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AFRPL-TR-67-200

THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER FOR HIGH ENERGY SOLID PROPELLANTS

by

D. E. Johnson, R. H. Quacchia, and A. J. DiMilo
Aerojet-General Corporation
Solid Propellant Operations
Sacramento, California

July 1967

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Air Force Rocket Propulsion Laboratory
Research and Technology Operations
Edwards, California
Air Force Systems Command
United States Air Force

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W.O. 1030

FOREWORD

This technical report was prepared under Contract No. AF 04(611)-11419 as partial fulfillment of the requirements of Project 3418 of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. The work reported was done in the Advanced Propellants Department of the Aerojet-General Corporation, Sacramento, California. This report was designated Aerojet-General Corporation Report 1030-81Q-5 and covers the results of work done during the interval 14 March to 13 June 1967. The project was a follow-on to the project completed under Contract AF 04(611)-10386, the results of which are reported in Report No. AFRPL-TR-66-40. Phases One to Three of this program have been completed and the results (including Phase Four results) are reported in AFRPL-TR-67-158. This report reports on Phases Four and Five. This project was monitored by Mr. Robert Corley.

Acknowledgement is made to the following persons who have contributed materially to the work performed during this period: J. L. Humphreys and T. F. Manning, Associate Chemists, F. H. Davidson, Liaison Engineer, Mechanical Properties Laboratories; and at the General Tire and Rubber Company to R. G. Chase, Technical Assistant to the Technical Coordinator, Research and Development.

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This technical report has been reviewed and is approved.

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ABSTRACT

The acquisition and characterization of hydroxy terminated Telagen S was continued. The functionalities by molecular weight to equivalent weight ratio continue to be below 1.7, but cured binders indicated functionalities in excess of 1.85. The equivalent weights determined by reaction with n-butyl isocyanate were within 2% of values obtained by the manufacturer of the prepolymers. Thin-layer chromatography was used to demonstrate the presence of nonfunctional and monofunctional fractions in Telagen S. Considerable effort was devoted to improving the low temperature properties which may be caused by the high concentration of polar groups in the saturated binder. The use of substitutes for CTI and catalysts studies to achieve room temperature cures were also pursued. PAPI gave good cures with Telagen S, but 1,2,6-hexanetriol has been eliminated as a substitute for CTI. The processing of Telagen S propellants at room temperature is apparently limited more by prepolymer viscosity than by cure rate. Burning rate studies indicate very similar rates for saturated and unsaturated polybutadiene propellants. Cyclic imides have been eliminated as a cure system for advanced oxidizers because of very slow reaction rate with hydroxy groups. The more rapid reacting acid anhydrides have more potential in this area. After two months of aging at 170°F and at relative humidities in excess of 25%, both Telagen S and Minuteman Wing VI Second Stage propellants are degraded.

TABLE OF CONTENTS

Page

TABLES

TABLE OF CONTENTS (Cont)

FIGURES

GLOSSARY

Ansul Ether 181	Tetraethylene glycol dimethyl ether
AR	Burning rate modifier, Aerojet-General proprietary compound
C_1 and C_2	Mooney-Rivlin Constants
CoAA	Cobalt acetylacetonate
CTI	Triisocyanate, proprietary item of the Aerojet-General Corporation
DOS	Dioctyl sebacate, product of the Deecy Products Division, Reichold Chemicals, Inc.
E_o	Initial uniaxial modulus
FeAA	Ferric acetylacetonate
GTRO	Glycerol triricinoleate
HAA	Acetylacetone
HDI	Hexamethylene diisocyanate
IDP	Isodecyl Pelargonate, product of Emery Industries, Inc.
kg/cm^2	Kilograms per square centimeter
meq/gm	Milliequivalents per gram
Methyl Nadic Imide	Imide of methylbicyclohepta-5-ene-2,3-dicarboxylic acid
mm/gm	Millimoles per gram
Nacconate H-12	Bis(4-isocyanatocyclohexyl)methane, product of the Allied Chemical Corporation
Niax D-22	Dibutyltin dilaurate, product of the Union Carbide Co.
PAPI	Polyphenyl polyisocyanate, product of the CPR Division, Upjohn Company
psi	Pounds per square inch

GLOSSARY (Cont)

T-18	Stannous type catalyst, product of Metal & Thermit Corp.
Telagen S	Functionally-terminated hydrogenated polybutadiene, product of The General Tire and Rubber Company
TDI	2,4-Toluene diisocyanate
Thermalite 25	Complex organotin compound, product of Metal & Thermit Corp.
v_2	Gel fraction
VPO	Vapor phase osmometer
ϵ_b	Uniaxial strain at break
ϵ_m	Maximum uniaxial strain
σ_b	Uniaxial break stress
σ_m	Uniaxial maximum stress

AFRPL-TR-67-200

THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER FOR HIGH ENERGY SOLID PROPELLANTS

I. INTRODUCTION

This is the fifth Quarterly Technical Report submitted in partial fulfillment of the requirements of Contract AF 04(611)-11419. The report covers the period 14 March through 13 June 1967.

II. OBJECTIVE

The objective of this program is to further develop and evaluate a solid propellant binder system specifically to meet the most rigid demands of advanced, high performance solid rocket motors. The solid propellant binder system consists of an isocyanate-cured, saturated hydrocarbon prepolymer developed and evaluated under Contract AF 04(611)-10386. Further development and evaluation will involve propellant optimization, testing of curatives for room temperature cures, replacing CTI, attaining better low temperature properties, determining the effect of burning rate modifiers, adaptation to advanced fuels and oxidizers, formulations containing both advanced fuels and oxidizers, and a study of environmental stability.

III. SUMMARY

A. Both a secondary and primary hydroxy terminated Telagen S have been received and characterized. The secondary hydroxy prepolymer, Lot 242AM-161AHR, has a functionality (MW:EW) of 1.49 and an actual functionality less than that of Lot 148AH and very similar to that of 158H. The primary hydroxy prepolymer, Lot 242AM-168H, has a functionality (MW:EW) of 1.63 and an actual functionality higher than that of 161AHR.

B. The equivalent weights of the prepolymers determined at Aerojet check within 2% of values determined at The General Tire and Rubber Company. The Aerojet determination involves reaction of the prepolymer with n-butyl isocyanate.

C. While Prepolymer 148AH cured more rapidly than either 158H or 161AHR, the amounts of isocyanate consumed by all three polymers in 18 hours were very similar. This leads to the conclusion that the faster cure rate of Prepolymer 148AH is due to a shorter gel time resulting from a higher functionality.

D. Hydroxy and carboxy terminated Telagen S were fractionated by thin-layer chromatography by silica gel on glass fibers. Non-acidic, moderately acidic, and strongly acidic fractions were obtained from the carboxy terminated prepolymer.

E. Since the low temperature behavior of Telagen S binders may be determined by the high carbamate content, low molecular weight diols have been added to Telagen S to further increase the carbamate content of binders and to determine its effect on the low temperature behavior. The first attempt with 1,4-dimethylolcyclohexane was not successful because the cyclohexane derivative was not compatible with Telagen S. While octanediol and decanediol were also incompatible, hexanediol and pentanediol were compatible. Mechanical data are not yet available.

F. PAPI and 1,2,6-hexanetriol have been used as replacements for CTI in Telagen S binders and propellants. While PAPI looks promising and is being investigated further, the hexanetriol shows no promise as a replacement for CTI. Glycerol triricinoleate is also being tried as a replacement for CTI.

G. Studies indicate that FeAA and Niax D-22 are active enough catalysts to cure Telagen S propellants at room temperature, but propellant studies show that the viscosity of the prepolymer affects the castability of the propellant and becomes the limiting factor in low temperature (< 110°F) processing.

H. Propellant studies have continued to verify and expand the results of binder studies. The best cure stoichiometry for propellants seems to be an NCO to OH ratio of 1.02 although the cure time is increased at this ratio.

I. Burning rates of propellants with saturated and unsaturated prepolymers are very similar. The pressure exponent increases from 0.4 to 0.9 between 600 and 1000 psia.

J. Acid anhydrides were shown to react rapidly and stoichiometrically with hydroxy functional groups in the presence of HAP. The reaction rate was slowest with the phthalic anhydride and the potential of this type of agent for curing HAP propellants is being pursued.

K. Cyclic imides were investigated as potential curing agents for HAP. Their rate of reaction with hydroxyl groups was very slow and was not catalyzed by HAP. This curing system has been abandoned because no method of increasing the reaction rate was available.

L. The synthesis of an azetidine (4-membered, nitrogen-containing ring system) derivative was initiated. The material will be investigated as a curing system for advanced oxidizers. Azetidines should be less prone to side reactions than aziridines.

M. After two months of aging, both Telagen S and Minuteman Wing VI Second Stage propellants show no degradation at -75, 0, and 77°F. At 170°F both types degraded seriously, especially under the influence of humidity.

IV. TECHNICAL DISCUSSION

A. PREPOLYMER

1. Material Acquisition

A batch of hydroxy terminated Telagen S requested for use in Phase IV of this program was delivered and evaluated. The properties of the material (Lot 242AM-161AHR) are shown in Table I.

Table I

PROPERTIES OF HYDROXY TERMINATED TELAGEN S

(Lot 242AM-161AHR)

Molecular Weight (VPO)	1670
Hydroxyl Content, meq/g	0.895
Equivalent Weight	1117
Functionality[a]	1.49
Unsaturation, mm/g	0.4
Brookfield Viscosity, poises at 25°C	132
Water Content, %	0.01
Volatiles, %	0.4
Sulfated Ash, %	0.04
Antioxidant, %	0.36

---

[a] Molecular weight/equivalent weight

Another batch of hydroxy (primary) terminated Telagen S, requested for use in Phase V of this program, was received and is being evaluated for a room temperature cured propellant. The primary hydroxyl groups will increase the rate of the cure reaction at lower temperatures. The properties of the material (Lot No. 242AM-168H) are shown in Table II.

Table II

PROPERTIES OF HYDROXY TERMINATED TELAGEN S
(Lot No. 242AM-168H)

Molecular Weight (VPO)	1800
Hydroxyl Content, meq/gm	0.904
Equivalent Weight	1108
Functionality[a]	1.63
Unsaturation, mm/gm	1.30
Brookfield Viscosity, poises at 25°C	159
Water Content, %	0.01
Volatiles, %	0.14
Sulfated Ash, %	0.07
Antioxidant, %	0.20

---

[a] Molecular weight/equivalent weight

The equivalent weight, determined by reaction with n-butyl isocyanate, was 1080.

B. PHASE V

1. Task One

a. Introduction

Task One will involve prepolymer characterization, improved low temperature properties, curing agent substitutes for CTI, the effects of plasticizer and burning rate modifiers, room temperature curing and boron-workhorse binder systems. A propellant designed for low temperature capability, a propellant cured at room temperature, and a propellant with a CTI replacement will be prepared for long-term aging.

b. Prepolymer Characterization

1) Equivalent Weights of Prepolymers

The equivalent weights of some prepolymers were examined using two methods. One involves varying the ratios of isocyanate (CTI) to prepolymers and the other method, used successfully by Dr. A.E. Oberth, involves the reaction of the prepolymer with butyl isocyanate.

The prepolymer 158H was cured with various ratios of prepolymer to CTI, (Figure 1). From the variation of the gel fractions with the prepolymer to CTI ratios, the equivalent weight of Prepolymer 158H was deduced to be slightly higher than 1130. Two binders, Nos. 139 and 140, Table IV, were prepared using 1190 as the equivalent weight and these were found to be softer than Nos. 133 and 134 which were based on an equivalent weight of 1132. This confirmed the vendor's equivalent weight of 1130.

While the above method is practical for determining equivalent weights under reaction conditions, the method is time consuming and not as accurate as other methods. Equivalent weights were obtained by reacting the polymer overnight with excess n-butyl isocyanate in toluene at room temperature and then determining the unreacted isocyanate. Controls were run to correct for isocyanate disappearance through side reactions. The data for various prepolymers are shown in Table III.

Table III

EQUIVALENT WEIGHTS OF TELAGEN S BY REACTION WITH C_4H_9NCO

Prepolymer Lot No.	Equivalent Weight Vendor	 C_4H_9NCO Method
I-47.1	980	960
148AH	1100	1075
158H	1130	1110
161AHR	1120	1110
161AHR	1120	1115
168H	1108	1080

Although all of the equivalent weights were slightly lower, the values are within 2% of the vendor analyses.

2) Cure Rate

During the preparation of binders, it was observed that prepolymer 148AH promoted faster cures than did other prepolymers. To

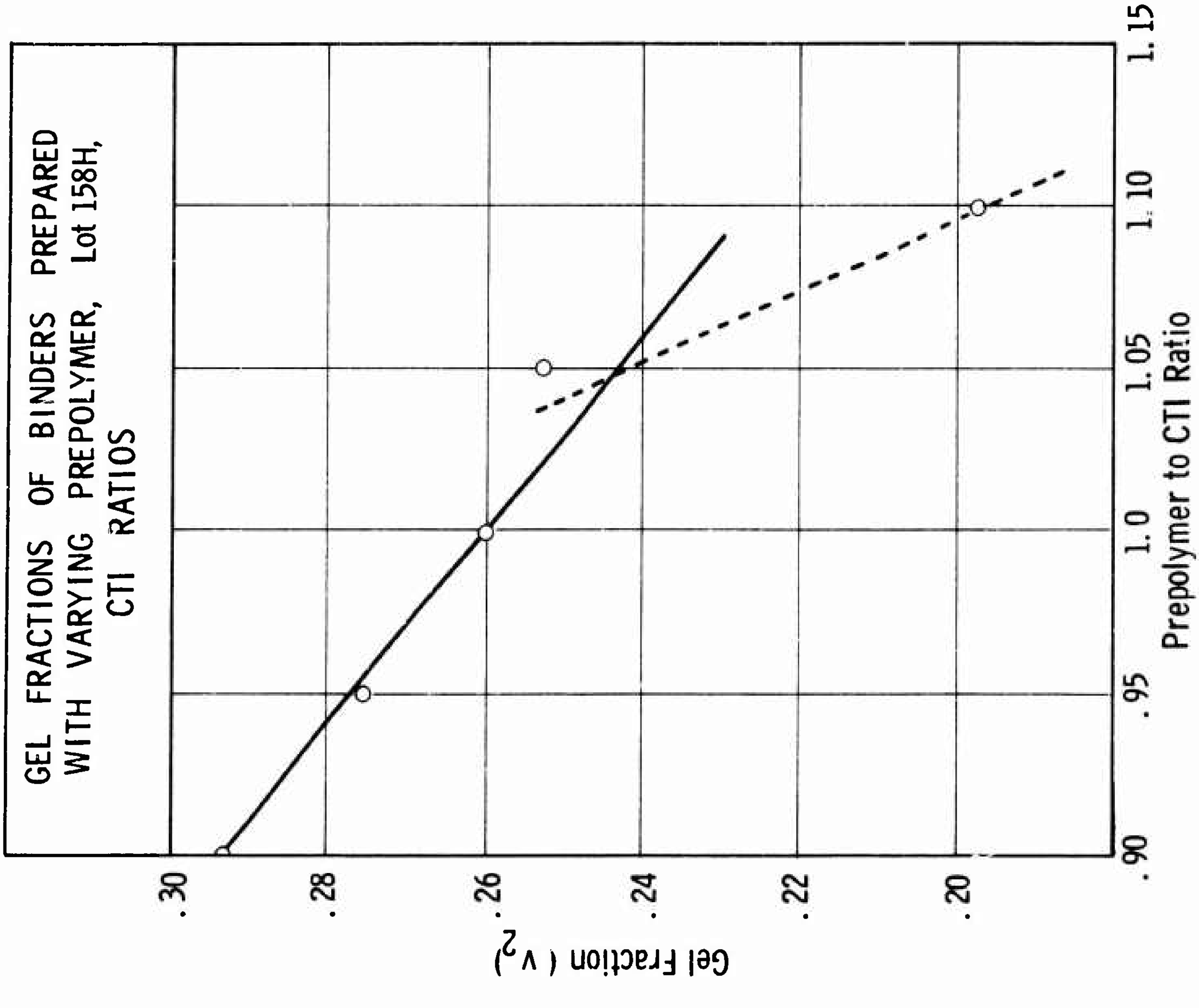
GEL FRACTIONS OF BINDERS PREPARED WITH VARYING PREPOLYMER, Lot 158H, CTI RATIOS

Figure 1

test this observation, 0.2N solutions of various prepolymers and phenyl isocyanate were made in toluene and the ensuing reaction was followed at room temperature by analysis for unreacted isocyanate. In 18 hours, 28.3% of the isocyanate remained in the solution containing Prepolymer 148AH. With Prepolymer 158H, 29.8% isocyanate remained and with Prepolymer 161AHR, 30.8% remained under the same conditions. These differences are not significant, however, a precipitate developed in 148AH and 158H which was identified as s-diphenylurea (carbanilide).

n-Butyl isocyanate was used in similar experiments and the results were similar except that this isocyanate reacted about 20 times slower. Definite color changes were observed during the first 3 days of these runs. The solution containing prepolymer 148AH became deep red-orange; 158H, a dark orange; and 161AHR remained straw colored.

The conclusion is that Prepolymer 148AH does not react more rapidly. The faster cure rate is the result of the higher functionality of 148AH which causes a shortening of the gel time. More definitive studies are in progress.

3) Prepolymer Chromatography

Gel determinations done under the present program and the functionality studies done by Esso Research and Engineering Company(1), indicate a significant amount of non- and/or monofunctional materials in these prepolymers. Both carboxy- and hydroxy-terminated prepolymers were fractionated by thin layer chromatography using basic silica gel on glass fibers. n-Hexane was used initially as the developing solvent and iodine as the indicator. The composition of these fractions was not determined.

Further work was done with the carboxy-terminated prepolymer, 148DH3, because bromcresol green could be used as an indicator for the functional groups. With ethyl acetate a non-acidic fraction (brown in presence of I_2; not affected by bromcresol green) was separated from the acidic fraction (Figure 2). A mixed benzene, ethanol, glacial acetic acid (90:16:4) solvent further separated the acid fraction into two fractions one of which, because of lower response to bromcresol green, was judged less acidic than the other which was not moved on the paper. It is possible that the less acidic material may be monofunctional but this is conjecture. Quantitative estimates of the amounts of each fraction could not be made. The technique is a rapid method of characterizing prepolymers, and it may, possibly, be developed as a semiquantitative method. Emphasis on other phases of this program has temporarily halted the work in this area.

c. Low Temperature Properties

The low temperature capabilities of Telagen S propellants have been mariginal up to the present time. Most recent evidence indicates

THIN-LAYER CHROMATOGRAM OF CARBOXY-TERMINATED TELAGEN S (Lot 148 DH3)

Solvent: Benzene-Ethanol-Acetic Acid (90:16:4)

Solvent: Ethyl Acetate

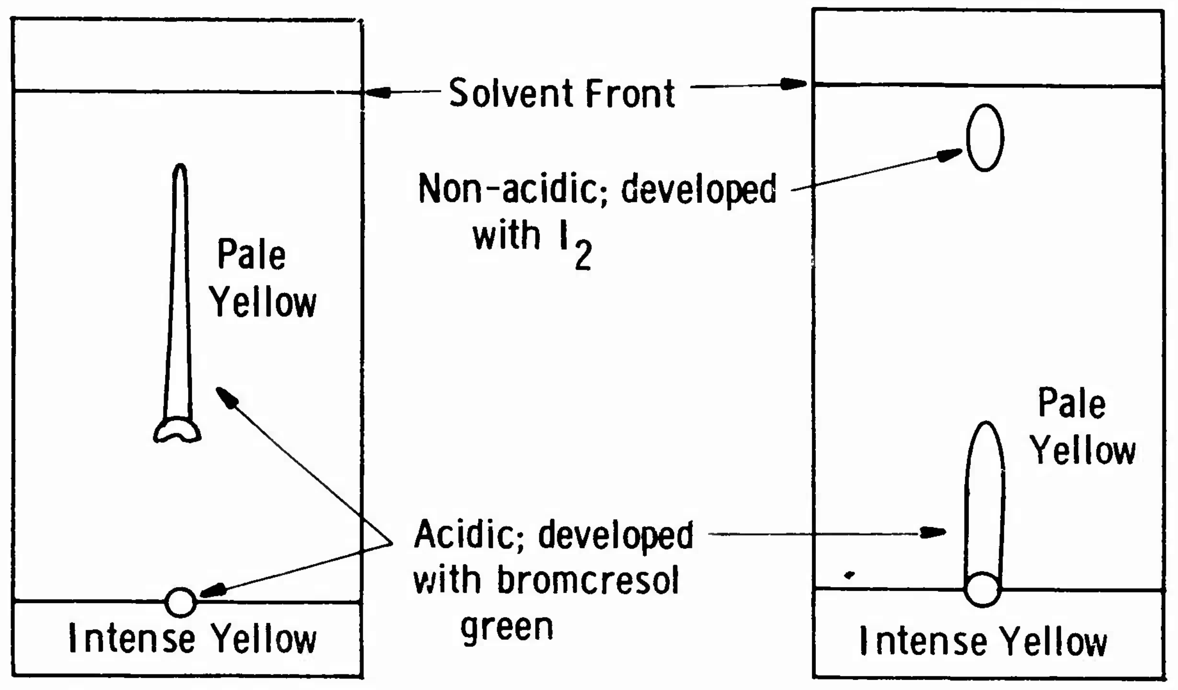

Figure 2

that motor grains of Telagen S propellants can be cycled to -40°F without cracking(2)(3). An improvement of this capability is being sought.

Previous work(2)(4) has indicated that crystallization of the prepolymer or binder is not a cause of the low temperature limitations. It is postulated that the high concentration of urethane groups caused by the use of a low molecular weight prepolymer is setting a limit on the low temperature properties. This effect is illustrated by the data for unsaturated prepolymers (Tables IV and V) which were obtained by Dr. Oberth and H. Michigian on Aerojet-General sponsored programs. The main effort is being devoted to substantiating this hypothesis for Telagen S.

Table IV

EFFECT OF PREPOLYMER[a] EQUIVALENT WEIGHTS ON THE LOW TEMPERATURE MODULI OF BINDERS

Prepolymer Equiv. Wt.	Initial Modulus, psi, at		
	77°F	-40°F	-75°F
3100	60	250	280
2833	15	60	110
2700	28	80	120
2400	84	250	270
1038	19	190	3950

---

[a] Unsaturated, hydroxy terminated polybutadienes

Table V

EFFECT OF PREPOLYMER[a] MOLECULAR WEIGHTS ON THE LOW TEMPERATURE MODULI OF PROPELLANTS

Prepolymer Molecular Wt.	Propellant Modulus at -75°F, psi
2000	11000
5000	8800

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[a] Unsaturated, hydroxy terminated polybutadienes

For this purpose, a series of prepolymers of molecular weights ranging from 1000 to 4000 has been ordered from The General Tire and Rubber Company. While these materials were being prepared, attempts were made to lower the average molecular weight of existing prepolymers by the addition of low molecular weight diols.

Binders were prepared using 1,4-dimethylolcyclohexane as part of the prepolymer in Binders 130 and 131 (Table VI) in order to increase the concentration of urethane linkages. The binders contained 1 and 5% of the low molecular diol, respectively, and had calculated crosslink densities of 10^{-5} and 10^{-4} mole branch points/gm. The gel fraction of No. 130, 0.050, was lower than is usual for this type of formulation and may indicate a poor cure. Binder No. 130 has approximately 15% more urethane linkages per gram than Binder No. 76.

1,4-Dimethylolcyclohexane is only partially soluble in these systems and this causes doubts as to the extent of cure. When 5% diol was used, many solid particles were present in the binder indicating a large amount of insolubles. The gel fractions of toluene swollen samples were high, but the effectiveness of toluene as a solvent for this system is not known.

Binders were prepared with hexanediol and pentanediol but octanediol and decanediol were incompatible with the prepolymer. Test results are not yet available.

d. Replacement of CTI

PAPI (polymethylene polyphenylisocyanate) and the crosslinker hexanetriol were studied as possible replacements for CTI. These materials were used because of their availability, but other crosslinkers will also be investigated.

Binders cured with PAPI and HDI are opaque, indicating PAPI was not completely soluble without a plasticizer.

Binders Nos. 136 to 138 and 141 (Table VI) contain varying ratios of PAPI and HDI. The gel fractions of these binders compared with those of Nos. 133-135 indicate the need for more equivalents of PAPI than CTI for binders of equivalent gel fractions. This reflects the lower functionality of or extent of cure with PAPI. PAPI is not completely compatible with Telagen S but it gives cures. Binder No. 142 which was cured with PAPI and contained treated IDP did not cure completely.

Hexanetriol was used in Binders Nos. 143-145. The crosslink densities of Binders Nos. 143 and 144 were calculated to be 10^{-5} and 10^{-4} mole branch points/gm, respectively. Binder No. 145 contains 25% treated IDP and can be directly compared with No. 143. It should be noted that there was very little change in the gel fractions when the plasticizer was added. In

Table VI

COMPOSITION AND PROPERTIES OF TELAGEN S BINDERS[a]

Reference No.	Prepolymer Lot No.	Plasticizer[b]		HDI/CTI equiv	Cure Time, days at 135°F	Mechanical Properties at 77°F				Mooney-Rivlin		Estimated Crosslink Density, moles chain per cc x 10^5			Gel Fraction v_2
		Type	Amount % Wt			σ_m psi	ϵ_m %	ϵ_b %	E_o psi	C_1 kg/cm^2	C_2 kg/cm^2	from C_1	From Compression Moduli	from v_2	
77[d]	148AH	none	0	4.0	7	29	400	400	34	0.10	0.22	1.0	-	1.2	0.061
79[d]	148AH	none	0	1.0	7	82	200	200	126	0.66	0.58	6.6	-	6.4	0.150
102	148AH	none	0	4.0	5	84	280	280	97	0.45	0.47	4.5	-	2.8	0.093
103	158H	none	0	4.0	5	78	630	630	53	0.14	0.43	1.4	-	0.90	0.055
104	148AH	none	0	4.0[e]	7	30	286	289	53	0.20	0.25	2.0	-	0.48	0.040
105	148AH	Toluene	25	4.0	7	21	487	487	20	0.06	0.13	0.6	0.73	0.80	0.052
111	158H	none	0	4.0[f]	7	27	699	699	10	0.02	0.24	0.2	-	0.84	0.053
112	148AH	none	0	4.0[f]	7	23	370	371	33	0.03	0.20	0.8	-	2.4	0.091
113	148AH	Toluene	10	4.0	6	-	-	-	-	-	-	-	-	1.45	0.070
114	148AH	Toluene	20	4.0	6	-	-	-	-	-	-	-	-	1.3	0.066
115	148AH	Toluene	30	4.0	6	-	-	-	-	-	-	-	-	0.82	0.054
122	148A[g]	none	0	4.0	6	-	-	-	-	-	-	-	1.64	1.5	0.072
123	148A[g]	none	0	2.0	6	-	-	-	-	-	-	-	3.98	2.95	0.101
124	148A[g]	none	0	6.0	6	-	-	-	-	-	-	-	1.19	0.92	0.056
125[a]	148AH	none	0	4.0	5	-	-	-	-	-	-	-	1.00	0.92	0.056
126[a]	148AH	none	0	4.0	5[h]	-	-	-	-	-	-	-	1.16	1.3	0.066
127[a]	148AH	none	0	4.0	5[h]	-	-	-	-	-	-	-	0.68	0.84	0.054
128[a]	148AH	none	0	4.0	5	-	-	-	-	-	-	-	0.99	1.15	0.063
130	148AH[i]	none	0	5.15	8	-	-	-	-	-	-	-	-	0.73	0.050
131	148AH[i]	none	0	8.5	8	-	-	-	-	-	-	-	-	0.84	0.054
133	158H	none	0	2.0	7	-	-	-	-	-	-	-	2.24	2.45	0.092
134	158H	none	0	4.0	7	-	-	-	-	-	-	-	0.38	0.38	0.036
135	158H	none	0	6.0	7	-	-	-	-	-	-	-	0.15	0.15	0.022
136	148H	none	0	0.33[j]	6	-	-	-	-	-	-	-	1.17	1.9	0.080
137[a]	158H	none	0	1.0[j]	6	-	-	-	-	-	-	-	0.43	1.2	0.064
138	158H	none	0	3.0[j]	6	-	-	-	-	-	-	-	0.19	0.36	0.035
139	158H[k]	none	0	2.0	7	-	-	-	-	-	-	-	0.75	0.95	0.057
140	158H[k]	none	0	4.0	7	-	-	-	-	-	-	-	0.20	0.18	0.024
141	158H	none	0	1.0[j]	6	40	530	530	30	0.10	0.15	1.0	0.65	0.85	0.054
142	158H	IDP	25	1.0[j]	6	-	-	-	-	-	-	-	-	incomplete cure	
143	148AH	none	0	5.0[l]	6	26	630	-[n]	25	0.04	0.18	0.4	0.31	0.41	0.037
144	148AH	none	0	1.85[l]	6	52	370	370	52	0.21	0.26	2.1	1.47	1.8	0.079

Table VI (Cont)

Reference No.	Prepolymer Lot No.	Plasticizer[b]		HDI/CTI equiv	Cure Time, days at 135°F	Mechanical Properties at 77°F				Mooney-Rivlin		Estimated Crosslink Density, moles chain per cc x 10^5			Gel Fraction v_2
		Type	Amount % Wt			σ_m psi	ϵ_m %	ϵ_b %	E_o psi	C_1 kg/cm^2	C_2 kg/cm^2	from C_1	From Compression Moduli	from v_2	
145	148AH	IDP	25	4.75[l]	6	12	560	560	4	0.04	0.01	0.4	0.32	0.33	0.033
155	161AHR	none	0	1.0	6	76	180	180	125	0.67	0.66	-	-	3.4[m]	0.14
156	161AHR	none	0	2.0	6	56	285	285	72	0.32	0.43	-	-	2.45[m]	0.091
157	161AHR	none	0	4.0	6	29	690	-[n]	29	0.04	0.23	-	-	1.25[m]	0.041
158	161AHR	none	0	6.0	6	8.3	720	-[n]	21	0.01	0.13	-	-	0.92[m]	0.020
159	161AHR	IDP	25	2.0	6	24	280	-[n]	23	0.18	0.07	-	-	1.0[m]	0.068
160	161AHR	IDP	25	4.0	6	-	-	-	-	-	-	-	-	-	0.028
168	148AH[o]	none	none	4.0	7	71	356	360	115	0.25	0.27	2.5	-	1.77	0.078
171	148AH	none	none	4.0[p]	5	54	440	440	42	0.21	0.10	2.1	-	-	-
172	148AH	none	none	2.0[p]	5	83	350	350	354	0.43	0.07	4.3	-	-	-
173	148AH	Ansul Ether 181	25	4.0	10	30	294	297	37	0.26	0.03	2.6	-	1.52	0.071
176	168H	none	none	4.0	7	-	-	-	-	-	-	-	-	0.87	0.054
177	175B	none	none	2.0	7	-	-	-	-	-	-	-	-	2.45	0.092
178	168H	none	none	2.0	6	100	240	240	151	0.74	0.35	7.4	-	3.2	0.105
179	168H	none	none	4.0	6	85	466	466	95	0.28	0.29	2.8	-	1.77	0.078
180	168H	none	none	6.0	6	70	443	445	100	0.22	0.29	2.2	-	1.05	0.059

---

[a] NCO/OH = 1.0 (except No. 137, 2.0), .04% FeAA cure catalyst (except Nos. 125 and 126, 0.05% Niax D-22; and Nos. 127 and 128, 0.2% Niax D-22).

[b] IDP passed through column of SiO_2, toluene redistilled from sodium and Ansul Ether 181 redistilled from Na.

[c] When other curing systems used, this column gives the equivalents ratio of extender to crosslinker.

[d] Prepared and tested in Phase One.

[e] HDI replaced with Nacconate H-12.

[f] HDI replaced with TDI.

[g] Unsaturated analog of 148AH.

[h] Cured at room temperature.

[i] Binder 130 contains 1% and Binder 131, 5% of 1,4-dimethylolcyclohexane.

[j] CTI replaced by PAPI.

[k] Binders prepared assuming equivalent weight of 1190

[l] Hexanetriol used as crosslinker.

[m] Estimated from E_o.

[n] Crosshead limit.

[o] Contains pentanediol.

[p] Prepolymer to CTRO ratio.

the usual binder preparations, the gel fraction would decrease more than that shown in This case.

The gel fractions of Binders Nos. 77 and 79 which have theoretical crosslink densities of about 10^{-5} and 10^{-4} mole branch points/gm when cured with CTI, are higher than those of binders containing hexanetriol. Also the gel fraction of Binder No. 77 should be closer to 0.090 than to the observed 0.060. This corroborates earlier work under Contract AF 04(611)-10386 which indicated hexanetriol was not as good a crosslinker as CTI.

A binder, containing glycerol triricinoleate, GTRO, was prepared for comparison. GTRO was compatible with this binder system and appeared to give a complete cure. Data will be reported when available.

e. Room Temperature Cures

Niax D-22 (dibutyltin dilaurate) was used as a catalyst for room temperature cures. A binder masterbatch was prepared and divided into two portions. To one portion was added 0.05% catalyst and to the other 0.2% catalyst, then each portion subdivided again and cured for 5 days at 135°F or at room temperature in a desiccator. Both cure temperatures gave equal gel fractions (equivalent cures).

The results are shown in Table VI, Binders 125 to 128. These results show that the room temperature cures were as good as those at 135°F. One attempt was made to prepare a propellant using Niax D-22 as the cure catalyst. While the castability of the propellant was poor, this system will be investigated further.

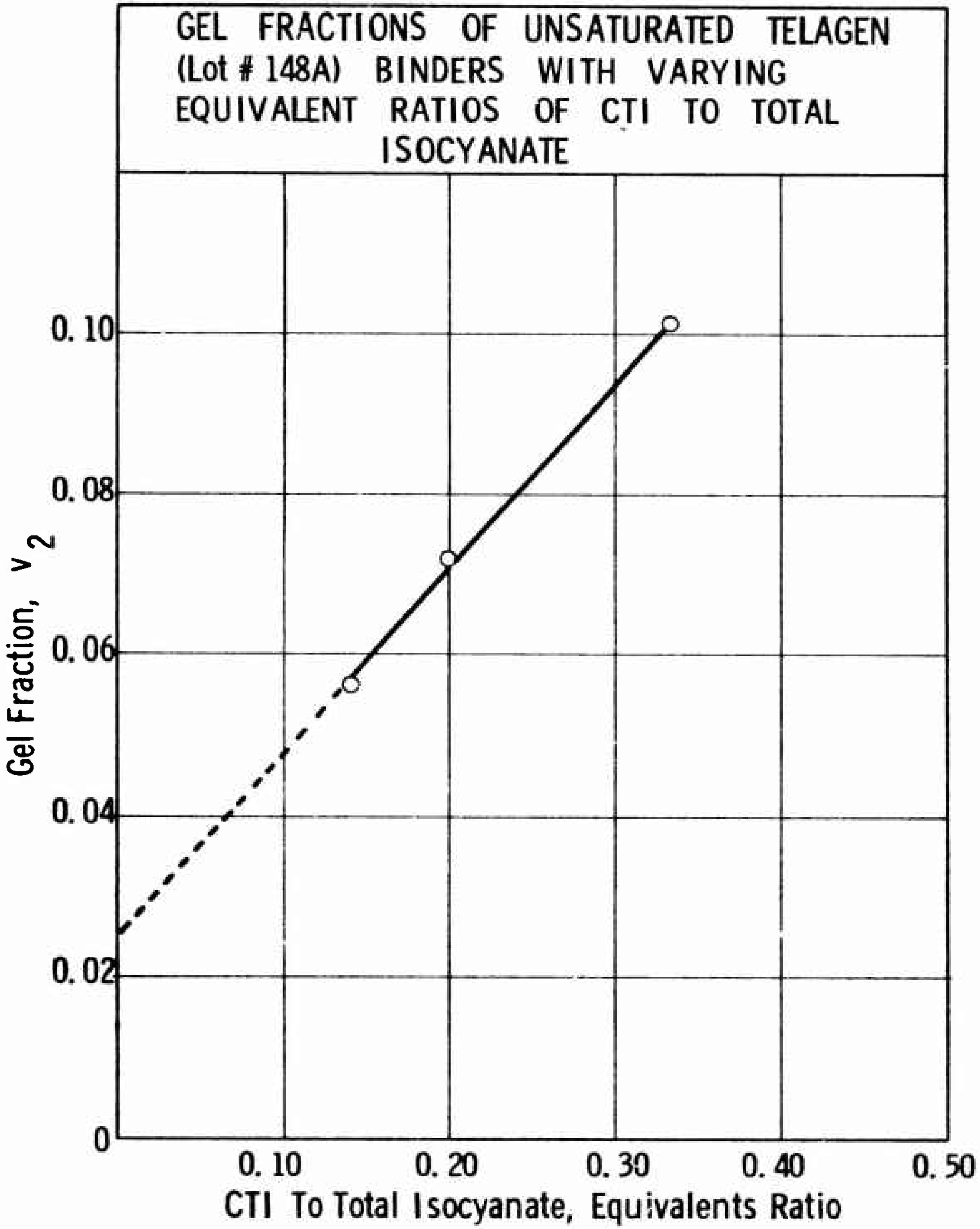
Catalyst studies made to further the effort on this objective are reported under the Task Three section of this report.

f. Unsaturated Binders

Binders Nos. 122-124 were prepared to compare an unsaturated prepolymer with a saturated one. These unsaturated binders were prepared at HDI to CTI ratios of 2, 4 and 6 (Table VI). A plot of gel fraction vs crosslinker content (Figure 3), indicates that the unsaturated prepolymer will cure with HDI only. If the gel fractions are correct, the results may be explained by additional crosslinks in this prepolymer due to oxidative crosslinking of chains.

g. Replacements for HDI

Binders were made using various isocyanates as replacements for HDI. For example, Binders 111-112 (Table VI) contained TDI as a replacement for HDI and can be compared with Binders 102 and 103. These binders also serve to compare Prepolymers 148AH and 158H. The gel fractions



GEL FRACTIONS OF UNSATURATED TELAGEN (Lot # 148A) BINDERS WITH VARYING EQUIVALENT RATIOS OF CTI TO TOTAL ISOCYANATE

Figure 3

of Binders 111 and 112 are suspect because they are too high compared to the E_0 and C_1 values. The mechanical properties data and the Mooney-Rivlin C_1 indicate that the HDI binders are better. The results also show that Prepolymer 148AH has a higher functionality than Prepolymer 158H.

Binder 104, cured with Nacconate H-12, had lower gel fraction and poorer mechanical properties than did the HDI cured Binder 102.

h. Plasticizer Studies

Only a minimum effort has been expended on plasticizer studies. Ansul Ether 181, which seriously interfered with the cure of Telagen S binders and propellants, was purified by refluxing over sodium for several days, filtering, then vacuum distilling it from more sodium. The plasticizer was used in a small binder sample which cured satisfactorily. Previously, a binder containing unpurified plasticizer did not cure. The binder is hazy, indicating that the plasticizer is not completely compatible.

Binders 105 and 113 to 115 were prepared with toluene as the plasticizer. The toluene will be removed under vacuum and the binders will be allowed to imbibe a plasticizer to determine plasticizing effects on a binder prepared in the presence of a diluent, but without cure effects. Possibly the effect of plasticizer at low temperatures may be determined in this way.

The gel fractions of these toluene binders are rather low considering that toluene does not interfere seriously with isocyanate curing agents.

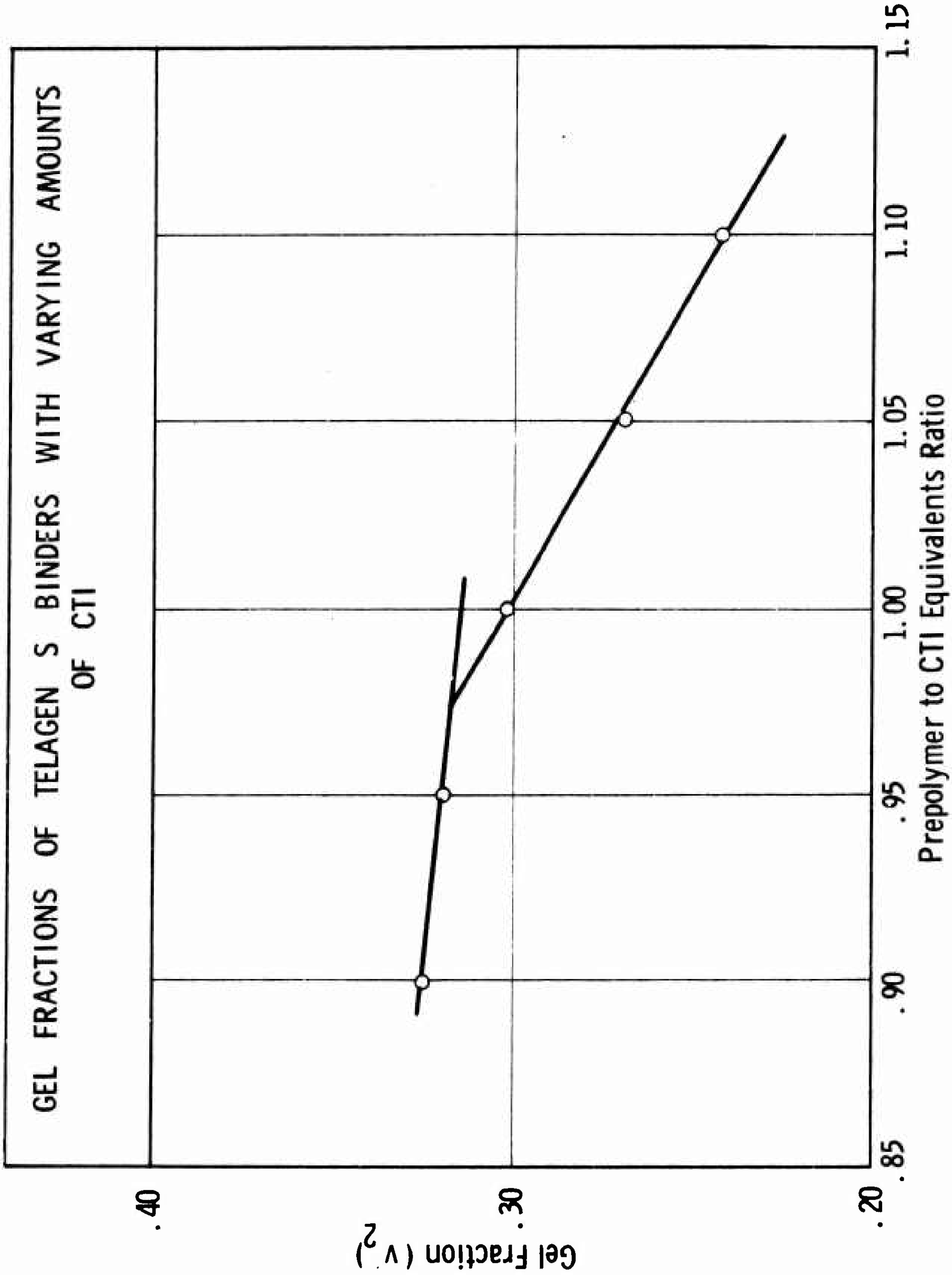
It was postulated that if more catalyst were added to plasticized binders and propellants, the faster rate of cure would overcome plasticizer interactions and other effects which inhibit the cure. Squalene, known to interfere with cure, was used as the plasticizer in four binders. The catalyst, FeAA, was varied from 0.075% to 0.3% and the samples kept at 135°F for 6 days. After curing, the binders were tested by swelling and all had gel fractions between 0.054 and .056. The level of catalyst within these limits had no effect. Apparently the catalyst catalyzed the cure-interference reactions as well as the cure reactions.

i. Cure Stoichiometry

Telagen S (Lot 242AM-148AH) was reacted with various amounts of CTI. The binders were swollen and the results are shown in Figure 4. With excess isocyanate, the gel fraction increased slowly. The excess isocyanate was either reacting with the urethane linkages or homopolymerizing slowly.

j. Prepolymer 161AHR

Binders were made of the new prepolymer, Lot 242AM-161AHR.



GEL FRACTIONS OF TELAGEN S BINDERS WITH VARYING AMOUNTS OF CTI

Figure 4

These binders (Nos. 155-160) are listed in Table VI. Although testing is not complete, the mechanical properties are similar to those of binders prepared from Prepolymer 148AH.

k. Propellant Studies

Propellants were made on both the 400-gram and 3200-gram scale. The composition and properties are reported in Table VII. Propellants 67-98-2 and -24 are samples from different cartons of 125-lb batch of propellant which is now being aged.

Propellant No. 9569, was prepared to replace aging samples lost when water leaked into the 77°F, 50% humidity oven. Four bars of this propellant were cut and will be used to spot check the aging results obtained at the above conditions. Propellant No. 9614 was prepared using dioctyl sebacate as the plasticizer in order to compare this plasticizer with IDP in propellants aged at 170°C and 25% humidity.

Two propellants were made using Prepolymer 158H, Nos. 9570 and 9615, to compare effects of an NCO to OH ratio of 1.00 and 1.02. The higher NCO ratio gave a better product, but required a longer cure period. The longer cure time was also observed in Propellants 137 and 138. After 7 days of cure, the propellant with the higher NCO content was not as hard as the other, but after about 14 days, Propellant 138 was harder. The explanation may be that at the NCO to OH ratio of 1.02, the binder ingredients are not stoichiometric and therefore would not attain as complete a cure (or achieve an equivalent hardness) as the binder in the propellant with the stoichiometric NCO to OH ratio. Thus an initially lower hardness is observed. However, with time slower secondary reactions of the excess isocyanate groups take place to increase the crosslink density (and hardness) beyond that obtained with the stoichiometrically formulated propellants. Figure 4 indicates that secondary crosslinking reactions do occur in the presence of excess isocyanate. The secondary reactions may be either dimerization of the isocyanate or allophanate formation.

Prepolymer 161AHR needs a lower HDI to CTI ratio, that is, more crosslinker, to achieve a given modulus. This reflects its lower functionality which was established by the binder studies.

A 125-lb batch of propellant with the prepolymer 161AHR will be mixed in the near future.

Hexanetriol was used as the crosslinker in Propellant 1601. The propellant is soft and emphasizes the problems that have been encountered with this triol. Possibly it is too polar for this system. It is unlikely the hexanetriol will be a suitable replacement for CTI.

PAPI was used as the curing agent in Propellant 1602 and it gave a good, fast cure. The values of the Shore A hardness and mechanical

Table VII

COMPOSITION AND PROPERTIES OF TELAGEN S PROPELLANTS[a]

(125-lb Batches)

Reference No.	Prepolymer Lot No.	HDI/CTI	NCO/OH	Cure Time, days at 135°F	Shore A Hardness Top	Shore A Hardness Side	Mechanical Behavior at 77°F σ_m psi	σ_b psi	ϵ_m %	ϵ_b %	E_0 psi
67-98-2	158H	3.5	1.02	16	68	57	123	116	35	45	605
67-98-24	158H	3.5	1.02	16	68	58	123	116	35	46	610
(3200-gram Batches)											
9569	148AH	4.0	1.02	7	62	56	119	118	32	34	546
				21	68						
9570	158H	3.5	1.02	7	67	53	81	77	44	53	291
				21	68						
				34			135	133	37	41	557
9614[a]	148AH	4.0	1.02	7	55	54					
				8	63	59	114	113	33	36	514
				20	66						
9615	158H	3.5	1.0	7	44	39					
				8	47	39	64	59	51	64	231
				20	50						
				34			103	97	41	51	455
137	158H	3.0	1.0	7	45	42	84	78	45	55	271
				14	43						
				28	53	43	73	65	48	64	282
138	158H	3.0	1.02	7	53	37	60	55	51	65	190
				14	62						
				28	72	62	141	139	38	42	581

Table VII (Cont)

Reference No.	Prepolymer Lot No.	HDI/CTI	NCO/OH	Cure Time, days at 135°F	Shore A Hardness		Mechanical Behavior at 77°F				
					Top	Side	σ_m psi	σ_b psi	ϵ_m %	ϵ_b %	E_o psi
1300[a]	161AHR	3.5	1.02	8	40	26					
				12	43	42	66	62	43	48	218
				21	47	45					
				(400-gram Batches)							
1601	148AH	2[b]	1.03	4	soft	-					
				7	soft	-					
				15	21	-					
1602	148AH	1[c]	1.02	4	75	60					
				7	68	75					
				15	75	70					
1603	161AHR	3.5	1.02	4	18	-					
				7	35	10					
				15	44	48					
1604	161AHR	3.0	1.02	4	31	-					
				7	54	31					
				15	59	61					
1761	161AHR	3.5	1.0	7	45	34					
				10	48	40					
1762	161AHR	3.0	1.0	7	48	44					
				10	50	46					
1912	148AH	4.0[d]	1.02	4	-	-					
1913	161AHR	3.0	1.02	4	32	-					
1914[e]	148AH	4.0	1.02	4	67	47					
				7	65	67					
1915[f]	158H	3.5	1.0	4	-	-					

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*Please see following page for footnotes.

Table VII (Cont)

Footnotes

[a] All propellants contain 88 wt% solids, 25% IDP purified by passing through silica gel (except 9614 which contains DOS), and 0.002% FeAA and 0.006% HAA.

[b] Prepolymer/hexanetriol.

[c] HDI/PAPI.

[d] TDI replaced HDI.

[e] Contains no HAA.

[f] Contains burning rate additive AR, supplied by Dr. R. S. Bruenner (AGC).

properties indicate that a higher HDI to PAPI ratio should be used to achieve more optimum product characteristics. PAPI may be a suitable replacement for CTI and is being investigated further.

Propellant 1914 was mixed at 110°F, with only FeAA as the catalyst and no HAA to modify the catalyst activity in order to obtain a cure at lower temperature. The castability of this propellant was poor and it cured to a much higher modulus. The higher prepolymer viscosity at lower temperatures may limit the processing of these propellants.

1. Burning Modifiers

Effort to define some combustion properties of Telagen S propellants are being made. Propellant 1915, Table VII, contains a burning rate modifier, but burning data are not available.

Pertinent to this effort is work done by Dr. W. S. Schmidt at Aerojet under Contract NAS-1-6323. He studied the uncatalyzed burning rates of two propellants; one with hydroxy-terminated, butadiene polymer, 148A and with the corresponding hydrogenated prepolymer 148AH. The 88 wt% solids propellants had the same burning rates (Figure 5). The pressure exponent is about 0.36 in the range 100 to 600 psia and about 0.9 at 1000 to 3000 psia. Between 600 and 1000 the exponent is increasing.

2. Task Two

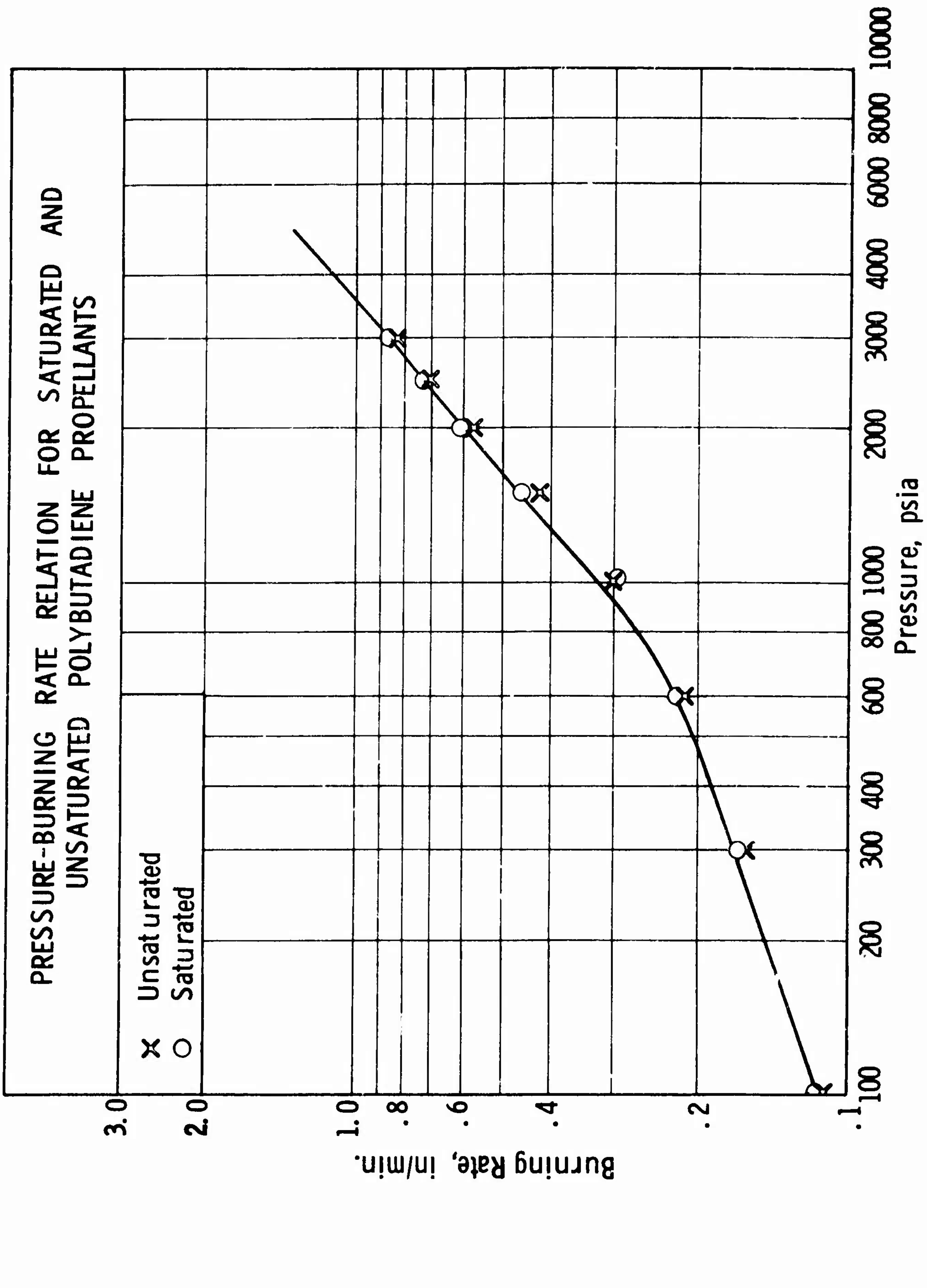
a. Introduction

Task Two involves the determination of the compatibility of the prepolymers and curing agents with combinations of advanced oxidizer and advanced fuel. Model compounds are being used to study the binder component interactions with the fuels and oxidizers and attempts are being made to improve systems which have poor compatibility. Compatible systems will be evaluated ballistically at the 1-lb scale.

b. Curing Agents for Advanced Oxidizers

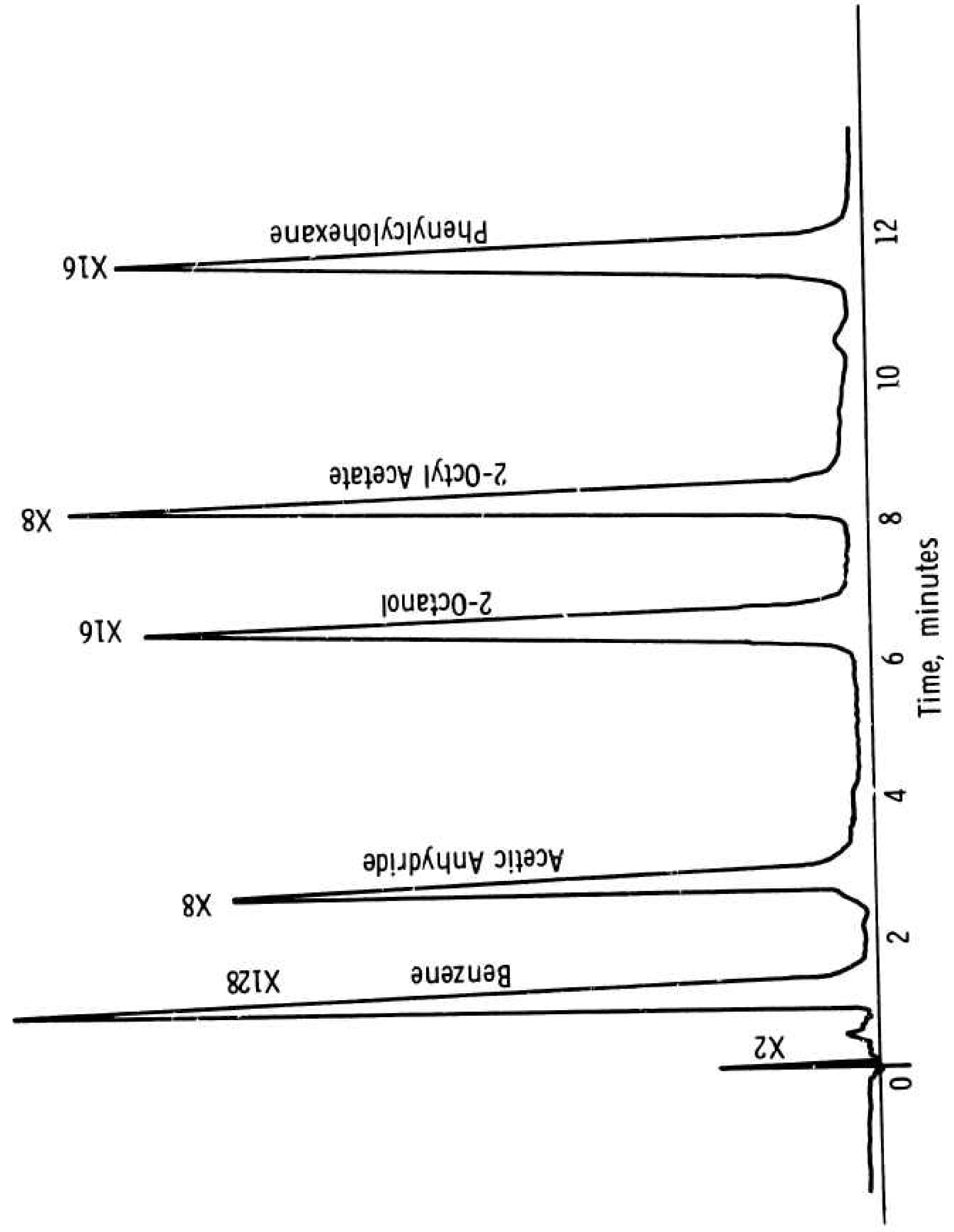
1) Acid Anhydrides

Studies of acid anhydrides as curing agents for hydroxy-terminated Telagen S prepolymer with the oxidizer HAP were initiated. Acetic anhydride, a model acid anhydride, was reacted with a 2-octanol in the presence of HAP. The chromatographic analysis of the model binder system (Figure 6) indicated that the reaction is complete after 15 minutes and that > 99% of the theoretical ester product (2-octyl acetate) is formed. The rates of reaction of 2-octanol with dodecenylsuccinic and phthalic anhydrides were investigated. The results are shown in Table VIII.



PRESSURE-BURNING RATE RELATION FOR SATURATED AND UNSATURATED POLYBUTADIENE PROPELLANTS

Figure 5



CHROMATOGRAM OF ACETIC ANHYDRIDE - 2-OCTANOL IN BENZENE

Figure 6

Table VIII

REACTION OF ACID ANHYDRIDES WITH 2-OCTANOL IN THE PRESENCE OF HAP AT ROOM TEMPERATURE

		Compound remaining, %		
Anhydride	Time, min	Alcohol	Anhydride	Product
Acetic	15	0	0	99
Dodecenylsuccinic	45	58.8	57.9	-
Phthalic	780	90.0	90.0	-

The reactions of the acid anhydrides with 2-octanol are quantitative in yield and the rates of reaction are very rapid and strongly dependent on the type of anhydride. The aromatic anhydrides were slowest and their potential as curing agents is being investigated further.

2) Cyclic Imides

The compatibility and fast reaction of acid anhydrides in the presence of HAP suggested a study of the less reactive cyclic imides as potential curing agents. A number of cyclic imides were reacted with 1-octanol in the presence of HAP. A typical chromatogram is shown in Figure 7. The N-n-butylsuccinimide and N-n-butylphthalimide showed no reaction with the alcohol after 18 hours at 50°C. The unsubstituted phthalimide did not react under the same conditions but the unsubstituted dodecenylsuccinimide showed 10% stoichiometric reaction.

Studies of the use of cyclic imides as possible crosslinking agents were continued. Various cyclic imides were prepared and reacted with 1-octanol in the presence of HAP (see Table IX). The present data indicate that cyclic imides are stable in the presence of HAP, and that HAP has no catalytic affect on the reaction of imides with alcohols. Unless, however, an effective catalyst can be found, the cyclic imides are unsuitable as crosslinking agents for low temperature cure propellants. Work along these lines has been discontinued.

3) Azetidines

Acyl and aroyl azetidines have been found to be considerably less susceptible to acid catalyzed polymerization than the related aziridines. Synthesis of a model compound to test its compatibility with the various advanced fuels and oxidizers and reactivity as a crosslinking agent has been initiated.

GAS-LIQUID CHROMATOGRAM OF 1-OCTANOL, HEXAHYDROPHTHALIMIDE, AND PHENYLCYCLOHEXANE IN BENZENE

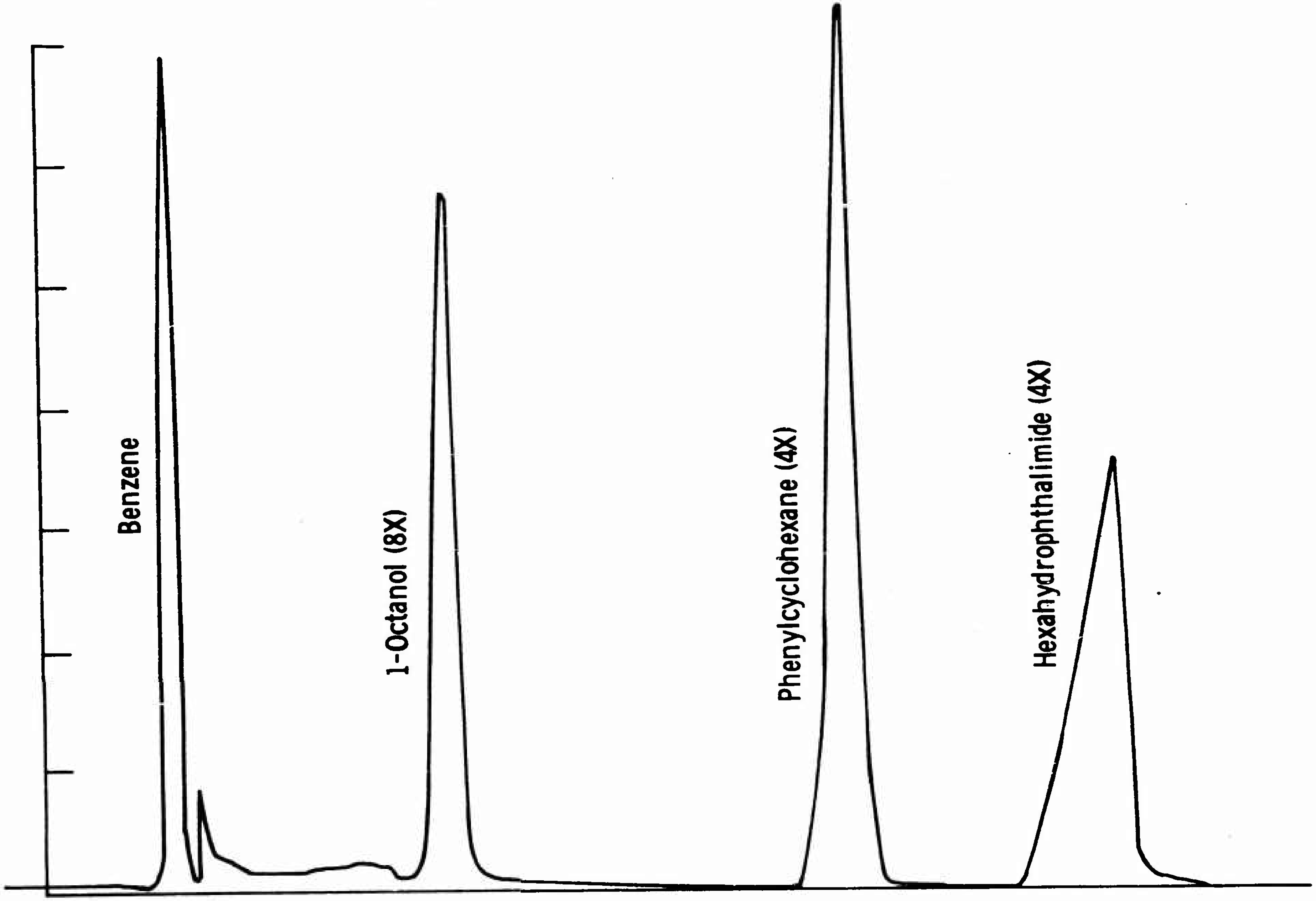


Figure 7

Table IX

REACTION OF VARIOUS CYCLIC IMIDES WITH 1-OCTANOL IN THE PRESENCE OF HAP AT 50°C

Cyclic Imide	Time Days	Observation
N-Butyltetrabromophthalic	3	no reaction
N-Butylmaleic	3	no reaction
Nadic methyl	3	no reaction
Hexahydrophthalic	1	~ 5%
3,4,5,6,7,7-Hexachlorobicyclo[2.2.1] hepta-4,5-ene-1,2-dicarboxylic	1	no reaction

3. Task Three

a. Introduction

The testing of curing agents and catalysts for achieving a room temperature cure and obtaining a suitable replacement for CTI are the main studies for Task Three. The synthesis of curing agents on an "as needed" basis is also being done.

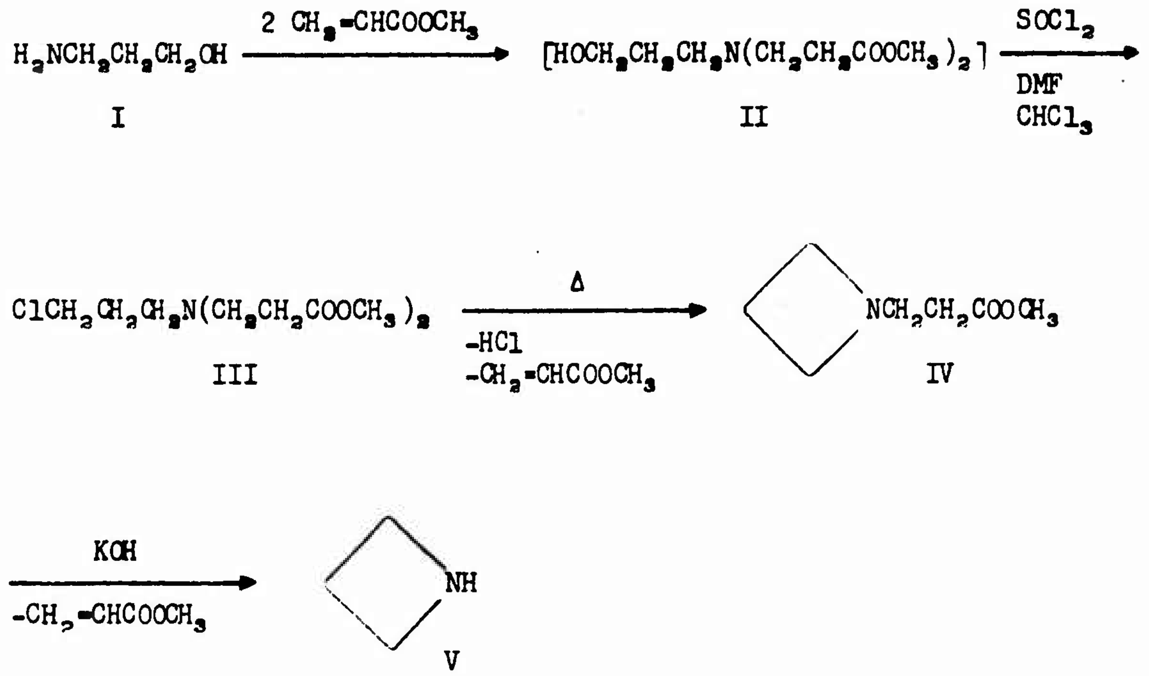
b. Synthesis of Imides

Phthalimide and dodecenylsuccinimide were prepared by reacting the anhydride with an excess of concentrated ammonia and refluxing the mixture for 2 hours. The water and ammonia were removed by distillation to yield the desired product.

The corresponding N-n-butyl derivatives were prepared in a similar manner by reacting the appropriate anhydride with a mole of n-butylamine. Results of tests with these materials are described in Section IV.B.2.b.(2).

c. Synthesis of Azetidine

1-(2-carbomethoxyethyl)azetidine (IV) has been prepared from the cyclization of dimethyl N-(3-chloropropyl)-2,2'-iminopropionate (III) by the method of Wadsworth(5).



The infrared spectra of the crude compounds II, III, and IV are shown in Figures 8-10. Compound (IV) will be converted to the parent azetidine (V) which will then be used to prepare various N-aroyl or acyl azetidines for compatibility studies with advanced fuels and oxidizers.

d. Room Temperature Cures

A screening of several catalysts was carried out to find suitable candidates for a room temperature cure. A 0.2N solution of Prepolymer 148AH and n-butyl isocyanate was prepared in toluene. Aliquots (33-ml) were transferred to volumetric flasks which contained 0.1 gm of catalyst. Five-ml aliquots were periodically analyzed for isocyanate, Table X.

The sampling techniques were not entirely suitable for the active catalysts because the initial points show considerable reaction. However, it is apparent that FeAA, Niax D-22 and Thermalite-25 are the most active. FeAA and Niax D-22 were used in propellants mixed at 110°F, but the castability of these was marginal.

4. Task Four

a. Introduction

Task Four includes Phase Four (propellants in aging before March 1967) and also involves the aging of propellants prepared under Tasks One and Two. It further includes the testing at 350°F of selected Task One propellants and the temperature cycling of propellants made with CTI replacement.

INFRARED SPECTRUM OF $HOCH_2CH_2CH_2N(CH_2CH_2COOCH_3)_2$

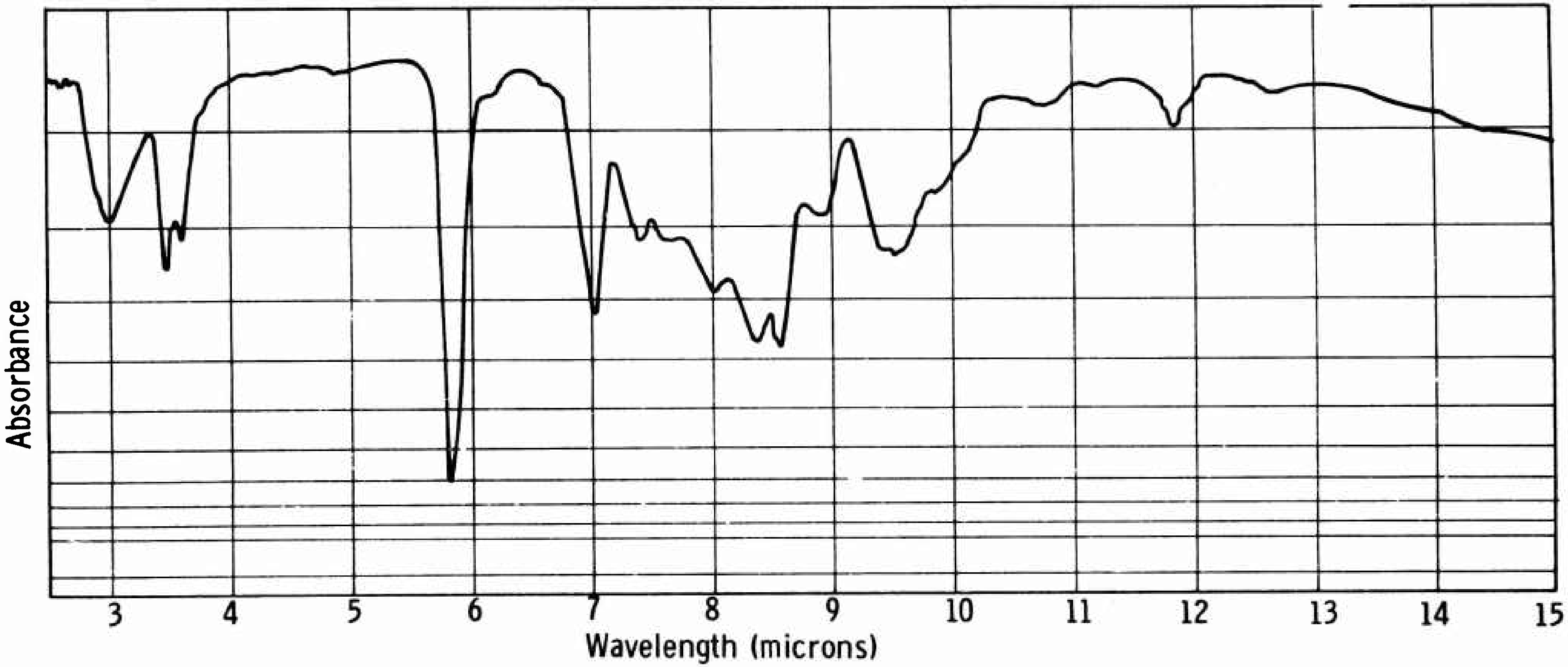


Figure 8

INFRARED SPECTRUM OF $ClCH_2CH_2CH_2N(CH_2CH_2COOCH_3)_2$

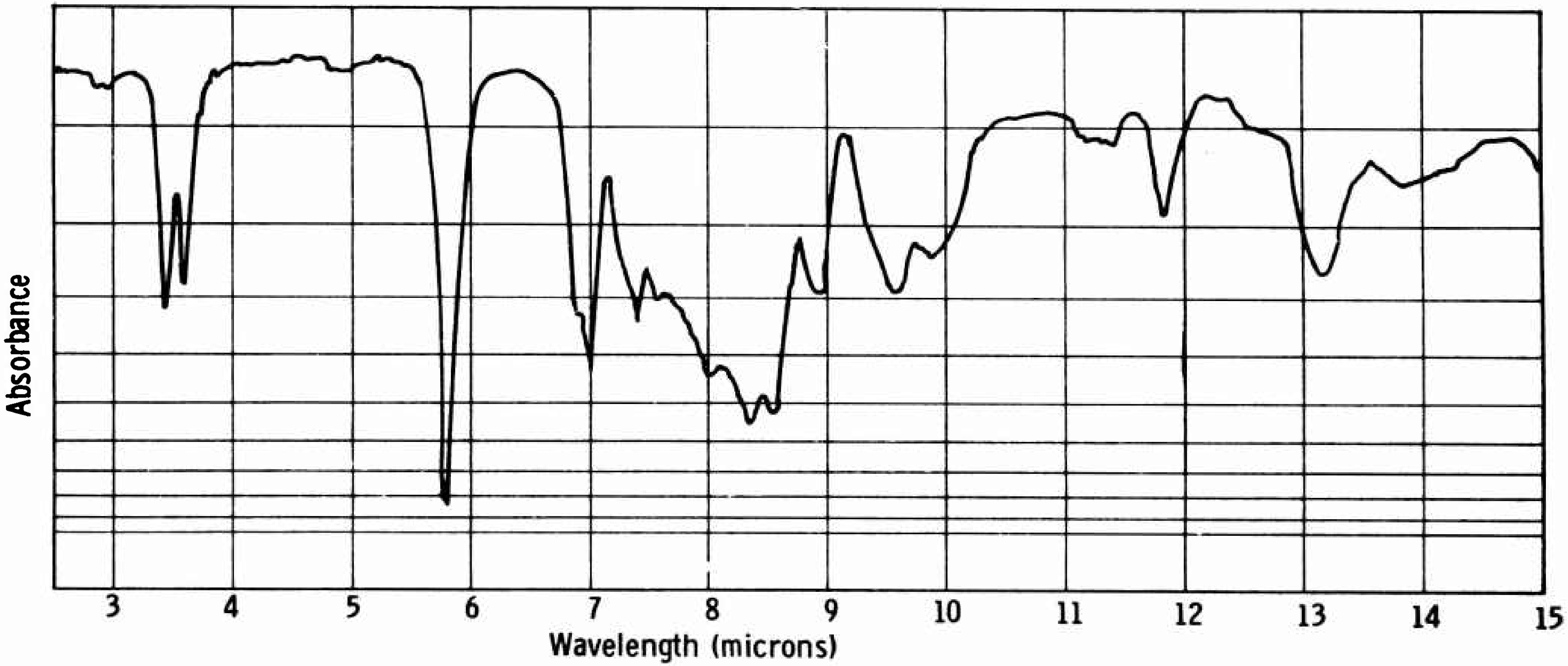


Figure 9

INFRARED SPECTRUM OF $NCH_2CH_2COOCH_3$

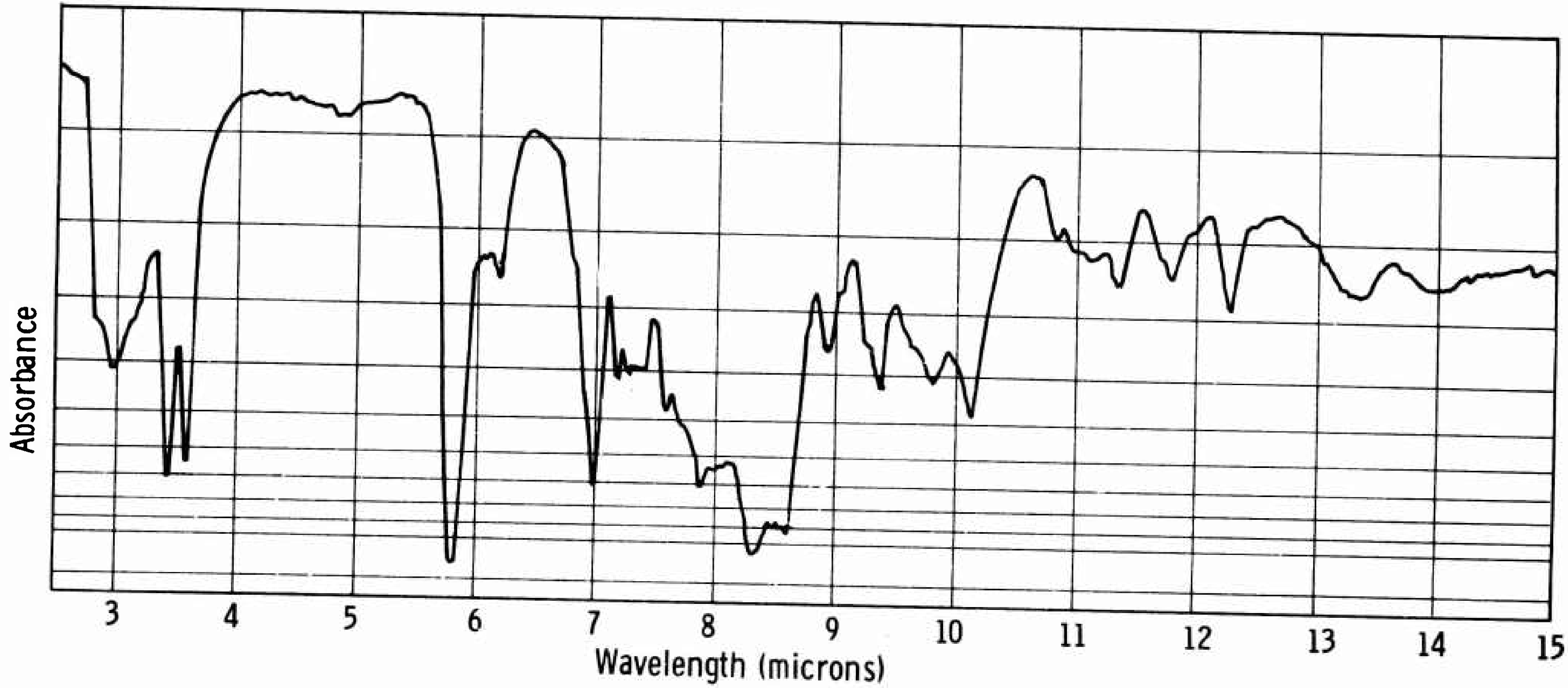


Figure 10

Table X

CATALYSIS OF THE REACTION OF N-BUTYL ISOCYANATE (0.2N) WITH PREPOLYMER 148AH (0.2N) IN TOLUENE AT ROOM TEMPERATURE[a]

	Catalyst[b]								
Time hrs	FeAA	FeAA HAA	Niax D-22	Niax D-22 HAA	Stannous Octoate	COAA	Thermalite 25	T-18	None
0[c]	0.691	0.988	0.789	0.703	0.872	0.908	0.772	0.988	0.99
4.5	-	-	-	0.243	0.778	0.836	0.216	0.920	-
18	0.017	0.570	0.023	-	-	-	-	-	-
24		-		0.029	0.537	0.625	0.009	0.665	-
90		0.190				0.195			0.588
120		-							
162		0.103							

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[a] Meq. isocyanate/5-ml aliquot is shown in table.

[b] Catalyst = 0.01 gm/33-ml, HAA = 0.03 gm/33-ml; FeAA = Ferric acetylacetonate, HAA = acetylacetone, Niax D-22 = dibutyltin dilaurate, CoAA = cobalt acetylacetonate, T-25 and T-18 = tin salts.

[c] Not a true zero time since it includes time to mix and to take first sample.

b. Conventional Propellants

The propellants for the aging program were cut into blocks, half of which were wrapped in aluminum foil. Wrapped and unwrapped samples were aged at the conditions shown in Table XI. A Minuteman Wing VI second stage propellant was included as a control. The Telagen S propellants being aged include Batch Nos. 66-954 and 67-98.

The control propellant, Minuteman Wing VI (No. 21-3066, DWM 001) was used in the qualification of prepolymers for production motors. After the regular 12-day cure cycle, this propellant had the following properties, $\sigma_m/\sigma_b/\epsilon_m/\epsilon_b/E$, 90/-/34/45/425. After this propellant had been held at room temperature for 6 weeks, pressed bars had the following properties, 108/-/22/32/760. These changes are not uncommon, because of the post cure immediately following the cure cycle. Later, when blocks were cut from liner boxes for the aging program, the properties were 135/133/16/19/1250. Again, the changes were partially due to post cure, and also to the fact that the bars were milled and that the orientation of the samples was varied. Thus, before the present aging program started, a considerable post cure had occurred in the control propellant at room temperature. This rapid a post cure is unusual, but the latter values for the properties have been used as control values. The aging data is summarized in Tables XII - XX.

Table XI

AGING CONDITIONS

Condition No.	Temp °F	Atmosphere	Relative Humidity, %
1	-75	carbon dioxide, stagnant	100
2	0	carbon dioxide, stagnant	100
3	77	nitrogen, stagnant	5
4	77	nitrogen, stagnant	50
5	77	air, circulating	25
6	77	air, circulating	50
7	77	air, stagnant	80
8	170	air, circulating	25
9	170	air, circulating	80

After 2 months of aging, only a few generalizations can be made since aging trends have developed only at 170°F. No discernible changes have occurred at either -75 or 0°F for any of the propellant and at 77°F for the Telagen S propellants. There are some incipient signs (very difficult to establish for certainty) of degradation of the Minuteman propellant at 77°F. Thus, note the lower moduli for 9 week data in Tables XV, XVI, XVII, and XVIII where the relative humidity was 25% or higher, but no modulus change in Table XIV where the relative humidity was 5%. These observed changes are difficult to separate from the experimental error, but data for 26 weeks, which should be available soon, may establish the trend more forcefully.

Table XII

MECHANICAL BEHAVIOR OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS[a]
AT -75°F AND 100% RELATIVE HUMIDITY IN CARBON DIOXIDE ENVIRONMENT

Time in Aging weeks	Mechanical Properties at 77°F, $\sigma_m/\sigma_b/\epsilon_m/\epsilon_b/E$					
	Unwrapped			Al Foil Wrapped		
	Telagen S		Minuteman	Telagen S		Minuteman
	66-954	67-98		66-954	67-98	
0	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]
1	-	129/123/39/42/770	-	-	131/124/31/42/770	-
2	111/96/21/30/826	141/136/35/43/743	135/133/16/19/1330	114/96/22/32/843	132/126/31/40/852	124/123/18/20/1009
4	115/100/24/33/754	132/123/33/44/756	136/130/16/22/1306	115/94/21/32/856	130/123/33/44/712	134/130/17/22/1173
9	111/100/23/30/843	-	128/124/17/21/1160	105/92/21/30/802	-	121/118/19/24/950

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[a] Propellants all contain 88 wt% solids.

[b] These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XIII

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS[a] AT 0°F AND 100% RELATIVE HUMIDITY IN CARBON DIOXIDE ENVIRONMENT

Time in Aging weeks	Mechanical Properties at 77°F, $\sigma_m/\sigma_b/\epsilon_m/\epsilon_b/E$					
	Unwrapped			Al Foil Wrapped		
	Telagen S		Minuteman	Telagen S		Minuteman
	66-954	67-98		66-954	67-98	
0	100/93/24/28/650	123/-/34/45/605	135/133/16/19/1250[b]	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]
1	112/108/21/26/808	129/124/34/43/672	135/133/16/19/1256	114/108/22/28/865	136/131/33/40/759	136/133/17/21/1167
2	107/100/18/28/800	143/136/33/42/789	113/112/14/20/1130	108/102/21/28/780	142/137/36/43/730	135/132/18/22/1110
4	110/103/21/28/800	131/124/35/43/682	131/129/17/20/1167	106/100/21/27/817	135/128/34/43/723	116/113/20/24/850
9	118/110/22/30/859	-	134/132/16/19/1265	104/96/21/27/789	-	133/130/18/21/1158

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[a] Propellants all contain 88 wt% solids.

[b] These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XIV

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS[a] AT 77°F AND 5% RELATIVE HUMIDITY IN STAGNANT NITROGEN ENVIRONMENT

Time in Aging weeks	Mechanical Properties at 77°F, $\sigma_s/\sigma_b/\epsilon_s/\epsilon_b/E$					
	Unwrapped			Al Foil Wrapped		
	Telagen S		Minuteman	Telagen S		Minuteman
	66-954	67-98		66-954	67-98	
0	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]
1	114/99/21/30/915	128/126/33/38/704	138/135/16/19/1459	118/100/22/32/852	129/124/33/40/732	129/128/19/19/1114
2	116/100/22/31/894	126/117/32/44/795	136/134/17/20/1156	109/106/19/24/784	124/121/27/33/688	136/134/15/18/1374
4	112/101/21/29/861	134/127/34/43/743	146/144/16/20/1374	111/94/22/31/808	126/121/33/42/686	141/139/17/19/1225
9	111/104/21/32/824	-	134/130/18/22/1112	112/107/21/30/824	-	127/125/16/19/1105

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[a] Propellants all contain 88 wt% solids.

[b] These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XV

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS[a] AT 77°F AND 50% RELATIVE HUMIDITY IN STAGNANT NITROGEN ENVIRONMENT

Mechanical Properties at 77°F, $\sigma_m/\sigma_b/\epsilon_m/\epsilon_b/E$

Time in Aging weeks	Unwrapped			Al Foil Wrapped		
	Telagen S		Minuteman	Telagen S		Minuteman
	66-954	67-98		66-954	67-98	
0	100/93/24/28/650	123/-/35/45/605	135/133/19/19/1250[b]	100/93/24/28/650	123/-/35/45/605	135/133/19/19/1250[b]
1	115/96/22/31/808	133/125/35/43/699	128/124/18/22/1101	114/98/22/30/822	124/116/30/42/798	141/139/16/19/1291
2	117/96/21/32/883	123/115/32/44/721	143/131/15/22/1549	115/98/21/30/861	121/113/30/42/769	138/131/16/19/1361
4	113/96/22/32/787	129/122/32/42/763	138/127/17/23/1254	110/90/21/32/835	129/120/32/44/743	133/116/17/25/1140
9	103/98/20/30/749	-	115/111/20/26/843	103/96/19/30/787	-	126/123/17/24/1077

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[a] Propellants all contain 88 wt% solids.

[b] These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XVI

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS[a] AT 77°F AND 25% RELATIVE HUMIDITY IN CIRCULATING AIR ENVIRONMENT

Time in Aging weeks	Mechanical Properties at 77°F, $\sigma_m/\sigma_b/\epsilon_m/\epsilon_b/E$					
	Unwrapped			Al Foil Wrapped		
	Telagen S		Minuteman	Telagen S		Minuteman
	66-954	67-98		66-954	67-98	
0	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]
1	118/99/21/30/933	130/124/33/42/743	124/121/19/23/1057	116/100/22/32/804	128/122/34/42/683	138/136/17/20/1250
2	118/100/23/33/789	127/118/32/43/839	140/137/19/22/1160	116/104/23/30/778	126/119/33/43/758	126/124/22/25/983
4	119/99/22/32/900	132/124/33/44/758	146/144/16/19/1402	115/96/22/32/856	129/121/33/44/756	146/143/16/20/1439
9	124/118/23/30/867	-	126/125/17/20/1099	114/109/21/30/850	-	118/115/20/23/922

---

[a] Propellants all contain 88 wt% solids.

[b] These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XVII

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS[a] AT 77°F AND 50% RELATIVE HUMIDITY IN CIRCULATING AIR ENVIRONMENT

Time in Aging weeks	Mechanical Properties at 77°F, $c_m/\sigma_b/\epsilon_m/\epsilon_b/E$					
	Unwrapped			Al Foil Wrapped		
	Telagen S		Minuteman	Telagen S		Minuteman
	66-954	67-98		66-954	67-98	
0	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]
1	116/100/22/30/870	131/124/33/41/737	140/136/16/20/1413	112/98/21/30/878	124/114/31/43/759	142/140/17/20/1234
2	-	121/115/32/42/758	136/133/18/20/1232	-	124/116/32/43/719	133/130/18/21/1162
4	-	125/119/33/43/671	112/108/19/26/870	-	127/118/32/44/725	132/129/16/24/1143
9	-	-	116/113/19/22/1020	-	-	133/130/16/19/1241

---

[a] Propellants all contain 88 wt% solids.

[b] These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XVIII

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS[a] AT 77°F AND 80% RELATIVE HUMIDITY IN STAGNANT AIR ENVIRONMENT

Mechanical Properties at 77°F, $\sigma_m/\sigma_b/\epsilon_m/\epsilon_b/E$

Time in Aging weeks	Unwrapped			Al Foil Wrapped		
	Telagen S		Minuteman	Telagen S		Minuteman
	66-954	67-98		66-954	67-98	
0	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]
1	108/96/20/27/841	130/124/32/41/754	137/135/16/18/1280	115/94/22/32/804	129/123/32/40/759	145/143/16/19/1350
2	107/92/21/30/776	118/104/31/45/677	143/141/15/19/1501	109/90/22/32/787	120/104/33/47/649	138/136/17/20/1195
4	96/75/21/31/688	120/110/32/44/664	134/121/16/24/1350	94/76/22/32/594	121/110/30/43/730	128/116/16/23/1243
9	60/50/22/35/439	-	115/115/15/22/1025	67/57/22/34/468	-	112/109/16/23/931

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[a] Propellants all contain 88 wt% solids.

[b] These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XIX

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS[a] AT 170°F AND 25% RELATIVE HUMIDITY IN CIRCULATING AIR ENVIRONMENT

Time in Aging weeks	Mechanical Properties at 77°F, $\sigma_m/\sigma_b/\epsilon_m/\epsilon_b/E$					
	Unwrapped			Al Foil Wrapped		
	Telagen S		Minuteman	Telagen S		Minuteman
	66-954	67-98		66-954	67-98	
0	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]
1	85/82/26/30/507	86/77/34/46/439	124/117/31/45/756	95/88/28/36/494	94/84/32/44/514	107/101/33/44/507
2	65/64/25/28/394	45/20/28/68/477	111/110,33/38/653	62/61/26/29/352	46/24/30/71/396	105/98/31/46/555
4	40/39/22/25/252	103/98/33/41/560	78/77/24/26/608	43/42/25/28/263	100/89/37/53/461	-
9	47/47/19/22/367	-	71/67/11/16/990	46/45/24/28/293	-	66/66/11/12/780

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[a] Propellants all contain 88 wt% solids.

[b] These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

Table XX

MECHANICAL PROPERTIES OF TELAGEN S AND MINUTEMAN WING VI SECOND STAGE PROPELLANTS[a] AT 170°F AND 80% RELATIVE HUMIDITY IN STAGNANT AIR ENVIRONMENT

Mechanical Properties at 77°F, $\sigma_m/\sigma_b/\epsilon_m/\epsilon_b/E$

Time in Aging weeks	Unwrapped			Al Foil Wrapped		
	Telagen S		Minuteman	Telagen S		Minuteman
	66-954	67-98		66-954	67-98	
0	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]	100/93/24/28/650	123/-/35/45/605	135/133/16/19/1250[b]
1	48/48/21/21/289	54/51/31/38/343	104/90/24/39/577	69/66/27/32/365	56/48/34/48/323	120/110/27/42/699
2	21/20/26/28/102	27/21/30/41/214	-	52/50/26/30/302	35/23/32/56/311	93/87/32/46/413
4	22/22/27/30/97	30/28/24/28/195	-	36/35/25/28/196	48/47/30/34/294	70/69/18/49/570
9	25/24/22/25/136	-	41/40/5/5/920	29/28/23/26/175	-	43/43/6/6/822

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[a] Propellants all contain 88 wt% solids.

[b] These values are values after aging at room temperature before storage begun. Properties after 12 day cure 90/-/34/45/425.

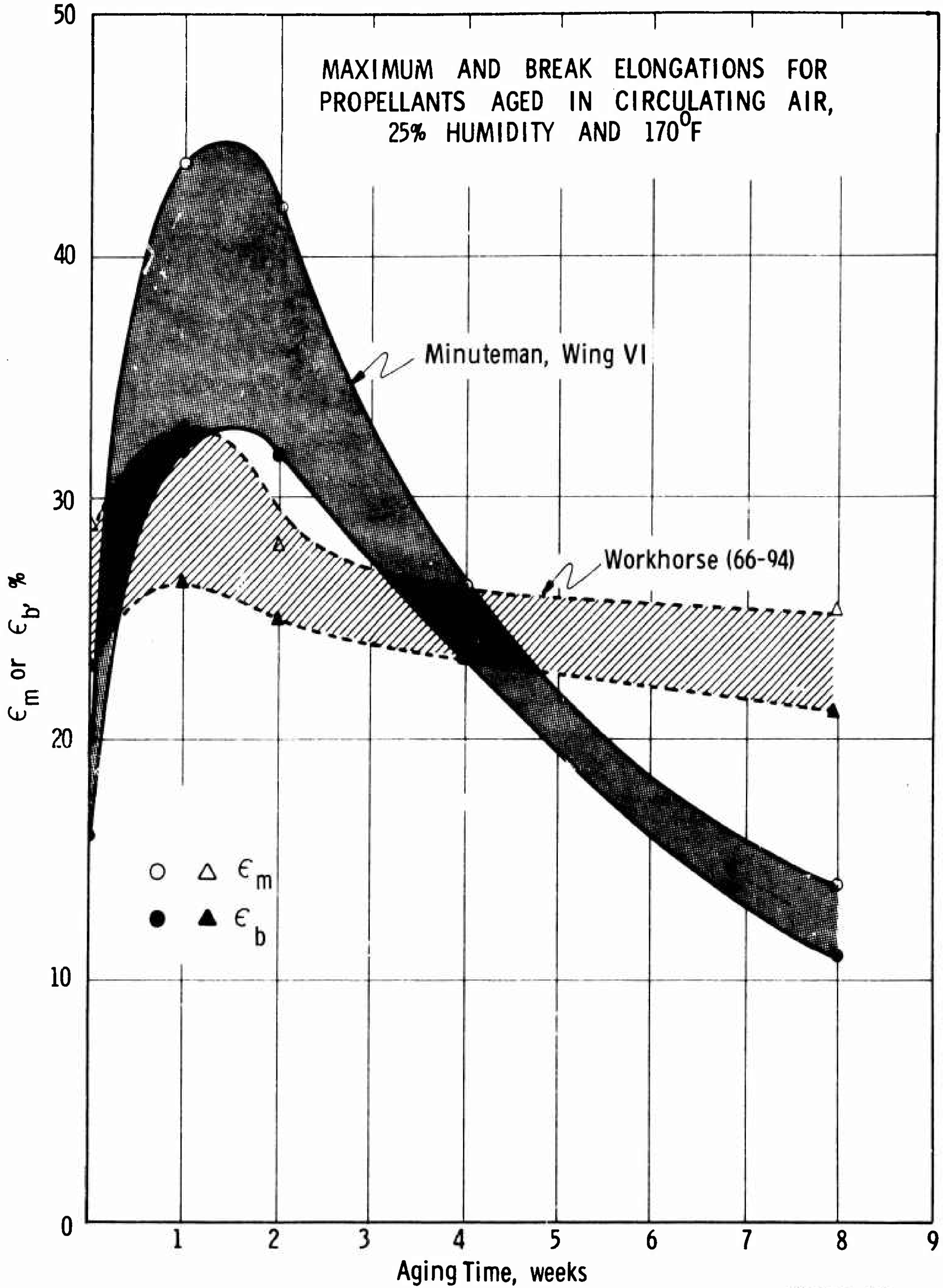
At 170°F both propellants have degraded rapidly. The Telagen S propellants rapidly lose tensile strength with little change of elongation. The unsaturated Minuteman propellant loses tensile strength while the elongation increases at first. The data at 9 weeks indicates that elongation of the unsaturated propellant decreases rapidly to very low values, probably because of oxidative crosslinking. There is some evidence that a recovery process may be occurring in the Telagen S propellant. This is best seen by comparing 4 week and 9 week data in Table XIX. The tensile strength and modulus have both increased. The same trend is seen in Table XX, but for these conditions (170°F and 80% relative humidity) the propellant has degraded far beyond usefulness. The effectiveness of the recovery process should be more clearly defined by 6 month data.

In general, there have been little differences between the aging behavior of wrapped and unwrapped samples. Only at 170°F and 80% relative humidity (Table XX) has there been a clear cut difference between the samples, the wrapped samples aging more slowly. At these conditions, however, the degradation was rapid for both the wrapped and unwrapped samples.

The aging data at 170°F is summarized in Figures 11-14.

c. Advanced Propellants

Telagen S propellants containing Be and LMH-2 were prepared and placed in aging in Phase Four of this program. After 6 months at 80°F and at 0 and 30% relative humidity, these propellants show no visual or hardness change. An LMH-1 Telagen S propellant was prepared as part of Task Four of Phase Five of this program and after 2 months at the above conditions, the propellant shows no visual or hardness change.



MAXIMUM AND BREAK ELONGATIONS FOR PROPELLANTS AGED IN CIRCULATING AIR, 25% HUMIDITY AND 170°F

Figure 11

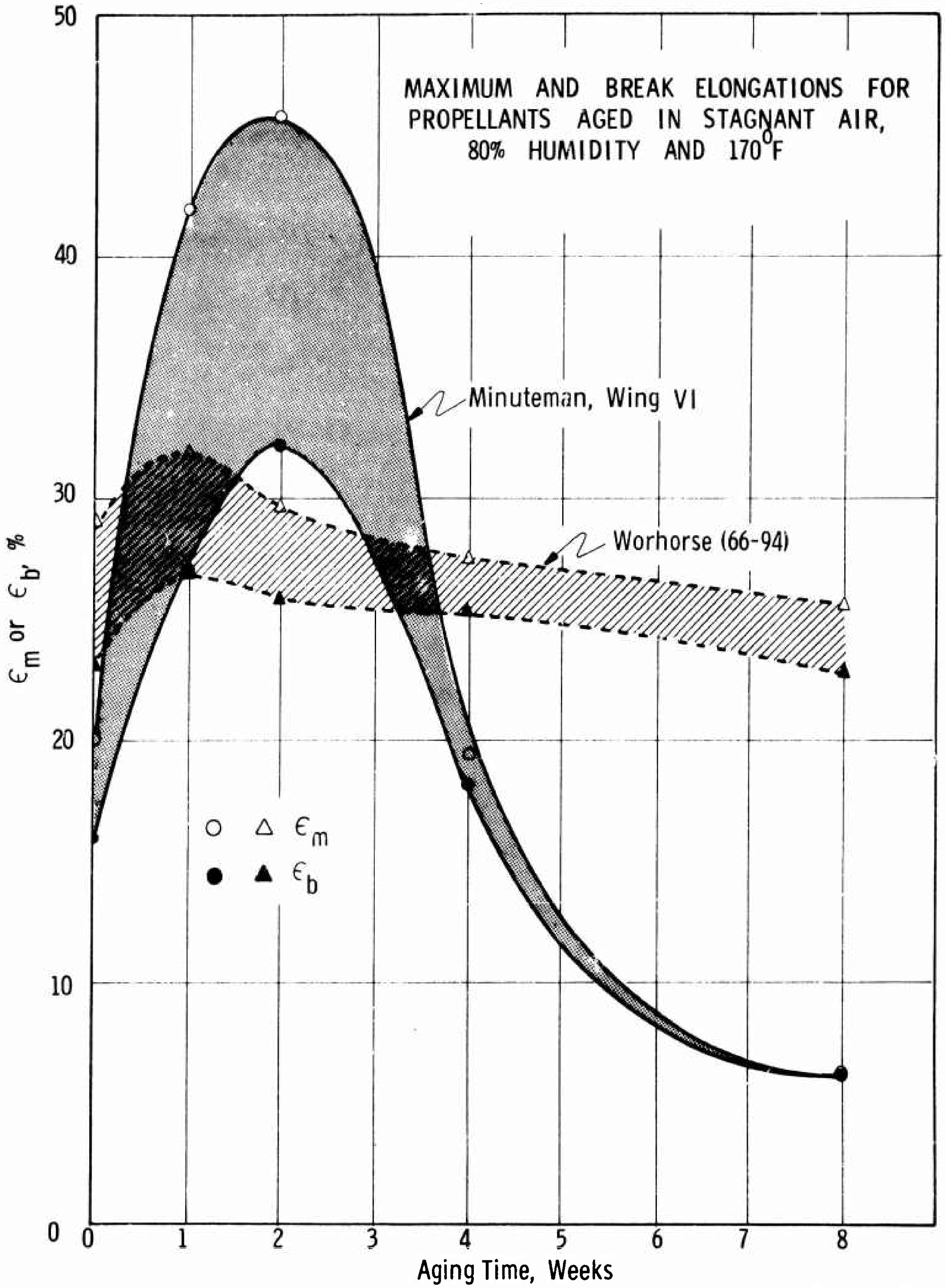

MAXIMUM AND BREAK ELONGATIONS FOR PROPELLANTS AGED IN STAGNANT AIR, 80% HUMIDITY AND 170°F
Minuteman, Wing VI
Worhorse (66-94)
○ △ ϵ_m
● ▲ ϵ_b
ϵ_m or ϵ_b, %
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
Aging Time, Weeks

Figure 12

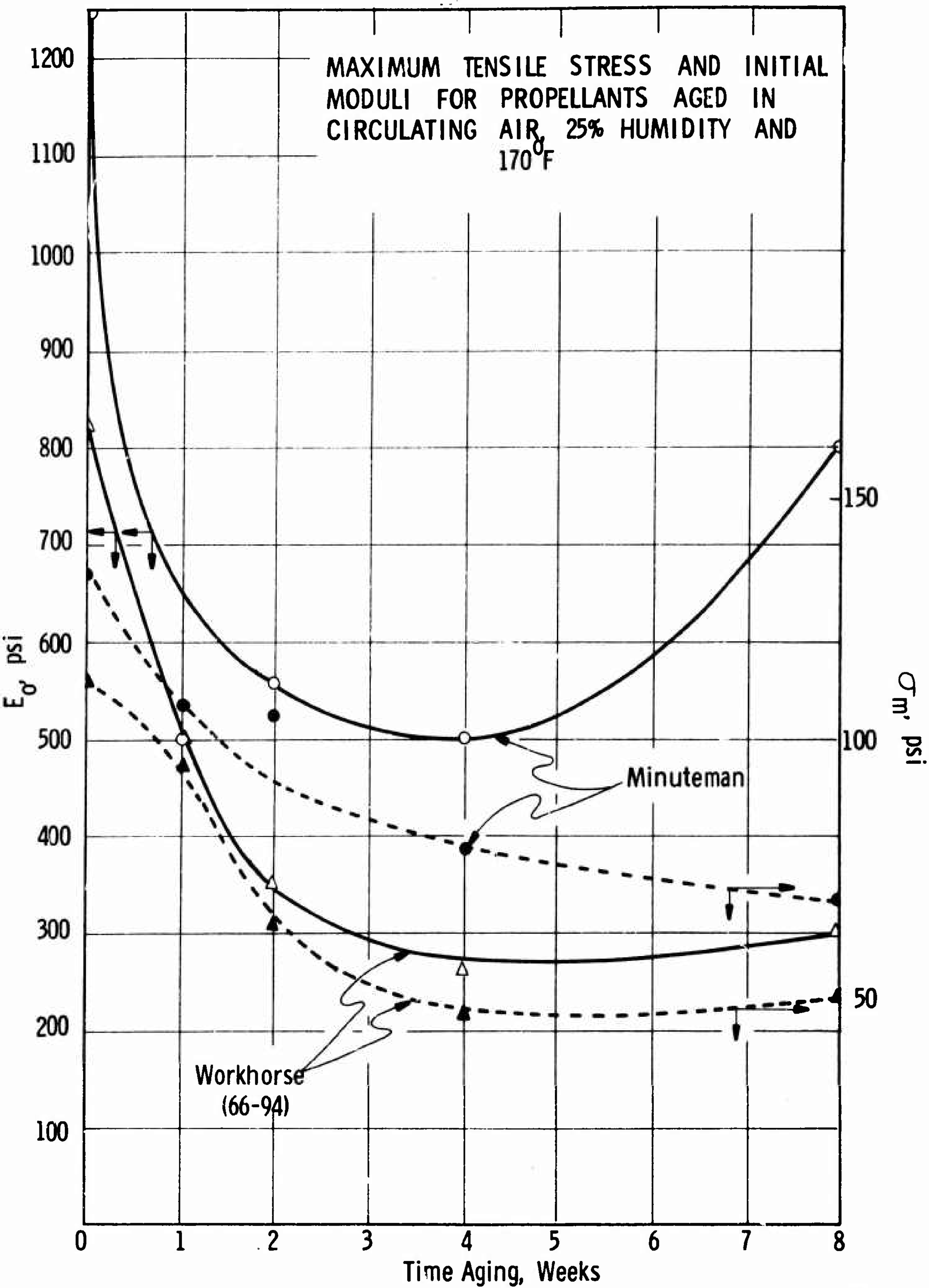

MAXIMUM TENSILE STRESS AND INITIAL MODULI FOR PROPELLANTS AGED IN CIRCULATING AIR, 25% HUMIDITY AND 170°F
1200
1100
1000
900
800
700
600
500
400
300
200
100
E_0, psi
150
100
50
σ_m, psi
Minuteman
Workhorse (66-94)
0
1
2
3
4
5
6
7
8
Time Aging, Weeks

Figure 13

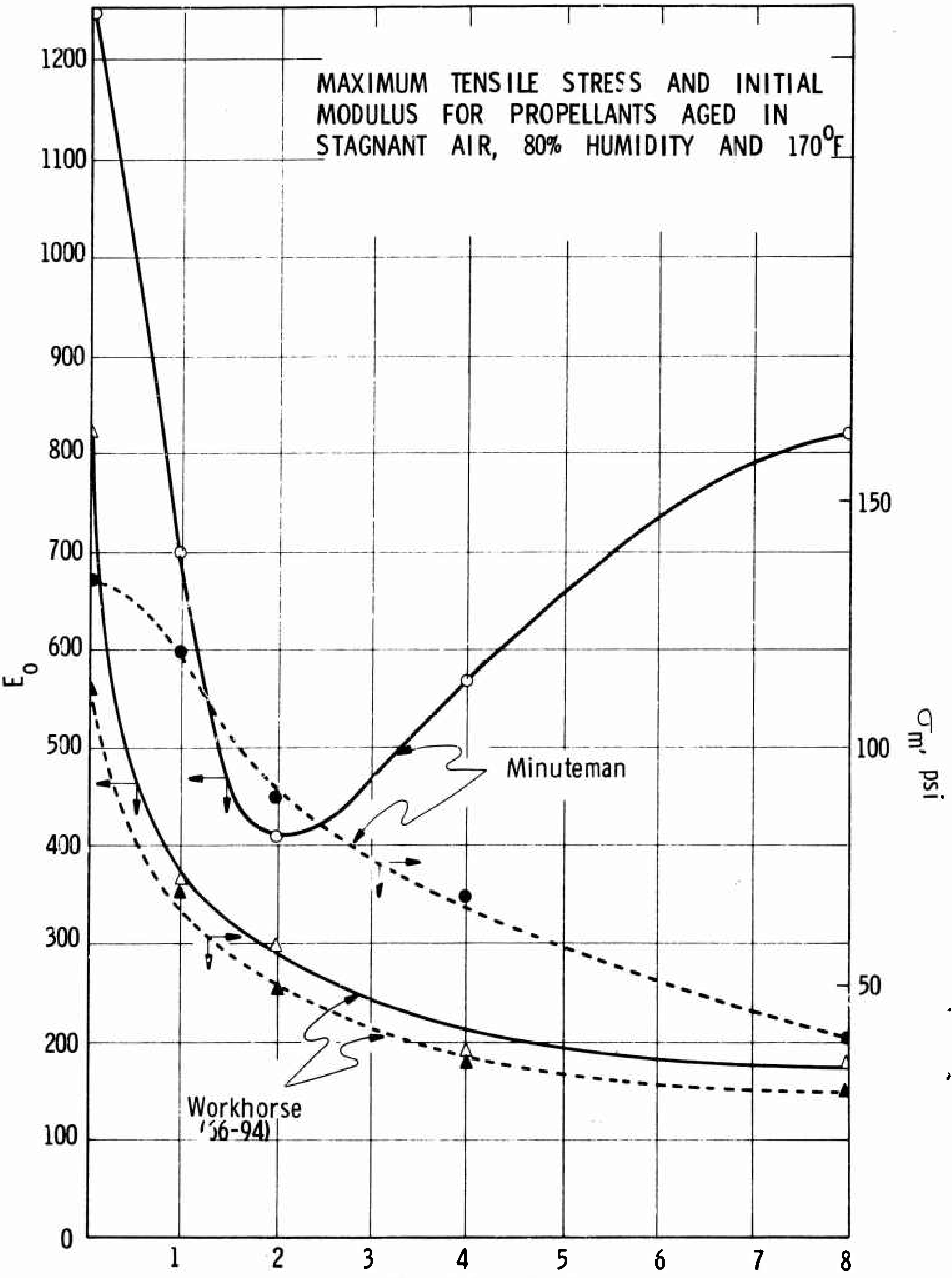

MAXIMUM TENSILE STRESS AND INITIAL MODULUS FOR PROPELLANTS AGED IN STAGNANT AIR, 80% HUMIDITY AND 170°F
E_0
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
σ_m, psi
150
100
50
Minuteman
Workhorse
(56-94)
1
2
3
4
5
6
7
8
Time Aging, Weeks

Figure 14

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(2) D. E. Johnson, R. H. Quacchia, and A. J. Di Milo, "The Development and Evaluation of a Hydrocarbon Binder for High Energy Solid Propellants" (U), Aerojet-General Corporation, Sacramento, California, AFRPL-TR-67-158, Contract AF 04(611)-11419, April 1967. (Confidential)

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(5) D. H. Wadsworth, J. Org. Chem., 32, 1184 (1967).

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13. ABSTRACT

The acquisition and characterization of hydroxy terminated Telagen S was continued. The functionalities by molecular weight to equivalent weight ratio continue to be below 1.7, but cured binders indicated functionalities in excess of 1.85. The equivalent weights determined by reaction with n-butyl isocyanate were within 2% of values obtained by the manufacturer of the prepolymers. Thin-layer chromatography was used to demonstrate the presence of nonfunctional and monofunctional fractions in Telagen S. Considerable effort was devoted to improving the low temperature properties which may be caused by the high concentration of polar groups in the saturated binder. The use of substitutes for CTI and catalysts studies to achieve room temperature cures were also pursued. PAPI gave good cures with Telagen S, but 1,2,6-hexanetriol has been eliminated as a substitute for CTI. The processing of Telagen S propellants at room temperature is apparently limited more by prepolymer viscosity than by cure rate. Burning rate studies indicate very similar rates for saturated and unsaturated polybutadiene propellants. Cyclic imides have been eliminated as a cure system for advanced oxidizers because of very slow reaction rate with hydroxy groups. The more rapid reacting acid anhydrides have more potential in this area. After two months of aging at 170°F and at relative humidities in excess of 25%, both Telagen S and Minuteman Wing VI Second Stage propellants are degraded.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Saturated Hydrocarbon Binders						
High Energy Solid Propellants						
Telagen S						
Burning Rate of Hydrocarbon Propellants						
Characterization of Saturated Prepolymers						
Thin-layer Chromatography						
Acid Anhydrides as Curing Agents						
Imides as Curing Agents						
Aging of Hydrocarbon Propellants						

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