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AFRPL TR-66-114

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**CHARACTERIZATION  
AND  
EVALUATION  
OF LIGHT METAL HYDRIDES**

LOCKHEED PROPULSION COMPANY  
REDLANDS, CALIFORNIA

TECHNICAL REPORT AFRPL-TR-66-114

JUNE 1966

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(UNCLASSIFIED TITLE)

CHARACTERIZATION AND EVALUATION OF LIGHT METAL HYDRIDES

Lockheed Propulsion Company  
P.O. Box 111  
Redlands, California

June 1966

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## FOREWORD

(U) This is the second quarterly report issued under Contract No. AF 04(611)-11219. This report was prepared by W. E. Baumgartner and G. Myers, Chemistry Department, Lockheed Propulsion Company (LPC). Contributors to the work reported herein include W. D. Allan, W. S. Baker, G. R. Cann, G. L. Horstman, T. A. Palmer, and D. R. Szymanski.

(U) The program is monitored by the Air Force Rocket Propulsion Laboratory (AFRPL), Edwards, California (Lt. John Rombouts, Lt. R. Bargmeyer).

(U) This report contains information regarding the use and the performance of light metal hydrides in solid propellants, and is classified CONFIDENTIAL.

(U) Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

John H. Bonin  
Director, Research Branch  
Lockheed Propulsion Company

## UNCLASSIFIED ABSTRACT

Evaluation of Beany material of recent production shows distinct improvements in the material's particulate structure. Propellant mixes using the newer materials gave low mix viscosity prior to ball milling. Analytical data are summarized.

A Beany double-base propellant was fired in a small motor at low chamber pressure. A significantly lower efficiency was obtained than was measured in a control motor fired under closely similar (mass flow rate, pressure) conditions.

Experimental work was continued in obtaining basic data for LMH-1 propellant shelf-life prediction. Initial data on gas generation rates, gas diffusion and solubility are reported.

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SECTION I  
INTRODUCTION

(C) The program effort conducted under Contract No. AF 05(611)-11219 is divided into two tasks: Task I, the characterization and evaluation of beryllium hydride, and Task II, the analysis of metal hydride propellant shelflife.

(C) 1. TASK I, CHARACTERIZATION AND EVALUATION OF BERYLLIUM HYDRIDE

(C) The primary objective of Task I is to provide a meaningful evaluation of beryllium hydride material forms for application in solid propellants.

(C) The first quarterly report issued under this contract gave a summary of ballistic data obtained in small motor tests. These tests served to define controlling parameters in beryllium hydride combustion in solid rocket motors. The data are now being used in establishing test conditions for a comparative Ethylene-Beany evaluation.

(C) In view of earlier difficulties in processing small grains containing the dense beryllium hydride, and as a prerequisite for further material evaluation, the phenomena underlying reactivity of dense  $\text{BeH}_2$  in propellant mixes are being analyzed further.

(U) 2. TASK II, METAL HYDRIDE PROPELLANT SHELF LIFE

(C) The use of a solid propellant ingredient, such as aluminum hydride, which exhibits a measurable rate of gas generation within the operational temperature range of a propellant (motor) creates the problem of internal gas pressure build-up. If this pressure becomes excessive, the grains will develop cracks.

(U) More precisely, grain failure in such systems is the consequence of an imbalance between gas generation rates and gas dissipation rates, the latter being highly dependent upon volumetric solid loading, grain size, and grain geometry. Because of this dependency, there are no simple means for predicting motor shelflife by extrapolation of laboratory surveillance test data. Instead, such data extrapolation has to rely on the use of a complex mathematical model, and requires precise information on gas solubilities in the binder, gas diffusion and gas generation rates, in addition to data on grain internal stress concentrations.

(U) The previous quarterly report discussed in detail a physical model of the gas generation-diffusion process, presented a mathematical analysis of that process and outlined the experimental program necessary to implement the analysis and predict shelflives of propellant motors. The present report describes the experimental procedures employed and the results obtained in the measurements of gas generation rate, gas diffusion and solubility constants and shelflives of laboratory specimens.

## SECTION II

## SUMMARY

## (C) 1. TASK I. CHARACTERIZATION AND EVALUATION OF BERYLLIUM HYDRIDE

(C) Analytical techniques for determining minor changes in sample composition during passivation and aging are being evaluated. These techniques include microcombustion analysis, analysis by KBr pellet technique, in combination with differential thermal analysis and differential scanning calorimetry. Specific information sought includes carbonate content, and concentration of active hydrogen (e. g., hydroxyl, surface moisture) not present as hydride hydrogen.

(U) Six samples of Beany material, all representing recent production lots, were received for evaluation. Analytical data and results of the evaluation of the materials in propellant mixes are reported. The data show a distinct improvement in particulate characteristics over samples of earlier production.

(C) Beryllium hydride was evaluated in double-base propellants containing 2,2-dinitropropanediol dinitrate (DNPDN) as an energetic plasticizer. A distinct stabilizer effect of  $\text{BeH}_2$ , comparable to the effect produced by the usual double-base propellant stabilizers, was observed in Taliani tests.

(C) A  $\text{BeH}_2$ /NIBTN double-base propellant (LPC-1032B) was test-fired in a  $1\frac{1}{2}$ -pound motor at low (270 psi) chamber pressure. A modified LPC-1005A propellant giving comparable mass flow rates at this pressure was used as a control. The data show low specific impulse efficiency for the beryllium hydride system (84.4% as compared to 93.8% for the control).

(C) Cracking cylinders prepared with LPC-1032C (15%  $\text{BeH}_2$ /NIBTN double-base propellant) were placed in elevated temperature storage. At  $140^\circ\text{F}$  the samples developed cracks between 10 and 18 days storage. All samples passed X-ray examination after 18 days at  $120^\circ\text{F}$ , and the tests are continuing.

(C) Further analysis of ballistic test data obtained during a preceding report period leads to more detailed understanding of  $\text{BeH}_2$  combustion in solid rocket motors (Section III, subsection g).

## (U) 2. TASK II. LIGHT METAL HYDRIDE PROPELLANT SHELF LIFE

## (U) a. Gas Diffusion and Solubility

Measurements of gas diffusion and solubility constants in propellant are being performed by means of a sorption technique.

(U) Preliminary values of gas diffusion coefficient and solubility have been obtained for propellant LPC-1018B without LMH-1 at several temperatures. Their magnitude, as well as that of a calculated energy of activation for diffusion, is consistent with literature values for  $\text{H}_2$  in various polymers.

## (U) b. Gas Generation Rate (LMH-1 Stability)

(U) A technique has been developed to replace the standard Taliani method for measuring gas generation rates and is now operating satisfactorily. It uses a thermal conductivity cell for measuring the  $H_2$  concentration in a carrier gas which purges sample cells after known periods of collection. As presently set up, six samples can be studied simultaneously. Data have been obtained for pure Dow 1451 (blend 97-131) at 100 and 140°F over a 700-hour period and for the same material in propellant (formulation A23-06) at 100 and 140°F over a 250-hour period. The pure Dow 1451 data agree well with the data from Dow derived with a pressure technique. In contrast to some other reports, however, these data indicate a significantly greater generation rate in propellant than in the pure state, particularly at 140°F. Propellant samples employed here were chopped into 1 to 2-mm particles to preclude any diffusional effects upon the measurements, which if not eliminated would make the observed generation rate lower than the true rate.

## (U) c. LMH-1 Propellant Surveillance

(U) Stainless steel surveillance containers have been fabricated and the appropriate quantities sent to Allegheny Ballistic Laboratory (ABL) and United Technology Center (UTC) for preparation of surveillance specimens of their propellant formulations. Samples to be shipped to LPC include specimens for measurements of gas generation rate, and diffusion and solubility constants. The surveillance containers are of such a geometry that the mathematical analysis of gas generation-diffusion is applicable and the effects of cure and thermally-induced internal stresses can be determined.

(U) Surveillance has been initiated at 75 and 115°F with propellant A23-06 containing blend 97-131 of LMH-1. Void formation occurs within a few days at 115°F, indicating that subsequent surveillance at this temperature will require the more stable LMH-1 samples expected shortly from Dow. Although the combined data are not yet sufficiently firm to warrant detailed analysis and correlation, preliminary calculations show the observed failure times to be consistent with the measured gas generation rates, diffusion constants and solubility.

SECTION III  
TECHNICAL EFFORT

(C) 1. TASK I, CHARACTERIZATION AND EVALUATION OF  
BERYLLIUM HYDRIDE

(U) a. Analysis by Microcombustion and Infrared Spectroscopy

(C) There is reason to believe that  $\text{BeH}_2$  material reactivity in propellant mixes is caused by two independently operating phenomena. Heating of the samples (especially the high density material) under vacuo affords a distinct improvement in relative propellant density; however, with this heat-treated material, some propellant porosity generally remains. This partial improvement can be attributed to the thermal decomposition, desolvation or desorption of yet undefined species during the vacuum heat treatment. A second phenomenon involves  $\text{BeH}_2$  particle surface reactivity with nitrate esters, and is believed to be associated with the existence of chemically active beryllium species, perhaps beryllium hydroxide, on the particle surface.

(C) To arrive at a better definition of  $\text{BeH}_2$  material reactivity various analytical techniques are being refined for measuring minor changes in material composition.

(U) b. Analysis by Microcombustion

(C) None of the currently used methods of analysis permits accurate distinction between hydrogen existing in the form of beryllium hydride, and hydrogen present as hydroxide (beryllium hydroxide, water). Moreover, it appears desirable to determine  $\text{CO}_2$  content, since passivation of amorphous  $\text{BeH}_2$  is accelerated in a  $\text{CO}_2$ -enriched atmosphere. To obtain the desired information, various suspected impurities are being studied in the pure state by differential thermal analysis, or differential scanning calorimetry to select specific operating conditions in microcombustion analysis. Additionally, infrared analysis is being evaluated.

(C) In the microcombustion analysis method the samples are pyrolyzed at different temperatures, either under an oxygen or argon stream, and the pyrolysis products are passed through a  $\text{CuO}$  furnace, or absorbed (water,  $\text{CO}_2$ ) direct.

(C) To test these various modes of operation, a variety of beryllium hydride samples were pyrolyzed under argon at 300 and 600°C, and the pyrolysis products were passed through the usual  $\text{CuO}$  furnace for converting the products to water and  $\text{CO}_2$ . The analytical data are summarized in Tables I and II for comparison with data reported by the Ethyl Corporation. The following comments apply:

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TABLE I

**CARBON-HYDROGEN ANALYSES OF LMH-2 - 300°C/ARGON**

Material	Lot No.	Hydrogen (%) LPC	Hydrogen (%) Ethyl	Carbon (%) LPC	Carbon (%) Ethyl
Beany, std.	79	16.89 16.96 16.98	17.51	0.96 0.64 0.48	1.49
Beany, std.	301-2	16.73 16.65 16.57	17.37	0.60 0.50 0.53	1.47
(4)	301-2	16.30 16.29	17.37	0.45 0.49	1.47
* Beany, std.	91	17.11 17.09	17.41	1.75 1.38	2.84
* Beany, std.	307-8	16.88 16.58	17.14	2.14 2.19	3.01
* Beany, std.	362-3	17.18 17.45	17.14	1.38 1.14	2.05
* Beany, std.	383-9	17.32 17.36	17.87	0.66 0.98	1.43
* Beany, std.	386-7	17.16 16.98	17.63	0.98 0.91	1.50
* Beany, std. (4)	386-7	17.47 17.12	17.63	1.63 1.35	1.50
Beany, dopad	338-7	15.21 15.71 15.95	17.32	0.92 0.74 0.92	1.53
(4)	338-7	15.87	17.32	0.75	1.53
Beany, dopad	328-1	16.27 16.36 16.18	17.78	0.96 1.12 1.19	2.23
Ethylene	E-46	15.57 15.68 15.66	-na-	1.11 1.18 1.18	-na-
Ethylene	E-81	15.68 15.24 15.32	-na-	1.27 1.12 1.26	-na-
Ethylene	E-89	15.93 16.03 15.78	-na-	0.95 0.95 0.97	-na-
(4)	E-89	15.96	-na-	0.82	-na-
Ethylene	E-120	15.48 15.47 15.47	-na-	1.13 1.03 1.08	-na-
(4)	E-120	15.41 15.55	-na-	0.81 0.84	-na-

\* Recent shipments  
 (1) Sample burned in stream of pure oxygen instead of argon.  
 (2) Sample pyrolyzed at 600°C instead of 300°C.  
 Beany = pyrolytically produced LMH-2.  
 Ethylene = higher density, pressure-fused LMH-2  
 na = not available.

TABLE II  
MICROANALYSIS DATA, BEANY SAMPLES

Lot No.	B-357-8	B-362-3	B-383-5	B-386-7	Lot 91
<u>Ethyl Corporation Data</u>					
Hydrogen content (%)	17.14	17.14	17.87	17.63	17.41
Carbon content (%)	3.01	2.05	1.43	1.50	2.84
Corrected hydrogen content (%) <sup>(1)</sup>	16.56	16.75	17.60	17.34	16.87
Calculated BeH <sub>2</sub> (%)	90.6	91.7	96.3	94.9	92.4
Reported BeH <sub>2</sub> (%)	92.0	92.5	96.5	95.6	91.9
<u>LPC Data (%)</u>					
Hydrogen content (%)	16.73±0.15	17.31±0.13	17.42±0.08	17.03±0.13	17.08±0.03
Carbon content (%) <sup>(2)</sup>	2.17±0.02	1.26±0.12	0.91±0.17	0.95±0.04	1.56±0.18
Corrected hydrogen content (%)	16.32	17.07	17.25	16.85	16.78
Calculated BeH <sub>2</sub> (%)	89.3	93.4	94.4	92.2	91.9
				17.01	
				93.1 <sup>(3)</sup>	

Analysis of Lot No. 388-391 not completed

- (1) Correction factor 0.191 is applied to carbon content to correct for hydrogen values for alkyls (assumed C<sub>4</sub>H<sub>9</sub>).  
 (2) Pyrolysis under argon stream, unless noted differently.  
 (3) Pyrolysis under oxygen stream.

(C) (i) With argon as a flush gas there appears to be a significant extent of conversion of beryllium alkyls or alkoxides to beryllium carbide, with resulting low values for total carbon content. Alternatively, beryllium alkyls might be lost by vaporization and condensation in the equipment.

(C) (ii) In duplicate or triplicate analyses somewhat better reproducibility is obtained with the dense Ethylene than with amorphous Beany. This is due to sample nonuniformity with the Beany.

(C) (iii) Freshly received (prepared) samples give data (hydrogen content) which are in generally good agreement with the manufacturer's data, although some samples show distinct discrepancies. There are constantly larger differences in the data with samples which have been stored for some time. This could be the result of autoxidation (e.g., doped samples), a slow degassing, or slow reaction between hydride and alkyls.

(C) Additional tests for improving the accuracy of the method will be performed. Analyses will then be repeated without the CuO furnace (argon flush gas) in an effort to determine surface-bound moisture and CO<sub>2</sub>.

(U) c. Analysis by Infrared Spectroscopy

(C) Initial studies have shown that analysis of BeH<sub>2</sub> samples by infrared spectroscopy (KBr pellet technique) holds promise for determining surface-bound moisture (including beryllium hydroxide) and beryllium oxide. Both moisture and hydroxide show a strong band centered at 3450 cm<sup>-1</sup>, while beryllium oxide absorbs at 860 cm<sup>-1</sup>. Efforts are under way to standardize the technique.

(C) d. Effect of BeH<sub>2</sub> Material Purity on Propellant Performance

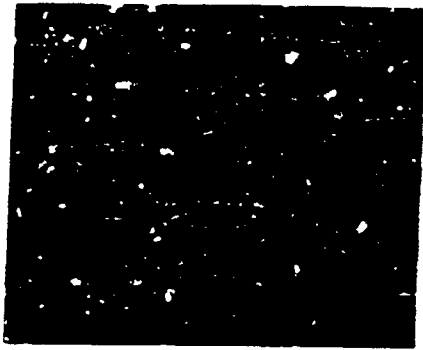
(C) In earlier performance calculations a BeH<sub>2</sub> material purity of 94.9% was assumed, and the impurities listed in Table III were programmed in the computer calculations. Following a review of analytical data with Ethyl Corporation personnel, the programs were revised to account for a somewhat different average material composition. The effects of these changes upon specific impulse and flame temperature are shown in Table III.

(U) e. Evaluation of Beany Samples

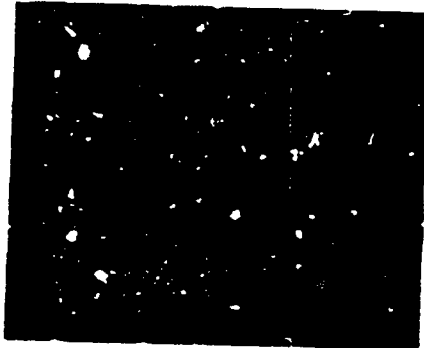
(C) Six samples of Beany material were received from the Ethyl Corporation for evaluation. Analytical data obtained with these materials (total hydrogen, total carbon) are shown in Table II. Photomicrographs are shown in Figures 1 and 2. The materials are now being evaluated in small scale propellant mixes, and preliminary data show a distinct reduction in mix viscosity over mix viscosities measured with previous Beany samples.

TABLE III  
THEORETICAL CALCULATIONS; LPC-1032AXM PROPELLANT

	Old	New Values	
	Values Beany	Beany	Ethylene
$T_c$ (°K)	3574	3584	3606
$T_e$ (°K)	2525	2537	2554
$c^*$	--	5825	5809
$I_{sp_{eq}}$	302.6	300.3	299.5
Density (gm/cc)	1.377	1.376	1.463
(lb/in. <sup>3</sup> )	0.050	0.050	0.053
LMH-2 purity (%)	94.9	92.9	89.6
<u>LMH-2 impurities (%)</u>			
Be metal	0.7	2.0	4.0
BeO	0	1.7	2.9
Alkyls			
C <sub>2</sub>	1.4	0.7	0.3
C <sub>4</sub>	1.6	1.5	0.6
Alkoxide (Et)	0.2	0.2	0.2
BeCl <sub>2</sub>	0	0.5	0.5
Carbon (free)	0	0.5	0.2
LiH	0	0	1.7
Ethyl ether	1.2	0	0
$H_f$ kcal/100 gm	-40.1	-58.4	-67.9



8357-8

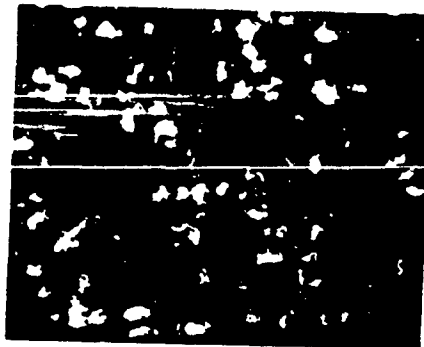


8356-7

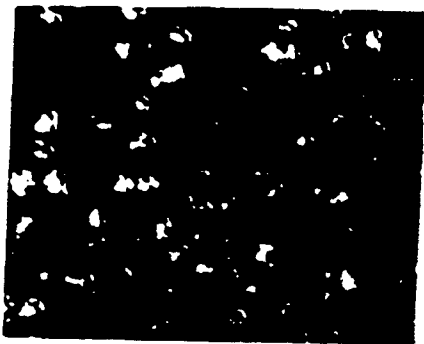


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Lot 91



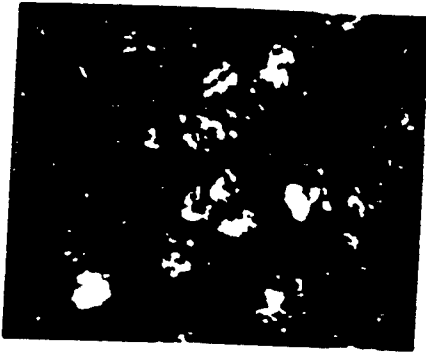
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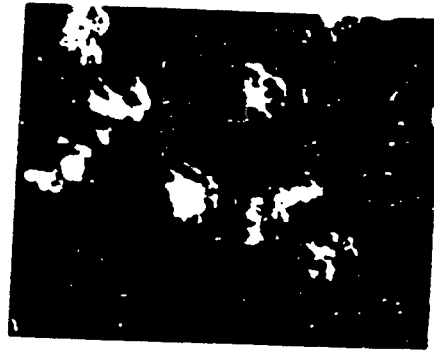
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100 microns

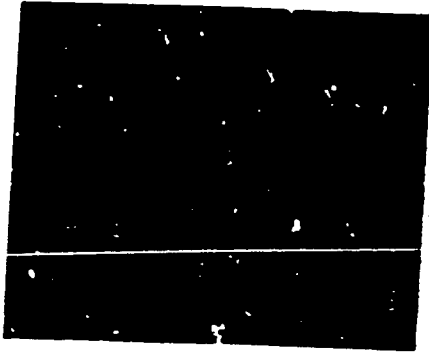
Figure 1 Amorphous Beryllium Hydride (Beany) Particles X65



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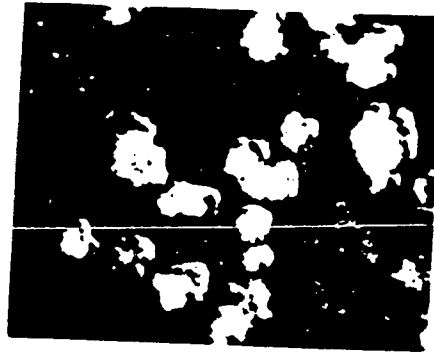


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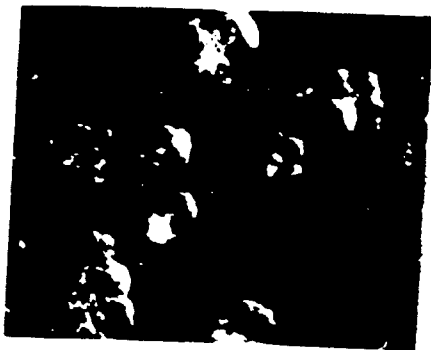


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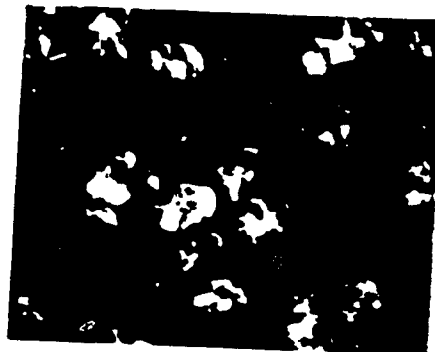
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Lot 22



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100 microns

Figure 2 Amorphous Beryllium Hydride (Beany) Particles X220

(C) f. Evaluation of Beryllium Hydride Propellants

(U) (1) Ballistic Evaluation

(C) A beryllium hydride double-base formulation (LPC-1032B, Table IV) was test-fired in a 1½-pound cartridge-loaded motor at a low chamber pressure. A modified LPC-1005A propellant<sup>1</sup> was used as the control, duplicating mass flow rates. The ballistic data are given in Table V. The same BeH<sub>2</sub> formulation, test-fired at 1000-psi chamber pressure, is expected to give a specific impulse efficiency only slightly less than control motor efficiency.

(C) The data, if confirmed in later firings, imply that lowering of burn rates in BeH<sub>2</sub> propellants (>15% BeH<sub>2</sub>) cannot be accomplished by firing at low chamber pressure without a serious loss in efficiency unless the propellants are reformulated (see subsection g, below).

(U) (2) Propellant Shelflife Studies

(C) Cracking cylinders containing LPC-1032C propellant (Table IV) were placed into elevated temperature storage for periodic examination by X-ray. At a storage temperature of 140°F (following 48-hour cure at 140°F) the samples developed cracks within a 10 to 18-day period. At a storage temperature of 120°F all samples passed X-ray examination after 18 days and the tests are continuing.

(C) Under an earlier program, BeH<sub>2</sub> double-base propellants containing conventional binders (TMETN) were stored for approximately one year at 120°F without the appearance of internal cracks.

(C) (3) Stabilizers for BeH<sub>2</sub> Double-Base Propellants

(C) Limited data available so far indicate that beryllium hydride (Beany) itself exerts a significantly stabilizing effect upon nitrate esters. A striking example is shown in the effect on the thermal stability of 2,2-dinitropropanediol dinitrate (Figures 3 and 4). Similar effects are observed in 90°C Taliani tests with NIBTN. On the other hand, the data show that some commonly used stabilizers (e.g., resorcinol) can adversely affect BeH<sub>2</sub>/nitrate ester mixture thermal stability. A more careful analysis of the relative merits of stabilizers in these systems is being conducted.

(C) g- Combustion of Beryllium Hydride in Solid Rocket Motors

(C) The conclusions regarding the controlling parameters in BeH<sub>2</sub> combustion which were derived from a small scale ballistic test program have been discussed in the preceding quarterly report<sup>1</sup>. The following supplements the earlier discussion.

<sup>1</sup>For description of test motor, control propellant, and preceding ballistic test data, see 1st Quarterly Report, AFRPL-TR-66-48.

TABLE IV  
COMPOSITION, LPC-1032 PROPELLANTS

	<u>LPC-1032B</u>	<u>LPC-1032C</u>
Plastisol grade nitrocellulose (%)	10.85	10.85
Nitroisobutanetriol trinitrate (%)	50.10	49.25
Diethyleneglycol dinitrate (%)	3.90	
Ethyleneglycol dinitrate (%)		3.90
Ammonium perchlorate, Type II, Size 1 (%)	20.15	20.00
2-Nitrodiphenylamine (%)		0.50 <sup>(1)</sup>
Ethyl centralite (%)		0.50 <sup>(1)</sup>
Beany (%)	15.00	15.00

(1) Beneficial effect of stabilizers, if any, in BeH<sub>2</sub> double-base propellants not established.

TABLE V  
BALLISTIC DATA, LOW PRESSURE FIRING

	<u>LPC-1032B</u>	<u>LPC-1005 Mod. 45μ</u>
Firing No.	P-16	P-14
Grain No.	218B	214A
Propellant wt		
Cast	1.335	1.714
Exhaust	1.288	1.681
Residue (%)	3.5	2.0
Nozzle Throat Area (in. <sup>2</sup> ), Average	0.711	0.737
Expansion Ratio	8.027	7.735
Burn Rate (r <sub>b</sub> )	0.452	0.378
Chamber Pressure, $\bar{P}_{ctq}$	270	278
Mass Flow Rate (ṁ)	1.16	1.28
c* (ft/sec)	5650	5313
Measured I <sub>sp</sub> (total time, $\bar{P}_{av}$ )	208.3	205.6
I <sub>1000</sub> <sup>0</sup> Corrected (lbf-sec)	258.38	251.39
Ign Corrected, I <sub>1000</sub> <sup>0</sup> Corrected (lbf-sec)	255.98	249.59
I <sub>sp</sub> Efficiency (%)	85.19	94.51
Ign Corrected, I <sub>sp</sub> Efficiency (%)	84.42	93.83

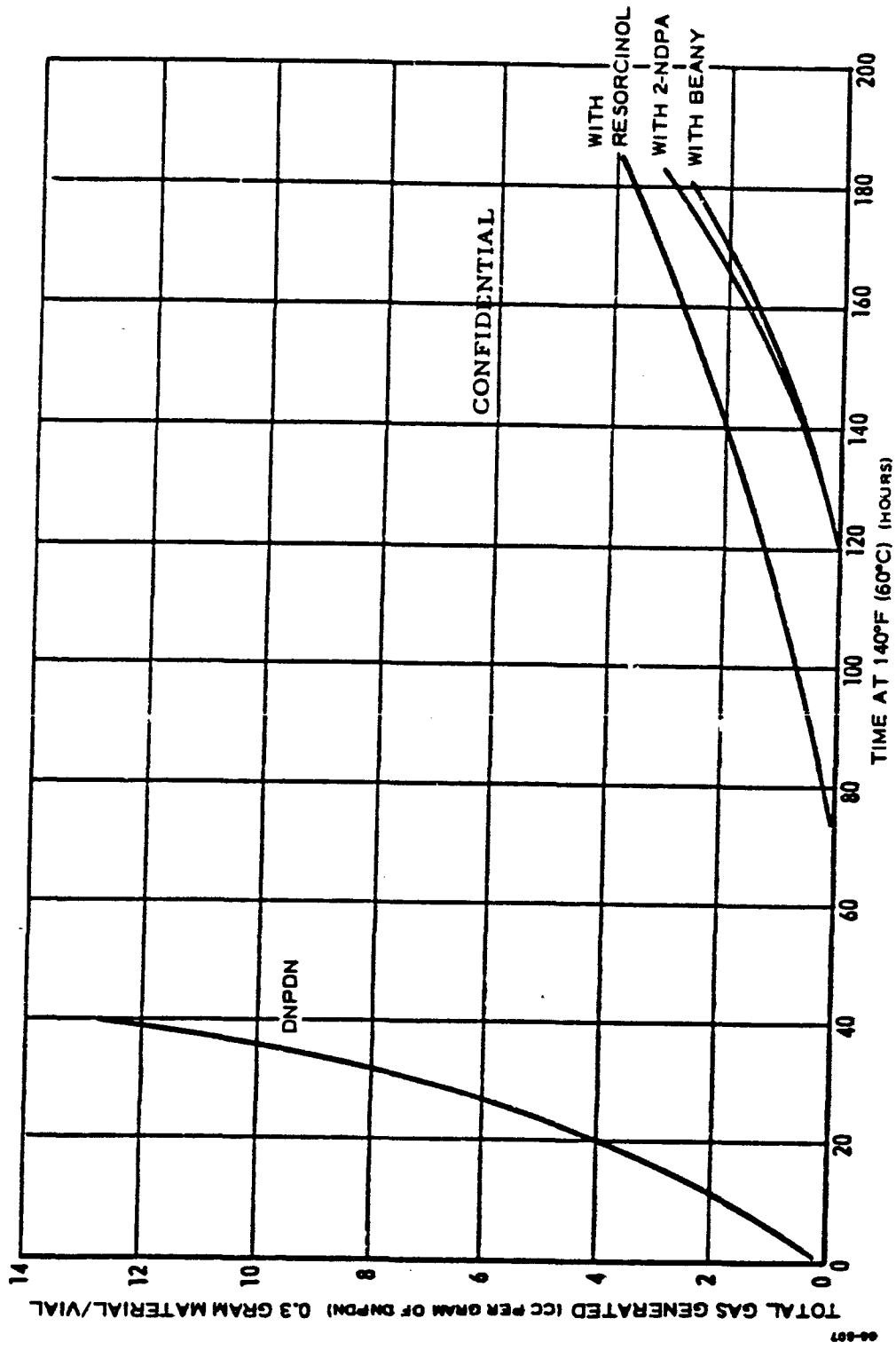


Figure 3 Taliani Data, DNPDI

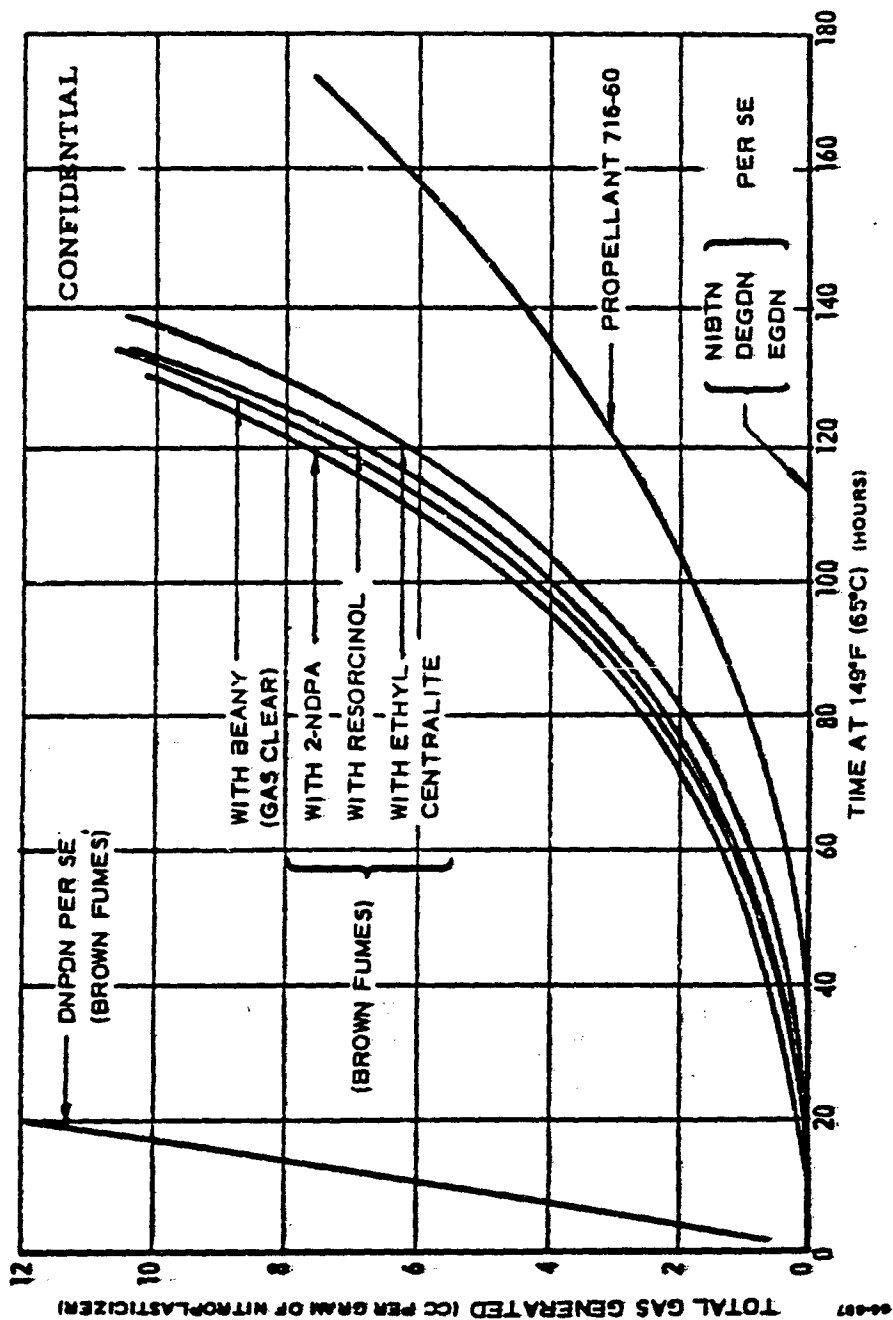


Figure 4 Talliani Data, DNPDN

(C) The existing small motor test data suggest two different modes of combustion of  $\text{BeH}_2$  and, as a result, differences in the controlling phenomena depending upon the predominant site of  $\text{BeH}_2$  pyrolysis.

(U) (1) Combustion Mode 1

(C) If beryllium hydride (or aluminum hydride) decomposes to a significant extent within the gaseous combustion zone rather than within the solid region, the controlling phenomenon is a nonequilibrium flame temperature that can be computed assuming no metal combustion, or only partial metal combustion. This temperature has to be in excess of a threshold value which is governed by the metal ignition point. Small scale motor tests indicate that high combustion efficiency is obtained if theoretical calculations, ignoring heat losses, afford a  $T^*$  value (0% metal combustion assumed) of 2300 to 2500°K. This temperature threshold is expected to vary with mass flow rates (heat loss effects), implying that  $\text{BeH}_2$  loadings can be slightly increased without reducing efficiency if heat losses are reduced (constant "effective"  $T^*$ ).

(U) In these Combustion Mode 1 systems variations in oxidizer particle-size distribution do not significantly affect the controlling parameter. This affords freedom in manipulating interior ballistic properties. Moreover, since  $T^*$  values in Combustion Mode 1 systems (relatively "cool" binders) increase with increasing AP loading, improvements in efficiency are paralleled by propellant density gains.

(C) Increasing the chamber pressure will cause a larger degree of metal hydride decomposition within the solid region, and produces a compensating surface-cooling effect. In extreme cases, this can give rise to very low pressure exponents. It can also result in an enhanced tendency toward metal agglomeration, complicating an analysis of chamber pressure effects on  $I_{sp}$  efficiency because of various counteracting effects.

(C) Typical Combustion Mode 1 systems are LPC-1029/LPC-1031 ( $\text{BeH}_2$ /TMETN base propellants), the UTC  $\text{AlH}_3$  nitrate polyester system, and the Thiokol AB-109  $\text{BeH}_2$ /NF-polymer system. It can also be assumed that some of the systems studied by the Atlantic Research Corporation represent Combustion Mode 1 systems, provided beryllium-metal loadings are sufficiently low to prevent excessive agglomeration.

(U) (2) Combustion Mode 2

(C) If beryllium hydride (or aluminum hydride) decomposes predominantly within the solid region, the controlling phenomenon is a nonequilibrium flame temperature that exists in the close vicinity of the surface. This temperature is difficult to evaluate theoretically since it is modified by chamber pressure (heat transfer to the surface), and solid oxidizer particle size (diffusion flame structure, varying degree of solid phase interaction). If these latter two variables are held constant, a theoretical comparison of systems is possible by calculating the flame temperature ( $T_f^*$ ) that would exist prior to

metal ignition, and ignoring any contribution from the solid oxidizer. Judging from the existing small motor data, high  $I_{sp}$  efficiency is obtained if these  $T_S^*$  values are in excess of 2100°K at 1000-psi chamber pressure.

(U) Implications, supported by the limited number of test data are:

(U) (i) Reducing solid oxidizer particle size will enhance heat transfer to the surface, thus improving  $I_{sp}$  efficiency (higher "effective"  $T_S^*$ ). In other words,  $I_{sp}$  efficiency is likely to be affected by attempting to modify interior ballistic properties.

(U) (ii) Reducing chamber pressure will adversely affect the "effective"  $T_S^*$ , and low  $I_{sp}$  efficiency can be expected at low chamber pressures unless  $T_S^*$  values are increased to compensate for this decrease in effective  $T_S^*$ .

(C) (iii)  $As BeH_2$  loadings are increased, AP loading has to be decreased to maintain  $T_S^*$ , and/or more energetic binders have to be used. A comparison of  $T^*$ ,  $T_S^*$ ,  $T_c$  and  $I_{sp}$  data for two different binder systems (NIBTN double-base binder versus DNPDN double-base binder) is given in Figure 5.

(C) (iv) Increasing AP loading in systems using an energetic binder is bound to decrease  $T_S^*$ , and to cause enhanced metal agglomeration (thermal and geometry effect). This gives rise to a large density penalty as  $BeH_2$  loading is increased.

(U) The existing data are still insufficient to state to what an extent burn rate and  $I_{sp}$  efficiency are interrelated in Combustion Mode 2 systems. There is reason to suspect that such a relationship exists, and that it will limit the range over which interior ballistic properties can be varied.

(U) 2. TASK II, LMH-1 PROPELLANT SHELF LIFE

(U) a. Gas Diffusion and Solubility

(U) (1) Experimental Procedure

(U) Diffusion coefficients of hydrogen in the propellants are being determined from rates of sorption, while the solubility is obtained from the equilibrium sorption. The apparatus is a modified safety (rupture) head fitting and is shown in Figure 6. To reduce the effects of temperature fluctuations, two such cells are employed and are connected to opposite sides of the oil manometer. One cell contains the propellant in the form of discs 2.9-inches in diameter and 0.1-inch thick, separated by glass filter paper or a thin metal screen. The second "blank" cell contains an equal number of aluminum discs similarly separated so that the free volume in the two cells is

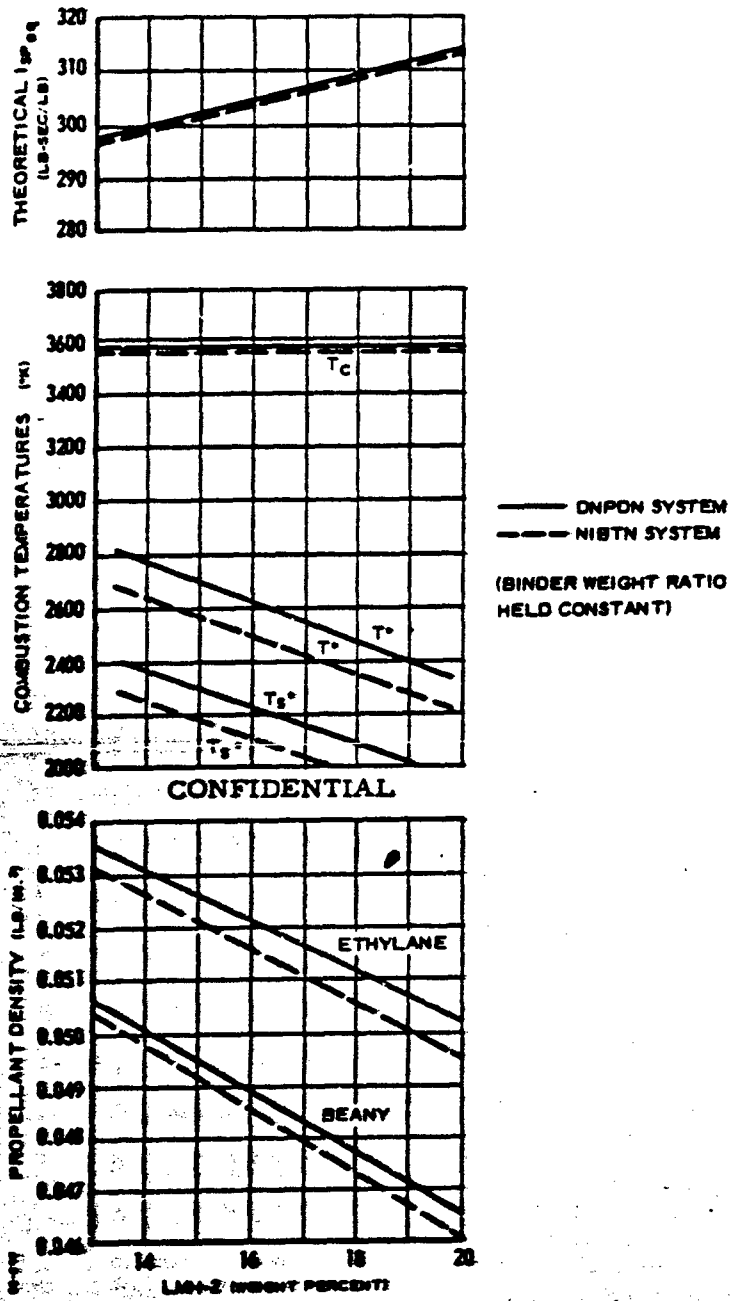


Figure 5 LMH-2/DNPDN and LMH-2/NIBTN Systems

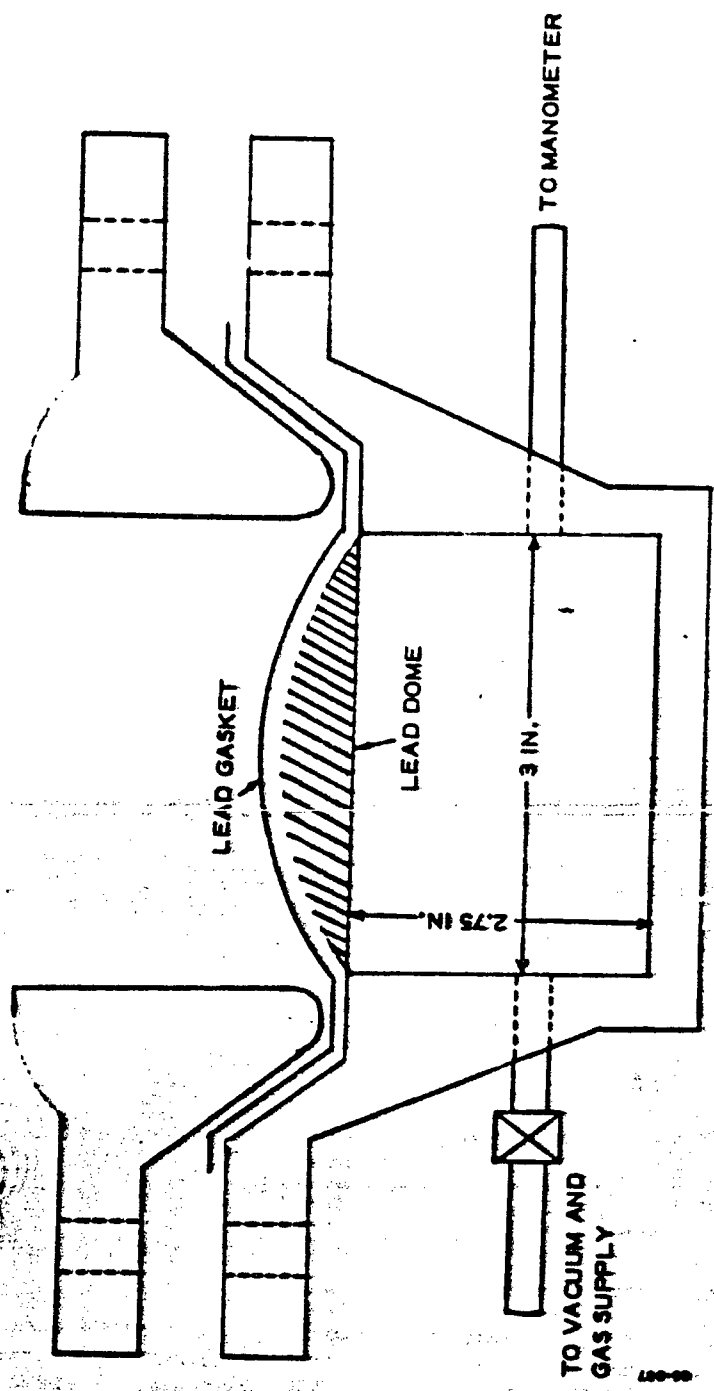


Figure 6 Gas Diffusion Cell

nearly identical. The lead dome below the rupture disc serves the dual purpose of supporting the gasket-rupture disc during evacuation of the cell and of reducing and holding constant the free volume. Difficulty was encountered initially in consistently obtaining a hydrogen-tight system with the aluminum gasket-rupture discs normally employed with such safety fittings. Substitution of a thin lead sheet appears to have solved this problem. (Plastic or rubber would of course be unsuitable in this application.)

(U) After assembly, both cells are checked for vacuum tightness with a helium leak detector, mounted in an oven and attached to the manometer through  $\frac{1}{8}$ -inch insulated copper tubing by means of Swagelok couplings. A second, more realistic check of gas tightness is then performed by reducing the air pressure within only the sample cell by an amount greater than expected during an actual sorption experiment and observing constancy of that pressure differential overnight. If the test is satisfactory, all air is removed from cells and propellant by pumping overnight or longer, hydrogen is let into both cells at the same pressure (essentially one atmosphere in experiments to date), and the rate of pressure drop due to hydrogen sorption by the propellant is measured.

(U) (2) Data Analysis

(U) Data analysis follows the suggestions of Crank (Ref. 2) and of Michaels, et al (Ref. 3). For sorption by a plane sheet immersed in a limited volume of solute the fractional equilibration, E, is given (Ref. 2) by

$$1-E = \sum_{n=1}^{\infty} \frac{2\gamma(1+\gamma)}{1+\gamma+\gamma^2 q_n^2} \exp\left[-4D q_n^2 t/L^2\right] = \frac{p(t) - P_f}{P_i - P_f} \quad (1)$$

(U) Here, D is the diffusion coefficient in  $\text{cm}^2/\text{sec}$ , t is time in seconds, and L is the thickness of propellant sheet in cm.  $\gamma$  is the ratio of initial pressure to total pressure drop, i. e.

$$\gamma = \frac{P_i}{P_i - P_f} \quad (2)$$

(U) The quantity  $q_n$  is a solution of the transcendental equation

$$\tan q_n = \gamma q_n \quad (3)$$

and is tabulated by Crank (Ref. 2).

(U) The initial pressure,  $P_i$ , cannot be directly measured. If the diffusion rate is too great,  $P_i$  may be obtained by an extrapolation of observed pressures back to zero time. This procedure appears to be satisfactory

in our experiments to date, although the contrary has been claimed for diffusion coefficients of the magnitude calculated from our data ( $D > 10^{-6}$  cm<sup>2</sup>/sec). Alternatively,  $p_i$  may be determined by an iterative procedure with a computer (Ref. 4).

(U) For  $1-E$  less than 0.3, equation (1) is given to good approximation by

$$1 - E = \frac{2\gamma(1+\gamma)}{1+\gamma+\gamma^2q_1^2} \exp \left[ -4Dq_1^2 t/L^2 \right] \quad (4)$$

Thus  $D$  may be obtained from the slope in the linear portion of a plot of  $\log(1-E)$  versus time.

(U) Hydrogen solubility under the above experimental conditions is given within sufficient accuracy by

$$S \left( \frac{\text{gH}_2}{\text{cc binder}} \right) = 2 \frac{(p_i - p_f)}{V_p \cdot V_B} \frac{V_F}{RT} \quad (5)$$

where  $V_p$  and  $V_F$  are respectively propellant volume and free volume within the cell. ( $V_F/V_p$  is approximately unity for the experiments reported herein), and  $V_B$  is the volume fraction of binder in the propellant.

(U) (3) Results

(U) Figure 7 represents the semi-log plots according to equation 4 for the data from two experiments. The straight lines were drawn by visual observation through the mid-portion of the points since the points at short times will not necessarily follow equation 4, while those at long times are inaccurate due to the subtraction of nearly equal numbers.

(U)  $D$  and  $S$  values calculated from the initial experiments which were carried out with propellant LPC-1018B without LMH-1 are given in Table VI.

(U) Literature values for hydrogen diffusion constant in various unplasticized polymers range between  $10^{-5}$  and  $10^{-7}$  cm<sup>2</sup>/sec. The values reported here would therefore seem to be of the proper magnitude, though they are perhaps somewhat larger than had been anticipated. The activation energy for diffusion calculated from these data (Figure 8) is approximately 9 kcal/mole. This is somewhat greater than the range of values reported for H<sub>2</sub> in unplasticized polymers above their glass transition, e. g., 6.6 kcal/mole and 7.6 kcal/mole for H<sub>2</sub> in neoprene and polyisobutylene, respectively (Ref. 5). Reproducibility of the solubilities is as yet quite poor but their magnitude is of the same order as reported for H<sub>2</sub> in polymers, e. g.,  $0.03 \frac{\text{cc H}_2 (\text{STP})}{1 \text{ atm} - \text{cc}}$  in poly

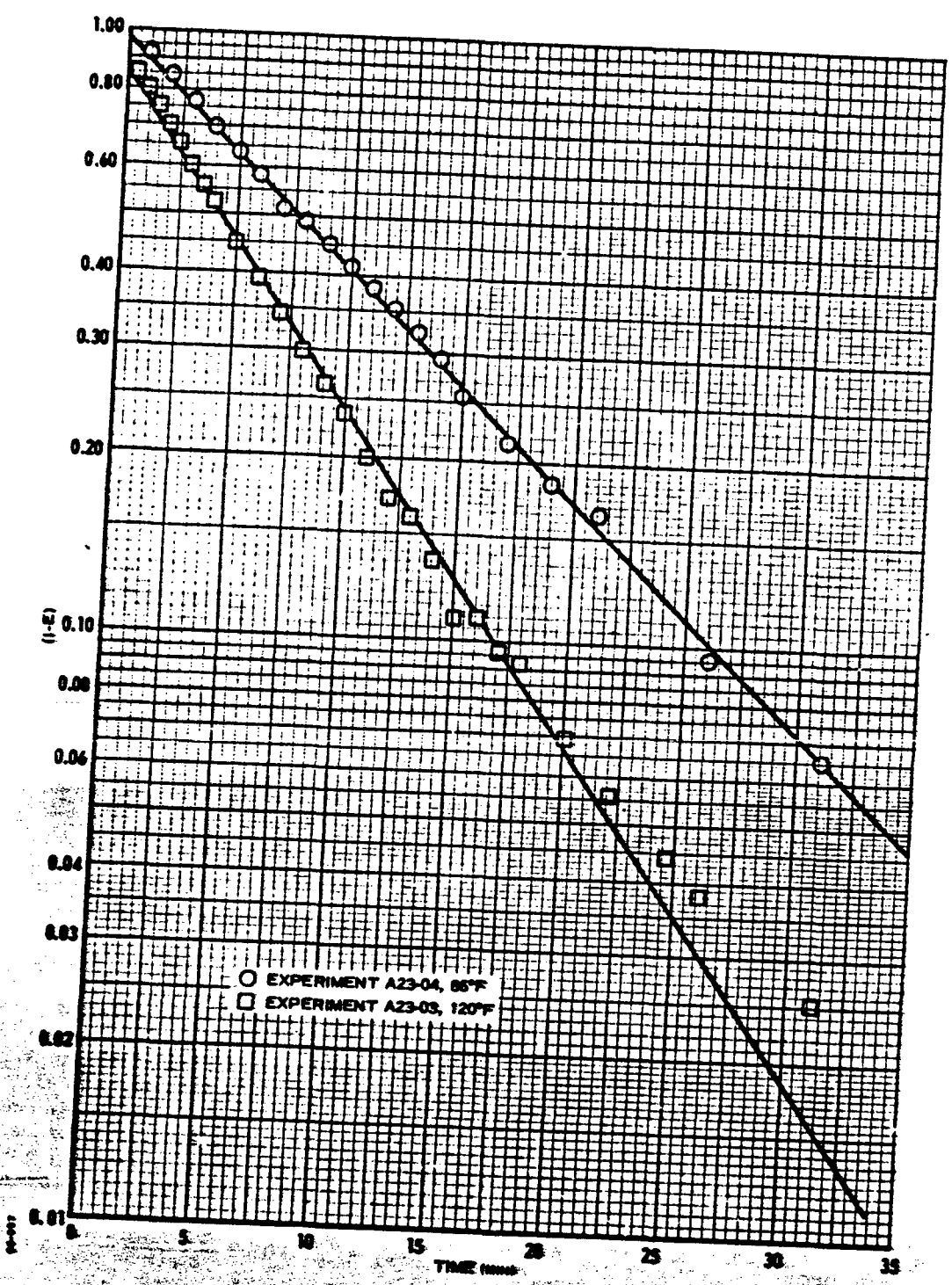


Figure 7 H<sub>2</sub> Sorption Rate Data

TABLE VI  
 DIFFUSION AND SOLUBILITY CONSTANTS FOR H<sub>2</sub>  
 IN PROPELLANT (LPC-1018B WITHOUT LMH-1)

<u>Experiment</u>	<u>Temperature (°F)</u>	<u>D (cm<sup>2</sup>/sec)</u>	<u>S* g H<sub>2</sub> 1 atm-cc binder</u>
A23-04	86	9 x 10 <sup>-6</sup>	1.2 x 10 <sup>-6</sup>
A23-11	90	4.1 x 10 <sup>-6</sup>	1.7 x 10 <sup>-6</sup>
A23-03	120	1.5 x 10 <sup>-5</sup>	1.7 x 10 <sup>-6</sup>
A23-03'	120	1.5 x 10 <sup>-5</sup>	1.4 x 10 <sup>-6</sup>
A23-13	140	2.3 x 10 <sup>-5</sup>	1.7 x 10 <sup>-6</sup>
A23-15	140	2.2 x 10 <sup>-5</sup>	1.9 x 10 <sup>-6</sup>

\* Average value of S in units of  $\frac{\text{cc H}_2 \text{ (STP)}}{\text{1 atm-cc binder}}$  is ~0.02

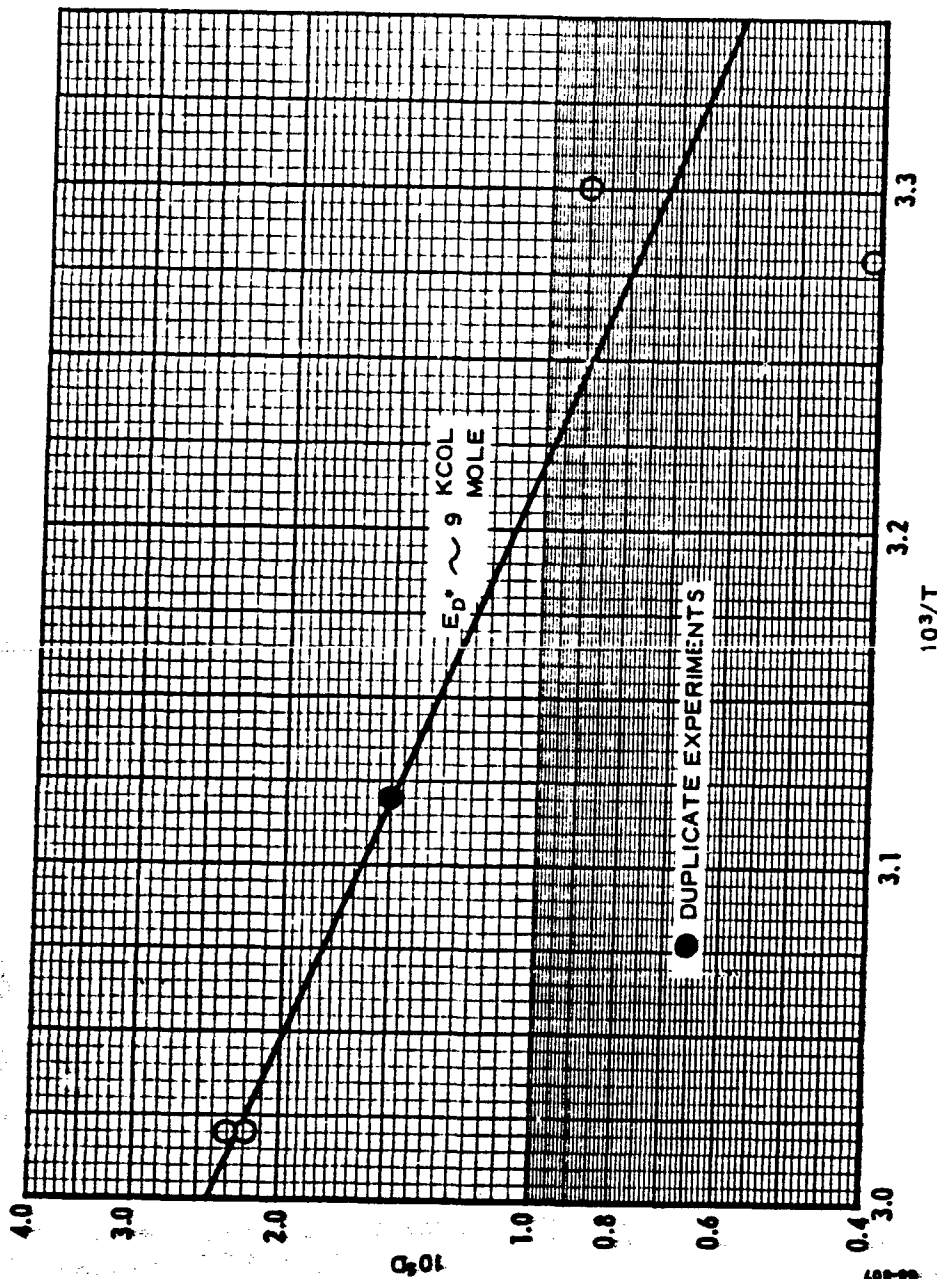


Figure 8 Temperature Dependence of D

(vinyl acetate) (Ref. 6) and  $0.14 \frac{\text{cc H}_2 (\text{STP})}{1 \text{ atm} - \text{cc}}$  in polycarbonates (Ref. 7).

Furthermore, Lawson quotes an estimated solubility for nitrogen in cordite of  $0.05 \frac{\text{cc N}_2 (\text{STP})}{1 \text{ atm} - \text{cc}}$  (Ref. 8).

(U) It should be pointed out that in both experiments at 140°F after the apparent cessation of pressure drop within the sample cell a very slow additional pressure drop was observed to occur over the next several hours. Whether this represents, for example, a second-stage diffusional process, a very slow leak, or a volume change of the lead gasket is not as yet clear. Because of this, however, and the preliminary nature of these first experiments, the present values of D and C must be considered tentative and any detailed discussion of their significance is unwarranted at this time.

(U) b. Gas Generation Rate (LMH-1 Stability)

(U) (1) Experimental Procedure

(U) A technique has been developed wherein the samples (LMH-1 by itself or in propellant) are sealed in H<sub>2</sub>-tight metal tubes which are connected to a thermal conductivity detector through a valving arrangement. After permitting the H<sub>2</sub> to collect in the thermostatted sample tube for known periods, the proper valves are opened, thus allowing a carrier gas (argon) to flush the collected H<sub>2</sub> into the detector. As presently set up, six samples can be studied simultaneously. A bypass loop around the valve assembly permits a continuous flow of carrier gas through the detector and it also contains a valve with a calibrated loop for calibration purposes. In principle, this apparatus is capable of being automated, although this has not yet been done. Considerable difficulties were encountered initially in obtaining a leak-tight system and with spurious liquid peaks but these have been resolved. Each sample tube is checked for tightness with an He leak detector before being placed in an oven and connected to the valve assembly. No significant pressure or flow effects are now observed unless collection times are extended to the point where an appreciable H<sub>2</sub> pressure has been built up. With the present LMH-1 sample (blend 97-131, a blend of Dow pilot-plant lots) for example, collection periods must be limited to only one or two hours at 140°F during the peak of the gas generation rate versus time curve. In general, the technique appears to be very satisfactory, its only serious drawback being the length of time required to purge the sample tubes completely of H<sub>2</sub> (up to one hour) and the consequent slow tailing-off of the detector curve.

(U) (2) Results

(U) Survey experiments were conducted to define the temperature range over which accurate measurements could be made with LMH-1 blend 97-131, within the limitations of reasonable sample size. It appears that 100°F is a practical lower limit, requiring about 5-g LMH-1 or 20-g propellant. For the upper limit 140°F was chosen since this has been the standard temperature for LMH-1 stability measurements, using 0.25 to 0.5-g sample, or 1 to 2-g propellant.

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(U) Measurements of H<sub>2</sub> generation rate as a function of time have been conducted upon LMH-1 blend 97-131 by itself and in propellants (formulation A23-06) at 100 and 140°F. Curves of gas generation rate  $\frac{\mu \ell H_2}{g \text{ LMH-1-hour}}$  versus time are shown in Figures 9 and 10. Numerical integration of the smooth curves drawn through the experimental points in Figures 9 and 10 yields the total amount of H<sub>2</sub> generated versus time, as shown in Figure 11. The more usual percent decomposition versus time curve can be obtained by multiplying the ordinates of Figure 11 by 10<sup>3</sup> (e.g., after 700 hours the pure LMH-1 at 140°F is 48% decomposed). The following points may be made regarding these data.

- (U) ● The rather large time gap in the data for pure LMH-1 at 100°F and 140°F resulted from a breakdown of the thermal detector.
- (U) ● The solid circles in Figure 9 result from measurements made after relatively long collection periods (at least overnight) wherein a sufficient H<sub>2</sub> pressure/flow surge occurred upon opening the valves. The instrument calibration would certainly be invalid under such conditions. Those points do parallel the curve drawn through the points obtained from short (1 to 5 hours) collection times.
- (U) ● The data scatter at 100°F is believed due to rather poor temperature control in that particular oven.
- (U) ● The agreement shown in Figure 11 between these data and those of Dow must be considered excellent in view of the total errors involved.
- (U) ● In agreement with past experience the temperature dependence of gas generation rate is very great. At 100 hours for pure LMH-1 the rate is approximately  $200 \frac{\mu \ell H_2}{hr - g \text{ LMH-1}}$  at 140°F and  $1\frac{1}{2} \frac{\mu \ell H_2}{hr - g \text{ LMH-1}}$  at 100°F; alternatively, it requires approximately 50 and 500 hours to attain 0.1% decomposition at 140 and 100°F, respectively. Calculation of true activation energies would, of course, necessitate kinetic analysis of the data. This has been done only in a very preliminary fashion in view of the limited data.
- (U) ● From the present limited data it appears that the LMH-1 decomposition rate is significantly greater in propellant than it is in the pure state. At 100°F this effect could conceivably be the result of the prior initiation of decomposition during the propellant cure at 115°F. However, this "pre-initiation" should have little influence upon the 140°F behavior, where the influence of propellant appears the greater.

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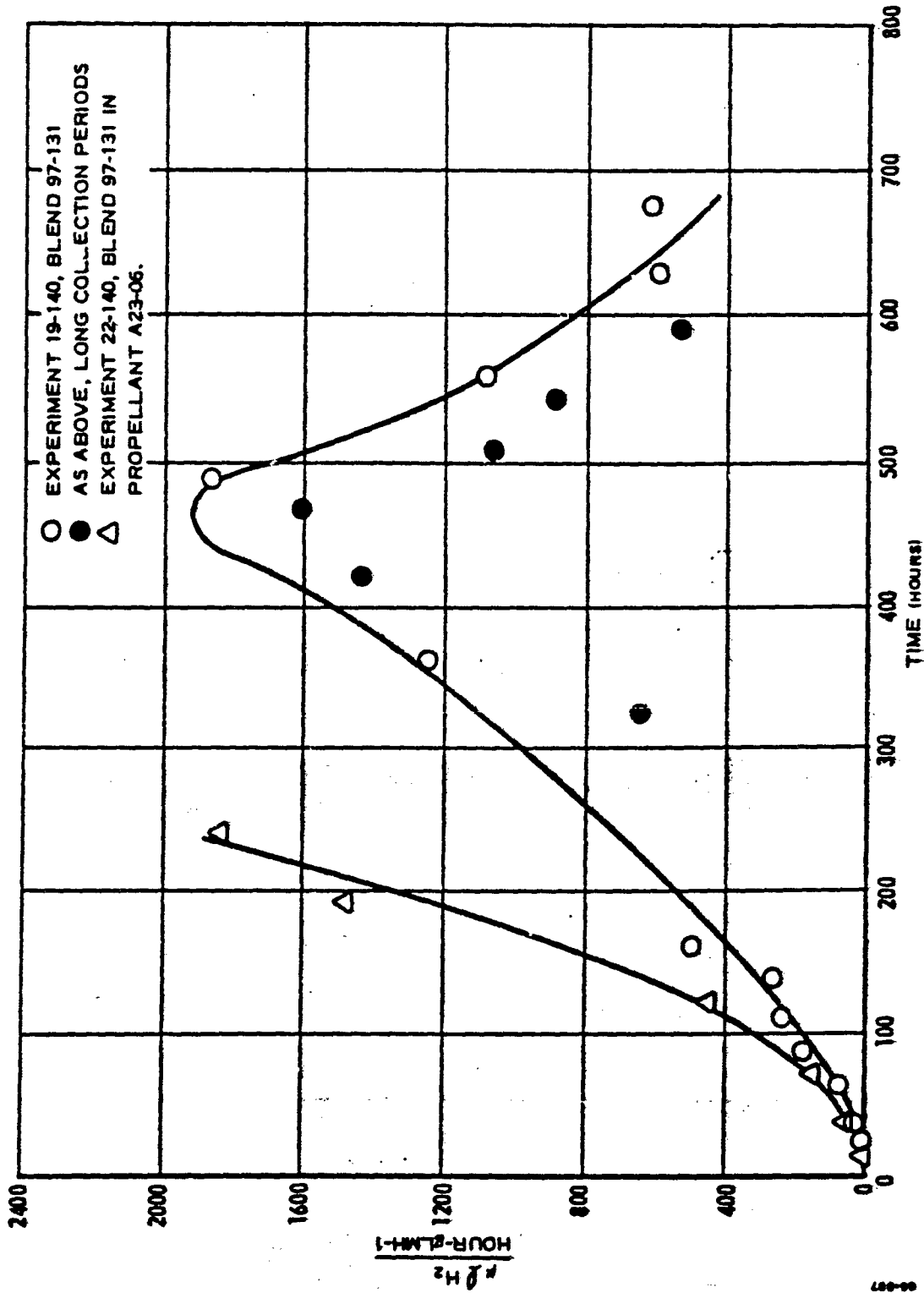


Figure 9 H<sub>2</sub> Generation Rate at 140°F for LMH-1

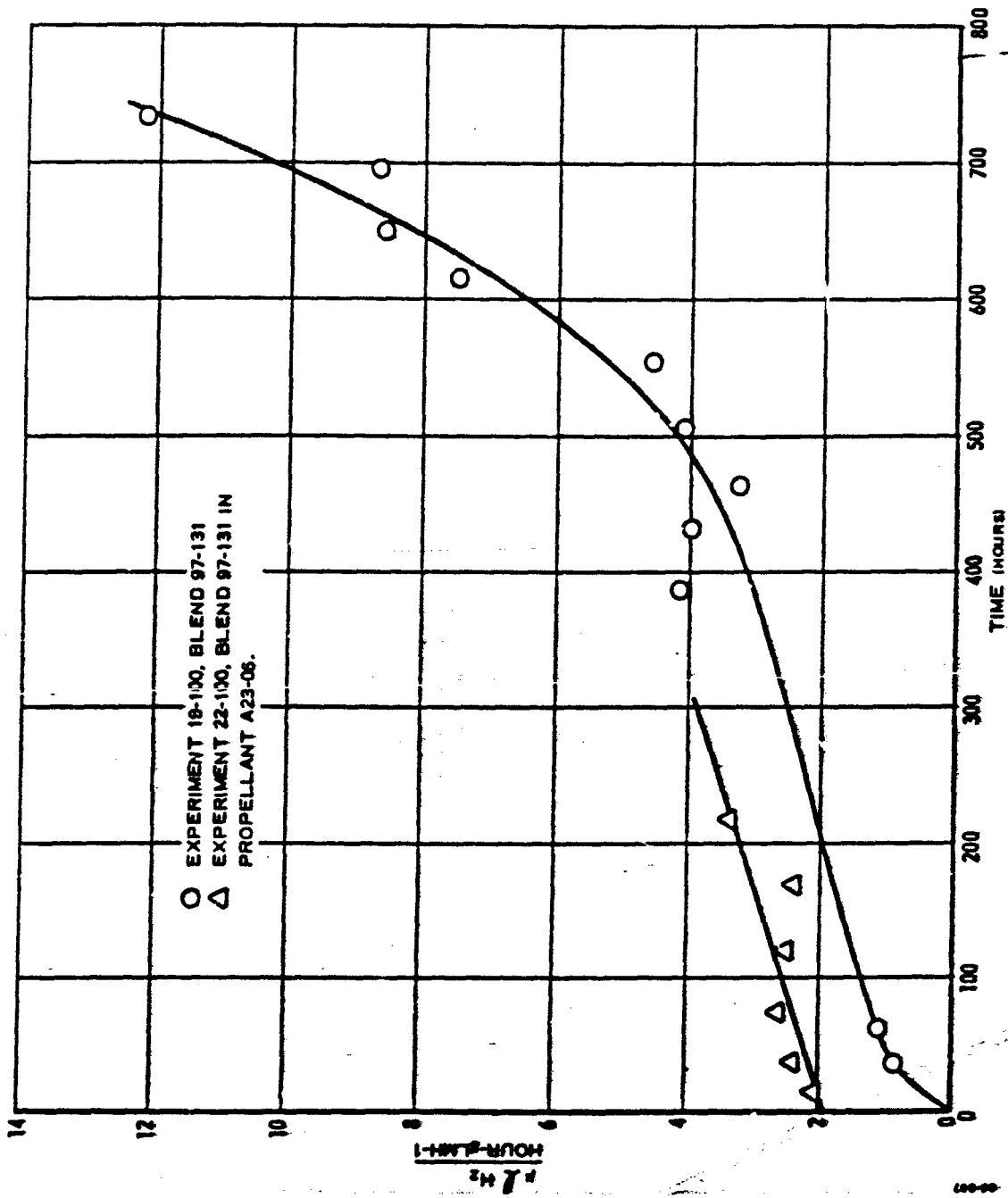


Figure 10 H<sub>2</sub> Generation Rate at 100°F for LMH-1

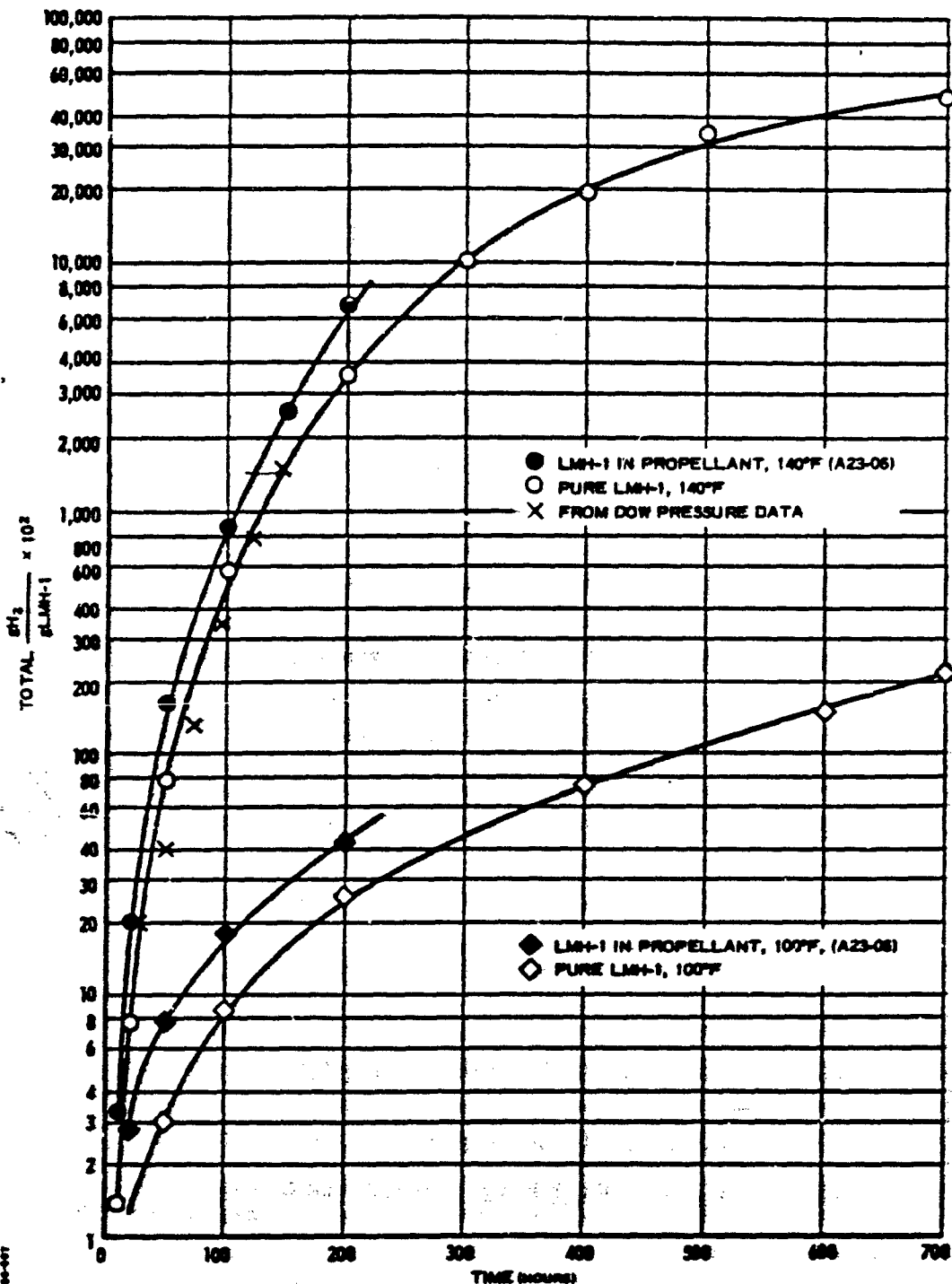


Figure 11 Total H<sub>2</sub> Generation versus Time

- (U) ● It has at times been reported that some lots of LMH-1 are stabilized by propellant ingredients (Ref. 9), in contrast to the present results. In such experiments, however, it is essential that the amount of gas which is dissolved within the total sample (propellant, liquid ingredient, or whatever) at any time is small compared to the total gas evolved up to that time. This implies primarily that the rate of gas diffusion to the sample surface(s) be large compared to the rate of gas generation, i. e., that the gas diffusion constant be not too small and the surface-to-volume ratio of sample be very large. For the experiments discussed herein the propellant was chopped into 1 to 2-mm particles, and for 2-mm cubes it may be calculated that with  $D = 10^{-6}$  cm<sup>2</sup>/sec the observed gas generation rate reaches about 50% of the true value some 5 hours after decomposition begins and about 97% of the true value after 10 hours.\* For a 2-cm cube the comparable times are 500 and 1000 hours. It might be objected that chopping the propellant into small particles would also cut LMH-1 particles, thus exposing fresh LMH-1 surfaces which might then lead to a significantly faster decomposition rate. However, chopping the propellant into 2-mm cubes at most would cut only about 0.1% of the LMH-1 particles.

(U) It had been hoped originally that the gas generation rate could be measured during both cure and storage in order to arrive at an expression for the rate which would exactly describe the complete generation process occurring in propellant surveillance samples. Unfortunately, the above diffusional effect necessitates a thin film (1 to 2 mm) of uncured propellant and it becomes impractical to obtain sufficient sample for accurate gas generation measurements.

- \* Weight of gas lost per cc of sample in which linear diffusion occurs to only one exposed surface is given by

$$G = v_d t - \bar{c}$$

where  $v_d$  represents the true rate of gas generation per cc and  $\bar{c}$  is the average gas concentration (g/cc) within the sample at time  $t$ . Further,

$$\bar{c} = \frac{v_d t^2}{D} \left[ \frac{1}{2} - \frac{32}{\pi^2} e^{-\left(\frac{\pi^2}{4} \frac{Dt}{l^2}\right)} \right]$$

where  $l$  is the maximum diffusion path length and  $D$  the diffusion constant. For the present case with a cube 2 mm on a side,  $l$  may be approximated by 0.66 mm.

(U) c. LMH-1 Propellant Surveillance

(U) (I) Experimental Procedure

(U) Propellant ingredients (for surveillance as well as for diffusion and gas generation measurements) are thoroughly dried and purified. Plasticizers, for example, are passed through a combined alumina-ion exchange bed and subsequently dried in a Rotovap at moderately elevated temperature. The LMH-1 employed to date is a blend of six lots of Dow pilot-plant material which was acrylonitrile-treated at Dow and subsequently retreated at LPC. Weighout of propellant ingredients is conducted in a dry box while mixing and casting are carried out in the humidity-controlled processing room of LPC's High Energy Laboratory. A given propellant preparation is considered satisfactory only when test specimens exhibit at least 98% of theoretical density after cure.

(U) Surveillance specimens are prepared by vacuum casting propellant into lined, cylindrical stainless steel cans. The primary specimens are contained in 1.1-inch ID cans with propellant depths (maximum diffusion path length) of 2, 3, and 6 cm. A minimum of 3 such specimens of each depth are prepared for each surveillance temperature or formulation variation. Such "case-bonded grains" have rather high length-to-diameter ratios and consequently may possess significant cure and thermal shrinkage-induced stresses which would complicate any quantitative interpretation of shelflife solely in terms of the gas generation-diffusion processes. Therefore, a limited number of specimens are also prepared in 4-inch ID cans of 2.5-cm depth. The middle portion of these large diameter specimens should possess very little cure or thermal shrinkage stress and also would be little affected by minor propellant-liner debonding which might greatly alter the diffusion process in the small diameter specimens.

(U) After cure the specimens are stored in ovens with a very slow nitrogen purge to maintain the exposed propellant surfaces essentially at zero hydrogen concentration. Periodically, specimens are removed briefly from the ovens and tested for the presence of voids by determining whether any dilation occurs under vacuum. For this test a specimen is placed in a bell jar with the plunger of a standard thickness gage resting on its top surface; any movement of the plunger upon brief evacuation is taken as evidence for the presence of voids. To minimize possible effects of this evacuation upon the integrity of the specimens, and hence upon measured shelflives, this vacuum dilation test is initially performed upon only one or two of those specimens expected to fail first, e. g., 6-cm and 4-cm deep. After void formation has been observed in this fashion, periodic X-rays of the specimens are obtained to provide a more concrete demonstration of the presence of voids and to assist in determining the locus of failure.

(U) Three formulations are used in this surveillance program. The first of these is a double-base system to be employed primarily as a vehicle for studying the physical chemistry of the gas generation-diffusion-shelflife

process, e. g., correlation of the parameters by means of the mathematical analysis and determination of such detailed factors as the influence of solids content upon diffusion rates, and hence upon shelflife. The basic formulation is designated A23-06 (24.6% PNC, 9.17% TEGDN, 29.5% TMETN, 1.6% stabilizers, 24.6% LMH-1). The other two basic formulations are a UTC polyester system and an ABL crosslinked double-base system. Samples of these latter systems are to be supplied to LPC by UTC and ABL for measurements of gas generation rate, diffusion/solubility constants, and shelflife of laboratory specimens.

(U) (2) Results

(U) Stainless steel surveillance containers were fabricated and sand blasted and the appropriate number shipped to UTC and ABL for the preparation of surveillance specimens from their formulations. The necessary quantity of LMH-1 from blend 97-131 was also shipped to UTC and ABL. Propellant samples are scheduled to be returned to LPC during the month of May.

(U) Table VII presents some preliminary surveillance data obtained at 115°F for propellant A23-06 (LMH-1 blend 97-131) in copper containers and in a plastic container. Although failure times are very short, obvious effects of diffusion path length and exposed surface area can be seen in the longer life of S<sup>1</sup>-2 cm and P compared to that of S<sup>1</sup>-6 cm and S<sup>1</sup>-4 cm. After the 48-hour tests had indicated voids in all metal containers by vacuum dilation but none by X-rays, attempts were made to determine whether the vacuum dilation increased regularly with time in the hope that a correlation might be made between extent of dilation and first appearance of voids by X-ray. No trend in dilation readings became apparent, however, even though an effort was made to reproduce evacuating time and final pressure. In all subsequent experiments, therefore, the vacuum dilation test is to be regarded as qualitative in nature and evacuation times are kept at a minimum (~ 15 seconds) in order to preclude any damages to the specimens.

(U) Surveillance data obtained to date for propellants A23-06 and A23-06C (control propellant with equal volume of aluminum substituted for blend 97-131 LMH-1) in the stainless steel containers are presented in Table VIII. The following comments may be made.

(U) The reason is not clear for the apparently shorter life of these 6 and 4-cm specimens compared with those of Table VII. In general, however, failure occurs too rapidly at 115°F with this formulation and the LMH-1 sample to permit any sensible study of the effects of variables or correlation with parameters. Subsequent measurements with this system will be restricted to 75°F storage or to the use of the more stable LMH-1 samples soon forthcoming from Dow.

(U) As in past experiments, the vacuum dilation test possesses greater sensitivity for voids than does X-ray. Since no other obvious correlation appears, both techniques must continue to be employed. It should be

TABLE VII  
 PRELIMINARY SURVEILLANCE DATA AT 115°F  
 FOR FORMULATION A23-06<sup>(a)</sup>

Sample <sup>(b)</sup>	Time to Observe Voids (Hours) <sup>(c)</sup>	
	Vacuum Dilatation	X-Ray
S'-6 cm	> 0; < 24	> 48; < 600
S'-4 cm	> 0; < 24	> 48; < 600
S'-2 cm	> 24; < 48	> 48; < 600
P	> 48	> 48; < 600

(a) Propellant density after cure in P container 98% of theoretical.

(b) S' samples in copper cans 1.0-inch ID and designated depth of propellant. P sample in polyethylene container, 3.8-cm diameter and 5-cm deep.

(c) Time beyond 17-hour cure at 115°F.

TABLE VIII

## SURVEILLANCE DATA AT 115°F AND 75°F FOR FORMULATION A23-06(a)

Sample (b)	Temperature (°F)	Time to Observe Voids (Hours)(c,d)	
		Vacuum Dilation	X-Ray
S-6 cm	115	45-115	45-115
S-4 cm	115	45-115	45-115
S-2 cm	115	45-115	> 200
L-2.5 cm	115	45-115	> 200(e)
Controls (A23-06C)	115	> 200	> 200
S-6 cm	75	139	146
S-4 cm	75	> 220	> 220
S-2 cm	75	> 220	> 220
L-2.5 cm	75	--	> 220
Controls (A23-06C)	75	> 220	> 220

(a) Propellant density 100% of theoretical after 16-hour cure at 115°F in small plastic container.

(b) S samples in stainless cans, 1.1-inch ID and designated depth of propellant.  
L samples in stainless cans, 4-inch ID and designated depth of propellant.  
Control samples prepared in S-6 cm, 4 cm, and 2 cm forms.

(c) Time beyond 16-hour cure at 115°F.

(d) Initial void formation in S generally appears approximately  $\frac{1}{3}$  of distance up from bottom and  $\frac{2}{3}$  of radial distance from center of cylinder. Shortly thereafter, perhaps simultaneously, the gas pressure at the bottom of the containers becomes great enough to break the liner-propellant bond and begins to push the propellant as a plug out of the can.

(e) L sample at 115°F actually contained voids near side wall at 115 hours but none in center. However, above plug movement was also occurring.

pointed out that holes  $\frac{1}{32}$ ,  $\frac{1}{16}$  and  $\frac{1}{8}$  inch in diameter and depth were drilled into the top surface of some of the control samples. Top-view X-rays showed the  $\frac{1}{16}$  and  $\frac{1}{8}$ -inch holes but not the  $\frac{1}{32}$ -inch.

(U) The observed upward "plug" movement of the propellant must be a consequence of the combined effects of the presence of maximum gas concentration at the bottom, of maximum cure and thermally-induced stresses in that region, and of rather poor liner-propellant bonding. Since this mode of failure creates new paths for diffusional losses of hydrogen, the interpretation of failure time and mode becomes cloudy for the central region of the L (4-inch diameter) samples, where cure and thermally induced stresses should be very small. It may be desirable, therefore, in the future to cure large diameter specimens of that depth, cut out the central portion and put it into S-4-cm containers.

(U) From the composition of propellant A23-06 it can be calculated that a hydrogen solubility of  $2 \times 10^{-6} \frac{\text{g H}_2}{\text{cc binder}}$  (c. f., Table VI) requires a total hydrogen generation of  $4 \times 10^{-6} \frac{\text{total g H}_2}{\text{g LMH-l}}$ . This in turn can be seen from Figure 11 to require about 10 hours at  $140^\circ\text{F}$  and 25 hours at  $100^\circ\text{F}$  in the absence of diffusional losses. Plotting the logarithm of these times versus reciprocal absolute temperature yields a first approximation the corresponding "saturation times" at  $115^\circ\text{F}$  and  $75^\circ\text{F}$  of 17 and 50 hours, respectively. These last numbers are both approximately  $\frac{1}{3}$  the observed shelflife of the 6-cm deep surveillance specimens. Considering the rather preliminary nature of the various data and the fact that some diffusional losses will have occurred in the surveillance specimens\*, such agreement at this stage must be considered encouraging.

(U) Exact analysis of surveillance data with the diffusion-gas generation equations necessitates having an analytic function for gas generation rate at the surveillance temperatures plus subsequent computer calculations of gas concentration as a function of time and geometry. In view of the preliminary status of all the data, such analyses are not yet warranted.

\* Diffusion may be neglected in general when  $Dt/l^2 < 0.05$ . At  $115^\circ\text{F}$  for a D of  $1 \times 10^{-9} \text{ cm}^2/\text{sec}$ , t of 150 hours, and l of 6 cm,  $Dt/l^2 = 0.15$ . At  $75^\circ\text{F}$  for a D of  $5 \times 10^{-10} \text{ cm}^2/\text{sec}$ , t of 50 hours and l of 6 cm,  $Dt/l^2 = 0.25$ . Thus, within our certainty in D some amount of diffusion almost certainly has taken place.

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SECTION IV  
BERYLLIUM HEALTH PHYSICS PROGRAM

(U) A summary of all monitoring sample data taken during February, March, and April is given in Table IX.

(U) During this period, air monitors in Building 119A laboratory were run during all working hours, the filters being analyzed for Be every 1, 2 or 3 weeks, depending upon the work load in the laboratory. During low work periods the monitors were allowed to run for a longer time period between analyses to enhance the detection of possible contamination.

(U) The strand burner equipment and operation (Building 114) were modified to accommodate Be propellant strand burning. An absolute filter was installed in the hood exhaust system with a corresponding increase in air flow out of the exhaust. The bomb vent was also adapted with an absolute filter to minimize air contamination. The burning procedure was modified to maintain surface contamination within the hood.

(U) Two motors containing beryllium hydride were tested at LPC's Potrero Production and Test Facility during this period. On April 28th, a 20-pound motor overpressurized and the propellant burned slowly out in the open<sup>1</sup>. Considerable air contamination was detected downwind from the test site, but the contamination was not considered serious because beryllium motors are tested only when the wind carries possible contamination away from personnel areas and into the unused portion of LPC's Potrero facility.

<sup>1</sup>Although this motor firing was conducted under a different program, all monitoring data are reported here.

TABLE IX  
BERYLLIUM MONITORING DATA

<u>Laboratory, Building 119A</u>	<u>Feb 28 - Mar 4</u> (5 days)	<u>Feb 28 - Mar 4</u> (6 days)	<u>Mar 15 - Mar 21</u> (5 days)	<u>Mar 22 - Apr 17</u> (18 days)	<u>Apr 18 - May 8</u> (15 days)
<u>Sample Station No. 1</u>					
m <sup>3</sup> air sampled	30	36	30	108	90
µg Be	3.8	nil	nil	1.4	2.0
µg Be/m <sup>3</sup>	0.13	--	--	0.02	0.02
<u>Sample Station No. 2</u>					
m <sup>3</sup> air sampled	30	36	30	108	90
µg Be	<0.1	nil	nil	nil	nil
µg Be/m <sup>3</sup>	nil	--	--	--	--
<u>Sample Station No. 3</u>					
m <sup>3</sup> air sampled	30	36	30	108	90
µg Be	<0.1	nil	nil	1.0	>50
µg Be/m <sup>3</sup>	nil	--	--	0.01	>0.55
<u>Sample Station No. 4</u>					
m <sup>3</sup> air sampled	30	36	30	108	90
µg Be	0.6	nil	nil	1.2	nil
µg Be/m <sup>3</sup>	0.02	--	--	0.01	--
<u>Sample Station No. 5</u>					
m <sup>3</sup> air sampled	30	36	30	108	90
µg Be	nil	nil	nil	nil	nil
µg Be/m <sup>3</sup>	--	--	--	--	--
<u>Sample Station No. 6</u>					
m <sup>3</sup> air sampled	30	36	30	108	90
µg Be	nil	nil	nil	3.6	nil
µg Be/m <sup>3</sup>	--	--	--	0.03	--

Processing Facility, Building 119

<u>Mix No.</u>	<u>217/218</u>		
	<u>April 21</u>		
<u>Date</u>	<u>m<sup>3</sup> air</u>	<u>µg Be</u>	<u>µg Be/m<sup>3</sup></u>
<u>Processing Room</u>			
Station 1 - upper head	4.0	nil	--
Station 2 - lower head	4.0	3.3	0.82
<u>Control Room</u>			
Station 3	4.0	nil	--

Strand Burning, Building 114

<u>Date</u>	<u>April 22</u>			<u>May 6</u>		
	<u>m<sup>3</sup> air</u>	<u>µg Be</u>	<u>µg Be/m<sup>3</sup></u>	<u>m<sup>3</sup> air</u>	<u>µg Be</u>	<u>µg Be/m<sup>3</sup></u>
Head	34	>50	>1.5	34	1.2	0.04
Bomb exhaust	34	nil	--	34	8.3	0.24

Potrero Open Air Firings, Beryllium Motors

<u>Date</u>	<u>April 28</u>		<u>May 3</u>	
	<u>10 minutes</u>		<u>5 minutes</u>	
<u>Sample Time</u>	<u>m<sup>3</sup> air</u>	<u>µg Be</u>	<u>m<sup>3</sup> air</u>	<u>µg Be</u>
<u>Crosswind Sample</u>				
m <sup>3</sup> air		5.6		2.8
µg Be		5.8		nil
µg Be/m <sup>3</sup>		0.68		--
<u>Downwind Sample</u>				
m <sup>3</sup> air		5.6		2.8
µg Be		>50		6.2
µg Be/m <sup>3</sup>		>9.0		2.2

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