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**(TITLE UNCLASSIFIED)
EVALUATION OF A HIGH-ENERGY BINDER**

**E. K. Ives
R. M. Kumagai
T. N. Scortia**

United Technology Center

**FINAL TECHNICAL REPORT
CONTRACT NO. F04611-67-C-0039**

JUNE 1969

**Group 4
DOWNGRADED AT 3 YEAR INTERVALS
DECLASSIFIED AFTER 12 YEARS
DOD DIR. 5200.10**

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FOREWORD

(U) This is the final report on the program conducted by UTC under Contract No. F04611-67-C-0039 to evaluate PBEP, a high-energy NF_2 binder, in prototype propellant formulations. Experimental work conducted at UTC facilities during the period 1 March 1967 through 28 February 1969 is covered.

(U) Classified information has been extracted from all documents listed under References.

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

W. H. Ebelke, Col, USAF
Chief, Propellant Division
AFRPL
Edwards, California

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CONFIDENTIAL ABSTRACT

(C) A sample of PBEP was fractionated into six fractions. The functionality of the fractions varied widely while the molecular weights varied between 1,200 and 6,500. The thermal stability of the lowest molecular weight fraction was poorest. As-received PBEP could not be cured in larger batches without increasing dibutyl tin diacetate catalyst to impractical levels. This effect was shown to stem from HF destruction of the catalyst. The formation of an HT-isocyanate adduct in the original polyol-containing formulations because of the slower PBEP reactivity complicated the cure problems. Work in the latter part of the program concentrated on a CTI system without polyol crosslinkers and on the use of treated PBEP and TVOPA. Raffinate PBEP required lower amounts of DBTDA for good cures than was necessary for as-received PBEP. Treatments of PBEP and TVOPA with molecular sieves were effective in removing unknown materials that absorb in the carbonyl range in IR. Formulations using these treated ingredients gave more reproducible and scaleable cures than controls in which neither the PBEP nor the TVOPA were treated. Adequate pot life and good cures were obtained with treated PBEP and TVOPA formulations when scaled from the 50-g to a 2,500-g size with the same catalyst level. CTI, in conjunction with HT or DPG, produced propellants with better physical properties than the properties of propellants cured with CTI alone. CTI or a mixture of CTI and a diisocyanate was the most effective cure system for PBEP propellants containing HAP as an oxidizer. HF-resistant catalysts were also studied as an approach to the cure scaleup problem. Of the HF-resistant catalysts tested for cure ability, Me_2SnCl_2 appeared to be the best. BuSnCl_3 produced a short pot life and erratic cures. Surveillance data showed that the aluminized PBEP system, with or without stabilizers, can be stored at 25° or 35°C for long periods of time without significant deterioration. However, the storage capability does vary from lot to lot of PBEP and/or TVOPA. AlH_3 propellants exhibited severe gassing at ambient storage temperatures in 2 to 4 weeks. Results of DTA studies and long-term surveillance at 80°F indicated that no apparent major incompatibilities existed in beryllium and BeH_2 propellants. Two 1-lb motors of a Be-AP-PBEP formulation with a theoretical I_{sp} of 284 sec gave an average delivered I_{sp} of 265.5 sec for an efficiency of 93.5%.

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ABBREVIATIONS AND SYMBOLS

Al	aluminum
AlH ₃	aluminum hydride
Al ₂ O ₃	aluminum oxide
AN	acrylonitrile
AP	ammonium perchlorate
AR	as-received
Be	beryllium
Beane	impure beryllium hydride
BeH ₂	beryllium hydride
BeCl ₂	beryllium chloride
BP	Baker-Perkins
BuSnCl ₃	butyl tin trichloride
Bu ₂ SnCl ₂	dibutyl tin dichloride
Bu ₃ SnCl	tributyl tin chloride
c*	characteristic exhaust velocity
CCl ₄	carbon tetrachloride
CH ₂ Cl ₂	methylene chloride
CH ₃	methyl group
CN	nitrile group
CTI	cyclohexane triisocyanate

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DBP	dibutyl phthalate
DBTDA	dibutyl tin diacetate
DBTDL	dibutyl tin dilaurate
DEBI	1,4-diethylbenzene- β , β' -diisocyanate
DHB	1,4-dihydroxybutane
DHCH	1,3-dihydroxycyclohexane
DHH	2,5-dihydroxyhexane
DMMDI	3,3'-dimethyl diphenylmethane-4,4'-diisocyanate
DPA	diphenyl acetylene
DPG	dipropylene glycol
DSC	differential scanning calorimeter
DTA	differential thermal analysis
FeAA	ferric acetylacetonate
4A	4A molecular sieves
GLC	gas-liquid chromatography
HAP	hydroxylamine perchlorate
HF	hydrogen fluoride
HMDI	hexamethylene diisocyanate
H ₁₂ MDI	dicyclohexylmethane-4,4'-diisocyanate
HT	1,2,6-hexanetriol
IPDI	isophorone diisocyanate
IR	infrared
Isonate 143L	a polyfunctional isocyanate from the Upjohn Company

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I_{sp}	specific impulse
JANAF	Joint-Army-Navy-Air Force
Kaiser NCO-10	poly(phenylisocyanates) from Kaiser Chemical Company
Kaiser NCO-20	
Kaiser NCO-120	
Mondur MR	polymethylene polyphenyl isocyanate from Molay Chemical Company
Me_2SnCl_2	dimethyl tin dichloride
NCO	isocyanate
NF_2	difluoramino group
N_2F_4	tetrafluorohydrazine
OH	hydroxyl group
PA	phenyl acetylene
PAPI	polyanisole polyisocyanate
PBEP	poly[1, 2-bis(difluoramino)2, 3-epoxy propane] (C)
P_c	chamber pressure
PF_3	phosphorous trifluoride
POF_3	phosphorous oxyfluoride
RAF	raffinate
r_b	burning rate
S	sulfur
TCP	tricresyl phosphate
TDI	tolylene diisocyanate

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TGA	thermogravimetric analysis
13X	13X molecular sieves
TTI	triphenylmethane triisocyanate
TVOPA	1, 2, 3-tris [1, 2-bis(difluoramino)vinoxy] propane (C)
UTC	United Technology Center

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SECTION I

INTRODUCTION

1. PROGRAM SCOPE

(C) Under Contract No. F04611-67-C-0039, UTC conducted a research program to evaluate PBEP, a high-energy NF_2 binder, in both metallized and nonmetallized propellants oxidized by conventional and high-energy oxidizers. The purpose of the program was to extend the utility of the 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 designed to develop NF_2 propellants with a range of burning rates, to provide test data on the stability of NF_2 propellants, and to develop stabilizers for these propellants.

(C) The program was divided into five phases. Phase I called for the investigation of various cure systems and plasticizers to yield an optimum gumstock. The sensitivity and compatibility of PBEP with all possible combinations of all plasticizers, fuels, and oxidizers were tested.

(C) Phase II called for the formulation of the optimized binder from phase I with nontoxic fuels and both conventional and advanced oxidizers to approach a theoretical I_{sp} goal of 300 sec (1,000 to 14.7 psia). The formulation developed under this phase was tested physically, mechanically, and ballistically in 1-lb motors.

(C) Phase III called for the formulation of the phase I optimized binder with toxic fuels and both conventional and advanced oxidizers to give propellants which approach a theoretical target I_{sp} of 325 sec (1,000 to 14.7 psia). The formulations were tested physically, mechanically, and ballistically in 1-lb motors.

(U) Phase IV called for long-term aging studies and temperature-cycling studies on formulations from phases II and III.

(U) Phase V called for investigation methods for improving the thermal stability and decreasing the burning rates of PBEP formulations.

(U) The program was redirected to emphasize investigations of various cure systems in phase I and to deemphasize the advanced oxidizer study in phase II.

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2. REPORT STATUS

(U) The present report covers the experimental work performed during 1 March 1967 through 28 February 1969.

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SECTION II

TECHNICAL DISCUSSION

1. INTRODUCTION

(C) PBEP is prepared by Shell Development Company 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 for the current material of 3,300 to 5,000.

(C) This program was a broad survey of the utility, compatibility, and stability of PBEP with various oxidizers, fuels, and curatives. The polymer was plasticized with TVOPA and cured with such systems as DMMDI and HT, CTI alone, CTI in conjunction with a diisocyanate, or CTI and a glycol.

(C) Early in the program it was discovered that there were cure and pot life problems on scaleup. Formulations that cured well at low catalyst levels in micromixes would not cure on scaleup. Increasing the catalyst level in the larger batches to obtain cure gave short pot life. Apparently some material in the binder was deactivating the commonly used cure catalyst, DBTDA. A study was undertaken to find cure catalysts that would not be deactivated and would give reproducible cures on scaleup.

(C) In the DMMDI-HT cure system the diisocyanate and triol reacted much more rapidly than the diisocyanate and PBEP, and the reaction product tended to separate from the binder. It was found that the CTI gave well-cured propellants when HAP was present. It was also found that CTI gave more reproducible cures on scaleup. However, the propellant with CTI as the only curative had very poor physical properties, and work was undertaken to improve these properties by the addition of a glycol or a diisocyanate.

(C) Efforts were made to avoid scaleup cure problems by treatment of the binder materials. Removal of the lower molecular weight fraction of PBEP helped in obtaining reproducible cures, but the resulting propellants were no more thermally stable and the physical properties were no better than those of propellants prepared with regular PBEP. Treatment of the PBEP and TVOPA with silaceous materials such as 13X molecular sieves also gave reproducible cures on scaleup but, at least in the case of PBEP, would revert with time to again deactivate the cure catalyst.

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2. EFFECT AND SOURCE OF HF

(C) When anhydrous HF is bubbled through a solution of DBTDA in benzene, a white precipitate is formed. Because any HF generated from a PBEP-TVOPA binder would react in the same manner in deactivating the catalyst, a study was undertaken to determine why this reaction occurred and to find the source of the HF.

a. Isolation and Identification of the Reaction Product of HF and DBTDA

(C) The white solid formed when anhydrous HF was bubbled through a DBTDA-benzene solution was insoluble in water, tetrahydrofuran, methylene chloride, and benzene but was soluble in hot, low-molecular weight alcohols. The precipitate after recrystallization in methanol had a melting point of 150° to 155°C. A precipitate obtained by heating PBEP-TVOPA blend with DBTDA at 60°C for 4 days was discolored. After repeated recrystallization and treatment of the hot methanol solution with Norite A, the precipitate was white and had a melting point of 152° to 155°C. The mixed melting point of these compounds was 151° to 156°C, indicating that the two products were the same.

(C) Analysis by DSC also gave similar results for the two compounds. The purified product from the PBEP-TVOPA-DBTDA reaction had endotherms at 163° and 211°C. The precipitate from the anhydrous HF-DBTDA reaction had endotherms at 163° and 216°C.

(C) Qualitative analysis of these solid precipitates showed the presence of tin and fluoride. Additional amounts of the precipitate from the reaction of anhydrous HF and the catalyst were prepared for quantitative elemental analysis. Analyses for carbon and hydrogen indicated the compound was dibutyl tin difluoride.

(C) IR analysis showed the compound from DBTDA and PBEP-TVOPA reaction contained C-H bands from both methyl and methylene groups but no carboxyl groups. The precipitate from anhydrous HF and DBTDA showed a spectrum similar to the material obtained from the mixtures of DBTDA and the NF₂ binder ingredients, although in the latter compounds there did appear to be an ionic carboxyl group present.

b. Determination of the Dominant HF Source

(C) To determine whether decomposition products of PBEP or TVOPA were the predominant reactants with DBTDA, two mixtures were prepared. One mixture was PBEP-DBP-DBTDA and the second was TVOPA-DBP-DBTDA. DBP was used as a high boiling diluent and was dried prior to

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use. Both mixtures were heated at 60°C for 4 days. A copious white precipitate was observed in the reaction vessel containing PBEP as opposed to a minute amount of precipitate in the TVOPA reaction vessel. The primary difference in appearance of the TVOPA mixture was a change from colorless to yellow upon heating. The precipitate from the PBEP reaction was found to be the same as the HF-DBTDA reaction product.

3. EFFECT OF IMPURITIES IN TVOPA

(U) Originally, it had been found at UTC that impurities in TVOPA, such as OH detected by IR, had little effect on the cure of the final polymer system. However, because difficulties in achieving both long pot life and good cures were encountered on scaleup, it was decided to investigate the importance of these impurities. AlH₃ formulations contain a higher TVOPA/PBEP ratio (60/40) instead of the usual 50/50 ratio used in aluminum systems. Thus, impurities in TVOPA would have a more pronounced effect in AlH₃ propellants than in aluminum propellants.

(C) An NCO/OH ratio of 0.65 was determined as being the minimum equivalents ratio that could be used to successfully cure PBEP lot 10001-186. If the OH in the TVOPA reacted with CTI to any extent, the system would probably not cure. Also, if no OH were present in the TVOPA, the system should cure. Formulations UTX 10264-6 and 10264-8 listed in table I contained TVOPA with no OH impurity as measured by IR. These formulations were well cured in 16 hr at 100°F. When the same NCO/OH ratios were used, UTX 10264-5 and UTX 10264-7, which included TVOPA that contained 0.23 wt-% of OH, failed to cure. Formulation UTX 10264-9, using TVOPA that had an OH wt-% of 0.31, also failed to cure. UTX 10264-10 mixed with TVOPA having 0.13 wt-% OH produced somewhat better but still incomplete cures. UTX 10274-1 was similar to UTX 10264-10 but the 0.13 wt-% OH in the TVOPA was compensated for by the addition of excess CTI. This propellant cured after 16 hr at 100°F; however, the propellant was physically inferior to the normal propellant. Apparently, the OH impurity in TVOPA can affect the cure, especially if the NCO level is just barely sufficient to cure the PBEP. This effect could explain some variations in cure; however, extrapolation to scaleup cure effects must be made cautiously because it has been established that lack of cure occurs even when the same lots are scaled up.

4. CURE CHARACTERISTIC STUDY

(U) Several methods have been tested to improve the cure characteristics and physical properties of PBEP-TVOPA propellants. Problems with pot life on scaleup and binder separation had occurred with the DBTDA-DMMDI-HT

TABLE I
(U) FORMULATIONS FOR TVOPA IMPURITIES STUDY

Formulation No.	UTX 10264-5	UTX 10264-6	UTX 10264-7	UTX 10264-8	UTX 10264-9	UTX 10264-9-2	UTX 10264-10-1	UTX 10264-10-2	UTX 10274-1
PBEP [†]	13.76	13.76	13.76	13.76	13.76	13.76	13.76	13.76	13.71
TVOPA	20.64	20.64	20.64	20.64	20.64	20.64	20.64	20.64	20.57
TVOPA lot	201	184-203B	201	184-203B	242	242	233	233	233
CTI	0.432	0.432	0.432	0.432	0.432	0.432	0.432	0.432	0.54
DBTDA	0.175	0.175	0.175	0.175	0.175	0.175	0.175	0.175	0.174
AP	49.50	49.50	49.50	49.50	49.50	49.50	49.50	49.50	49.50
AlH ₃	15.50	15.50	15.50	15.50	15.50	15.50	15.50	15.50	15.50
Wt-% OH in TVOPAF	0.23	0.00	0.23	0.00	0.31	0.31	0.13	0.13	0.13
NCO/OH [‡]	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65 on PBEP 1.0 on TVOPA
Cure temperature, °F	100	100	100	100	100	100	100	100	100
Cure time, hr	168	16	504	16	168	168	168	168	16
Remarks	Uncured	Cured	Uncured	Cured	Uncured	Uncured	Poor cure	Poor cure	Cured

[†]PBEP lot was 10001-186 in all formulations.
[‡]These values are taken from the TVOPA analyses supplied by Aerojet-General Corporation.
[§]These numbers are based on an OH equivalents value of 0.70 meq/g for the PBEP.

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cure systems. The HT reacted much faster with the diisocyanate than PBEP and the reaction product tended to separate from the rest of the binder. The cure catalyst, DBTDA, at levels necessary for adequate cure of the propellant gave too short a pot life on scaleup. At lower levels the catalyst was deactivated by HF or some other binder ingredient and no cures were obtained. Several crosslinking systems were examined. Among these were polyisocyanates, polyisocyanates plus a glycol, and mixtures of poly- and diisocyanates. Catalysts, as a replacement for DBTDA, were evaluated for resistance to HF attack, efficiency of cure ability, and compatibility with binder ingredients.

a. Miscellaneous Polyisocyanates Evaluation

(C) Preliminary testing in gumstocks indicated that TTI produced adequate cures without any additional crosslinker. Two formulations were prepared, one using only TTI and the other using TTI in conjunction with the diol DPG. The all-TTI formulation cured in 16 hr and the resulting propellant had a tensile of 66 psi and an elongation of 6%. The formulation with TTI and DPG had somewhat improved values of 126 psi and 11%. TTI appeared to produce essentially the same cure results as those obtained with CTI.

(U) Another isocyanate, Isonate 143L, manufactured by the Upjohn Company, with a functionality of about 2.2 to 2.3 was tested in gumstock samples without the use of a diol or triol. Adequate cures were obtained but there was gassing and discoloration of the samples, indicating some incompatibility with the binder. Therefore, testing of Isonate 143L was terminated.

(U) Three isocyanates made by Kaiser Chemical Company were tested. These compounds have an average functionality of 2.3, 2.6, and 3.2 and are all various adducts of diphenyl methane diisocyanate.

(C) Gumstocks prepared from PBEP and Kaiser isocyanates cured at a 1 to 1 ratio of NCO/OH but failed to cure at ratios of 0.9 and 1.1. The cured samples had very poor tensile properties.

(C) A mixture of DMMDI and the Kaiser NCO-110 isocyanate gave cures in gumstocks when the DMMDI content was low, but at higher DMMDI percentages the gumstocks failed to cure. Those gumstocks that did cure had very poor tensile properties. Even poorer cures were achieved in gumstocks prepared from mixtures of TDI and Kaiser 3.2.

(U) The Kaiser materials were also incompatible with HAP and, therefore, these isocyanates were not further evaluated.

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b. CTI and CTI-Glycol Evaluation

(1) CTI

(C) Gumstocks, when prepared with CTI alone, cured but had poor tensile properties. This was also true for propellant formulations that contained no crosslinker other than CTI. For example, formulations UTX 9825-1 and UTX 9825-3 listed in tables II and III had a tensile of 50 to 42 psi and an elongation of 37% and 27%, respectively. The NCO/OH was varied from 0.86 to 1.24 in these propellants with no significant changes in mechanical properties. The use of a different lot of PBEP in UTX 9878 or the use of a different catalyst in UTX 11766-1 also failed to give any improvement in properties.

(C)

TABLE II

(U) CTI PROPELLANT FORMULATIONS

<u>Formulation No.</u>	<u>UTX 9825-1</u>	<u>UTX 9825-2</u>	<u>UTX 9878-1</u>	<u>UTX 11766-1*</u>
PBEP	17.68	17.68	13.67	13.74
PBEP Lot	9557-99A	9557-99A	10001-186	10316-172
TVOPA	17.68	17.68	20.46	20.61
CTI	1.14	1.14	0.49	0.49
Catalyst	0.64	0.64	0.35	0.04
Type of Catalyst	DBTDA	DBTDA	DBTDA	Me ₂ SnCl ₂
AP	48.86	48.86	50.00	49.33
Aluminum	14.00	14.00	15.00	14.80
NCO/OH	0.86	1.24	0.75	0.80
Cure time, days	6	7	3	3
Cure temperature, °F	120	120	100	100
Remarks	Cured	Uncured	Cured	Cured

*These formulations also contained 0.99 wt-% 13X molecular sieves.

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(U)

TABLE III

(U) PHYSICAL PROPERTY DATA
FOR CTI FORMULATIONS

<u>Formulation No.</u>	<u>True Physical Properties</u>	
	<u>Tensile, psi</u>	<u>Elongation, %</u>
UTX 9825-1	50	37
UTX 9825-2	42	27
UTX 9878-1	30	25
UTX 11766-1	40	14

(2) CTI-HT

(U) Physical property data for the all-CTI cure system indicated that some loss of elongation could be sacrificed for a gain in tensile value. Therefore, HT was added to increase the tensile strength. Normally a long chain diol would be preferred with CTI, but use of HT had given very good cures with CTI in gumstock samples.

(C) Table IV lists the CTI-HT containing various curative ratios as well as different catalyst levels. The series 232-54-1 to 232-54-3 were prepared to test the effect of the DBTDA level. The samples were well cured in 16 hr, even at a level of 0.19 wt-% catalyst.

(C) Sample series 232-55-1 to 232-55-7 and 232-56-1 to 232-56-8 had triol/PBEP(OH) ratios varying between 0.21 and 1.14 and NCO/OH ratios of 0.83 to 1.49. All samples were well cured after 16 hr at 120° F, except 232-55-1 which contained no cure catalyst.

(C) Gumstock samples 232-57-1 to 232-57-4 contained DBTDA levels of 0.06 to 0.20 wt-% and high curative ratios of 1.14 triol/PBEP(OH) and 1.00 NCO/OH. All samples were well cured after 16 hr and the samples at the higher catalyst levels cured in 1 hr.

(C) Formulation 232-56-3 appear to be about the optimum of the gumstock samples tested for use in propellant mixes. This formulation had NCO/OH ratio of 0.94, a catalyst level of 0.58 wt-% and a triol/PBEP(OH) ratio of 0.42. Although the level of

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TABLE IV

(U) CTI-HT GUMSTOCK FORMULATIONS

Formulation No.	232-54-1	232-54-2	232-54-3	232-55-1	232-55-2	232-55-3	232-55-4	232-55-5	232-55-6	232-55-7	232-56-1
PBEB	37.85	37.99	38.14	37.92	37.85	37.78	38.28	38.17	38.02	38.05	37.85
TVOPA	56.78	56.99	57.21	56.88	56.78	56.67	57.43	57.25	57.03	57.08	56.78
CTI	3.52	3.53	3.55	3.91	3.90	3.89	3.25	3.55	3.91	3.91	3.52
HT	0.91	0.91	0.91	1.29	1.29	1.28	0.46	0.46	0.46	0.76	0.91
DBTDA	0.95	0.57	0.19	---	0.19	0.38	0.57	0.57	0.57	0.57	0.57
Triol/PBEP(OH)	0.80	0.80	0.80	1.14	1.14	1.14	0.42	0.42	0.42	0.64	0.80
NCO/OH	1.10	1.10	1.10	1.00	1.00	1.00	1.23	1.35	1.49	1.17	1.10
Cure time, hr *	0.50	16.0	16.0	120.0	16.0	16.0	16.0	16.0	16.0	16.0	0.50
Formulation No.	232-56-2	232-56-3	232-56-4	232-56-5	232-56-6	232-56-7	232-56-8	232-57-1	232-57-2	232-57-3	232-57-4
PBEB	38.70	38.58	38.43	38.02	37.85	37.71	38.26	37.90	37.88	37.87	37.84
TVOPA	58.05	57.87	57.65	57.03	56.78	56.56	57.38	56.85	56.83	56.80	56.77
CTI	2.21	2.51	2.88	3.92	3.90	3.88	3.56	3.90	3.90	3.90	3.90
HT	0.46	0.46	0.46	1.00	0.91	1.28	0.23	1.29	1.29	1.29	1.29
DBTDA	0.58	0.58	0.58	0.57	0.57	0.57	0.57	0.06	0.10	0.15	0.20
Triol/PBEP(OH)	0.42	0.42	0.42	0.42	0.80	1.14	0.21	1.14	1.14	1.14	1.14
NCO/OH	0.83	0.94	1.09	1.49	1.21	1.00	1.20	1.00	1.00	1.00	1.00
Cure time, hr	16.0	16.0	16.0	1.0	1.0	72.0	72.0	16.0	16.0	1.0	1.0

Cure temperature was 120 °F for all samples. All samples were well cured in the designated times except 232-55-1 which failed to cure.

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cure catalyst was relatively high, the gumstocks still had adequate pot life for scaleup to the micromixer, which was probably due to the lower NCO/OH ratio of 0.94.

(C) Table V lists CTI-HT propellant formulations and mechanical properties. UTX 11700-1 with high curative ratios and a high catalyst level of about 1.9 wt-% of the binder cured too rapidly to be cast. A second formulation, UTX 11701-1, with the same curative ratios but a lower catalyst level of 0.30 wt-% cured firmly in 15 min. The next three formulations using a triol/PBEP(OH) ratio of 0.38 and an NCO/OH ratio of 0.85 cured with a low catalyst level of 0.048 wt-% of the binder. UTX 11704-1 with 0.024 wt-% only gelled after 72 hr at 100°F.

(C) Physical properties of UTX 11701-1 and U7X 11702-1, listed in table V, were very similar with tensile values of approximately 85 psi and elongations of 13% to 15%. The tensile values were an improvement over the values of 20 to 40 psi usually obtained with an all-CTI system.

(C) Several formulations were prepared to evaluate the level of DBTDA catalyst necessary for cure at different cure ratios. UTX 11706-1 with a catalyst level of 0.008 wt-% was well cured in 120 hr at 100°F. This formulation had a triol (OH)/PBEP(OH) ratio of 0.40 and an NCO/OH ratio of 0.92. Physical properties of this system were a tensile of 57 psi and an elongation of 18%. In UTX 11709-1 and UTX 11709-2, the triol (OH)/PBEP(OH) was 0.2 and NCO/OH was 1.05. These two mixes gave propellants with similar tensile values of 77 and 74 psi and elongations of 18% and 17%.

(3) CTI-Diol

(C) Three diols were tested with CTI during gumstock studies in the PBEP cure system. The diols were DPG, 1, 4-butanediol, and 1, 4-dihydroxy cyclohexane. DPG and 1, 4-butanediol gave well-cured gumstocks, but 1, 4-dihydroxy cyclohexane was immiscible in the system, and the samples failed to cure. DPG has secondary hydroxyl groups and would have a slower reaction rate than 1, 4-butanediol. The DPG binders were less opaque than the butanediol binders, indicating the PBEP reaction was more competitive in this system.

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TABLE V
(U) CTI-GLYCOL PROPELLANT FORMULATIONS

Formulation No.	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX
	11700-1	11701-1	11702-1	11703-1	11704-1	11706-1	11709-1	11709-2	11710-1	DBTDA	DBTDA
PREP	13.60	13.60	13.60	13.61	13.61	13.60	13.63	13.63	13.54	13.63	13.63
TVOPA	20.40	20.50	20.40	20.41	20.42	20.39	20.45	20.45	20.31	20.45	20.45
CTI	1.26	1.26	0.78	0.78	0.78	0.85	0.66	0.66	1.03	0.66	0.66
Glycol	0.38	0.38	0.16	0.16	0.16	0.17	0.084	0.084	0.32	0.084	0.084
Type of glycol	HT	HT	HT	HT	HT	HT	HT	HT	DPG	HT	HT
Catalyst	0.64	0.18	0.035	0.016	0.008	0.008	0.024	0.024	0.016	0.024	0.024
Type of catalyst	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA
AP	50.00	50.40	50.01	50.02	50.02	50.00	50.12	50.12	49.97	50.12	50.12
Aluminum	15.00	15.10	15.00	15.01	15.01	15.00	15.04	15.04	14.93	15.04	15.04
OH/PBEP(OH)	0.90	0.90	0.38	0.38	0.38	0.40	0.20	0.20	0.50	0.20	0.20
NCO/OH	1.04	1.04	0.85	0.85	0.85	0.92	1.05	1.05	1.05	1.05	1.05
Cure time at 100°F, hr	0.08	0.12	0.25	16	72	120	20	20	48	20	20
Remarks	Cured	Cured	Cured	Cured	Cured	Cured	Cured	Cured	Cured	Cured	Cured
True physical property data											
Tensile, psi	---	85	85	---	---	57	77	74	74	74	74
Elongation, %	---	13	15	---	---	18	18	17	20	17	20

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TABLE V

(U) CTI-GLYCOL PROPELLANT FORMULATIONS (Continued)

Formulation No.	11726-1*		11727-1*		11728-1*		11729-1*		11730-1*		11732-1*		11733-1*		11735-1*		11730-1		
	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	
PREP	13.42	13.47	13.47	13.53	13.53	13.53	13.56	13.48	13.53	13.53	13.53	13.53	13.48	13.53	13.53	13.53	13.53	13.53	13.53
TVOPA	20.11	20.22	20.22	20.30	20.30	20.30	20.33	20.22	20.31	20.31	20.33	20.33	20.22	20.31	20.31	20.31	20.31	20.31	20.31
CTI	1.030	0.693	0.693	0.673	0.673	0.693	0.693	0.698	0.674	0.674	0.693	0.693	0.698	0.674	0.674	0.674	0.674	0.674	0.674
Glycol	0.317	0.317	0.317	0.317	0.317	0.317	0.317	0.317	0.317	0.317	0.317	0.317	0.149	0.317	0.317	0.317	0.317	0.317	0.317
Type of glycol	DPG	DPG	DPG	DPG	DPG	DPG	DPG	DPG	DPG	DPG	DPG	DPG	DPG	DPG	DPG	DPG	DPG	DPG	DPG
Catalyst	0.032	0.26	0.26	0.12	0.12	0.26	0.04	0.024	0.002	0.002	0.04	0.04	0.024	0.006	0.006	0.006	0.010	0.010	0.010
Type of catalyst	DBTDA	DBTDA	DBTDA	Me ₂ SnCl ₂	Me ₂ SnCl ₂	Bu ₂ SnCl ₂	Me ₂ SnCl ₂	Me ₂ SnCl ₂	BuSnCl ₃	BuSnCl ₃	Me ₂ SnCl ₂	Me ₂ SnCl ₂	BuSnCl ₃	BuSnCl ₃	BuSnCl ₃	BuSnCl ₃	BuSnCl ₃	BuSnCl ₃	BuSnCl ₃
AP	49.30	49.30	49.30	49.30	49.30	49.30	49.30	49.30	49.30	49.30	49.30	49.30	49.70	49.40	49.40	49.40	49.40	49.40	49.40
Aluminum	14.80	14.80	14.80	14.80	14.80	14.80	14.80	14.80	14.80	14.80	14.80	14.80	14.90	14.80	14.80	14.80	14.80	14.80	14.80
OH/PBEPI(OH)	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.24	0.50	0.50	0.50	0.50	0.50	0.50
NCO/OH	1.06	0.71	0.71	0.70	0.70	0.71	0.76	0.87	0.71	0.71	0.76	0.76	0.87	0.69	0.69	0.69	0.69	0.69	0.69
Cure time at 100°F, hr	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72
Remarks	Cured	Uncured	Uncured	Cured	Cured	Cured	Cured	Cured	Uncured	Uncured	Cured	Cured	Cured	Uncured	Uncured	Uncured	Uncured	Uncured	Uncured
True Physical Property Data																			
Tensile, psi	92	---	---	49	49	59	68	55	---	---	68	55	---	---	---	---	---	---	---
Elongation, %	19	---	---	32	32	29	27	13	---	---	27	13	---	---	---	---	---	---	---

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TABLE V

(U) CTI-GLYCOL PROPELLANT FORMULATIONS (Continued)

Formulation No.	UTX 11737-1*	UTX 11769-1*	UTX 11770-1*	UTX 11771-1*
PBEP	13.52	13.52	13.53	13.53
TVOFA	20.31	20.28	20.29	20.29
CTI	0.674	0.73	0.73	0.73
Glycol	0.317	0.30	0.30	0.30
Type of glycol	DPG	DPG	DPG	DPG
Catalyst	0.040	0.07	0.04	0.02
Type of catalyst	BuSnCl ₃	Me ₂ SnCl ₂	Me ₂ SnCl ₂	Me ₂ SnCl ₂
AP	49.40	49.31	49.32	49.34
A1	14.80	14.79	14.79	14.80
OH/PBEP(OH)	0.50	0.5	0.5	0.5
NCO/OH	0.69	0.8	0.8	0.8
Cure time at 100°F, hr	1.0	1	1	1
Remarks	Cured	Cured	Cured	Cured
True physical property data				
Tensile, psi	---	---	81	79
Elongation, %	---	---	16	19

*These formulations also contained 0.99 wt-% 13X molecular sieves.

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(C) The first micromix using DPG was UTX 11710-1 (see table V). This formulation cured in 48 hr at a catalyst level of 0.016 wt-%. The physical properties of this formulation were a tensile of 74 psi and an elongation of 20%.

(C) UTX 11711-1 with 0.032 wt-% cure catalyst had physical properties of 92 psi tensile and 19% elongation.

c. Mixed Isocyanate Studies

(C) One possible method of obtaining better physical properties than those obtained from an all-CTI cure system is the use of mixed poly- and diisocyanates as curatives. Three triisocyanates were tested with several diisocyanates. However, only CTI was given a systematic evaluation. DBTDA was used initially as a cure catalyst until HF resistant catalysts such as BuSnCl_3 and Me_2SnCl_2 became available.

(C) Formulation, UTX 9834-1, (table VI) with a diisocyanate/triisocyanate ratio of 1.0, failed to cure. The next three formulations with a low diisocyanate/triisocyanate ratio cured but had poor physical properties of 29 to 34 psi tensile and 17% to 29% elongation, as listed in table XXVI. The majority of the curatives were CTI formulations, and the physical properties were very similar to those obtained from an all-CTI system. Formulation UTX 9881-1, which contained a ratio of H_{12}MDI to CTI of about 1.8, showed some improvement with a tensile of 31 psi and an elongation of 54%. All of the next 1,4 formulations failed to cure completely and were discarded.

(C) UTX 11731-1 contained a mixture of TDI to CTI at a ratio of 1.8 and only gave a soft cure. FeAA was used as a catalyst instead of DBTDA in an attempt to obtain a better cure. The cure was somewhat better but was still inadequate for further testing of the propellant. The use of mixed isocyanates apparently requires use of a more active catalyst than DBTDA. The formulations using a tin-chloride catalyst gave better cures but no improvement in mechanical properties was obtained. UTX 11734-1, which contained IPDI and CTI at a ratio of 0.4 and with BuSnCl_3 as the catalyst was cured after 72 hr. However, the physical properties of 30 psi tensile and 21% elongation, listed in table VII, are still inadequate. UTX 11748-1, UTX 11756-1, UTX 11757-1, and UTX 11758-1 varied only in the diisocyanates used in the cure system. Of the four diisocyanates tested, HMDI and DEBI gave better cures than either IPDI or TMDI.

TABLE VI

(U) MIXED ISOCYANATE PROPELLANT FORMULATIONS

Formulation No.	UTX 9834-1	UTX 9875-2	UTX 9876-1	UTX 9877-1	UTX 9881-1	UTX 9883-1	UTX 9884-1	UTX 9885-1	UTX 9892-1
PBEP	17.68	13.65	13.64	13.62	13.55	13.55	13.56	13.48	13.62
TVOPA	17.68	20.47	20.46	20.43	20.33	20.33	20.33	20.22	20.43
Triisocyanate	0.33	0.33	0.33	0.33	0.23	0.23	0.23	0.40	0.23
Type of triisocyanate	CTI	CTI	CTI	CTI	CTI	CTI	CTI	CTI	CTI
Diisocyanate	1.06	0.20	0.213	0.27	0.54	0.54	0.53	0.54	0.06*
Type of diisocyanate	DMMDI	TMDI	IPDI	H ₁₂ MDI	H ₁₂ MDI	H ₁₂ MDI	DMMDI	H ₁₂ MDI	H ₁₂ MDI
Catalyst	0.64	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.052
Type of catalyst	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA
AP	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00
Aluminum	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00
Di- /triisocyanate	1.0	0.37	0.37	0.37	1.12	1.12	1.12	0.67	1.43
NCO/OH	0.80	0.75	0.75	0.75	0.75	0.75	0.75	1.00	0.55
Cure time at 100° F, days	6	3	4	3	7	5	5	5	5
Remarks	Uncured	Cured	Cured	Cured	Cured	Uncured	Soft cure	Soft cure	Uncured

TABLE VI

(U) MIXED ISOCYANATE PROPELLANT FORMULATIONS (Continued)

Formulation No.	UTX 9893-1	UTX 9894-1	UTX 11705-1	UTX 11707-1	UTX 11714-1	UTX 11718-1	UTX 11719-1	UTX 11720-1
PBEP	13.54	13.52	13.40	13.44	13.58	13.51	13.51	13.51
TVOPA	20.31	20.27	20.10	20.16	20.48	20.36	20.36	20.37
Triisocyanate	0.164	0.097	0.096	0.195	0.328	0.172	0.172	0.326
Type of triisocyanate	CTI	CTI	CTI	CTI	CTI	CTI	CTI	CTI
Diisocyanate	0.81	0.94	0.805	0.398	0.341	0.397	0.397	0.210
Type of diisocyanate	H ₁₂ MDI	H ₁₂ MDI	H ₁₂ MDI	H ₁₂ MDI	H ₁₂ MDI	TDI	IPDI	H ₁₂ MDI
Catalyst	0.175	0.175	0.99	1.00	0.35	0.99	0.99	0.99
Type of catalyst	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA
AP	50.00	50.00	49.70	49.85	49.90	49.67	49.67	49.68
Aluminum	15.00	15.00	14.91	14.97	14.98	14.90	14.90	14.90
Di-/triisocyanate	2.40	4.67	0.46	1.00	0.50	2.00	1.13	0.42
NCO/OH	0.85	0.85	0.85	1.00	0.74	0.75	0.51	0.71
Cure time at 100°F, days	5	5	3	3	3	3	3	3
Remarks	Soft Cure	Uncured	Uncured	Uncured	Uncured	Uncured	Uncured	Uncured

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TABLE VI

(U) MIXED ISOCYANATE PROPELLANT FORMULATIONS (Continued)

Formulation No.	UTX 11724-1	UTX 11731-1	UTX 11734-1	UTX 11738-1	UTX 11739-1	UTX 11742-1	UTX 11746-1	UTX 11747-1	UTX 11748-1
PREP	13.58	13.38	13.76	13.72	13.72	13.51	13.69	13.69	13.69
1VOPA	20.48	20.16	20.75	20.58	20.57	20.36	20.18	20.54	20.54
Triisocyanate	0.33	0.169	0.333	0.13	0.13	0.17	0.26	0.26	0.26
Type of triisocyanate	CTI	CTI	CTI	CTI	CTI	CTI	CTI	CTI	CTI
Diisocyanate	0.34	0.393	0.225	0.64	0.64	0.40	0.33	0.33	0.33
Type of diisocyanate	H ₁₂ MDI	TDI	IPDI	IPDI	TMDI	TDI	HMDI	HMDI	HMDI
Catalyst	0.35	0.98	0.01	0.01	0.02	0.02	0.02	0.02	0.03
Type of catalyst	DBTDA	FeAA	BuSnCl ₃	BuSnCl ₃	BuSnCl ₃	BuSnCl ₃	BuSnCl ₃	BuSnCl ₃	Me ₂ SnCl ₂
AP	49.93	49.20	49.20	49.18	49.18	49.65	49.34	49.34	49.34
Aluminum	14.98	14.80	14.80	14.75	14.75	14.90	14.81	14.81	14.81
-Di- /triisocyanate	0.5	1.8	0.40	3.0	3.0	1.8	1.0	1.0	1.0
NCO/OH	0.85	0.73	0.71	0.80	0.80	0.80	0.80	0.80	0.80
Cure time at 100 F, days	3	3	3	3	3	0.05	0.05	0.05	0.05
Remarks	Uncured	Soft Cure	Cured	Uncured	Uncured	Cured	Cured	Cured	Cured

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TABLE VI

(U) MIXED ISOCYANATE PROPELLANT FORMULATIONS (Continued)

Formulation No.	UTX 11749-1	UTX 11750-1	UTX 11751-1	UTX 11752-1	UTX 11753-1	UTX 11754-1	UTX 11755-1	UTX 11756-1	UTX 11757-1
PREP	13.67	13.66	13.64	13.46	13.61	13.89	13.61	13.65	13.67
IVOPA	20.51	20.49	20.47	20.28	20.41	20.72	20.54	20.48	20.49
Triisocyanate	0.20	0.26	0.20	0.17	0.54	0.27	0.26	0.26	0.26
Type of triisocyanate	CTI	CTI	CTI	CTI	CTI	CTI	CTI	CTI	CTI
Diisocyanate	0.44	0.33	0.44	0.40	0.26	0.33	0.33	0.44	0.40
Type of diisocyanate	HMDI	HMDI	HMDI	TDI	HMDI	HMDI	HMDI	IPDI	TMDI
Catalyst	0.03	0.24	0.24	0.03	0.03	0.04	0.03	0.03	0.03
Type of catalyst	Me ₂ SnCl ₂	Bu ₂ SnCl ₂	Bu ₂ SnCl ₂	Me ₂ SnCl ₂	Me ₂ SnCl ₂	Me ₂ SnCl ₂	DBTDA	Me ₂ SnCl ₂	Me ₂ SnCl ₂
AP	49.34	49.32	49.24	49.47	49.34	49.79	49.34	49.34	49.34
Aluminum	14.81	14.78	14.78	14.84	14.81	14.90	14.81	14.81	14.81
Di-/triisocyanate	2.0	1.0	2.0	1.0	1.0	1.0	1.0	1.0	1.0
NCO/OH	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Cure time at 100 F., days	3	3	3	3	3	3	3	3	3
Remarks	Cured	Soft Cure	Uncured	Cured	Cured	Uncured	Uncured	Soft Cure	Soft Cure

TABLE VI

(U) MIXED ISOCYANATE PROPELLANT FORMULATIONS (Continued)

Formulation No.	UTX 11758-1#	UTX 11759-1#	UTX 11760-1#	UTX 11761-1#	UTX 11762-1#	UTX 11763-1#	UTX 11764-1#	UTX 11765-1#
PREP	13.66	13.55	13.55	13.63	13.72	13.73	13.15	13.06
TVOPA	20.49	20.33	20.32	20.44	20.59	20.59	19.72	19.58
Triisocyanate	0.26	0.43	0.41	0.44	0.24	0.24	0.24	0.23
Type of triisocyanate	CTI	TTI	TTI	Mondur MR	CTI	CTI	CTI	CTI
Diisocyanate	0.41	0.50	0.53	0.30	0.31	0.31	0.30	0.29
Type of diisocyanate	DEBI	DMM	DMM	TDI	HMDI	HMDI	HMDI	HMDI
Catalyst	0.03	0.07	0.07	0.07	0.04	0.02	0.07	0.05
Type of catalyst	Me_2SnCl_2	Me_2SnCl_2	Me_2SnCl_2	Me_2SnCl_2	Me_2SnCl_2	Me_2SnCl_2	Me_2SnCl_2	Me_2SnCl_2
AP	49.34	49.32	49.32	49.32	49.35	49.36	50.43	50.63
Aluminum	14.81	14.81	14.81	14.81	14.81	14.81	15.14	15.19
Di-/triisocyanate	1.0	1.0	1.1	1.0	1.0	1.0	1.0	1.0
NCO/OH	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Cure time at 100° F. days	3	3	3	3	3	3	3	3
Remarks	Cured	Cured	Cured	Cured	Uncured	Uncured	Soft cure	Soft cure

*These formulations also contained 0.99 wt-% 13X molecular sieves.

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(U)

TABLE VII

(U) PHYSICAL PROPERTY DATA FOR
MIXED ISOCYANATE FORMULATIONS

<u>Formulation No.</u>	<u>True Physical Properties</u>	
	<u>Tensile, psi</u>	<u>Elongation, %</u>
UTX 9875-2	34	29
UTX 9876-1	29	24
UTX 9877-1	32	17
UTX 9881-1	31	54
UTX 11734-1	30	21
UTX 11759-1	52	18
UTX 11760-1	57	20
UTX 11761-1	38	29

d. Candidate Cure Catalyst Evaluation

(U) The commonly used catalyst, DBTDA, readily reacts with any HF generated by the PBEP-TVOPA binder or is deactivated by some ingredient in the binder. The use of excess DBTDA leads to a short pot life on scaleup formulations. Several catalyst candidates were tested at UTC for HF resistance and improved compatibility. The initial test was visual observation for reaction between anhydrous HF and the catalyst. If no visible reaction occurred, the compound was tested further for compatibility with the binder by DTA and for cure in gumstocks and micromix formulations. Esso has found several tin catalysts that were resistant to HF attack and cured PBEP gumstocks. These catalysts were further evaluated in propellant studies at UTC.

(1) Reaction with Anhydrous HF

(U) Suitable reaction solvents could be found for only four of the candidate catalysts. Of these four, aluminum acetylacetonate gave a definite precipitate, while solutions of chromium neodecanoate, tetrabutyl tin, and chromic octoate were only slightly turbid after treatment with HF. Because it was difficult to find suitable solvents, the HF screening procedure was not used for all compounds studied.

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(2) Differential Thermal Analysis Studies

(C) Of the 14 compounds originally tested for compatibility (see table VIII), five were thermally unstable with PBEP-TVOPA. The onset to the exotherm as well as the first exotherm peak listed in table IX were lowest for silver oxide with an onset of 73°C and a peak temperature of 95°C. These compare to values of 145° and 205°C for onset and peak temperatures for the PBEP-TVOPA. As expected, all additives lowered either the onset temperature, peak temperature, or both temperatures, although none of the more compatible five candidates had an onset temperature lower than 129°C or a peak temperature lower than 174°C.

(C) Neat BuSnCl_3 by DTA gave an endotherm peaking at 249°C. This catalyst when tested with PBEP lowered the onset and peak exotherm to 112° and 187°C from 144° and 205°C for neat PBEP. BuSnCl_3 lowered the onset and peak values of TVOPA from 202° and 256°C to 164° and 213°C, respectively.

(C) Although this catalyst appears to have some high-temperature incompatibility with PBEP and TVOPA the onset and peak exotherms found by DTA are still far above any processing or storage temperatures anticipated for propellants containing these ingredients.

(C) The compatibilities of the candidate catalysts (Bu_2SnCl_2 , Bu_3SnCl , Me_2SnCl_2 , and Bu_4Sn) with PBEP and TVOPA were also tested by DTA. DBTDA was included in the tests as a control. The catalysts did not exhibit any low-temperature exotherms. The lot of PBEP used in these evaluations had an onset of 144°C and a first peak value of 205°C. The TVOPA used had an onset of 202°C and a first peak value of 256°C. DBTDA was the least compatible of the catalysts tested with onset and peak temperature values of 121° and 170°C with PBEP and 138° and 170°C with TVOPA. The catalyst most compatible with PBEP was Bu_2SnCl_2 with onset and peak values of 135° and 186°C, while the most compatible with TVOPA was Me_2SnCl_2 with values of 192° and 250°C. None of the catalysts tested had onset values below 120°C with either PBEP or TVOPA (see table X).

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TABLE VIII

(U) CATALYST COMPATIBILITY BY DTA

<u>Sample Composition</u>	<u>Exotherms Onset/Peak °C</u>	<u>Endotherms Onset/Peak °C</u>
PBEP	144/205	---
TVOPA	202/256	---
DBTDA (liquid)	---	251/289
DBTDA + PBEP	121/170	---
DBTDA + TVOPA	138/170, 173/178	---
Bu ₂ SnCl ₂ (crystalline)	---	39/45
Bu ₂ SnCl ₂ + PBEP	135/186, 191/194	---
Bu ₂ SnCl ₂ + TVOPA	176/215	---
Bu ₃ SnCl (liquid)	---	None to 270
Bu ₃ SnCl + PBEP	137/181, 183/187	---
Bu ₃ SnCl + TVOPA	156/193	---
Me ₂ SnCl ₂ (solid)	---	103/111, 193/220
Me ₂ SnCl ₂ + PBEP	120/161, 178/208	83/84
Me ₂ SnCl ₂ + TVOPA	192/250	---
Bu ₄ Sn + PBEP	146/163, 167/189	---
Bu ₄ Sn + TVOPA	151/189	---
PBEP/Tin	143/210	---
TVOPA/Tin	128/194, 209/224, 229/234	---
Bu ₂ SnCl ₂ (50% toluene solution)	---	125/134
Bu ₂ SnCl ₂ + PBEP	128/176, 183/189, 195/196	---
Bu ₂ SnCl ₂ + TVOPA	162/213	---

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TABLE IX

(U) DIFFERENTIAL THERMAL ANALYSIS STUDIES
OF CANDIDATE CATALYSTS

<u>Sample*</u>	<u>Onset to First Exotherm °C</u>	<u>First Exotherm °C</u>	<u>Second Exotherm °C</u>
Lead oxide	80	110	200
Silver oxide	73	95	---
Cadmium nitrate	89	131	183
Bismuth nitrate	111	127	176
Hydroxylamine hydrochloride	90	125	138
Aluminum resinate	85	211	---
Aluminum oleate	129	204	---
Chromic octoate	---	55 [†]	---
Tetrabutyl tin	130	174	---
Tetraphenyl tin	134	185	---
Nickel naphthenate	119	139	184
Ferrous naphthenate	131	164	---
Stannous naphthenate	114	123	161
Titanium neo-decanoate	111	127	176

*All samples were 50 wt-% catalyst in PBEP-TVOPA binder. This binder without additives had an onset of 145°C and a first exotherm of 205°C.

†This mixture had an endotherm at 51°C.

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(C)

TABLE X

(U) BuSnCl_3 DTA COMPATIBILITY DATA

<u>Sample</u>	<u>Exotherms Onset/Peak °C</u>
PBEP	144/205
TVOPA	202/256
BuSnCl_3	(249-Endotherm)
BuSnCl_3 /PBEP	112/187
BuSnCl_3 /TVOPA	164/213
PBEP/TVOPA	147/221
BuSnCl_3 /PBEP/TVOPA	126/201

(3) Gumstock Cure Tests

(C) Of the catalysts listed in table XI only samples containing nickel naphthenate and titanium neo-decanoate showed any sign of cure when tested in gumstocks. Since HAP propellants tend to cure rapidly, HAP and hydroxylamine hydrochloride were tested as catalysts. Neither gave any sign of cure at the 10 wt-% level.

(C) Of the four HF-resistant catalysts recommended by Esso for curing the PBEP-TVOPA binder, BuSnCl_3 and Me_2SnCl_2 were the most effective, although Bu_2SnCl_2 showed some activity. Using the all-CTI cure system, high catalyst levels of 0.59 and 0.40 wt-% were necessary to obtain adequate cures with Me_2SnCl_2 compared to a level of 0.16 wt-% for DBTDA. BuSnCl_3 was a very active catalyst in the gumstock cure studies, listed in table XII. This catalyst, at levels of 0.08 to 1.6 wt-%, cured the samples in less than 5 min at 75°F. Both catalysts, as well as Bu_2SnCl_2 , were evaluated in a number of propellant formulations.

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TABLE XI

(U) CATALYST CURE STUDIES

<u>Sample*</u>	<u>Cure</u>
Tetrabutyl tin	No cure
Tri-n-butyl tin chloride	No cure
Titanium neo-decanoate	Cured
Bismuth nitrate	No cure
Lead oxide	No cure
Lead dioxide	No cure
Iron naphthenate	No cure
Tin naphthenate	No cure
Lead naphthenate	No cure
Nickel naphthenate	Cured
Hydroxylamine hydrochloride	No cure
Hydroxylamine perchlorate	No cure
Nickel dimethylglyoxime	No cure

*All samples contained PBEP, TVOPA, and CTI, and all candidate catalysts were added at about 10 wt-% level.

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TABLE XII

(U) CATALYST CURE STUDIES*

<u>Catalyst</u>	<u>Catalyst Concentration wt-% of Binder</u>	<u>Degree of Cure</u>
DBTDA	0.16	Firm cure
Bu ₂ SnCl ₂ (toluene solution)	0.04	None
Bu ₂ SnCl ₂ (crystalline)	0.22	Partial cure
Bu ₃ SnCl	0.15	None
Bu ₃ SnCl	0.30	None
Me ₂ SnCl ₂	0.15	Partial cure
Me ₂ SnCl ₂	0.59	Firm cure
BuSnCl ₃	0.08	Firm cure
BuSnCl ₃	0.40	Firm cure
BuSnCl ₃	0.75	Firm cure
BuSnCl ₃	1.6	Firm cure

*The cure was at ambient temperature.

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(4) Micromix Formulations

(C) The cure catalyst, BuSnCl_3 , was evaluated in micromix propellant formulations. A curative system using CTI and DPG was utilized, varying only in the percentage of BuSnCl_3 catalyst. The initial gumstock studies had indicated that an extremely low level of BuSnCl_3 was sufficient to obtain well-cured samples. Therefore, the initial micromix formulation, UTX 11740-1 shown in table XIII contained only 0.008 wt-% BuSnCl_3 . This mix failed to cure. Subsequent mixes at 0.012 and 0.016 wt-% catalyst cured too rapidly to be cast. A repeat of UTX 11740-1 at the 0.008 wt-% level also cured too rapidly. Several mixed isocyanate systems (see table VI) were prepared using BuSnCl_3 . One system cured with 0.01 wt-% BuSnCl_3 , while a second system containing 0.02 wt-% failed to cure.

(U)

TABLE XIII

(U) CATALYST CONCENTRATION STUDY

Formulation No.	<u>UTX 11740-1</u>	<u>UTX 11741-1</u>	<u>UTX 11743-1</u>	<u>UTX 11740-2</u>
BuSnCl ₃ , wt-% of binder	0.008	0.016	0.012	0.008
Cure Time at 100°F, min	No cure	4	3	6

(C) Because BuSnCl_3 appeared to be too active above a given wt-% level and appeared erratic below that level, testing of this catalyst was discontinued.

(C) UTX 11733-1 (listed in table V) containing 0.024 wt-% DBTDA was prepared as a control. This formulation cured to a shore A hardness value of 55 with stress-strain properties of 55 psi tensile and 13% elongation. Two formulations containing Me_2SnCl_2 at 0.12 and 0.04 wt-% levels cured and gave propellant with better physical properties than the control. UTX 11729-1 had a tensile of 49 psi and an elongation of 32% while UTX 11732-1 with the lower wt-% of Me_2SnCl_2 had stress-strain values of 68 psi and 27%. UTX 11728-1 containing n- Bu_2SnCl_2 at a 0.26 wt-% level cured to a Shore A hardness value of 55 and physical properties of 59 psi tensile and 29% elongation.

(C) Bu_2SnCl_2 was tested in formulations UTX-11750-1 and UTX 11751-1 at 0.24% catalyst level and two triisocyanate/diisocyanate levels. Neither formulation cured adequately.

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These formulations were similar to UTX 11748-1 and UTX 11749-1 with 0.03% Me_2SnCl_2 as cure catalyst instead of Bu_2SnCl_2 . Of the three catalysts tested in micromix formulations, Me_2SnCl_2 appeared to give better cures than Bu_2SnCl_2 and also appeared to be more predictable than BuSnCl_3 .

(C) UTX 11754-1 using Me_2SnCl_2 but with PBEP and TVOPA that had not been treated with 13X molecular sieves failed to cure. UTX 11758-1, an identical formulation but with treated binder materials, cured very well. Apparently, even with Me_2SnCl_2 it is still preferable to treat PBEP and TVOPA with molecular sieves.

(C) UTX 11752-1 using CTI and TDI as curatives was well cured after 72 hr at 100°F. This formulation had been tested previously using DBTDA and FeAA as the catalyst. The mix containing DBTDA failed to cure completely while the FeAA formulation gave a soft cure. Me_2SnCl_2 is a better catalyst for this system than FeAA or DBTDA, even at a much lower level.

(C) DBTDA at a 0.03 wt-% level was retested in formulation UTX 11755-1 that contained a diisocyanate/triisocyanate ratio of 1.0 HMDI to CTI. This mix failed to cure. Another formulation, UTX 11747-1, with BuSnCl_3 as the catalyst cured in 1 hr.

(C) The last four formulations listed in table VI were prepared to evaluate the effect of varying the amount of the cure catalyst, Me_2SnCl_2 , in a mixed isocyanate system. This formulation with 0.04 wt-% catalyst and with PBEP lot 10001-186 previously had given propellant with physical properties of 68 psi tensile and 27% elongation. However, with PBEP lot 10316-172 this formulation gave incomplete cures even at a 0.07 wt-% catalyst level. The degree of cure was in the correct order with the formulations containing the higher catalyst levels curing somewhat firmer. No explanation is apparent other than the fact that different lots of PBEP were used.

(C) Since the mixed isocyanate system did not cure adequately enough to be tested for physical properties, a 50 g micromix, UTX 11766-1, was prepared with CTI as the only curative and with a 0.04 wt-% Me_2SnCl_2 . This formulation had a pot life of at least 4 hr and was well cured in 72 hr. A scaleup mix, UTX 11766-2, to the 200 g batch size duplicated the times of cure and pot life of the micromix formulation.

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(C) The last three formulations listed in table VI used CTI and DPG as curatives and had wt-% levels of Me_2SnCl_2 of 0.02, 0.04, and 0.07. All three formulations had less than 1-hr pot life and were well cured in 16 hr at 100°F. The three formulations had similar physical properties with tensile values between 66 and 81 psi and elongations between 14% and 19%. As noted previously, with DBTDA and FeAA, Me_2SnCl_2 appears to be a more efficient cure catalyst with an all-CTI or CTI-DPG cure system than with the mixed isocyanate system.

(C) Formulations UTX 11759-1 and UTX 11760-1 were prepared with a mixture of DMMDI and TTI at respective diisocyanate to triisocyanate ratios of 1.0 and 1.1. The true physical properties of the two formulations were quite similar. UTX 11759-1 had a tensile value of 52 psi and an elongation of 18%, while UTX 11760-1 had values of 57 psi and 20%. These are somewhat better than values for an all-CTI formulation, UTX 11766-1, of 40 psi and 14%.

(C) Formulation UTX 11761-1 in table VI was prepared using Mondur MR, a polymethylene polyphenyl, isocyanate, and TDI. The physical properties were somewhat poorer than those obtained with the TTI-DMM system. The tensile value was 38 psi and the elongation was 29%.

(C) The last formulations were prepared to test Me_2SnCl_2 as a catalyst and will be discussed in the next section.

5. FRACTIONATION OF PBEP

(U) The major areas of needed improvement in the PBEP prepolymer are: (1) improved thermal stability, and (2) more reproducible cure characteristics. While the use of stabilizers such as TCP has extended the thermal stability of some PBEP propellants, greater stability is needed to meet many service requirements. Cure reproducibility and variations in pot life of compositions have presented problems in scaleup which do not appear to stem from the problem of isocyanate-triol adduct formation but from some component of the PBEP-TVOPA binder. Formulation experience had shown that there was some variation in functionality and rate of cure from lot to lot of the PBEP received previously.

(U) In an attempt to correlate thermal stability and functionality with molecular weight, a representative lot of PBEP was separated into six fractions by solvent-nonsolvent precipitation. The functionality of the six fractions was characterized by molecular weight and gel equivalence determinations. Thermal stability of the fractions were studied by DSC and TGA.

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a. Fractionation Method

(U) PBEP lot 9557-14 as received in methylene chloride was further diluted with methylene chloride to a concentration of 4.3 wt-% PBEP. The solution was placed in a three-necked reaction flask equipped with a high-speed, air-driven stirrer, and the flask flushed continuously with nitrogen. The rapidly stirred solution was titrated with ligroin from a separatory funnel. Each fraction was isolated from the supernatant liquid by decantation after a 20-hr settling period. The last fraction was obtained by evaporation of the ligroin-methylene chloride solution by nitrogen sparging.

(U) Essentially no precipitation occurred until the ligroin was increased to the 10% level. Approximately 90% of the polymer was precipitated by the time the ligroin level had reached 65% of the total solution. A distinct color variation was observed from a pale amber for the last (lowest molecular weight) to a very dark brown for the first (highest molecular weight) fraction.

b. Molecular Weight Distribution

(U) The number average molecular weight for each fraction was determined by a Mechrolab Osmometer, using ethylene chloride as a solvent. The methylene chloride-ligroin solution was concentrated by nitrogen sparging after which the fraction was vacuum stripped at 60°C. The neat fraction was redissolved three times in ethylene chloride and stripped. The fractions were then examined by GLC and found to be free of residual methylene chloride.

(C) Solutions of the fractions at a concentration of 20% by weight were prepared with ethylene chloride and molecular weights obtained by osmometer. The distribution of number average molecular weights was between 1,200 and 6,500. The molecular weight determination of the highest molecular weight fraction did not appear to be as reliable as the lower fractions. This distribution is shown in figure 1.

c. Functionality Determinations

(U) Functionalities of the PBEP fractions were measured by the use of a gel technique. Stock solutions of CTI, a triisocyanate, in DBP were freshly prepared and 1 g of the stock solution mixed with varying aliquots of the test fraction. Prior to curing at 60°C, 2% DBTDA was added. The samples were examined for initial signs of gelling, after

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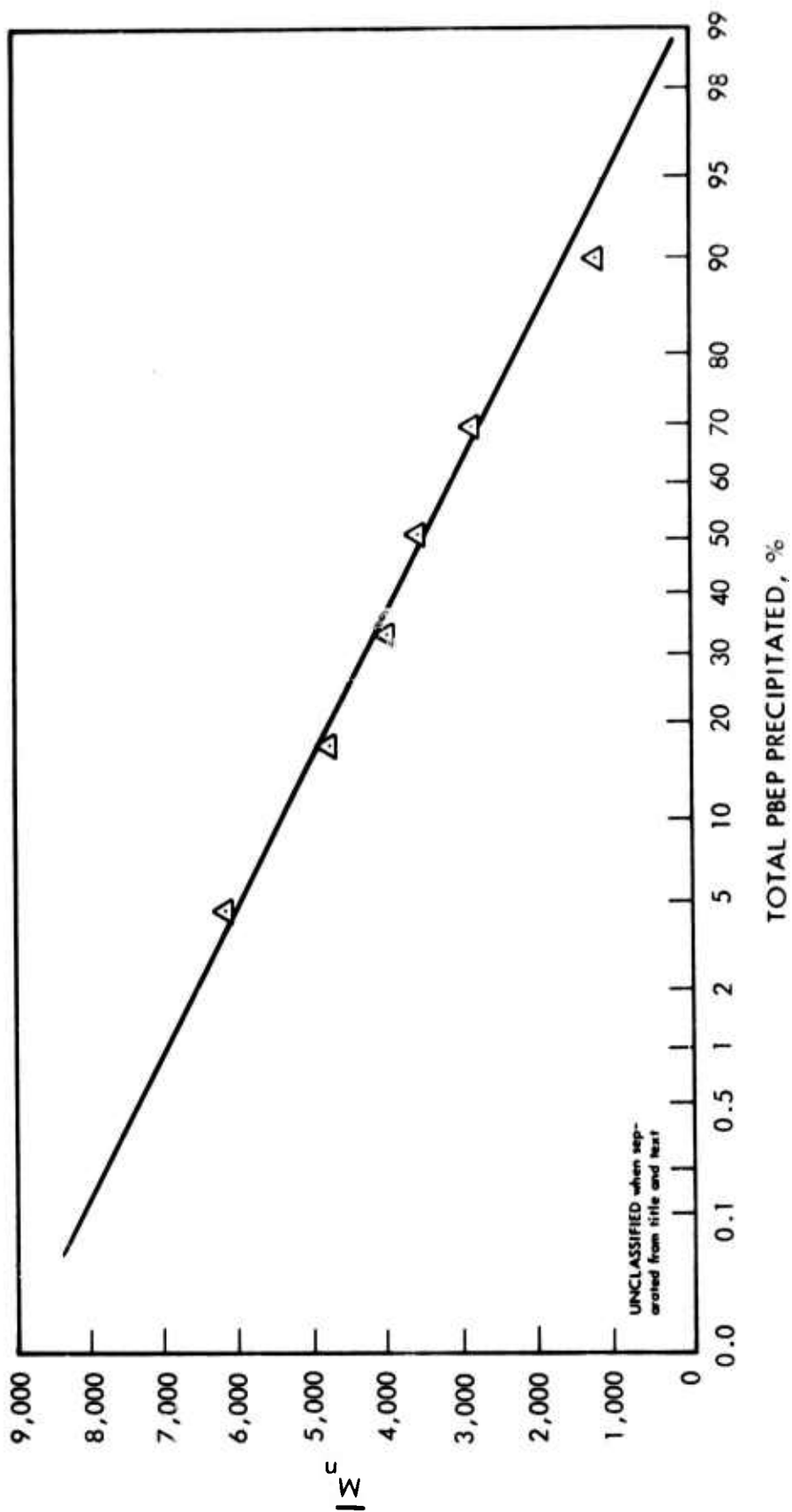


Figure 1. (U) Fractionation and Molecular Weight Distribution of PBEP

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which they were placed horizontally on a flat surface. Relative flow rates were assumed to be directly proportional to viscosity and, therefore, proportional to degree of gel.

(C) Because of the limited amounts of each fraction, only three isocyanate concentrations were used. As a result, peak viscosity was not bracketed in every instance. However, sufficient data were generated to allow the plotting of the approximate equivalence versus molecular weight curve in figure 2. When this technique was used, the equivalent weights increased with molecular weight. The two highest molecular weight fractions exhibited functionalities of 4.4 and 6.1. The increase in functionality above 3.0 with molecular weight is unexpected because the glycerol-initiated polyepichlorohydrin, which is the precursor of PBEP, is ideally trifunctional, regardless of the molecular weight. However, gel time gives an apparent equivalence value that relates adequately to values used in propellant formulations and is an acceptable technique for effective functionality.

(C) All fractions were examined by IR and exhibited a peak at $3,600\text{ cm}^{-1}$. Fraction six (the lowest molecular weight) showed a minor peak at $3,450\text{ cm}^{-1}$ which might stem from the presence of secondary hydroxyl groups. Fraction 1 showed a peak at $3,350\text{ cm}^{-1}$ as well as the expected hydroxyl peak at $3,600\text{ cm}^{-1}$. Adsorption in this area in the presence of difluoramino groups is not well defined but could be caused by an amine group. Comparison of the IR analyses of fractions 1 and 6 in this range is shown in figure 3. When the areas under the adsorption peaks in this area were integrated, fractions 2, 3, 4, and 5 gave essentially identical values while both fractions 1 and 6 gave higher values stemming from the secondary peaks.

d. Thermal Stability Studies

(C) Fractions 1, 3, 6, and the as-received PBEP were evaluated by both DSC and TGA. The TGA results showed a markedly poorer stability for fraction 6, the lowest molecular weight fraction, at 80°C and a 50-micron vacuum. The rate of decomposition of various fractions, followed by TGA, is shown in figure 4. Fraction 6 had a steady decomposition rate of 0.101% wt-loss/hr, compared with weight losses from 0.03% to 0.05% for the other samples. Fraction 6 gave a high initial weight loss of 10% in the first 12-hr period. The thermal stability of the polymer would, therefore, be most affected by fraction 6, the lowest molecular weight material.

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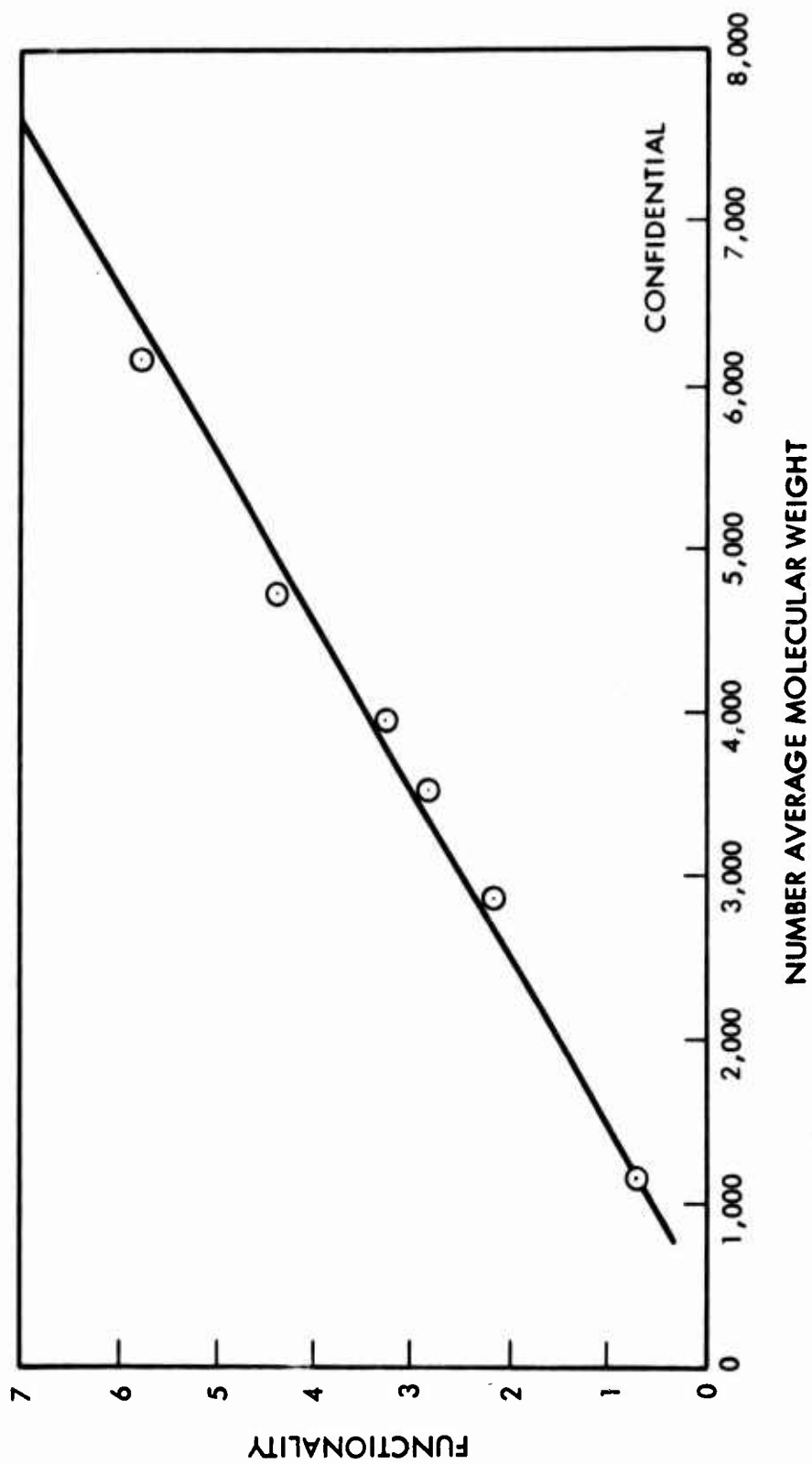


Figure 2. (U) Correlation of Functionality with Molecular Weight

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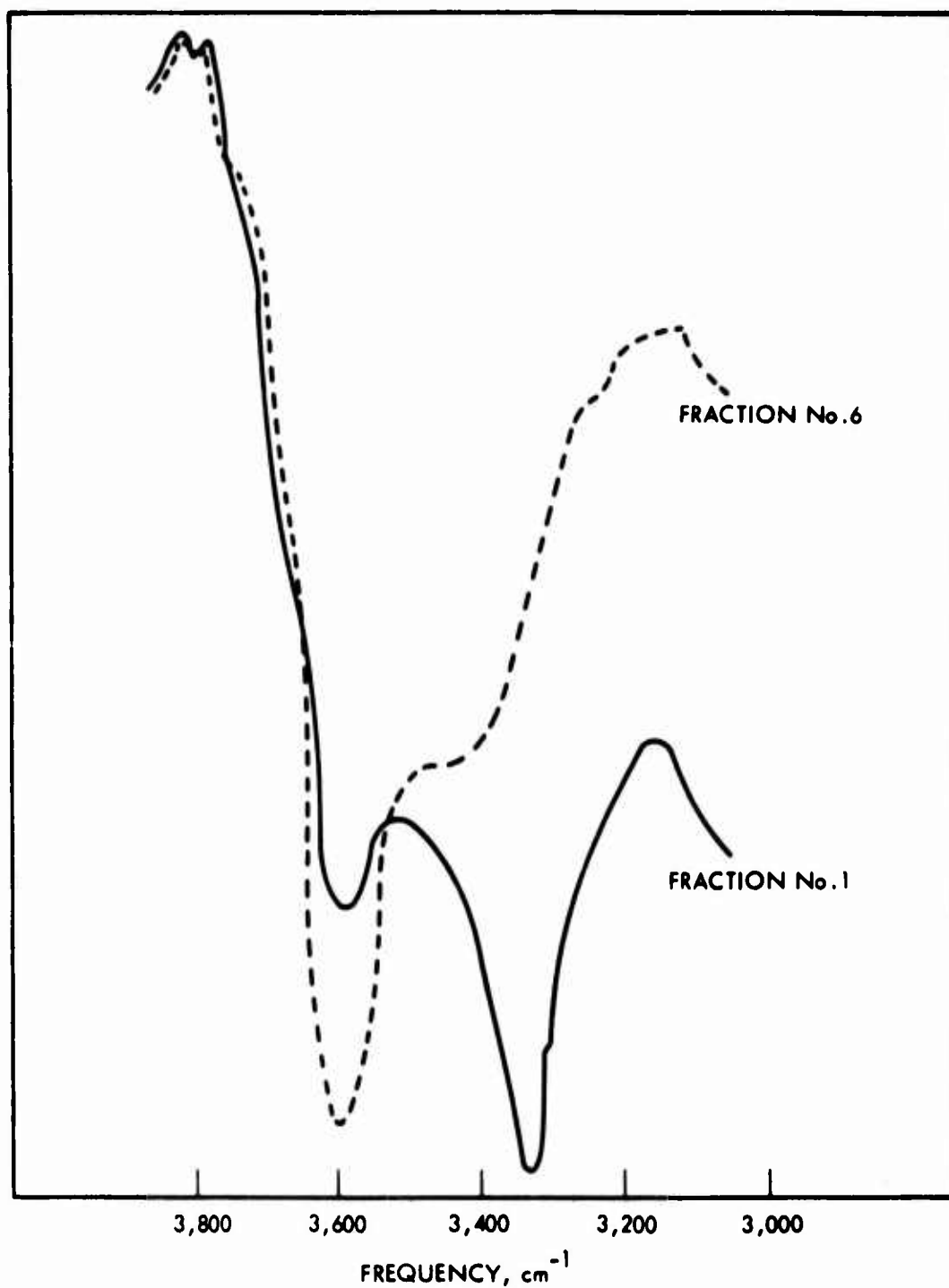


Figure 3. (U) Comparison of IR Analyses of Two Fractions

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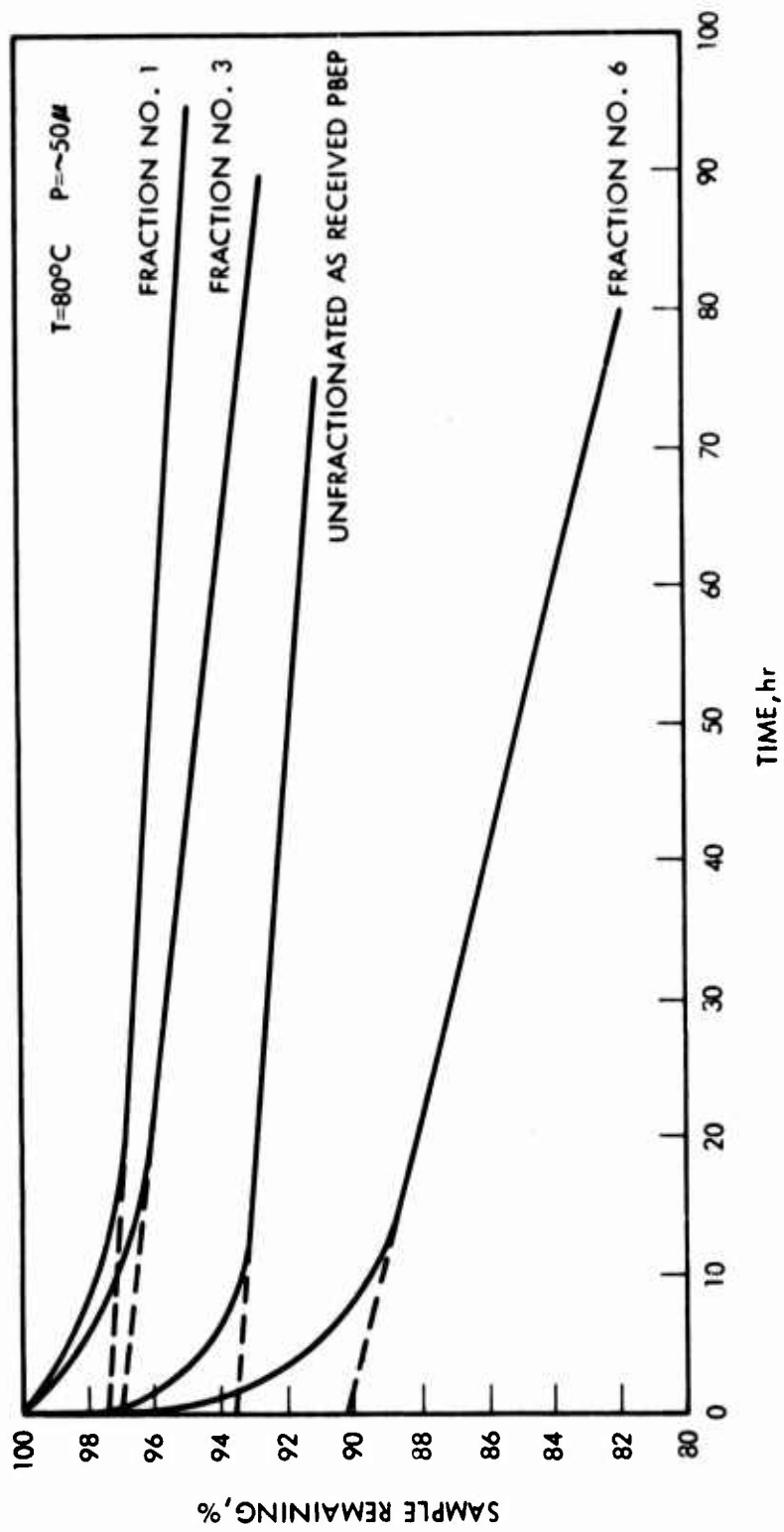


Figure 4. (U) TGA Weight Loss of PBEP and PBEP Functions

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(U) The DSC results listed in table XIV are difficult to analyze.

(U)

TABLE XIV

(U) DIFFERENTIAL SCANNING CALORIMETER STUDIES

<u>Fractions</u>	<u>Run</u>	<u>Endotherms Onset/Peak °C</u>	<u>Exotherms Onset/Peak, °C</u>
1	a	+1/---	179/200, 213
	b	-0.5/---	
	c	-3.0/---	
3	a	---	164/212
6	a	-56, 34.5/-50	---
	b	-58, -34/-47	---
	c	-59, -34/-50	---
	d	+77/91.5	172/192, 240

Fractions 1 and 3 gave normal traces with fraction 1 having a glass transition point of -1°C . Fraction 6 showed endotherms at -34° and -58°C . The -58°C endotherm had the characteristic shape of a melting point while the -34°C endotherm appeared to be the glass transition point. The endotherm at 77°C appeared to be a boiling point. On cooling, the sample failed to show the 77°C endotherm. These phase change endotherms may be associated with residual ethylene chloride which has a melting point of -35.3°C and a boiling point of 83.5°C .

6. RAFFINATE AND EXTRACT STUDIES

(C) Shell Development Company has prepared raffinate PBEP by deposition of PBEP on an acid-washed Chromosorb W column followed by elution with CCl_4 and then CH_2Cl_2 . The raffinate prepared by this method had better cure characteristics and a different IR spectrum than the original PBEP. Dr. F. Roberto at Edwards Air Force Base had developed an alternate preparation of raffinate PBEP by adding a poor solvent, such as Freon 11, to the as-received PBEP- CH_2Cl_2 solution in a volume ratio of 4 to 1. The raffinate precipitates and is isolated by decantation of the supernatant solution. This latter procedure was adopted for preparation of raffinate at UTC.

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a. Test of Shell Raffinate PBEP

(U) Approximately 200 g of raffinate PBEP were received from Shell Development Company and has been tested by the usual methods for any new lot of PBEP. These tests included hazard classification, thermal stability, and cure studies.

(C) Evaluation of raffinate PBEP for hazard classification yielded results similar to those obtained for PBEP lot 10001-186. The values for impact sensitivity, listed in table XV, were essentially the same at 26 to 27 kg-cm. Also, both samples were negative with no grit on the ESSO friction tester but positive with Pyrex grit. Neither gave positive tests on spark sensitivity up to 9.8 joules.

(C) The raffinate had autoignition values of 525° F for 10 sec and 465° F for 30 sec. These values are similar to those obtained from other lots of PBEP.

(C) The original PBEP lot 10001-186 had an onset of 134°C and a first exotherm of 175°C. With TVOPA as a diluent, the onset rose to 152°C, and a first exotherm was 216°C. The raffinate did not show this change when mixed with TVOPA. The onset values listed in table XVI for both the neat PBEP and the PBEP-TVOPA mixture were 155°C, and first exotherms were 204°C. The thermograms of the raffinate and the original PBEP indicate the raffinate was somewhat more stable, with an onset of 155°C and a first exotherm of 204°C compared to values of 134° and 175°C for the original PBEP.

(U)

TABLE XV

(U) RAFFINATE HAZARD DATA

<u>Sample</u>	<u>Raffinate</u>	<u>Raffinate + TVOPA</u>	<u>Lot 10001-186</u>
Friction sensitivity	+ Pyrex grit	+ Pyrex grit	+ Pyrex grit
Spark sensitivity, j	> 9.8	> 9.8	> 9.8
Impact, kg-cm	27	45	26

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(C)

TABLE XVI

(U) DIFFERENTIAL THERMAL ANALYSIS

<u>Sample</u>	<u>Onset to First Exotherm, °C</u>	<u>First Exotherm, °C</u>
PBEP lot 10001-186	134	175
PBEP lot 10001-186 + TVOPA	152	216
Raffinate	155	204
Raffinate + TVOPA	155	204

(U) The only difference between the spectrum of the raffinate PBEP and lot 10001-186₁ was the disappearance of a band in the raffinate spectrum at $1,725 \text{ cm}^{-1}$ in the carbonyl range.

(C) Gel time studies at UTC gave similar results for the OH equivalents of the raffinate as reported by Shell Development Company. Initially (at least in the first few hours), an NCO/OH value of 1.0 based on 0.7 meq OH/g PBEP appeared to give the optimum cure rates. Continued observation of the samples, however, indicated that a value of less than 0.6 meq/g was more nearly correct. This compares very favorably to a value of 0.56 meq OH/g PBEP reported by Shell Development Company.

b. Evaluation of UTC Raffinate and Extract PBEP

(U) Raffinate and extract PBEP prepared at UTC were evaluated for thermal stability and cure characteristics. The materials were also analyzed by IR for variations between different samples and for differences between the samples and the original PBEP.

(C) Fifty ml of concentrated PBEP in CH_2Cl_2 solution was added to a round bottom flask. Two hundred ml of Freon 11 was added slowly from a separatory funnel to the PBEP- CH_2Cl_2 solution. The extract solution was decanted and the raffinate was washed 3 times with 25 ml of Freon 11. The effect of Freon 11 addition times on yields and raffinate stability are listed in table X. In most tests the yield of raffinate was higher when the addition time was shorter. The non-solvent reached a high of 75% with an addition time of 5 min in run

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186H-5. The lowest yield was 36.2% with an addition time of 74 min in run 186H-2. Variation in laboratory temperatures could account for some of the variation in yield at the same addition times since no effort was made to maintain a constant temperature. Carbon tetrachloride was used in test 186H-7 where a yield of over 85% was achieved. This lack of reproducibility indicates a need for careful control of experimental variables.

(C) The thermal stability of the raffinates and extracts were evaluated by DTA and DSC. These data are given in table XVII. Only one sample, 186H-2, gave a significant improvement in onset temperature although an improvement in peak values was shown by all samples. Raffinate 186H-2 was also the lowest yield sample.

(C) The raffinate samples showed a 20°C improvement in onset to gassing temperature as measured by the DSC effluent analyzer.

(3) PBEP

(C) The IR data for all of the raffinate and extract PBEP samples that have been prepared are listed in table XVIII. Two of the nine raffinate samples gave two peaks in the 1,725 to 1,750 cm^{-1} region instead of the usual single peak. There was normally only one peak, with the total absorbancy in this region decreased. There was very little difference between the spectrum of 186H-5 raffinate prepared using Freon 11 and raffinate 186H-7 prepared using CCl_4 . No correlation could be made between the IR spectra and the percent yields from the preparations.

(C) Gumstocks were prepared to test the optimum NCO-OH equivalents ratio for a blend of the raffinates prepared from all the samples except for lot 2. The best cures were obtained at an NCO-OH ratio of 1.0 when the OH equivalents value for PBEP was assumed to be 0.55 meq/g. This number compares favorably to values of 0.54 and 0.62 meq/g for the two lots of raffinate PBEP prepared at Shell Development Company by the column method.

c. Propellant Evaluation of Shell and UTC Raffinate

(C) The first three micromixes listed in table XIX were used to evaluate the cure characteristics of raffinate PBEP received from

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TABLE XVIII

(U) IR ANALYSIS OF RAFFINATE AND EXTRACT PBEP

Lot No.	Relative Strength of IR Bands*					
	1625	1725	1740	1750	C \equiv N	OH
10001-186H (AR)	0.10	0.47	---	0.36	0.13	0.150
186H1 (RAF)	0.09	0.18	---	0.36	0.11	0.072
186H1 (Extract)	0.07	---	0.20	---	0.08	0.081
186H2 (RAF)	0.13	---	0.41	---	0.14	0.091
186H2 (Extract)	0.06	---	0.18	---	0.07	0.078
186H3 (RAF)	0.05	---	0.28	---	0.07	0.067
186H3 (Extract)	0.08	0.50	---	0.28	0.09	0.110
186H4 (RAF)	0.08	0.26	---	0.21	0.07	0.077
186H4 (Extract)	0.09	---	0.31	---	0.08	0.057
186H5 (RAF)	0.13	---	0.36	---	0.12	0.12
186H5 (Extract)	0.13	---	0.29	---	0.11	0.13
186H6 (RAF)	0.19	---	0.55	---	0.18	0.18
186H6 (Extract)	0.12	0.28	---	0.26	0.08	0.12
186H7 (RAF)	0.10	---	0.33	---	0.11	0.11
186H7 (Extract)	0.16	---	0.37	---	0.26	0.17
186H8 (RAF)	0.20	---	0.32	---	0.16	0.15
186H8 (Extract)	0.12	0.52	---	0.31	0.09	0.11
186H9 (RAF)	0.26	---	0.60	---	0.25	0.19
186H9 (Extract)	0.11	0.34	---	0.26	0.07	0.089
10469-160-2 (RAF)†	0.06	---	0.33	---	0.09	0.070

*The strength of these bands is compared to the strength of the CH₃ band which was arbitrarily assigned a value of 1.00.

†This lot of raffinate PBEP was prepared by Shell Development Company.

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IDENTIFICATION	CURRENT STATEMENT	AUTHORITY
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AD-882 874
 UNITED TECHNOLOGY CENTER
 JUVENILE CAMP
 Evaluation of a High-Energy Radar. (U)
 Final rept. 1 Mar 67. 25 Feb 68.
 Rept. no. UTC-2262-FR
 Jun 68
 Contract F04611-67-C-0039

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 28 Jan 68



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TABLE XIX
(U) RAFFINATE PROPELLANT FORMULATIONS

Formulation No.	UTX 10270-1	UTX 10271-1	UTX 10272-1	UTX 10273-0	UTX 10273-3	UTX 10281-1	UTX 10295*	UTX 11726-0
Raffinate PBEP	9.87	9.87	13.78	13.78	13.78	12.60	11.02	13.78
Raffinate lot	10469-119-2	10469-119-2	10469-119-2	10469-119-2	10469-160-2	10469-160-2	10469-160-2	UTC
TVOPA	24.68	24.67	20.66	20.66	20.67	18.90	16.53	20.67
AlH ₃	15.50	15.50	15.50	15.50	15.50	20.00	22.00	15.50
AP	49.50	49.50	49.50	49.50	49.50	48.00	49.80	49.50
CTI	0.41	0.38	0.30	0.52	0.52	0.48	0.42	0.52
DBTDA	0.035	0.035	0.035	0.035	0.035	0.032	0.28	0.035
PBEP (meg OH/g)	0.60	0.55	0.45	0.55	0.55	0.55	0.55	0.55
NCO/OH	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.0
Cure time at 100° F, hr	16	16	72	48	72	48	48	24
Remarks	Well cured	Well cured	Soft cure	Well cured	Well cured	Well cured	Well cured	Cured

*These formulations also contained 0.2 wt-% Alrowet D65 as a surfactant.

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Shell Development Company. The first two mixes using NCO/OH ratios of 1.0 based on 0.60 and 0.55 meq OH/g PBEP were well cured after 16 hr at 100°F. A third formulation using a value of 0.45 meq/g was only partially cured after 72 hr at this temperature. The most significant change in the raffinate, compared to a usual lot of PBEP, was the small amount of DBTDA catalyst necessary for cure. Very good cures were produced with 0.035 wt-% catalyst, which was less than one-third the amount usually needed.

(C) Formulations UTX 11726-1 and UTX 11726-2 contained UTC-prepared raffinate polymer, and UTX 10273-1 contained Shell-prepared material. In addition, the raffinate in UTX 11726-2 was treated with 13X molecular sieves.

(C) The Shore A hardness and physical property data are listed in table XX. The 13X sieve treatment appears to give more complete cures as UTX 11726-2 cured to a Shore A hardness reading of 68 compared to a value of 52 for UTX 11726-1. The physical property values for UTX 11726-2 were also somewhat better. The tensile value of 41 psi for UTX 11726-2 was much better than the value of 29 psi for UTX 11726-1. However, the elongations were similar at about 8%. UTX 10273-3 prepared from Shell raffinate had intermediate values for both Shore A hardness and physical properties between the other two formulations.

(C)

TABLE XX

(U) PHYSICAL PROPERTIES OF RAFFINATE PBEP PROPELLANTS

<u>Formulation No.</u>	<u>True Physical Properties</u>		
	<u>Tensile, psi</u>	<u>Elongation, %</u>	<u>Shore A Hardness</u>
UTX 10270-1	58	7	---
UTX 10273-1	48	6	---
UTX 10273-3	24	5	55
UTX 11726-1	29	8	52
UTX 11726-2*	41	8	68

* This lot was treated with 13X molecular sieves.

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(C) UTX 10273-2 and 10281-1 were scaleup mixes of about 500 g. At the same catalyst levels of the micromix formulations, these formulations were both well cured in 48 hr at 100°C. Scaleup of formulations UTX 10295-1 and UTX 10295-2 to 500 and 2,400 g, respectively, resulted in similar pot life and both were well cured in 48 hr.

7. BINDER COMPONENT TREATMENT STUDIES

(C) Raffinate PBEP which cures reproducibly on scaleup and at a much lower catalyst level than regular PBEP has an IR spectrum similar to PBEP except that a band at $1,725\text{ cm}^{-1}$ is missing.

(C) Because the preparation of PBEP raffinate by Shell Development Company involved deposition of PBEP on an acid-washed Chromosorb W column followed by elution, it was postulated that some ingredient may be selectively removed or destroyed by the Chromosorb W or by a silaceous component of the Chromosorb W. A study was therefore initiated to determine if the $1,725\text{ cm}^{-1}$ peak could be removed by use of selected absorbants or reactants. Because a similar effect on propellant cure had been noted with TVOPA without a $1,740\text{ cm}^{-1}$ peak, it was included in the study.

a. Initial Studies On Treatment of PBEP and TVOPA

(C) A list of materials used to treat PBEP, as well as their effect on certain IR bands, is given in table XXI. In most cases treatment of PBEP caused changes in the carbonyl range with the bands at $1,725$ and $1,750\text{ cm}^{-1}$ merging into one band approximately $1,740\text{ cm}^{-1}$. Most treatments also reduced the total absorption in this region. Both 13X and 4A molecular sieves showed promise for lowering these bands and the ensuing treatment work used these materials.

(C) Fluorine analysis of PBEP treated for 24 hr with 13X molecular sieve pellets showed an increase of 1.0 wt-% fluorine. The sieves were possibly removing an unstable, low molecular weight fraction of PBEP which is found in fluorine.

(C) Results of the treatment of TVOPA are listed in table XXII. Chromosorb W had the most effect with elimination of the IR spectral bands at $1,660$ and $1,740\text{ cm}^{-1}$. Powdered 13X sieves eliminated the band at $1,740\text{ cm}^{-1}$. Alon C and Celite eliminated the band at $1,660\text{ cm}^{-1}$.

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TABLE XXI

(U) IR EVALUATION OF TREATED PBEP

<u>Treatment Material</u>	<u>Relative Strength of IR Bands*</u>				
	<u>1725 cm⁻¹</u>	<u>1740 cm⁻¹</u>	<u>1750 cm⁻¹</u>	<u>C ≡ N</u>	<u>OH</u>
Control	0.44	---	0.38	0.10	0.094
Alon C (Al ₂ O ₃)	---	0.62	---	0.07	0.081
Alumina	0.26	---	0.26	0.10	0.086
Powdered 13X sieves	0.33	---	0.33	0.07	0.110
Powdered 5A sieves	0.26	---	0.26	0.08	0.075
Powdered 4A sieves	0.35	---	0.35	0.10	0.093
NaF	0.31	---	0.31	0.09	0.082
Celite	0.30	---	0.30	0.09	0.071
Silica gel	0.25	---	0.25	0.08	0.072
Ni dimethylglyoxime	Treatment material dissolved				
Cabosil	0.55	---	0.44	0.15	0.16
Cabolite	0.36	---	0.30	0.08	0.085
Dowex 50W	---	0.12	---	0.17	0.12
Chromosorb W	0.60	---	0.39	0.14	0.10

*The strength of these bands is compared to the strength of the CH₃ band which was arbitrarily assigned a value of 1.0.

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TABLE XXII

(U) IR EVALUATION OF TREATED TVOPA

<u>Treatment Material</u>	<u>Relative Strength of IR Bands*</u>				<u>OH</u>
	<u>1620 cm⁻¹</u>	<u>1660 cm⁻¹</u>	<u>1740 cm⁻¹</u>	<u>1840 cm⁻¹</u>	
Control	0.04	0.03	0.04	0.06	0.01
Alon C (Al ₂ O ₃)	0.06	No band	0.12	0.07	0.01
Activated aluminum	0.03	0.06	0.03	0.12	0.005
Powdered 13X sieves	0.07	0.03	No band	0.06	No band
Powdered 5A sieves	0.06	0.03	0.04	0.07	0.01
Powdered 4A sieves	0.08	0.05	0.03	0.07	0.02
NaF	0.06	0.04	0.06	0.07	0.01
Celite	0.07	No band	0.16	0.08	0.01
Silica gel	0.11	0.07	0.04	0.11	0.01
Ni dimethylglyoxime	0.04	0.06	0.14	0.06	0.01
Chromosorb W	0.06	No band	No band	0.06	0.01

*The strength of these bands is compared to the strength of the CH₃ band which was arbitrarily assigned a value of 1.0.

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Fluorine analysis of TVOPA treated with sieves showed a decrease in fluorine content of 1.4 wt-%.

b. Preliminary Propellant Evaluation Using Treated Binder Ingredients

(C) The initial micromixes referenced in table XXIII were prepared using either treated PBEP or TVOPA. The control, formulation UTX 10804-1, contained minimum amounts of CTI and DBTDA and failed to cure completely. UTX 10804-2 used TVOPA treated with Chromosorb W and with the same CTI and DBTDA levels as the control. This formulation cured more completely than the control but was not as well cured as formulation UTX 10804-3 which included TVOPA treated with 13X molecular sieves. The next two formulations, UTX 10804-4 and 10804-5, contained PBEP treated with 4A and 13X molecular sieves, respectively, and were fully cured in 72 hr. The formulation containing 13X-sieve-treated PBEP cured to a Shore A hardness of 52 while the formulation containing 4A-sieve-treated PBEP cured to a hardness of 38.

(C) A repeat of the IR analysis of PBEP lot 10001-186C showed the untreated material had only one peak in the $1,725$ to $1,750$ cm^{-1} range and not two peaks as observed previously. These are shown in run 2 of table XXIV. Formulation UTX 10804-6 was processed using this single peak PBEP. The propellant cured to a Shore A hardness value of 20. Treatment of this lot with 4A molecular sieves resulted in an IR analysis as shown by run 3 in table XXIV. Formulation UTX 10804-5 processed with this sieve-treated PBEP cured to a Shore A hardness value of 52.

c. Scaleup of Treatment Method for PBEP and TVOPA Evaluation

(C) The molecular sieve treatment for PBEP was scaled up to a continuous column process. Both a top-feed glass column and bottom-feed stainless steel column were constructed. The sieves used in both columns were oven dried for 24 hr at 600°F and consisted of a blend of 65 wt-% 4A molecular sieves and 35 wt-% 13X molecular sieves. The 4A molecular sieves were crushed pellets with particles of less than 351 microns in size removed. The 13X molecular sieves were in a powder form with the particle size ranging from 1.0 to 4.5 microns.

(C) Column treatment of PBEP lots 10001-186E and 10001-186G produced a product with a single peak in the $1,725$ to $1,750$ cm^{-1} range,

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TABLE XXIII

(U) MICROMIXER FORMULATIONS USING TREATED BINDER MATERIALS

Formulation No.	UTX 10804-1	UTX 10804-2	UTX 10804-3	UTX 10804-4	UTX 10804-5	UTX 10804-6	UTX 10804-7	UTX 10804-8	UTX 10804-9	UTX 10804-10
PBEP*	13.78	13.78	13.78	13.78	13.78	13.78	13.78	13.78	13.78	13.78
PBEP treatment	---	---	---	4A sieves	13X sieves	---	4A/13X sieves	---	4A/13X sieves	4A/13X sieves
TVOPA	20.68	20.68	20.68	20.68	20.68	20.68	20.68	20.68	20.68	20.68
TVOPA treatment	---	Chromo- sorb W	13X sieves	---	---	---	4A sieves	4A sieves	---	4A/13X sieves
CTI	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
DBTDA	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
AlH ₃	15.50	15.50	15.50	15.50	15.50	15.50	15.50	15.50	15.50	15.50
AP	49.50	49.50	49.50	49.50	49.50	49.50	49.50	49.50	49.50	49.50
NCO/OH †	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Cure time at 100° F, hr	72	72	72	72	72	72	72	72	72	72
Shore A hardness	---	5	53	38	52	20	45	5	20	33
Remarks	Uncured	Soft Cure	Cured	Cured	Cured	Cured	Cured	Soft Cure	Cured	Cured

*PBEP lot was 10001-186 in all formulations.

†These numbers are based on an OH equivalents value of 0.70 meq/g for the PBEP.

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TABLE XXIV

(U) IR ANALYSIS OF PBEP

<u>Run No.</u>	<u>Lot No.</u>	<u>Treatment</u>	<u>Relative Strength of IR Bands*</u>					<u>OH</u>
			<u>1625</u>	<u>1725</u>	<u>1740</u>	<u>1750</u>	<u>C \equiv N</u>	
1	186CB	Untreated	0.11	0.46	---	0.34	0.10	0.12
2	186CB	Untreated	0.17	---	0.44	---	0.15	0.16
3	186CB	4A-batch	0.20	0.47 ²	0.47	---	0.17	0.16
4	186E	13X + 4A-column	0.08	0.24 ²	0.24	---	0.10	0.08
5	186G	Untreated	0.13	---	---	0.38	0.13	0.12
6	186G	13X + 4A-column	0.24	---	0.52	---	0.22	0.17
7	186G	13X + 4A-column	0.18	---	0.50	---	0.17	0.17
8	Reanalysis of 7 after 3 days at 0° F.		0.10	0.36	---	0.29	0.10	0.10

*The strength of these bands is compared to the strength of the CH₃ band which was arbitrarily assigned a value of 1.00.

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listed as analyses 4 and 6 in table XXIV. Two micromixes were processed using treated and untreated PBEP lot 10001-186G. UTX 10804-7 using treated PBEP cured to a Shore A hardness value of 45 and UTX 10804-8 using untreated PBEP with a double peak cured to a Shore A hardness value of 5. A 400-g batch, UTX 10804-9, was then processed to determine if the treated PBEP would allow formulation scaleup without the usual necessary increase in catalyst level. This mix, using PBEP analyzed as run 6 in table XXIV, cured to a Shore A hardness of 20, which was less than obtained in the micromix but better than would be normally expected for this batch size and catalyst level.

(C) The effect of batch treatment with 4A molecular sieve pellets is shown by comparing the IR sample run 1 in table XXV, which was untreated TVOPA, and run 2, which was the same TVOPA after treatment. A stainless steel column was constructed for sieve treatment of the TVOPA. This column was packed with crushed 13X sieves. Comparison of the TVOPA before and after column treatment is given in table XXV by runs 3 and 4, respectively. Column treatment removed only 60% of the material absorbing at $1,740\text{ cm}^{-1}$ compared with 100% removal by the batch method. Since column treatment did not appear to be as efficient as the batch method, the column-treated TVOPA was further treated with powdered 13X molecular sieves using the batch process. Formulation UTX 10804-10 was then processed using the column- and batch-treated TVOPA. The PBEP used in mix UTX 10804-10 also had a double treatment. After column treatment, the PBEP gave the IR analysis shown in run 7, table XXIV. After three days of storage at 0°F , the PBEP gave the analysis shown by run 8, showing a reappearance of a double peak in the $1,725$ to $1,750\text{ cm}^{-1}$ range. The PBEP was then batch-treated with powdered 13X molecular sieves. UTX 10804-10 cured to a Shore A hardness value of 33 after 18 hr at 100°F .

(C) Rheometer data was also obtained for both 400-g batches and is given in table XXVI. Both mixes, UTX 10804-9 with only PBEP-treated ingredients and UTX 10804-10 with both PBEP and TVOPA treated ingredients, have flow rates comparable to previously processed formulations containing untreated binder ingredients with the same volume percent binder. The difference in the two flow rates can be attributed to a more rapid cure in UTX 10804-10. In addition, the final cure in the last mix was firmer, as shown by the higher Shore A hardness value of 33, compared to a value of 20 for UTX 10804-9.

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(C)

TABLE XXV

(U) IR ANALYSIS OF TVOPA

Run No.	Lot No.	Treatment	Relative Strength of IR Bands *				
			1620	1660	1740	1840	OH
1	BT184D	Untreated	0.05	None	0.04	0.08	0.01
2	BT184D	4A-batch	0.08	0.06	None	0.07	0.01
3	BT184E	Untreated	0.07	0.14	0.05	0.08	0.02
4	BT184E	13X-column	0.07	0.07	0.02	0.06	None

*The strength of these bands is compared to the strength of the CH₃ band which was arbitrarily assigned a value of 1.00.

(U)

TABLE XXVI

(U) RHEOMETER DATA FOR SYSTEMS USING TREATED BINDER MATERIALS

Time After DBTDA Addition min	Flow Rate, g/min	
	UTX 10804-9	UTX 10804-10
33	59.8	---
43	49.1	33.3
53	42.7	27.6
63	36.1	22.8
72	---	18.5

8. AlH₃ PROPELLANT STUDIES

(U) AlH₃ studies involved formulation, hazard characterization, and thermal stability. All DMMDI-HT, CTI, and CTI-glycol systems were evaluated. Hazard data included impact, friction, spark, and autoignition tests.

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a. AlH_3 Formulations

(C) UTX 8462-1 and UTX 8462-2, listed in table XXVII, contained 21 wt-% AlH_3 and had a total solids loading of 73 wt-%. Crosshead physical property data from UTX 8462-1, listed in table XXVIII, was 200-psi tensile and 15% elongation. UTX 8462-2 produced crosshead data of 114-psi tensile and 6% elongation. UTX 8462-2 had a longer cure time than UTX 8462-1, accounting for the variation in physical properties between the two mixes.

(C) Two AlH_3 formulations, UTX 11711-1 and UTX 11712-1 with catalyst levels of 0.016 and 0.017 wt-%, were well-cured in 16 hr at 120°F. UTX 11711-1 was nearly cured in 3 hr. UTX 11712-1, with one-half the catalyst level as in the other two formulations, failed to cure in 72 hr. A similar formulation, UTX 11706-1, with aluminum as the fuel, had cured in this time period but a longer residence time in the mixer was used during processing than was used in the preparation of UTX 11712-1.

(C) Two formulations, UTX 10263-1 and UTX 10263-2, were prepared to evaluate the reproducibility of the system relative to cure characteristics. All three mixes cured to a Shore A value of 60 after 16 hr at 100°F. The fourth formulation, UTX 10263-4, was prepared to investigate longer solvent strip times. The cure appeared to be somewhat faster than usual, but the final state of cure was the same as that of the propellant having a Shore A value of 60. UTX 10263-7, which has a very short solvent strip time, also gave the same final cure with the propellant again having a Shore A value of 60.

(U) UTX 10263-6 contained 0.1 wt-% UTEFLO A-2 as a processing aid. It was hoped that this additive would help to lower the viscosity of the propellant for better casting characteristics. However, no great difference was noted in the viscosity of the propellant during casting.

b. AlH_3 Propellant Hazard Data

(C) Autoignition data on propellant containing AlH_3 , listed in table XXIX, are similar to those obtained from propellant containing aluminum as a fuel with a 30-sec value of about 465°F and 10 sec-value of 570°F. Spark sensitivity on this propellant was greater than 9.8 joules, which was similar to aluminum-containing propellant. Friction sensitivity varies with occasional positive values obtained without added grit. Pyrex grit was usually necessary for a positive test.

TABLE XXVII

(U) AIH₃ FORMULATIONS

Formulation No.	UTX 8465-5	UTX 8466-2	UTX 8466-3	UTX 8462-1	UTX 8462-2	UTX 8465-1	UTX 11704-J	UTX 11711-J	UTX 11712-1
PREP	14.43*	12.13*	12.13*	12.13*	12.13*	14.43*	11.62†	12.23†	13.67†
TVOPA	14.43	12.13	12.13	12.13	12.13	14.43	16.42	17.28	20.51
Isocyanate	2.33	1.96	1.96	2.20	2.20	2.23	0.73	0.76	0.86
Type of isocyanate	DMMDI	DMMDI	DMMDI	DMMDI	DMMDI	DMMDI	CTI	CTI	CTI
Glycol	0.17	0.14	0.14	0.24	0.24	0.17	0.14	0.15	0.17
Type of glycol	HT	HT	HT	HT	HT	HT	HT	HT	HT
DBTDA	0.64	0.64	0.64	0.29	0.29	0.64	0.016	0.017	0.008
AP	48.00	52.00	52.00	52.00	52.00	48.00	51.06	50.56	49.33
Aluminum	20.00	21.00	21.00	21.00	21.00	20.00	20.02	18.97	15.45
OH/PBEP(OH)	0.25	0.25	0.25	0.40	0.40	0.25	0.40	0.40	0.20
NCO/OH	0.85	0.85	0.85	0.85	0.85	0.85	0.92	0.92	1.05
Cure time, days	5	5	5	10	10	10	1	1	3
Cure temperature, °F	75	75	75	75	75	75	100	100	100
Remarks	Soft Cure	Soft Cure	Soft Cure	Cured	Cured	Cured	Cured	Cured	Uncured

TABLE XXVII

(U) AIH₃ FORMULATIONS (Continued)

Formulation No.	UTX 11713-1	UTX 11715-1	UTX 11716-1	UTX 11717-1	UTX 11721-1	UTX 11722-1	UTX 10263-2	UTX 10263-3	UTX 10263-4	UTX 10263-5	UTX [†] 10263-6	UTX 10263-7
PBEP	13.63†	13.63†	13.45†	13.61†	13.57†	13.46†	13.34†	13.34†	13.34†	13.34†	13.34†	13.34†
TVOPA	20.44	20.44	20.28	20.41	20.46	20.29	21.02	21.02	21.02	21.02	21.02	21.02
Isocyanate	1.037	1.037	1.247	0.78	0.83	1.247	0.465	0.465	0.465	0.465	0.465	0.465
Type of isocyanate	CTI	CTI	CTI	CTI	CTI	CTI	CTI	CTI	CTI	CTI	CTI	CTI
Glycol	10.32	0.32	0.38	0.16	0.224	0.38	---	---	---	---	---	---
Type of glycol	DPG	DPG	HT	HT	DHI	HT	---	---	---	---	---	---
DBTDA	0.016	0.032	0.032	0.032	0.032	(DBTDL) 0.057	0.175	0.175	0.175	0.175	0.175	0.175
AP	49.16	49.15	14.94	50.01	49.91	49.67	49.50	49.50	49.50	49.50	49.40	49.50
AIH ₃	15.40	15.39	14.94	15.00	14.97	14.94	15.50	15.50	15.50	15.50	15.50	15.50
OH/PBEP(OH)	0.50	0.50	0.91	0.38	0.34	0.91	---	---	---	---	---	---
NCO/OH	1.05	1.05	1.00	0.85	0.94	1.00	0.70	0.70	0.70	0.70	0.70	0.70
Cure time, days	3.0	1.0	0.1	0.2	0.2	1.0	1.0	1.0	1.0	0.3	1.0	1.0
Cure temperature, °F	100	100	100	100	100	100	100	100	100	100	100	100
Remarks	Cured	Cured	Cured	Cured	Cured	Cured	Cured	Cured	Cured	Cured	Cured	Cured

* Formulation contained PBEP lot 9557-99A.

† Formulation contained PBEP lot 10001-186.

‡ Formulation contained 0.1% UTEFLO-A-2.

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(C)

TABLE XXVIII

(U) PHYSICAL PROPERTY DATA FOR
AlH₃ FORMULATIONS

<u>Formulation No.</u>	<u>True Physical Properties</u>	
	<u>Tensile, psi</u>	<u>Elongation, %</u>
UTX 8462-1	200*	15*
UTX 8462-2	114*	6*
UTX 11715-1	74	17
UTX 11716-1	108	18
UTX 11717-1	82	13
UTX 11721-1	67	16

* This value is crosshead data.

(C) The high impact values of 19.6 and 22.4 kg-cm for UTX 8462-1 and UTX 8462-2 were obtained on humid days. Reruns on UTX 8462-2 on less humid days, as well as on propellant retained in a desiccator until testing, produced more realistic values of 12.6 to 14.9 kg-cm. Impact values on UTX 8465-4 and UTX 8466-2 varied from 6.0 to 7.8 kg-cm. UTX 8466-3 was very well cured and had an impact value of 12.0 kg-cm. These values are higher than values obtained previously on formulations with lower solids loadings.

9. HAP STUDIES

(U) HAP used as a solid oxidizer has two distinct advantages over AP used as an oxidizer. HAP has a higher density of 2.06 g/cc compared to a density of 1.95 g/cc for AP, and higher specific impulses of about 15 sec are attainable with HAP-oxidized propellants at comparable solids loadings.

(U) The main disadvantages of HAP are its moisture sensitivity, its incompatibility with commonly used curative ingredients, and poor compatibility with the PBEP-TVOPA binder.

TABLE XXIX
(U) AlH₃ PROPELLANT HAZARD EVALUATION

Formulation No.	Impact Kg-cm	Friction		Diamond Grit	Autoignition °F		Spark Sensitivity joules
		No Grit	Pyrex Grit		30 sec	10 sec	
UTX 8462-1	19.6	-	+	+	470	570	-----
UTX 8462-2							
Test 1	22.4	-	+	+	465	585	9.80
Test 2	14.1	+	+	+	---	---	-----
Test 3	12.6	---	---	---	---	---	-----
Test 4 (Desiccated)	14.9	---	---	---	---	---	-----
UTX 8465-1	7.8	---	---	---	---	---	-----
UTX 8465-6							
Uncured	6.0	-	+	+	---	---	-----
UTX 8465-4							
Cured	7.8	---	---	---	---	---	-----
UTX 8466-2							
Uncured	7.6	-	+	+	---	---	9.80
3 days ambient cure	7.8	+	+	+	---	---	-----
UTX 8466-3							
Cured	12.0	-	+	+	---	---	-----

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a. HAP Compatibility Testing

(U) Various candidate binder ingredients were visually tested for compatibility and solubility with HAP. The materials and results are shown in table XXX. The diisocyanate, DMMDI, and HAP appear to be compatible. Slight discoloration of these two HAP/diisocyanates were noted after 18 days, but this is a longer time period than the normal cure cycle would require. HAP was not soluble in PARI, a poly-functional isocyanate, and color changes could not be observed. The liquid isocyanate, Isonate 143L, was not compatible with HAP. The solid triisocyanate, CTI, was compatible with the oxidizer.

(U) Of the three triols investigated, HAP was compatible with DB oil and 11-80. The oxidizer was soluble in HT but did not appear to react with this triol. No discoloration or oxidizer solubility was observed when HAP was mixed with DBTDA cure catalyst or TCP stabilizer.

(C) The thermal compatibility of candidate binder ingredients with HAP were studied by DTA. The experimental results are shown in table XXXI. The HAP/CTI thermogram had an exotherm at 94°C, directly after the melting point of the oxidizer. The exotherm was small and reproducible. Samples containing PBEP had exotherm peak temperatures near 140°C, or approximately 20°C lower than expected. This would indicate reaction between PBEP and HAP.

(C) Onsets to the first exotherm varied in samples containing HAP from 90°C for HAP and CTI to 118°C for the PBEP/TVOPA/HAP/CTI/DBTDA mixture. None of the onsets were as low as the temperatures expected for use in processing or storage of HAP propellants.

(C) When tested for thermal stability by DSC and DTA, cured propellants containing HAP and either aluminum or AlH_3 exhibited no exothermic activity below 100°C. The onsets to the first exotherms listed in tables XXXI and XXXII for the aluminum- or AlH_3 -fueled HAP propellants were very similar. Aluminized formulations, UTX 10805-1 and UTX 10806-1, when tested by DTA had initial onsets of 111° and 102°C, respectively. UTX 10807-1 which contained AlH_3 had an onset temperature of 104°C. The initial peak temperatures varied only between 116° and 127°C. DSC indicated very slight differences between HAP-aluminum and HAP- AlH_3 propellants. Onsets varied only between 120° and 137°C and first peak temperatures between 146° and 150°C. Using the DSC effluent analyzer, the onset of gas evolution was between 139° and 148°C for either type of HAP propellant.

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TABLE XXX

(U) COMPATIBILITY AND SOLUBILITY STUDY OF HAP

<u>Binder Ingredient</u>	<u>HAP Solubility</u>	<u>Color Change</u>	
		<u>1 day</u>	<u>35 days</u>
H ₁₂ MDI	No	None	Slight yellow
DEBI	No	None	Brown
DMM	No	None	None
PAPI	No	None	None
Isonate 143 L	No	Brown	None
CTI	No	None	None
HT	Yes	---	---
11-80	No	None	Slight yellow
DB Oil	No	None	Slight yellow
PBEP + TVOPA	No	None	Darker brown
DBTDA	No	None	None
TCP	No	None	None

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TABLE XXXI

(U) DIFFERENTIAL THERMAL ANALYSIS COMPATIBILITY DATA

	<u>Endotherms</u> <u>Onset/Peak, °C</u>	<u>Exotherms</u> <u>Onset/Peak, °C</u>
HAP	55/58, 81/93	164/174
CTI	34/45	None to 240°C
TVOPA	---	159/240
AIH ₃	167/182	190/194
PBEP	---	134/175, 186/199
PBEP/TVOPA/HAP	57/60, 80/88	96/101, 120/140
HAP/CTI	34/43, 56/59, 80/89	90/94, 142/163
HAP/TVOPA	54/57, 80/90	115/164
PBEP/TVOPA/HAP/CTI	53/56, 95/87	117/137
PBEP/TVOPA/HAP/CTI/DBTDA	53/57, 81/92	118/138
PBEP/TVOPA/HAP/CTI/AIH ₃ / DBTDA	52/54, 76/86	98/139
UTX 10805-1	111/124, 131/138, 144/151, 162/171	53/57, 80/91
UTX 10806-1	102/127, 134/143 145/147, 154/166	54/59, 75/90
UTX 10807-1	104/116, 119/126, 129/133, 143/151, 179/192	54/58, 80/88

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(U)

TABLE XXXII

(U) DSC DATA

<u>Formulation No.</u>	<u>Exotherms Onset/Peak, °C</u>	<u>Endotherms Onset/Peak, °C</u>	<u>Effluent Analyzer Onset of Gassing, °C</u>
UTX 10805-1	127/150, 197/214	52/58, 77/85	148
UTX 10806-1	137/146, 156/161, 197/216	50/52, 79/85	139
UTC 10807-1	120/146	77/87, 177/201	141

(U) HAP has been evaluated for compatibility by DTA with various binder ingredients. Although all ingredients showed lower exotherms when mixed with HAP, these exotherms and their onsets were usually much higher than HAP propellants will ever experience during processing or storage. Data from gumstocks and gumstocks plus HAP showed that CTI or CTI-diisocyanate was the preferred cure system.

b. Formulation of HAP Propellants

(U) Hand mixes were prepared with HAP-compatible ingredients to determine cure characteristics of various binder systems. When possible, candidate components were distilled to ensure purity and low-moisture content. With the exception of solvent stripping, all weighing and mixing operations were conducted in controlled atmosphere chambers with dew points of -60°F or lower. The PBEP and TVOPA solutions were dried over sodium sulfate, and the HAP was dried at 10^{-6} mm Hg. The H-5 aluminum was oven-dried at 200°C and the AlH_3 was AN-treated. HAP was added to one-half of the mixed binders to determine the effect of oxidizer on binder cure.

(U) CTI formulations 12-1, 13-2, 13-3, 14-4, 14-5, and 15-6, (see table XXXIII) were prepared to vary the NCO/OH ratio and to check the effect of different DBTDA cure catalyst concentrations. The best cure was obtained at an NCO/OH ratio of 0.75. Mixes 15-6, 14-5, and 12-1 contained 0.10, 0.25, and 0.50 wt-% cure catalyst, respectively, but were identical in all other respects, including NCO/OH ratios. Observing the cures of these three mixes for 5 days, the mix with the highest catalyst wt-% cured the fastest, as expected.

TABLE XXXIII

(U) FORMULATION STUDIES WITH HAP

Formulation No.	12-1	13-2	13-3	14-4	14-5	15-6	17-1	19-1	19-2	20-3	20-4	21-5	21-6	25-1	25-2	26-1	26-2	29-1	
PREP	1.21	1.59	1.37	1.14	1.21	1.06	0.64	0.81	0.80	0.88	0.87	1.03	1.20	0.89	1.36	1.42	1.03	1.03	1.03
VOFA	0.69	0.91	0.78	0.65	0.69	0.60	0.36	0.81	0.80	0.88	0.87	1.03	1.20	0.89	1.36	1.42	1.03	1.03	1.03
DMM	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	0.022	---	---
DEBI	---	---	---	---	---	---	---	---	---	---	---	---	---	---	0.024	0.022	---	---	---
HMDI	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	0.012	---	---
F ₁₂ MDI	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	0.021
NCO-120	---	---	---	---	---	---	---	---	---	---	---	---	---	0.057	---	0.071	---	---	---
CTI	0.045	0.064	0.049	0.039	0.046	0.040	0.032	0.028	0.029	0.034	0.035	0.045	0.055	---	0.052	---	0.025	0.040	0.040
Polyglycol 11-80	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
DRTDA	0.011	0.011	0.014	0.011	0.005	0.002	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020
Triol/PBEP (OH)	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
NCO/OH	0.78	0.85	0.75	0.70	0.70	0.79	1.00	0.70	0.75	0.80	0.85	0.90	0.80	0.80	0.80	0.80	1.00	1.00	1.00
Cure at ambient																			
Binder	Cured tacky	Cured tacky	Cured tacky	Cured tacky	Cured tacky	Gel	Cured tacky	Cured tacky	Cured tacky	Cured tacky	Cured tacky	Cured tacky	Cured tacky	Cured tacky	---	Uncured	---	---	---
Binder + HAP	Cured tacky	Cured tacky	Cured tacky	Soft cure	Soft cure	Soft cure	Cured tacky	Cured tacky	Cured tacky	Cured tacky	Cured tacky	Cured tacky	Cured tacky	Cured tacky	Soft cure	Uncured weak	Cured weak	Cured weak	Cured weak

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(U) Formulation 17-1 was prepared to check AlH_3 for compatibility and stability in the CTI binder. A void-free sample containing both HAP and AlH_3 was obtained.

(U) Formulation 19-1 19-2, 20-3, 20-4, 21-5, and 21-6 were prepared at different NCO/OH ratios to determine optimum cure equivalents. The NCO/OH levels investigated were 0.70 to 0.95. The best cures were obtained at NCO/OH ratios of 0.75 and 0.80.

(U) Formulations 25-1 and 26-1 were mixed using the polyfunctional isocyanate Kaiser NCO-120 which has a reported 3.2 NCO functionality. The NCO-120 was found to be insoluble in PBEP-TVOPA, and further studies were discontinued.

(U) In formulations 25-2, 28-1, 28-2, 29-3, an attempt was made to incorporate a triisocyanate with a diisocyanate to obtain a binder system with more elongation. The equivalents were 0.8 triisocyanate and 0.2 diisocyanate to 1.0 equivalent PBEP (OH). Poor cures were observed with all mixes. This may have been caused by using too high an NCO/OH ratio.

c. Scaleup Formulations

(C) Mechanical property samples were cast from a 60-g HAP formulation prepared in the micromixer. This formulation, UTX 10802-1, was viscous because no attempt had been made to optimize the solids loading distribution. Casting voids were observed in the cured specimens. The true mechanical properties of the mix were 73-psi tensile and 18% elongation.

(C) Three micromixes listed in table XXXIV were also prepared with HAP as the oxidizer. UTX 10805-1 contained as-received PBEP while UTX 10806-1 contained raffinate PBEP. Both formulations had aluminum as the fuel. The physical properties listed in table XXXV were similar with a tensile of 58 psi and elongation of 13% for UTX 10805-1, and 51-psi tensile and 11% elongation for UTX 10806-1. UTX 10807-1 contained AlH_3 and had crosshead physical properties of 43-psi tensile and 43% elongation. No evidence of gas was observed; however, a shorter pot life than for comparable AP formulations was noted.

(U) Formulations containing HAP have a much shorter pot life and cure time than similar AP formulations. An AP- AlH_3 formulation

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TABLE XXXIV
(U) HAP FORMULATIONS

Formulation No.	UTX 10802-1	UTX 10805-1	UTX 10806-1	UTX 10807-1	UTX 10808-1	UTX 10809-1
PBEP*	19.95	16.73	16.73	18.10	18.11	16.72
TVOPA	19.95	25.09	25.17	27.15	27.16	25.09
CTI	0.77	0.65	0.51	0.70	0.71	0.65
DBTDA	0.043	0.043	0.043	0.043	0.02	0.04
AlH ₃	---	---	---	12.00	---	12.50
Aluminum	12.50	12.50	12.50	---	12.00	---
HAP	46.00	45.00	45.00	42.00	42.00	45.00
NCO/OH	0.80	0.80	0.80	0.80	0.80	0.80
Cure time at ambient temperatures, hr	16	16	16	16	3.0	16

*PBEP was lot 10001-186 in all formulations.

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(C)

TABLE XXXV

(U) PHYSICAL PROPERTY DATA FOR HAP FORMULATIONS

True Physical Properties

<u>Formulation No.</u>	<u>Tensile, psi</u>	<u>Elongation, %</u>	<u>Shore A</u>
UTX 10802-1	73	18	---
UTX 10805-1	58	13	59
UTX 10806-1	51	11	53
UTX 10807-1	43*	43*	60
UTX 10808-1	15*	38*	45*

*These data are crosshead rather than true physical properties.

that cures in 16 hr will be well cured in less than 1 hr when the AP is replaced by HAP. The HAP propellant, both aluminum and AlH_3 exhibited binder reversions in week at $35^\circ C$. Apparently, the HAP catalyzes breakdown of the curve linkage.

(U) Formulation UTX 10809-1, listed in table XXXIV, was well cured after 16 hr at ambient temperatures. This propellant produced stable combustion when well restricted and had a burning rate of 1.75 in./sec at 1,000 psi and a pressure exponent of 0.72. These values are comparable to AP propellants that usually have burning rates of 1.55 to 1.65 in./sec at 1,000 psi and pressure exponents of 0.65 to 0.75.

10. TOXIC PROPELLANT STUDIES

(C) PBEP-TVOPA propellants yield a theoretical I_{sp} of 289 sec with beryllium and 310 to 315 sec with BeH_2 . The beryllium formulations show its peak I_{sp} of 289 sec at 11 to 12 wt-% beryllium and 40 to 50 wt-% binder. Processing limitations determine the highest practical impulse with PBEP and BeH_2 .

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(C) Both beryllium and BeH_2 have a history of poor combustion and impulse efficiency in both composite and double-base propellants. One of the primary objectives of this part of the program was to see if beryllium and BeH_2 -PBEP propellants showed the high motor efficiencies demonstrated in aluminized NF_2 propellants.

(U) A second goal was to evaluate the stability of beryllium and BeH_2 with PBEP-TVOPA in laboratory and long-term surveillance studies.

a. Factors Affecting Delivered Specific Impulse of Beryllium and BeH_2 Propellants

(C) There are numerous factors which affect the motor performance of a propellant. Among the more important variables are flame temperature; O/F ratio; metal fuel content, which affects two-phase flow losses; and heat loss (in small motors).

(C) A theoretical study of these factors affecting the performance in beryllium- and BeH_2 -Domino propellants was conducted to determine if additional information could be gained to aid in formulation of beryllium and BeH_2 propellants. Two-phase flow losses have been shown to be approximately proportional to the Z factor, (the ratio of condensed species mass flow to gas mass flow). Analysis of the Z factor and oxidation-fluorination ratios suggested the possibility of achieving a higher efficiency at lower BeH_2 loadings, which might compensate for the lower theoretical specific impulse at these lower solids loading.

b. Analysis of BeH_2 Lots

(C) Three lots of BeH_2 were obtained from the Ethyl Corporation for the initial screening studies. The analysis data for these lots are given in table XXXVI. The results of the preliminary screening study were used as the basis for selection of one lot for scaleup to the 1-lb motor size. In these studies, the Beane was used as received with no ball milling or heat treatment.

c. Stability Studies of Propellant Ingredients

(C) The preliminary screening work depended on visual inspection of binder-fuel mixtures for gassing and DTA studies. Samples of PBEP-TVOPA-beryllium and beryllium at 90°F were under surveillance

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TABLE XXXVI

(U) ANALYTICAL DATA FOR BEANE*

<u>Composition, wt-%</u>	<u>Lot No.</u>		
	<u>B403-7</u>	<u>B433-5</u>	<u>B439-41</u>
Total carbon	1.51	1.23	1.90
Total hydrogen	17.75	17.87	17.68
BeH ₂	96.6	96.2	95.4
Beryllium metal	1.0	3.6	1.0
BeC/2	0.03	0.07	0.08
Beryllium alkoxide	0.13	0.05	0.08
Beryllium alkyls			
(C ₄ H ₉) ₂ Be	1.8	1.0	2.0
(C ₃ H ₇) ₂ Be	0	0	0.1
(C ₂ H ₅) ₂ Be	0.6	0.5	0.6
Volatiles	0	0	0.04
True density, g/cc	0.64	0.63	0.65
Bulk density, g/cc	0.30	0.35	0.38

*Analysis supplied by Ethyl Corporation.

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for several weeks with no visible signs of gassing. DTA analysis of the binder-fuel mixtures, shown in table XXXVII, indicated no major compatibility problem. Of the three Beane lots, lot B403-7 exhibited the poorest stability with an exotherm onset of 143°C and peak of 167°C compared with values of 164° and 180°C for the other two lots.

(U) Addition of beryllium or Beane resulted in a lowering of the exotherm peak temperature. This does not necessarily indicate a compatibility problem. Under normal processing, no compatibility problem between binder and fuel was observed.

d. Thermal Stability of Beryllium and BeH₂ Propellants

(U) DTA studies of cured and uncured propellant formulations were conducted as shown in table XXXVIII. The complete formulations had a lower onset temperature and a more uniform first exotherm peak temperature. Beane lot B403-7 showed somewhat poorer stability. The uncured propellant had slightly lower values, but this is not considered a significant variation. All samples exhibited satisfactory stability to permit propellant processing under normal conditions. All samples were well cured after 3 days ambient cure with no signs of gassing.

e. Impact Sensitivity of Propellant Formulations

(C) The impact sensitivities for the beryllium and BeH₂ propellants listed in table XXXIX compared favorably with an aluminum propellant with the same solids loading. The values of 13 kg-cm for uncured and 16 kg-cm for cured propellant containing aluminum were similar to values of 12 and 14 kg-cm for beryllium propellant and 11 and 13 kg-cm for Be-BeH₂ propellant. No undue impact sensitivity was noted in any of the samples tested.

(U) All three formulations, tested for friction sensitivity with the ESSO friction tester, produced negative results with no grit but positive results with Pyrex grit.

f. Toxic Propellant Formulations

(C) UTX-9860-1, listed in table XL contained beryllium as the fuel. The mix was cast as microtensile specimens and was well cured after 8 days at ambient temperatures. UTX-9860-2 and UTX 9860-3 were cast into a 1-lb motor. This motor was well cured after 10 days.

TABLE XL

(U) TOXIC PROPELLANT FORMULATIONS

Formulation No.	UTX 9860-1	UTX 9860-2	UTX 9860-3	UTX 9861-1	UTX 9861-2	UTX 9862-1	UTX 9860-4	UTX 9860-5	UTX 9860-6	UTX 9860-7	UTX 9860-8
PBEP	14.75	14.75	14.75	17.29	17.29	21.25	14.75	14.75	14.75	14.75	14.75
TVOPA	14.75	14.75	14.75	17.29	17.29	21.25	14.75	14.75	14.75	14.75	14.75
DMMDI	2.60	2.60	2.60	3.06	3.06	3.73	2.60	2.60	2.60	2.60	2.60
HT	0.34	0.34	0.34	0.40	0.40	0.48	0.34	0.34	0.34	0.34	0.34
DBTDA	0.53	0.53	0.53	0.62	0.62	0.77	0.53	0.53	0.53	0.53	0.53
AP	51.10	51.10	51.10	43.81	43.81	38.40	51.10	51.10	51.10	51.10	51.10
Beryllium	16.00	16.00	16.00	---	---	10.60	16.00	16.00	16.00	16.00	16.00
BeH ₂	---	---	-	17.52	17.52	3.53	---	---	---	---	---
Triol/PBEP(OH)	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70
NCO/OH	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Cure at ambient temperature, days	8	8	8	1	1	10	10	10	10	10	10

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(C)

TABLE XXXVII

(U) DTA STUDIES OF BERYLLIUM ON BeH_2 SYSTEMS

<u>Sample No.</u>	<u>Composition*</u>	<u>BeH_2 Lot</u>	<u>Onset to First Exotherm, °C</u>	<u>First Exotherm, °C</u>
234-1	PBEP/TVOPA	- - -	166	205
234-3-2	Beryllium	- - -	162	190
234-4-3	BeH_2	B403-7	143	167
234-5-1	BeH_2	B433-5	163	183
234-5-2	BeH_2	B439-441	165	179
234-4-2	AP	- - -	160	213
234-6-1	AP-Beryllium	- - -	167	175
234-6-2	AP- BeH_2	B433-5	168	184
234-6-3	AP- BeH_2	B403-7	145	183
234-6-4	AP- BeH_2	B439-441	160	179

*All samples contain PBEP and TVOPA.

(C) UTX 9861-1 and UTX 9861-2 were prepared to establish the variability of processibility of two different lots of BeH_2 in a viscous propellant formulation. As expected, these mixes containing 18% BeH_2 were extremely viscous. They could be cast but failed to flow after casting.

(C) UTX 9862-1 contained a BeH_2/Be ratio of 75/25. The mix was cast as microtensile specimens and was well cured in 10 days.

(U) Three 1-lb beryllium motors were cast from formulations UTX 9860-4 through UTX 9860-9. These were all well cured after 10 days at ambient temperatures. Two of the grains had casting

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(C)

TABLE XXXVIII

(U) DTA STUDIES OF BERYLLIUM AND BeH₂ PROPELLANTS*

<u>Sample No.</u>	<u>Cure</u>	<u>Beryllium or BeH₂ Lot</u>	<u>Onset to First Exotherm, °C</u>	<u>First Exotherm, °C</u>
234-8-1	Uncured	Beryllium	150	174
	Cured	Beryllium	157	172
234-8-2	Uncured	B433-5	148	174
	Cured	B433-5	150	175
234-8-3	Uncured	B403-7	143	174
	Cured	B403-7	151	177
234-8-4	Uncured	3439-441	150	177
	Cured	B439-441	155	179

*All samples are complete propellants containing 40% binder, 40% AP, and 20% beryllium or BeH₂.

(U)

TABLE XXXIX

(U) IMPACT SENSITIVITY

<u>Fuel</u>	<u>Cure</u>	<u>Impact Value, kg-cm</u>
Aluminum	Uncured	13
Aluminum	Cured	16
Beryllium	Uncured	12
Beryllium	Cured	14
Be-BeH ₂	Uncured	11
Be-BeH ₂	Cured	13

TABLE XL

(U) TOXIC PROPELLANT FORMULATIONS

Formulation No.	UTX 9860-1	UTX 9860-2	UTX 9860-3	UTX 9861-1	UTX 9861-2	UTX 9862-1	UTX 9860-4	UTX 9860-5	UTX 9860-6	UTX 9860-7	UTX 9860-8
PBEP	14.75	14.75	14.75	17.29	17.29	21.25	14.75	14.75	14.75	14.75	14.75
TVOPA	14.75	14.75	14.75	17.29	17.29	21.25	14.75	14.75	14.75	14.75	14.75
DMMDI	2.60	2.60	2.60	3.06	3.06	3.73	2.60	2.60	2.60	2.60	2.60
HT	0.34	0.34	0.34	0.40	0.40	0.48	0.34	0.34	0.34	0.34	0.34
DBTDA	0.53	0.53	0.53	0.62	0.62	0.77	0.53	0.53	0.53	0.53	0.53
AP	51.10	51.10	51.10	43.81	43.81	38.40	51.10	51.10	51.10	51.10	51.10
Beryllium	16.00	16.00	16.00	---	---	10.60	16.00	16.00	16.00	16.00	16.00
BeH ₂	---	---	-	17.52	17.52	3.53	---	---	---	---	---
Triol/PBEP(OH)	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70
NCO/OH	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Cure at ambient temperature, days	8	8	8	1	1	10	10	10	10	10	10

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TABLE XL

(U) TOXIC PROPELLANT FORMULATIONS (Continued)

Formulation No.	UTX 9860-9	UTX 9863-1	UTX 9863-2	UTX 9863-3	UTX 9863-4	UTX 9863-5	UTX 9864-1	UTX 9865-1	UTX 9866-1	UTX 9867-1	UTX 9868-1
PBEP	14.75	15.97	15.97	15.97	15.97	15.97	15.39	15.55	15.83	15.10	15.90
TVOPA	14.75	15.97	15.97	15.97	15.97	15.97	19.28	22.35	22.70	22.56	23.85
DMMDI	2.60	2.83	2.83	2.83	2.83	2.83	2.79	2.80	2.82	3.27	2.65
HIT	0.34	0.37	0.37	0.37	0.37	0.37	0.36	0.37	0.37	0.43	0.35
DBTDA	0.53	0.58	0.58	0.58	0.58	0.58	0.56	0.58	0.58	0.55	0.58
AP	51.10	54.30	54.30	54.30	54.30	54.30	49.09	46.70	45.80	46.06	45.80
Beryllium	16.00	10.00	10.00	10.00	10.00	10.00	---	---	---	---	---
BeH ₂	---	---	---	---	---	---	12.53	11.70	11.90	12.00	11.87
Triol/PBEP(OH)	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.60	0.50
NCO/OH	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.80	1.00
Cure at ambient temperature, days	10	5	10	10	10	10	3	3	3	10	10

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TABLE XL

(U) TOXIC PROPELLANT FORMULATIONS (Continued)

Formulation No.	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX	UTX
	9869-1	9870-1	9871-1	9873-1	9873-2	9873-3	9873-4	9873-5	9873-7	9873-8	9874-1	
PBEP	15.90	15.90	21.25	21.53	21.53	21.53	21.53	21.53	21.53	21.53	20.61	20.61
TVOPA	23.85	23.85	21.25	21.53	21.53	21.53	21.53	21.53	21.53	21.53	20.61	20.61
DMMDI	2.65	2.65	3.73	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.32	2.32
HT	0.35	0.35	0.48	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14
DBTDA	0.58	0.58	0.77	0.77	0.77	0.77	0.77	0.77	0.77	0.77	0.75	0.75
AP	45.80	45.80	38.40	39.20	39.20	39.20	39.20	39.20	39.20	39.20	40.74	40.74
Beryllium	---	---	3.53	3.60	3.60	3.60	3.60	3.60	3.60	3.60	3.43	3.43
BeH ₂	11.87	11.87	10.60	10.70	10.70	10.70	10.70	10.70	10.70	10.70	10.30	10.30
OH/PBEP(OH)	0.50	0.50	0.50	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
NCO/OH	1.00	1.00	1.00	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90
Cure at ambient temperature, days	10	10	10	8	5	8	8	8	8	14	14	14

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voids down one side where the propellant had failed to flow evenly. Because of the uneven burning surface, the conclusion was that it was unsafe to fire these motors. The formulation was modified to improve castability, and two motors were made from the UTX 9863 formulation. These motors were well cured after 10 days at 80°F. X-ray analysis indicated that no motor had more than three very small voids.

(U) UTX 9864-1 and UTX 9865-1, containing BeH₂, were castable but did not flow well after casting. Increasing the TVOPA/PBEP ratio in these formulations did not give adequate flow characteristics.

(C) UTX 9866-1, UTX 9867-1, UTX 9868-1, and UTX 9870-1 (listed in table XL) containing all BeH₂ and various particle sizes of AP, were prepared in a processing study. Even at a level of 12% BeH₂ and a TVOPA/PBEP ratio of 60/40, these formulations were too viscous to flow after casting.

(C) UTX 9871-1 was prepared to obtain the goal of a theoretical I_{sp} of 300 sec. It contained a mixture of BeH₂ and beryllium at a 75/25^{sp} ratio. This mix was very fluid without high TVOPA levels.

(U) Formulation UTX 9873-1 which contained a mixture of beryllium and BeH₂, cured in 5 days at ambient temperatures. The next six formulations listed in table XL were used to prepare three 1-lb motors. The last two formulations were cast as specimens for surveillance studies.

g. Microtensile Data

(C) The tensile data listed in table XLI demonstrate that good physical properties could be achieved with most lots of PBEP. The formulation containing Be-BeH₂ with PBEP lot 10001-186 had a crosshead tensile value of 93 psi and an elongation of 60%. One-pound motors were prepared using this formulation. Two formulations containing beryllium as the fuel but two different lots of PBEP had similar tensile values of 126 and 105 psi and identical elongations of 44%.

h. One-Pound Motor Data

(C) Three 1-lb motors containing beryllium with a theoretical I_{sp} of 284 sec were tested. During one firing the transducer part plugged

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(U)

TABLE XLI

(U) PHYSICAL PROPERTY DATA (CROSSHEAD)

<u>Fuel</u>	<u>PBEP Lot</u>	<u>Tensile, psi</u>	<u>Elongation, %</u>
Beryllium	9237-163A	126	44
Beryllium	9557-14	105	44
Be-BeH ₂	10001-186	93	60

and no values for characteristic exhaust velocity or specific impulse were obtained. The values in table XLII for the other two motors give an average I_{sp} of 265.5 sec for a 93.5% efficiency.

(C) A 1-lb motor containing both beryllium and BeH₂ and with a theoretical I_{sp} of 300 sec was test fired. The system overpressurized, and no data were obtained.

11. STABILIZATION STUDY

(U) Stabilization of PBEP propellants during long-term storage may be necessary if these propellants are to be feasible for use in many propulsion systems. One possibility is the use of additives as chemical stabilizers. A laboratory study was undertaken for the purpose of screening compounds in small gumstock samples.

(U) Various candidate stabilizers have been screened by DTA prior to their incorporation in propellant. Because TCP had appeared to stabilize a propellant cube over long-term storage, several similar compounds were incorporated into this screening program. Except for phosphites, most of the compounds tested were compatible with the PBEP-TVOPA binder system.

(U) Assuming that HF is the primary decomposition product from the binder, the product from the reaction of HF and a stabilizer were examined by IR. Results from this study indicated that the stabilization does proceed via fluoride addition to the stabilizer.

a. Compatibility Tests by DTA

(U) (U) Because TCP used as an additive had shown a stabilization effect during long-term storage for PBEP-TVOPA propellant, several

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(C)

TABLE XLII

(U) BERYLLIUM MOTOR DATA

<u>Motor No.</u>	<u>Propellant Weight, g</u>	<u>r_b in./sec</u>	<u>P_c psia</u>	<u>c^* ft/sec</u>	<u>I_{sp}^\dagger sec</u>
UTX 9860-6 and UTX 9860-7	403.4	0.708	521.1	5,570	266.6
UTX 9863-4 and UTX 9863-5	297.4	0.577	---	---	---
UTX 9863-2 and UTX 9863-3	346.0	0.255	284.3	5,383	264.4

[†] The I_{sp} values are ideal and corrected for a 0° half angle and 14.7 psia.

phosphorous-containing compounds were tested as stabilizer candidates. Phenyl acetylene was also screened as a possible stabilizer because it is known to add HF across the triple bonds. DTA tests, listed in table XLIII, were run on these compounds. These tests were conducted to find out if any special hazards would arise from adding these compounds to propellants. The tests were not expected to produce data to predict the additives effect as stabilizers.

b. Gumstock Studies

(C) The candidate stabilizers listed in table XLIV at the 0.5 wt-% level were tested in binder formulations stored at 60°C . The effectiveness of these additives were tested by following the weight loss of the samples. PA was the only compound that acted as a stabilizer after storage of 30 and 90 days. The sample containing this additive had a weight loss of 1.12% after 30 days and 4.34% after 90 days. This compares to the weight loss of standard samples except for the one containing activated charcoal, which had somewhat lower weight loss than the standard after storage of 30 and 90 days.

(U) The failure of TCP or other phosphorous compounds to exhibit any apparent stabilization may be caused by the formation of volatile products such as PF_3 or POF_3 . Under these storage conditions, the

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TABLE XLIII

(U) TEST OF STABILIZERS BY DTA*

<u>No.</u>	<u>Additive</u>	<u>Onset to First Exotherm, °C</u>	<u>First Exotherm, °C</u>	<u>Second Exotherm, °C</u>
1	(PBEP-TVOPA)	167	218	---
2	Trimethyl phosphate	135	179	190
3	Triethyl phosphate	126	182	197
4	Triphenyl phosphate	170	192	204
5	Tripropyl phosphate	128	176	200
6	Tris(2, 3-dibromo-propyl) phosphate	137	176	190
7	Tricresyl phosphate	152	191	193
8	Tributyl phosphate	141	188	207
9	Tris-n-butyl phosphine	160	Volatile	---
10	Triphenyl phosphine sulfide	132	139	---
11	Triethyl phosphite	39	72	---
12	Tris(2-chloroethyl) phosphite	55	93	178
13	Trilauryl trithio phosphite	86	102	177
14	Trimethyl phosphate	38	66	182
15	Tri-isopropyl phosphite	33	56	---
16	Triethyl phosphoro-acetate	122	176	197
17	Trimethyl phosphoro-acetate	132	172	---
18	Phenyl acetylene	140	171	---
19	Triallyl phosphate	119	178	---

*PBEP lot was 9557-14 in all samples.

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TABLE XLIV

(U) STABILIZER STUDY IN GUMSTOCKS*

<u>Stabilizer Candidate</u>	<u>Weight Loss, %</u>	
	<u>30 days</u>	<u>90 days</u>
Control-no stabilizer (average of three samples)	1.62	6.10
Tris (2, 3-dibromopropyl) phosphate	1.78	7.75
Triisopropyl phosphite	1.78	9.54
Tributyl phosphate	1.59	7.57
Triphenyl phosphate	2.17	8.33
Activated charcoal	1.35	5.59
Triphenyl phosphine sulfide	2.20	8.60
TCP	1.76	7.30
PA	1.12	4.34
Triallyl phosphate	2.13	7.20
Tris (2-chloroethyl) phosphite	2.01	6.95
Triethyl phosphate	1.63	7.36
Triethyl phosphono acetate	1.62	7.55
Triphenyl phosphine	2.03	8.50
Trilauryl phosphine	1.45	8.57
Linseed oil	1.83	6.65

*Storage temperature was 60°C.

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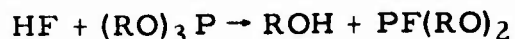
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stabilizer could have been used up too rapidly by the evolution of HF. This does not account for the decrease in stability observed in the 90-day storage for the samples containing the candidate stabilizers. It is possible that at this storage temperature and conditions, a secondary reaction is occurring that catalyzes further decomposition. Possibly the POF_3 or PF_3 products are reacting with moisture from the air to release HF, which then catalyzes further decomposition.

c. IR Studies on the Effect of Stabilizers

(U) Candidate stabilizers were investigated by IR analysis in an effort to gain some basic information about the stabilization mechanism. The pure compounds were first examined by IR, and the product was reexamined after HF was added. HF is assumed to be a major decomposition product (at least at low temperatures) from PBEP-TVOPA binder.

(U) One proposed mechanism by which a compound such as TCP could act as a stabilizer is outlined in the following equation



Examination of the product from reaction by IR indicates the appearance of bands for PF and OH indicating that the above mechanism has some validity.

12. ACCELERATED THERMAL TESTS FOR DETERMINATION OF STORAGE STABILITY OF PROPELLANTS

(U) The data from standard autoignition and DTA tests are not adequate to predict long-term storage stability of propellants. The adiabatic calorimeter has been used successfully by Rohm and Haas Company to predict stability of propellant systems. However, this apparatus was not available at UTC. Therefore, isothermal DTA and the Shell syringe test were evaluated.

a. Isothermal DTA

(U) The possibility that an isothermal DTA might be useful for determination of stability was explored. The usual DTA size samples of about 100 mg of standard propellant tested over a period of several

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days gave inconclusive results at 100°, 120°, 160°, and 170°C. The samples did not produce erratic temperature profiles that could not be related to either time or the temperature. Tests with a 2-g propellant at 160°C and a sample of PBEP at 170°C also produced inconclusive results. This method was abandoned as an accelerated thermal test.

b. Shell Syringe Test

(U) A series of tests were run to determine the feasibility of using the Shell gas evolution syringe test for prediction of storage stability of propellants. A standard propellant had less than 0.5 cc of gas per gram of sample in 9 days at 80°C. A sample of neat PBEP had approximately 4 cc/g in 6 days at 80°C, and a sample of PBEP containing 1.5% TCP had approximately 3 cc/g. Running the test in triplicate indicated that a wide scattering of data occurs. From the limited number of tests performed, as much as 20% scatter can be expected from this test technique. Therefore, only fairly gross differences in gassing rates can be considered meaningful unless numerous tests are run.

13. SURVEILLANCE STUDIES

(U) PBEP's thermal stability during long-term storage at elevated and ambient temperatures is important to its use as a high-energy binder for propellant systems. Surveillance studies of formulations with various lots of PBEP unstabilized and containing candidate stabilization additives have been made. Four types of surveillance samples were used: 1-lb motors; aluminum- and AlH₃-containing 2-in. cubes and microtensile specimens. All surveillance samples, listed in tables XLV and XLVI, were stored in a desiccated air atmosphere.

a. Microtensile Specimens

(C) Microtensile specimens of formulation UTX 8422 were stored at 25°C for 630 days without gross deterioration (see table XLVII). The physical properties after 630 days were 152-psi tensile and 29% elongation, compared with initial values of 130 psi and 23% elongation.

(C) This same formulation stored at 35°C exhibited behavior similar to the samples stored at 25°C. The tensiles, listed in table XLVIII, increased from an initial value of 130 psi to a value of 215 psi after 60 days, then decreased to 175 psi after 240 days of storage. The elongations increased slowly from an initial value of 23% to 30% during the 240-day test period.

TABLE XLV

(U) ALUMINUM SURVEILLANCE FORMULATIONS

Formulation No.	UTX 8422	UTX 8423-1	UTX 8430-1	UTX 8430-7	UTX 8430-8	UTX 9835-2	UTX 9836-2	UTX 9839-1	UTX 9840-1	UTX 9841-2	UTX 9842-1
PBEP	18.31	18.31	17.68	17.68	17.68	17.76	17.76	17.68	17.68	17.68	17.68
PBEP lot	9557-84	9088-180	9557-99A	9557-99A	9237-163A	9557-14	9557-14	9557-84	9557-84	9557-84	9557-84
TVOPA	18.31	18.31	17.68	17.68	17.76	17.76	17.76	17.68	17.68	17.68	17.68
Isocyanate	2.18	2.18	4.81	4.81	4.81	3.15	3.15	2.81	2.70	2.70	2.70
Type of isocyanate	TDI	TDI	DMMDI	DMMDI	DMMDI	DMMDI	DMMDI	DMMDI	DMMDI	DMMDI	DMMDI
HT	0.50	0.50	0.74	0.74	0.41	0.37	0.37	0.41	0.41	0.41	0.41
Catalyst	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64
Type of catalyst	FeAA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	FeAA
AP	47.05	47.05	45.18	45.18	46.28	46.66	46.66	46.39	45.89	46.89	46.89
Aluminaum	13.01	13.01	12.77	12.77	14.00	14.00	14.00	14.00	14.00	14.00	14.00
Stabilizers	---	---	0.50	0.50	---	---	---	0.50	0.50	---	---
Type of stabilizers	---	---	TCP	TCP	---	---	---	TCP	TCP-S	---	---
OH/PBEP(OH)	0.83	0.83	0.80	0.80	0.70	0.70	0.70	0.70	0.70	0.70	0.70
NCO/OH	0.98	0.98	1.00	1.00	1.00	1.00	1.00	0.86	0.86	0.86	0.86
Cure time, days	3	3	3	3	3	3	3	3	6	2	2
Cure temperature, °F	120	120	120	120	120	120	120	120	120	120	120

TABLE XLV

(U) ALUMINUM SURVEILLANCE FORMULATIONS (Continued)

Formulation No.	UTX 9850-1	UTX 9850-2	UTX 9851-1	UTX 9851-2	UTX 9852-1	UTX 9852-2	UTX 9853-1	UTX 9853-2	UTX 9854-1	UTX 9854-2
PREP	17.23	17.23	17.14	17.14	17.05	17.05	17.05	17.05	17.05	17.05
PIREP lot	9557-99A	9557-99A	9557-99A	9557-99A	9557-99A	9557-99A	9557-99A	9557-99A	9557-99A	9557-99A
TVOPA	17.23	17.23	17.14	17.14	17.05	17.05	17.05	17.05	17.05	17.05
Isocyanate	3.73	3.73	7.71	3.71	3.69	3.69	3.69	3.69	3.69	3.69
Type of isocyanate	DMMDI	DMMDI	DMMDI	DMMDI	DMMDI	DMMDI	DMMDI	DMMDI	DMMDI	DMMDI
HT	0.50	0.50	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49
Catalyst	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61
Type of catalyst	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA
AP	47.56	47.56	47.33	47.33	47.09	47.09	47.09	47.09	47.09	47.09
Aluminum	13.14	13.14	13.08	13.08	13.02	13.02	13.02	13.02	13.02	13.02
Stabilizers	---	---	0.50	0.50	0.50-0.50	0.50-0.50	0.50-0.50	0.50-0.50	0.50-0.50	0.50-0.50
Type of stabilizers	---	---	S	S	S-PA	S-PA	S-TCP	S-TCP	S-DPA	S-DPA
OH/PREP(OH)	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
NCO/OH	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90
Cure time, days	10	16	16	16	16	16	16	16	16	16
Cure temperature, °F	75	75	75	75	75	75	75	75	75	75

TABLE XLVI

(U) AIH₃ SURVEILLANCE FORMULATIONS

Formulation No.	UTX	UTX	UTX	UTX	UTX	UTX
	<u>10281-1</u>	<u>10282-1</u>	<u>10282-2</u>	<u>10284-1</u>	<u>10285-1*</u>	<u>11745-1</u>
PBEP	12.60	12.55	12.55	12.60	12.60	12.60
PBEP Lot	Raffinate †	10001-186E	10001-186E	10001-186E	10001-186E	10001-186H UTC Raffinate
TVOPA	18.89	18.83	18.83	18.91	18.91	18.89
AIH ₃	20.00	20.00	20.00	20.00	---	20.00
AIH ₃ Lot	02147A	02147A	02147A	02147A	---	02147A
Aluminum	---	---	---	---	20.00	---
AP	48.00	48.00	48.00	48.00	48.00	48.00
DBTDA	0.03	0.16	0.16	0.03	0.03	0.03
CTI	0.48	0.46	0.46	0.46	0.46	0.48
NCO/OH †	1.00	0.75	0.75	0.75	0.75	1.00

*This cube has an identical formulation to UTX 10284-1, except that aluminum is the fuel instead of AIH₃.

†This was raffinate PBEP lot 10469-160-2 from Shell Development Company

‡UTX 10281-1 NCO/OH ratio was based on 0.55 meq/g PBEP. All other formulations were based on 0.70 meq/g.

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TABLE XLVII

(U) SURVEILLANCE SAMPLES
(MICROTENSILE SPECIMENS AT 25° C)

<u>Days</u>	<u>UTX 8422*</u>	
	<u>Tensile, psi</u>	<u>Elongation, %</u>
0	130	23
90	222	22
180	195	27
270	163	25
365	151	25
450	158	25
540	159	29
630	152	29

*The PBEP lot was 9557-84, and the cure catalyst was FeAA.

TABLE XLVIII

(U) SURVEILLANCE SAMPLES
(MICROTENSILE SPECIMENS AT 35° C)

<u>Days</u>	<u>UTX 8422*</u>	
	<u>Tensile, psi</u>	<u>Elongation, %</u>
0	130	23
60	215	24
108	197	25
150	192	26
180	186	27
210	187	27
240	175	30

*The PBEP lot was 9557-84, and the cure catalyst was FeAA.

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(C) Microtensile specimens of formulation UTX 8430, which differed from UTX 8422 in both PBEP lot and cure catalyst, behaved differently when stored at 35°C. The tensiles listed in table XLIX increased from an initial value of 130 psi to 324 psi after 150 days, then remained almost constant for the next 120 days. The elongation values remained essentially constant, varying only between 15% and 18% during the surveillance time. Apparently, no gross deterioration occurred during storage at either 25° or 35°C.

b. One-Pound Motors

(C) Data from 1-lb motors stored for 18 months at 25°C are listed in table L. The motor stored for 18 months had a burning rate of 2.06 in./sec at 708 psi and gave a delivered I_{sp} of 251.0 sec at 0° half-angle corrected to 1,000 psi. The burning rate of this formulation was 1.26 in./sec at 867 psi with a delivered I_{sp} of 253 sec in the motor fired immediately after cure. The increase in burning rate was due mostly to separation between the propellant and the case wall. This separation also caused erratic burning rates for several other motors.

(C) Weight changes after storage are also listed in table L. Five of the motors remained essentially at the same weight. The only motor that had any significant change with a weight loss of 0.22% was the one in storage for only 3 months. The change was small enough to be caused by a slight weighing error. There was no significant performance loss.

c. Aluminum Surveillance Samples with Various PBEP Lots

(C) Several formulations for 2-in. surveillance cubes using different lots of PBEP are listed in table LI. Of the various formulations, only those containing either PBEP lot 9237-163A or lot 9557-84 have survived 284 days with no deterioration detectable by X-ray. UTX 9841-2, with PBEP lot 9557-84 and DBTDA as the cure catalyst, and UTX 9842-1, with the same lot of PBEP but with FeAA as the cure catalyst, have both shown no change after 574 days of storage. The least stable formulation, UTX 8431-1, containing PBEP lot 9557-99A, was terminated after 85 days as was UTX 8430-8, a similar formulation.

d. Aluminum Surveillance Samples - Stabilized Formulations

(C) Data for several 2-in. cubes containing stabilizers are listed in table LII. The test of UTX 8430-8 with no added stabilizer was

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TABLE XLIX

(U) SURVEILLANCE SAMPLES
(MICROTENSILE SPECIMENS AT 35°C)

UTX 8430*

<u>Days</u>	<u>Tensile, psi</u>	<u>Elongation, %</u>
0	130	18
45	230	18
66	170	17
100	215	15
120	287	16
150	324	17
240	314	15
270	319	16

*The PBEP lot was 9557-99A, and the cure catalyst was DBTDA.

TABLE L

(U) SURVEILLANCE SAMPLES
(ONE-POUND MOTORS)

<u>Time at 25°C months</u>	<u>Propellant Weight, g</u>	<u>r_b in. /sec</u>	<u>P_c psia</u>	<u>c* ft/sec</u>	<u>I_{sp}† sec</u>	<u>Weight Change, %</u>
0	451.0	1.263	867.0	5,302	253.0	---
3	402.3	1.289	658.1	5,097	244.0	-0.22
6	324.8	1.524	587.0	5,198	251.9	+0.02
9	401.0	1.506	694.0	5,254	250.8	+0.05
12	420.0	1.470	666.0	5,140	248.0	0.00
15	333.9	1.490	733.6	5,057	251.9	0.00
18	391.6	2.060	708.0	5,258	251.0	+0.02

†The I_{sp} values are ideal and corrected for 0° half-angle and 14.7 psia.

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TABLE LI

(U) ALUMINUM SURVEILLANCE SAMPLES*
(PBEP LOT VARIATION)

<u>Formulation No.</u>	<u>Storage Time days</u>	<u>PBEP Lot No.</u>	<u>Cure Catalyst</u>	<u>Status of Test</u>
UTX 8423-1	172	9088-180	DBTDA	Terminated
UTX 8431-1	85	9557-99A	DBTDA	Terminated
UTX 9835-2	532	9237-163A	DBTDA	Continued
UTX 9836-2	284	9557-14	DBTDA	Terminated
UTX 9841-2	574	9557-84	DBTDA	Continued
UTX 9842-1	574	9557-84	FeAA	Continued

*The storage temperature was 35° C for all samples

TABLE LII

(U) ALUMINUM SURVEILLANCE SAMPLES*
(STABILIZED FORMULATIONS)

<u>Formulation No.</u>	<u>Storage Time days</u>	<u>PBEP Lot No.</u>	<u>Stabilizer</u>	<u>Status of Test</u>
UTX 8430-8	85	9557-99A	---	Terminated
UTX 8430-7	668	9557-99A	TCP	Continued
UTX 9839-1	244	9557-84	TCP	Terminated
UTX 9840-1	244	9557-84	TCP-S	Terminated

*The storage temperature for all samples was 35° C, and the cure catalyst was DBTDA in all formulations.

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terminated after 85 days. UTX 8430-7, the same formulation with TCP added as a stabilizer, has survived over 668 days at 35°C with no signs of decomposition. Tests of formulations containing PBEP lot 9557-84 with either TCP or TCP and sulfur as stabilizers were both terminated after 244 days. However, UTX 9841-2 and UTX 9842-1 (listed in table LI), which contain PBEP lot 9558-84 but no stabilizers, were still being tested after 574 days of storage. It appears that TCP may stabilize PBEP lot 9557-99A but may actually be compatible with PBEP lot 9557-84. There was enough variation between lots that a stabilizer for one lot may not have been a stabilizer for a second lot.

e. Aluminum Surveillance Samples - Stabilized Formulations at Two Temperatures

(C) Ten 2-in. cubes of five identical formulations were prepared to test the relative effectiveness of stabilizers at both 35° and 45°C. The first two formulations listed in table LIII were prepared without stabilizers as controls. Formulation UTX 9850-1 survived 112 days at 35°C and only 98 days at 45°C. The only formulation to last more than 98 days at 45°C without decomposition was UTX 9851-2, which contained sulfur as a stabilizer. However, tests of this formulation at 35°C were terminated at the same time. The only formulation to survive any significant length of time at either temperature was UTX 9852-1, which was stored at 35°C and which contained sulphur and PA as stabilizers. Variation of TVOPA lots among the surveillance formulations had not been taken into account. This variation may explain discrepancies of the data in the various surveillance tables.

f. AlH₃ Surveillance Samples

(C) All 2-in. cubes containing AlH₃ (see table LIV) failed within 2 weeks at either 35° or 45°C. Even UTX 10281-1, which contained raffinate PBEP from Shell Development Company, failed within this time period. These samples showed deterioration at ambient temperatures with the deterioration accelerating at the higher temperatures. A cube of formulation UTX 11745-1 using raffinate PBEP prepared at UTC has shown no decomposition detectable by X-ray after storage for 5 weeks at 25°C. Formulation UTX 10285-1, a control with aluminum instead of AlH₃ as the fuel, is still intact after storage for 144 days at 35°C.

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TABLE LIII

(U) ALUMINUM SURVEILLANCE SAMPLES*
(STABILIZED FORMULATIONS AT TWO TEMPERATURES)

<u>Formulation No.</u>	<u>Storage Time days</u>	<u>Storage Temperature °C</u>	<u>Stabilizers</u>	<u>Status of Test</u>
UTX 9850-1	112	35	---	Terminated
UTX 9850-2	98	45	---	Terminated
UTX 9851-1	140	35	S	Terminated
UTX 9851-2	140	45	S	Terminated
UTX 9852-1	406	35	S-PA	Continued
UTX 9852-2	98	45	S-PA	Terminated
UTX 9853-1	98	35	S-TCP	Terminated
UTX 9853-2	98	45	S-TCP	Terminated
UTX 9854-1	168	35	S-DPA	Terminated
UTX 9854-2	98	45	S-DPA	Terminated

*In all formulations, the PBEP lot was 9557-99A, and the cure catalyst was DBTDA.

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(C)

TABLE LIV

(U) AlH_3 SURVEILLANCE SAMPLES
(2-in. Cubes)

<u>Formulation No.</u>	<u>Storage Time days</u>	<u>Storage Temperature °C</u>	<u>PBEP Lot</u>	<u>Results</u>
UTX 10281-1	14	45	10469-119-2 (raffinate)	Terminated
UTX 10282-1	14	45	10001-186	Terminated
UTX 10282-2	14	45	10001-186	Terminated
UTX 10284-1	14	35	10001-186	Terminated
UTX 10285-1*	144	35	10001-186	Continued
UTX 11745-1	28	25	10001-186	Continued

*This cube had an identical formulation to UTX 10284-1 except aluminum was the fuel instead of AlH_3 .

g. HAP Propellant Surveillance

(C) Formulation UTX 10808-1 in table XXXIV contained HAP and AlH_3 as the fuel. The propellant had poor crosshead physical properties of 15-psi tensile, 38% elongation and a Shore A of 45. After storage for 1 week at 35°C, the samples had degraded to a soft mass and were discarded. A sample of UTX 10809-1 containing aluminum instead of AlH_3 also showed similar degradation after 1 week at 35°C.

h. Surveillance Studies of Beryllium and BeH_2 Propellants

(C) Samples containing beryllium and Be- BeH_2 were stored for 1 year at 80°F. Shore A measurements, listed in table LV, were taken before and after storage. All values increased during this time by 10 to 20 which could be expected from postcure. No deterioration was noted by visual inspection, and the specimens were still quite flexible.

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(C)

TABLE LV

(U) BERYLLIUM AND BeH₂ SURVEILLANCE STUDIES*

<u>Formulation No.</u>	<u>Fuel</u>	<u>Shore A Measurement</u>	
		<u>Initial</u>	<u>Final</u>
UTX 9860-1	Beryllium	65	85
UTX 9862-1	Be-BeH ₂	60	80
UTX 9863-1	Beryllium	55	70
UTX 9871-1	Be-BeH ₂	55	65
UTX 9873-1	Be-BeH ₂	60	70

*These samples were stored for 1 year at 80° F.

i. Summary and Conclusions from Surveillance Studies

(C) Microtensile specimens stored at either 25° or 35° C for periods of up to 630 days have shown little degradation of physical properties during surveillance. Much of the change found in the physical properties during storage could be attributed to postcure rather than deterioration of the specimens.

(C) Large variations in surveillance stability was found among various lots of PBEP. Formulations containing some lots only survived 85 days at 35° C; other lots survived 284 to over 500 days.

(C) TCP and PA have shown promise as stabilizers for PBEP propellants. However, their stabilizing effect will vary, depending on the lot of PBEP used in the formulation.

(C) AlH₃-PBEP-TVOPA propellants will not survive storage for any reasonable time period unless a more stable binder system can be developed.

(C) HAP propellants, at least with the all-CTI cure system, will not age (even at 35° C) without complete degradation of physical properties.

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(C) Beryllium and BeH_2 propellants are apparently stable for long periods at temperatures near ambient conditions. The only change noted in the surveillance samples was an increase in Shore A values, which is probably due to postcure and not degradation.

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SECTION III

SUMMARY AND CONCLUSIONS

(U) Beryllium and BeH_2 showed no major incompatibility with PBEP-TVOPA binders, either by DTA tests or by long-term surveillance at 80°F . The samples stored at 80°F for 1 year contained both beryllium and BeH_2 . The only change noticed after aging was an increase in Shore A values, which could have been due to postcure. Beryllium and BeH_2 propellants have similar impact sensitivities as aluminum propellants.

(U) Isothermal DTA and the Shell syringe test were evaluated as methods for predicting long-term storage stability of propellants. Results for either method were too scattered to be useful.

(U) The polyfunctional isocyanates (especially CTI) which were tested did not produce cured propellants with physical properties as good as obtained with DMMDI and hexanetriol. Improvements were noted over an all-CTI system when CTI was used in conjunction with a diol.

(U) The lowest molecular weight fraction of the six separated from a sample of PBEP contributes to the thermal instability of the unfractionated polymer. Its functionality of less than 1.0 is unattractively low. The highest molecular weight fraction had an apparently higher functionality than would be predicted from an ideal polymerization of epichlorohydrin. The results of this study were from a single lot of PBEP which was thought to be representative. Until studies of other lots confirm these findings, any conclusions drawn must be tentative. Nevertheless, it appears that improvement in thermal stability should result from the elimination of the lowest molecular weight fraction and that cure reproducibility could be improved by the elimination of the highest and lowest molecular weight fractions.

(C) The preferred cure systems for HAP propellants appeared to be the aliphatic polyisocyanate, CTI, in conjunction with an aliphatic diisocyanate such as H_{12} MDI or HMDI. HAP propellants gave stable combustion in strand tests when well restricted. The burning rate and pressure exponent were similar to those obtained with comparable AP propellants.

(U) PBEP propellant that will withstand long-term storage at elevated temperatures (at least at 35°C) can be prepared. One aluminized 2-in. cube completed storage for more than 600 days at this temperature with no

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apparent decomposition when examined by X-ray. One-pound motors fired after 18 months storage at 25° C produced data indicating very little loss in weight or in ballistic performance during storage. Tensile data from specimens stored at 25° or 35° C indicated that no gross deterioration of the samples had occurred during surveillance.

(U) The raffinate prepared at Shell Development Company had hazard properties similar to other PBEP lots. DTA studies indicated that the raffinate PBEP was more thermally stable than the precursor lot of PBEP. The most significant difference between the raffinate and standard PBEP was the very low level of catalyst necessary to cure the raffinate. The treatment by Shell Development Company not only took out low molecular weight ends (as witnessed by an increase in molecular weight from approximately 4,000 to about 6,000) but also took out other impurities as indicated by the lack of the carboxyl band in the IR spectra of the raffinate.

(C) Raffinate PBEP prepared at UTC by the Roberto method was found to have similar cure characteristics and IR spectra as raffinate PBEP prepared at Shell Development Company. The resulting propellants in either case had no better physical properties than propellants prepared from untreated PBEP.

(U) The OH impurity in TVOPA appeared to affect the cure of PBEP at NCO/OH ratios that were just high enough to cure the PBEP. However, propellant formulations included enough isocyanate curative to compensate for the OH in the TVOPA.

(U) Of the HF-resistant catalysts tested for cure efficiencies in propellants, two recommended by ESSO, Me_2SnCl_2 and BuSnCl_3 , appearing to be the most effective. However, BuSnCl_3 produced too short a pot life at about 0.008 wt-% and erratic cures below this wt-% load. Me_2SnCl_2 appeared to be a very good catalyst, with good pot life on scaleup, with either all-CTI or CTI-DPG cure system but was less efficient with a mixed isocyanate system.

(C) Treatment of PBEP and TVOPA with 13X molecular sieves improved the reproducibility of cure on scaleup. A fixed catalyst level could be used on increasing the batch size from 50 to 2,500 g. Previously, the large amount of catalyst necessary to obtain cures on scaleup led to problems with pot life. Using the treated materials, less catalyst was necessary for scaling the batch size, thus, adequate pot life and a well-cured propellant were obtained.

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13. ABSTRACT Unclassified Abstract Toxic propellant fuels were compatible with the PBEP-TVOPA binder. Samples of propellants containing these ingredients stored at ambient temperatures for 1 year showed no apparent deterioration. The polyfunctional isocyanates (especially CTI) which were tested did not produce cured propellants with physical properties as good as those obtained with DMMDI and hexanetriol. The preferred cure systems for HAP propellants appeared to be the aliphatic triisocyanate, CTI, in conjunction with an aliphatic diisocyanate such as H ₁₂ MDI or HMDI.			

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
PBEP						
TVOPA						
HAP						
beryllium						
BeH ₂						
AlH ₃						