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(TITLE UNCLASSIFIED)
EVALUATION OF HIGH-ENERGY BINDER

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United Technology Center

TECHNICAL REPORT AFRPL-TR-67-111
June 1967

Group 4
DOWNGRADED AT 3 YEAR INTERVALS
DECLASSIFIED AFTER 12 YEARS

AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND, UNITED STATES AIR FORCE
EDWARDS, CALIFORNIA

UTC 2200-FR

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UTC 2200-FR

FOREWORD

(U) This report is the final report on Contract No. AF 04(611)-11404 under which United Technology Center (UTC) has conducted a program to evaluate the high-energy NF_2 binder, PBEP, in prototype propellant formulations. This report covers the experimental work conducted at UTC's Sunnyvale, California, research laboratories during the period 1 March 1966 to 28 February 1967. The work performed under this project is in response to requirements of AFFTC Project 3148, Program Element No. 62405184, BPSN 623148. The AFRPL project engineer is Mr. F. Roberto, AFRPL, Edwards Air Force Base, California.

(U) Classified information has been extracted from (asterisked) documents listed under References on page 75.

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

(U) This technical report has been reviewed and approved.

Col. W. H. Ebelke
Chief, Propellant Division
AFRPL
Edwards Air Force Base, California

ABSTRACT

(U) The high-energy binder, PBEP, has been evaluated in prototype propellant formulations. Cure problems encountered have been resolved by introducing changes in the original process variables. There appears to be no basic incompatibility between AlH_3 and the PBEP/TVOPA binder system. A 100-g motor has been successfully fired based on these ingredients with AP as oxidizer. Good cures were obtained on AlH_3 propellant with a high binder level with one ambient cured formulation giving a stress of 121 psi and strain of 52%. Surveillance studies of 2-in. cubes of propellant have indicated that DBTDA cure catalyst may have better aging characteristics than a cube with FeAA cure catalyst, although the two cubes did contain different PBEP lots. HAP appears to be compatible in either the NF_2 binder/Al system or NF_2 binder/AlH_3 system. Samples of these formulations have been stored for several months under dry conditions with no signs of deterioration.

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TABLES (Continued)

ABBREVIATIONS AND SYMBOLS

1, 2, 6-HT	1, 2, 6-hexanetriol
Al	aluminum
AlH_3	aluminum hydride
Al_2O_3	aluminum oxide
AP	ammonium perchlorate
ARC	Altantic Research Corporation
Be	beryllium
BeH_2	beryllium hydride
BTU	bis[tris(difluoramino)]methyl urea (C)
Bu_2SnAc_2	dibutyltin diacetate
CT	carboxy terminated
DBP	dibutyl phthalate
DBTDA	dibutyltin diacetate
DMM	3, 3'-dimethyldiphenylmethane-4, 4'-diisocyanate
DTA	differential thermal analysis
FeAA	ferric acetylacetonate
Fe_2O_3	ferric oxide
HAP	hydroxylamine perchlorate
$H_{12}MDI$	dicyclohexylmethane-4, 4'-diisocyanate
HP-2	hydrazine diperchlorate
HPE	hexakis(difluoramino)propyl ether (C)
ICRPG	Interagency Chemical Rocket Propulsion Group
JANAF	Joint Army-Navy-Air Force
LiF	lithium fluoride
Mg	magnesium
MgO	magnesium oxide

ABBREVIATIONS AND SYMBOLS (Continued)

N_2	nitrogen
N_2F_4	tetrafluorohydrazine
NF_2	difluoramino group
NP	nitronium perchlorate
OPE	1,2 bis 2,2,3-tris(difluoramino)propoxy 1,2-bis difluoramino ethane (C)
PBAA/AN	polybutadiene-acrylic acid-acrylonitrile
PBEP	poly[1,2-bis(difluoramino) 2,3-epoxy propane] (C)
QMB-3	tetramethyl ammonium hydrotriborate, a product of Callery Chemical Company
S	sulfur
TDI	tolylene diisocyanate
TGA	thermogravimetric analysis
TVOPA	1,2,3-tris[1,2-bis(difluoramino)vinoxy]propane (C)
UTC	United Technology Center
VOAA	vanadyl acetylacetonate
XL	crosslinked

SECTION I

INTRODUCTION

1. PROGRAM SCOPE

(C) Under Contract No. AF 04(611)-11404, UTC has conducted a research program to evaluate a high-energy NF_2 binder in both metallized and non-metallized propellants oxidized by conventional and high-energy oxidizers. The purpose of the program was the extension of the utility of PBEP binder with state-of-the-art fuels and advanced fuels to yield advanced propellants of high performance, high density, and high-performance efficiency. In addition to these objectives, the program was also designed to develop a high burning rate NF_2 propellant and to provide test data on the stability of NF_2 propellants. Work under this contract began on 1 March 1966.

(C) The program was divided into three phases. Phase I was concerned with the development of propellants with aluminum and boron as fuels. Phase II was devoted to the exploitation of the PBEP binder as a high-energy replacement for existing high-performance systems. Aluminum hydride was formulated with a variety of oxidizers and plasticizers. Phase III was devoted to the development of techniques for measuring the stability of NF_2 propellants and for the characterization of these propellants using manometric and physical deterioration measurements.

(C) The primary goals of this work were:

A. Development of a boron and aluminum propellant with a theoretical impulse of 300 sec

B. Development of a propellant with an impulse greater than current state of the art (265 sec) and a density greater than 0.065 lb/in.^{3}

C. Development of a propellant with a burning rate of from 1.0 to 10.0 in./sec at 1,000 psi.

D. Obtain data on the long-term aging stability of Domino propellants based on the PBEP binder.

2. REPORT STATUS

(U) This final report covers the experimental work performed during the year 1 March 1966 to 28 February 1967.

SECTION II

TECHNICAL DISCUSSION

(C) PBEP is prepared by Shell Chemical Co. by the direct addition of N_2F_4 to the unsaturated carbon-to-carbon double bonds in dehydrochlorinated polyepichlorohydrin which has been glycerol initiated. PBEP is a tan-colored, highly viscous polymer with a typical molecular weight in the range of 3,600 to 4,500. The specific gravity at 25°C of a typical prepolymer is 1.58 g/cc. The typical analysis is:

Carbon	25.8%
Hydrogen	3.6%
Nitrogen	15.6%
Fluorine	40.9%
Difluoramino groups	58.0%
Equivalent wt OH/100g	0.040

(C) Successful formulation of PBEP propellants is dependent upon the use of plasticizers to lower the viscosity of the prepolymer. The polymer may be cured successfully with a diisocyanate used in conjunction with a crosslinker such as 1,2,6-hexanetriol or glycerol.

1. THEORETICAL CALCULATIONS

(C) The calculation conventions used at UTC are those used previously under Air Force Contract No. AF 04(611)-10540.[1]* A calculated heat of formation of -43.675 kcal/100g based on the elemental analysis of a crosslinked PBEP binder as reported by Shell Development Co.[2] is now used in all performance calculations. This lowers the NF_2 content and results in a more negative heat of formation. The term "PBEP XL" refers to the crosslinked binder. The heat of formation used for TVOPA is -199.45 kcal/mole.

a. Aluminum Systems

(C) The performance of aluminum in the AP-oxidized PBEP XL/TVOPA binder is shown in figure 1. The peak performance occurs at 15 wt-% aluminum in a very fluid area of high binder content.

* Superscript numbers denote references appearing on page

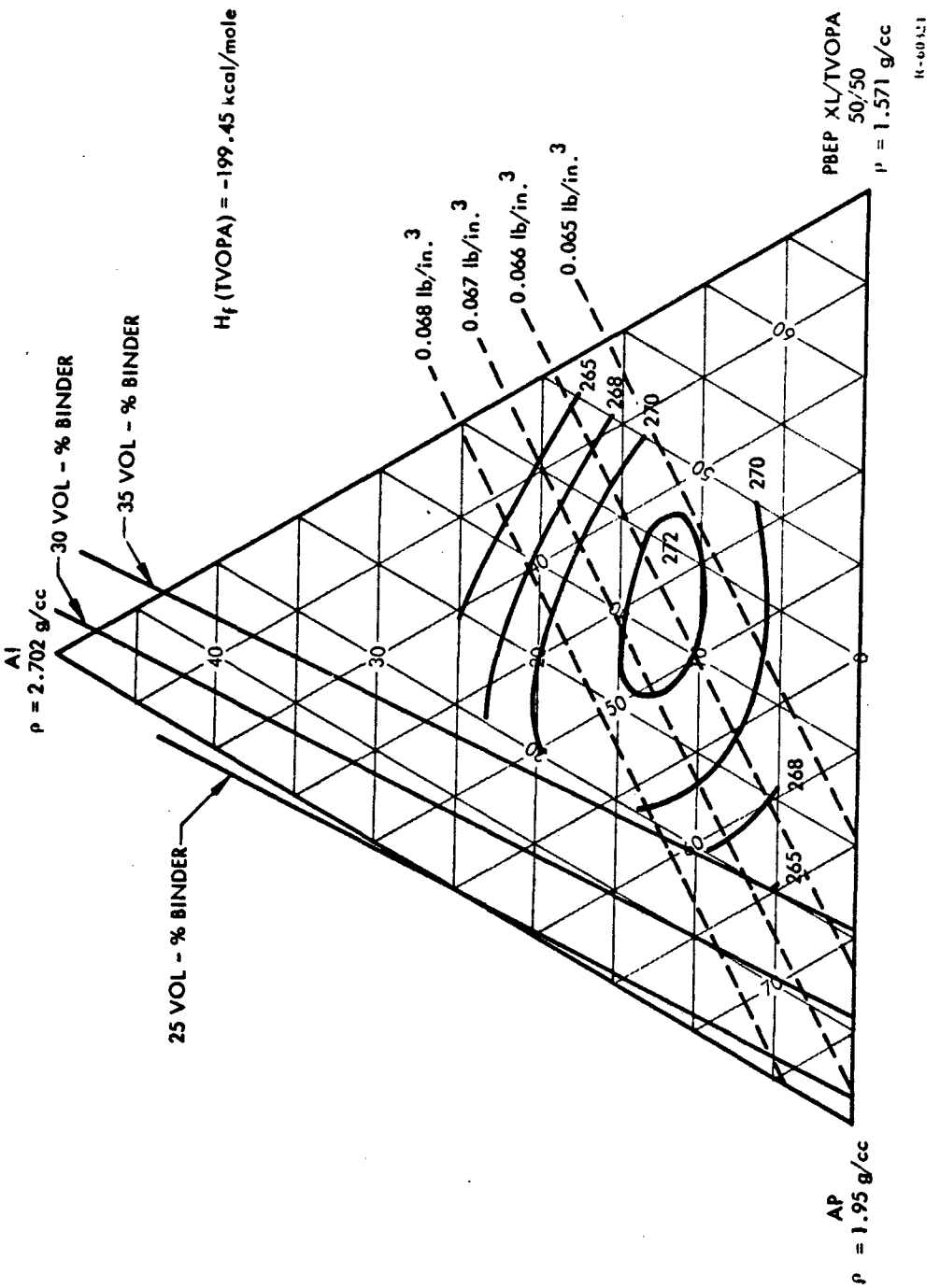

Figure 1. (U) Performance in the Al/AP/PBEP XL/TVOPA Binder System

The density of this composition is approximately 0.068 lb/in.^{3} The theoretical specific impulse of the peak is 272 sec. Substitution of OPE for TVOPA gives approximately a 5-sec impulse improvement. With OPE's high density (1.713 g/cc) this system appears very attractive with propellant densities in the 0.067 to 0.069/in.^{3} region.

(C) The use of an energetic nondifluoramino oxidizer is shown in figure 2, where HP-2 has been substituted for AP in the PBEP XL binder. The system reaches a peak performance of 274.1 sec at 10 wt-% aluminum with a density of 0.070 lb/in.^{3} The use of HAP oxidizer increases the peak theoretical impulse to 274 sec, as shown in figure 3. No density improvement at peak performance is obtained with HAP even though it has a higher density than AP. This is because of the lower oxidizer requirements in the HAP system. However, a density of 0.070 lb/in.^{3} can be obtained at an impulse of 272 sec.

(C) The use of a difluoramino oxidizer such as BTU with the aluminum system requires AP or a similar source of working fluid because the other three constituents are poor in hydrogen. The BTU/AP/Al systems peak between 5 wt-% and 10 wt-% aluminum at a value of approximately 289 sec. However, because of the extreme sensitivity of BTU, its application is highly questionable.

b. Aluminum Hydride as Fuel

(C) Aluminum hydride in the AP-oxidizer PBEP XL system peaks in an unprocessable region. If the composition is chosen on the ternary, shown in figure 4, at the intersection of the 25 vol-% binder line and the 25 wt-% AlH_3 line,* the theoretical performance is 287 sec. The density of this composition is approximately 0.0615 in./sec.^{3} As might be expected, the addition of HP-2 or HAP will increase this performance. Figure 5 illustrates the effect of substituting HAP for AP in this system. The performance at this same intersection is now about 292 sec, a gain of 5 sec, and the density of the composition is now 0.0632 lb/in.^{3}

* (C) The choice of 25 wt-% AlH_3 as the fuel level is influenced by the performance efficiencies experienced in AP-CHON system under Contract No. AF 04(611)-9570. However, the higher efficiencies achieved in the Al-AP-PBEP system suggest that higher AlH_3 contents without loss of efficiency are possible.

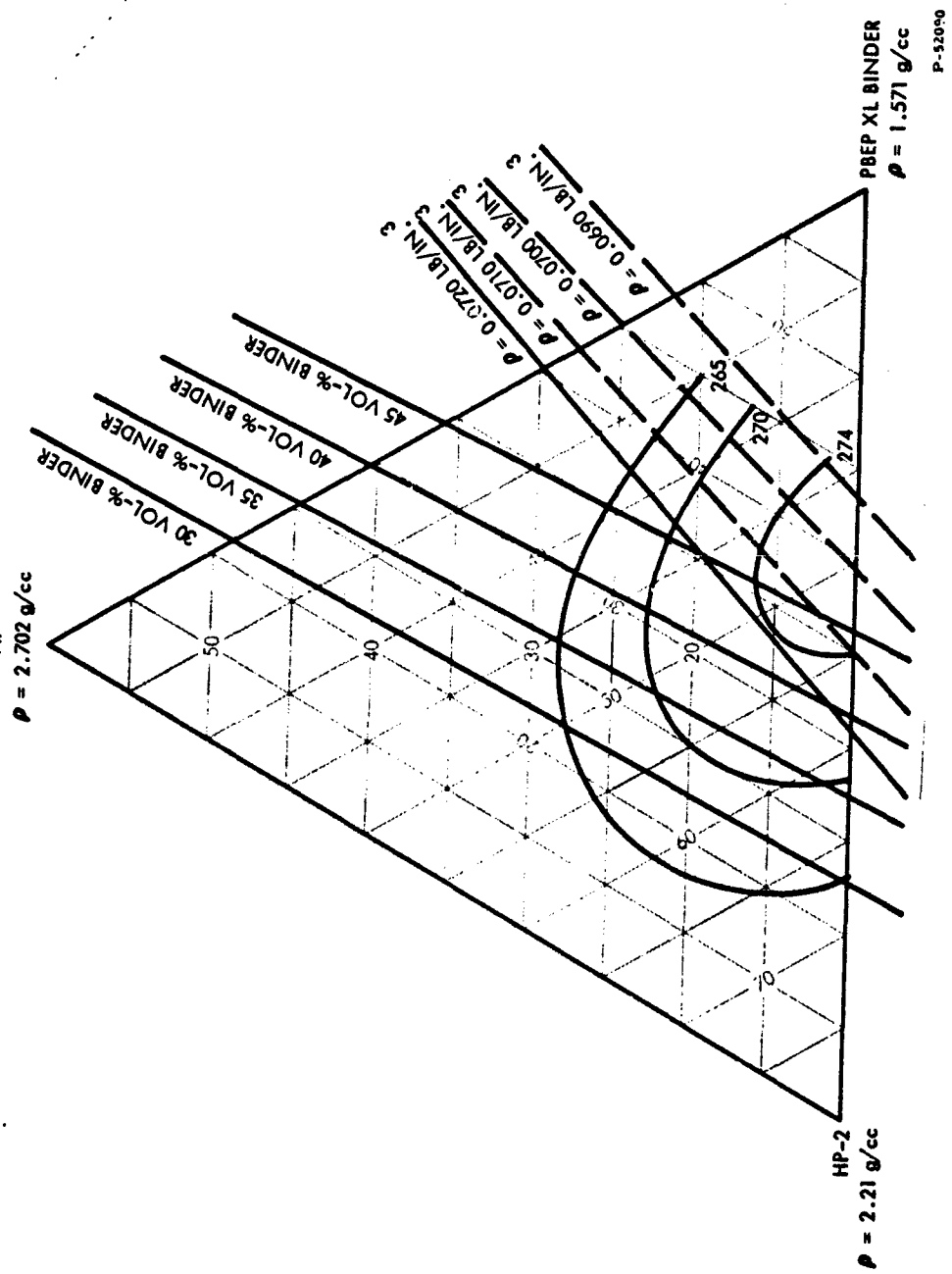

Figure 2. (U) Performance in the Al/HP-2/PBEP XL Binder System

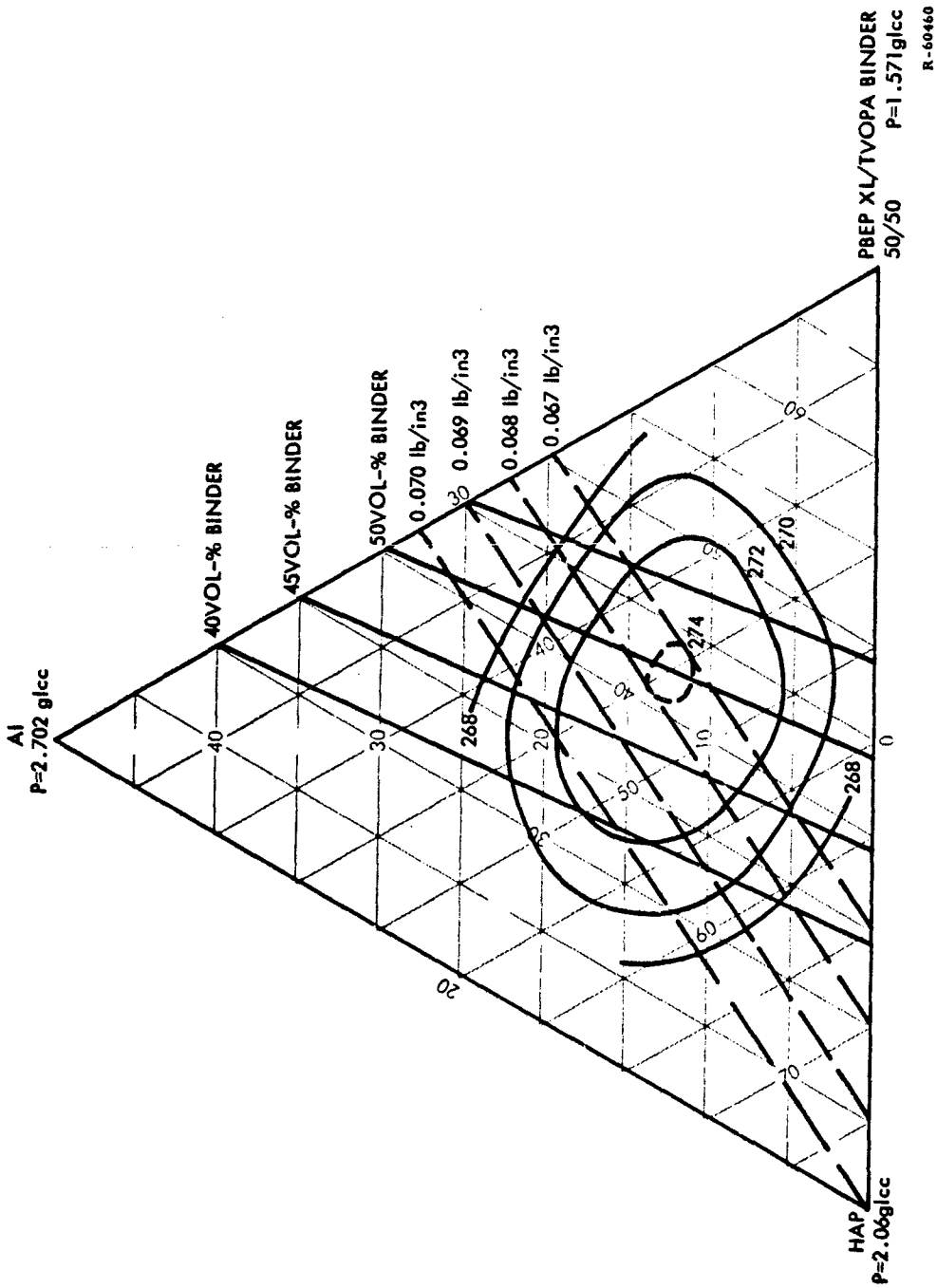

Figure 3. (U) Performance in the Al/HAP/PBEP XL/TVOPA Binder System

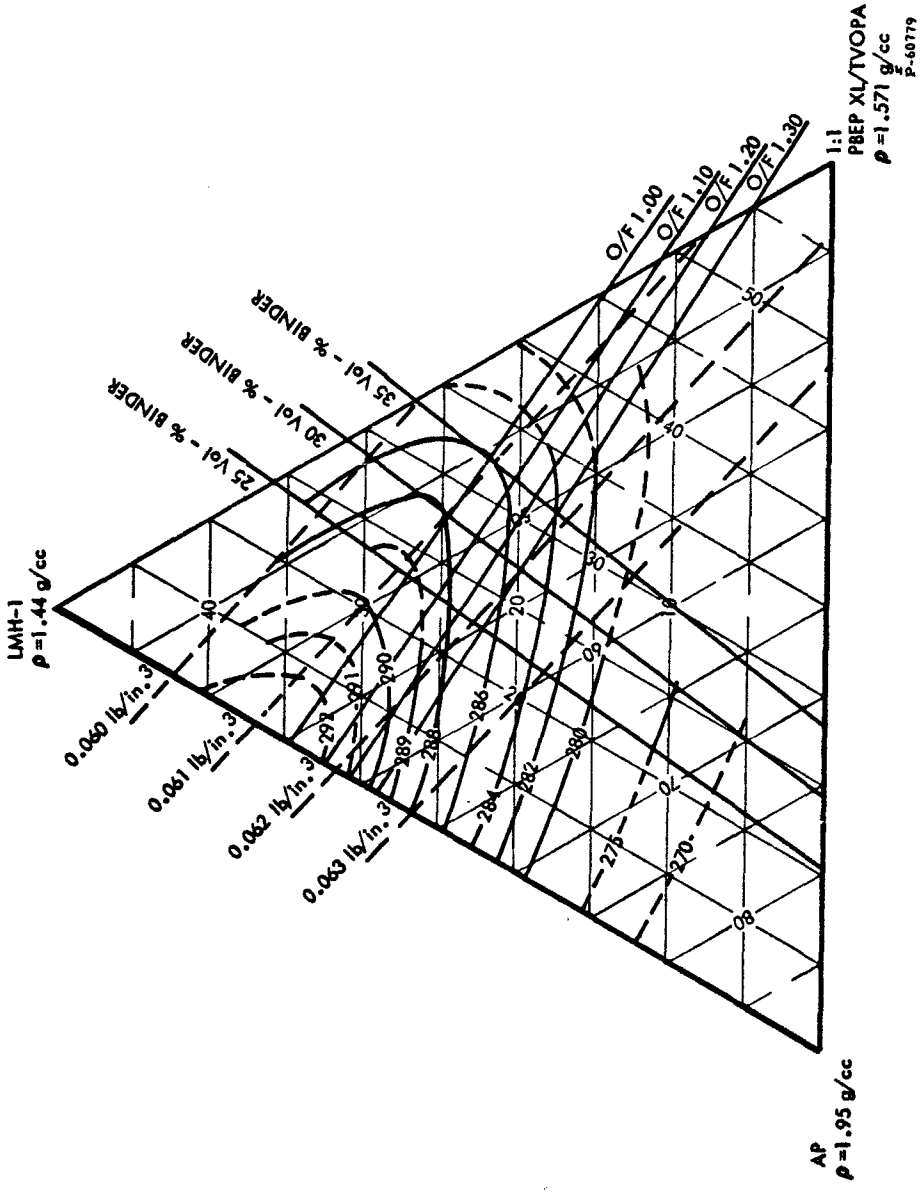

Figure 4. (U) Performance in the AlH_3/AP/PBEP XL Binder System

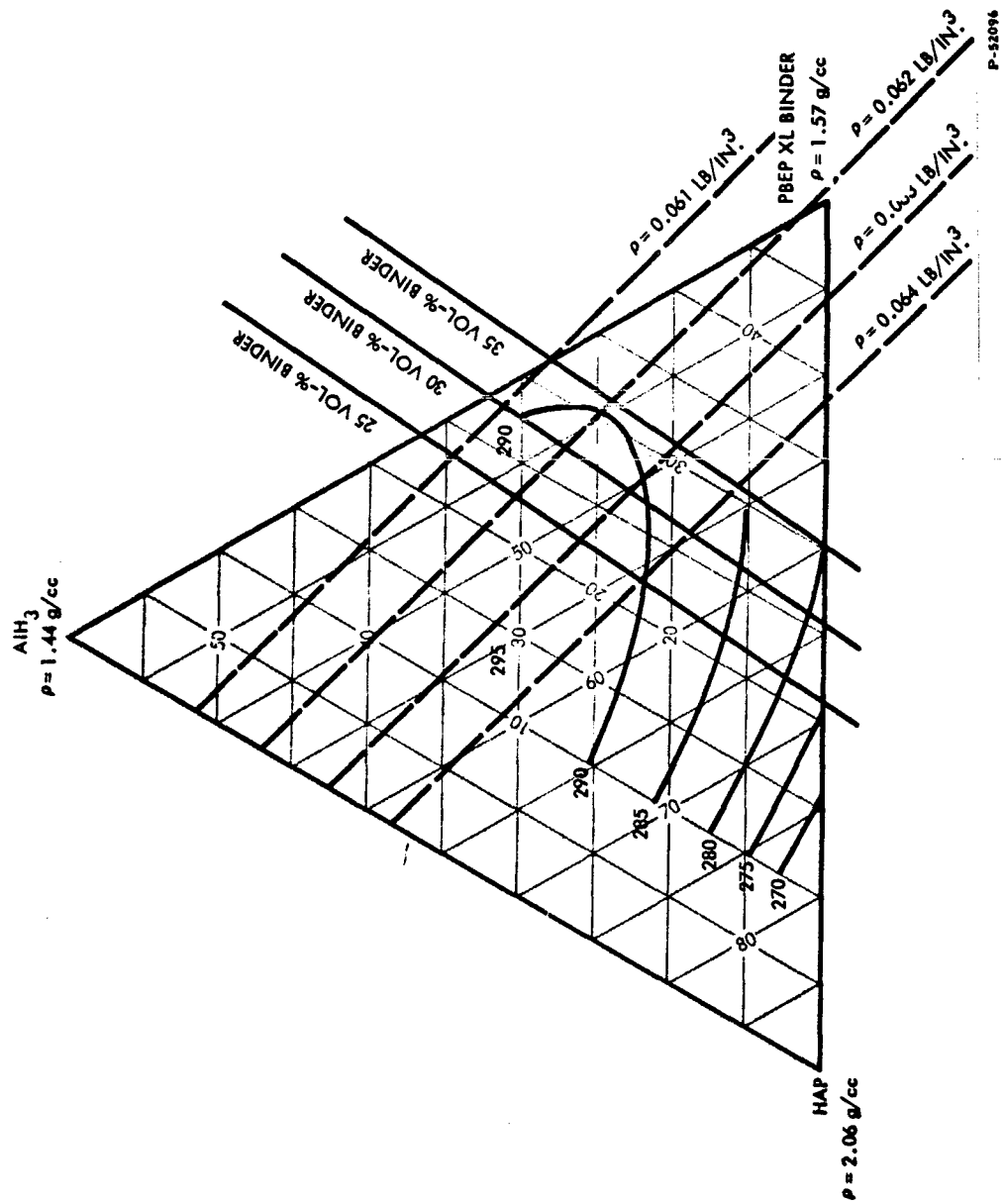

Figure 5. (U) Performance in the AlH_3/HAP/PBEP XL Binder System

(C) Because the location of this intersection is influenced positively by the density of the solid phase, the use of the more dense HP-2 should add another second to the value of this intersection.

c. Beryllium and Beryllium Hydride

(C) Both beryllium and beryllium hydride are of special interest in view of the reasonable probability that higher combustion efficiencies can be achieved with these materials in NF_2 systems. The performance of beryllium in an AP-oxidized PBEP XL binder is shown in figure 6. The system peaks at 290+ sec with a metal content of 15 wt-%. The density of this formulation is about 0.0630 lb/in.^{3} The addition of HAP or HP-2 to this system should result in a peak of approximately 294 sec.

(C) The performance of BeH_2 in an AP-oxidizer PBEP XL binder, figure 7, seeks a peak in areas of unprocessability. However, using the density of crystalline beryllium hydride of the type now prepared by Ethyl Corporation, and processing at 25 vol-% binder, a performance of 315 sec at a level of 22 wt-% hydride appears possible.

2. PBEP AND PBEP PROPELLANT STABILITY STUDIES

(U) The thermal stability of PBEP and PBEP propellants have been tested by mass spectrograph, DTA, TGA and other methods. Propellant surveillance samples indicate that FeAA cure catalyst may be more unstable in propellant than the DBTDA catalyst.

a. PBEP Decomposition Study by Mass Spectrograph

(U) The gaseous decomposition products of PBEP were identified by mass spectrographic analysis of the gaseous products from the decomposition of PBEP at 70° to 85°C. Pressure changes at these temperatures correlated with decomposition observed previously in TGA analysis. The heated PBEP sample had darkened with an increase in volume caused, perhaps, by trapped gases.

(C) The mass spectrum of the gas sample was obtained with a CEC Model 21-103C mass spectrometer by Stanford Research Institute. The results are listed below. Quasi-quantitative values are given only to indicate relative orders of abundance.

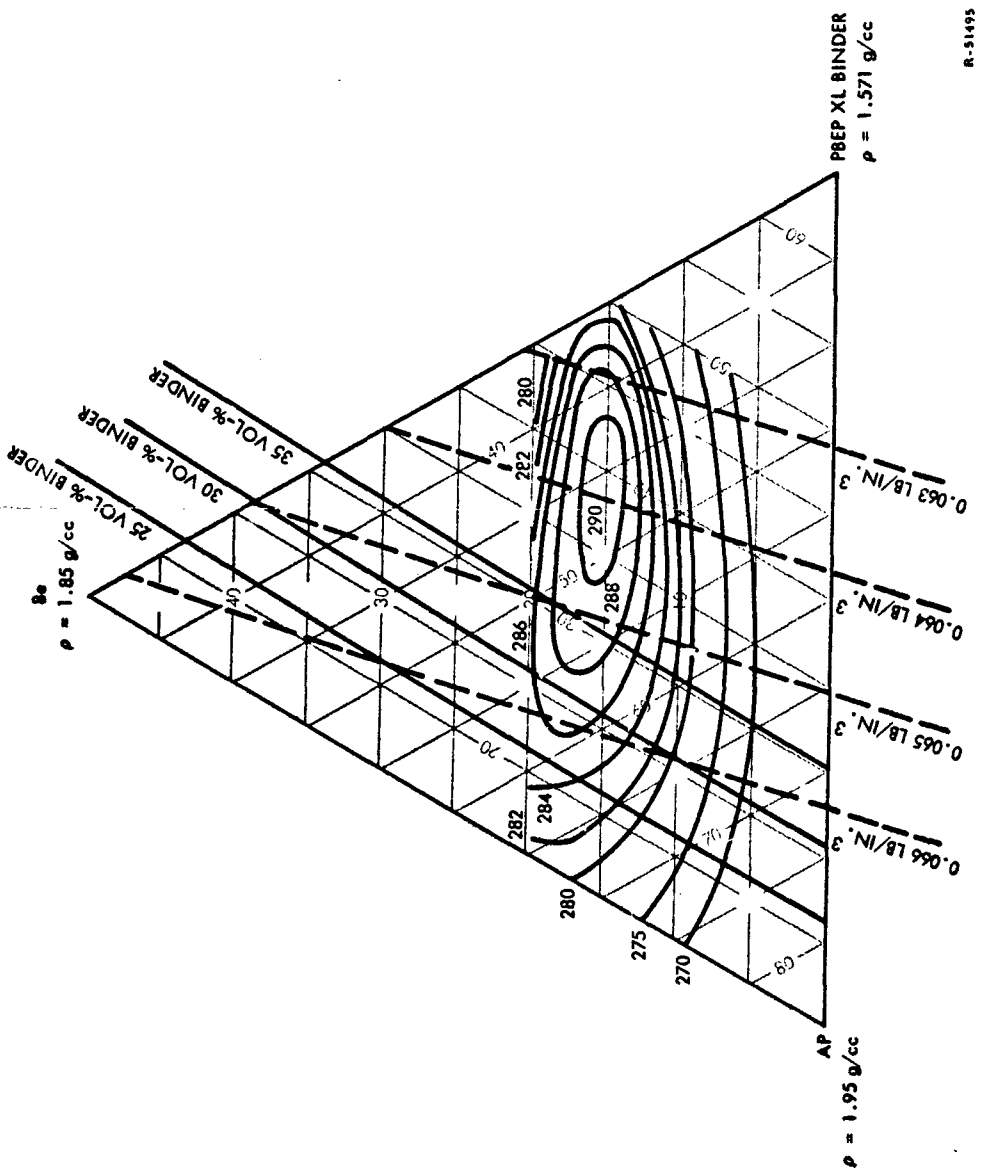

Figure 6. (U) Performance in the Be/AP/PBEP XL Binder System

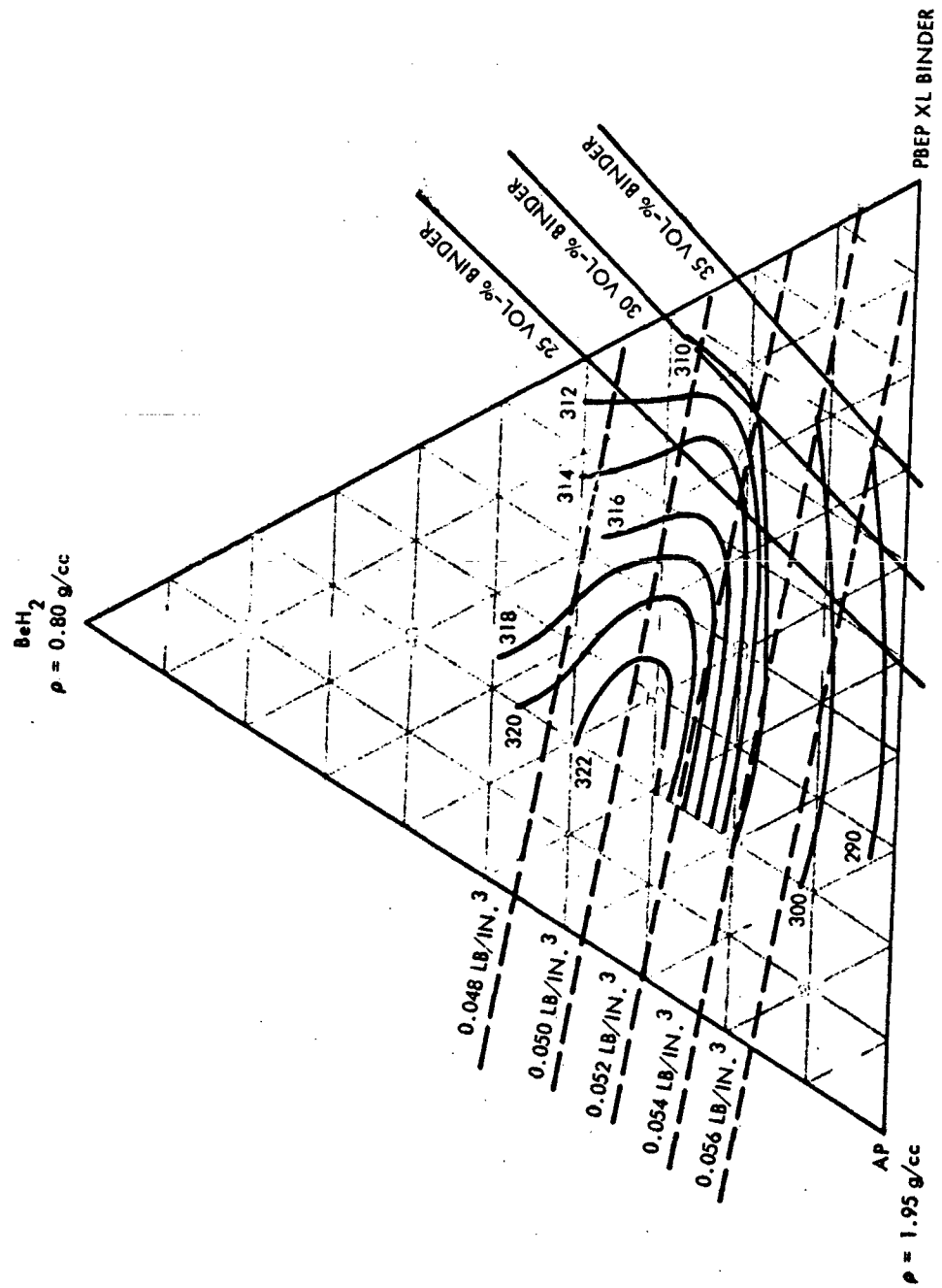

Figure 7. (C) Performance in the BeH_2/AP/PBEP XL Binder System

Component	Mol-%	Component	Mol-%
H_2	48	CO_2	4
H_2O	14	Air	7
N_2, C_2H_4, CO	15	C_6H_{14} (branched)	3
CH_2Cl_2	8	HF	0.1
Unidentified	1		

The gas was also sampled after evacuation at liquid nitrogen temperature, but the spectrum showed no difference except in the loss of hydrogen and air.

(U) The lack of HF concurrent with the high percentage of H_2 probably results from the interaction of HF with the steel walls of the container. The presence of the branched hydrocarbon as well as CO_2, and possible C_2H_4 and CO, indicates some degradation of the polymer backbone. No NF_2-containing material was found.

b. Effect of Cure Ingredients

(C) DTA results indicated that addition of a large percentage of the cure additives FeAA, TDI, and 1,2,6-hexanetriol decreases the stability of PBEP. Of the several propellant ingredients tested with PBEP, 1,2,6-HT, FeAA, and Bu_2SnAc_2 showed the least compatibility under higher temperature conditions. The onset of the mixture of 1,2,6-HT and PBEP as compared to that of pure PBEP was lowered from 146° to 111°C and the first major exotherm from 204° to 153°C. FeAA and Bu_2SnAc_2 gave onsets that were lowered by about 50°C. The least incompatibility was exhibited by TDI and PBEP with very little change in either the onset or first exotherm peak. These materials were tested at a 25% level which exaggerates any incompatibility that might be found under normal conditions where only a small percentage of the material is actually used.

(U) Based on the DTA results, PBEP lot 9165-107 samples with these additives were conditioned at 45°C and the weight losses measured. The effect of the urethane linkages on stability were evaluated by adding the urethanes of methyl alcohol and TDI and DDI were added to PBEP. As shown in table I, there is evidence that the urethane linkage causes some instability.

TABLE I

(U) EFFECT OF CURE ADDITIVES ON PBEP STABILITY

68 Days at 45 °C

	Wt Loss, %
PBEP neat	1) 2.34 2) 2.37
PBEP + 10% 1,2,6-HT	8.01
PBEP + 10% FeAA	8.82
PBEP + 10% TDI	14.39
PBEP + 10% (MeOH + DDI urethane)	3.62
PBEP + 10% (MeOH + TDI urethane)	4.75

(U) The large weight loss with TDI possibly is caused by volatilization of the excess TDI. The apparent instability induced by the urethanes is, however, significantly less than that induced by excess FeAA or 1,2,6-HT.

c. Stabilizing PBEP by Additives

(C) UTC has conducted DTA tests to screen possible candidate stabilizers. Based on the results of the DTA tests, a number of candidate stabilizers were chosen for screening in accelerated aging tests. Table II lists the results of these tests conducted for 72 days at 45 °C. Tricresyl phosphate was found to be the best stabilizer followed by resorcinol and Ca_3PO_4.

(C) Other samples containing 2% urea, LiF, or sulfur were conditioned at 60 °C for 111 days. The results in table III show that there is some improvement with sulfur. Urea and LiF, which are candidate burning rate modifiers and/or stabilizers, were found to be ineffective as stabilizers.

d. Effect of Burning Rate Catalysts on Stability

(U) Weight loss measurements made of samples of UTX 8407 with 1% of each of four burning rate catalysts are shown in table IV. All of these accelerated the decomposition loss rate. Cured PBEP/TVOPA binder and cured PBEP samples also were tested for comparison purposes.

TABLE II

(U) EFFECT OF SELECTED STABILIZERS ON PERCENT WEIGHT LOSS

Exposure Time = 72 Days at 45 °C

Order of Effectiveness	0.5% Additive to Basic UTX 8407 Formulation	Wt Loss, %
1	Tricresyl phosphate	0.49
2	Resorcinol	1.17
3	$Ca_3(PO_4)_2$	1.18
4	K_3PO_4	1.31
5	Na_3SeO_3	1.34
6	No additive (UTX 8407)	1.35
7	Sodium barbituate	1.37
8	Tetrabromophthalic anahydride	1.51
9	Na_3PO_4	1.53

TABLE III

(U) EFFECT OF STABILIZERS AT ELEVATED TEMPERATURES

111 Days at 60 °C

	Wt-% Lost, %
UTX 8407	8.89
UTX 8407 + 2% S	6.42
UTX 8407 + 2% urea	9.04
UTX 8407 + 2% LiF	10.19

TABLE IV

(U) EFFECT OF BURNING RATE CATALYSTS ON STABILITY

67 Days at Ambient Temperature

	Wt-% Lost, %
UTX 8407	0.12
UTX 8407 + 1% milori blue	0.38
UTX 8407 + 1% Fe_2O_3	0.62
UTX 8407 + 1% Fe_3O_4	0.65
UTX 8407 + 1% Cu2O2	0.71
PBEP + TVOPA 50/50 (cured)	0.34
PBEP (cured withough TVOPA)	1.95

e. Surveillance Study

(U) The surveillance schedule includes six 1-lb motors stored at ambient temperature and fired every 3 months. The schedule also includes microtensile specimens stored at ambient for 2 years and at 35 °C for 1 year. Several 2-in. cubes are in storage at 35 °C with any deterioration being followed by X-ray analysis.

(U) The measured physical property data listed in table V from samples of UTX 8422 stored at 35 °C for 150 days gave a tensile value of 192 psi* and 26% elongation. These are equivalent to values obtained after 108 days at 35 °C, which had a tensile of 197 psi and elongation of 25%. Although a cube of this formulation showed some gassing between 60 and 80 days at this temperature, the physical properties indicate no polymer deterioration after 150 days. A 2-in. cube of UTX 8423 formulation, listed in table VI, which contained DBTDA instead of FeAA as a cure catalyst and a different lot of PBEP than UTX 8422 did not gas after 108 days at 35 °C.

* All tensile strength and elongation values gives in this report are true values, reduced from crosshead values using bonded extension gauges.

TABLE V

(U) SURVEILLANCE DATA[1]

Formulation Number	True Tensile Data		Storage Temperature, °C	Storage Time, days
	Elongation, %	Tensile, psi		
UTX 8422	23	130	Ambient	0
UTX 8422	22	222	Ambient	90
UTX 8422	24	215	35	60
UTX 8422	25	197	35	108
UTX 8422	26	192	35	150

(1) The cure catalyst was FeAA, and the PBEP lot in all formulations was 9557-84.

(C) Additional cubes have been placed in storage, one containing 0.5% tricresyl phosphate as stabilizer and one of an NFPA formulation. The other cubes are duplicates of the first cubes using, however, a DMM and DBTDA cure system.

(C) Several 1-lb motors are in storage at ambient temperature. One motor has been fired after 3 months storage. The motor gave a burning rate of 1.29 in./sec at 658 psia which indicates very little change of data from an unaged motor with a rate of 1.350 in./sec at 763 psia.

f. PBEP Propellant Diffusion Tube Specimens

(U) To evaluate the effect of specimen geometry, a number of propellants were evaluated in special closed-end tubes. The specimens had a 1 cm^2 cross section and were about 5 cm in length, with a weight of approximately 2 g. UTX 8407, the standard Al/AP/PBEP/TVOPA propellant, had a weight loss of 0.16% at ambient after 200 days and 0.67% after 200 days at 45°C, as listed in table VII. Some swelling of the samples was observed at 45°C after approximately 100 days. A control formulation, UTP 8298, a 50% TMETN-plasticizer polyether binder, lost 0.044% at ambient and 0.25% at 45°C for the same period.

TABLE VI

(U) SURVEILLANCE FORMULATIONS

Formulation Number	UTX 8422-11	UTX 8422-12	UTX 8422-13	UTX 8422-14	UTX 8422-15	UTX 8422-16
PBEP (lot 9557-84)	18.31	18.31	18.31	18.31	18.31	18.31
TVOPA	18.31	18.31	18.31	18.31	18.31	18.31
TDI	2.18	2.18	2.18	2.18	2.18	2.18
1, 2, 6-HT	0.50	0.50	0.50	0.50	0.50	0.50
FeAA	0.64	0.64	0.64	0.64	0.64	0.64
Al	13.01	13.01	13.01	13.01	13.01	13.01
AP	47.05	47.05	47.05	47.05	47.05	47.05
Triol/PBEP(OH)	0.83	0.83	0.83	0.83	0.83	0.83
NCO/OH[1]	0.98	0.98	0.98	0.98	0.98	0.98
Cure at 120°F, hr	72	72	72	72	72	72
Remarks[2]	Soft cure, voids	Well cured	Soft cure, voids	Soft cure, voids	Soft cure, voids	Soft cure, voids

(1) The Triol/PBEP(OH) and NCO/OH ratios are based on 0.041 hydroxyl equivalents per 100g of polymer determined by infrared (Shell Chemical) rather than a value of approximately 0.075 as determined by gel time studies.

(2) All the mixes listed as giving soft cures after 72 hours at 120°F will postcure in an additional 7 to 10 days at ambient to very tough, flexible propellant.

TABLE VII

(U) WEIGHT LOSS THROUGH A 5 cm WEB
1 cm^2 BY 5 cm LONG TUBE SAMPLES

Exposure Time = 200 Days

Formulation	Percent wt Lost at Ambient Temperature	Percent wt Lost at 45 °C Temperature
UTX 8407[1,2] (PBEP/TVOPA Binder)	a. 0.16	a. 0.65 - sample swelled
	b. 0.16	b. 0.69 - sample swelled
UTP 8298[3] (Uteflex/TMETN Binder)	0.044	0.25
UTX 8410[1,2] (PBEP/DBP Binder)	0.16	0.68

(1) These samples contain 50% AP and 15% Al
(2) PBEP was Lot 9165-107
(3) Contains 16% Al, 66.4% AP

The effect of plasticizer volatility was evaluated in UTX 8410. TVOPA was replaced by the less volatile DBP. No change in weight loss was observed by this variation.

g. Effect of Sample Environment on DTA Thermogram

(U) Because etching of the glass walls occurs during the DTA run, platinum inserts were used to avoid direct contact of PBEP and glass. The onsets for the first exotherm were the same in both cases as shown in table VIII, but the first two major exotherms were lowered considerably. This may be explained by a catalytic effect of platinum on the PBEP decomposition.

(C) Several other effects were tested – the effect of air versus N_2 atmosphere, effect of purification of the PBEP, and the effect of small amounts of moisture. The thermograms were the same from these tests as from the standard tests.

TABLE VIII

(U) EFFECT OF SAMPLE ENVIRONMENT OF DTA THERMOGRAM OF PBEP (LOT 9165-107)

Run	Onset to First Exotherm °C	First Exotherm °C	Second Exotherm °C	Third Exotherm °C	Remarks
1	146	190	213	- -	Platinum sample holders
2	146	186	202	219	Platinum sample holders
3	145	206	213	---	N_2 atmosphere
4	145	187	201	214	Dried over molecular sieves
5	146	204	219	---	"Washed" sample
6	146	200	216	---	Control

h. Evaluation of an Aged Lot of PBEP

(U) PBEP lot 9237-86B which has been aging for a year at about 5 °C was retested in a series of formulations listed in table IX. The lot cured over a range of Triol/PBEP(OH) and NCO/OH ratios similar to that which had been used successfully when the lot was originally received. Apparently, no functionality deterioration has occurred, at least as far as cure ratios are concerned, with this lot of PBEP.

i. Gas Evolution Studies

(U) The JANAF vacuum stability apparatus was evaluated as a tool for measuring the thermal stability of PBEP samples. The reproducibility was found to be poor because of the inability to compensate for the rapid evolution of residual solvent during the testing. Three samples of PBEP propellant and one NFPA propellant were tested. Under the test conditions, 76 °C and vacuum, the NFPA exhibited the best stability. However, extensive plasticizer evolution occurred in all samples creating an uncertainty in the weight of the sample actually being tested. Possibly the use of lower temperatures would improve this situation.

TABLE IX

(U) EVALUATION OF AN AGED LOT OF PBEP[1]

Formulation Number	215-188-1	215-188-2	215-188-3	215-188-4
PBEP[2]	45.75	45.96	46.17	46.42
TVOPA	45.75	45.96	46.17	46.42
TDI	5.54	5.24	4.89	4.41
1,2,6-HT	1.09	1.01	0.92	0.88
DBTDA	1.83	1.84	1.85	1.86
Triol/PBEP (OH)[3]	1.43	1.31	1.20	1.19
NCO/OH[3]	1.49	1.48	1.43	1.36
Cure at 120°F, hr	72	72	72	72
Remarks	Cured	Cured	Cured	Cured

(1) All values for ingredients are in wt-%
(2) PBEP lot in all samples was 9237-86B
(3) The Triol/PBEP(OH) and NCO/OH ratios are based on 0.038 hydroxyl equivalents per 100 g of polymer as determined by infrared by Shell Development Co.

(U) The TGA method for measuring thermal stability was evaluated. The results of these tests are shown in figure 8. Duplicate runs on PBEP lot No. 9557-99A gave excellent reproducibility. The results of the TGA analysis on lot No. 9557-84 also are shown. Utilizing the slope of the percent of sample remaining per hour as a criteria for stability, it is apparent that the 99A lot is less stable than lot No. 9557-84. Because of the reproducibility of the results of this study, TGA is now used as the primary tool for measuring thermal stability of the neat PBEP samples.

(U) An Arrehenius plot of rate versus 1/T over the temperature range of 60° to 90°C gave an energy of activation of -24.5 kcal/mole. It should be noted that the TGA covers only approximately 6% decomposition.

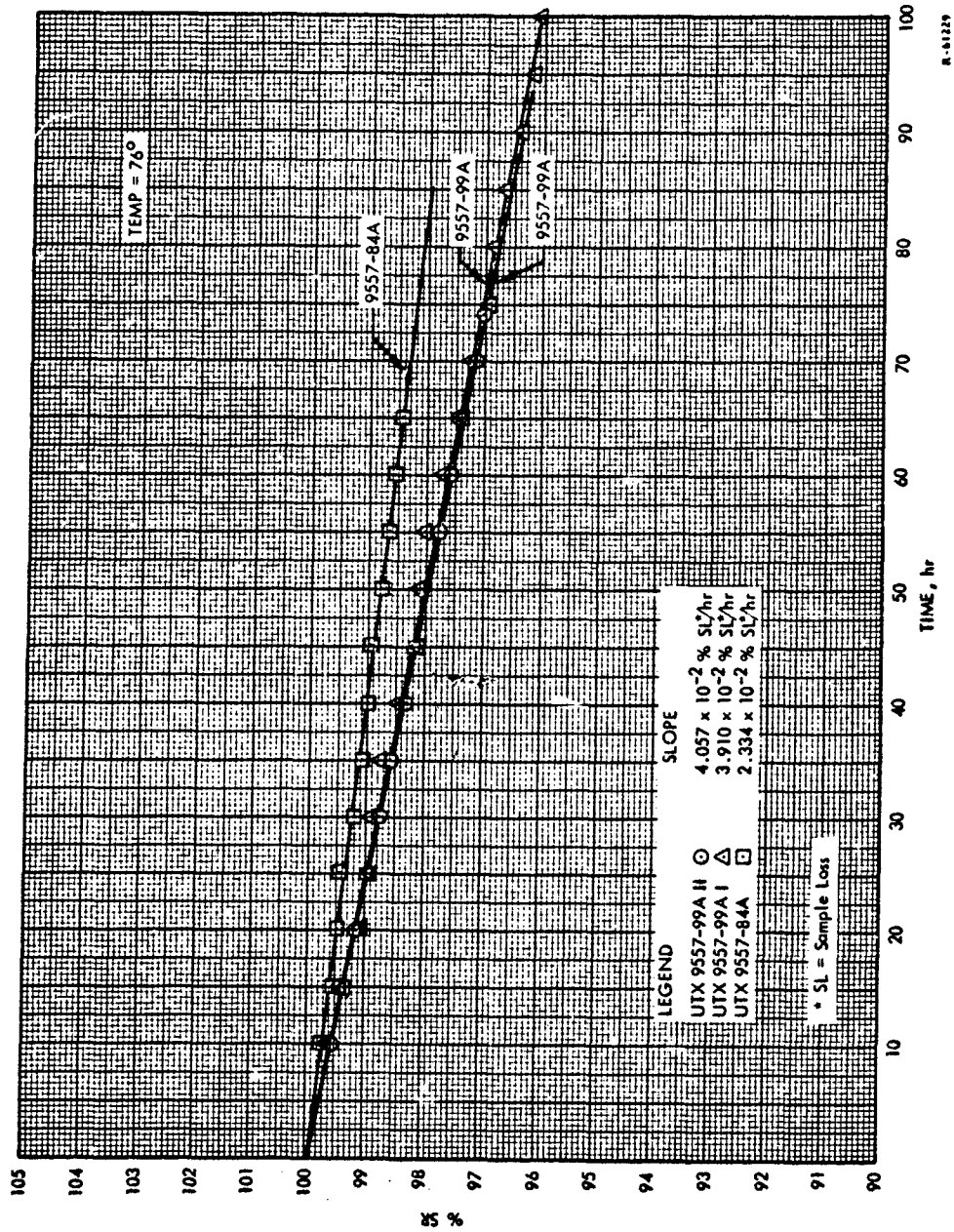

Figure 8. (U) Vacuum TGA Results of Neat PBEP

3. ALUMINUM HYDRIDE EVALUATION

(U) One route to increased performance is by addition of a high-energy fuel such as AlH_3. Previous experience in handling AlH_3 at UTC has shown that AlH_3 propellants can be expected to have a high sensitivity to impact and friction. To evaluate fully the AlH_3-PBEP propellant, a thorough compatibility and hazard evaluation study was made prior to commencing cure studies. The results of these studies as well as cure studies are discussed in the following sections.

a. Aluminum Hydride Compatibility Tests by DTA

(C) The compatibility of AlH_3 with PBEP and TVOPA as well as with OPE and HAP were evaluated by DTA. Two different lots of AlH_3 were investigated. One lot was standard AlH_3, DL-528, and the second lot was an experimental Dow sample, QX022, which is a magnesium-doped AlH_3. Table X presents the test results for the neat materials and mixtures.

(C) Thermograms of AlH_3/PBEP mixtures show an absence of the first PBEP exotherm. The difluoramino group causing the first PBEP exotherm is possibly reacting with decomposed AlH_3 products (Al and H_2) at lower temperatures. Thermograms were run to determine the compatibility of PBEP with magnesium and magnesium oxide powders which could be present on the magnesium-treated AlH_3. All PBEP exotherm onset temperatures occurred at higher than normal temperatures. Either the PBEP is somewhat stabilized or is merely diluted with apparent raising of the onset. Both lots of PBEP exploded with MgO at the first PBEP exotherm peak temperature, but no explosion was noted with the magnesium and PBEP mixture. Magnesium oxide may be basic enough to aid in decomposition of PBEP at higher temperatures.

(C) The thermograms of PBEP/TVOPA/AlH_3 and PBEP/HPE/AlH_3 showed exotherms at temperatures where the AlH_3 endotherm was usually located indicating a reaction between the binder and the decomposed AlH_3 products.

(C) An OPE/QX022 mixture showed a major exotherm at 169°C, again at the same temperature that the hydride is decomposing. An OPE/Al thermogram did not display this exotherm but was similar to the thermogram of pure OPE. A PBEP/OPE/FeAA mixture exploded at 208°C which is the

TABLE X

(U) COMPATIBILITY TESTS BY DTA

Sample[1] Composition	First Endotherm °C	Second Endotherm °C	Onset to First Exotherm °C	First Exotherm °C	Second Exotherm °C	Third Exotherm °C	Fourth Exotherm °C
AlH_3 (QX 022)	168	---	---	---	---	---	---
AlH_3 (DL 528)	181	---	---	---	---	---	---
PBEP	---	---	138	208	219	---	---
PBEP + AlH_3 (QX 022)	185	---	134	227	---	---	---
PBEP + AlH_3 (QX 022)	178	---	144	217	---	---	---
PBEP + AlH_3 (DL 528)	172	---	143	222	---	---	---
PBEP + Mg	---	---	175	217	---	---	---
PBEP + MgO	---	---	157	202[2]	---	---	---
PBEP + MgO	---	---	164	203[2]	---	---	---
PBEP + TVOPA	---	---	152	206	224	---	---
PBEP + TVOPA + AlH_3 (QX 022)	---	---	155	170	185	217	---
PBEP + HPE	---	---	137	186	223	---	---
PBEP + HPE + AlH_3 (QX 022)	---	---	176	186	218	---	---
OPE	---	---	149	225	245[2]	---	---
OPE (2 days old)	---	---	140	215	239	---	---
OPE + AlH_3 (QX 022)	---	---	156	169	191	227	237
OPE (2 days old) + Al (H-5)	---	---	160	223	---	---	---
PBEP + OPE + FeAA	---	---	124	195	208[2]	---	---
PBEP + OPE + FeAA + AlH_3 (QX 022)	---	---	136	199[2]	---	---	---
PBEP + OPE + FeAA + AlH_3 (QX 022) + HAP	---	---	77	134	140[2]	---	---
HAP	57	93	154	176	---	---	---
HAP + AlH_3 (QX 022)	59	93	148	171[2]	---	---	---
HAP + AlH_3 (DL 528)	50	95	143	181[2]	---	---	---
PBEP + TVOPA + AlH_3 (QX 022) + HAP	---	---	---	---	---	---	---

(1) All PBEP was lot 9165-107.
(2) Explosions occurred at these exotherm temperatures.

peak temperature for the first PBEP exotherm. A PBEP/OPE/FeAA/AlH_3 mixture exploded at 199°C. Aluminum hydride is more reactive in the NF_2 binder than aluminum, but no thermal reactions occurred at any temperatures near where propellant is processed.

(C) DTA studies were conducted on AlH_3 and HAP mixtures. The HAP thermogram displayed two endothermic changes below 100°C and an exothermic decomposition above 150°C. The HAP/QX022 and HAP/DL-528 mixtures exploded at the HAP exothermic peak temperature. A PBEP/TVOPA/QX022/HAP mixture exploded at 140°C, the onset temperature for a HAP/AlH_3 exotherm. As expected, HAP lowers the stability of the system below that of the AP/AlH_3 system, but no unusual thermal behavior was noted near temperatures at which propellant will be processed.

b. Impact Sensitivity

(U) The factors affecting the impact sensitivity of AlH_3-containing propellants were studied. Among the factors which could affect the impact sensitivity of AlH_3-PBEP propellants are PBEP sensitivity, the oxidizer concentration, and the TVOPA level. These variables were evaluated, and the results are shown in tables XI, XII, and XIII. In formulations 178-102-1 and 178-102-2, PBEP lot 9165-180, which had shown extremely good impact sensitivities in the range of 70 to 80 kg-cm, was evaluated with AlH_3 to determine if the impact sensitivity of the propellant was improved. No significant improvement in impact was obtained by using this lot of PBEP. In these studies two types of AlH_3 were evaluated: magnesium-doped material and acrylonitrile-treated AlH_3. Those mixes made with acrylonitrile-treated AlH_3, in general, gave somewhat higher impact values. At this time, it is not known if this is caused by an intrinsic characteristic of the hydride or if the difference is caused by micro-porosity which could have occurred with the use of magnesium-doped AlH_3.

(U) Previous experience with PBEP/TVOPA/AP/Al propellant has shown that addition of AP resulted in an improved impact sensitivity. In formulations 178-102-6 through -8, shown in table XII, the effect of the addition of AP is shown. No improvement in impact sensitivity was noted with addition of AP oxidizer. No effect attributable to concentration of AP was observed. Again, in these mixes, notably between -6 and -7, an improvement in impact sensitivity of 2.6 to 4.2 kg-cm is observed by use of acrylonitrile-treated AlH_3.

TABLE XI

(U) ALUMINUM HYDRIDE IMPACT DATA[1]

Sample	178-102-1	178-102-2	178-103-3	178-103-4	178-103-5
Binder PBEP/TVOPA, wt-%	100	91.6	84.2	88.6	83.0
Ratio, PBEP:TVOPA	1/1	1/2	1/1	1/1	1/1
AlH_3, wt-%	---	8.4[2]	15.8[3]	11.4[2]	17.0[3]
Impact sensitivity, E_{50} kg-cm, uncured	12	1.5	3.5	2.0	3.5
Impact sensitivity, E_{50} kg-cm, cured	70	3.0	4.2	3.8	5.0

TABLE XII

(U) EFFECT OF AP CONCENTRATION ON IMPACT[1]

Sample	178-102-6	178-102-7	178-102-8
Binder	56.4	57.2	47.7
AlH_3	15.2[2]	13.5[2]	10.1[3]
AP, MS-4	28.4	29.3	42.2
Impact sensitivity, E_{50} kg-cm, uncured	2.0	3.0	2.5
Impact sensitivity, E_{50} kg-cm, cured	2.6	4.2	4.9

TABLE XIII

(U) EFFECT OF INCREASING TVOPA CONCENTRATION ON IMPACT SENSITIVITY[4]

Sample	178-105-1	178-105-2	178-105-3	178-105-4
PBEP/TVOPA ratio	1/2	1/3	1/2	1/3
AlH_3, wt-%	---	---	20	20
Impact sensitivity, E_{50} kg-cm, uncured	15	14	2.25	1.5
Impact sensitivity, E_{50} kg-cm, cured	32	40	6.0	4.0

(1) All values for ingredients are in wt-%
(2) Magnesium-doped AlH_3
(3) Acrylonitrile-treated AlH_3
(4) PBEP Lot 9088-180

(U) In formulations 178-105-1 through -4 listed in table XIII, the effect of TVOPA concentration was evaluated. Formulations 178-105-1 and -2 were the controls with a PBEP/TVOPA ratio of 1 to 2 and 1 to 3, respectively. The formulations with the increased TVOPA level gave a lower impact sensitivity in the uncured state than did the 1/1 PBEP/TVOPA binder which was probably a result of running the test in the open-cup tester. No improvement in impact sensitivity was obtained in the uncured propellant, although the cured propellant in one case did give a slightly improved impact sensitivity. In all cases an improvement in impact sensitivity was obtained with the cured propellant.

c. Propellant Development

(C) Because impulse and density improvements are obtained by substitution of HAP for AP in the AlH_3/PBEP system, a concurrent evaluation of these oxidizers was performed. The diisocyanate, 3,3'-dimethyl-phenylmethane-4,4'-diisocyanate (DMM) previously gave satisfactory cures in HAP propellants. However, in-house work with HAP propellants has shown that some incompatibility exists between HAP and the cure catalyst FeAA. Accordingly, a series of hand mixes evaluating FeAA and DBTDA was prepared. Formulations tested are shown in table XIV. Control mixes of Al-AP and Al-HAP were included in this study.

(C) A color change from red to reddish brown was noted when HAP was added to the FeAA-containing binder. The mixes were stiff and gave a somewhat porous cure. However, propellants containing DBTDA were fluid and cured to a firm rubbery propellant. The presence of AlH_3 in these mixes appeared to have no effect on the cure.

(U) A micromixer capable of processing up to 50 g of high-energy propellant is utilized in preliminary propellant evaluation studies. The micromixer itself is installed in an inert atmosphere box. This box is equipped with two socket-type tongs and is designed to withstand the detonation of 100 g's of Composition B. A number of AlH_3 and HAP propellant formulations have been made in this equipment. Because this mixer is not of the high-shear type, it is necessary to hold the AlH_3 loadings to a relatively low percentage. An arbitrary limit of 15% AlH_3 was established. Previous studies with AlH_3 had

TABLE XIV

(U) CURE CATALYST STUDY[1]

Formulation Number	178-109-1	178-109-2	178-109-3	178-109-4	178-116-1	178-116-2	178-116-3
AlH_3	16.7	18.5	---	---	---	11.6	10.2
Al	---	---	20.7	20.5	11.5	---	---
AP	---	37.0	---	34.2	---	---	20.3
Binder	50.0	44.5	44.8	45.3	65.5	65.3	69.5
Cure catalyst	FeAA	FeAA	FeAA	FeAA	DBTDA	DBTDA	DBTDA
Triol/OH	1.4	1.4	1.4	1.4	1.4	2.7	1.4
NCO/OH	1.5	1.5	1.5	1.5	1.5	1.0	1.5
Results	Cured, porous	Cured, surface bubbles	Cured, surface bubbles	Soft cure	Cured	Cured	Cured

(1) DMM was the diisocyanate used.

established that at this level problems with curative or incompatibility should be evaluated sufficiently to allow scaling factors to be made once the system is taken to a high-shear mixer. Table XV lists the processed formulations of AlH_3 and HAP propellant.

(C) Aluminum hydride formulations UTX 8455 and UTX 8457 with H_{12} MDI both cured firmly at an ambient cure temperature. UTX 8455 had a tensile value of 121 psi and an elongation of 51.8%, and UTX 8457 had values of 45 psi and 93.4%. The latter formulation had 2 days less cure time which could account for the difference in physical properties. These two formulations had impact values of 4.2 kg-cm and had similar sensitivities of friction, both being sensitive on the ESSO friction tester with no grit. Autoignition values also were similar with a 30-sec value of approximately 480°F and a 10-sec value of approximately 570°F. These formulations are as stable as those with aluminum as far as autoignition goes but are much more impact sensitive and friction sensitive.

(U) To determine the extent of cure obtained at ambient temperatures, formulations UTX 8455, 8456, and 8457 were post-cured at 120°F. The further cure was followed by measuring the increase in Shore A hardness values. The zero Shore A readings of 20 to 54 were the readings at the conclusion of the ambient cure period. Near maximum values of approximately 70 were obtained after 4 days of additional cure on all specimens.

(U) Formulation UTX 8459 which contained HAP as an oxidizer yielded a soft cure. The propellant reacted with moisture while being trimmed outside of the dry box and was discarded. It is apparent that stringent handling techniques and moisture disciplines will be required to permit the successful processing and handling of HAP propellant.

(U) Formulations UTX 8460 and UTX 8461 were made to compare the effects of AlH_3 with aluminum in a HAP propellant. Soft cures were obtained in both of these propellants, but no void formulation or gassing was observed. These propellants were stored at ambient temperature for 3 months with no degradation.

(U) Formulation studies were continued to develop an optimized NF_2 binder/AP/AlH_3 propellant using the ARC mixer. The AlH_3 used in this investigation was UTC acrylonitrile-treated for four days to improve its stability. Table XVI presents formulations of all the mixes investigated.

(U) The initial mix, UTX 8462-1, contained 21 wt-% AlH_3, 27 wt-% NF_2 binder, and 52 wt-% AP. This mix partially cured during mixing and was discarded.

(U) The second mix, UTX 8462-2, was mixed for a shorter period after addition of the diisocyanate. This mix was more fluid than the previous batch and flowed enough after casting to obtain tensile specimens.

(U) In UTX 8462-3, an adjustment was made in the coarse-to-fine ratio to gain more fluidity. No improvement in propellant viscosity was noticed by increasing the amount of coarse particles. In UTX 8462-4, further adjustment was made in the particle size distribution. A larger particle size AP MS-19 with an average 300μ size was employed in place of the MS-4 AP with an average 190μ size. A small gain in castability was obtained with the larger AP.

(U) To determine if the DBTDA was causing the rapid cure, a mix – UTX 8464-1 – was prepared with no cure catalyst. The cast mix was "fluffy," and a decrease in fluidity was noticed. Apparently, the DBTDA also acts as a surfactant in PBEP propellant.

(U) Formulation UTX 8465-1 contains an additional 5 vol-% binder. The first mix was very castable and a 100 g end burning grain was prepared. A 1/2-lb end burning grain and a ballistic 1-lb motor also were prepared using formulation UTX 8465.

(U) Using the binder system from UTX 8465 at 35 vol-% binder, a mix – UTX 8466 – with 30 vol-% binder was prepared. This mix was castable but not as fluid as the higher vol-% mix.

d. Ballistic Data

(C) A 100 g grain of formulation UTX 8465, gave a good firing trace (illustrated in figure 9) with a burning rate of 1.029 in./sec at 580 psia. A 1/2-lb grain appeared to have liner separation during the firing, and the overpressurization blew the nozzle.

TABLE XV

(U) AlH_3 FORMULATIO

Formulation Number	UTX[2] 8451	UTX[2] 8452	UTX[2] 8453	UTX[2] 8454	UTX 8455	UTX 8456	UTX 8457	UTX 8458
PBEP	16.00[3]	22.85[3]	18.28[3]	20.56[3]	19.86[4]	20.56[4]	18.83[4]	19.83[4]
TVOPA	16.00	22.85	18.28	20.56	19.86	20.56	18.83	19.83
1,2,6-HT	0.32	0.45	0.36	0.41	0.49	0.51	0.49	0.49
Catalyst	0.62	0.90	0.72	0.81	0.70	0.70	0.70	0.70
Catalyst type	FeAA	FeAA	FeAA	FeAA	DBTDA	DBTDA	DBTDA	DBTDL
Diisocyanate	2.06	2.95	2.36	2.66	4.09	2.67	4.15	4.15
Diisocyanate type	TDI	TDI	TDI	TDI	DMM	TDI	H_{12} MDI	H_{12} MDI
AlH_3	20.00	10.00	15.00	10.00	15.0	15.0	15.0	15.0
AP	45.00	40.00	45.00	45.00	40.0	40.0	40.0	40.0
HAP	---	---	---	---	---	---	---	---
Coarse/fine ratio	70/30	70/30	70/30	70/30	60/40	60/40	60/40	60/40
Triol/PBEP(OH)	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
NCO/OH	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Cure at ambient, days	3	3	4	4	7	5	5	5
Remarks	Uncured	Uncured	Cured	Cured	Cured	Soft cure	Cured	Soft cure

(1) All values for ingredients are in wt-%.
(2) These mixes were cured at 120°F.
(3) PBEP was lot 9165-107.
(4) PBEP was lot 9088-180
(5) PBEP was lot 9557-99A
(6) The fuel was Al instead of AlH_3.

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E XV

MULATIONS[1]

UTX 8458	UTX 8459	UTX 8460	UTX 8461	UTX 8462	UTX 8463	UTX 8464	UTX 8465	UTX 8466
19.83[4]	24.30[4]	24.35[4]	22.82[4]	12.13[5]	12.20[5]	12.27[5]	14.43[5]	12.13[5]
19.83	24.30	24.35	22.82	12.13	12.20	12.27	14.43	12.13
0.49	0.60	0.60	0.57	0.24	0.24	0.24	0.17	0.14
0.70	0.70	0.70	0.70	0.29	0.15	0.15	0.64	0.64
DBTDL	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA
4.15	5.10	5.00	4.69	2.20	2.21	2.22	2.33	1.96
H_{12} MDI	H_{12} MDI	DMM	DMM	DMM	DMM	DMM	DMM	DMM
15.0	10.0	10.0	9.00[6]	21.00	21.00	21.00	21.00	21.00
40.0	---	---	---	52.00	57.20	51.22	51.03	53.17
---	35.0	35.0	39.40	---	---	---	---	---
60/40	70/30	60/40	60/40	50/50	55/45	50/50	60/40	60/40
1.4	1.4	1.4	1.4	0.40	0.40	0.40	0.25	0.25
1.5	1.5	1.5	1.5	0.86	0.86	0.86	0.86	0.86
5	5	7	7	(7)	(7)	(7)	(7)	(7)
Soft cure	Cured porous	Soft cure	Soft cure	---	---	---	---	---

(7) All formulations are curing at ambient temperatures but have not been tested as yet.

AlH_3.

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TABLE XVI

(U) HYDROXYLAMINE PERCHLORATE CURE STUDIES

Formulation Number	215-27-1	215-27-2	215-27-3	215-27-4	215-39-1	215-39-2	215-39-3
PBEP	22.00	22.10	22.05	27.75	18.80	18.80	18.70
TVOPA	22.00	22.10	22.05	27.75	18.80	18.80	18.70
Curative	2.37(1)	0.35(1)	0.44(1)	---	4.88(2)	5.06(2)	5.24(2)
1,2,6-HT	0.26	0.35	0.44	---	0.45	0.51	0.57
FeAA	0.88	0.88	0.88	0.91	0.75	0.74	0.74
Al	8.80	8.84	8.82	9.10	---	---	---
HAP	44.00	44.20	44.10	45.50	56.90	56.40	56.20
Triol/PBEP(OH)	---	0.93	1.13	---	1.36	1.50	1.70
NCO/OH	1.78	1.90	1.51	---	1.93	1.87	1.77
Cured at 120°F, hr	48	48	48	---	96	96	96
Remarks	Cured, porous	Cured, porous	Cured, porous	Uncured propellant	Good cure	Good cure	Good cure

(1) Curative was TDI.
(2) Curative was 3,3'-dimethyldiphenylmethane – 4,4'-diisocyanate.

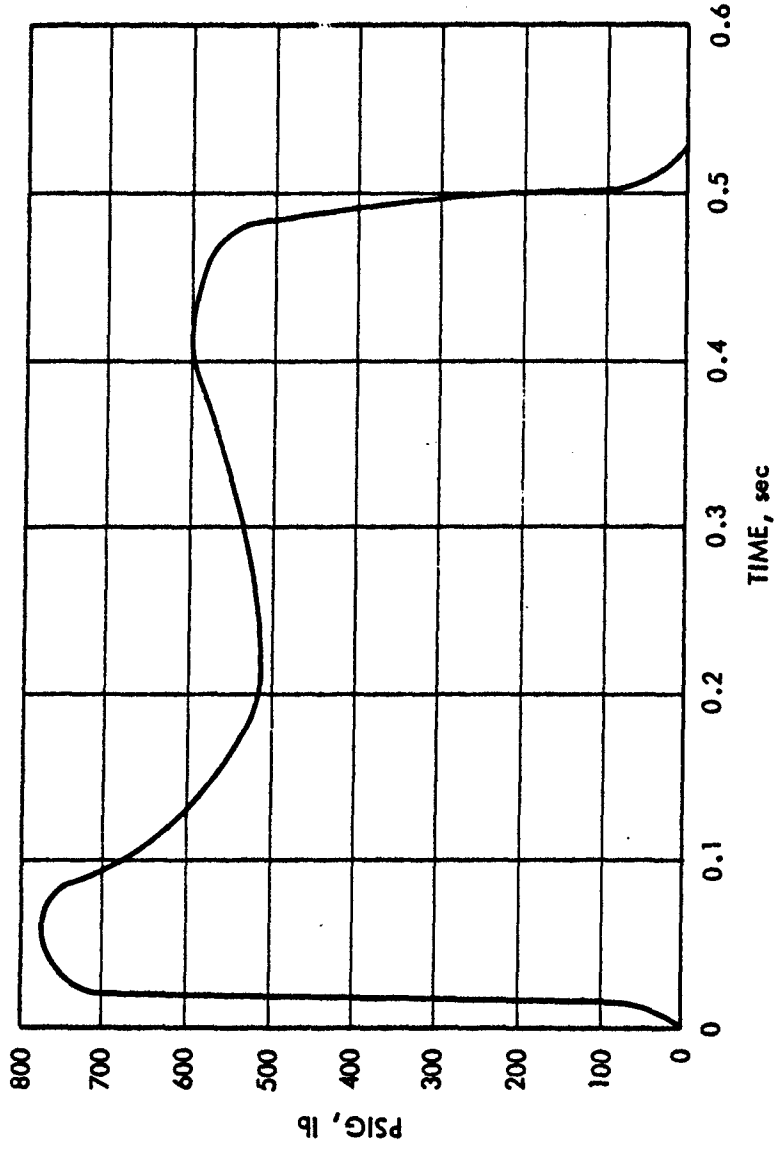

Figure 9. (U) AlH_3 Propellant Firing Trace

The standard 1-lb grain was cured at ambient for only 7 days before the mandrel was extracted. Although the propellant was partially cured it was too soft for the mandrel to be pulled successfully.

4. HYDROXYLAMINE PERCHLORATE EVALUATION

a. Hydroxylamine Perchlorate Cure and Catalyst Studies

(C) The series 215-27, containing HAP (table XVI), all cured but exhibited gassing during cure. Because UTC-sponsored work had demonstrated that HAP is incompatible with TDI, this diisocyanate was replaced with 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate as a curative. Gumstocks cured very well with this diisocyanate, and propellants containing HAP, 215-39-1 to -3, were prepared. These propellants gave a good cure and appeared to have no compatibility problems. However, it is necessary to use a dry atmosphere to successfully process HAP propellants.

(C) A series of mixes was formulated with H_{12}MDI, a diisocyanate produced by National Analine Division of Allied Chemical Co. The cure catalysts which were tested were VaOAA, TiOAA, and DBTDL. A complete list of ingredients and formulations is given in table XVII. As the HAP was added to the vanadium and titanium catalyzed mixes, an immediate color change was observed which was ascribed tentatively to the reduction of the catalyst. All six hand mixes, however, cured firmly.

(C) The six mixes in series 132 were prepared to evaluate the aliphatic diisocyanate, HMDI. No cures were obtained with this curative system, and gassing was observed on the surface of the samples.

(C) Additional mixes were made with the cure catalyst chromic 2-ethyl hexoate and H_{12}MDI and DMM as the curatives. In this series, good cures were obtained with the H_{12}MDI-containing mixes. However, the DMM curatives failed to give adequately cured propellant. In past mixes with DMM curative, the propellant had cured well using DBTDA and FeAA as the cure catalysts.

TABLE XVII

(U) HAP HAND MIX FORMULATIONS

Formulation No.	178-128-1	178-128-2	178-128-3	178-128-4	178-128-5	178-128-6	178-132-1	178-132-2	178-132-3
PBEP	29.47	29.47	29.47	29.47	29.47	29.47	30.57	30.57	30.57
TVOPA	29.47	29.47	29.47	29.47	29.47	29.47	30.57	30.57	30.57
Curative	6.08	6.08	6.08	6.08	6.08	6.08	3.86	3.86	3.86
Curative type	H_{12}MDI	H_{12}MDI	H_{12}MDI	H_{12}MDI	H_{12}MDI	H_{12}MDI	HMDI	HMDI	HMDI
1, 2, 6-HT	0.77	0.77	0.77	0.77	0.77	0.77	0.79	0.79	0.79
Catalyst	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32
Catalyst type	VaOAA	TiOAA	DBTDL	VaOAA	TiOAA	DBTDL	VaOAA	TiOAA	DBTDL
Al	10.96	10.96	10.96	---	---	---	10.96	10.96	10.96
AlH_3	---	---	---	10.96	10.96	10.96	---	---	---
HAP	21.93	21.93	21.93	21.93	21.93	21.93	21.93	21.93	21.93
Triol/PBEP(OH)	1.47	1.47	1.47	1.47	1.47	1.47	1.49	1.49	1.49
NCO/OH	1.44	1.44	1.44	1.44	1.44	1.44	1.47	1.47	1.47

Formulation No.	178-132-4	178-132-5	178-132-6	178-134-1	178-134-2	178-134-3	178-134-5	178-134-6	178-134-7
PBEP	30.57	30.57	30.57	29.38	29.38	29.38	29.45	29.45	29.45
TVOPA	30.57	30.57	30.57	29.38	29.38	29.38	29.45	29.45	29.45
Curative type	HMDI	HMDI	HMDI	H_{12}MDI	H_{12}MDI	H_{12}MDI	DMM	DMM	DMM
Curative	3.86	3.86	3.86	6.19	6.19	6.19	6.14	6.14	6.14
1, 2, 6-HT	0.79	0.79	0.79	0.84	0.84	0.84	0.75	0.75	0.75
Catalyst	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32
Catalyst type	VaOAA	TiOAA	DBTDL	Cr_2Eth	Cr_2Eth	Cr_2Eth	Cr_2Eth	Cr_2Eth	Cr_2Eth
Al	---	---	---	10.96	---	10.96	---	10.96	10.96
AlH_3	10.96	10.96	10.96	---	10.96	---	10.96	---	---
HAP	21.93	21.93	21.93	---	21.93	21.93	---	21.93	21.93
Triol/PBEP(OH)	1.49	1.49	1.49	1.60	1.60	1.60	1.44	1.44	1.44
NCO/OH	1.47	1.47	1.47	1.39	1.39	1.39	1.50	1.50	1.50

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b. Hydroxylamine Perchlorate

(C) The HAP hazard data are given in table XVIII. An uncured propellant containing HAP, TVOPA, AL, and PBEP gave an impact value of 19 kg-cm. Sample 215-27-4 containing HAP and Al in an uncured NF_2 binder gave a positive test without added grit.

(C) An uncured propellant containing HAP gave 30- and 10-sec autoignition values of 330° and 390°F, which are approximately 100°F below similar systems containing AP. As expected, HAP propellants appear more thermally unstable than AP propellants. A DTA of the HAP/Al/PBEP/TVOPA propellant showed an exotherm onset at 119°C terminating in an explosion at 130°C.

5. OPE EVALUATION

a. OPE Hazard Evaluation Studies

(C) The results of the OPE laboratory hazard testing are given in table XIX. Neat OPE has an impact sensitivity of 1.5 kg-cm. It gave a positive test with pyrex glass grit and negative results with no grit on the ESSO-type friction tester. The 10-sec autoignition temperature is 500°F. The sensitivity of OPE/PBEP(50/50) blends is dependent upon the sensitivity of the PBEP. The higher the impact of the PBEP, the higher the impact of the blend. OPE-plasticized propellants will undoubtedly be more sensitive than the equivalent TVOPA system; however, the data obtained to date indicate that the propellant can be formulated successfully.

(C) DTA tests were run on neat OPE and mixtures containing OPE. The neat OPE had an exotherm onset at 149°C and peaked at 225°C and 245°C. The 245°C peak terminated in an explosion. Aging neat OPE 2 days at ambient temperature caused the material to turn cloudy. The DTA onset temperature decreased only slightly, but the peak temperatures decreased 40°C. Apparently some hydrolysis or reaction with the glass container occurred which decreased the OPE stability.

(C) Both aluminum and FeAA lowered the exotherm peak temperature of OPE. The FeAA also lowered the onset temperature. Aluminum gave an apparent stabilization to the onset; however, this could be a result of the diluent effect of the aluminum.

TABLE XVIII

(U) HYDROXYLAMINE PERCHLORATE HAZARD EVALUATION TEST RESULTS

	HAP	HAP/PBEP/ TVOPA	HAP/PBEP/ TVOPA/Al
Impact sensitivity, E_{50}, kg-cm	150 (smoke, no flame)	44.8	19.1
Friction sensitivity:			
No grit	-	+	-
Pyrex grit	-	-	+
Autoignition:			
30 sec, °F	---	330	330
10 sec, °F	---	390	390
DTA, endotherm, °C	57.5/9.4	87	82
Exotherm:			
Onset, °C	156	140	119
Peak, °C	170	171/180	136

b. OPE/PBEP Cure Studies

(C) The direct substitution of OPE for TVOPA was accomplished with no difficulties. Formulations 178-95-1 through 215-35-3 in table XX were hand mixes to check the cure characteristics of PBEP/OPE gumstock and propellants. UTX 8412 is a 5 g scaleup mix. The propellant was well cured and gave good propellant.

6. HPE CURE STUDIES

(C) Previous work under Air Force Contract No. AF 04(611)-11404[1] indicated that no apparent compatibility or stability problem existed between HPE and PBEP. However, good cures could not be obtained with HPE as plasticizer. The initial studies used TDI, 1,2,6-HT, and FeAA as the cure system. These studies were continued under the present contract using a different crosslinker and cure catalysts. The results of these studies are shown in table XXI. Glycerol and VOAA gave a soft cure in 48 hours at 120°F. However, the samples showed extreme darkening and showed signs of obvious degradation. The sample using Bu_2SnAC_2 failed to cure past the gel point and also appeared to have undergone some degradation.

TABLE XIX

(U) OPE HAZARD EVALUATION TEST RESULTS

Composition	PBEP Lot	Impact Sensitivity kg-cm	Autoignition Graph Data, °F		No Grit	Diamond Grit	Pyrex Glass Grit	Exotherm Onset	Exotherm Peak
			30 sec	10 sec					
OPE in Freon 113 (20%)	---	120	---	---	-	-	-	---	---
OPE (100)	---	1.5	Evaporated	500	-	+	+	149	225/245
OPE/Al	---	---	---	---	-	-	-	160	170/223
PBEP/OPE cured gumstock	9165-107	43.1	370	450	-	+	+	---	---
PBEP/OPE/FeAA	9165-107	---	---	---	-	-	-	124	195/208
PBEP/OPE uncured gumstock	9165-107	3.0	Evaporated	475	-	+	+	---	---
PBEP/OPE uncured gumstock	9088-180	51.0	---	---	-	-	-	---	---
PBEP/OPE/Al/AP uncured	9088-180	8.5	485	525	+	+	+	---	---
PBEP/OPE cured gumstock	9088-180	7.6	446	541	-	+	+	---	---
PBEP/TVOPA cured gumstock	9088-180	120	445	525	+	-	-	---	---
OPE 2 days ambient aging	---	---	---	---	-	-	-	140	161/203

TABLE XX

(U) OPE CURE STUDIES

Formulation No.	178-95-1	178-97-1	215-35-1	215-35-2	215-35-3	UTX 8412
PBEP	45.7	45.7	16.1	16.0	16.2	15.90
OPE	45.7	45.7	16.1	16.0	16.2	15.90
TDI	5.9	5.9	2.32	2.69	2.14	2.06
1,2,6-HT	0.9	0.9	0.37	0.40	0.47	0.39
FeAA	1.8	1.8	0.64	0.64	0.64	0.64
Al	---	---	16.1	16.1	16.2	15.00
AP	---	---	48.3	48.0	48.6	50.0
Triol/PBEP(OH)	1.40	1.12	1.30	1.40	1.44	1.40
NCO/OH	1.50	1.70	1.74	1.90	1.48	1.50
Cure at 120°F, hr	72	72	48	72	96	72
Remarks	Cured	Cured	Well cured	Well cured	Well cured	Well cured

TABLE XXI

(U) HPE CURE STUDIES[1]

Formulation No.	215-21-1	215-21-2	215-21-3	215-25-1	215-25-2	215-25-3
PBEP	45.5[2]	44.3[2]	42.7[2]	45.5[3]	44.3[3]	44.1[3]
HPE	45.5	44.3	42.7	45.5	44.3	44.1
TDI	6.82	8.81	11.26	6.82	6.82	10.03
Glycerol	0.50	0.79	1.26	0.50	0.68	0.97
Catalyst	1.82	1.77	1.70	1.82	1.81	8.80
Type of catalyst	VOAA	VOAA	VOAA	Bu_2SnAc_2	Bu_2SnAc_2	Bu_2SnAc_2
Triol/PBEP(OH)	9.91	1.41	2.30	0.91	1.21	1.73
NCO/OH	2.30	2.30	2.38	2.30	2.20	2.30
Cure at 120°F, hr	48	48	48	144	144	144
Remarks	Darkened, soft cure	Darkened, soft cure	Darkened, soft cure	Strong gel	Strong gel	Strong gel

(1) All values for ingredients are in wt-%.
(2) PBEP lot number was 9088-180.
(3) PBEP lot number was 9165-107.

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(U) Because of the cure problems and the questionable applicability of HPE in propellants because of its high vapor pressure, no further work was done with this material.

7. BURNING RATE STUDY

(C) One of the objectives of this program was to develop a series of domino-propellants with burning rates of 1.0 to 10.0 in./sec at 1,000 psi. The typical formulation, such as UTX 8407, has a burning rate of approximately 1.6 in./sec. Various combustion modifiers including the usual AP burning rate catalysts, binder decomposition catalysts, AP burning rate depressants, and polymer flame retardants were tested. Also, high TVOPA-plasticized formulations which have high burning rates without added catalysts were examined. Initially, the compatibility and hazard characteristics of the NF_2 binder and these various additives were tested by DTA, impact, friction, spark, and autoignition tests.

a. Effects of Ammonium Perchlorate Catalysts on Cure and Stability

(U) DTA results have shown that AP burning rate catalysts decrease the exotherm onset and peak temperatures of PBEP. It was thought that the cure of the PBEP/TVOPA binder might also be affected by these burning rate catalysts.

(C) Small hand mixes were made of UTX 8407 containing 1% catalyst to determine the compatibility of these additives in the propellant formulation and to determine the effects on cure. These formulations are listed in table XXII. The results indicate that Cu2O2, Fe_2O_3, Fe_3O_4, and Milori blue are compatible in UTX 8407 and cure well, while both QMB-3 and $(Et)_4NB_r$ cured slowly into a spongy propellant. There appears to be a compatibility problem with these quaternary amines. Further studies will be required to determine if quaternary amines can be used in PBEP propellants. DTA results listed in table XXIII show that Fe_3O_4 does not decrease PBEP stability to any large extent, and Cu2O2 does decrease stability.

b. Burning Rate Depressant Compatibility Studies

(C) DTA studies have previously shown that most candidates for burning rate suppressants apparently decrease the DTA stability of PBEP. Hand mixes of UTX 8407 formulation containing these additives, listed in table XXIII, all gave good cures.

TABLE XXII

(U) BURNING RATE CATALYSTS FORMULATIONS

Formulation Number	LA 45-1	LA 45-2	LA 45-3
UTX 8407	99%	99%	99%
Additive	1%	1%	1%
Results	Cu2O2, cured	Fe_2O_3, cured	QMB-3,[1] cured slowly, porous

Formulation Number	LA 45-4	LA 45-5	LA 45-6
UTX 8407	99%	99%	99%
Additive	1%	1%	1%
Results	Milori blue, cured	$(Et)_4NBr$,[2] cured slowly, porous	Fe_3O_4, cured

(1) Quaternary methyl ammonium triborate, Callery Chemical
(2) Quaternary ethyl ammonium bromide

TABLE XXIII

(U) DTA RESULTS

Sample Composition[1]	Onset °C First Exotherm	Peak °C First Exotherm	Peak °C Second Exotherm	Endotherms
PBEP + K_3PO_4 (75/25)	70	100	186	140, 177
PBEP (100)	146	204	219	---
PBEP + Cu2O2 (75/25)	96	152	---	---
PBEP + Fe_3O_4 (75/25)	156	206	---	---
PBEP + $(NH_4)\ C_2O_4 \cdot H_2O$ (75/25)	127	152	195	114
PBEP + tricresyl phosphate (75/25)	142	195	199	---

(1) All PBEP was lot 9165-107

These additives include such things as sodium barbituate as a burning rate depressant, tetrabromophthalic anhydride as a flame retardant, as well as others with similar properties.

(C) Tricresyl phosphate and ammonium oxalate mixed with PBEP also were studied by DTA. The tricresyl phosphate-PBEP mixture gave no appreciable change in the thermogram when compared to the thermogram of neat PBEP. However, adding ammonium oxalate decreased the onset by about 20°C, the first exotherm peak by 52°C, and the second exotherm peak by 24°C. The oxalate was a monohydrate, and the water of hydration may have had some effect on the thermogram.

(U) Table XXIV indicates that the several depressants tested in propellant formulations did not affect the impact sensitivity of the propellant.

c. High TVOPA Level Effect on Propellant Sensitivity

(U) It was thought that this higher TVOPA level would increase the impact and friction sensitivity of the propellant. The results in table XXIV show just the opposite effect for impact. A TVOPA/PBEP ratio of 2:1 gave a value of 17.6 kg-cm and a 3:1 ratio gave a value of 20.5 kg-cm. This compares to a value of 11.8 kg-cm for a 1.1 ratio. The friction sensitivity remained essentially the same at all levels.

d. Preparation of Strands for Burning Rate Evaluation

(C) Several formulations, listed in table XXV, for burning rate strands were prepared at the 100 g level in the ARC mixer. These included a mix containing Cu_2O_2 as an additive as well as formulations varying the particle size and TVOPA level. Table XXV shows the burning rate at 1,000 psi, and the strand results are given in figure 10.

(C) Formulations UTX 8482 and UTX 8481 had some porosity which may have contributed to their high rates. A burning rate of 2.6 in./sec at 1,000 psi was obtained in formulation UTX 8482 containing 1% Cu_2O_2, a 4:1 ratio of fine to coarse AP, and 2:1 TVOPA/PBEP. Using all coarse AP (350) in formulation UTX 8480 resulted in a decrease of only 0.06 in./sec from the standard formulation UTX 8478.

TABLE XXIV

(U) HAZARD EVALUATION RESULTS

Formulation Number	PBEP Lot No.	Impact Sensitivity kg-cm	Friction Results No. Grit	Friction Results Diamond Grit	Friction Results Pyrex Grit	Remarks
UTX 8407	9165-107	11.8	-	+	+	1:1 TVOPA/PBEP
UTX 8476-1	9165-107	17.6	-	+	+	2:1 TVOPA/PBEP
UTX 8477-1	9165-107	20.5	-	+	+	3:1 TVOPA/PBEP
LA 41-5	9165-107	12.0				1% tetrabromo phthalic oxhydride
LA 41-4	9165-107	11.5				1% tricresyl phosphate
LA 41-8	9165-107	13.0				1% sodium barbiturate

TABLE XXV

(U) STRAND BURNING RATE FORMULATIONS

Formulation No.	UTX 8478	UTX 8479	UTX 8480	UTX 8481	UTX 8482
PBEP	15.70	15.70	14.70	10.47	10.37
TVOPA	15.70	14.70	14.70	20.93	20.72
TDI	1.84	1.84	1.84	1.84	1.82
1,2,6-HT	0.56	0.46	0.46	0.46	0.46
FeAA	0.65	0.39	0.39	0.39	0.39
Al	15.20	15.20	15.20	15.20	15.04
AP, 180μ	35.15	10.14	---	10.14	10.04
AP, 350μ	---	---	50.71	---	---
AP, 8-10μ	15.00	40.57	---	40.57	40.16
Variable	Control	80/20 fine/ coarse AP	350μ AP	2/1 TVOPA/ PBEP	1.00% Cu2O2
r_b, in./sec at 1,000 psi	1.46	1.72	1.40	2.40	2.60
n	0.66	0.66	0.68	0.50	0.50

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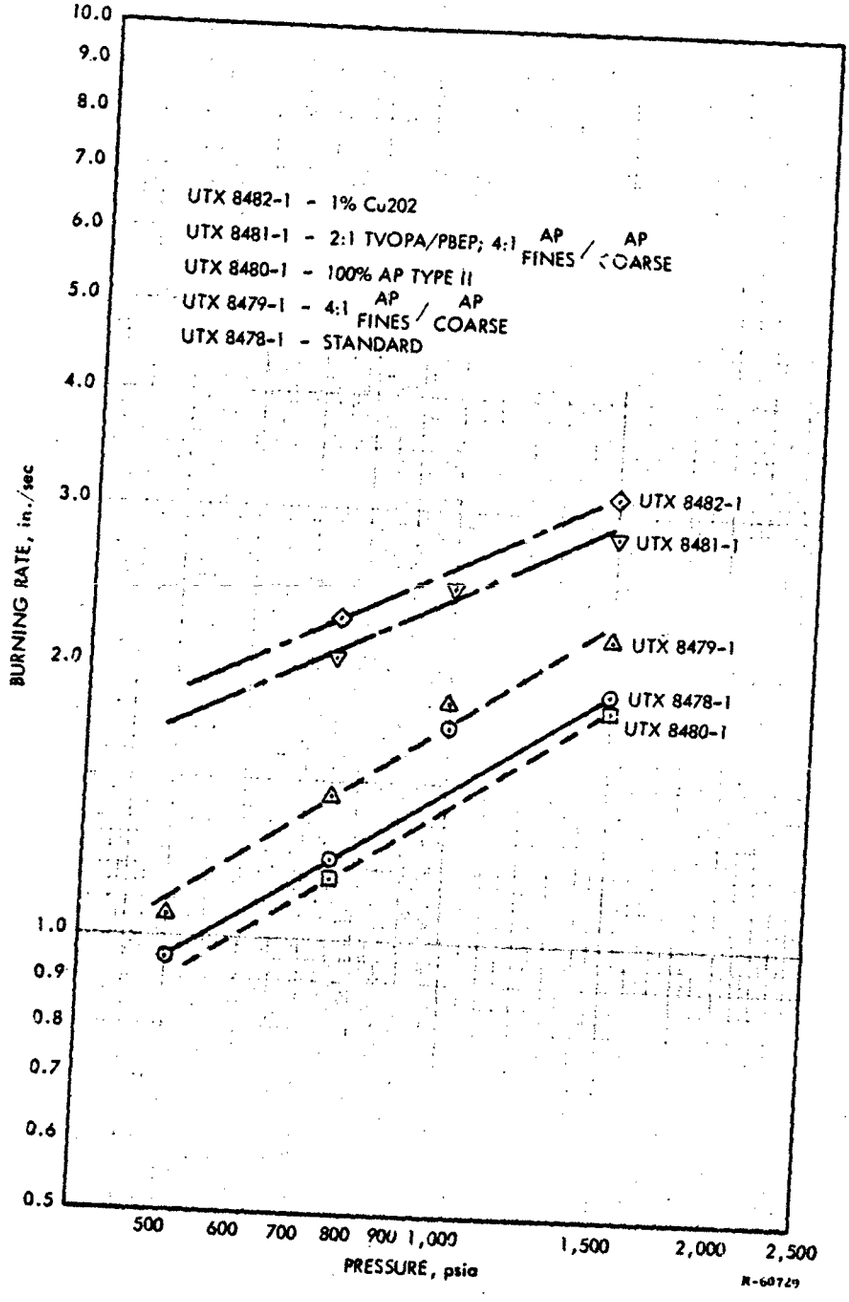

Figure 10. (U) Strand Burning Rate Data

8. VARIATION OF CURE INGREDIENTS AND BINDER LEVEL

a. Low Volume-Percent Binder Level Study

(U) AlH_3/AP propellants must be formulated with high solids loadings to approach an optimum specific impulse value. With aluminum as a substitute for AlH_3, propellants were prepared to a 25 vol-% binder level. The formulations listed in table XXVI processed adequately, were quite fluid on casting, and cured well at either 120°F or ambient temperatures.

1. Physical Properties

(C) Lower binder level formulations whose physical properties are listed in table XXVII gave the expected higher true tensile and lower true elongation values than the higher binder formulations. A 35 vol-% binder formulation had a tensile of 221 psi and an elongation of about 14% when cured at ambient temperatures. This same formulation when cured at 120°F gave values of 179 psi and 12%. A 30 vol-% binder formulation had a tensile of 297 psi and 7.4%. This latter formulation with a lower binder level also contained less crosslinking. This could account for the elongation values being approximately the same for the two formulations of different vol-% binder.

(U) All these formulations have tensile values that are sufficiently high that elongation could be increased at the expense of tensile by reformulation at different curative levels.

2. Hazard Data

(C) Propellants with higher solids loadings of AP and aluminum are less impact sensitive. UTX 8443 with a solids loading of 60 wt-% had an impact value of 17 kg-cm, and UTX 9814-1 with 71% solid and UTX 9816-1 with 76% solids have values of 25.3 and 35.6 kg-cm, respectively. The friction was similar on the ESSO tester to a standard formulation. Added grit was necessary for a positive test.

TABLE XXVI

(U) Al/AP FORMULATIONS WITH LOW VOLUME-PERCENT BINDER[1]

Formulation Number	UTX 9819-1	UTX 9816-1	UTX 9814-1
PBEP[2]	9.21	10.48	12.66
TVOPA	9.22	10.48	12.66
DMM	1.67	2.31	2.79
HT	0.18	0.36	0.43
DBTDA	0.22	0.37	0.46
AP (MS-4)[3]	46.55	44.10	40.60
AP (12μ)	19.95	18.90	17.40
Al	13.00	13.00	13.00
Triol/PBEP(OH)	0.40	0.71	0.71
NCO/OH	0.86	0.86	0.86
Cure at 120°F, hr[4]	48	48	72
Vol-% binder	25	30	35
Remarks	Cured	Cured	Cured

(1) All values for ingredients are in wt-%.
(2) PBEP lot number was 9557-99A in all formulations.
(3) MS-4 AP has average particle size of 180μ to 200μ.
(4) These formulations also cured in several days at ambient temperatures.

TABLE XXVII

(U) PHYSICAL PROPERTIES OF PROPELLANTS AT VARIOUS BINDER LEVELS

Formulation Number	Vol-% Binder	True Physical Property Data	
		Tensile, psi	Elongation, %
UTX 9819-1	25	227	7.4
UTX 9816-1	30	297	7.1
UTX 9814-1(1)	35	221	13.9
UTX 9814-1	35	179	11.7

(1) Cured at ambient temperature

b. Catalyst Level Studies

(C) Table XXVIII lists formulations containing lower DBTDA cure catalyst levels than the 0.64% normally used. This series was required to determine if a lower catalyst level could be used to extend pot life on the highly loaded AlH_3/AP propellants and still obtain ambient cure to avoid thermal degradation.

(C) Both objectives were achieved as the pot life on UTX 9815-1 with 0.3% catalyst was roughly double that of a standard formulation with 0.64% catalyst. Also, ambient cures were obtained in 1 week with these formulations.

(U) The physical properties of these formulations are listed in table XXIX. The true tensile properties varied from 109 to 156 psi with the elongations about constant at 27% to 28%.

(C) With FeAA as the cure catalyst, the formulations listed in table XXX all cured well down to 0.1 wt-%. The measured physical properties are listed in table XXXI. The elongations varied from 17.3% to 20.0% and the tensile varied from 100 to 210 psi.

TABLE XXVIII

(U) VARIATION OF DBTDA PERCENTAGES

Formulation Number	UTX 9815-1	UTX 9821-1	UTX 9822-1
PBEP (9557-99A)	17.68	17.68	17.68
TVOPA	17.68	17.68	17.68
DMM	3.89	3.89	3.89
HT	0.60	0.60	0.60
AP	46.71	46.61	46.51
Al	13.14	13.14	13.14
DBTDA	0.30	0.40	0.50
Triol/PBEP(OH)	0.70	0.70	0.70
NCO/OH	0.86	0.86	0.86
Cure at 120°F, hr(1)	72	72	72
Remarks	Cured	Cured	Cured

(1) These formulations also cured at ambient temperatures in about 1 week.

TABLE XXIX

(U) PHYSICAL PROPERTY DATA FROM PROPELLANT WITH DIFFERENT DBTDA LEVELS

Formulation Number	DBTDA %	True Physical Property Data: Tensile psi	True Physical Property Data: Elongation %
UTX 9815-1	0.30	156	27.1
UTX 9821-1	0.40	109	28.0
UTX 9822-1	0.50	122	27.7
UTX 9813-1	0.64	137	27.2

TABLE XXX

(U) VARIATION OF FeAA CATALYST LEVEL FORMULATIONS

Formulation	UTX 8415-1	UTX 8416-1	UTX 8417-1	UTX 8418-1	UTX 8411-4
PBEP (lot 9546-16)	16.1	16.1	16.0	16.02	16.01
TVOPA	16.1	16.1	16.0	16.02	16.01
TDI	1.92	1.91	1.92	1.92	1.91
1,2,6-HT	0.44	0.44	0.44	0.44	0.44
FeAA	0.10	0.20	0.30	0.40	0.64
Al	15.10	15.0	15.00	15.00	15.00
AP	50.40	50.3	50.25	50.15	50.04
Triol/PBEP (OH)	1.55	1.55	1.55	1.55	1.55
NCO/OH	1.30	1.30	1.30	1.30	1.30
Cure at 120°F, hr	120	96	72	48	24
Remarks	Uncured	Cured	Cured	Cured	Cured

TABLE XXXI

(U) PHYSICAL PROPERTY DATA OF PROPELLANT WITH VARIOUS FeAA CATALYST LEVELS

Formulation Number	% FeAA	True Data Tensile psi	True Data Elongation %	Temperature °F
UTX 8416-1	0.20	158	25.0	+76
UTX 8417-1	0.30	164	20.8	+76
UTX 8418-1	0.40	210	20.4	+76
UTX 8411-4	0.64	160.	17.3	+76
UTX 8419-1	0.32	100	23.2	+76

c. Variation of Tensile Properties with Cure Ratios

(U) The series formulations listed in table XXXII were prepared to study the optimization of cure ratios based on the physical properties of the resultant propellant. Microdogbone specimens were prepared from each mix and their physical properties evaluated.

(C) The true tensile properties in table XXXIII varied from 55 psi tensile and 37% elongation in UTX 9805-1 with cure ratios of Triol/PBEP(OH) of 0.61 and NCO/OH of 0.84 to 125 psi tensile and 25% elongation in UTX 9805-1 with ratios of Triol/PBEP(OH) of 0.81 and NCO/OH of 0.85.

(U) UTX 9808-1 which had original values of 99 psi tensile and 29% elongation on 2 additional days of cure at 120°F gave an increased tensile value of 163 psi and decreased elongation to 23%.

(U) UTX 8430-2 is a formulation prepared several months prior to the other formulations. At that time higher cure equivalents of isocyanate were used for good cures.

(U) The physical properties of PBEP propellant can be varied widely depending upon the cure system. These properties also could be varied to give properties tailored for a specific purpose.

(U) UTX 9810-1 with the same formulation as UTX 9808-1 was a 1,000 g mix in the Bramley-Bekin 1/2 gal. mixer. The propellant cured very well in 48 hours with no voids.

d. Effect of Test Temperature on Physical Properties

(U) Mixes UTX 9813-1 to 5 were prepared to obtain microtensile specimens for testing at various temperatures. Ambient cures were included in the investigation. Tables XXXIV and XXXV present the experimental results and figure 11 is a graph of the data.

(U) Formulation UTX 9813-3 had an elongation of 25% and a tensile of 125 psi. At 120°F the elongation and tensile dropped to 22% and 80 psi, respectively. The elongation dropped to 6% at -20°F and the tensile increased to 1,000 psi. The physical properties change rapidly from 0° to 20°F with about -10° being the limiting temperature for this formulation and this lot of PBEP.

TABLE XXXII

(U) SCALEUP FORMULATIONS

Formulation Number	UTX 9800-1	UTX 9801-1	UTX 9802-1	UTX 9803-1	UTX 9804-1	UTX 9805-1	UTX 9806-1	UTX 9807-1	UTX 9808-1	UTX 9809-1	UTX 9810-1	UTX 9812-1	UTX 9807-2
PBEP	17.68	17.68	17.68	17.68	17.63	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68
TVOPA	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68
DMM	2.81	3.20	2.68	3.65	3.71	3.57	4.11	3.89	4.09	3.97	4.09	4.81	3.89
1,2,6-HT	0.17	0.34	0.17	0.51	0.51	0.68	0.60	0.68	0.60	0.60	0.68	0.74	0.60
DBTDA	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64
Al	13.30	13.19	13.38	13.07	12.88	12.90	12.73	12.80	12.73	12.78	12.73	12.77	12.80
AP	47.72	47.27	47.77	47.77	46.90	47.02	46.48	46.71	46.50	46.65	46.50	45.18	46.71
Triol/PBEP (OH)	0.20	0.40	0.20	0.61	0.61	0.61	0.61	0.71	0.81	0.71	0.81	0.90	0.71
NCO/OH	0.88	0.86	0.84	0.86	0.87	0.84	0.86	0.86	0.85	0.87	0.85	0.96	0.86
Cure at 120°F, hr	260	120	260	96	96	96	---	72	48	120	48	24	72
Remarks	Uncured	Cured	Uncured	Cured	Cured	Cured	Cured	Cured voids	Cured	Cured voids	Cured	Cured	Cured

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TABLE XXXIII

(U) VARIATION OF TENSILE PROPERTIES WITH CURE RATIOS

Formulation Number	Cure Ratios		True Tensile Data	
	Triol/PBEP(OH)	NCO/OH	Tensile, psi	Elongation, %
UTX 9801-1	0.40	0.86	81	32
UTX 9803-1	0.61	0.86	71	43
UTX 9804-1	0.61	0.87	78	32
UTX 9805-1	0.61	0.84	55	37
UTX 9813-1	0.71	0.86	125	25
UTX 9808-1	0.81	0.85	99	29
UTX 9801-1(1)	0.81	0.85	163	23
UTX 8430-2(2)	0.90	1.00	200	20

(1) These specimens had 2 days of postcure at 120°F.

(2) UTX 8430-2 was prepared several months prior to the other formulations.

TABLE XXXIV

(U) FORMULATIONS FOR TEMPERATURE VERSUS PHYSICAL PROPERTY STUDY

Formulation Number	UTX 9813-1	UTX 9813-2	UTX 9813-3	UTX 9813-4	UTX 9813-5
PBEP (9557-99A)	17.68	17.68	17.68	17.68	17.68
TVOPA	17.68	17.68	17.68	17.68	17.68
DMM	3.89	3.89	3.89	3.89	3.89
1,2,6-HT	0.60	0.60	0.60	0.60	0.60
DBTDA	0.64	0.64	0.64	0.64	0.64
AP	46.71	46.71	46.71	46.71	46.71
Al	12.80	12.80	12.80	12.80	12.80
Triol/PBEP(OH)	0.40	0.40	0.40	0.40	0.40
NCO/OH	0.86	0.86	0.86	0.86	0.86
Cure at 120°F, hr	72	72	72	72	72
Remarks	Cured	Cured	Cured	Cured	Cured

TABLE XXXV

(U) EFFECT OF TEST TEMPERATURE ON PHYSICAL PROPERTIES

		Crosshead		True	
Formulation Number	Temperature °F	Tensile psi	Elongation %	Tensile psi	Elongation %
UTX 9813	140	53	28	---	---
UTX 9813	120	61	28	80	22
UTX 9813	100	84	33	109	23
UTX 9813	76	100	37	125	25
UTX 9813	40	186	37	232	25
UTX 9813	20	255	32	311	22
UTX 9813	0	368	25	424	17
UTX 9813	-20	950	9	1,001	6
UTX 9813	-30	1,090	5	---	---
UTX 9813	-54	660	2	---	---

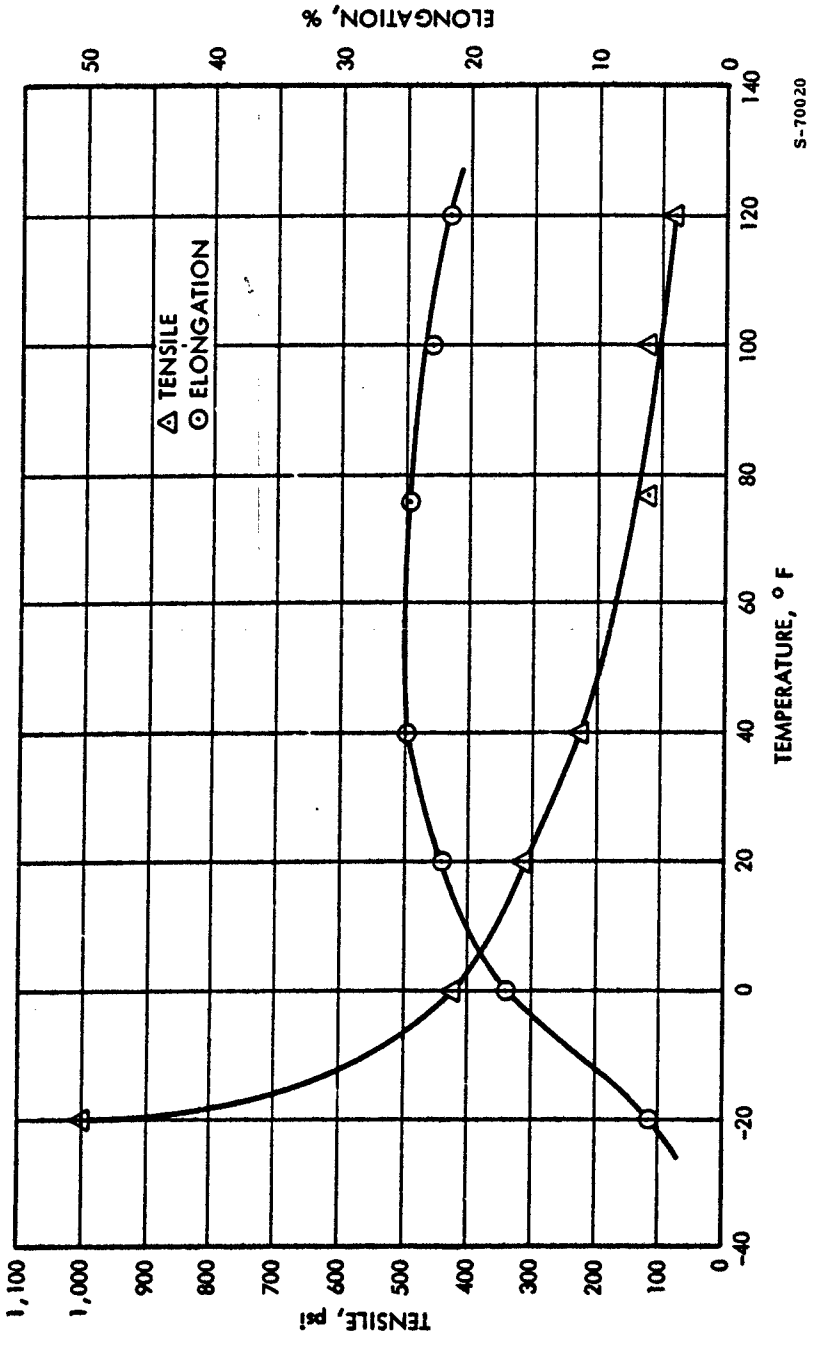

Figure 11. (U) Physical Property Data

(U) Formulation UTX 8418 was tested at temperatures ranging from -10° to -54°F. The data listed in table XXXVI indicate that the major changes in crosshead tensile properties for this propellant formulation are between -20° and -30°F. The values for both tensile and elongation are essentially the same at -30° and -54°F. Between -30° and -20°F both tensile and elongation values increase by a factor of about 2.5, indicating that the material changes from a glass to a cold plastic somewhere in this range. This formulation actually contained 5 wt-% less binder than UTX 9813 and also had a different lot of PBEP. However, the glass transition temperature is about 10°F below that for UTX 9813. The lower temperature limits of PBEP propellant appear amenable to modification by formulation techniques.

e. Evaluation of a New Triisocyanate

(C) A new triisocyanate, CTI, obtained from Aerojet-General Corporation was evaluated in a series of hand mixes listed in table XXXVII. The last four formulations with NCO/OH ratios of 1.00 to 1.20 failed to cure in 120 hours. The series 215-183-1 to -4 which contained 1,2,6-hexanetriol as well as PBEP and the triisocyanate cured in 24 hours. All samples showed some gassing, even those prepared in a dry box.

TABLE XXXVI

(U) VARIANCE OF TENSILE PROPERTIES WITH TEMPERATURE

Formulation Number	Temperature, °F	Crosshead Data	
		Tensile, psi	Elongation, %
UTX 8418-3	-54	288	2.0
UTX 8418-4	-30	371	1.7
UTX 8418-4	-20	911	5.2
UTX 8418-4	-10	727	15.9

TABLE XXXVII

(U) FORMULATIONS FOR EVALUATION OF CTI

Formulation Number	215-183-1	215-183-2	215-183-3	215-183-4	215-184-1	215-184-2	215-187-1	215-187-2
PBEP (9557-99A)	43.88	43.76	43.95	44.03	46.42	46.34	45.42	45.25
TVOPA	43.88	43.76	43.95	44.03	46.42	46.34	45.42	45.25
CTI(1)	6.67	6.79	6.59	6.52	3.45	3.61	3.72	4.05
1,2,6-HT	2.06	2.19	1.98	1.89	---	---	---	---
DBTDA	3.51	3.50	3.52	3.52	3.71	3.70	5.45	5.45
Triol/PBEP (OH)	1.00	1.05	0.95	0.90	---	---	---	---
NCO/OH	1.03	1.01	1.03	1.04	1.00	1.05	1.10	1.20
Cure at 120°F, hr	24	24	24	24	120	120	120	120
Remarks	Cured	Cured	Cured	Cured	Uncured	Uncured	Uncured	Uncured

(1) CTI is cycloheyxl triisocyanate received from Aerojet General Corporation.

(U) Reformulation to lower isocyanate equivalents resulted in good cures, and these formulations were scaled up to a 100 g batch size. No diisocyanate chain extender was used on these studies. No gassing or incompatibility was noted on the cured propellant. Further tests will be required using mixed di- and triisocyanates for complete evaluation.

f. Gel Time Studies

(C) Because lower cure ratios than expected were giving the best cures on PBEP lot 9557-99A, a sample of this lot from UTC was retested by Shell Development Company. A value of 0.097 hydroxyl equivalents per 100 g of polymer was obtained, compared with an original value of 0.108. Gel time studies run at UTC gave a value of 0.90 hydroxyl equivalents per 100 g of polymer.

(C) The UTC gel time studies on lot 9557-99A were done with three isocyanates: TDI, DMM, and CTI. The tests with TDI and CTI gave excellent agreement with CTI giving gelled samples overnight at 50°C. The TDI samples only thickened. Both samples gave isocyanate values of 0.090 equivalents per 100 g of polymer. The DMM sample gave somewhat misleading results because of an incrustation that formed on the top of the sample.

(C) Gel time studies also were carried out on PBEP lots 9088-180 and 9557-84. The data indicated that an NCO/OH value of 1.8 is required in lot -180. Lot -84 appears to have undergone a decrease in hydroxyl equivalents similar to lot 9557-99A. Initial tests indicate that the new hydroxyl value is approximately 80% to 85% of the previously used value. Further testing will be required to verify this.

(C) A 100 g mix UTX 9824-1 was prepared using PBEP lot 9088-180. Physical property data were 159 psi tensile and 29% elongation. Although the hydroxyl equivalents had changed after long term storage at -5°F, the polymer could still be cured to give good propellant.

9. BINDER CONTAMINATION STUDIES

(C) Because some cure problems had been encountered during scaleup, samples of binder containing equal amounts of PBEP and TVOPA were taken from the Bramley-Bekin mixer at various times for water and solvent analysis by GLC at Shell Development Company. After evaporation

of methylene chloride solvent overnight at 110°F, the system was evacuated for 5 hours at 120°F. Samples of the binder were taken at 2.5, 3.5, and 5 hours after vacuum was initiated. As shown in table XXXVIII, the water content dropped to 0.066% after 5 hours from the previous high of 0.087% at 2.5 hours. The methylene chloride level dropped from 0.25% to 0.083% during the same period. Neither the solvent nor water content appeared to be large enough to completely retard propellant cure. However, if even small amounts of moisture are introduced with other ingredients such as AP and aluminum, this value could have more significance in retarding cure and causing gassing. The small percentage of acetone probably remains in the PBEP from the preparation. (C)

10. PBEP/TVOPA MISCIBILITY STUDY

(U) Some workers have reported that TVOPA is not completely miscible with PBEP at equal levels. Because some turbidity was noted in gumstocks prepared for evaluation of PBEP lot 9557-99A and because poor cures on scaleup have been obtained with earlier lots of PBEP, a study was initiated in the laboratory to determine the cause of this apparent binder separation. Numerous gumstock samples, shown in table XXXIX, were prepared for this study.

(U) A 200 g gumstock mix was prepared which had an opaque appearance when cast from the mixer and failed to cure in several days. The binder showed separation into a heterogeneous mixture. The uncured binder was extracted with acetone, leaving an insoluble white residue. This residue was insoluble in the several common organic solvents tried and apparently

TABLE XXXVIII

(U) ANALYSIS OF A PBEP-TVOPA(2) MIXTURE

Evacuation Time, hr	Contamination, wt-% Water	Methylene Chloride	Acetone
2.5	0.087	0.259	0.018
3.5	0.083	0.156	0.015
5.0	0.066	0.083	0.012

(1) These analyses were run on a GLC by Shell Development Corporation.

(2) PBEP lot number was 9557-99A. GLC of Shell's retainer sample of this lot gave a value of 0.013% water in the solution or 0.04% based on PBEP.

did not react with sodium hydroxide solution but obviously reacted with sulfuric acid. Infrared analysis indicated that it was not PBEP, contained some NCO, and had aliphatic C-H and carbonyl groups.

(C) The product of the reaction of TDI and 1,2,6-hexanetriol prepared in the absence of PBEP had a similar spectrum. The apparent rapid rate of reaction of TDI and the triol, as compared to the reaction rate of TDI and PBEP(OH) with resultant separation to a heterogeneous system, would cause either slow cures of lack of cure. This could be the reason for slow cures obtained in the scaleup mixes. The formation of this precipitate also explains the reported opacity of the PBEP/TVOPA gumstock during cure.

(C) Several hand mixes listed in table XXXIX were prepared from three lots of PBEP to check if this separation was unique in one lot or a group of lots. All hand mixes were milky after a few minutes of heating. Formulation 215-140-2 using FeAA instead of DBTDA as in 215-140-1 had the same opaqueness. Mixes 215-146 and 215-150 using DMM instead of TDI appeared the same except that 215-146 cured in 3 hours instead of 24 hours. Reducing the percent of TVOPA to only 60% of the normal amount gave the same type of opaqueness as the higher plasticized gumstock.

(C) Formulations 215-164-1 and -2 were prepared to test the effect of 1,2,6-HT versus glycerol in the same formulations. The white product appeared about 10 min after addition of all ingredients in each case. Even with heating after stepwise addition of each component, no cloudiness was observed until the binder system was complete. Replacement of TVOPA with dibutylphthalate or by systematically replacing each UTC curative ingredient with one from Shell Development still gave gumstocks with the same appearance.

(U) Because solvent and/or water retention could be adding to the cure problem, a PBEP/TVOPA mixture was stripped at 80°C instead of the usual 50°C for several hours. A sample was sent to Shell Development for analysis by GLC. The water percentage was 0.069% which was similar to the percentage found in a sample stripped in a mixer at 50°C.

(U) However, no acetone was found; and the methylene chloride level dropped from 0.083% in the 50°C sample to 0.005% in the 80°C stripped material. Because it may be difficult to remove moisture below this level by vacuum stripping at a reasonable temperature, the binder materials are now being dried over molecular sieves while in solvent.

11. EVALUATION OF PBEP LOTS

(U) PBEP lot evaluation formulations are listed in tables XL, XLI, and XLII. The lots tested were 9557-84, 9088-180, 9546-16, and 9557-99A. This is a study that is routinely performed on all new lots of PBEP to establish the optimum NCO and triol levels for the given lot. Experience has shown that the formulations evaluated as a control technique by Shell Development on these lots have exhibited satisfactory properties in the PBEP/TVOPA/AP/Al propellant systems. In general, triol-to-diol and NCO-to-OH ratios have been chosen in the middle ranges of those evaluated by Shell.

(U) The cure was usually more rapid at the lower equivalents level, although ultimately most samples reached approximately the same degree of cure and exhibited approximately the same physical properties.

12. IMPACT SENSITIVITY OF PBEP AND PBEP PROPELLANTS

(U) The impact sensitivities of PBEP that have been reported by UTC have been obtained on an Olin Mathieson Impact Tester using an open-cup method. It was felt that the properties of PBEP, such as its extremely high viscosity, placed this material more in the category of an uncured propellant rather than that of a liquid sample. However, as some companies have reported closed-cup impact values for PBEP much lower than those reported by UTC's open-cup data or by Shell Development's closed-cup data, several lots of PBEP were reevaluated using open- and closed-cup methods. These data are listed in table XLIII for the neat PBEP. Data on PBEP/TVOPA blends and on PBEP propellants are listed in table XLIV.

(U) In table XLIII both open-cup and closed-cup data are given. These tests were run on freshly stripped material by the same operator in the same time period. Where there is no closed-cup data reported, it was because of the lack of material to rerun the test; and these data are reported from the original work on PBEP. Of the numerous lots of PBEP retested, only three lots gave an impact value of less than 11.6 kg-cm by either open- or closed-cup methods. These lots were 8976-110, 8976-112, and 9088-180. Lot No. 8976-110 and No. 8976-112 were the first two samples of PBEP received. Lot No. 9088-180 gave a value of 5.8 kg-cm in a closed-up test – once after the material had been aged for approximately 1 month at room temperature – in the neat stage. This value is, therefore, considered somewhat questionable as being representative of that of normal PBEP. Considerable variation was observed in lot No. 9088-180 over its test history. Impacts as high as 90 kg-cm and as low as 17 kg-cm were observed for this material. It is believed that the variation in these values is a result of the difficulty in obtaining reproducible samples of extremely viscous PBEP. However, from the testing at UTC, no samples of PBEP appear to be unduly sensitive to impact.

TABLE XXXIX

(U) FORMULATIONS FOR THE MI

Formulation No.	215-138[1]	215-139[1]	215-140-1[2]	215-140-2[2]	215-1
PBEP	44.29	44.25	45.77	45.77	45.
PBEP lot	9557-99A	9557-99A	9557-84	9557-84	9546
TVOPA	44.29	44.25	45.77	45.77	45.
Diisocyanate	8.00	7.99	5.49	5.49	5.
Type of diisocyanate	TDI	TDI	TDI	TDI	TD
1, 2, 6-HT	1.85	1.84	1.25	1.25	1.
Catalyst	1.57	1.59	1.65	1.65	1.
Type of Catalyst	DBTDA	DBTDA	DBTDA	FeAA	DBTI
Triol/PBEP(OH)[1]	0.90	0.90	1.58	1.58	1.
NCO/OH[1]	1.00	1.00	1.32	1.32	1.
Cure at 120°F, hr	7?	24	24	24	24
Remarks	Uncured	Cured	Cured	Cured	Cur

Formulation No.	215-164-1	215-164-2	215-167	215-168-1	215-16
PBEP (9557-99A)	44.29	44.53	44.29	44.48	44.
Plasticizer	44.29	44.53	44.29	44.48	44.
Type of plasticizer	TVOPA	TVOPA	DBP	TVOPA	TVOI
TDI	7.99	8.04	7.99	8.01	7.9
Triol	1.84	1.29	1.84	1.26	1.7
Type of triol	1, 2, 6-HT	Glycerol	1, 2, 6-HT	Glycerol	1, 2, 6-
DBTDA	1.56	1.60	1.56	1.78	1.7
Triol/PBEP(OH)[1]	0.87	0.87	0.87	0.87	0.8
NCO/OH[1]	1.02	1.02	1.02	1.02	1.0
Cure at 120°F, hr	24	24	24	48	48
Remarks	Cured	Cured	Cured	Cured	Cur

(1) The triol/PBEP(OH) and NCO/OH ratios are based on 0.108 hydroxyl equivalents per 100

(2) The triol/PBEP(OH) and NCO/OH ratios are based on 0.041 hydroxyl equivalents per 100

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ABLE XXXIX

FOR THE MISCIBILITY STUDY

(2)	215-141[2]	215-142[1]	215-143[2]	215-144[2]	215-145[2]	215-146[2]	215-150[1]
	45.77	57.61	60.74	60.74	45.77	44.35	53.76
	9546-16	9557-99A	9546-16	9557-84	9557-84	9557-84	9557-99A
	45.77	24.69	26.03	26.03	45.77	44.35	23.03
	5.49	12.41	8.70	8.70	5.49	8.42	18.23
	TDI	TDI	TDI	TDI	TDI	DMM	DMM
	1.25	2.86	1.98	1.90	1.25	1.20	2.68
	1.65	2.47	2.60	2.60	1.65	1.60	2.30
	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA
	1.58	0.90	1.58	1.58	1.58	1.58	0.90
	1.32	1.00	1.32	1.32	1.32	1.32	1.00
	24	24	24	24	24	3	24
	Cured	Cured	Cured	Cured	Cured	Cured	Cured

215-168-2	215-168-3	215-168-4	215-170-1	215-170-2	215-170-3	215-170-4
44.25	44.25	44.98	45.62	45.33	45.03	44.74
44.25	44.25	44.98	45.62	45.33	45.03	44.74
TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA
7.96	7.96	8.10	6.07	6.46	6.85	7.25
1.78	1.78	0.13	0.87	1.07	1.28	1.49
1,2,6-HT	1,2,6-HT	Glycerol	1,2,6-HT	1,2,6-HT	1,2,6-HT	1,2,6-HT
1.77	1.77	1.80	1.82	1.81	1.80	1.79
0.87	0.87	0.87	0.40	0.50	0.60	0.70
1.02	1.02	1.74	1.00	1.00	1.00	1.00
48	48	48	48	48	48	48
Cured	Cured	Cured	Cured	Cured	Cured	Cured

ents per 100 g of polymer as determined by gel time studies by Shell Development.
ents per 100 g of polymer as determined by infrared by Shell Development.

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TABLE XL

(U) PBEP LOT EVALUATION FORMULATIONS

Formulation No.	215-51-1	215-51-2	215-51-3	215-51-4	215-51-5	215-51-6	215-51-7	215-51-8	215-52-1
PBEP	46.5	45.9	45.7	45.5	45.35	45.5	45.5	45.9	46.5
PBEP Lot	9088-180	9088-180	9088-180	9088-180	9088-180	9088-180	9088-180	9088-180	9546-16
Plasticizer	46.5	45.9	45.7	45.5	45.35	45.5	45.5	45.9	46.5
Type of Plasticizer	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA
TDI	4.09	5.05	5.43	5.82	6.14	5.93	5.66	5.32	4.09
1,2,6-HT	1.18	1.27	1.25	1.23	1.20	1.13	1.08	1.06	1.18
FeAA	1.81	1.83	1.82	1.81	1.81	1.81	1.81	1.83	1.81
Triol/PBEP/(OH)	1.45	1.55	1.55	1.55	1.50	1.40	1.30	1.30	1.45
NCO/OH	1.10	1.20	1.30	1.40	1.50	1.50	1.50	1.40	1.10
Cure at 120°F, hr	72	72	72	72	72	72	72	72	72
Remarks	Gel	Tacky cure	Well cured	Well cured	Slightly tacky cure	Slightly tacky cure	Slightly tacky cure	Well cured	Gel

Formulation No.	215-52-2	215-52-3	215-52-4	215-52-5	215-52-6	215-52-7	215-52-8	215-53-1	215-53-2
PBEP	45.9	45.7	45.5	45.35	45.5	45.5	45.9	46.5	45.9
PBEP Lot	9546-16	9546-16	9546-16	9546-16	9546-16	9546-16	9546-16	9099-180	9088-180
Plasticizer	45.9	45.7	45.5	45.35	45.5	45.5	45.9	46.5	45.9
Type of Plasticizer	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA
TDI	5.05	5.43	5.82	6.14	5.93	5.66	5.32	4.09	5.05
1,2,6-HT	1.27	1.25	1.23	1.20	1.13	1.08	1.06	1.18	1.27
FeAA	1.83	1.82	1.81	1.81	1.81	1.81	1.83	1.81	1.83
Triol/PBEP/(OH)	1.55	1.55	1.55	1.50	1.40	1.30	1.30	1.45	1.55
NCO/OH	1.20	1.30	1.40	1.50	1.50	1.50	1.40	1.10	1.20
Cure at 120°F, hr	72	72	72	72	72	72	72	72	72
Remarks	Gel	Slightly tacky cure	Gel	Well cured	Well cured	Tacky cure	Tacky cure	Gel	Semicured

Formulation No.	215-53-3	215-53-4	215-53-5	215-53-6	215-53-7	215-53-8	215-55-1	215-55-2	215-55-3
PBEP	45.7	45.5	45.35	45.5	45.5	45.9	45.7	45.7	45.7
PBEP Lot	9088-180	9088-180	9088-180	9088-180	9088-180	9088-180	9088-180	9088-180	9088-180
Plasticizer	45.7	45.5	45.35	45.5	45.5	45.9	45.7	45.7	45.7
Type of Plasticizer	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA
TDI	5.43	5.82	6.14	5.93	5.66	5.32	5.43	5.43	5.43
1,2,6-HT	1.25	1.23	1.20	1.13	1.08	1.06	1.25	1.25	1.25
FeAA	1.82	1.81	1.81	1.81	1.81	1.83	1.82	1.82	1.82
Triol/PBEP/(OH)	1.55	1.55	1.50	1.40	1.30	1.30	1.55	1.55	1.55
NCO/OH	1.30	1.40	1.50	1.50	1.50	1.40	1.30	1.30	1.30
Cure at 120°F, hr	72	72	72	72	72	72	96	96	96
Remarks	Well cured	Well cured	Semicured	Well cured	Well cured	Slightly tacky cure	Very tacky	Semicured	Semicured

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TABLE XLI

(U) PBEP LOT 9557-84 EVALUATION FORMULATIONS

Formulation	215-76-1	215-76-2	215-76-3	215-76-4	215-76-5
PBEP[1]	46.1	45.8	45.2	44.6	44.45
TVOPA	46.1	45.8	45.2	44.6	44.45
TDI	5.58	6.06	7.15	8.26	8.26
1,2,6-HT	1.30	1.48	1.54	1.41	1.74
FeAA	0.92	0.91	0.91	0.90	0.90
Triol/PBEP(OH)[2]	---	---	---	---	1.30
NCO/OH[2]	---	---	---	---	1.40
Cure at 120°F, hr	24	24	72	96	72
Remarks	Cured	Cured	Cured	Cured	Cured

(1) PBEP lot was 9557-84.
(2) The triol/PBEP(OH) and NCO/OH ratios are based on 0.075 hydroxyl equivalents per 100 g of polymer determined by gel time studies rather than a value of approximately 0.041 as determined by infrared.

TABLE XLII

(U) PBEP LOT 9557-99A GUMSTOCK EVALUATION FORMULATIONS

Formulation	215-130-1	215-130-2	215-130-3	215-130-4	215-130-5
PBEP	44.64	44.25	44.05	43.95	44.84
TVOPA	44.64	44.25	44.05	43.95	44.84
TDI	7.86	8.41	8.85	9.03	7.71
1,2,6-HT	1.98	2.05	2.05	2.15	1.81
DBTDA	0.89	0.88	0.88	0.88	0.90
Triol/PBEP(OH)[1]	0.94	1.0	1.00	1.05	0.87
NCO/OH[1]	0.96	1.0	1.05	1.05	0.97
Cure at 120°F, hr	72	72	72	72	72
Remarks	Well cured	Well cured	Well cured	Well cured	Well cured

(1) The triol/PBEP(OH) and NCO/OH ratios are based on 0.108 hydroxyl equivalents per 100 g of polymer determined from gel time studies by Shell Chemical.

TABLE XLIII

(U) IMPACT SENSITIVITIES OF PBEP SAMPLES

PBEP Lot	Open Cup E_{50} kg-cm	Closed Cup E_{50} kg-cm	PBEP Lot	Open Cup E_{50} kg-cm	Closed Cup E_{50} kg-cm
8976-110	6.0	---	9237-163A	11.6	35.2
8976-112	6.0	---	9165-107	14.3	---
8976-126	28.9	---	9088-180	17.0(1)	20.2(2)
8976-130	23.8	---	9088-180	60-90(3)	---
8976-182	---	22.2	9088-180	18.4(4)	15.4
9305-8	55.4	27.6	9557-84	28.0	42.0
9305-9	20.2	---	9456-16	21.2	17.8
9305-14	16.0	---	9537-14	---	25.8
9237-68D	17.8	41.4	9557-84	40.0	42.0
9237-86B	17.3	21.8			

(1) Shell stripped material
(2) An impact of 5.8 obtained after one month ambient aging
(3) Original values
(4) Rerun

TABLE XLIV

(U) IMPACT SENSITIVITIES
OF GUMSTOCK AND PROPELLANT

PBEP	E_{50}(1) kg-cm	PBEP/TVOPA	E_{50}(1) kg-cm	Propellant	E_{50}(1) kg-cm
8976-126	28.9	1/1 (U)(2)	10.2	(U)	15.0
8976-126	---	1/1 (C)(3)	17.2	(C)	27.6
8976-130	23.8	1/1 (U)	15.8	(U)	15.6
9165-107	14.3	---	---	UTX 8407 (U)	16.1
				UTX 8407 (C)	8.3/ 11.6/ 11.4/ 14.2/ 11.8(4)
---	---	---	---	UTP 3001	24.4
9237-68D	17.8	1/1 (C)	10.2	(C)	15.0
9557-84	28.0	---	---	---	---
9456-16	17.8	---	---	UTX 8419-2	7.5
9083-180	90.0	1/1 (C)	120	(C)	31
9088-180	---	1/1 (C)	51	---	---
9088-180	---	1/1 (U) PBEP/OPE	51.0	---	---
9165-107	14.3	1/1 (U) PBEP/OPE	3.0	---	---
9088-180	---	1/1 (U)	12.0	---	---
9088-180	---	1/1 (C)	70	---	---
9088-180	18.4	1/1 (U)	40(5)	---	---
9088-180	---	1/1 (U)(6)	19.2	---	---
9557-84	40	---	---	UTX 8422 (C)	13.6/ 13.3/ 13.6(7)

(1) Open cup
(2) Uncured
(3) Cured
(4) Results of five batches
(5) Smoke at 8 kg-cm
(6) Closed cup
(7) Results of three batches

(U) A closed-cup impact value for TVOPA of 2.66 kg-cm was obtained on a sample of Aerojet-synthesized material as compared with a previous value on Rohm and Haas-synthesized TVOPA of 1.5 kg-cm. These values are comparable and appear to be representative of the sensitivity of neat TVOPA.

(U) No explanation could be given for the low values for the impact sensitivity of PBEP reported by Rohm and Haas. However, because there is no need at UTC for manual handling of either PBEP or TVOPA – or the binder materials without being diluted by solvent, the impact sensitivity of the propellant appears to be more important than the sensitivity of the binder. Impact values for propellant, such as those listed in table XLIII, usually fall between 8 to 16 kg-cm depending upon the lot of PBEP and the state of cure. Reproducibility of the impact values obtained from numerous batches of the PBEP propellant is indicative of the impact sensitivity that can be expected of PBEP-TVOPA propellant. The impact sensitivity range of the cured propellant permits manual handling – such as for transportation purposes – but does, however, preclude any manual trimming or sawing type of operation. It should be noted, however, that PBEP propellant has been successfully sawed and milled in the UTC remote-milling facility without incident.

(U) The reproduction of methods of testing at UTC was checked by resubmitting a sample of PBEP lot 8976-182 that had given a value of 24.7 kg-cm 9 months earlier. A second value of 26 kg-cm was obtained which indicates not only a consistency of method but also that this lot has remained at about the same impact sensitivity for at least 9 months.

13. NFPA BINDER EVALUATION

(C) Currently, there are only limited data available comparing PBEP with the Rohm and Haas NFPA binder. The NFPA binder is based upon 2,3-bis(difluoramino)propyl acrylate monomer. This binder is copolymerized with approximately 5% acrylic acid to form a prepolymer with carboxy functional groups. The prepolymer is cured by crosslinking with UNOX 221, a diepoxide manufactured by Union Carbide Company.

(U) Samples of Rohm and Haas formulation SE-103A were prepared for both physical property, hazard, and thermal stability evaluation. These results are directly comparable with PBEP samples under identical test conditions.

(U) Impact sensitivity of the prepolymer (PPAA-3-1011) was 8.0 kg-cm (E_{50} in OM open cup tester) and 11.0 kg-cm for the cured propellant. Friction sensitivity by the ESSO Tester for the prepolymer and propellant was positive with Pyrex glass grit at 100 ft-lb and 38 ft-lb, respectively.

(U) The Rohm and Haas formulation SE-103A was scaled up to the ARC mixer, and physical property data were obtained on the propellant. Crosshead values of tensile and elongation were 44.2 psi and 21.9%. True values were 50.4 psi tensile and 13.6% elongation. The tensile values were comparable to those reported by Rohm and Haas, but elongation was lower than reported. However, no attempt was made to optimize the physical properties of NFPA propellant.

SECTION III

CONCLUSIONS

(U) In the preparation of the 1-lb motors for the surveillance program, a number of mixes were scheduled in the 2-qt Bramley-Bekin mixer. However, a problem was encountered in this work in that these mixes failed to cure properly and exhibited signs of porosity. This problem has been thoroughly discussed in the quarterly reports. Several initial changes listed below were evaluated as an answer to this problem:

A. The hot binder was evacuated before the FeAA cure catalyst was added.

B. The order of addition of ingredients was changed.

C. Various mix temperatures and cure temperatures were evaluated.

D. Analysis for residual solvent and water after evacuation were run.

E. The cure catalyst level was varied.

F. Extended solvent evacuation was attempted.

G. The mixer was renovated for better vacuum.

(C) These variations did not completely cure the problem but did give somewhat better propellant than previously. Conclusions that may be drawn from experimental results based on these changes are as follows:

A. There is enough residual HF in the hot binder at least to deactivate part of the FeAA.

B. 1,2,6-hexanetriol added last after a prereaction of the diisocyanate and PBEP does give better propellant, but the cures can be too rapid.

C. The standard 120°F mix and cure temperature was adequate.

D. Extended evacuation does decrease the residual solvent and water.

E. An FeAA level of at least 0.2% based on total formulation was necessary.

(C) Although the propellant was somewhat improved by these variations, the major problem was not identified until it was discovered that the 1,2,6-hexanetriol reacts much more rapidly than PBEP does with the diisocyanate. The triol-diisocyanate reaction product separates from the surrounding binder. This leads to either very slow cure or no cure at all. The cure problems were remedied by a longer residence time in the mixer after all ingredients had been added. Additionally, lower cure ratios were used than might have been expected from the qualitatively determined hydroxyl equivalents. These changes gave well · ·ed propellant from both the ARC and Bramley-Bekin mixers.

(C) No basic incompatibility apears to exist between AlH_3 and the PBEP/TVOPA binder. No gassing appears to occur on cure of the propellant or even after 3 months at ambient temperatures with AP or HAP as the oxidizer. The resultant propellant is impact and friction sensitive. However, HAP— either with AlH_3 or Al in the NF_2 binder — lowers the autoignition temperature. The HAP propellant has about the same impact and friction sensitivity as if AP were the oxidizer. HAP propellant is much more hygroscopic and must be handled in dehumidified atmospheres.

REFERENCES

1. "Evaluation of PBEP, a High-Energy Binder (U)," Final Report, UTC 2175-FR, Contract No. AF 04(611)-10540. United Technology Center, May 1966. (CONFIDENTIAL)*

2. "Synthesis of High-Energy Solid Oxidizer Binder Propellants (U)," Quarterly Report No. 7, April – June 1964. Shell Development Company. (CONFIDENTIAL)*

3. "Evaluation of High-Energy Binder (U)," Quarterly Progress Report No. 1, UTC 2200-QPR1, 1 March to 31 May 1966, United Technology Center, 1966. (CONFIDENTIAL)*

4. "Evaluation of High-Energy Binder (U)," Quarterly Progress Report No. 2, Technical Report AFRPL-TR-66-255, UTC 2200-QPR2, 1 June to 31 August 1966, United Technology Center, September 1966. (CONFIDENTIAL)*

5. "Evaluation of High-Energy Binder (U)," Quarterly Progress Report No. 3, Technical Report AFRPL-TR-66-354, UTC 2200-QPR3, 1 September to 30 November 1966, United Technology Center, December 1966. (CONFIDENTIAL)*

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The high-energy binder, PBEP, has been evaluated in prototype propellant formulations. Cure problems encountered have been resolved by introducing changes in the original process variables. There appears to be no basic incompatibility between AlH_3 and the PBEP/TVOPA binder system. A 100-g motor has been successfully fired based on these ingredients with AP as oxidizer. Good cures were obtained on AlH_3 propellant with a high binder level with one ambient cured formulation giving a stress of 121 psi and strain of 52%. Surveillance studies of 2-in. cubes of propellant have indicated that DBTDA cure catalyst may have better aging characteristics than a cube with FeAA cure catalyst, although the two cubes did contain different PBEP lots. HAP appears to be compatible in either the NF_2 binder/Al system or NF_2 binder/AlH_3 system. Samples of these formulations have been stored for several months under dry conditions with no signs of deterioration.

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