladder materials for service with dinitrogen tetroxide (N_2O_4) and hydrazine (N_2H_4) propellants. During that Contract, considerable emphasis was placed on understanding the nature of propellant/bladder permeability and compatibility, and on improving these properties through novel chemical approaches.

A following program, Contract NAS7-702 (Reference 2), was based on the previous work but shifted attention to investigation of commercially available elastomers usable with the mild cryogenic, space storable propellants OF_2 and B_2H_6. As these propellants are to be stored at low temperatures, an additional requirement of flexibility at low temperature was introduced. During NAS7-702, compounds based upon cis 1,4-polybutadiene were identified as being potentially useful for service with OF_2. Compounds based upon acrylonitrile/butadiene copolymers (nitriles) were identified as being potentially useful with B_2H_6. Compatibility measurements, permeability measurements and the determination of low temperature stiffening points for the candidate compounds indicated that these materials were attractive candidates, but that additional optimization was required.

The present program, funded under Contract NAS7-770, was performed to optimize the mechanical properties of the candidate elastomers through formulation and curing studies, to assess the compatibility of the optimized compounds through dynamic testing in OF_2 and B_2H_6 at the storage temperatures, and to determine the long-term static compatibility and permeability of the optimized compounds at various temperatures. At the outset of this project, available information for storage temperatures indicated that the vapor pressure of the propellants should not exceed 300 psia (Appendix E), which relates to a temperature maximum of -12°C for B_2H_6 and -87.5°C for OF_2. Since -87.5°C is a difficult temperature to maintain in the laboratory, -78.5°C (dry ice) was adopted for OF_2 testing for the majority of this program.

The previous study had utilized only one nitrile base polymer which appeared to be compatible with the B_2H_6. However, a homopolymer of butadiene included in the same tests was degraded by the propellant. (A homopolymer of butadiene is analogous to a nitrile polymer with 0% acrylonitrile.) From these results it was concluded that the acrylonitrile units stabilized the polymer against the effects of B_2H_6. Thus, in the present work, a trade-off was sought between low temperature elasticity (low acrylonitrile) and compatibility with the propellant (high acrylonitrile).

As the previous program had been primarily a survey of commercially available materials, little effort was expended in developing optimum mechanical properties (tensile strength and elongation at break). Additional work was indicated to optimize these properties as they are imperative to proper expulsion bladder performance.

The use of CIS-4-1203 Polybutadiene (Phillips Petroleum Co., 98% cis 1,4-structure) was suggested by the prior compatibility test results. Silicon dioxide (Cabot Corporation Cab-O-Sil M-5, fumed SiO_2) and a peroxide curative were used (as in the previous work). This composition (Compound 60-1) while immersed in propellant was strained to failure, initiated a fire, and apparently was consumed. A modification of Compound 60-1, which utilized the same base polymer but was reinforced with Al_2O_3 (ALON, Cabot Corp.) was recovered essentially quantitatively from the tensile test conducted in propellant. This material, Compound 202-1, eventually was determined to be the prime candidate elastomer compound developed under this program for OF_2 service.

In the preceding contract, a carboxylated nitrile (Hycar 1072), was identified as compatible with B_2H_6 in the static tests at low temperature. However, this particular polymer became stiff and non-elastomeric at temperatures considerably above the desired B_2H_6 storage temperature, caused by the high acrylonitrile content and carboxy groups. In the present work, four nitrile copolymers were obtained ranging between 20 and 45 mole-percent acrylonitrile. A similar compound was made using each of these four materials and each was subjected to tensile tests between -30° and -60°C. Short, static compatibility tests in B_2H_6, monitored by change in weight and retention of mechanical properties, indicated that between the stated limits of acrylonitrile content, B_2H_6 compatibility was not affected. On this basis, the 20 mole-percent copolymer was selected for further work because it had the best low temperature properties. This polymer, Chemigum N-9 (Goodyear Chemical Company), was subjected to a brief compounding study to optimize its room temperature mechanical properties. During this study it was determined that peroxide was an unsatisfactory vulcanizing agent for this polymer.* A formulation of Chemigum N-9 (Compound 215-3) reinforced with fumed silica and cured by sulfenamide-accelerated sulfur was found to have acceptable mechanical properties at room temperature and at -40°C. A short, static compatibility test was conducted with this compound in B_2H_6 to determine if the new cure system had affected the compound's propellant compatibility. Weight change and retention of mechanical properties indicated compatibility equivalent with the peroxide-cured precursor. Dynamic (tensile) tests conducted in B_2H_6 at ambient room temperature showed essentially no reaction at break.

The long-term compatibility of properly cured polybutadiene (Compound 202-1) with OF_2, also monitored by weight change and property retention measurements, showed that either relaxed or strained specimens were unaffected by the propellant at -78.5°C. Long-term compatibility test of Compound 215-3 in B_2H_6 at -20°C showed that the propellant was reacting slowly with the base polymer. It was not determined if this incompatibility was due to the low acrylonitrile content, the accelerated sulfur cure system, or to a combination of causes.

Permeability of Compound 202-1 to OF_2 at -78.5°C was extremely low. A plot of pressure (ordinate) <u>versus</u> time (abscissa) over the test period was a smooth curve with a slightly decreasing slope as the test period progressed. Thus, permeability decreased with time. Permeability of this compound to OF_2 at -95°C was unmeasurably low. However, from knowing the sensitivity and dimensions of the permeability apparatus, it was calculated that less than 13 mg/day of OF_2 would permeate through a 0.020-inch thick, 10-inch diameter Compound 202-1 bladder at -95°C, a temperature at which this compound is elastomeric. This use temperature relates to a vapor pressure of 225 psia for OF_2 which is below the system limit as discussed in Appendix E.

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*Appendix A discusses possible reasons for the poor mechanical properties found for this polymer.

The permeability of Compound 215-3 by B_2H_6 was measured at three temperatures. After the induction periods, essentially linear data were obtained in all three cases. Calculation of the permeability coefficients over the linear periods gave values considerably higher than those observed for Compound 202-1 with OF_2, but they did decrease with lower temperatures, as expected. An Arrhenius plot of the coefficients provided a nearly straight line. The -40°C test temperature relates to a B_2H_6 vapor pressure of only 135 psia which is well within the system limit as discussed in Appendix E.

Each prime candidate compound was tested with the respective propellant in a small size expulsion bladder test apparatus. For OF_2, Compound 202-1 was used as an expulsion diaphragm actuated by nitrogen.* At -78.5°C the elastomer successfully expelled the propellant forty times without failure. For B_2H_6, Compound 215-3 was used as the expulsion diaphragm also actuated by nitrogen. At -45°C the diaphragm expulsed B_2H_6 twenty times. On the 21st cycle, a leak developed and the test was stopped. Investigation of the cause for leakage showed that the specimen was cracked radially in a manner strongly suggesting low temperature stress-induced failure rather than chemical failure. In the case of Compound 215-3, -45°C is about the glass transition temperature of the base polymer. It appeared as though the sample was forced to stretch by the nitrogen ullage gas beyond the elastic limit of the material. Both expulsion diaphragms were retrieved from the test cells apparently free from chemical attack.

The results of this work established that further study is warranted to determine the lower use temperature limit for Compound 202-1, and to develop further a nitrile compound for better low temperature properties and lower propellant permeability.

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*Maximum calculated elongation for the diaphragms in their fully extended position was 200%.

2. TECHNICAL ACCOMPLISHMENTS

This section reports the technical progress made under the present program, its relationship to laboratory findings of the previous program, and to bladder requirements.

2.1 TASK I - PREPARATION OF OPTIMIZED ELASTOMER COMPOUNDS FOR OF_2 and B_2H_6 SERVICE

2.1.1 Polybutadiene Compounds for OF_2 Service

Laboratory investigations carried out during contract NAS7-702 defined peroxide-cured cis 1,4-polybutadiene reinforced with silica as the prime candidate material for further investigations with OF_2. A brief compounding study initiated the present work to develop formulations with the best mechanical properties (tensile strength/elongation at break) using the previously identified ingredients in various ratios. Cure times and temperatures also were studied to reach the same goal. The compounds described in Table 1 were prepared and tested with the result that three were identified for further evaluation. Selected compounds included the one with the highest tensile strength at room temperature (60-1 cured 20 minutes at 300°F), the compound with the lowest filler volume (60-3 cured 10 minutes at 320°F) and the compound with the highest tensile strength at the lowest temperature at which stress/strain measurements were made (60-7 cured 10 minutes at 320°F).

During concurrent Task II tests, one compound representative of the three selected compounds was strained to breaking while immersed in propellant (discussed in Section 2.2.3) which generated fires in the apparatus as a result of these tests (Appendix B). Subsequent analysis of the problem indicated that the silica (SiO_2) reinforcement may have reacted with the OF_2. Although it was likely that the polybutadiene also could react with OF_2 at the test temperature (Reference 3), this base polymer was retained due to its compatibility relative to the other polymers available (established during the previous program) and due to its excellent low temperature properties. Therefore, the filler was recognized as the most likely ingredient which could be changed to improve the composites' compatibility.

TABLE 1. FORMULATIONS AND PROPERTIES OF OF_2 CANDIDATE ELASTOMER COMPOUNDS

Component/Compound No.	60-1	60-3	60-4	60-5	60-6	60-7
CIS-4 Polybutadiene, Phillips Petroleum Company	100	100	100	100	100	100
Cab-O-Sil M-5, Cabot Corporation	40	10	40	40	40	40
HYSTL Hydroxy PB Resin, G-2000, HYSTL Development Company					50	
di-*t*-butyl peroxide, Wallace and Tiernan	2.5	2.0	1.5	3.5	5.0	
Di-Cup R, Hercules Powder Company						2.5
Total	142.5	112.0	141.5	143.5	195.0	142.5

		Tested at -78.5°C[b]				Tested at 22°C[b]				
Compound No.	Press Cure[a]	M_{300},psi	T_B,psi	E_B,%	Set,%	M_{300},psi	T_B,psi	E_B,%	Set,%	Shore A
60-1	10/300	5100	6800	500	5	1800	2700	500	5	80
60-1	10/320	4550	6150	500	5	--	2200	250	0	80
60-1	10/350	--	3850	200	0	--	1500	75	0	85
60-1[c]	20/300	4700	6600	570	10	2100	2800	500	0	80
60-1	20/320	4850	6850	510	5	--	2250	250	0	80
60-1	20/350	5350	7100	450	10	--	2300	240	0	85
60-3[c]	10/320	1500	3750	625	0	--	240	50	0	70
60-4	10/320	4500	6650	600	10	1800	2500	440	0	85
60-5	10/320	4750	6200	430	5	--	2000	160	0	85
60-6	10/350	2800	4250	500	0	--	1100	200	0	70
60-7[c]	10/320	4950	7150	600	10	1100	1400	440	10	75

a) Minutes at temperature shown in degrees Fahrenheit. The Fahrenheit scale has been used as a matter of rubber compounding custom. All samples were oven post cured for four hours at 225°F.

b) Crosshead speed 20 inches per minute. Modulus at 300% elongation and ultimate elongation data were taken from the Instron chart. Set value was measured at temperature shown. Temperature control was ±5°C.

c) These samples were selected for evaluation in Task II.

Interaction between SiO_2 and OF_2 is favored on a thermodynamic basis according to Equation (1):

$$SiO_2 + 2OF_2 \rightarrow \underset{\text{(b.p. = -65°C at 181mm)}}{SiF_4} + O_2 \qquad \Delta F° = -224\ \frac{\text{kcal}}{\text{mole}} \qquad (1)$$

Slight warming would vaporize the SiF_4 (b.p. = -65°C at 181mm) and expose fresh SiO_2 surface for further reaction with the propellant. Reaction between Al_2O_3 and OF_2 leads to the formation of thermally stable AlF_3, as shown in Equation (2), and would tend to passivate the surface of each filler particle exposed to the propellant.

$$Al_2O_3 + 3OF_2 \rightarrow \underset{\text{(subl. 1300°C)}}{2AlF_3} + 3O_2 \qquad \Delta F° = -381\frac{\text{kcal}}{\text{mole}} \qquad (2)$$

Although this point is considered thermodynamically and not kinetically, replacement of SiO_2 with Al_2O_3 proved to be advantageous, as described below.

Polybutadiene reinforced with Al_2O_3, such as ALON (Cabot Corporation fumed alumina), provides somewhat different properties than the SiO_2 reinforced counterpart. A brief compounding study was undertaken to optimize the mechanical properties of the Al_2O_3 reinforced composite. Three representative formulations are described in Table 2. Although room temperature properties are somewhat less than those of conventional performance rubber compounds, at low temperature (-78.5°C), all three candidates have outstanding mechanical properties which are considered to be satisfactory for a bladder material. Compound 202-1 was selected for further evaluations as it has the best properties at low temperature, and it has a high volume loading of Al_2O_3 (which is speculated to be passivated by OF_2 and to provide a thermal sink to quench potential degradation reactions).

2.1.2 Nitrile Compounds for B_2H_6 Service

During Contract NAS7-702, carboxylated acrylonitrile/butadiene copolymer was shown to be compatible with B_2H_6. Also during those tests, butadiene homopolymer was shown to be not compatible with B_2H_6. It was not clear whether the polymer was stabilized by the nitrile groups, by the carboxylic acid groups, or both. In the present work, commercially available nitriles (without carboxylic acid groups) covering the range of 20-45 mole-percent

Table 2. Candidate Polybutadiene Compounds For OF_2 Service

Component/Compound No.	212-1	212-2	202-1
CIS-4 Polybutadiene, Phillips Petroleum Co.	100	100	100
ALON Fumed Alumina, Cabot Corporation	40	40	60
Di-Cup R, Hercules Powder Company	2.5	2.5	--
Di-*t*-butyl Peroxide, Wallace and Tiernan	--	--	2.5
Total Parts	142.5	141.5	162.5
Press Cure, Min/°F a)	10/350°	20/350°	30/300°
Oven Post Cure, Hours/°F a)	2/225°	2/225°	2/225°
Property at Ambient Temperature b)	**212-1**	**212-2**	**202-1**
Modulus at 100% Elongation, psi	280	225	410
Tensile Strength, psi	375	450	1100
Elongation at Break, %	160	260	350
Shore A Hardness	73	70	86
Property at -78.5°C (-110°F) b)	**212-1**	**212-2**	**202-1**
Modulus at 100% Elongation, psi	590	870	1250
Tensile Strength, psi	3650	4925	6450
Elongation at Break, %	345	445	450

a) Fahrenheit temperatures are used as a matter of rubber compounding custom.

b) Stress/strains tested at indicated temperature, cross-head speed 20"/min using ASTM micro-tensile die specimens. Values are from the second highest of three specimens.

acrylonitrile were obtained for testing. This represents the range of nitriles presently available (described in Table 3), and represent brittle points from -18°C to ≺57°C. These brittle points were calculated according to the relationship described by Wiley and Brauer (Reference 2) of Tg = +1.2°C for every one mole-percent of acrylonitrile added.

Four of the five selected base polymers* were made into a formulation which was relatively similar except that the acrylonitrile volume fraction was assumed not to accept filler (loading varied with butadiene content) and not to vulcanize (curative varied with butadiene content). As shown in Table 4, tensile test data were obtained at temperatures selected to be above and below the calculated Tg of each base polymer. The data were inconclusive and indicated that all compounds were quite brittle at -30°C and below. (Possible causes for this are discussed in Appendix A.)

All four compounds were stored with B_2H_6 for 100 hours at -20°C to test compatibility. Although there is some data scatter due to the small number of specimens tested (Table 5), it was concluded that all four compounds were equally compatible with the propellant, insofar as a short, static test could determine. Chemigum N-9 , known to have the lowest acrylonitrile content, appeared to be compatible with the propellant, and certainly would have the lowest brittleness temperature of commercially available nitriles. Therefore, this base polymer was chosen for formulation optimization.

Table 6 shows representative formulations prepared to provide the best room temperature properties from Chemigum N-9. Formulations 202-3 and 203-1, among others, demonstrated that N-9 was not satisfactorily cured by dicumyl peroxide. Accelerated sulfur cures, such as used in Compound 202-2, provided much better mechanical properties. Short, static compatibility tests were used to show that this cure system would not affect compound/ propellant interaction. The loss of tensile strength observed (about 25%) was not considered conclusive in light of the low number of data points and experimental error inherent in tensile testing. In retrospect, however, it would appear as though an accelerated sulfur cure is less compatible with B_2H_6 than a peroxide cure. A modification of Compound 202-2 was made in

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*Chemigum N-206 was not received from Goodyear until after the test had been begun.

TABLE 3.
ACN/BD POLYMERS CHOSEN FOR B_2H_6 COMPATIBILITY TESTING

Designation	ACN Content (%wt)	Brittle Point (Wiley and Brauer)
Chemigum N-9	20.	-57°C
Chemigum N-608	32.	-43°C
Chemigum N-300	38.5	-32.5°C
Chemigum N-206	45.	-22°C
(Control) HYCAR 1072	25-30	(Measured) -18°C

TABLE 4.
FORMULATIONS AND PROPERTIES OF SELECTED CANDIDATE ACN/BD POLYMERS

Component	57-1	57-2	57-3	68-1
Chemigum N-9, Goodyear Chemical	100			
Chemigum N-608, Goodyear Chemical		100		
Chemigum N-300, Goodyear Chemical			100	
HYCAR 1072, B. F. Goodrich				100
Cab-O-Sil M-5, Cabot Corporation	32.	27.	25.	40
di-t-butyl peroxide	1.8	1.6	1.5	2.5
Cure time/temp, min./°F a)	20/350	20/350	20/350	20/350
Oven post cure, hrs/°F	18/225°	18/225°	18/225°	18/225°
M_{300}, psi at ambient b)	---	400	650	1150
Tensile, psi at ambient	950	2000	1675	2775
Elongation, % at ambient	150	700	500	550
Tensile Set, % at ambient	0	10	5	10
Shore A Hardness at ambient	84	68	75	83
	-60°C	-50°C	-40°C	Not Tested at Low Temp.
Tensile, psi c)	850	1000	2100	
Elongation, %	40	35	15	
Tensile Set, %	0	0	15	
	-50°C	-40°C	-30°C	Not Tested at Low Temp.
Tensile, psi c)	600	2800	2850	
Elongation, %	35	65	50	
Tensile Set, %	20	40	0	

a) Fahrenheit temperatures are used as a matter of rubber compounding custom.

b) Stress/strains tested at 72°F, cross-head speed 20"/min using ASTM micro-tensile die specimens.

c) Stress/strains tested above and below reported Tq (Wiley and Brauer). Values are from the second highest of three specimens.

TABLE 5.

MECHANICAL PROPERTIES OF NITRILE COMPOUNDS EXPOSED TO B_2H_6

Component	57-1	57-2	57-3	68-1*
Chemigum N-9, Goodyear Chemical	100			
Chemigum N-608, Goodyear Chemical		100		
Chemigum N-300, Goodyear Chemical			100	
HYCAR 1072, B. F. Goodrich				100
Cab-O-Sil M-5, Cabot Corporation	32.	27.	25.	40
di-<u>t</u>-butyl peroxide	1.8	1.6	1.5	2.5
Cure time/temp, min./°F a)	20/350	20/350	20/350	20/350
Oven post cure, hrs/°F	18/225°	18/225°	18/225°	18/225°
M_{300}, psi at ambient b) c)	---	400	650	1150
Tensile, psi at ambient	950	2000	1675	2775
Elongation, % at ambient	150	700	500	550
Tensile Set, % at ambient	0	10	5	10
Shore A Hardness at ambient	84	68	75	83
Properties following exposure to B_2H_6 at -20°C for 100 hours				
Tensile, psi at ambient c)	970	1850	1950	3560
Elongation, % at ambient c)	120	600	500	520

a) Fahrenheit temperatures are used as a matter of rubber compounding custom.

b) Stress/strains tested at 72°F, cross-head speed 20"/min using ASTM microtensile die specimens.

c) Values are from the second highest of three specimens.

*Control compound investigated during Contract NAS7-702.

TABLE 6.

TEST COMPOUNDS BASED ON LOW ACRYLONITRILE COPOLYMER FOR B_2H_6 SERVICE

Component/Compound No.	101-1	101-3	202-3	203-1	202-2
Chemigum N-9, Goodyear Chemical a)	100	100	100	100	100
Cab-O-Sil M-5, Cabot Corp.	20	30	50	50	50
Lupersol 101 Peroxide, Wallace & Tierman	1.5	2.5			
Di-Cup R, Hercules			5.0	2.0	
Zinc Oxide Reagent				5.0	5.0
Sulfur, Rubbermakers					1.8
Santocure, Monsanto					1.2
Total Parts -	121.5	132.5	155.0	157.0	158.0
Press Cure, Min./°F	30/325°	30/325°	30/325°	30/325°	30/325°
Oven Post Cure, Hours/°F	2/225°	2/225°	2/225°	2/225°	2/225°
Properties b)	101-1	101-3	202-3	203-1	202-2 c)
Tensile Strength, psi d)	675	825	1300	1550	4100
Elongation at Break, % d)	40	20	20	50	460
Shore A Hardness d)	86	92	97	95	88

a) Reported to be 20%w acrylonitrile/80%w butadiene.

b) Stress/strains tested at 22°C, cross-head speed 20"/min. using ASTM microtensile die specimens.

c) This compound has not been demonstrated to be compatible with B_2H_6.

d) Values are from the second highest of three specimens.

which the filler and curative levels were decreased to lower the compound's room temperature and low temperature hardness. These changes provided better flexibility, and the formulation prepared as a result of this work, Compound 215-3, was identified as a prime candidate for Task II evaluation

2.1.3 Mechanical Property Tests

Mechanical property tests were run parallel with the compounding studies described above, and the results were described in Tables 5 and 6. Test specimens for stress/strain and hardness measurements were placed in a Hoke S-10 stainless steel cell for storage with propellant. Molded slabs 0.020 and 0.050-inch thick were used interchangeably, but with appropriate property calculation corrections. Tensile tests were conducted using an Instron tensile test machine with a crosshead speed of 20 inches per minute.

Low temperature tensile tests were conducted in a Missimers environmental chamber attached to the Instron tensile test machine. Liquid nitrogen was used as the coolant and temperature control was about ± 5°C. Samples were conditioned for a minimum of five minutes at the reported temperature prior to testing. No attempt was made to correct the reported temperature (which was actually the atmospheric temperature in the box) for heating effects caused by stretching the rubber during test. The importance of this point will be discussed later in this report. Serially lowered test temperatures were employed for each candidate compound to determine its low temperature brittleness limits.

Although the polybutadiene (Compound 202-1) remained highly compliant at -120°C, it retained an extremely high permanent deformation (set) at this temperature. The nitrile was elastomeric at -45°C, but was brittle at -50°C under these test conditions.

2.1.4 Selection of Candidates for Task II

Table 7 shows the formulations of the two prime candidate compounds chosen for evaluation under Task II, their room temperature mechanical properties and their mechanical properties at the lowest temperature (±5°C) at which they are judged to be elastomeric.

TABLE 7.

PRIME CANDIDATE COMPOUNDS FOR OF_2 AND B_2H_6 EXPULSION BLADDERS

Component/Compound No.	202-1(OF_2)	215-3(B_2H_6)
CIS-4 Polybutadiene, Phillips Petroleum Co.	100	
Chemigum N-9, Goodyear Chemical		100
ALON Fumed Alumina, Cabot Corporation	60	
Cab-O-Sil M-5, Cabot Corporation		20
Di-*t*-butyl Peroxide, Wallace & Tiernan	2.5	
Sulfur, Rubbermakers		1.5
Santocure NS, Monsanto		1.0
Total Parts -	162.5	122.5
Press Cure, Min./°F	30/300°	15/325°
Air Oven Post Cure, Hours/°F	2/225°	2/225°

Property at Ambient Temperature [a]	202-1(OF_2)	215-3(B_2H_6)
Modulus at 100% Elongation, psi	410	200
Modulus at 300% Elongation, psi	825	450
Tensile at Break, psi	1100	1300
Elongation at Break, %	350	725
Tensile Set, %	10	5
Shore A Hardness	86	63

Property at Indicated Temperature [a]	202-1 At -100°C	215-3 At -45°C
Modulus at 100% Elongation, psi	1775	2650
Modulus at 300% Elongation, psi	3700	3000
Tensile at Break, psi	5825	3000
Elongation at Break, %	450	300
Tensile Set, %	170	20

a) Stress/strain tests at 20 inches per minute using ASTM microtensile die specimens. Values are from the second highest of three specimens.

2.2 TASK II - STATIC AND DYNAMIC COMPATIBILITY TESTS OF OPTIMIZED COMPOUNDS

Work under the previous contract and the initial work under the present contract utilized storage tests in which elastomer specimens were placed in the propellant and held for several days. Weight change analysis of the specimens and mechanical property retention were the measure of compatibility. Although this test procedure is adequate for screening purposes, an expulsion bladder is a dynamic device, and ultimately must be tested in a mode resembling its end-use requirements. This section describes the series of tests conducted to demonstrate the usefulness of the candidate elastomers for OF_2 and B_2H_6 expulsion bladders. Tests varied from short, static conditions to actual "propellant expulsions".

2.2.1 Static Compatibility Tests

Results of static compatibility tests were described in Section 2.1 of this report. The apparatus used for these tests was built under the previous Contract (NAS7-702), and was described in the Final Report (Reference 2). Storage temperatures were -78.5°C for OF_2 (dry ice) and -20°C for B_2H_6 (freezer appliance).

As a result of 100-hour storage periods, no information was obtained to show that either propellant reacted significantly with any compound prepared during this program. There was a higher level of compatibility with both propellants than was anticipated originally. Thus, a more severe static test procedure was employed to explore further the elastomer/propellant compatibility by contacting the specimens with propellant at higher temperature.

A sample of alumina-reinforced polybutadiene (Compound 202-1) measuring 1.2 x 0.25 x 0.050-inch was covered by about 1.5cc of OF_2 at -196°C in a stainless steel cylinder. The liquid nitrogen coolant then was allowed to evaporate slowly. The propellant slowly warmed to 0°C (vapor pressure was higher than the 2500 psi limit of the transducer being used), and contacted the elastomer for nearly a half-hour at this temperature, with no reaction observed. After venting the OF_2, the elastomer was retrieved apparently unaffected. A fire was anticipated at a temperature above 0°C (see Appendix C), thus the test was stopped at this temperature in order to recover the specimen for evaluation rather than to risk its destruction.

A similar test was conducted using the nitrile (Compound 215-3) with B_2H_6. It was observed that no reaction took place between the elastomer (static) and the propellant after one-half hour at room temperature (22°C). This specimen also appeared unaffected by the exposure.

2.2.2 Dynamic Compatibility Tests

A small test cell (Figure 1) was built to strain elastomer specimens to failure while immersed in propellant. Some of the results of this test have been presented in previous sections of this report (Section 2.1.1). Silica filler for polybutadiene was eliminated from contention as a result of this test, and was replaced by the more stable alumina filler.

Alumina-reinforced polybutadiene (Compound 202-1) was cut to form a 67.3 milligram strip which was placed in the apparatus. While immersed in OF_2 at -78.5°C, the specimen was strained to breaking. A fire was initiated when the rubber broke, the stainless steel apparatus ruptured and was oxidized severely. The broken rubber was recovered, weighed and reassembled. Weight of the recovered specimen was 58.2 milligrams (13.5%w loss) and although the surface was slightly charred, the bulk remained elastomeric. One sliver of the specimen was not found, and it is believed that this might account for the weight loss (a further narrative of this test is reported in Appendix B).

Analytical examination of the specimen provided no helpful information. There was no evidence of surface fluorination, as shown by comparing Attenuated Total Reflectance infrared spectra of unexposed material with the test sample. No discreet absorption bands were found for either sample at 8.4, 8.9, 10.4 and 11.0μ. This indicates that the specimen was not fluorinated to a high degree, or that fluorinated species were pyrolyzed by the heat of the reaction. Temperatures of >200°C probably were encountered in this instance, as this is the temperature at which fluorine reacts with stainless steel. Scanning electron photomicrographs of the specimens are shown in Figure 2.

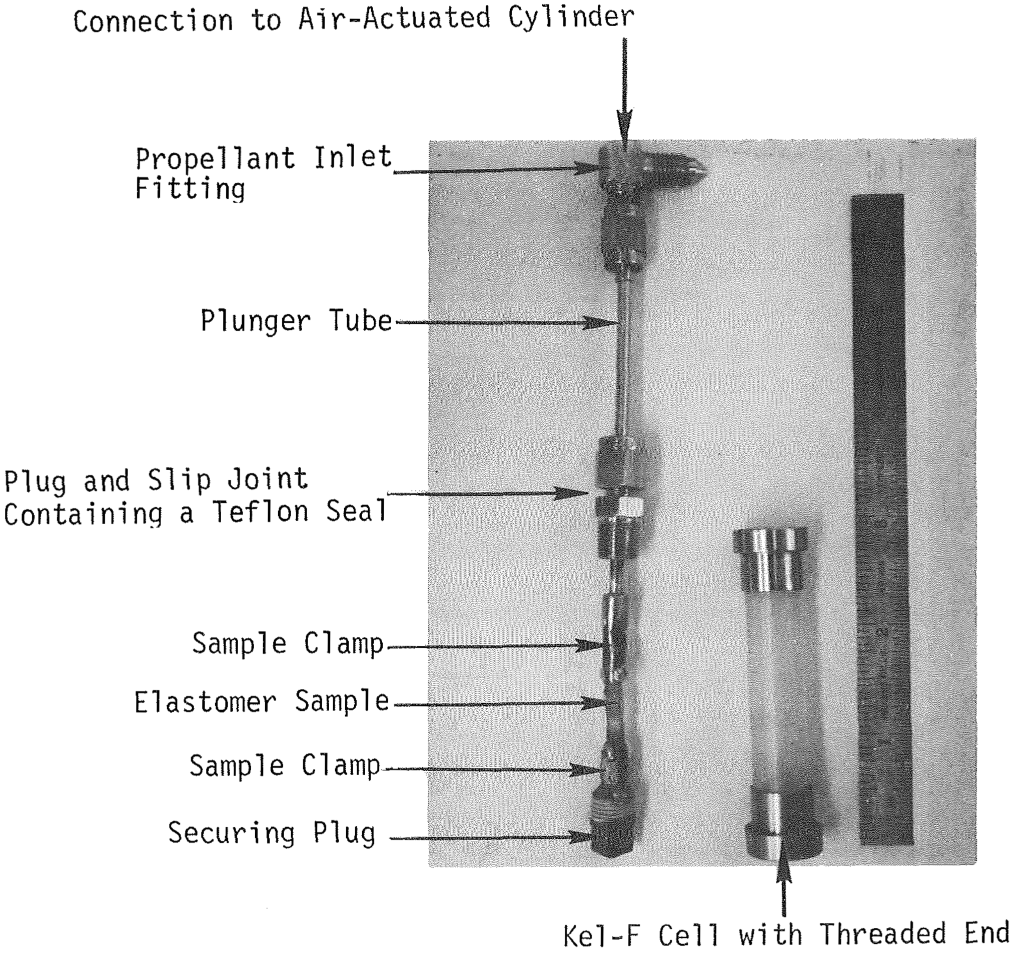
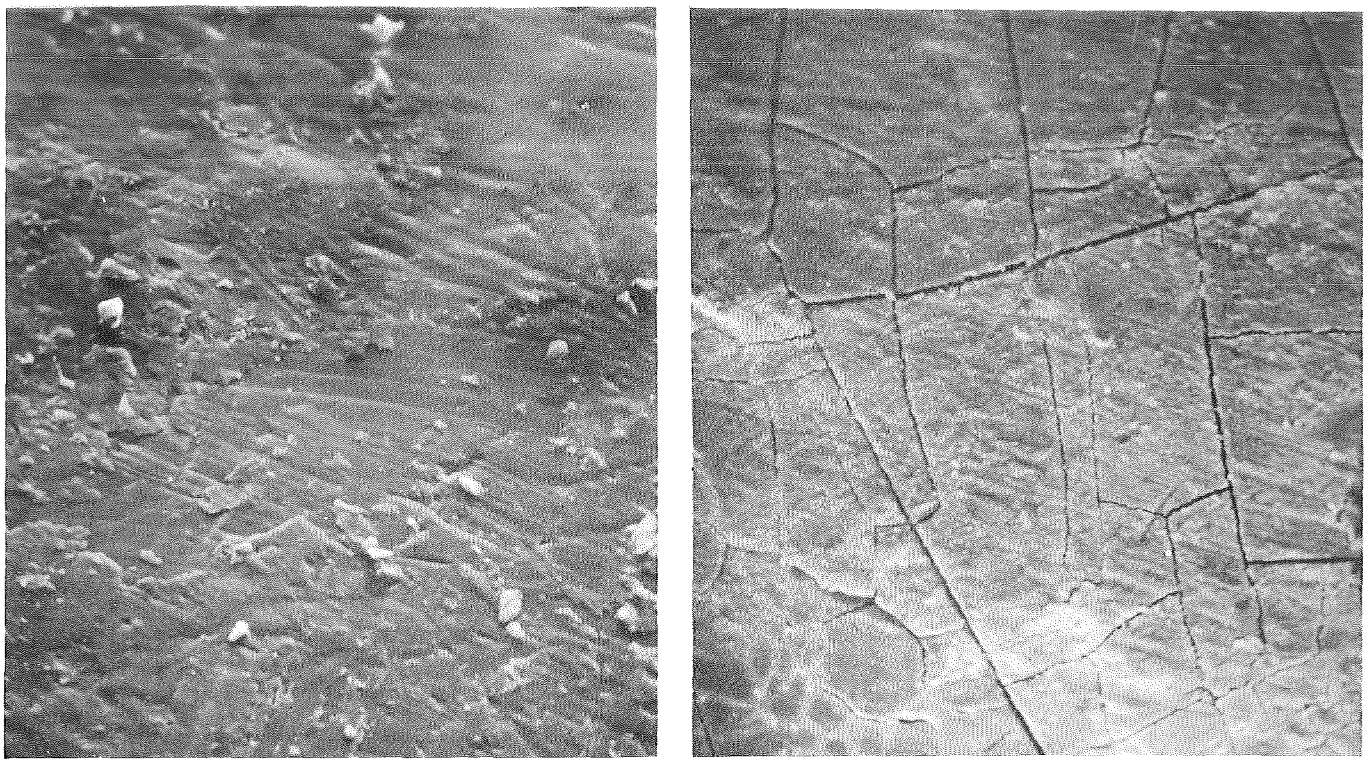
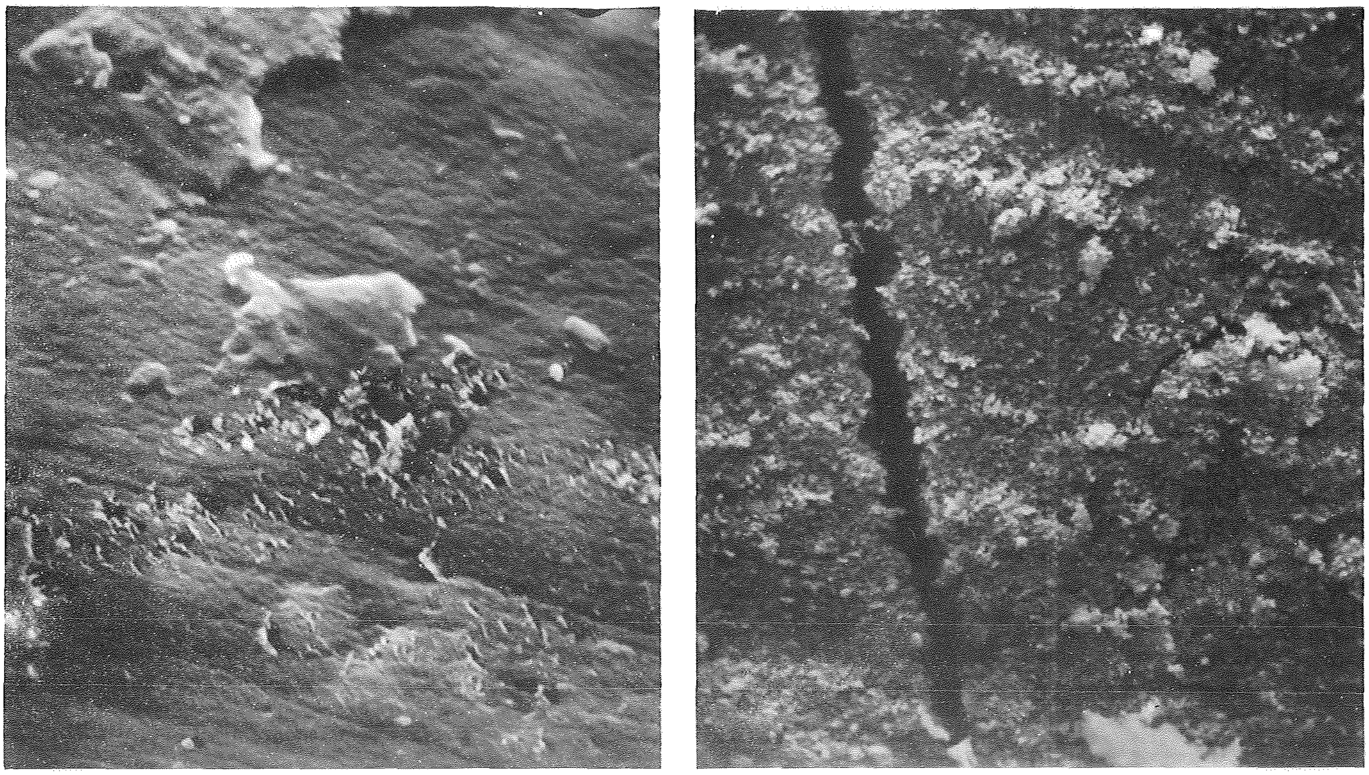


Figure 1. Test Apparatus Built to Break Elastomer Samples While They Are Immersed in Propellant



Compound 202-1 Control. 100X Magnification Compound 202-1 Exposed. 100X Magnification



Compound 202-1 Control. 1000X Magnification Compound 202-1 Exposed. 1000X Magnification

Figure 2. Surfaces Of Rubber Specimens Prior To And After Being Strained To Breaking In OF_2 at -78.5°C.

Strain to failure of the nitrile (Compound 215-3) was performed while the specimen was immersed in B_2H_6 at room temperature (about 22°C). There was no indication of chemical reaction, and the sample was recovered quantitatively. Attenuated Total Reflectance infrared analysis of the specimen showed no evidence of boron-carbon or boron-hydrogen functional groups on the surface of the specimen. This conclusion is reached by the absence of absorption bands at 3.85 and 4.0μ (Reference 4). Scanning Electron photomicrographs of the specimens are shown in Figure 3.

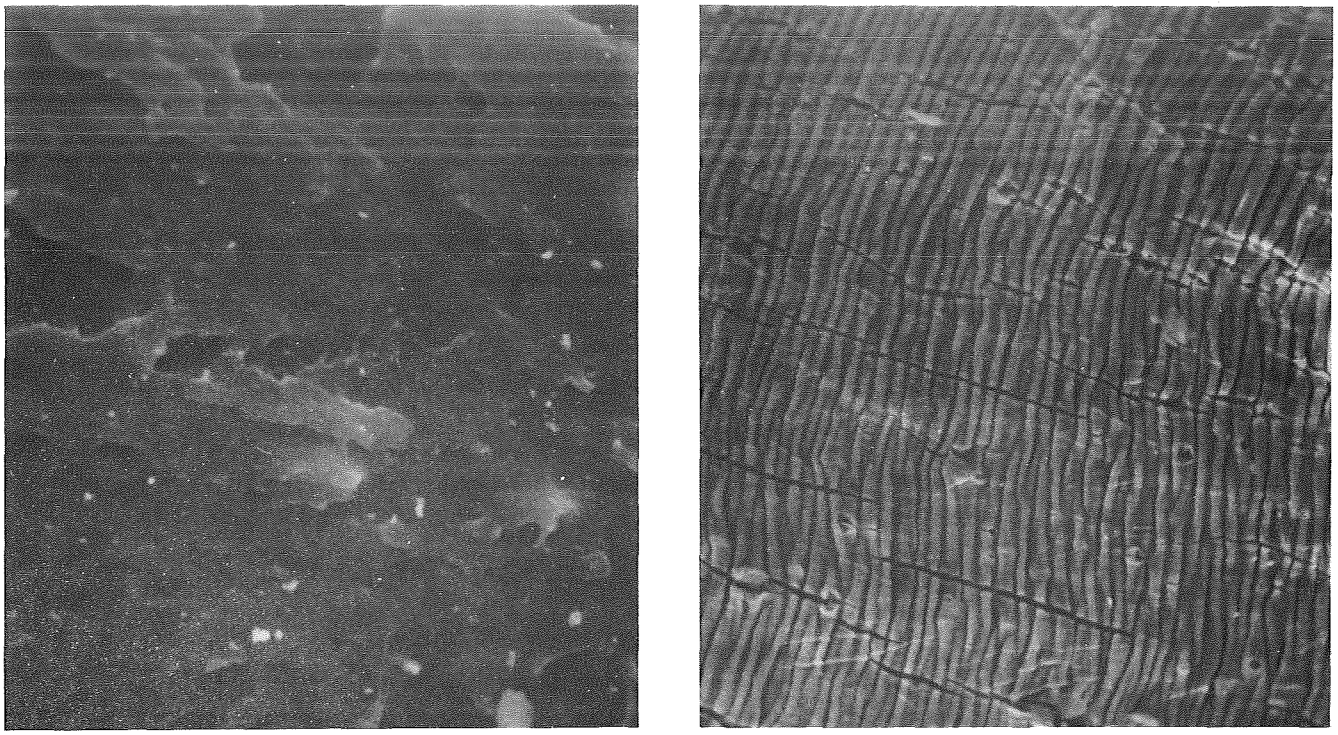
2.2.3 Diaphragm Expulsion Tests

Laboratory tests are satisfactory for screening purposes, but authentic, in-use tests are far more useful in the assessment of the feasibility of using the candidate materials as expulsion bladders. Such an in-use test was devised to evaluate flat sheets of elastomer as expulsion diaphragms.

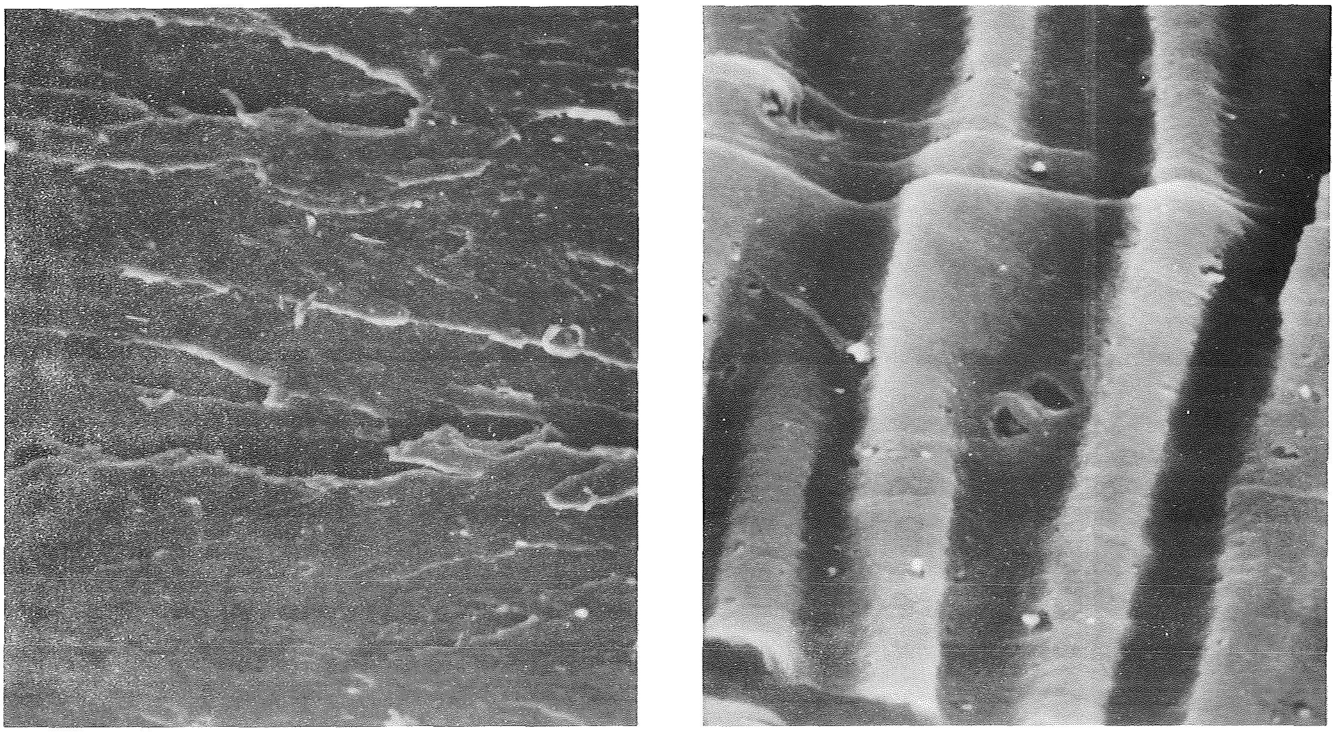
A test apparatus was built as shown in Figure 4 to serve as a small-size expulsion device. Compound 202-1, molded 0.050-inch thick, was used as the expulsion membrane for OF_2 to be actuated by nitrogen. The apparatus was cooled to -78.5°C (vapor pressure of OF_2 at this temperature is about 450 psia), and was connected both to an OF_2 supply source and to a nitrogen tank, as indicated in the diagram. At low nitrogen pressure, the check valve tandem would accumulate about five ml of liquid OF_2 on one side of the elastomer membrane. Raising the nitrogen pressure would flex the elastomer and expel the accumulated propellant to the receiving tank. After forty such cycles, the receiving tank had reached a pressure of over 100 psig. At this point, the experiment was stopped and the OF_2 vented from the receiving tank.

The specimen was retrieved apparently unaffected. It had taken a "set" as shown in the photograph of Figure 5, but was as elastomeric (judged by hand testing) as the pretest material.

A similar test was conducted with Compound 215-3 used to expel B_2H_6. In this experiment the equipment was immersed in a stirred slush bath of dry ice/chlorobenzene (m.p. = -45°C), providing a propellant



Compound 202-2 Control. 100X Magnification Compound 202-2 Exposed. 100X Magnification



Compound 202-2 Control. 1000X Magnification Compound 202-2 Exposed. 1000X Magnification

Figure 3. Surfaces Of Rubber Specimens Prior To And After Being Strained To Breaking In B_2H_6 At Ambient Temperature.

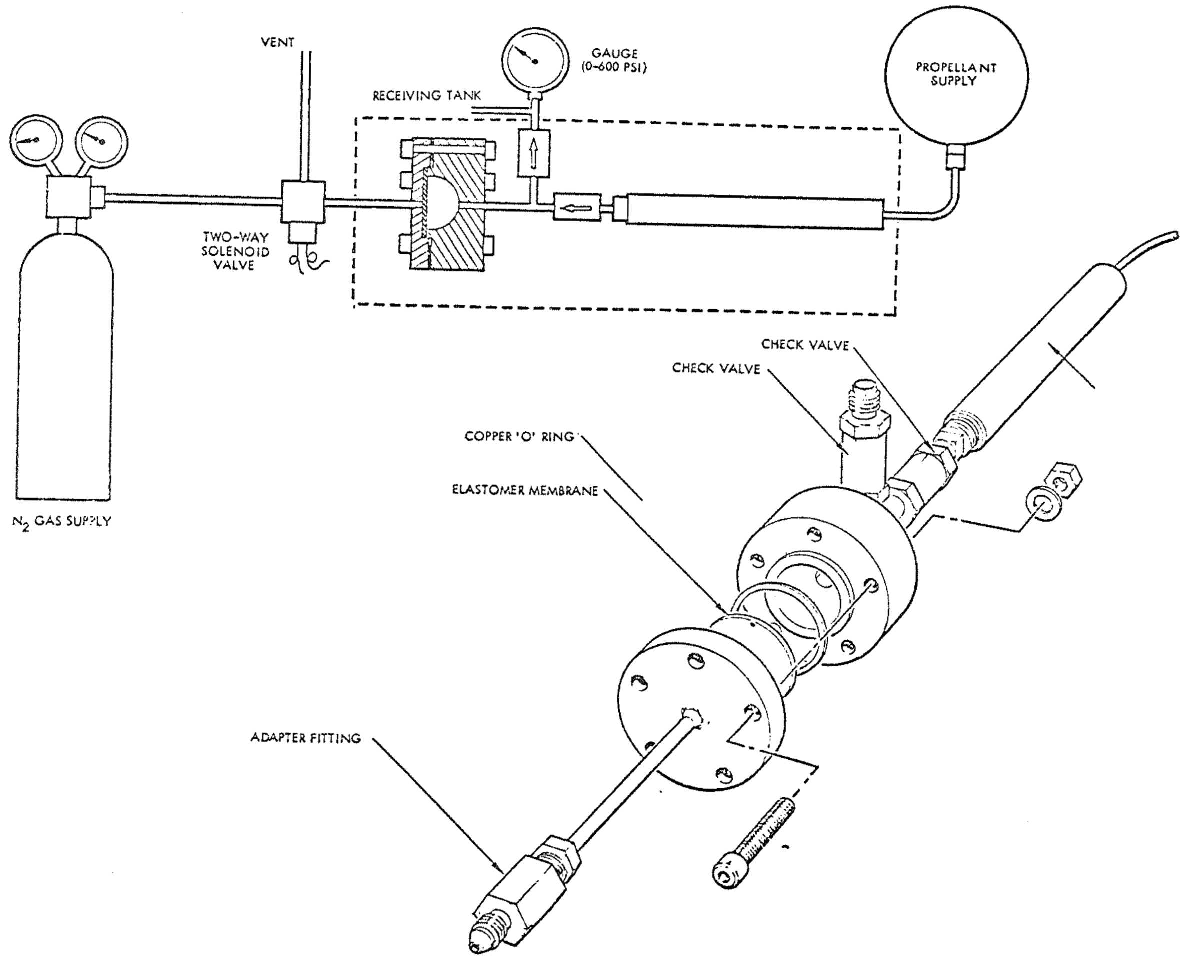


Figure 4. Diagram of Small-Size Expulsion Test Apparatus And Isometric View of Specimen Holder

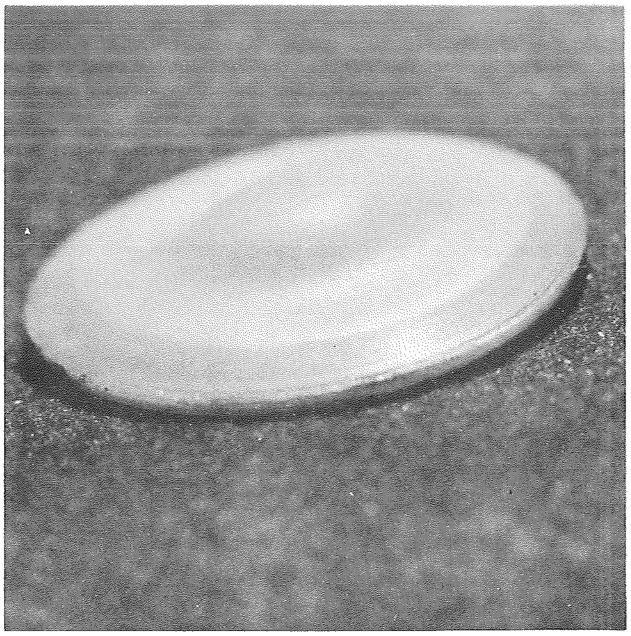


Figure 5. Specimen of Compound 202-1 Used To Expulse OF_2 Forty Times At -78.5°C. Original Specimen Was Flat.

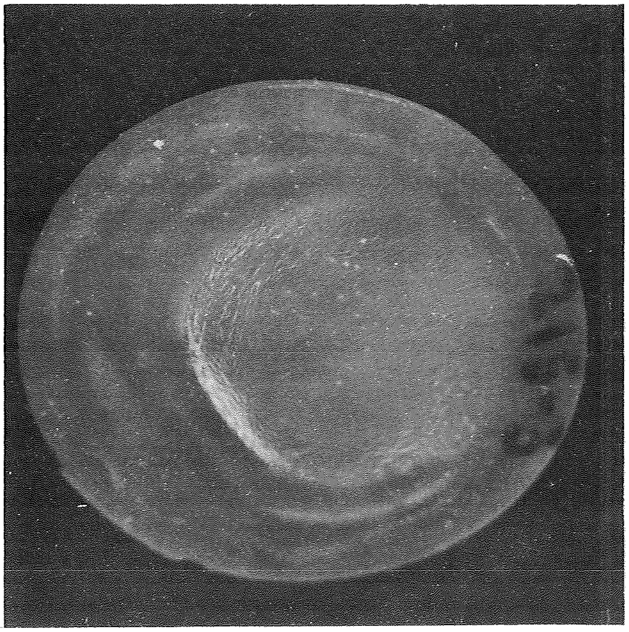


Figure 6. Specimen of Compound 215-3 Used To Expulse B_2H_6 Twenty Times At -45°C. Original Specimen Was Flat.

vapor pressure of about 250 psi. After 20 expulsions of B_2H_6 which generated a pressure of about 100psi in the receiving tank, the membrane appeared to be leaking pressure, and the experiment was stopped. Upon removal, the membrane was found to be cracked as shown in the photograph of Figure 6.

Investigation of the possible mechanism of cracking leads to the conclusion that the specimen was being flexed in a near-brittle state. Concentric stress cracks were found near the center of the sample, and these appeared to be initiated from the nitrogen gas pressurant side as opposed to the B_2H_6 side. The specimen was not stiffened, and it did not show evidence of chemical attack. It is believed strongly that the cracking was due to mechanical damage caused by straining the low temperature-stiffened membrane beyond its elastic limit.

Although the tensile test data reported in Table 7 show the nitrile compound is elastomeric at -45°C, it must be realized that the specimen may have warmed somewhat during the test. Also, control of the tensile test chamber was about $\pm 5°C$. During the expulsion tests, liquid B_2H_6 contacted the membrane and would provide more efficient cooling than the nitrogen atmosphere of the tensile test apparatus. It is concluded that the expulsion tests were performed with the elastomer somewhat cooler than in the tensile tests, and this small change was enough to stiffen the membrane significantly.

The successful expulsions of OF_2 and B_2H_6 by elastomeric membranes are considered to be most significant result of this program, but exposure time to the propellants was short during these tests. Therefore, long-term compatibility and permeability measurements were made to further characterize the materials usefulness for projected OF_2 and B_2H_6 service.

2.3 TASK III - LONG-TERM COMPATIBILITY AND PERMEABILITY BY OF_2 AND B_2H_6

There are two procedures which can be used to test long-term compatibility between materials and propellants. The more obvious is to store the materials in the propellant for periods of time approximating the in-use requirement. A more economical alternative is to store the materials for shorter periods of time at higher storage temperatures. However, there is a trade-off between excessively long tests and the introduction of new chemical reactions at higher temperatures which would not take place at in-use storage temperatures. This section describes tests conducted for the longest period of time available within the contract period at temperatures 42°C above the potential lower use limit of Compound 202-1 and about 25°C above the potential lower use limit of Compound 215-3.

2.3.1 Long-Term Compatibility of Compound 202-1 with OF_2

Compound 202-1 was stored in OF_2 at -78.5°C for 42 days. Three specimens were stored relaxed and three were stored bent double; three specimens were stored bent double without propellant to serve as controls. Table 8 presents the data obtained from these specimens for change in weight and retention of mechanical properties.

It is concluded from the data that properly cured (see Appendix D) alumina-reinforced, peroxide-cured cis 1,4-polybutadiene is highly compatible with liquid OF_2 at -78.5°C. Impact sensitivity has not been determined (aside from the dynamic test described in Section 2.2.2), but this important consideration was outside of the scope of this program.

Mechanical property changes were considered to be minor for the relaxed specimens as was the weight increase. The bent specimens appeared to be affected slightly by the propellant.

In the conclusions (Section 3) based upon the work during this project, a calculated estimate was made regarding the anticipated lifetime of Compound 202-1 in a strained configuration with OF_2 at -120°C. While this calculated lifetime estimate is shorter than present mission goals, it is several-fold greater than was anticipated prior to this program.

2.3.2 Long-Term Compatibility of Compound 215-3 With B_2H_6

Compound 215-3 was stored with B_2H_6 at -20°C for 48 days. Three specimens were stored relaxed and three were stored bent double; three

TABLE 8. COMPATIBILITY OF COMPOUND 202-1 WITH OF_2 a)

Conditions	Specimen Thickness, Inch	M_{100}, psi b)	T_B, psi b)	E_B, % b)	Set, % b)	Shore A	Weight Change, %
Bent Double, -78.5°C, in air (Control)	0.050	155	2075	700	17	62	+0.27 c)
Bent Double, -78.5°C, In OF_2	0.050	155	1750	600	15	62	+0.77
Relaxed, -78.5°C, In OF_2	0.050	155	2050	650	14	67	+0.44

a) Stored in propellant at -78.5°C for 42 days, except as noted. Tensile tests were conducted at room temperature using ASTM microtensile die specimens pulled at 20"/min. crosshead speed. Values reported are the second highest of three specimens.

b) Values are from the second highest of three specimens.

c) There is no obvious explanation for the weight gain.

were stored bent double without propellant to serve as controls. Table 9 presents the data obtained from these specimens for change in weight and retention of mechanical properties.

It is concluded from the data that silica-reinforced, sulfur-cured low acrylonitrile content butadiene copolymer is relatively compatible with B_2H_6 at -20°C. However, the propellant does react slowly with the base polymer. This is reflected by loss of tensile strength and breaking elongation, and by surface embrittlement. Reaction between propellant and polymer apparently is a surface phenomenon as a 0.050-inch thick specimen is less affected than a 0.020-inch thick specimen both stored relaxed in B_2H_6 at -20°C. Based upon the short-term compatibility test results using peroxide-cured nitriles (Table 5) and sulfur-cured nitrile (Table 9), it appears as though the sulfur cure system may be the primary cause for the observed degree of propellant incompatibility.

2.3.3 Permeability of Compound 202-1 by OF_2

Specimens of Compound 202-1 were clamped into the permeability test cell (Figure 7) and permeated by OF_2 at two temperatures. Pressure rise in the downstream compartment was plotted as a function of time. Permeability coefficients, P, were calculated over the linear portion of the curve, independent of the induction periods which typically were 3-4 days. Table 10 presents the pertinent data used in calculating the P values in the units of:

$$P = \frac{(\text{ccSTP gas})(\text{cm thick specimen})}{(\text{cm}^2\text{ specimen})(\text{seconds})(\text{cmHg pressure drop})}$$

From these P values, long-term leak rates may be calculated for a bladder of given configurations and operating conditions. For example, a 10-inch diameter bladder 0.050-inch thick made from Compound 202-1 and containing OF_2 at -78.5°C would leak about 0.35%w of the contained propellant per year.* At -95°C, the leakage would be unmeasurably low, but using the upper limit of permeability detection as the criteria, it may be calculated that a bladder as described above would leak less than 0.10%w of the contained propellant per year.

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*Assumptions: Density of OF_2 at -78.5°C = 1.25 g/ml
ΔP across bladder = 450 psia
OF_2 assumed to be a perfect gas
Leakage is linear with time

TABLE 9. COMPATIBILITY OF COMPOUND 215-3 WITH B_2H_6 a)

Conditions	Specimen Thickness Inches	M_{100}, psi	T_B psi	E_B %	Set, %	Shore A	Weight Change %
Original Properties	0.050	200	1300	725	5	63	--
Bent Double, -20°C, in air (Control)	0.020	170	1225	550	12	59	+1.8 c)
Relaxed, -20°C, In B_2H_6	0.020	140	340	150	0	b)	+2.2
Bent Double, -20°C, In B_2H_6	0.020	165	410	290	0	b)	d)
Relaxed, -20°C, In B_2H_6 e)	0.050	115	550	440	5	b)	+0.4

a) Stored in propellant at -20°C for 48 days, except as noted. Tensile tests were conducted at room temperature using ASTM micro tensile die specimens pulled at 20"/min. crosshead speed. Values reported are the second highest of three specimens.

b) The surface is brittle, but the bulk is elastomeric.

c) There is no obvious explanation for the weight gain.

d) When removed from the test cell the surfaces flaked and sufficient elastomer material was lost to render the weighings invalid.

e) Stored in propellant at -20°C for 64 days.

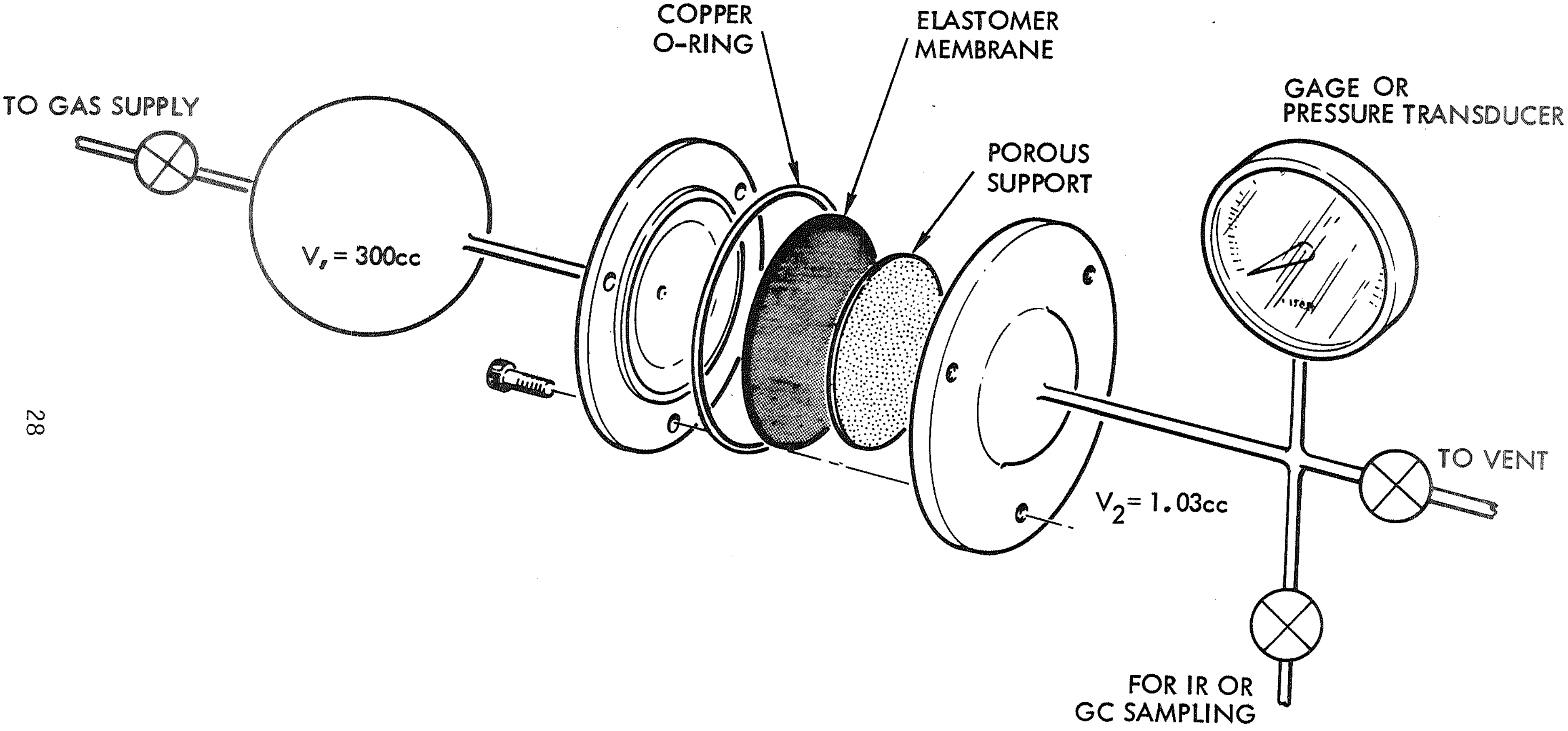

Figure 7. Diagram of Propellant Permeability Apparatus

TABLE 10.

PERMEABILITY COEFFICIENTS FOR THE PRIME CANDIDATE ELASTOMER COMPOUNDS AS A FUNCTION OF TEST TEMPERATURE

Compound No.[a)]	Test Temperature	ΔP, psia	Test Period, days [b)]	P X 10^{10} [c)]
202-1 (OF_2)	-95°C	235	25	Nil
201-1 (OF_2)	-78.5°C	415	18	0.00011
215-3 (B_2H_6) [d)]	- 6°C	350	19	2.3
215-3 (B_2H_6)	-20°C	235	16	1.36
215-3 (B_2H_6)	-45°C	110	19	0.17

a) Specimens were nominally 0.050-inch thick and 1-inch diameter.

b) Only linear data were used in the calculation of the permeability coefficient. Typical induction periods were 3-4 days.

c) Units are: $\dfrac{\text{(cc STP) (cm thick)}}{\text{(cm}^2\text{ area) (sec) (cm Hg pressure)}}$

d) The B_2H_6 analyzed 99% pure with 1% hydrogen.

2.3.4 Permeability of Compound 215-3 by B_2H_6

Compound 215-3 was permeated by B_2H_6 in the same cell as was used for OF_2 (Figure 7). Permeability coefficient values calculated for three temperatures are shown in Table 10. They are higher than the values for Compound 202-1, but it must be noted that the test temperatures are significantly higher and extrapolation of the P values to temperatures in the range of -90°C are more consistent with the 202-1 values.

Calculation of leakage rates for a 10-inch diameter bladder prepared from Compound 215-3 at -45°C shows that about 10.4% of the contained propellant would permeate per year.

2.3.5 Final Selection of Candidate Compounds

As a result of the work reported herein, Compound 202-1 (see Table 7) appears to be attractive for further evaluation as a possible expulsion bladder material for OF_2. At low temperatures, it is highly compatible with the propellant, it can be safely flexed in the propellant, and it is highly processable and could be fabricated readily into a bladder.

While not as fully developed as the OF_2 candidate, Compound 215-3 (see Table 7) shows high feasibility for service in B_2H_6. Certain modifications in the material will be suggested in Section 2.4, but the goals for these changes are defined clearly. While not recommended for long mission B_2H_6 bladders in its present form, simple modifications are feasible to bring it to the state of usefulness represented by the OF_2 candidate material. From this program, however, Compound 215-3 is the best overall elastomeric material available for B_2H_6 service. The following section suggests modifications and further study indicated by the present findings.

2.4 RECOMMENDATIONS FOR FUTURE WORK

The polybutadiene compound for OF_2 service is at an advanced stage of development. However, it must be demonstrated that a bladder can be molded from the material. Also, the impact sensitivity of the material must be examined further to determine the role played purely by impact in the tests described in Section 2.2.2. During those tests it appeared as though the elastomer was significantly more charred in the vapor contact area as opposed to the liquid contact area. It needs to be determined if Compound 202-1 will ignite a fire, even under impact, in an OF_2 liquid environment. Calculations of initiation kinetics indicate that the elastomer may not initiate a fire under these conditions.

For B_2H_6 service, it must be determined if a peroxide-cured nitrile would be more compatible with the propellant than the sulfur-cured Compound 215-3. Data discussed in this report indicate that this may be the case. Of equal importance is the investigation of alternative base polymers to provide better low temperature properties. At lower temperatures the permeability would certainly decrease to a more desirable level. Further work should be directed toward developing better mechanical properties either from peroxide-cured Chemigum N-9 or from an alternative polymer.

3. CONCLUSIONS

It is concluded that a reasonable demonstration was performed for candidate OF_2 expulsion bladder material with TRW Compound 202-1. Additional evaluations are necessary to establish its capabilities and limitations.

It is concluded that TRW Compound 215-3 was demonstrated to be a favorable candidate material for B_2H_6 expulsion bladders. However, some of the limitations of this material are known and must be overcome to a assure reliable performance during long missions.

Projections of useful lifetimes have been made based upon the long-term tests conducted during this program. The following assumptions have been made:

- Permeability is linear with time
- Degradation is linear with time
- Rate of degradation doubles for every 10°C temperature rise
- Tensile strength is the most important mechanical property for a folding-type bladder.

Table 11 shows the projected rates of bladder function degradation.

TABLE 11.

PROJECTED RATES OF BLADDER FUNCTION DEGRADATION

Compound	Propellant	Temperature	Permeability	Mechanical Properties
202-1	OF_2(225)*	-95° C	<0.10% loss of propellant/year	0.3% loss of strength/year
215-3	B_2H_6(135)*	-40° C	10.4% loss of propellant/year	23% loss of strength/year

*Values in parentheses are the vapor pressures of the propellants in psia at the indicated use temperatures.

4. NEW TECHNOLOGY

During this program it was determined that fumed alumina (Al_2O_3) is an attractive reinforcing agent for cis 1,4-polybutadiene both from a mechanical property standpoint and from an OF_2 compatibility standpoint. The improvement in compatibility with OF_2 was predicted by thermodynamics in that a more stable reaction product is formed by OF_2 reacting with Al_2O_3 than by OF_2 reacting with SiO_2. This reaction is believed to passivate the Al_2O_3 surface. Other factors undoubtedly contribute to the observed improvement in compatibility, but it appears as though the thermodynamic approach to the selection of rubber compounding ingredients for service in highly corrosive environments is a useful one.

5. REFERENCES

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APPENDIX A

FACTORS INFLUENCING THE MECHANICAL PROPERTIES OF VULCANIZED NITRILE COMPOUNDS

During the formulation optimization studies with Chemigum N-9, it was determined that peroxide cures did not develop sufficiently good mechanical properties from this type of low acrylonitrile content base polymer. A brief survey of the literature was made in order to discover a solution to the problem.

Williams (Reference A-1) reports that a nitrile copolymer with stereospecific 1,4-polybutadiene theoretically is stronger than natural rubber, but that 1,2-structure is the single most harmful structural feature. Based upon the >4000 psi tensile strength developed from the Chemigum N-9 using an accelerated sulfur curative, it must be concluded that a high percentage of the butadiene units are of 1,4-structure. On the other hand, Sebrell and Dinsmore (Reference A-2) showed that 1,2-structure increases with lower acrylonitrile contents. Thus, Chemigum N-9 (low acrylonitrile) would be expected to have the lowest tensile strength of a series of nitriles, all other factors the same.

Hofmann (Reference A-3), in noting that the energy to dehydrogenate rubber varies with types, indicates that nitriles are intermediate in vulcanization efficiency between e.g. ethylene/propylene terpolymer (excellent) and butyl rubber (degraded). Hofmann points out the advantage in nitrile rubber of using zinc oxide in conjunction with the peroxide. This procedure was used unsuccessfully as demonstrated by Compound 203-1, reported in Table 6 of the text.

Cab-O-Sil M-5 reinforcing silica used in the compounding study has a pH of about 4 (water slurry) and acidic materials are known to decrease the efficiency of peroxides by favoring heterolytic oxygen cleavage. Compounds containing silica may be more effectively cross-linked by special peroxides such as tetrachloro-di-*t*-butyl peroxide, but this approach was not investigated during this program.

Antioxidants also can influence the peroxide cure of nitrile rubbers by inhibiting free radical formation. In the case of Chemigum N-9, the antioxidant content was not known and therefore no adjustment in peroxide level was made due to antioxidant.

Improved peroxide vulcanizates often can be obtained by using an auxiliary crosslinking agent such as triallyl cyanurate (Reference A-4) or m-phenylene-bis-maleimide (Reference A-5). These procedures were not investigated during this program.

Effect of varying levels of peroxide on mechanical properties as described by Hofmann (Reference A-6), indicates that the compounding study reported herein utilized too much peroxide. The nitrile groups have a high activation effect on the diene portion of the polymer, and thus require less peroxide to reach a satisfactory state of cure than, say, ethylene/propylene polymers. However, the addition of very small amounts of sulfur and accelerator in conjunction with peroxide markedly increases the elongation at break, and tends to increase the tensile strength compared with the pure peroxide cure employed. Low elongations at break were the obviously poor characteristic of the peroxide-cure nitriles described in Table 6 of the text. It is concluded that additional compounding work could provide a peroxide-cured compound based on Chemigum N-9 with mechanical properties satisfactory for bladder requirements.

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APPENDIX B.

RESULTS OF TENSILE TESTING A POLYBUTADIENE COMPOUND IMMERSED IN OF_2

Samples of rubber (Compound 60-3, prepared from cis 1,4 polybutadiene, silica and peroxide) were elongated to rupture in liquid/gaseous OF_2 at a vapor pressure of 400 to 500 psig (-78.5°C). The sample ignited and destroyed the test apparatus in both instances.

The apparatus used for this experiment is shown in Figure B-1. It is essentially a "U" tube attached to a vacuum system by a 1/8" AN fitting. One leg of the "U" tube served as a receiver for the liquid OF_2 and was chilled with LN_2. The other leg of the "U" tube was a sample cell chilled with dry ice. It contained a sample holder for the test rubber. One end of the sample holder was attached to the bottom of the sample cell, which in turn was bolted to the floor. The other end was attached to a 1/8" rod operated by a power actuator. This rod was drawn through a Teflon-sealed Swagelok fitting.

In operation, the liquid OF_2 was condensed in the left arm of the tube with LN_2 coolant. The right arm of the tube was pre-chilled with dry ice. In this way the rubber did not experience temperatures below -78.5°C. Approximately 1.5 to 2.0 cc of liquid OF_2 was distilled into the LN_2 cooled arm at pressures up to one atmosphere. When the measured amount was transferred as evidenced visually and by reduction of the vapor pressure below 0.1 psig, the tube leading to the transfer line was sealed with two valves. The LN_2 bath was removed to allow liquid OF_2 to warm and distill into the dry ice cooled sample cell. When the pressure increased to the normal vapor pressure of oxygen difluoride at -78.5° (equilibrium pressure is about 450 psia) two samples were elongated to breaking. Both experiments resulted in fires and extensive damage to the apparatus.

Rubber held in the jaws of the holder showed extensive charring. No other rubber material was found. Much of the metal apparatus and tubing leading to the ruptured equipment was burned and corroded.

A previous attempt to observe this rupture in a Kel-F test cell also resulted in an explosion. Since the apparatus was not of "U" tube design the cell was being chilled with LN_2 to transfer the oxygen difluoride. It was anticipated that the cell would be warmed with dry ice prior to breaking the rubber sample; however, an explosion occurred when only a small amount of the OF_2 had transferred. Since shattered, unburned rubber was recovered, it is believed that the Kel-F cracked and ignited without igniting the test sample. No charred samples of Kel-F were found.

As a result of this test, a reformulation study was conducted resulting in preparation of a similar compound (202-1) in which the silica was replaced by alumina. This compound was recovered almost quantitatively from a subsequent elongation to break test in OF_2.

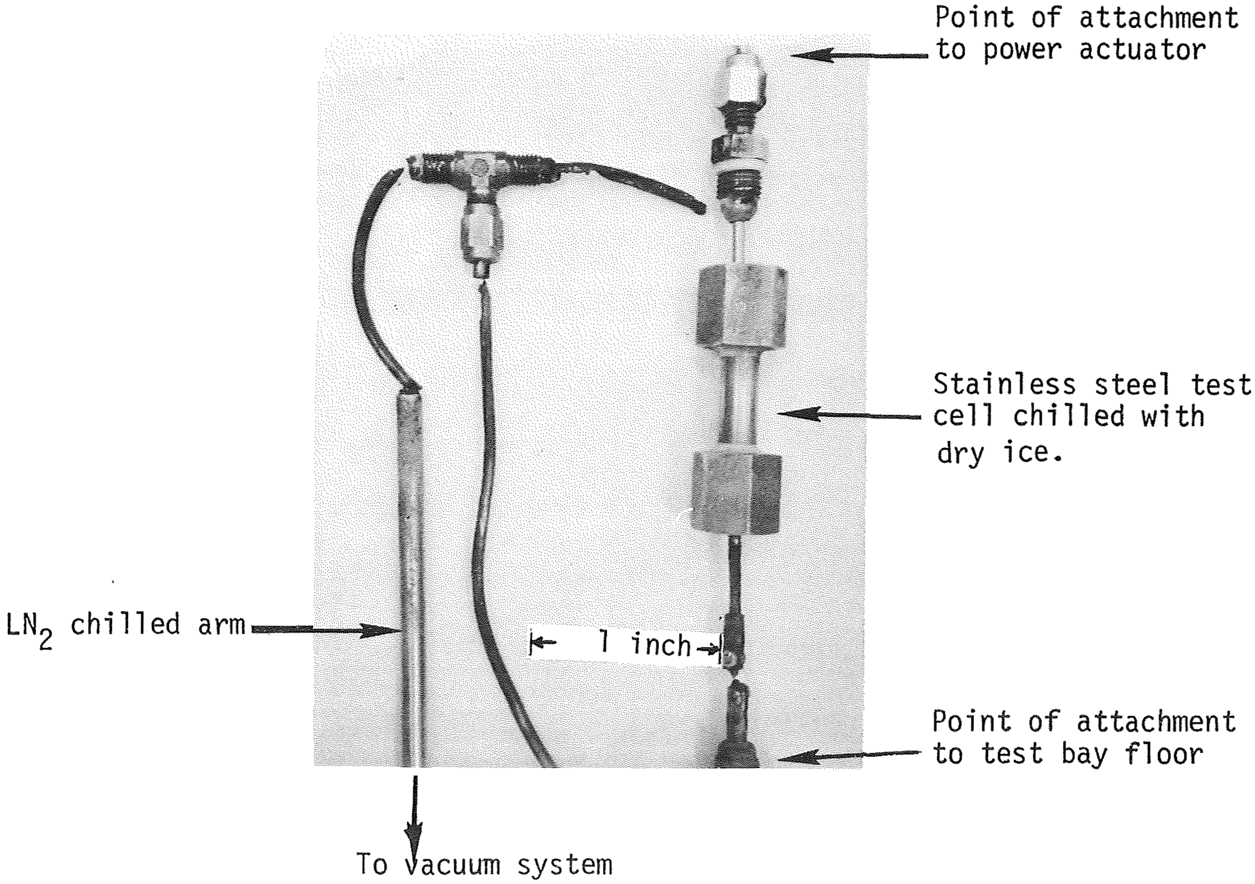

Figure B-1. Apparatus Used to Rupture Rubber Sample 60-3 Leading to an Explosion. Some of the Damage to the Stainless Steel is Evident.

APPENDIX C.

A DETONATION OF OF_2 IN THE PRESENCE OF POLYBUTADIENE

Storage tests described in this Report are conducted in stainless steel cylinders which are immersed in appropriate cryogenic slush baths. In the case of OF_2 storages, the bath is composed of dry ice and trichloroethylene. During long storage periods the dry ice sublimes and must be replaced. The replacement frequency is typically every three days.

The slush bath is exposed to outdoor atmosphere and often freezes moisture from the air, forming a plug of ice near the top of the Dewar flask which contains the bath. During a storage period in which Compound 202-1 was being tested with OF_2, an ice plug apparently formed; the Dewar appeared to be full of dry ice when it was actually only partially full.

Two days after adding the short supply of dry ice, the storage apparatus was destroyed by an explosion. The mechanism of initiation was not determined, but it is believed that the storage cells reached ambient air temperature (about 20-25°C). Compound 202-1 is reported in Section 2.2.1 of this report to be compatible with OF_2 (static test) at 0°C.

APPENDIX D

EFFECT OF STATE-OF-CURE ON POLYBUTADIENE/OF_2 COMPATIBILITY

A set of specimens prepared from Compound 202-1 for storage with OF_2 were prepared from uncured stock which had been stored in a refrigerator for approximately two months. When OF_2 at -78.5°C was added to the cured specimens, a fire resulted which was believed to be caused by undercured polybutadiene.

Green and Levine (Reference D-1) previously reported than an undercured polybutadiene had detonated in the presence of OF_2. Therefore, a short study was conducted to determine the state of cure of the specimen which caught fire. Results of the study are described in Table D-1.

Compound 202-1A was the material placed in OF_2. Its formulation requires 2.5 phr of di-t-butyl peroxide in order to obtain an optimum cure in 30 minutes at 300°F. From the benzene swelling data, it appears as though this compound had significantly less than the required amount of curative. A drawback to the use of di-t-butyl peroxide as the curative is its relatively high volatility (b.p. = 111°C at one atmosphere pressure) combined with its thermodynamic incompatibility with the base polymer and its low viscosity (liquid at the refrigerator temperature). These factors contribute to peroxide migration and evaporation from the compound.

A secondary result of this experiment is that the peroxide concentration and cure conditions were firmly established to be 2.5 phr peroxide cured 30 minutes at 300°F to provide a tight cure (as indicated by low swelling in benzene) with a strong, tough composite.

Reference D-1: Green, J. and N. B. Levine, "Elastomeric and Compliant Materials For Liquid Rocket Fuel and Oxidizer Application", Report No. ML-TDR-64-107, Air Force Materials Laboratory, March 1964, page 5.

TABLE D-1. SWELLING OF POLYBUTADIENE/Al_2O_3 COMPOUNDS IN BENZENE a)

Component/Compound No.	243-3	243-4	243-5	202-1	202-1A
CIS-4 Polybutadiene, Phillips Petroleum	100	100	100	100	100
ALON Fumed Alumina, Cabot Corp.	60	60	60	60	60
di-*t*-butyl peroxide, Wallace & Tiernan	4.	2.5	3.5	2.5	b)
Cure Time/Temperature; Min./°F	30/300°	30/350°	60/300°	30/300°	30/300°
Oven Post Cure; Hrs./°F	2/225°	2/225°	2/225°	2/225°	2/225°
Results	243-3	243-4	243-5	202-1	202-1A
Volume Swell in Benzene, %	50	50	57	59	142
Remarks	Low Strength	Brittle	No Better Properties Than 202-1	Control	Sample Which Caught Fire In OF_2

a) Specimens were stored in excess room temperature benzene for 96 hours. All specimens were approximately one inch square by 0.020 inch thick prior to immersion. Values were obtained in duplicate.

b) Concentration not known. Determination of this value was the reason for the experiment.

APPENDIX E

ENGINEERING REQUIREMENTS FOR BLADDER MATERIALS

At the onset of Contract NAS7-702, it was determined through discussion with systems engineering personnel at JPL that a propellant vapor pressure of 400-500 psia would be the probable upper limit for OF_2/B_2H_6 propulsion systems. Revision of this allowable pressure range was made prior to the start of efforts on the present Contract (NAS7-770). The revised allowable propellant vapor pressure range was 100-300 psia.

Figures E-1 and E-2 are plots of propellant vapor pressure as a function of temperature for OF_2 and B_2H_6, respectively. The lowest temperature at which each candidate elastomer compound remains flexible,and the corresponding propellant pressure at that temperature, is as follows:

- <u>Compound 202-1 for OF_2</u>

  -95°C (-139°F), OF_2 vapor pressure = 225 psia

- <u>Compound 215-3 for B_2H_6</u>

  -40°C (-40°F), B_2H_6 vapor pressure = 135 psia

It is apparent that the two materials meet the 300 psia limit imposed by system requirements.

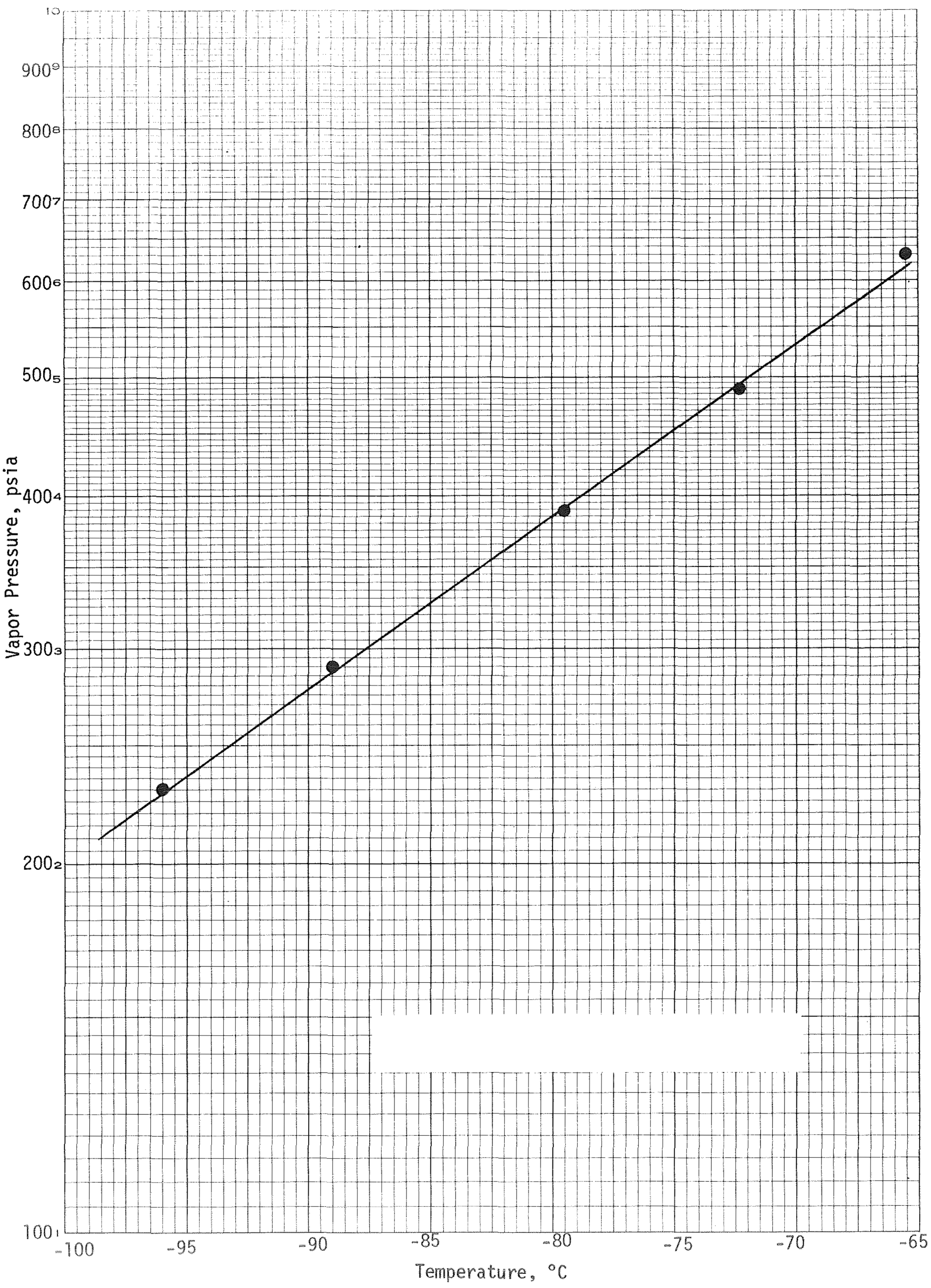

Figure E-1. Oxygen Difluoride Vapor Pressure vs Temperature

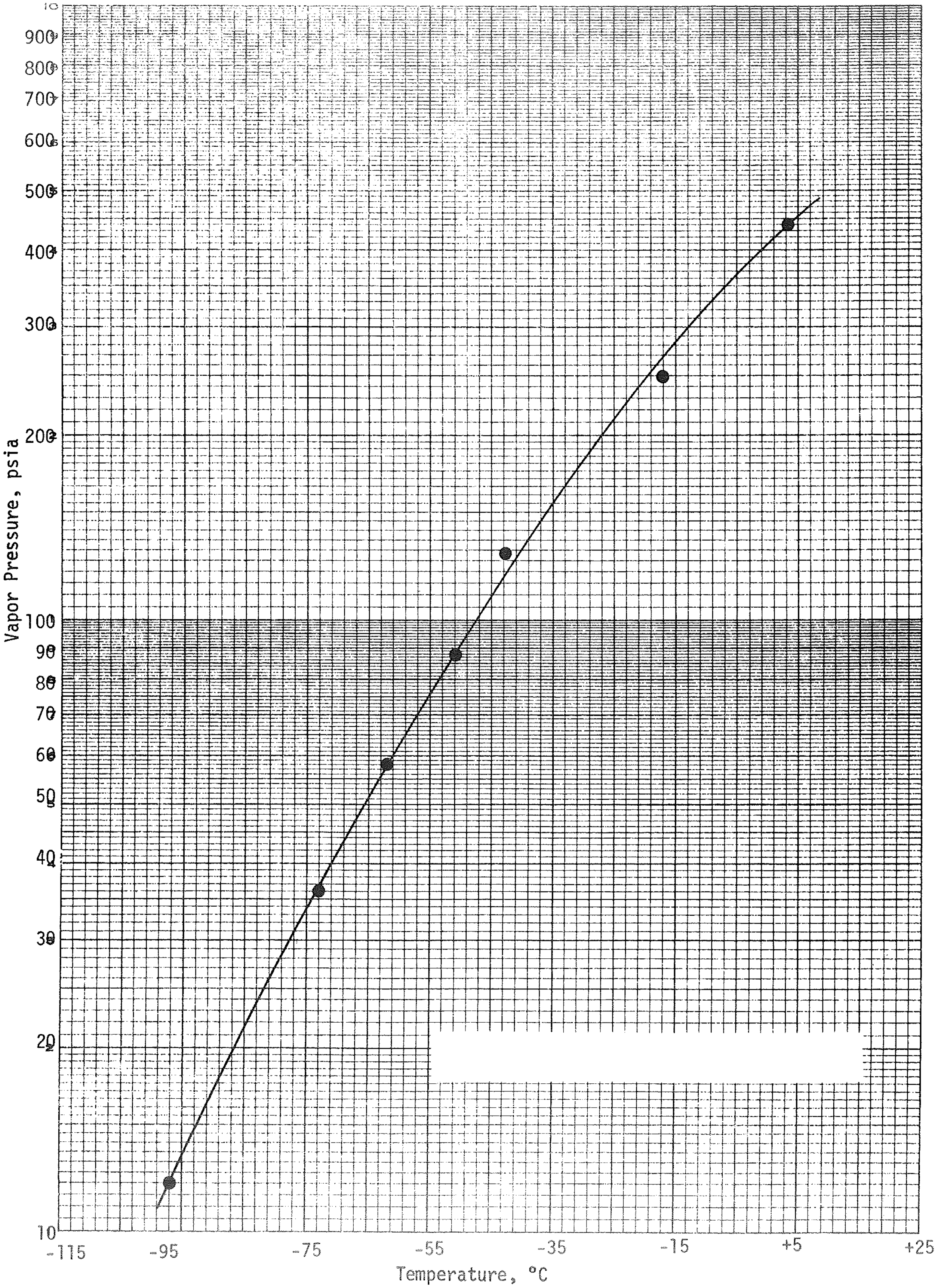

Figure E-2. Diborane Vapor Pressure vs Temperature

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SUMMARY OF CONTRACT - 2 SEPTEMBER 1969 to 1 JULY 1970

OBJECTIVE: TO INVESTIGATE ELASTOMERIC MATERIALS FOR OF_2 AND B_2H_6 EXPULSION BLADDERS

TASK I - _cis_ 1,4-polybutadiene was compounded for optimum mechanical properties for OF_2 service.

Acrylonitrile/butadiene was compounded for optimum mechanical properties for B_2H_6 service.

Short-term, static compatibility tests were performed in propellants at low temperatures, monitored by weight change and property retention measurements.

TASK II - Dynamic tests: candidate elastomers were strained to breaking in propellant.

Lowest temperature was determined at which candidate compounds are elastomeric.

Highest temperature was determined at which relaxed elastomers and respective propellants apparently do not react.

Small-scale diaphragm expulsion tests were performed successfully.

TASK III - Long-term relaxed and stressed specimens were tested for compatibility at low temperature, monitored by weight change and property retention measurements.

Long-term permeability was measured at several temperatures.

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