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AD 525314

DEVELOPMENT AND TEST OF A NEW PROPELLANT

FINAL TECHNICAL REPORT, AFRPL-TR-73-25

APRIL 1973

HERCULES INCORPORATED
BACCHUS WORKS
MAGNA, UTAH

D D C

[redacted]

AFRPL-TR-73-25

(Unclassified Title)

DEVELOPMENT AND TEST OF A HIGHLY ENERGETIC DOMINO PROPELLANT

FINAL TECHNICAL REPORT, AFRPL-TR-73-25

April 1973

HERCULES INCORPORATED
Bacchus Works, Magna, Utah

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FOREWORD

(U) This is the final report to be issued under Contract F04611-C-68-0081, "Development and Test of a Highly Energetic "DOMINO" Propellant." The technical work was performed by the Research and Development Group, Bacchus Works, Chemical Propulsion Division, Hercules Incorporated.

(U) Preparation of this report is authorized under Contract F04611-68-C-0081 in accordance with Item B005, Exhibit B, Contract Data Requirements List. This contract is sponsored by the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California. The project officers have been Richard Pallett from June 1968 to July 1970, Capt James W. Hold, Jr. from July 1970 to February 1971, Capt Dayton Silver from March 1971 to August 1971, and Capt Arnold M. Crelier from September 1971 to the conclusion of the effort.

(U) The report deals with the use of classified propellant ingredients and is, therefore, classified "Confidential".

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

ARNOLD M. CRELIER
Capt, USAF, Project Officer

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CONFIDENTIAL ABSTRACT

(C) The objective of this program was to demonstrate a practical high energy propellant containing a difluoramine binder, AlH_3, and the advanced oxidizer, hydroxylammonium perchlorate (HAP).

(C) While considerable technology had been demonstrated with these energetic ingredients, there were several problems which had to be solved before the attractive specific impulse and density of an advanced system could be realized in a practical propellant. This program was designed to explore the problems of in-process hazards, system compatibility and stability, and reproducible cures. Included in this program were (1) a comparison of TVOPA plasticized P-BEP binder with low energy polymers highly plasticized with TVOPA, (2) scale up of propellants based on TVOPA/AP/AlH_3, and (3) a study of the feasibility of incorporating HAP into a difluoramino binder.

(C) Results obtained early in the program indicated that HAP is not usable in the difluoramine binders. Compatibility testing indicated considerable interaction, and coating the HAP did not resolve the problem. A 2-in. cube of P-BEP/HAP propellant ignited after 10 hr at 75° C placing this propellant in the ICC forbidden category. Effort on developing HAP propellants was, therefore, discontinued in favor of increased efforts in binder development.

(C) Two DOMINO binders were developed and scaled up with AlH_3 fuel and HMX and/or AP oxidizer. The primary effort was placed on developing a TVOPA plasticized P-BEP binder. An alternate binder based on a low energy polymer highly plasticized with TVOPA (TVOPA/polymer ratio of 7/1) was developed and propellant using this binder was scaled up when aging problems developed with the P-BEP binder.

(C) The development of the TVOPA plasticized P-BEP binder required extensive ingredient characterization and catalyst studies to achieve satisfactory mechanical properties and cure rate/pot life trade off. Impurities in the P-BEP and in the TVOPA interfered with the cure reaction by reacting with the isocyanate and by poisoning the catalyst. Careful adjustment of the cure stoichiometry and protection of the catalyst by placing it on molecular sieves produced AlH_3-AP propellant having satisfactory mechanical properties and a reproducible cure. Five pound motor firings of the P-BEP/TVOPA/AP propellant containing 18-percent AlH_3 produced a delivered impulse (I^{15}_{1000}) of 266 sec with an efficiency of 94 percent. Accelerated aging studies of the P-BEP propellants, both with Al and AlH_3 fuels, indicate very short shelf life for these propellants. The primary cause of failure is CO_2 gassing from the binder. Because of the short shelf life of the P-BEP binder propellants, effort was concentrated on developing and scaling up propellants based on an alternate binder.

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(C) Three low energy polymers were evaluated for use with TVOPA in the alternate binder development. An ethyl acrylate-acrylic acid (EAAA) copolymer cured with an epoxide shows considerable promise. However, an adequate low temperature cure which is required to prevent gassing from AlH_3 was not achieved; therefore, emphasis was placed on urethane cured polymers which do cure at low temperatures. An ethyl acrylate-hydroxy ethyl acrylate (EA-HEA) copolymer failed to give satisfactory mechanical properties, but a copolymer of diethylene glycol-adipic acid (Multron R-18) did give satisfactory mechanical properties, especially when the TVOPA was purified to remove an isocyanate reactive impurity.

(C) The TVOPA/R-18 binder was scaled up to 10-quart Hobart and 5-gallon Day mixes. Two propellants were fired in 5-lb motors: VKU contained 22 percent AlH_3 and all AP oxidizer, and VKW containing 18 percent AlH_3 and 10 percent of the AP replaced with HMX. Both gave the same delivered impulse (265.3 sec); so the more dense VKW propellant was selected for scaleup to a 15-lb motor. The delivered impulse I^{15}_{1000} of 267.0 sec and efficiency of 94.5 percent indicate that high efficiency and impulse is achievable from the DOMINO AlH_3 propellant system.

(C) Accelerated aging testing of the VKW propellant was performed on 2-in. cracking cubes and by off-gas analysis. Results indicate that when a rapid low temperature cure is achieved, 2-in. cubes have a reasonable shelf life with a predicted life of 5 years at 25° C. However, if the cure rate is slow, general microporosity will occur. CO_2 generation during cure is sufficient to cause porosity if the propellant remains in a low modulus state for more than a day or two. Shelf life prediction of a 70-lb BATES motor resulted in similar conclusions. With a rapid cure the propellant will survive cure and will not fail until the hydrogen generation from AlH_3 accelerates markedly from its normal generation rate.

(U) A time extension of this contract permitted the preparation of a 40-pound motor of related propellant which was developed on the follow-on contract, F04611-70-0067. The propellant (VML) was similar to VKW, except the ratio of TVOPA to polymer was lowered and the HMX was replaced by AP to reduce the sensitivity and improve the shelf life of the VML propellant. Extensive in-process and in-use hazards, shelf life, and ballistic testing was performed on VML in the follow-on contract.

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LIST OF ABBREVIATIONS

Abbreviation	Meaning
AFRPL	Air Force Rocket Propulsion Laboratory
Al	aluminum
AlH_3	aluminum hydride
Alon C	submicron Al_2O_3
Al_2O_3	aluminum oxide
AP	ammonium perchlorate
CO	chromium octoate
CO_2	carbon dioxide
CWX-105	Linde molecular sieves containing 10 weight percent DBTDL
DBDTA	dibutyltin diacetate
DBTDL	dibutyltin dilaurate
DMDI	diphenyl methane diisocyanate
EAAA	ethyl acrylate acrylic acid
EA-HEA	ethyl acrylate-hydroxyethyl acrylate
E/C	epoxy/carboxyl ratio
ESD	electrostatic discharge
F	fluorine
FeAA	ferric acetyl acetonate
FHA	double base propellant containing AlH_3
FJAI	Fisher-John autoignition
H_2	hydrogen
HAP	hydroxylammonium perchlorate
HCN	hydrogen cyanide
HDI	hexamethylene diisocyanate

LIST OF ABBREVIATIONS (Cont)

Abbreviation	Meaning
HF	hydrogen fluoride
HMX	cyclotetramethylene tetranitramine
H_2O	water
HT	1,2,6 hexanetriol
ICC	Interstate Commerce Commission
IR	infrared
I_{sp}	specific impulse
LPC	Lockheed Propulsion Company
mq	milliequivalents
mg	milligrams
Mondur TM	triphenylmethane triisocyanate-20 weight percent in methylene dichloride
NBA	n-butylamine
N_2	nitrogen
N_2O	nitrous oxide
NCO	isocyanate
NF_2	difluoramino
OH	hydroxyl
PAPI	polymethylene poly-phenylisocyanate
P-BEP	poly [1,2-bis(difluoramino) - 2, 3-epoxy-propane]
P-K-r	pressure-S/A_t-rate
PPG-2025	polyoxypropylene glycol of 2,000 molecular weight
R-18	polydiethylene glycol adipic acid

LIST OF ABBREVIATIONS (Cont)

Abbreviation	Meaning
STP	standard temperature, pressure
TCP	tricresyl phosphate
TDI	toluene diisocyanate
TPMTI	triphenylmethane triisocyanate
TVOPA	1,2,3-tris [α, β-bis (difluoramino) ethoxy] propane
UNOX 221	old trade name for ERL 4221 (3, 4-Epoxy-cyclohexylmethyl-3, 4-epoxy-cyclohexane carboxylate)
UTC	United Technology Center
VKN	non-AlH_3 DOMINO propellant
VKO	23-percent AlH_3 DOMINO propellant
VKP	18-percent AlH_3 DOMINO propellant

SECTION I

INTRODUCTION

A. BACKGROUND

(C) Difluoramino binder materials have demonstrated three advantages over conventional materials: Specific impulse, density, and specific impulse efficiency. P-BEP, poly [1,2 bis(difluoramino) 2, 3 epoxy propane], offers these advantages with the potential of good ambient temperature properties. TVOPA, 1,2,3, tris[a,β-bis (difluoramino) ethoxy] propane, is an available energetic plasticizer for P-BEP. Propellants based on P-BEP and TVOPA in conjunction with aluminum hydride (AlH_3) offer important improvements in delivered specific impulse over other "non-toxic" propellants. By employing an advanced oxidizer such as HAP, the density penalty incurred with AlH_3 can be avoided and additional specific impulse can be gained.

(C) An alternative to the P-BEP binder is a low energy polymer such as the epoxy-cured EAAA prepolymer plasticized with TVOPA. This system offers essentially the same delivered impulse potential and density as the P-BEP binder.

(C) While considerable technology has been demonstrated with these energetic ingredients under previous programs, there are several problems which must be solved before the attractive specific impulse and density of an advanced system are realized in a practical propellant. These problems include: (1) greater in-process hazards, (2) poorer system compatibility and stability, (3) ingredient hygroscpoicity, and (4) obtaining optimum and reproducible cures from P-BEP. In addition, final utilization of the propellant will also be limited unless techniques are developed to significantly decrease the intrinsically high burning rate associated with difluoramino binders and to improve the comparatively poor shelf life resulting from the incorporation of present quality AlH_3.

B. OBJECTIVE

(C) The objective of this program was to demonstrate a practical high energy propellant based on a difluoramino binder containing AlH_3 and an advanced oxidizer. The ultimate performance objective was a delivered impulse of 272 lbf-sec/lbm (15 degree half-angle, 1000/14.7 psia) at a propellant density of 0.063 lb/in.^{3}.

C. PROGRAM DEFINITION AND SCOPE

(U) The technical program was accomplished in three phases. Phases I and II were carried out concurrently with the early part of Phase III. In Phase I, a comparison of P-BEP and TVOPA plasticized acrylate binders in combination with AP and HAP were made. In this phase the ingredient control and process studies were conducted to support a successful scaleup

(U) effort. In Phase II, the P-BEP/TVOPA/AlH_3/AP system was more fully explored and selected propellants scaled up through the 70-lb level. The Phase III effort was designed to demonstrate the feasibility of a difluoramino binder with HAP.

(C) Early in the program, insurmountable compatibility problems were encountered with HAP, which led to the abandonment of this oxidizer in favor of additional effort with AP and a combination of AP and HMX. A serious problem of shelf life with P-BEP led to the replacement of this polymer in the program by the low energy polymers EAAA and a hydroxyl terminated copolymer of diethylene glycol and adipic acid (R-18).

SECTION II

INGREDIENT CHARACTERIZATION AND COMPATIBILITY STUDIES

(U) Previous work by Hercules under contract AF33(615)-5420[1] had shown that a potential compatibility problem exists between the advanced oxidizer, HAP, and the P-BEP binder. These results indicated the need for additional analysis and testing to determine whether a safe system could be found for processing a HAP/DOMINO propellant.

(U) The stability of P-BEP and AlH_3, both neat and in propellant, were also of major concern. As a consequence, additional effort was required to provide gas generation rate data from these materials in propellants and to refine shelf life prediction models.

(C) In addition to the compatibility problem between the P-BEP binder and HAP, problems concerning the cure of P-BEP have also seriously limited the development of P-BEP propellants. These problems have been characterized by poor reproducibility in mechanical properties and propellants that have failed to cure upon scaleup which had previously cured well in the laboratory. A serious problem with catalyst demand increasing as mix size increases has been reported by United Technology Center[2] in conjunction with the scaleup problem. As a consequence, it was desirable to compare the properties of a difluoramino binder utilizing an epoxy cure to the P-BEP urethane cured system. The epoxy-cured EAAA prepolymer, plasticized with TVOPA, offers promise of approaching the performance levels of the P-BEP system. A comparison of the two binder systems containing AlH_3 and both AP and HAP was desirable.

(U) The effort discussed in this section is divided into:

(1) Ingredient characterization

(2) Stability and compatibility testing

A. INGREDIENT CHARACTERIZATION

(U) Preliminary characterization of the three basic ingredients, P-BEP, TVOPA, and AlH_3 was conducted early in the Phase I effort. This characterization provided support for the compatibility and stability testing in Phase I.

[1,2] Refer to List of References

1. P-BEP and TVOPA

a. General Testing

(C) Analytical testing of the major fluorine containing propellant ingredients, P-BEP and TVOPA, was in essence performed as outlined by previous investigators with the exception of a few necessary and appropriate modifications. Unlike most previous work on these types of materials, the analytical methods used for the characterization were designed to accommodate macro-sized samples. Thus, small changes in samples might more easily be measured. For instance, percent carbon, hydrogen, and nitrogen (C, H, and N) were determined by weighing gram quantities of the sample, diluting of and taking an aliquot for analysis. Measurements of fluorine in P-BEP and TVOPA were scaled up to a macro technique by performing appropriate base hydrolyses on macro-sized samples. The fluoride was then measured by a direct titration with lanthanum (III), using a fluoride ion specific electrode. The micro technique, used previously for this purpose, utilized a Schoniger combustion with a colorimetric determination for fluoride.[3]

(C) Hydroxyl determinations on P-BEP were made directly by infrared (IR) and indirectly by an isocyanate demand technique. This latter method, developed by Hudson, et.al., at Esso,[4] depended on reaction of the sample hydroxyl functionality with toluenesulfonyl isocyanate (TSNCO) and measurement of the isocyanate (NCO) take-up by IR. This isocyanate demand method was also applied to TVOPA as this compound was found to consume a significant amount of isocyanate. This determination on TVOPA replaced IR hydroxy and vinoxy determinations since adequate standards for the measurement of these functional groups were not available.

(U) Solids in "as received" P-BEP and TVOPA were determined gravimetrically after vacuum stripping of solvent. Moisture and residual solvent determinations were performed by gas chromatographic techniques.

(C) As previously stated, the determination of elemental fluorine in P-BEP incorporated a base-hydrolysis step. Though P-BEP was very difficult to hydrolyze, a thorough hydrolysis was obtained through the use of a combination of piperidine (suggested in a report by Fokin et.al.)[5] and tetrabutyl-ammonium hydroxide in ethanol. The hydrolyzed fluoride was then determined by a potentiometric titration with lanthanum (III), using a fluoride ion specific electrode as recommended by Lingane.[6]

---

3 through 6 Refer to List of References

(C) This fluorine determination initially constituted a problem as the fluorine content of the samples varied with the degree to which the samples were stripped of residual solvent. Invariably, longer evacuations of samples produced lower elemental fluorine analyses. For instance, an incoming P-BEP sample, still in methylene chloride, was found to be composed of 42.3 percent fluorine. After a 22 hr nitrogen purge, this value remained unchanged. However, after a 48-hr evacuation the fluorine content dropped to 41.5 percent. The fluorine content of this sample was further diminished to 39.8 percent by extended exposure of the sample to water-saturated methylene chloride, followed by a stripping of this solvent.

(C) This volatile fluorine compound, lost by P-BEP, was identified as hydrogen fluoride (HF). Identification was accomplished by titrating both the hydrogen and fluoride ions in water washes of incoming methylene chloride solutions of P-BEP. A typical wash was titrated with 0.05N tetrabutyl-ammonium hydroxide to measure the equivalents of strong acid present. Then, the sample solution was adjusted to a pH of 4.0 and titrated with 0.2N lanthanum (III) nitrate in a manner already described to determine the equivalents of fluoride. The equivalents of hydrogen and fluoride ions were invariably identical in every wash.

(C) The effect of stripping P-BEP was also followed by elemental nitrogen analysis and isocyanate demand determinations. No measurable changes were observed in the nitrogen content of P-BEP. The isocyanate demand of P-BEP, however, did change with evacuation. This change is discussed in paragraph b.

(C) The characterization of TVOPA was performed in a manner similar to that used for P-BEP. Again, the elemental fluorine content of TVOPA was determined after a base hydrolysis step. However, a complete hydrolysis was obtained with sodium hydroxide in methanol with this compound. Once hydrolyzed, the fluoride was determined in the same manner described for P-BEP. In contrast to P-BEP, however, TVOPA stripping was readily accomplished without loss in fluorine. Moreover, HF was never detected in Freon solutions of this compound. The determination of solids, trace water, and Freon in TVOPA was performed as described earlier for P-BEP. Although TVOPA was used in this program as a plasticizer, it was found that neat TVOPA contained substantial amounts (up to half the reactivity of P-BEP in some cases) of an isocyanate-reactive functional group. Consequently, isocyanate demand determinations were performed on TVOPA also. A continued discussion of this determination is presented in paragraph b.

b. Isocyanate Demand Test

(U) The use of TSNCO for the determination of the hydroxyl equivalent of polymeric binder materials is based on a one-to-one equivalent reaction of the isocyanate with the hydroxyl groups of the polymer. The high reactivity of this isocyanate allows the reaction with secondary hydroxyl groups to be complete in approximately 24 hr in the absence of

(U) a catalyst. Possible side reactions which may alter the one-to-one isocyanate-to-hydroxyl reaction ratio will affect the method.

(C) The isocyanate demand test was run by allowing either P-BEP, TVOPA, or a mixture of the two materials to react with a known amount of TSNCO for 24 hr. The TSNCO was standardized by reaction with a known amount of n-Butanol. The isocyanate content of the solution was measured by an IR method before and 24 hr after addition of the material to be analyzed. The amount of isocyanate, consumed during the 24 hr period, was used to calculate the hydroxyl equivalent of the material.

(C) The P-BEP polymer was received from the manufacturer as a 27 percent solution in methylene chloride. The equivalent weight of the P-BEP polymer (Lot No. 10316-134), as determined by the above isocyanate demand method, was found to be 1670 gm after correction for the solids level of the solution. The water content of the P-BEP solution was found to be 0.08 percent by a gas chromatographic method.

(C) The equivalent weight of "neat" P-BEP (Lot No. 10316-134) was found to average 2240 gm using the TSNCO method. This agreed with an average value of 2210 gm as determined by a direct IR method using polypropylene glycol as a standard. The "neat" P-BEP had been stripped of methylene chloride by sparging with dry nitrogen and storing in a vacuum dessicator for 24 hr. The water content of the "neat" P-BEP was found to be 0.09 percent by a gas chromatographic method. (The presence of both water and HF in the "as received" P-BEP solution was thought possible to cause side reactions and thus cause the differences in the equivalent weight of the P-BEP before and after stripping. Therefore, additional studies were undertaken to explore these possible side reactions.)

(U) In order to study the effects of water on the isocyanate demand test, known amounts of water were added to a solution of TSNCO. Thus, the reaction of the added water could be followed by the rate of disappearance of the isocyanate band at 2235 cm^{-1}. The reaction curves of several water concentrations are plotted in Figure 1. The curves show that the reaction of TSNCO with water is essentially complete in 3 to 4 hr. The amounts of isocyanate which were consumed in a 23-hr period corresponded approximately to a one-to-one equivalent reaction. This reaction was confirmed by the IR identification of pure P-toluenesulfonamide in the dried residue from a methylene chloride solution containing TSNCO and water.

(C) Water was thus found to react very rapidly with toluenesulfonyl isocyanate. The reaction rate of water was comparable to the reaction of sample hydroxyl groups. Thus, the presence of 0.1 percent water in a stripped P-BEP sample would add to the isocyanate demand and cause a decrease in the reported equivalent weight of approximately 10 percent. On the other hand, a typical moisture of 0.1 percent in "as received", 30-percent P-BEP in methylene chloride solution would cause an error of greater magnitude, decreasing the equivalent weight by about 30 percent. Thus, most of the difference existing in measured equivalent weights between stripped and unstripped P-BEP can be attributed to residual H_2O.

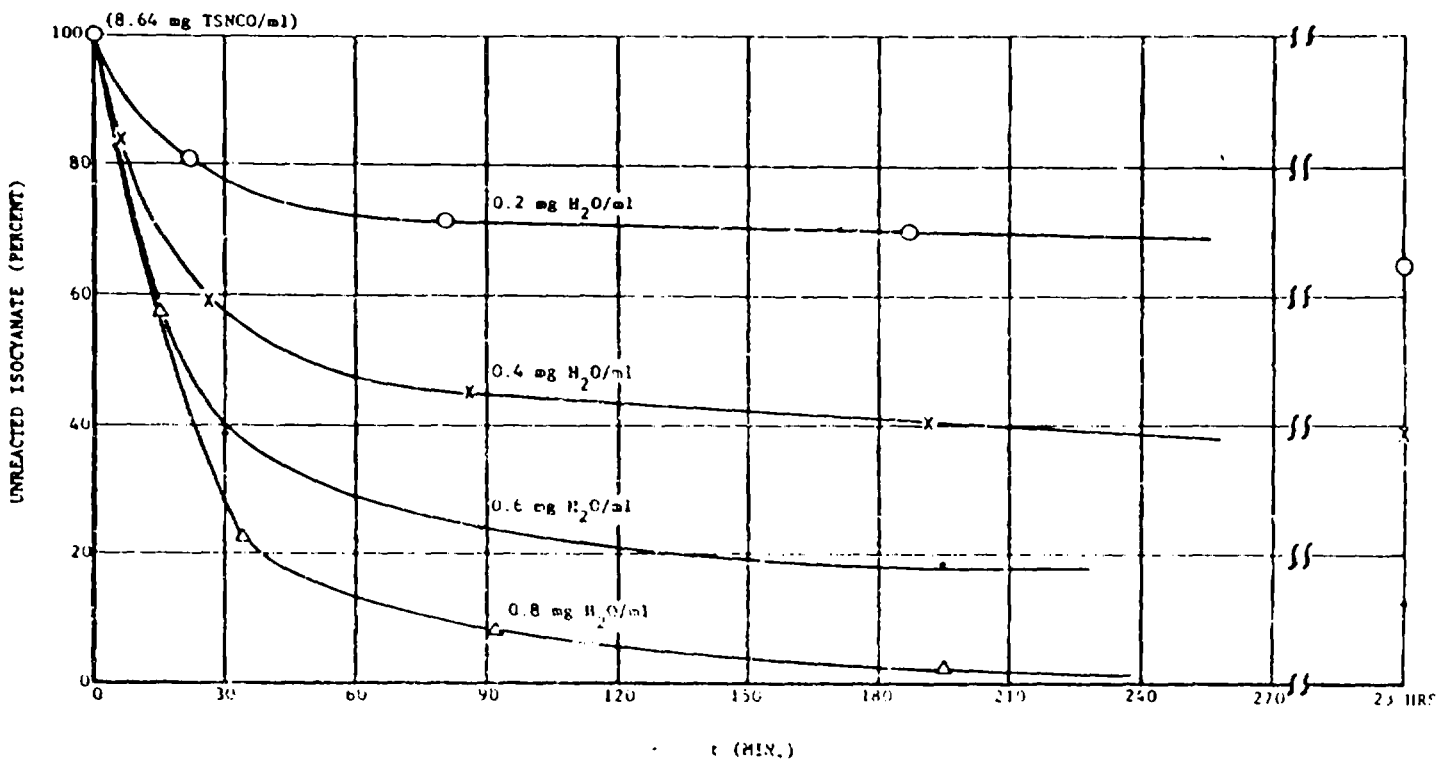

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Figure 1. Reaction of Toluenesulfonyl Isocyanate and Water at 25° C (BC-157-15)

(C) The reaction rates of TDI and water with respect to P-BEP systems have been studied at Shell.[7] Water was found to react very slowly with TDI when uncatalyzed; however, with a catalyst the rate was comparable to that of P-BEP. Thus, in actual propellant mixes, most water will react. Therefore, the moisture content is important to the overall reaction of P-BEP and isocyanate. The equivalent weights obtained by the TSNCO method on P-BEP should not be corrected for moisture present if the P-BEP is to be used in propellant mixes. For baseline data on P-BEP, the moisture correction should be applied.

(C) The isocyanate demand test was applied to TVOPA in place of the direct IR determination of the hydroxyl functionality because standard materials were not available for the IR method. The measurement is expressed in grams per OH equivalent for convenience. The stripped TVOPA was allowed to react with TSNCO in the same manner as for P-BEP.

(C) Vacuum stripping of TVOPA was accomplished more easily than for P-BEP due to its lower viscosity. The water content of stripped TVOPA was found to be lower than that of P-BEP. The equivalent weight of a sample of clear, freshly-stripped TVOPA (Lot No. 20339) containing less than 0.01 percent water was determined. The equivalent weight was found to be 6880 gm. This equivalent weight was probably due to the hydroxyl containing impurities in the TVOPA.

(C) A sample of TVOPA which had been standing at room temperature for several weeks was found to develop a straw-yellow color. The aged TVOPA was evacuated in a dessicator for 24 hr and the isocyanate demand did not change significantly. This indicated that the isocyanate reactive material was nonvolatile. The yellow color did not decrease. The yellow material was believed to be a polymeric material and is not necessarily a factor in the NCO demand.

(C) Stripping of all residual solvent and water from the viscous P-BEP has been found to be very difficult. However, for propellant production purposes this stripping is accomplished by preparing a 1:1 mixture of P-BEP and TVOPA. This mixture does not tend to form surface films and thus may be vacuum stripped to water and methylene chloride levels of less than 0.01 percent.

(C) The use of 1:1 P-BEP-TVOPA mixtures in propellant formulations suggested that the isocyanate demand be run on this mixture. A 1:1 P-BEP-TVOPA premix was reacted with TSNCO for 24 hr. The equivalent weight was determined in the same manner as for P-BEP. A 1:1 P-BEP-TVOPA premix containing less than 0.01 percent water had an equivalent weight of 3135 gm. This value was lower than would be expected if the P-BEP were diluted with an inert material. The relatively high isocyanate demand of the water-free 1:1 P-BEP-TVOPA mixture probably was caused by the isocyanate reactive material in the TVOPA.

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[7] Refer to List of References

(U) Tables I and II show typical analyses of P-BEP and TVOPA used throughout the program.

TABLE I

EVALUATION OF P-BEP, LOT 10316-134

Polymer Characterization	Shell Analysis	Hercules Analysis
Percent N, weight	16.2	15.3, 15.6
Percent F, weight	42.3	41.4 (neat) 42.3 (MeCl solution)
Hydroxyl functionality IR-PPG, gm/equivalent Toluene sulfonyl isocyanate (ESSO)	2180	2210 2240
Percent H_2O	PPM	< 0.01%
DTA (5° C/min)	--	Initial infl.-154° C Maximum exo.-213° C
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TABLE II

EVALUATION OF TVOPA, BATCH 4A-768

Determination	Hercules Analysis
Percent N	17.3
Percent F	47.4
Percent H_2O	0.02
Percent alcohol	Replaced by NCO demand test
Percent vinoxy	Replaced by NCO demand test
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2. TVOPA Characterization

(C) Previous work had shown that the TVOPA (Aerojet) being used on this program has an isocyanate demand approximately one-third that of P-BEP on a weight basis. The implications of this were not known but it was felt that a reactive species in the TVOPA could interfere in primary cure reactions. As a result, preliminary studies were initiated to determine means of eliminating the TVOPA isocyanate demand.

(C) Previous work at Hercules' ABL facility indicated that silica gel might be effective for removal of the isocyanate-reactive species. Using this concept, as-received TVOPA was passed through a column of chromatographic grade silica gel (0.2 to 0.5 mm). The eluate was stripped and desiccated overnight. The neat recovered TVOPA was then analyzed by the previously reported isocyanate demand technique (meaning toluene sulfonyl isocyanate uptake measured by IR). It was found that the isocyanate demand was completely removed in the above technique.

(C) After elution, a yellow band was found at the top of the column - obviously separated material. An ether elution was successful in removing only one component. An IR spectrum of this material closely resembled TVOPA, but had a significant absorbance in the bonded OH portion of the spectrum which was not moisture. A difference was also noticed in the IR spectra of TVOPA before and after treatment. A measurable decrease was observed in the O-H absorbance and in the previously reported carbonyl absorbance after the column treatment.

(C) Apparently, several compounds were removed with this cleanup procedure, one possibly being a hydroxy containing TVOPA-like compound and the other an aliphatic carbonyl compound.

3. AlH_3

(C) Prior to starting this program, Dow Chemical had reported improved thermal stability for neat AlH_3 through the use of an n-butylamine (NBA)/ water hydrolysis treatment. Previous work at Hercules had used AlH_3 treated by an acrylonitrile (AN) hydrolysis. As a result, a preliminary comparison of the stability of neat AlH_3, obtained from both the NBA and AN treatments, was made.

(C) To aid in this analysis a technique was developed to determine AlH_3 from an active hydrogen analysis. Previous methods have not differentiated between active hydrogen and that from various hydrates. Purity analysis from oxygen determination is also contingent upon knowing the particular hydrate forms. Several approaches were investigated for the purity determination including volumetric, X-ray diffraction, pyrolysis, and hydrolysis techniques. A combination of X-ray diffraction and hydrolysis/ oxidation proved to be the most successful. In this technique, several

(C) tenths of a gram of the AlH_3 sample was hydrolyzed in an aqueous sodium hydroxide solution. The hydrogen liberated by the hydrolysis was dried and then oxidized to water. The water was collected on magnesium perchlorate and determined gravimetrically. Both AlH_3 and any aluminum metal present yielded hydrogen. Thus, X-ray diffraction was used to determine any aluminum metal present at levels greater than 1 percent.

(C) The two passivation treatments consisted of adding three parts liquid to two parts AlH_3 and agitating slowly at 60° C. A water add was made to both liquids to adjust the total water content to 1.8 percent by weight. A composite blend of 26 lots of AlH_3 was used. Incremental withdrawals were made at periods of 3, 7, 14, and 21 days. The treated AlH_3 was then vacuum baked 1 hr at 100° C to remove residual solvents. The stability of the resulting material was then determined both neat and in propellant by Taliani testing at 60° C. Purity, mix viscosity, and particle shape by photomicrographs were monitored as a function of treatment time. Selected propellant samples were also cured and the resulting grains studied for signs of porosity.

(C) Figure 2 shows the effect of treatment time on percent decomposition of the neat AlH_3 at 4 days at 60° C for both the acrylonitrile and NBA treatments. As shown, both treatments improved the stability of neat AlH_3 by an order of magnitude after approximately 7-days treatment.

(C) Figure 3 shows AlH_3 assay as a function of treatment time. Assuming the diphenylacetylene is removed during the treatment cycle, both treatments showed almost a linear decrease in purity with time. After 7 days the purity loss exceeds 1 percent and some decrease in ballistic performance could be expected.

(C) Figure 4 shows photomicrographs as a function of time for the NBA treatment. After 14 days crystal structural damage, i.e., particle shape and size changes are apparent and extensive damage is evident after 21 days. The acrylonitrile treatment showed extensive damage after even only 3 days of treatment. Increasing mix viscosities with increasing treatment times followed the trend that would be expected from the photomicrographs. As a result of the purity decrease and structural damage evidenced in both treatments, Dow personnel were contacted and have indicated that in similar treatment cycles only approximately 1-percent purity loss (as calculated from oxygen analysis) was obtained with no evidence of structural damage. A comparison of treatment cycles gave apparent differences only in the amount of agitation during treatment and the possibility of a slightly higher water content in the Hercules cycle. Based on these results, it appears the AlH_3 water hydrolysis treatments are fairly sensitive to process variables and that purity analysis during the treatment cycle is important. Based on these preliminary results, a 7-day NBA treatment cycle was selected for the initial formulation effort. Further evaluation of the NBA treatment for AlH_3 in propellant is discussed in Section VI.

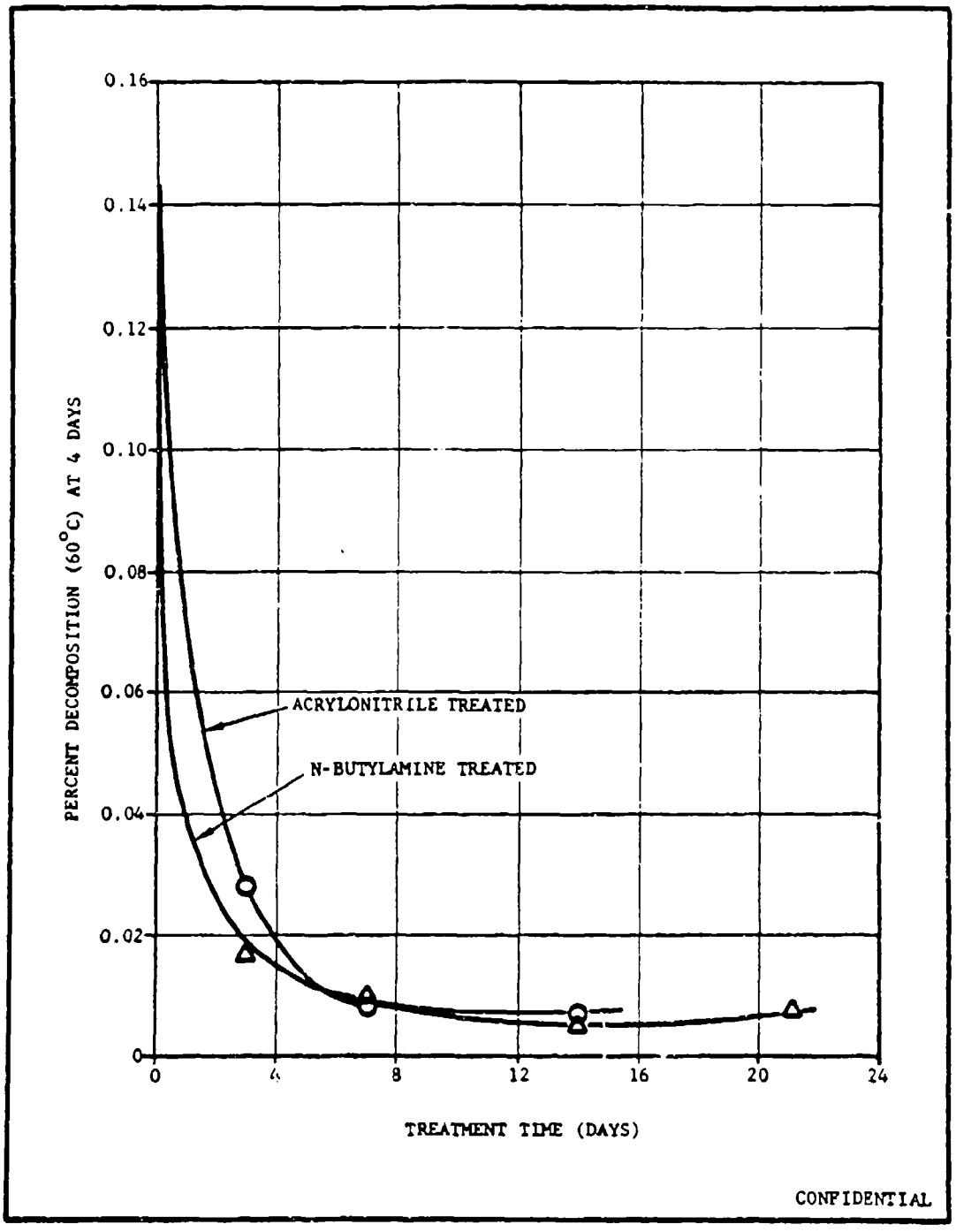


Figure 2. Effect of Treatment on Stability of Neat AlH_3

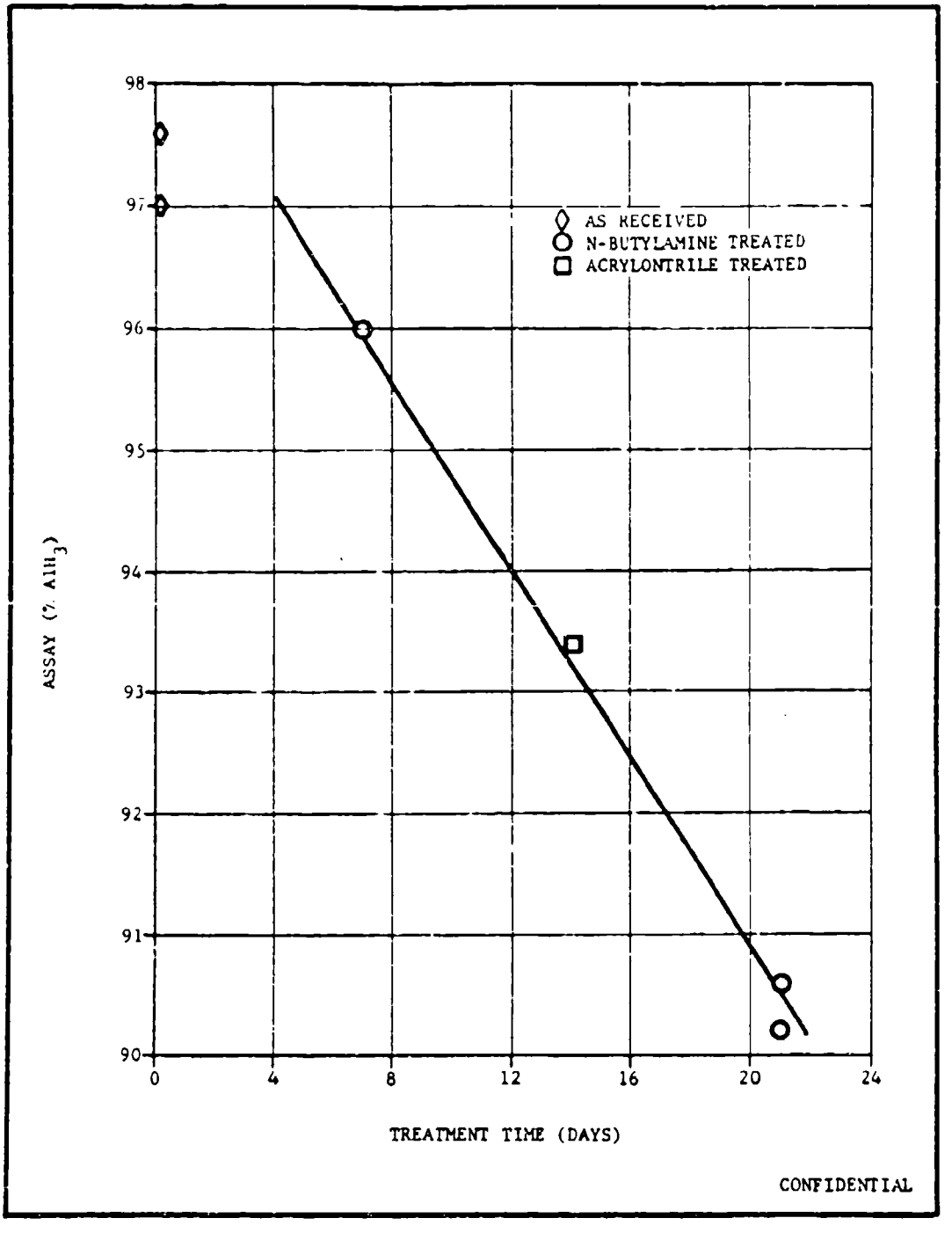
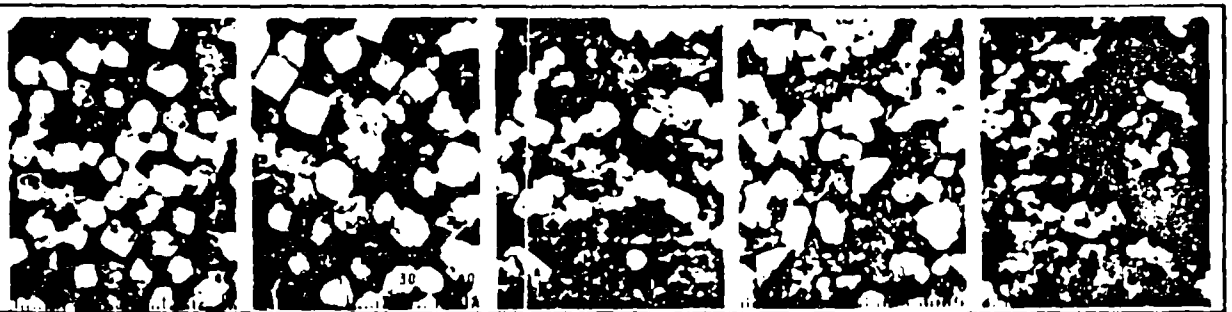


Figure 3. Effect of Treatment Time on AlH_3 Assay



	AS RECEIVED	3-DAY TREATMENT	7-DAY TREATMENT	14-DAY TREATMENT	21-DAY TREATMENT
ASSAY % AlH_3	97.0 97.6		96.0		90.2 % AlH_3 90.6
STABILITY % DECOMPOSITION @ 60 °C					
A. HEAT DECOMPOSITION AFTER 4 DAYS	0.143 *	0.0138 **	0.0098	0.005	0.007
B. IN DOUBLE BASE PROPELLANT DECOMPOSITION AFTER 4 DAYS		0.0438	0.0048	0.011	0.038

* DOW DATA (AVERAGE OF 26 LOTS)
** DECOMPOSITION AFTER 3 DAYS

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Figure 4. Effect of 60° C n-Butylamine Treatment on AlH_3 Stability

B. SYSTEM COMPATIBILITY AND STABILITY

1. Compatibility of HAP with P-BEP

(C) The key to successful development of a difluoramino binder containing an advanced oxidizer lies in development of a compatible and stable cure system. Previous work by Hercules under Wright-Patterson Contract AF33(615)-5420[1] had shown that a potential compatibility problem exists between the advanced oxidizer, HAP, and the P-BEP binder. Results of stability testing of final propellant mixes including a triisocyanate curative and the DBTDA catalyst are listed in Table III, and results of multicomponent testing by differential thermal analysis (DTA) are presented in Table IV.

TABLE III

STABILITY TESTING OF TVOPA/P-BEP PROPELLANTS

Test	Formulation*		
	AP/Al	HAP/Al	HAP/AlH3
Fischer-Johns Autoignition (°C)	227	178	176
DTA Onset (°C)	170	123	130
Peak Exo (°C)	196	161	152

*Matrix contained P-BEP/TVOPA/triphenylmethane triisocyanate/DBTDA

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(C) Results in Table IV show that the HAP system is significantly less thermally stable than the AP system, and indicates that a fundamental incompatibility exists between HAP and the binder at elevated temperatures. Although the ignition temperatures for the HAP systems are above the normal operating temperatures, these results show that the safety margins for thermal initiation during processing were markedly reduced.

(C) To determine the effect of coating HAP and of adding potential HF scavengers on the stability of HAP, an additional compatibility study was performed. The following systems were studied:

(a) P-PAPI coated HAP:TVOPA

(b) Al_2O_3 over P-PAPI coated HAP:TVOPA

(c) 3A molecular sieves over P-PAPI coated HAP:TVOPA

(d) P-PAPI coated HAP:P-BEP:TVOPA

TABLE IV

SYSTEM COMPATIBILITY BY DTA

System	Initial Exotherm (°C)	Major Exotherm (°C)	Other Peaks (°C)	Results
P-BEP	151	203	193 exo	Autoignition
TVOPA	240 endo	253 endo	--	Evaporation
HAP	173	189	90 endo	Autoignition
AlH_3	180 endo	200	180 endo	Autoignition
P-BEP/TVOPA 1:1	187	222	--	Explosion
P-BEP/AlH_3-1 1:1	124	215	174 exo	Autoignition
TVOPA/AlH_3	170	182	--	Autoignition
TVOPA/HAP	159	166	--	Explosion
HAP/AlH_3	139	164	96 endo 203 exo	Autoignition
P-BEP/TVOPA/HAP	128	164	--	Explosion
TVOPA/HAP/AlH_3	134	156	--	Explosion
P-BEP/TVOPA/HAP/AlH_3	120	142	--	Explosion

Note: DTA test programmed at 5°C/min

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(C) As shown, P-PAPI coated HAP was used in all tests. Previous results have shown that the PAPI coating significantly reduced the HAP:TVOPA interaction.

(C) The samples were heated to 50° C for approximately 140 hr in the off-gas analyzer. The gases were then determined and the sample residues were analyzed for TVOPA via residual fluorine and HAP via the hydroxylammonium ion.

(C) Table V presents a grid of the experiment together with fluorine and HAP recoveries on the sample residues. Table VI presents the off-gas data. Both the residue analyses and the off-gas determinations demonstrated that P-PAPI-caoted HAP alone was the best coating treatment. The other treatments with Al_2O_3 and molecular sieve either caused additional compatibility problems of themselves or demonstrated that the additional treatments possibly removed some of the P-PAPI coating by abrasion or fracturing of the crystals. Similar treatment of a mixture of only TVOPA with molecular sieve or Al_2O_3 may be worthwhile. Perhaps the most outstanding finding was the degree to which P-BEP was incompatible with HAP. This incompatibility was much more pronounced than any demonstrated before with TVOPA-HAP systems.

(C) It is concluded from these results that the use of HAP with P-BEP binder is not feasible due to a basic incompatibility of HAP with P-BEP. A study of the compatibility of HAP with another potential binder (EAAA) was undertaken to determine whether HAP could be used with this binder.

2. Compatibility Screening with EAAA Binder

(C) Compatibility screening of the EAAA prepolymer with the proposed ingredients was accomplished. These results for the various ingredient combinations are presented in Table VII. The EAAA was found to be compatible with both the HAP and AlH_3. However, the diepoxide (ERL 4221, the curative) when in combination with the HAP, either in the binder (TVOPA/EAAA/ERL 4221) or by itself, lowered the ignition temperatures. The HAP/ERL 4221 combination gave a major exotherm at 151° C and that for the HAP/binder was 132° C. It should be noted that the concentration of the ERL 4221 was in considerable excess (about 30 to 40 times) of that which would orindarily be in actual propellant formulations. The remaining possible ingredient combinations were considerably more thermally stable. The major exotherm by DTA for HAP was found to be 165° C. This value is lower than that (180° C) reported in the literature; however, for purposes of this compatibility study, test results are relative.

TABLE V

EXPERIMENTAL GRID PLUS RECOVERY OF FLUORINE AND HAP

Sample	HAP Treatment	Fluorine[1] Added Via TVOPA (mg)	HAP Added (mg)	Analyses After Off-gas Study	
				Fluorine Recovered (mg)	HAP Recovered (mg)
1	P-PAPI-coated HAP	F-239.6 (TVOPA-510.6 mg)	446.7	235.4 (98.2%)[3]	466.3[2] (104.4%)[3]
2	Al_2O_3 over P-PAPI-coated HAP	F-239.8 (TVOPA-511.0 mg)	571.3	227.8 (95.0%)	572.3 (100%)
3	3A molecular sieve over P-PAPI-coated HAP	F-240.6 (TVOPA-512.7 mg)	549.6	230.7 (95.9%)	527.6 (96.0%)
4	P-PAPI-coated HAP	F ~ 225 (TVOPA-254.8 mg) (P-BEP-254.8 mg)	599.0	166.4 (74.0%)	550.6 (91.9%)

[1]Fluorine contents added were based on nominal values of 46.9 percent for TVOPA and 41.5 percent for P-BEP

[2]Result was confirmed by a rerun

[3]Percent recovery

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TABLE VI

OFF GASES FROM COMPATIBILITY TESTS OF TREATED HAP
(cc/gm)

Sample	N_2	CO	N_2O	HCN	HF	Other	Total
1	0.11	0.09	0.12	0.0045	ND**	ND	0.32
2	0.13	0.38	1.01	0.042	0.05	0.004	1.6
3	0.17	0.41	0.96	0.033	0.09	0.01	1.7
4*							>2.1

*Cell leaked
**None detected

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(C) The effect of the polymethyl polyphenyl isocyanate (PAPI) coating (used to improve handling characteristics) on the thermal stability of HAP was also checked. Apparently, this coating has no effect on the stability of the HAP by itself, butan earlier autoignition (173° C on the Fischer-Johns test) did occur when the coated HAP was placed in combination with the ERL 4221. However, essentially the same exothermic condition (157° C) was found as that for the uncoated HAP for this combination on DTA.

(C) For the AlH_3/ingredient combinations, good thermal stability was found. Under 60° C/23 hr Taliani test conditions, very minimal pressure increases were indicated.

(C) Using the binder/AP/Al combination as a control, relative thermal stabilities of the AP/AlH_3 and HAP/AlH_3 propellant systems were established. As expected, the AP/AlH_3 system was slightly less thermally stable than the control. The HAP/AlH_3 system showed a significantly lower thermal stability of the same order as the P-BEP/HAP/AlH_3 propellants.

3. Propellant Stability Testing

(C) Compatibility testing of the oxidizer, fuel combination under consideration with TVOPA plasticized EAAA binder was continued in propellant cure studies. (Refer to Table VIII.)

TABLE VII

ETHYL ACRYLATE-ACRYLIC ACID (EAAA) PREPOLYMER COMPATIBILITY

System	Ambient[1]	EJAI, °C[1]	DTA, °C[2] Exotherm	Taliani @ 60° C,[3] mm of Hg after 23 Hr
HAP	--	>300	165	182, 123
HAP/EAAA	No reaction[7]	>300	170	--
HAP/ERL 4221	No reaction	270	154, 152	32, 25
HAP Polymer[5]	No reaction	>300	154	--
HAP/TVOPA	No reaction	>300	167	129, 67
HAP/Binder[6]	No reaction	158	132	137
HAP/AlH_3	No reaction	215	167	0 (@ 46° C)
HAP-C[8]	No reaction	>300	167	--
HAP-C/EAAA	No reaction	>300	--	--
HAP-C/ERL 4221	No reaction	173	157	--
AlH_3	--	>300	186	11, 13
AlH_3/EAAA	No reaction	>300	195	9, 6
AlH_3/ERL 4221	No reaction	>300	No change[9]	3

Refer to end of table for legend

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TABLE VII (Cont)

ETHYL ACRYLATE-ACRYLIC ACID (EAAA) PREPOLYMER COMPATIBILITY

System	Ambient[1]	FJAI, °C[1]	DTA, °C[2] Exotherm	Taliani @ 60° C,[3] mm of Hg after 23 Hr
AlH_3/Polymer	No reaction	>300	No change	--
AlH_3/TVOPA	No reaction	>300	188	20
AlH_3/ Binder	No reaction	213	172	20
TVOPA	--	>300	231	5, 7
Binder	--	220	182	3, 0
Binder/AP/Al	No reaction	235	217	0, 0
Binder/AP/AlH_3	No reaction	215	176	18
Binder/HAP/AlH_3	No reaction	158	132	20

Legend:
[1]Equal volumes of ingredients were used with a total of 10-15 mg
[2]Equal volumes of ingredients were used with a total of 30-50 mg
[3]Equal volumes of ingredients were used with a total of 0.3 to 0.6 gm
[4]Equal volumes of ingredients were used with a total of 25-30 mg
[5]Polymer - EAAA + ERL 4221
[6]Binder - Polymer + TVOPA
[7]Held for at least 1 hr
[8]Coated with polymethylene polyphenyl isocyanate (PAPI)
[9]No endothermic or exothermic condition from 0° to 300° C at a heat-up rate of 5° C/min

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TABLE VIII

ETHYL ACRYLATE-ACRYLIC ACID PREPOLYMER PROPELLANT CURE STUDIES

Ingredients	Control	Control	Control	AP/LMH-1	AP/LMH-1	HAP/LMH-1	HAP/LMH-1	HAP/LMH-1	HAP/LMH-1
TVOPA/EAAA (7/1)	39.0	39.0	39.0	40.0	30.0 (5/1)	40.0	40.0	40.0	40.0
ERL-4221 (add)	0.47	0.94	0.94	0.97	0.97	0.97	0.47	0.97	0.97
AP	46.0	46.0	46.0	40.0	45.0	--	--	--	--
Al	15.0	15.0	15.0	--	--	--	--	--	--
LMH-1*	--	--	--	20.0	25.0	--	--	--	--
LMH-1**	--	--	--	--	--	20.0	20.0	20.0	20.0
HAP	--	--	--	--	--	40.0	--	--	--
HAP (P-PAPI coated)	--	--	--	--	--	--	40.0	40.0	40.0
Cure temp (°F)	140	140	120	140	140	140	140	140	115
E/C***	1.0	2.0	2.0	2.0	2.0	2.0	1.0	2.0	2.0
Propellant condition	Excellent, soft, rubbery, nonporous	Excellent, firm, rubbery, nonporous	Excellent, firm, rubbery, nonporous	Fair, soft, rubbery, nonporous	Good, firm, rubbery, nonporous	Cured, gassed	Cured, gassed	Cured, gassed	Uncured, gassed

*n-Butylamine treated

**Acylonitrile treated

***Epoxy-to-carboxyl ratio

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(C) When AP was replaced with HAP, profuse gassing occurred. Because the magnitude of gassing indicated significant decomposition of one or more major ingredients, attempts were made to analyze the resulting propellants for the major ingredients. Two propellants which had been cured for several days at 140° F were analyzed.

(C) The propellants were first extracted with methylene chloride to remove TVOPA and other soluble fluorine compounds. This extract was analyzed for fluorine by base-hydrolysis and titration with lanthanum (III), using an ion specific electrode. The residue was then extracted with water and the HAP concentration was determined by titrating the hydroxyl ammonium and perchlorate ions separately. The residue from the water wash was analyzed by X-ray diffraction for percent Al_2O_3. Both IR and TLC were used for confirming the constituents in the various extracts. Off-gas analyses were also performed on these samples.

(C) Data from the propellant analyses are presented in Table IX. As can be seen, TVOPA underwent a major decomposition, losing one out of three fluorine atoms. In addition, entire difluoramine groups were lost as evidenced by the presence of HCN in off-gas analyses and in the HAP titrations as well. IR studies indicated that the basic skeletal structure of TVOPA had not changed but that the intensity of several characteristics N-F bands did, in fact, decrease. The TVOPA-like material in the propellant was compared to pure TVOPA by TLC. No TVOPA could be found in the TLC analysis.

(C) The HAP concentration did not change as severely as did TVOPA. The perchlorate ion, generally regarded as one of the poorest oxidizers under these conditions, was present in slightly higher concentrations than the hydroxylammonium ion, which indicated that a decomposition in the cationic portion of the molecule had occurred. The fact that most of the HAP was still present was confirmed by IR. The hydroxylammonium ion titrations also served to measure the presence of a strong acid entity and probably HCN in the water washes. The fact that a relatively large amount of strong acid was present together with an excess of ClO_4 suggests that a least some perchloric acid could be present in the sample together with HF and perhaps HNO_3. This strong acid entity could be a result of both TVOPA and hydroxylammonium ion decompositions.

(C) The preceding analysis indicated that a serious TVOPA stability problem existed in the presence of HAP and that a more thorough understanding of the binary HAP-TVOPA system was necessary. As a result, a study was designed for this purpose as discussed in the following paragraphs.

TABLE IX

PROPELLANT ANALYSIS

Sample	Ingredient	Percentage of Ingredient Added	Precentage of Ingredient Determined
BC-158-20 (140° F cure)	TVOPA	35%; 16.1% fluorine	TVOPA not present - 10.5% fluorine
	HAP uncoated	40.0%	41.9% - from ClO_4^- determination 37.5% - from NH_3OH^+ deterionation Additional findings: 0.17m Eq strong/acid/g propellant 0.26m Eq HCN/g propellant
	LMH-1	20.0%	21.8%
BC-158-22 (140° F cure)	TVOPA	35%; 16.1% fluorine	10.6% fluorine
	HAP PAPI-coated	40.0%	39.1% - from ClO_4^- determination 36.6% - from NH_3OH^+ determination Additional findings: 0.10m Eq strong acid/g propellant 0.18m Eq HCN/g propellant
	LMH-1 light fraction	20.0%	22.2%

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4. Reaction of HAP and TVOPA - Off-Gas Analysis and Recovery Study

(C) Several one-to-one mixtures of HAP and TVOPA were placed in the stainless steel off-gas analysis system. No gas was evolved after several days at room temperature. The temperature was then raised to 50° C and the decomposition products evolved as shown in Table X.

TABLE X

OFF-GAS ANALYSIS OF HAP-TVOPA MIXTURES AT 50° C

Sample	Gas Evolved (cc/gm) 24 hr	Gas Evolved (cc/gm) 120 hr
Control, TVOPA only	None	None
TVOPA + dried HAP	CO_2-0.019 N_2O-0.14	CO_2-0.025 N_2O-0.26 N_2-0.29 HF - present NF compounds - present
TVOPA + PAPI-coated HAP	CO_2-0.084 N_2O-0.15	CO_2-0.06 N_2O-0.15 N_2-0.18 HF - not present NF compounds - not present
TVOPA + ultra dry HAP	CO_2-0.024 N_2O-0.12	CO_2-0.07 N_2O-0.11 N_2 - present, not measured HF - present NF compounds - present

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(C) The off-gas analysis shows that there was a definite reaction of the TVOPA and HAP at 50° C. The reaction was controlled to some extent by the PAPI coating of the HAP surface. All gases, except CO_2, were reduced in the sample containing the PAPI-coated material.

(C) The samples were washed from the stainless steel tubes and the amounts of fluorine as TVOPA and fluoride as HF and TVOPA decomposition were measured. the HAP was determined as hydroxylammonium ion. The results are presented in Table XI.

TABLE XI

RECOVERY STUDY OF TVOPA-HAP REACTION AT 50° C
(STAINLESS STEEL TUBES)

Sample	Percent F as TVOPA Recovered	Percent F as HF Recovered*	Percent HAP Recovered
TVOPA only	101.5	None	None
TVOPA + dried HAP	90.4	9.1	72.1
TVOPA + PAPI-coated HAP	97.3	2.1	97.7
TVOPA + ultra-dry HAP	89.9	6.9	78.3

*Represents HF remaining in tube after off-gas analysis

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(C) The reaction of HAP and TVOPA was evident in all cases, but was reduced in the system containing PAPI-coated HAP.

(C) Several HAP-TVOPA binary mixtures were tested after a 7-day German test at 50° C. The HAP crystals had changed to a brown color while the TVOPA had lost its initial straw-yellow color. The TVOPA layer (clear liquid) was found to contain a strong carbonyl band at 1735 cm^{-1}. The significance of the band has not been determined. Some etching was noted on all glass tubes containing mixtures of TVOPA and HAP. No etching was seen on the tube containg TVOPA only.

(C) The contents of the German tubes were removed and the contents analyzed for organic fluorine in TVOPA, fluoride as HF from TVOPA decomposition, and HAP as hydroxylammonium ion. The results are presented in Table XII.

(C) Compared to reactions in the stainless steel tubes, German tube reactions were somewhat reduced. This may have been due to the presence of glass which would absorb HF and prevent its further reaction. However, the binary reaction did occur in all mixtures although the reaction was reduced by the PAPI coating on the HAP surface.

TABLE XII

RECOVERY STUDY OF TVOPA-HAP REACTION AT 50° C
(GERMAN TUBES)

Sample	Percent F as TVOPA Recovered	Percent F as HF Recovered	Percent HAP Recovered
TVOPA only	100	None	--
TVOPA + dried HAP	88	0.8	98
TVOPA + PAPI-coated HAP	95	2.5	97
TVOPA + ultra-dry HAP	93	2.5	97
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(C) Results of the binary testing of HAP and TVOPA mixtures coupled with the propellant cure studies indicate there is a strong interaction of HAP and TVOPA at elevated temperatures. Although this interaction is reduced by the PAPI coating and a stabilizing environment such as molecular sieves or glass, it appeared doubtful that a stable system could be achieved.

5. ICC Thermal Stability and Cracking Cube Tests

(U) One critical test to establish the practicality of a propellant is the ICC thermal stability test. In this test a 2-in. cube of propellant is placed in an oven. The temperature is raised to 75° C and maintained for 48 hr. If the test results in either explosion, burning, or marked decomposition of the sample, the material will be classified as ICC "Forbidden."

(C) Samples of five propellants were subjected to this test as shown below:

Propellant	1	2	3	4	5
Basic System	DB/AlH_3	P-BEP/AP	P-BEP/AP/AlH_3	P-BEP/HAP/Al	EAAA/AP/AlH_3

The P-BEP/HAP propellant samples were obtained from a one-pint Baker-Perkins mix. Al was substituted for AlH_3 to reduce sensitivity problems and some AP was used to obtain better solids loadings.

(C) The mix was cast into a 2-in. cube for ICC testing. The cube was well cured after 24 hr at 80° F, and it was nonporous. Table XIII shows the composition of the propellants tested and the test results. The P-BEP binder with AP (VKN) survived the test with very little change. Aluminum hydride incorporation caused no noticeable changes in the double-base (FHA) or ethyl acrylate binder (BC-158-28), but did show evidence of some gassing (swelling), and softening of the propellant in the P-BEP/TVOPA binder (VKO). The sample containing HAP in the P-BEP/TVOPA binder (BC-165-2) burned after 10 hr and 15 min. The oven door was blown open and the tray that the sample was sitting on was ejected, but there was only superficial damage to the interior of the oven. These results indicate that of the systems tested, only the P-BEP/HAP system fell in the ICC "Forbidden" category.

(C) From the results of the ICC tests it was recommended that no further work be performed with the P-BEP/HAP system. Based on the compatibility tests, development of a practical HAP propellant in a difluoramine environment with AlH_3 appears extremely unlikely and no additional HAP formulation work was conducted.

TABLE XIII

RESULTS OF ICC THERMAL STABILITY TESTS

Propellant Designation or Reference	FHA	VKN	VKO	BC-158-28	BC-165-2
	1	2	3	4	5
NC	8.0				
NG	27.4				
TEGDN	2.6				
BDNPA	2.0				
NDPA	0.3				
MgO	0.5				
PGA-TDI	0.7				
HMX	15.0				
AP	20.5	62.7	36.9	45	19.0
AlH_3	23.0		23.0	25	
P-BEP		17.6	19.0		19.0
TVOPA		17.6	19.0	25	19.0
TCP		0.5	0.5		0.5
Mondur TM		1.68	1.82		1.7
EAAA				5	
Epoxy				1	
CWX-105		0.2	0.2		1.0
HAP					26.0
Al					15.0
Test Results					
Weight change (%)	+0.05	-0.05	-0.12	-0.05	
Volume change (%)	0	+1	+6	0	
Appearance	No significant change	Color darkened	Color darkened. Bulged out in center. Cracked on one face	No significant change	Sample burned after 10-1/4 hr
Durometer Hardness (A Scale)					
Before		51	44	56	32
After	77	49	34	56	

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SECTION III

BINDER STUDIES

(U) The major goal of this effort was to make the P-BEP binder work. However, since there were a number of known problems associated with P-BEP, considerable effort was also expended on alternate binder systems.

A. P-BEP BINDER

(C) Although the theoretical hydroxyl functionality of P-BEP is 3, the actual functionality is less than 2. Thus, P-BEP cannot be cured directly with diisocyanates. Either a diisocyanate/triol combination or a triisocayante must be employed to obtain adequate cures. Problems resulting from the low functionality coupled with a rather poor stability characterized by the probable elimination of HF have precluded the systematic development of P-BEP propellants. An additional problem which places severe constraint upon P-BEP/AlH_3 propellants is the need for rapid development of propellant modulus at low cure temperatures to prevent formation of porosity. Probably as a result of a combination of the above problems, United Technology Center[2] has reported problems with P-BEP/AlH_3 propellants characterized by non-reproducible cures and non-cures during scaleup.

(U) To eliminate the problems of nonreproducible cures, initial cure studies with P-BEP were directed towards the use of curatives with a functionality greater than 2 and the search for catalysts less susceptible to HF poisoning than the standard organotin catalysts.

(C) Initial curing studies were conducted with propellants containing a 50:50 mixture of P-BEP/TVOPA binder crosslinked with triphenylmethane triisocyanate (TPMTI). The NCO:OH ratio was varied from 0.6 to 1.6. (The equivalent weight used for the P-BEP was based on the IR functionality.) The catalyst level was maintained at 0.1 percent dibutyltin diacetate (DBTDA) to ensure sufficient catalyst for adequate cures in all cases. The binder was filled with AlH_3 and AP at a solids loading of approximately 60 percent. Table XIV summarizes the results of this study.

(C) No firm cures were obtained at NCO:OH ratios of 0.6, 0.8, or 1.0. Reasonably good cures were obtained at an NCO:OH ratio of 1.2 and excellent cures at NCO:OH ratios of 1.4 and 1.6. The pot life was extremely short for the 1.6 NCO:OH ratio mix. Based on these results, the optimum NCO:OH ratio appeared to be in the range of 1.2 to 1.4 for formulation purposes. The NCO:OH ratio of 1.2 (based on the IR equivalent weight for P-BEP) is basically the same ratio as was found in previous work to give good cures at the 1-lb level. This NCO:OH ratio corresponds to 0.88 based on the equivalent weight of P-BEP determined by the TDI method.

TABLE XIV

OPTIMUM FUNCTIONALITY DETERMINATIONS

Formulation	NCO:OH Ratio*					
	0.6	0.8	1.0	1.2	1.4	1.6
P-BEP	20.00	20.00	20.00	20.00	20.00	20.00
TVOPA	20.00	20.00	20.00	20.00	20.00	20.00
TCP	0.50	0.50	0.50	0.50	0.50	0.50
TPMTI	0.68	0.90	1.13	1.35	1.58	1.80
DBTDA	0.10	0.10	0.10	0.10	0.10	0.10
AlH_3	18.00	18.00	18.00	18.00	18.00	18.00
AP	40.73	40.50	40.26	40.05	39.92	39.60
Cure Characteristics	Very little cure	Increasing cure	Increasing cure	Cured, slight surface tack. Can indent surface	Fully cured, no surface tack	Fully cured, short pot life.

*Equivalent weight used for P-BEP was the IR value. If TDI equivalent weight is used for P-BEP, the above NCO:OH ratios must be multiplied by 0.74

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(C) The functionality test samples were split and cured at both 50° and 115° F. Complete cure was basically achieved within 24 hr. Very little postcuring was achieved after the first day. No real difference in cure rate was seen between the two temperatures, possibly because of the high catalyst levels.

(C) To determine the effect of catalyst type and level on cure properties, a series of 25-gm mixes were made. The propellant formulation used in all mixes is presented in Table XV. The NCO:OH ratio was constant at 1.4:1.0. The following catalyst systems were evaluated:

(1) DBTDA

(2) DBTDL

(3) CW-X105 (Linde Company), molecular sieves loaded with 10-percent DBTDL

(4) CW-X156A, molecular sieves loaded with 20-percent methyl-diethanolamine

(5) CW-X116, molecular sieves loaded with 15-percent triethylamine

(C) The two straight organo-tin salts were evaluated over a catalyst level from 0.01 to 0.1 percent. All mixes were cured at 50° to 60° F. Table XV also summarizes the results of mixes made with both catalysts. In general, the DBTDA showed slightly greater catalytic activity as evidenced by faster cures and a lower minimum catalyst level necessary for curing. The greater activity of DBTDA is to be expected based on a higher total tin content. A minimum DBTDA catalyst for cure was approximately 0.02 percent while 0.04 percent was required for the DBTDL system.

(C) The three molecular sieves containing catalysts were also evaluated in the formulation presented in Table XV at an active catalyst level of 0.05 percent. The mixes containing CW-X-156A (loaded with 20 weight percent methyl-diethanolamine) and CW-X116 (loaded with 15 weight percent dibutyltin dilaurate) cured well. Apparently, the teriary amines are not strong enough urethane catalysts for the P-BEP-OH/TPMTI reaction. This is in line with other work which has shown teriary amines to have much less catalytic effect than the organo-tin compounds. No further work is planned with the teriary amine catalysts.

TABLE XV

P-BEP CURE - CATALYST STUDY

FORMULATION	
Ingredient	Percent
P-BEP	19.0
TVOPA	19.0
TCP	0.50
TPMTI	1.50
AP	41.80
AlH_3	18.0
Catalyst	Variable
NCO/OH	1.4

MIX RESULTS		
Catalyst Type	Catalyst Level	Cure Results
DBTDL	0.1	Cured
	0.05	Cured
	0.04	Cured
	0.02	Uncured
	0.01	Uncured
DBTDA	0.1	Cured
	0.05	Cured
	0.02	Marginal cure
	0.01	Uncured

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(C) The CW-X105-loaded molecular sieves were also evaluated at a DBTDL catalyst level of 0.02 percent. A good cure was obtained in 4 days at a cure temperature of 50° to 60° F. In contrast, a mix containing 0.02 percent DBTDL added directly to the formulation would not completely cure. This suggests the possibility that some catalyst deactivation is prevented by the molecular sieves. In the use of chemically loaded molecular sieves, the catalyst is theoretically only released by displacement with HF, H_2O, or other species with similar molecular diameters. Thus, the use of the molecular sieves may provide a means for reducing the total catalyst level and improving pot life while still maintaining good cures. A detailed study of the effect of HF on the cure catalysts was made. This work is described in Appendix A. This effort proved that HF poisons the catalyst, and molecular sieves provide some protection of the catalyst. Based on the above catalyst study, the CW-X105 catalyst was chosen for further evaluation and for comparison with the unprotected catalyst DBTDA.

(C) Initial pot-life studies were conducted using mixes containing 0.1 percent DBTDA catalyst (based on total propellant formulation). This was the same catalyst level used in the functionality tests. For these mixes, the initial viscosity increased from 200,000 to 750,000 cps within 30 min, showing an undesirably short pot life existed at this catalyst level.

(C) As a result, additional pot-life studies were made at lower catalyst levels. Figure 5 shows viscosity as a function of time for the formulation presented in Table I made with near minimal catalyst levels of 0.02 percent for both the DBTDA and CW-X105 catalyst systems. Also shown is the uncatalyzed system for comparison purposes. Both catalyzed systems show a rapid increase in viscosity for the first 2 hr followed by an apparent decrease in the cure rate particularly for the DBTDA system. The apparent change in cure rate may be due to partial catalyst deactivation by HF.

(C) Even at 0.02 percent catalyst level the rapid increase in initial viscosity shown in Figure 5 could limit obtaining the desired high solids loadings. As a result, the catalyst level was further reduced and an elevated temperature cure cycle employed. Propellants formulated with no catalyst and 0.004 percent DBTDA and DBTDL were evaluated in cure studies with a 115° F cure. At the 0.004 percent catalyst level, a good cure was obtained with the use of both catalysts in 4 to 6 days. The propellant formulation containing no catalyst cured in 8 to 10 days; however, it was somewhat softer than catalyzed formulations. In the several samples cured without a catalyst, porosity was detected in each. This may be due to slow development of physical properties coupled with gassing from either the isocyanate-water reaction or AlH_3 decomposition.

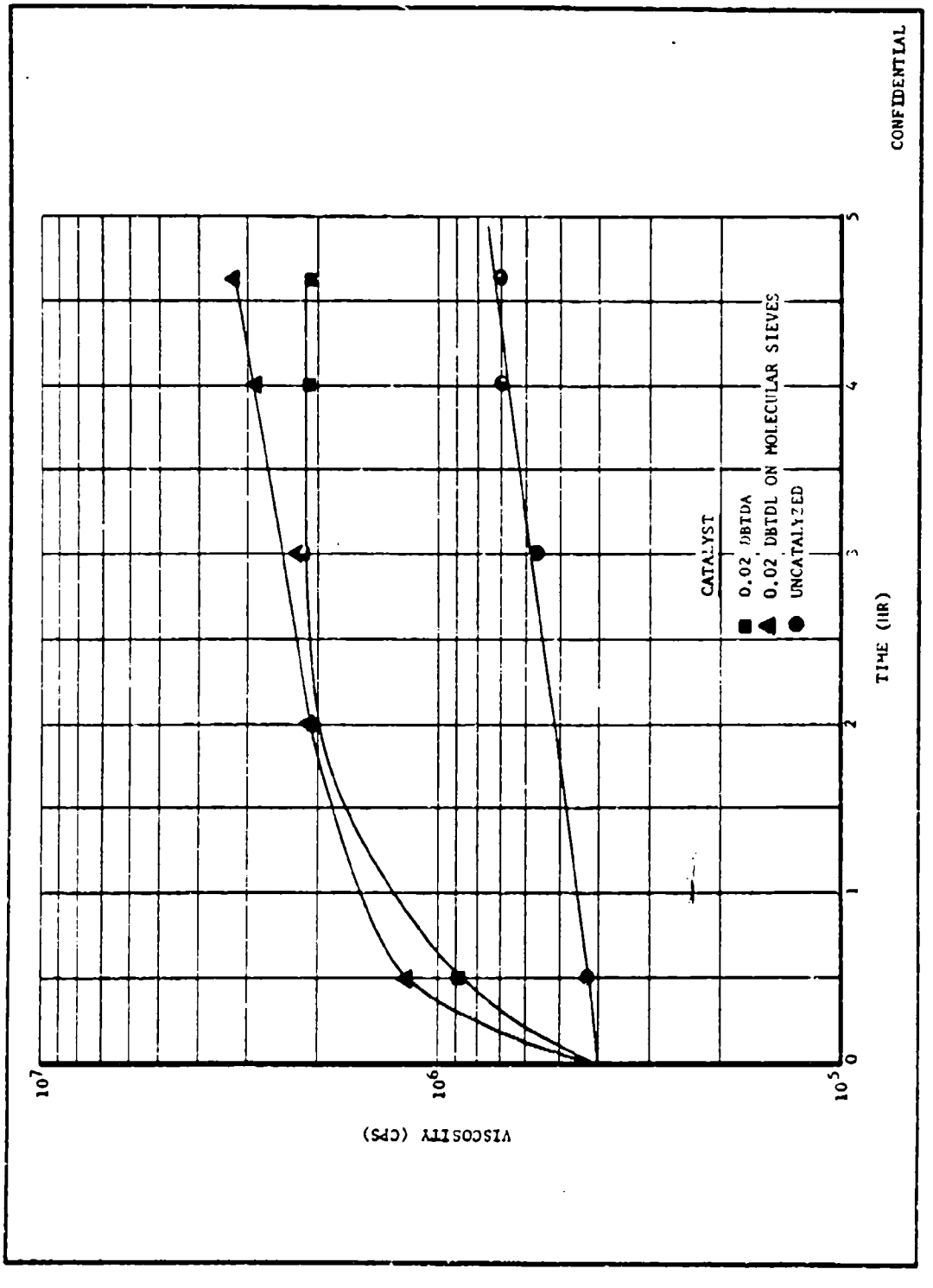

Figure 5. Viscosity as a Function of Time for P-BEP Propellants at 75° F

(C) Based upon the results of the above cure studies, pot life studies were made at 75° and 120° F for propellant formulations containing DBTDA and DBTDL catalyst levels ranging from 0 to 0.02 percent. For the 120° F studies, the mixes were made at 75° F, the viscosity measured, and the mix then heated to 120° F. The results are plotted in Figure 6. A catalyst level of 0.004 percent gave a good pot life at both 75° and 120° F. The 120° F temperature mix cycle reduced the propellant viscosity by approximately one-half, and a pot life in excess of 4 hr was indicated. It is concluded that a good balance between pot life and cure time is obtained with an active catalyst level of 0.004 percent, whether the catalyst was supported or not.

(U) Since changes in cure have been noted during scaleup, which could be blamed on increased poisoning by HF, the catalyst supported on molecular sieves (CWX 105) was chosen for use in this program.

(C) The efficiency of the DBTDL catalyst introduced through molecular sieves was also investigated to determine if the molecular sieves would influence the optimum NCO:OH. A propellant formulation containing the DBTDL catalyst, added directly, was used as a reference. The composition was formulated at NCO:OH ratios of 1.0 and 1.2 and at a catalyst level of 0.02 percent. No difference in state of cure was detected for the catalyst addition method in the propellant at corresponding NCO:OH ratios. The lower the NCL:OH ratio, the poorer was the cure.

(C) In conjunction with temperature considerations to reduce propellant mix viscosity, a study was conducted to determine the feasibility of increasing the TVOPA:P-BEP ratio to achieve this objective. Propellant compositions were formulated at TVOPA/P-BEP levels of 1.5 to 1.0 and 2.0 to 1.0. The propellants were cured with triphenylmethane triisocyanate at NCO:OH ratios ranging from 1.4 to 1.8. Cure results are reported in Table XVI. As the TVOPA level is increased, the NCO:OH ratio must be increased to achieve a good cure. This is probably explained by the isocyanate demand of TVOPA which has been found to exist. The 2.0-TVOPA/1.0-P-BEP binder system in the propellant, cured at an NCO:OH ratio of 1.8, looked very good. The viscosity of this propellant was so low that all the solids settled; whereas, in the same formulation containing a 1-TVOPA/1-P-BEP binder there was no solids settling. Thus, there is room to significantly increase solids loading by considering eleveated mix temperature and in increasing the TVOPA percentage in relation to P-BEP in the binder.

(C) A preliminary evaluation was also made of four alternate isocyanate curatives shown below as a replacement for TPMTI:

(1) Mondur MRS (Upjohn)

(2) Isonate I-500 (Upjohn)

(3) PAPI (Upjohn)

(4) Mondur CB-75 (Mobay)

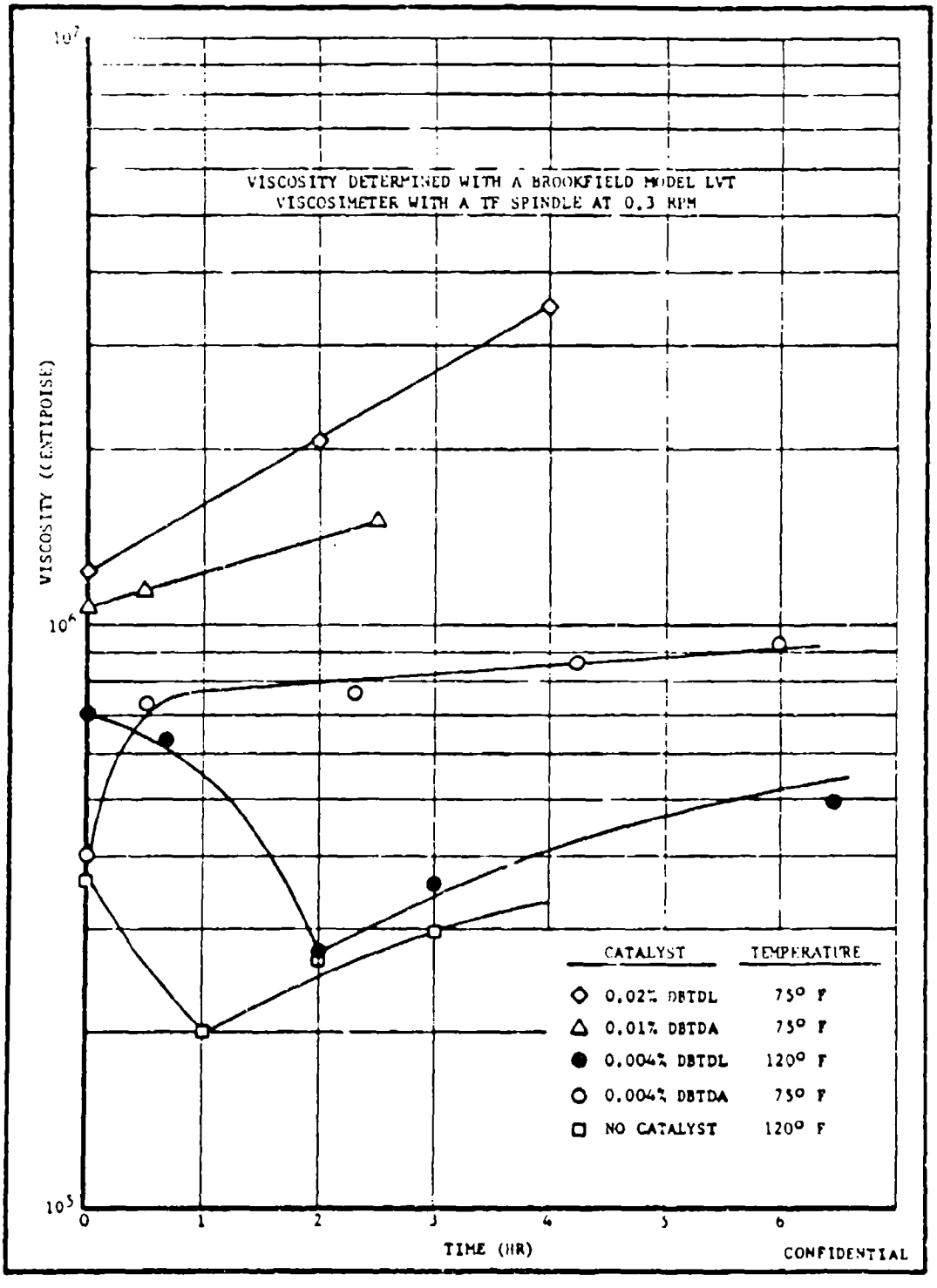

Figure 6. Viscosity as a Function of Time for P-BEP Propellants

TABLE XVI

CURE RESULTS OF P-BEP/TVOPA PROPELLANTS WITH INCREASED LEVELS OF TVOPA

	P-BEP/TVOPA Ratio			
	1.0/1.5		1.0/2.0	
NCO:OH ratio	1.4	1.6	1.6	1.8
Cure results Days @ 115° F	Poor cure 14	Good cure 5	Poor cure 9	Good cure 5

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(C) The results of this evaluation are presented in Table XVII. The first three curatives are derivatives of 4,4'diphenylmethane diisocyanate and the Mondur CB-75 is the TDI adduct of 1,2,6 hexane triol. The CB-75 is tri-functional and the other three curatives are polyfunctional. Initial cure studies were performed with the MRS, I-500, and CB-75 in the basic formulation at an NCO:OH ratio of 1.4 to 1.0 and a DBTDA catalyst level of 0.2 percent. All mixes were cured at room temperature. None of these mixes gave a good cure. Additional cure studies were performed with the PAPI and the I-500 curatives at a catalyst level of 0.02 percent over an NCO:OH range of 1.4 to 2.2. All mixes were cured at a temperature of 115° F. Table XVII shows that in order to obtain a good cure from these isocyanates, a much higher NCO:OH ratio was required compared to the TPMTI curative. In addition, all cured propellant showed evidence of some porosity. These results indicate steric hinderance may have inhibited the cure rate and allowed the water-isocyanate reaction to occur. As indicated, none of the alternate curatives evaluated showed any significant improvement over TPMTI.

B. ALTERNATE BINDER STUDIES

1. Objective

(U) The objective of this effort was to evaluate an alternate binder as a back up for P-BEP. Major emphasis has been placed in obtaining a good, reliable cure and eliminating compatibility problems. The prime objective is to develop a binder system that retains high TVOPA levels and possesses adequate pot life, processibility, and mechanical properties when cured in the 75° to 100° F range.

TABLE XVII

ALTERNATE CURATIVE EVALUATION FOR P-BEP

Curative	MRS	I-500	CB-15	I-500	I-500	I-500	PAPI	PAPI	PAPI
Catalyst type	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	CWX-105	DBTDA	DBTDA	CWX-105
Catalyst level	0.2	0.2	0.2	0.02	0.02	0.02	0.02	0.02	0.02
NCO:OH	1.4	1.4	1.4	1.4	1.8	2.2	1.4	1.8	2.2
Cure temp (°F)	75	75	75	115	115	115	115	115	115
Cure conditions	Uncured	Uncured	Uncured	Poor cure, porous	Firm cure, porous	Firm cure, porous	Poor cure, porous	Firm cure, porous	Firm cure, porous

Data evaluated in Table I formulation

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2. Background

(C) Two types of prepolymer, acrylates, and polyesters, were evaluated as binders for the TVOPA-AlH_3 propellant in this program. Acrylate prepolymers were first evaluated in TVOPA plasticized propellants by the Rohm & Haas Co. Copolymers of ethyl acrylate and acrylic acid (having carboxylic acid functionality) were crosslinked with epoxides by Rohm & Haas giving TVOPA-Al propellants with acceptable mechanical properties. These propellants were cured at 140° F and there was no evidence in the literature that highly filled carboxyl-epoxy systems could be cured at 100° F or below. Therefore, a cure study was needed to determine whether a low temperature cure could be obtained through the use of cure catalysts. Simultaneously, a study of the acrylate prepolymers containing hydroxyl functionality seemed warranted since hydroxyl functional prepolymers can be cured at low temperatures with isocyanates.

(U) Copolymers of HEA/EA that were supplied by Dow Chemical were used for this evaluation.

(U) The polyester prepolymer (Multron R-18) used in this investigation is a diethylene glycol adipate polymer terminated with hydroxyl groups. Cure was obtained with a diisocyanate and crosslinking with a triol.

3. EAAA Prepolymer

(C) Since Rohm & Haas had characterized the EAAA/TVOPA binder in alu[illegible]zed propellants, Hercules first step in the EAAA evaluation was to repr[illegible] one of the Rohm & Haas formulations and compare the results to ensure that Rohm & Haas properties could be achieved with the particular lots of ingredients available for this program.*

(C) Attempts were made to duplicate the mechanical properties of both the Rohm & Haas U-105 (40 percent binder, 5:1 TVOPA:EAAA) and U-110 (40 percent binder, 7:1 TVOPA:EAAA) formulations. Table XVIII is a summary of 1-lb mixes made with a 95:5 EAAA prepolymer with both the 5:1 and 7:1 TVOPA:EAAA formulations. It was readily apparent that neither the Rohm & Haas reported 60-hr cure rate at 140° F nor their mechanical properties were being obtained in the initial propellant mixes. (Refer to mix No. 158-29 in Table XVIII.) These mixes were made without the Al_2O_3-C coated AP, with 10μ Al in place of 3μ Al, and with Aerojet TVOPA in place of Rohm & Haas TVOPA. Propellant cures were characteristically much longer and tensile strengths much lower than reported by Rohm & Haas. Although changes in the epoxy/carboxy ratio significantly affected the propellant elongation, little improvement was obtained in tensile strengths. As a result, attempts were made to determine which of the three variables (Al_2O_3-C coated AP, Al particle size or TVOPA source) was affecting the

*Rohm & Haas supplied the prepolymers used for this program.

TABLE XVIII

MECHANICAL PROPERTIES OF ROHM & HAAS CONTROL PROPELLANTS

Mix No.	E/C	TVOPA/EAAA	Particle Size, μ Al	Particle Size, μ AP	Cure Time & Temp (Days @ °F)	Tensile (psi)	Elongation (%)	Modulus (psi)
158-29	2.0	7/1	10	50μ	5/140	35	29	129
158-44	2.0	7/1	10	50μ	68 hr/140	18	163	21
					10/140	28	44	68
158-47	1.5	7/1	10	50μ	73 hr/140	26	47	72
					10/140	20	117	29
158-48	2.0	5/1	10	50μ	68 hr/140	21	175	20
					10/140	42	35	130
158-50	1.5	5/1	10	50μ	68 hr/140	35	43	96
158-60	2.5	7/1	10	50μ	90 hr/140	20	145	23
					12/140	34	33	109
158-62	2.5	5/1	10	50μ	9/140	35	17	221
158-88	2.0	7/1*	5	50μ-C	5/140	36	125	36
					9/140	62	32	197
					21/140	66	28	250
158-91	2.0	7/1	5	50μ-C	5/140	55	63	95
					9/140	61	45	141
158-92	2.0	7/1	10	50μ-C	7/140	44	38	131
					10/140	39	42	115

*Purified TVOPA

(C) mechanical properties and cure rate. Mixes made (No. 158-88 through 158-92) to study these variables are summarized in Table XIX. Since no Rohm & Haas TVOPA was available, the Aerojet material was purified with a silica gel treatment which had been shown previously to remove residual hydroxyl functional material. As shown in Table XIX, all three of these variables affected the propellant mechanical properties but not the cure rate. To provide further confirmation of the importance of these variables, Rohm & Haas was contacted and requested to duplicate their control propellant using the same prepolymer furnished to Hercules.

TABLE XIX

RH-U-105 PROPELLANT PROPERTIES AND CURE RATE

Mix No.	Variables	Cure Time (at 140° F)	Tensile (psi)	Elongation (%)
158-44	10μ Al, non-coated AP, Aerojet TVOPA	68 hr 10 days	18 28	163 44
158-92	Al_2O_3-C coated AP, 10μ Al Aerojet TVOPA	7 days 10 days	44 39	38 42
158-91	Al_2O_3-C coated AP, 5μ Al Aerojet TVOPA	5 days 9 days	55 61	63 45
158-88	Al_2O_3-C coated AP, 5μ Al purified Aerojet TVOPA	5 days 9 days 21 days	36 62 66	125 32 28
Rohm & Haas	Control	60 hr	68	44

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(C) The results (Table XIX) show that by using the finer Al and Al_2O_3 coated AP, mechanical properties comparable to those obtained by Rohm & Haas were obtained. However, the cure rates were substantially longer for the Hercules propellants. Removal of the hydroxyl functionality in the Aerojet TVOPA in conjunction with the fine Al and coated AP decreased the propellant elongation with little change in tensile strength and did not significantly affect the cure rate.

(U) Although the Rohm & Haas mechanical properties were duplicated for the EAAA propellants, the slower cure rate is a serious problem with AlH_3 propellants.

(C) Initial mixes of AlH_3 propellants with the EAAA binder are summarized in Table XX. As shown, several mixes have been processed at the 30-percent binder level with a 5:1 TVOPA:EAAA ratio. Mechanical properties for these propellants ranged from 40 to 55 psi tensile strength and 15 to 25 percent elongation at an epoxy-to-carboxyl ratio of 2.0. All mixes were cured at 120° F for 1 to 2 weeks. In comparing the cure rates of Al and AlH_3 propellants in Tables XIX and XX, and from small propellant mixes, there is a strong indication that AlH_3 is actually catalyzing the cure. (Mechanical properties of AlH_3 propellants stabilized at 120° F is approximately 8 days while it took the same time for Al propellants to stabilize at 140° F). However, the AlH_3 cure rates were still too slow and resulted in varying degrees of propellant porosity with all but the most stable AlH_3 lots.

a. Cure Studies

(U) As a result of the porosity during cure, the laboratory effort was directed towards developing a suitable low temperature cure for the EAAA binder. Several approaches were tried with the goal of a 100° F cure in 2 days:

(1) A comparison of cure rates with TVOPA purity

(2) Evaluation of catalysis systems

(3) Evaluation of other epoxy curatives

(4) Evaluation of a higher acid content prepolymer (93/7 EA:AA)

1) TVOPA Purity

(C) As mentioned above, purification of TVOPA with silica gel did not increase the cure rate, so the Rohm & Haas cure rate was not matched. Rohm & Haas treats their TVOPA with Amberlyst-15 which is a sulfonic acid type ion exchange resin. Since sulfonic acids are catalysts for many reactions, the possibility existed that traces of the acid were released into the TVOPA during treatment which then catalyzed the epoxy-carboxyl reaction. To check this theory, some Aerojet TVOPA was treated with Amberlyst-15 following the method used by Rohm & Haas and identical propellants were made with untreated and treated TVOPA. No difference could be detected in the cure rate. Therefore, the Amberlyst treatment is not responsible for the difference in cure rates.

TABLE XX

MECHANICAL PROPERTIES OF EAAA/AlH_3 PROPELLANTS

Mix. No.	E/C	TVOPA/EAAA	Binder Level	Cure Time & Temp (Days @ °F)	Tensile (psi)	Elongation (%)	Modulus (psi)
158-17	2.0	7/1	40	2/140			
				+5/120	17	24	81
				+7/120	18	27	76
158-32	2.0	7/1	40	9/120	22	30	93
				16/120	22	28	101
158-37	2.0	5/1	30	7/120	18	33	69
158-39	2.0	5/1	30	7/115	33	22	212
				14/115	41	15	337
158-41	2.0	5/1	30	7/120	47	20	319
				14/120	55	23	360
158-97	2.0	5/1	30	5/120	14	75	39
				8/120	44	22	264
				21/120	41	25	213
158-98	2.5	5/1	30	5/120	18	40	54
				8/120	46	12	370
				15/120	48	12	437

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2) Evaluation of Catalysts and Other Epoxides

(U) Investigation of catalysis with the EAAA using chromium octoate (CrOct) and ferric acetyl acetonate (FeAA) has shown both catalysts react with EAAA prepolymer to give stable gel. However, catalyst levels that significantly increase cure rates have resulted in unacceptable pot life.

(U) Binder studies with a dual catalyst consisting of chromium octoate and tetraethyl ammonium bromide (TEAB) indicated fast low temperature cures with TVOPA/EAAA/Unox 221 were achievable. (Refer to Table XXI.) However, the addition of solids slowed the cure rate markedly so that slower cures occurred in 10-gm propellant mixes. All solids tested appeared to slow the reaction to the same extent, and the effect is much larger than would be expected from simple dilution of the system. Even 4 percent Alon-C slowed the rate to the same extent as much larger quantities of either Al or AP. A possible explanation for this behavior is that one of the functional groups could be adsorbing onto the solids, thus making them inaccessible to the other reactant. For example, the acid group of the EAAA could absorb on the solids in such a way that the epoxide could not reach it, thus preventing reaction. This theory remains to be tested.

TABLE XXI

BINDER STUDIES WITH DUAL CATALYST

Cat. CO	Conc.* TEAB	Cure Temp (°F)	Cure Time (days)	Condition of: Gumstock	Propellant
16	4	80	13	--	Partially cured
16	4	100	13	--	Almost cured
4	1	80	12	--	Uncured
4	1	100	12	--	Partially cured
4	1	80	5	Cured	Uncured
4	1	100	5	Cured	Uncured
0	0	80	5	Partially cured	Uncured
0	0	100	5	Almost cured	Uncured

*In the epoxy (%)

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(U) While testing the effect of solids on the epoxide-carboxyl reaction, it was discovered that AP catalyzes the polymerization of Unox 221 - a solid polymer being achieved in one day at 120° F. This could explain why the optimum stoichiometry for RH-U-105 propellant is an E/C ratio of 2 rather than the expected ratio of 1 or less. To determine whether AP polymerized all epoxies, a different type of diepoxide, DER 332, was tested with AP. No noticeable polymerization was found with DER 332 at 120° F.

(U) Since DER 332 is not affected by AP, it was chosen for additional study as curative for the EAAA binder. Binder studies indicated that it did not cure any faster than Unox 221, but that it could be catalyzed by either chromium octoate or the dual catalyst. Solids were found to affect this reaction in the same manner as the Unox 221, but low temperature cures were achieved on 10-gm propellant mixes when high chromium octoate levels were used. (Refer to Table XXII.) Overnight cures at 120° F were achieved with 0.05 or 0.1 percent chromium octoate with partial cure in 4 days at 100° F. Three-hundred-gm mixes were then made with both 0.05 and 0.1 percent chromium octoate and cured at both 100° and 120° F. Cures were much slower than in the 10-gm mixes as seen in Table XXII. The mix with 0.1 percent catalyst finally cured in 10 days at 120° F but extensive porosity had developed in this time. Therefore, chromium octoate by itself is not an acceptable catalyst for this reaction.

TABLE XXII

CHROMIUM OCTOATE CATALYST PROPELLANTS

Mix No.	BC-138-19	BC-138-23	BC-172-36	BC-172-37
TVOPA/EAAA	29.5	29.0	29.0	29.0
DER 332	0.5	1	1.0	1.0
Cr Oct	0.05	0.1	0.05	0.1
AlH_3	22	22	22	22
AP	48	48	48	48
Mix Size (gm)	10	10	300	300
Cure At 100° F	--	Soft cure, 5 days	Slight cure in 8 days, porous	No cure in 7 days
At 120° F	Soft cure, 1 day	Cured in 1 day	Soft cure in 8 days, porous	Cured in 7 days, porous

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(U) A number of additives were tested in the chromium octoate catalyzed system to increase the cure rate. TEAB was added to detect the dual catalyst effect. Calcium tetraborate (CTB), an efficient HF scavenger, was added to test whether HF was interfering and ERL 0510 was added to determine whether a tertiary amine would catalyze the reaction. ERL 0510 was chosen since it is compatible with TVOPA (Fisher-Johns hot plate test and Taliani at 60° C) and it is also a triepoxide, thus providing additional crosslinking (which may or may not be helpful). These mixes were made with binder plus some AP since the addition of other solids in addition to AP is not expected to alter the reaction rate and AP can alter the stoichiometry by polymerizing epoxy whereas Al or AlH_3 do not influence the stoichiometry, only the rate. The results (Table XXIII) indicate that CTB increases the cure rate slightly, adding a quaternary ammonium salt has no effect, but adding ERL 0510 greatly increases the rate.

TABLE XXIII

EFFECT OF ADDITIVES ON CHROMIUM OCTOATE CATALYZED BINDERS

Formulation, Parts	1	2	3	4	5	6
TVOPA/EAAA	39	39	39	39	39	39
DER 332	1.0	1.0	1.0	1.0	1.0	1.0
Cr Oct	0.05	0.1	0.008	0.008	0.008	0.008
AP	10	10	10	10	10	10
Calcium Tetraborate	--	--	--	1	--	--
TEAB	--	--	--	--	0.03	--
ERL 0510	--	--	--	--	--	0.5
Cure at 120° F						
1 day	Slight	Soft	No	No	No	Cured
2 days	Cured	Cured	No	Slight	No	--
6 days	--	--	No	Slight	No	--

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(U) Additional studies of this effect with binder plus AP have demonstrated that ERL 0510 reacts with the acid but it also catalyzes the reaction of DER 332 and that chromium octoate and ERL 0510 are both needed to get rapid low temperature cures. These mixes are presented in Table XXIV. As little as 0.05 parts of ERL 0510 per 30 parts of binder is sufficient to achieve complete cure overnight at 120° F (mix III-1) with 0.05 parts of chromium octoate, but without chromium octoate rapid cure is not achieved even with 0.5 parts of ERL 0510. Thus, the two catalysts are synergistic and both are needed to achieve rapid low temperature cures. To ensure that no other ingredients interfere with the cure, a 10-gm mix was made. This mix cured at 120° F in 16 hr.

TABLE XXIV

CURE STUDY WITH ERL 0510

Composition, Parts	1	2	3	4
TVOPA/EAAA (10/1)	2.95	2.95	2.95	2.95
DER 332	0.05	0.05	0.05	--
Cr Oct	0.005	0.005	0.005	--
AP	1	1	1	1
ERL 0510	0.005	0.01	0.05	0.05
Pot Life	1 hr	1 hr	<30	OK
16 hr	Cured	Cured	Cured	No*

*Cured in 5 days

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(U) A 300-gm mix was then made to [illegible]mine whether scaleup will interfere with cure. Using the same binder [illegible] 2 in Table XXIV and filling with solids to a 70 weight percent solids loading, a short pot life was obtained resulting in a mix which only partially cast into the mold. (Refer to Table XXV.) A second mix, with the chromium octoate level reduced by one half, mixed and cast well. Both of these mixes cured in 16 hr at 100° F. These results indicated that the use of ERL 0510 in combination with chromium octoate and DER 332 would give a low temperature cure of the TVOPA/EAAA system.

TABLE XXV

300-GM MIXES WITH ERL 0510

Formulation	BC-172-38	BC-172-39
TVOPA/EAAA (10/1)	29.5	29.5
DER 332	0.5	0.5
ERL 0510	0.1*	0.1*
Cr Oct	0.05*	0.025*
AlH_3	22	22
AP	48	48
Pot Life (min)	20**	>30
Cure Time at 100° F		
16 hr	Complete	Soft Rubber
40 hr		Complete

*Additive

**Partially setup during casting

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3) Higher Acid Content Prepolymers

(U) Rohm & Haas has reported higher cure rates with prepolymers containing higher acrylic acid levels; therefore, the 95/5 EAAA prepolymer used in the above studies was compared with a 93/7 EAAA prepolymer also obtained from Rohm & Haas. There was no noticeable difference in the cure rate of the two prepolymers in the catalyzed system.

b. Mechanical Property Studies with EAAA

(C) The effect of a number of variables on the mechanical properties of EAAA/TVOPA/AlH_3/AP propellants was examined. These variables include carboxyl/epoxy ratio, tri/di epoxy ratio, AP particle size distribution, TVOPA/EAAA ratio, EAAA ratio in prepolymer, and the binder level. Comparison was made using JANNAF Type II dogbones from 300-gm mixes made in a Baker-Perkins mixer.

(C) A wide variation in E/C ratio at two different tri/di epoxy ratios resulted in remarkably little change in rather poor mechanical properties. (Refer to Table XXVI and Figure 7.) At an E/C ratio near 1, the modulus increased but without a corresponding change in tensile strength.

(C) Changing the TVOPA/EAAA ratio did not markedly improve the properties as presented in Table XXVII. With the 5/1 ratio, the binder level was raised to 35 percent (to reduce the viscosity) and even this change failed to significantly improve the mechanical properties.

(C) Changing the AP particle size distribution has a significant effect on the mechanical properties with a 1/1 ratio of 50 and 5μ AP giving the best results (Table XXVIII), but the best properties are far from acceptable.

(C) According to Rohm & Haas, the composition of the prepolymer significantly affects the mechanical properties of EAAA/TVOPA propellants, but with this AlH_3 propellant, little benefit was noted in changing from a 95/5 EAAA ratio to 93/7. (Refer to Table XXIX.)

(U) Increasing the binder level to 35 percent also gave little improvement in mechanical properties with normal cure times. (Refer to Table XXX.) However, after extended cure at 100° F a composition containing a large excess of UNOX 221 cured to give good mechanical properties. A similar composition containing an excess of DER 332 did not post cure and, therefore, had much inferior properties. Since the ability of UNOX 221 to homopolymerize under these conditions has been established, it is believed that the improved properties are due to homopolymerization of the epoxide. Therefore, contrary to expectations, the clean reaction of epoxide is desirable.

(U) Using the above findings, the binder level was then lowered back to 30 percent and formulation was made using a large excess of UNOX 221 with the 93/7 EAAA prepolymer. After 23 days cure, this propellant also gave high modulus and tensile strength. (Refer to Table XXXI.)

(C) The above results would indicate that the search for improvement in EAAA properties should concentrate on the use of epoxides that homopolymerize readily. Catalysts which promote this homopolymerization will be required to achieve low temperature cure in reasonable times.

4. EA-HEA

(C) An alternate method of achieving a low cure temperature for the TVOPA plasticized acylate binders is the use of an EA-HEA copolymer and a urethane cure. Dow Chemical supplied copolymers for this effort. (Table XXXII summarizes these copolymers evaluated.) These prepolymers were cured with 3-nitraza 1,5-pentane diisocyanate (XIII diisocyanate), HDI, DMDI, and Mondur TM at NCO:OH ratios of 1.0, 1.5, 2.0, and 2.5. The NCO:OH ratio is based on the combined equivalent weight of the TVOPA and EA-HEA. Because of the relatively large quantities of TVOPA used (87.5 percent in the 7:1 TVOPA:EA-HEA prebinder) its isocyanate demand becomes quite significant.

TABLE XXVI

EFFECT OF E/C RATIO ON MECHANICAL PROPERTIES OF EAAA PROPELLANTS

	BC 172-39*	BC 172-41*	BC 172-43*	BC 172-44*	BC 172-46*	BC 172-47*	BC 172-58*
Ingredients							
DER 332	0.5	0.5	1.0	0.25	0.25	1.0	0.1
ERL 0510	0.1	0.05	0.1	0.1	0.05	0.05	0.1
E/C ratio	1.6	1.4	2.9	1.0	0.8	2.7	--
Di/tri wt ratio	5/1	10/1	10/1	2.5/1	5/1	20/1	1/1
Mechanical Properties**							
Cure time, days	8	6	5	4	7	6	4
Tensile, psi	28	23	27	32	30	26	30
Elongation (max), %	25	42	21	17	22	38	21
Modulus	130	70	160	230	170	90	158
Cure time, days	15	13	12	11	14	13	
Tensile, psi	28	23	27	33	31	25	
Elongation (max), %	25	38	19	15	23	33	
Modulus	130	80	170	260	170	90	
Cure time, days		20	19				
Tensile, psi		26	32				
Elongation (max), %		41	23				
Modulus		80	170				

*Composition contains 30 percent binder, 9/1 TVOPA/EAAA, 22 percent ERL-1, and 48 percent AP.

**Type II JANAF dogbones conditioned at 77° F and pulled at a rate of 0.2 in./in./min.

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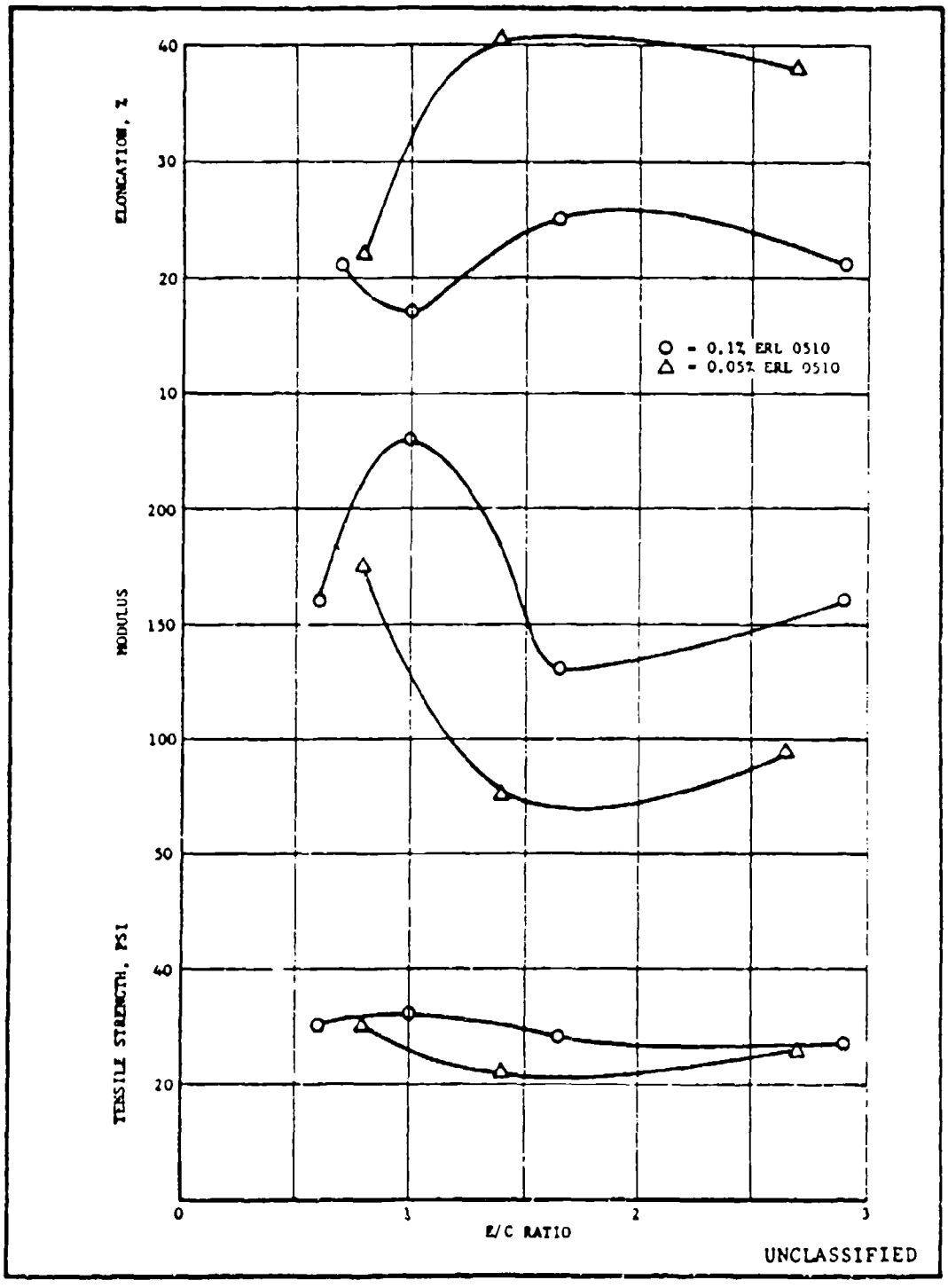

Figure 7. Effect of Stoichiometry on Mechanical Properties

TABLE XXVII

EFFECT OF TVOPA/EAAA RATIO ON MECHANICAL PROPERTIES

Mix Number	41	50	75
TVOPA/EAAA Ratio	8/1	7/1	5/1*
Mechanical Properties			
Tensile, psi	23	26	34
Elongation (max), percent	42	38	38
Modulus	70	90	100

*Thirty-five percent binder

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TABLE XXVIII

EFFECT OF AP PARTICLE SIZE ON MECHANICAL PROPERTIES FOR EAAA PROPELLANTS

	BC 172-50	BC 172-51	BC 172-58	BC 172-64
AP Size				
400μ, %	--	--	--	50
200μ, %	50	--	50	--
50μ, %	--	50	--	--
15μ, %	50	--	50	25
5μ, %	--	50	--	25
Mechanical Properties				
Tensile, psi	26	36	30	29
Elongation (max), %	38	36	21	31
Modulus	90	120	160	120

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TABLE XXIX

EFFECT OF PREPOLYMER COMPOSITION ON MECHANICAL PROPERTIES

EA/AA Ratio	95/5	93/7
E/C	1.5	1.0
Di/Tri	4/1	4/1
Mechanical Properties		
Tensile (psi)	26	34
Elongation (%)	26	33
Modulus (psi)	120	120
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TABLE XXX

MECHANICAL PROPERTIES OF HIGHER BINDER LEVEL PROPELLANTS

Mix No.	75	76
TVOPA/EAAA	5/1	7/1
Binder Level (%)	35	35
EA/AA ratio	95/5	95/5
DER 332	0.9	--
UNOX 221	--	1.0
ERL 0510	0.1	0.1
Cure time (days)	19	19, 26
Mechanical Properties		
Tensile (psi)	34	76
Elongation (%)	38	24
Modulus (psi)	100	320
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TABLE XXXI

HIGH E/C RATIO EAAA FORMULATION

TVOPA/EAAA		7/1	
Binder Level		30%	
EAAA Ratio		93/7	
UNOX 221 Level		0.9%	
ERL 0510 Level		0.1%	
E/C Ratio		2.4	
Cure Time	9	16	23
Mechanical Properties			
Tensile (psi)	39	57	77
Elongation (%)	21	13	12
Modulus (psi)	215	470	700
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TABLE XXXII

PROPERTIES OF ETHYL ACRYLATE-HYDROXYETHYL ACRYLATE COPOLYMERS

EA/HEA	No. Average Molecular Weight (gm)	Equivalent Weight (gm)
90/10	97,000	1280
90/10	22,000	2000
90/10	7,800	1790
90/10	15,000	1120
95/5	8,200	1030
85/15	13,000	720
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(C) It was found from initial gumstock work that cures were obtained at 80° F after 5 days with EA-HEA copolymers of molecular/equivalent weight of 97,000/1280, 22,000/2000, and 13,000/720 (the molecular/equivalent weight for the EAAA copolymer is approximately 25,000 to 30,000/1409). No significant change in the properties of these gumstocks was observed when further cured at 100° F for 2 weeks. Generally, the properties of the resulting cured gumstocks were of poor quality having low tear strengths (soft, gel-like and brittle). These poor properties are possibly a result of a nonoptimum crosslinked density, excess isocyanate, TVOPA chemical interaction or concentration, or combined effects of these factors.

(C) The DMDI seemed to yield more promising properties, but was somewhat immiscible in the TVOPA:EA-HEA prebinder. However, because of these more promising properties, this grid was repeated at NCO:OH ratios of 1.0, 1.5, and 2.0 (based on the total TVOPA:EA-HEA prebinder). The prebinder (5:1 TVOPA:EA-HEA) and DMDI were heated to 140° F (MP of DMDI ~90° to 100° F); however, a small portion of the DMDI remained insoluble. These gumstocks were well cured in 4 days at 100° F. However, the properties were poor. The samples were quite firm but very brittle and broke apart easily. As concluded earlier, these poor properties may be the result of the TVOPA chemical interaction or concentration and/or too high an isocyanate concentration.

(C) Control TVOPA/EA-HEA/AP/Al propellants were prepared with these prepolymers. As expected from gumstock results, marginal mechanical properties were obtained. However, these results were viewed as being quite promising, since this was the first attempt with this new polymeric system. The resulting properties are summarized in Table XXXIII.

(U) Based on these results, additional studies with the 29,000 and 40,000 molecular weight EA-HEA copolymers were completed. Each copolymer was crosslinked with various stoichiometric levels of 4,4-methylene bis (cyclohexyl diisocyanate) (Nacconate H-12), HDI, XIII diisocyanate, and 2/1 mol ratios of HDI and methane triisocyanate (TMTI). The same propellant composition and ingredients were used for each propellant. All were cured at 100° F until stable mechanical properties were obtained. Suitable catalyst (DBTDA) levels (0.000 to 0.002 percent) were used and essentially stable mechanical properties were obtained after 7-days cure. These results are summarized in Table XXXIV. In general, increased stoichiometry increased tensile strengths only slightly with an appreciable loss in percent elongation. The 40,000 mw copolymer gave slightly lower tensile strengths and appreciably higher percent elongations than the 29,000 mw copolymer. As a consequence, by increasing the crosslink density of the 40,000 mw copolymer with the addition of a TMTI in a more ratio of 2/1 (di/tri), tensile was improved. The mechanical properties of 48 psi tensile strength and 35 percent elongation obtained with the dissocyanate/triisocyanate blend and the higher molecular weight copolymer represent the best compromise of stress and strain capabilities obtained with the EA-HEA system. However, these properties must be compared with 61 psi tensile strength and 45 percent elongation obtained from the aluminized EAAA systems with the same basic propellant. It is felt that through continued binder

TABLE XXXIII

MECHANICAL PROPERTIES OF CONTROL PROPELLANT USING EA-HEA COPOLYMERS

(Cure Temp = 100° F)

EA-HEA Lot	TVOPA/EA-HEA	Curative	NCO/OH[1]	Catalyst[2]	Cure Time (Days)	Tensile (psi)	Elongation (%)	Modulus (psi)
97,000	5.4	XIII-Diisocyanate[3]	4.0	0.000	4	22	25	89
					7	33	17	199
					14	50	17	306
					21	79	15	548
					28	83	15	535
97,000	4.9	XIII-Diisocyanate	4.0	0.000	6	22	21	110
					12	26	20	134
					19	37	18	216
					27	71	16	466
97,000	4.4	XIII-Diisocyanate	2.4	0.000	3	38	14	284
					10	39	14	293
13,000	5.0	DMDI[4]	1.5	0.000	2	43	12	360
					7	50	10	486
					14	61	10	626
29,000	5.0	Nacconate H-12[5]	1.5	0.000	14	22	39	61
					22	26	35	77
					28	26	32	85
29,000	5.0	Nacconate H-12	1.0	0.002	5	30	32	116
					9	34	25	123
					14	36	28	132
29,000	5.0	Nacconate H-12	0.75	0.002	1	32	41	83
					5	34, 38	37, 36	84, 112
					14	35	37	96
29,000	5.0	Nacconate H-12	0.50	0.002	2	26	65	47
					7	29	53	59
					14	25	46	59
29,000	5.0	MDI[6]	1.00	0.002	6	32	42	77
					14	31	41	81
29,000	5.0	MDI	0.75	0.002	3	23	89	28
					7	27	69	34
					17	25	66	35
29,000	5.0	MDI	0.50	0.002	4	20	130	19
					7	18	110	19
					18	21	118	20

Notes:
[1] Based on equivalent weight of copolymer
[2] Dibutyltin diacetate
[3] 3-nitraza 1,5-pentane diisocyanate
[4] Diphenyl methane diisocyanate
[5] 4,4-methylene Bis(cyclohexyl diisocyanate)
[6] Hexamethylene diisocyanate
[7] Toluene diisocyanate
[8] Triphenyl methane triisocyanate

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TABLE XXXIV

MECHANICAL PROPERTIES OF EA-HEA PROPELLANTS

Copolymer 29,000			
Nacconate H-12[1]			
NCO/OH	Tensile, psi	Elongation, %	Modulus, psi
0.50	25-29	46-53	59
0.75	34-35	33-37	102-108
1.00	36	28	132
HDI[2]			
0.50	21	118	29
0.75	25	68	38
1.00	30	40	81
XIII-Diisocyanate[3]			
0.75	31	54	63
TDI[4]			
0.75	34	37	91
HDI/TMTI[5] **(1/1)**			
0.75	36	30	123
Copolymer 40,000			
Nacconate H-12			
0.75	28	54	55
HDI			
0.50	20	203	35
0.75	22	98	20
TDI			
0.75	30	65	55
HDI/TMTI (1/1)			
0.75	48	35	134
EAAA/ERL-4221	61	45	141

[1] 4,4-methylene bis(cyclohexyl diisocyanate)
[2] Hexamethylene diisocyanate
[3] 3-nitraza 1,5-pentane diisocyanate
[4] Toluene diisocyanate
[5] Triphenyl methane triisocyanate

Constants for each propellant:

A. Composition: TVOPA / EA-HEA 5:1 — 32.5; 6.5; Diisocyanate — As indicated (above); AP 50μ 1% Al_2O_3-C — 46.0; Al 5μ

B. Cure cycle 100° F until stable mechanical properties were obtained.

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(U) optimization the EA-HEA properties could be further improved. However, promising results with the R-18 prepolymer (Refer to Paragraph 5) negates much of the advantage of the EA-HEA binder; therefore, additional work on this system did not appear warranted.

5. R-18 Prepolymer

(U) Multron R-18 is a hydroxyl terminated copolymer of diethylene glycol and adipic acid. This structure gives R-18 two advantages and one potential disadvantage compared to EAAA. The advantages are (a) the hydroxyl functionality allows low temperature cure with isocyanates, and (b) R-18 has a much lower bulk viscosity than EAAA giving lower propellant mix viscosity. The potential disadvantage of R-18 is its history of poor hydrolytic stability.

a. Cure Studies

(C) The R-18/isocyanate cure reaction occurs very readily at low temperature with the use of small amounts of catalyst, the limiting factor being the pot life. Using 0.005 percent DBTDA, 2-days cure at 100° F is obtained with a pot life at 100° F in excess of 4 hr. This system cures at 80° F in 3 to 4 days. Increasing the catalyst level to 0.01 percent reduced the pot life to an unacceptable level. DBTDL placed on molecular sieves so that the catalyst is not immediately available for cure has produced good cure with adequate pot life. This approach aids catalyst dispersion also.

(C) As with P-BEP propellants, Hercules found that the impurities in TVOPA interfere with the cure of the R-18 system, mainly by reacting with the isocyanate. Even when accounting for the isocyanate demand of TVOPA, a considerable excess of isocyanate is required in order to obtain a cure with the R-18 system as seen in Table XXXV. (Hexane triol was used to crosslink the system.) No complete cures occurred at an NCO:OH ratio of 1.15 or below, but most systems cured when the NCO:OH ratio was 1.3 or greater. The data also indicate that the triol-to-diol ratio is important in obtaining cure. Two low a triol-to-diol ratio will prevent cure even at an NCO:OH ratio of 1.30.

b. Propellant Mechanical Properties

(C) A number of AlH_3/AP compositions containing a 6.5/1 TVOPA/R-18 ratio and 30 percent binder were tested with good results. At this low binder level, the particle size distribution of the solids is very important in the R-18 system. Even though the mix viscosity of R-18 compositions is fairly low, casting difficulties were encountered due to the thixotropic nature of the mix. Results of 10-gm mixes with a number of AP size distributions (Table XXXVI) indicate that a mixture of very large and very small AP casts best with AlH_3 propellants. A viscosity index of greater than 8 is not considered to be castable by ordinary methods.

TABLE XXXV

CURE STUDY WITH R-18 BINDER*

NCO/OH**	Triol/Diol Ratio	Cure After 5 Days @ 100° F
1.00	1.7	Uncured
1.00	1.4	Uncured
1.00	1.1	Uncured
1.00	0.8	Uncured
1.15	1.7	Partial Cure
1.15	1.4	Partial Cure
1.15	1.1	Partial Cure
1.15	0.8	Uncured
1.30	1.7	Soft Cure
1.30	1.4	Soft Cure
1.30	1.1	Soft Cure
1.30	0.8	Uncured
1.45	1.7	Cured
1.45	1.4	Cured
1.45	1.4	Cured
1.45	0.8	Cured

*10 gram propellant mixes using TDI curative and hexane triol catalyzed with DBTDA

**NCO/OH ratio is calculated based on an isocyanate demand value of 17,000 for TVOPA

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TABLE XXXVI

EFFECT OF AP SIZE DISTRIBUTION ON THE CASTABILITY OF R-18 PROPELLANT

Mix No.	1	2	3	4	5	6	7
Binder	30	30	30	30	30	30	30
600 μ	20	24	34	14	24	24	--
200 μ	14	--	--	--	--	--	--
15 μ	14	--	--	--	12	24	24 (50)
5 μ	--	24	14	34	12	--	24
AlH_3	22	22	22	22	22	22	22
Viscosity index	8.2	8.6	8.4	8.8	8.0	8.3	8.5

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(C) Formulation 5, when made in a 300-gm mix, cast easily with vibration. Replacing the 600μ AP with 400μ AP did not reduce the castability, and replacing the 5μ AP with 8μ HMX or with 15μ AP also resulted in castable mixes.

(C) The effect of particle size of AP on the mechanical properties of the R-18 TVOPA/AlH_3/AP propellant is presented in Table XXXVII. Use of AP sizes which pack poorly (mix No. 40) gives high modulus and low elongation. Use of a 50:50 course-to-fine blend gave lower modulus and higher elongation. Small changes in size and replacement of fine AP with fine HMX did not markedly change the properties.

(C) As mentioned above in the cure studies, a considerable excess of isocyanate is needed to achieve good cures with the R-18. The effect of isocyanate/OH ratio on mechanical properties of R-18 propellants is presented in Table XXXVIII at several ratios of triol to diol. The best properties were achieved with an isocyanate/OH ratio of 1.3 and a triol/diol ratio of 1.7.

(U) The above stoichiometry studies were made with "as received" TVOPA lots. As received TVOPA contains a number of impurities, at least one of which contains an isocyanate reactive functional group (probably OH). Therefore, all TVOPA lots have an appreciable isocyanate demand which interferes directly with the cure. To obtain cure, excess isocyanate must be added to the mix to account for the isocyanate demand of TVOPA. When calculating the cure stoichiometry (iso/OH) in the above mixes the TVOPA isocyanate demand was included as part of the OH level of the formulation.

TABLE XXXVII

EFFECT OF AP SIZES ON MECHANICAL PROPERTIES OF R-18 PROPELLANT

Mix Number[a]	BC 138-40	BC 138-43	BC 138-49	BC 138-59	BC 138-97	BC 138-93
AP Content, %						
600 μ	--	20	24	--	--	--
400 μ	--	--	--	24	24	24
200 μ	20	14	--	--	--	--
50 μ	28	--	--	--	--	--
25 μ	--	14	12	12	24	12
5 μ	--	--	12	12	--	--
5 μ HMX						
Mechanical Properties						
Tensile, psi	65	62	57	59	62	62
Elongation, %	14	23	26	27	23	28
Modulus	680	410	260	260	310	280

[a] 300 series mixes 30 percent binder, 7/1 TMOPA/polymer ratio, iso/OH = 1.3, di/tri = 1.7, AlH_3 12%, AP = 45

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TABLE XXXVIII

EFFECT O STOICHIOMETRY ON THE MECHANICAL PROPERTIES OF R-18 PROPELLANTS

Mix Number	BC 138-83	BC 138-86	BC 138-65	BC 138-73	BC 138-85
NCO:OH Ratio	1.15	1.30	1.45	1.45	1.1[illegible]
Diol:Triol Ratio	1.7	1.7	1.7	0.8	2.0
Mechanical Properties					
Tensile (psi)	50	67	67	38	58
Elongation (%)	28	24	21	32	25
Modulus	220	370	340	150	270
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(U) This approach worked well for most lots of TVOPA giving fairly good mechanical properties as seen above. However, with some lots of TVOPA, good cures were not achieved.

(U) This effect was first encountered in a 70-lb mix in which a blend of a number of lots of TVOPA was used. Even though the isocyanate demand was measured and accounted for, the cure was very slow and the mechanical properties inferior. Extensive studies with a blend of TVOPA lots, similar to those used in the above 70-lb mix, revealed that no ratio of iso/OH or triol/diol would give good cure (Table XXXIX), [illegible] TVOPA (Lot 280019) used in earlier studies gave fairly good propert[illegible]. A possible explanation for this behavior is that the nature of the isocyanate reactive impurity varies from lot to lot. Perhaps the impurity is mainly difunctional in some lots, thus providing chain extension of the R-18 binder, whereas in other lots the impurity is monofunctional, thus chain terminating the binder preventing crosslinking.

(U) Based on this theory, an extensive investigation was undertaken to purify the TVOPA to remove the reactive species. A description of the procedure developed in included in Appendix B. Use of purified TVOPA greatly improved the mechanical properties. (Refer to Table XXXIX.)

6. Binder Aging Comparison

(C) R-18 binder appears to have several advantages over EAAA. The major question mark for R-18 is the aging characteristics. The thermal aging of EAAA binder has been demonstrated by Rohm & Haas to be excellent, whereas considerable data is available for R-18 in other systems to indicate that a potential aging problem exists. The R-18 polymer is subject to

TABLE XXXIX

MECHANICAL PROPERTIES OF VKW PROPELLANT

TVOPA Lot No.	2BC019	Blend	Blend	Blend	Blend	Blend	Purified
Iso/OH Ratio	1.3	1.15	1.3	1.45	1.3	1.3	1.3
Tri/Di Ratio	1.7	1.7	1.7	1.7	2.0	2.3	1.7
Mechanical Properties							
Tensile (psi)	68	No Cure	25	No Cure	27	37	79
Elongation (%)	26	No Cure	60	No Cure	53	43	26
Modulus	290	No Cure	60	No Cure	70	110	340

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(C) hydrolysis of both the ester and the urethane linkages, either of which would cause cleavage of the polymer chain. This could create serious problems in tactical weapons which are subject to extreme temperature and humidity conditions. In a strategic application in which temperature and humidity can be controlled, the problem will be less serious. Some recent data to support this concept is given in Table XL. Storage under dry conditions at 100° F does not degrade the mechanical properties in 110 days. However, exposure to relatively low humidity levels (~35 percent) causes rapid degradation of the R-18 binder and 80° C testing at very low humidity caused complete breakup of dogbones in 42 days.

7. Binder Selection

(C) A comparison of the EAAA and R-18 binders is given in Table XLI. As a result of this comparison, the R-18 binder was chosen for scaleup. The EAAA binder looks promising but still requires a better low temperature cure whereas the R-18 gives good mechanical properties with a low temperature cure. The R-18 binder still has a serious question mark concerning its aging ability, but aging studies proved that it [illegible] enough to complete this program. Therefore, in an attempt to complete the scaleup portion within the time and funds of the contract, effort to find a cure system for EAAA was abandoned on this program and the R-18 binder was selected as the back-up binder for P-BLP.

TABLE XL

AGING STUDIES ON R-18 PROPELLANTS

	BC 138-43	BC 138-44	BC 138-49	BC 172-59	BC 138-57
Special Characteristics	3.95% R-18 polymer 26.04% TMPA 27.[illegible]% Al_2O_3 Trimodal blend of AP (600, 200, and 1[illegible] μ.	Identical to -43 except purified TMPA used	Identical to -43 only 20 μ AP replaced with 5 μ AP	Same as -49 only 30 μ AP replaced 60 μ AP	Identical to -57 except inert silicone process aid
Cure Time* @ 100° F, days	3	3	2	6	[illegible]
Tensile, psi	49	53	70	59	57
Elongation, %	24	14	26	27	31
Modulus	274	340	310	[illegible]	290
Cure Time @ 100° F, days	7	[illegible]	17	13	
Tensile, psi	53	54	70	77	
Elongation, %	23	[illegible]	23	25	
Modulus	390	520	310	[illegible]	
Cure Time @ 100° F, days	60	112	107	100	[illegible]
Tensile, psi	62	91	[illegible]	75	77
Elongation, %	23	18	25	27	26
Modulus	410	[illegible]	350	320	390

*Cure occurred in a heated, dry building

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TABLE XLI

COMPARATIVE BINDER CRITERIA

Comparative Criteria	R-18	LAAA
Polymer Availability	Readily available.	Would have to be manufactured, but synthesis is simple and straightforward as demonstrated by Rohm & Haas.
Solids Loading Potential	Allows higher solids loading. Limit not presently defined.	Present higher molecular weight polymers will allow processible propellant at the solids loading required to meet performance targets, however, a more easily processible system would be desired and can be obtained through tailoring of the LAAA polymer molecular weight.
Mechanical Properties	Yields better mechanical properties.	Although mechanical properties are lower, adequate or even comparable properties are indicated through polymer tailoring.
Structural Stability	Has history of structural instability. However, this instability has been shown to be retarded through the use of stabilizers under limited aging studies.	Has been demonstrated to have extremely good and reliable structural stability.
Shelf Life Potential	Not adequately defined, needs stabilization and will be dependent on temperature and humidity.	Excellent under controlled humidity at high temperatures, needs stabilization, and better definition of humidity limitations.
Stability in Scavenged Propellants	Hydrogenation could break polymer chains.	Hydrogenation breaks very few polymer chains since most ester groups are on side chains

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SECTION IV

SCALEUP

(C) Two binder systems were scaled up on this program. The P-BEP/TVOPA propellant was scaled up to 5PC motors, but was abandoned when a serious shelf life problem with the P-BEP/TVOPA/AlH_3 propellants were encountered. AlH_3 propellants with an R-18/TVOPA binder were then scaled up to 15- and 40-lb motors.

A. P-BEP PROPELLANT SCALEUP

1. Performance Optimization

(C) Theoretical performance calculations were made using the thermochemical data shown in Table XLII for the P-BEP/AP/AlH_3 system. Specific impulse and density as a function of P-BEP binder level and AlH_3 loadings is shown in Figure 8. Theoretical specific impulse peaks at low binder and high AlH_3 laodings, thus, processibility determines the upper limit to formulating from a theoretical standpoint.

TABLE XLII

THERMOCHEMICAL DATA USED IN PERFORMANCE CALCULATIONS

Ingredient	ΔH_f K-cal/mole	Formula	ρ(gm/cc)
P-BEP binder	-42.3	$C_{2.16}H_{3.09}O_{p.75}N_{1.17}F_{2.24}$	1.570
AlH_3	- 2.17	AlH_3	1.474
TVOPA	-197.7	$C_9F_{12}H_{14}N_6O_3$	1.54

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(C) To better define the formulation region of interest, predictions of delivered impulse were made on the basis of two-phase flow considerations. Figure 9 shows the calculated effect of weight percent Al_2O_3 in an exhaust on specific impulse efficiency. Figure 10 shows specific impulse efficiency as a function of mass flow rate for both fluorine and oxygenated binders. As shown, the fluorine binders give significantly higher impulse efficiencies than oxygenated binders even at relatively high mass flow rates. The high impulse efficiencies obtained with the fluorine containing propellants can be explained in terms of improved combustion efficiency (particularly in small motors and at high fuel loadings), and a reduction in two-phase flow losses. The reduction in two-phase flow losses at constant mass flow rate can be related to a reduction in weight percent condensables and a possible reduction in the oxide particle size. In order to fully

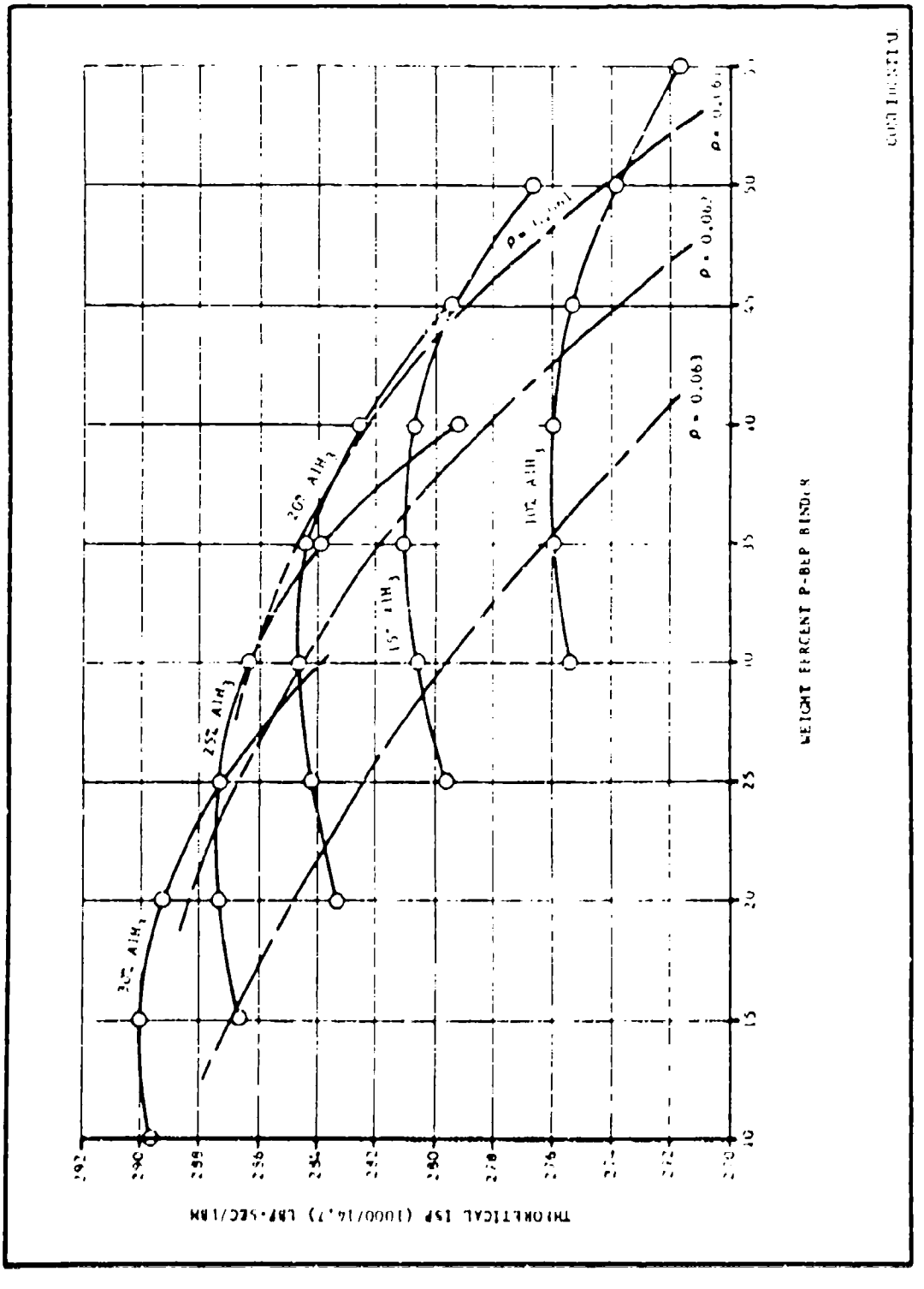

Figure 8. Theoretical Specific Impulse as a Function of Binder Level for P-BEP/AlH_3/AP System

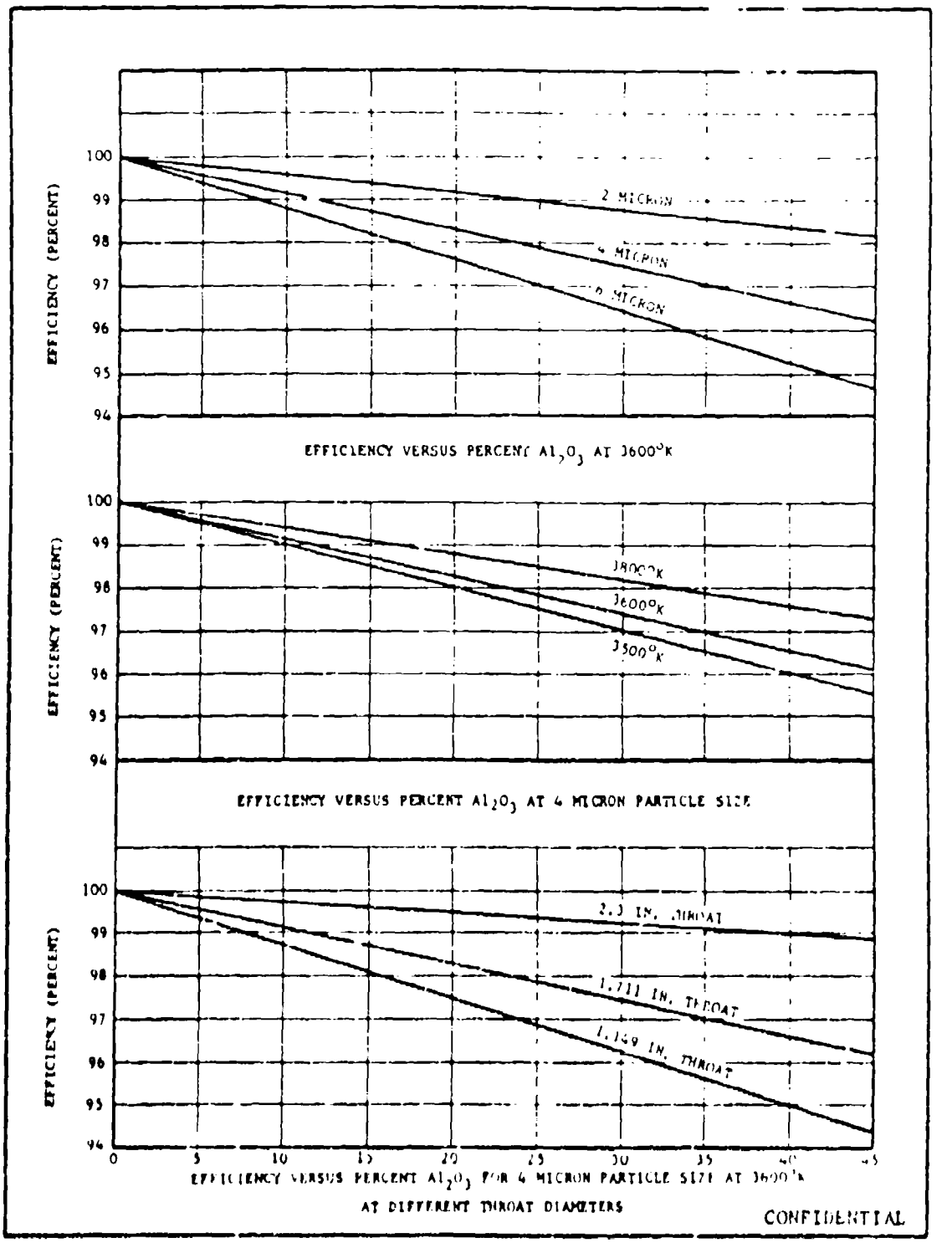

Figure 9. Calculated Particle Lag Losses

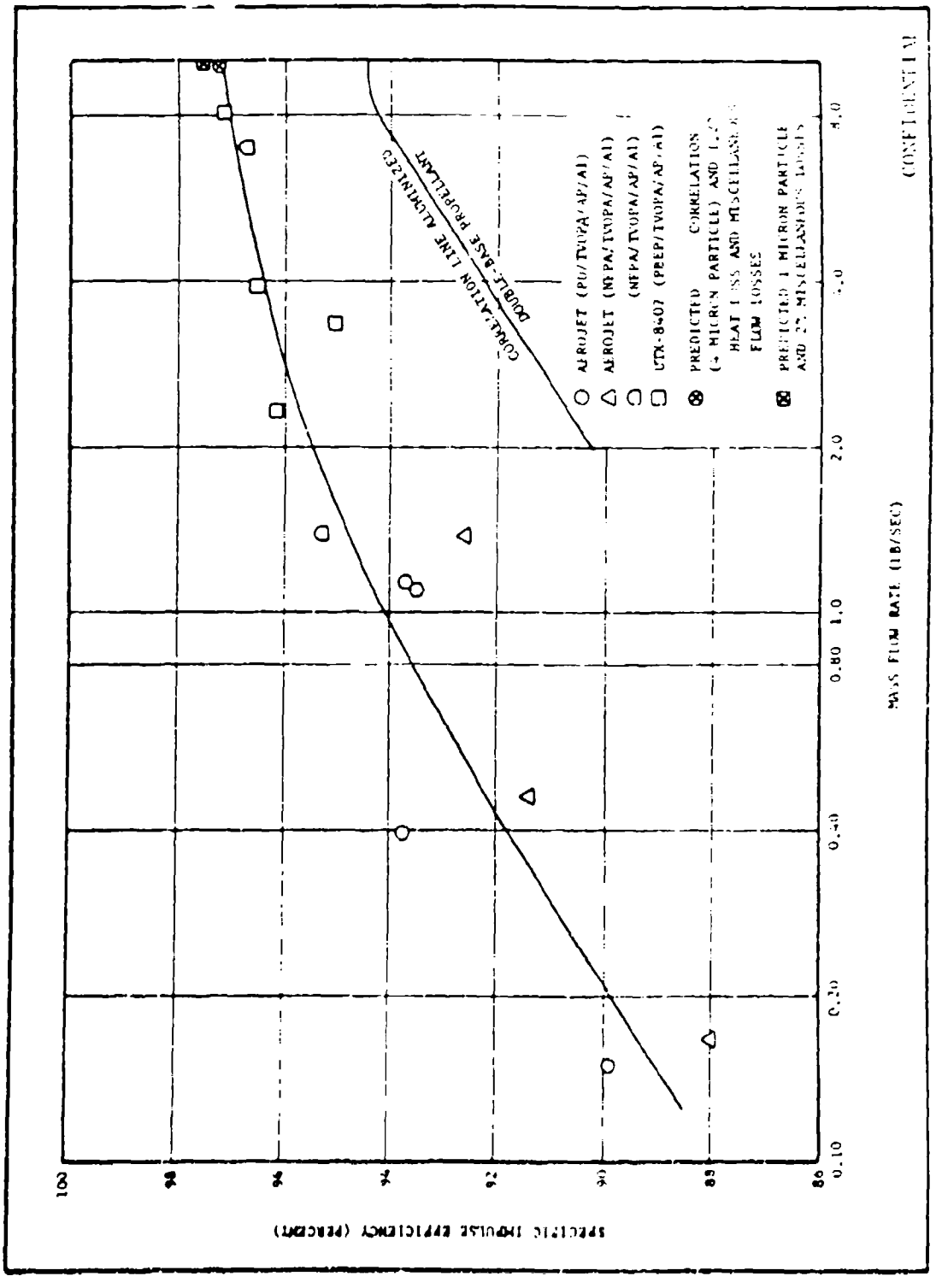

Figure 10. Effect of Mass Flow Rate on Specific Impulse Efficiency of Aluminized Propellants

(C) account for the differences in efficiency between fluorine and oxygen systems, the assumption of either a 1-micron oxide particle must be made, or if a 4-micron oxide particle is present, a reduction of approximately 1.0 percent in miscellaneous losses. For example, the impulse losses of a double-base propellant containing approximately 18 percent aluminum (34 percent condensables) at a mass flow of 8 lb/sec can be broken down as follows:

Basis (percent)	100
Particle lag loss (4 micron Al_2O_3)	-2.5
Heat loss	-1
Miscellaneous losses	-2
Specific impulse efficiency	94.5

(C) For comparable aluminum loadings, the weight percent condensables of the fluorine systems is approximately one-half that of the double-base systems with an indicated impulse efficiency of approximately 97 percent. As shown in Figure 10, this reduction in percent condensables can only account for approximately 1.6 percent of the 2.5 percent difference in efficiency between binders if a 4-micron oxide particle is assumed. Thus, under this assumption miscellaneous losses must be reduced by approximately 1 percent to account for the difference between binders. On the other hand, the assumption at a 1-micron particle could almost entirely account for the 2.5 percent efficiency difference. These factors are further illustrated in Figure 11.

(C) It is obvious from the above analysis that the efficiency data on fluorine systems is too limited to allow rigorous prediction of the effect of propellant and motor parameters on delivered impulse efficiency. Thus, further refinement of the efficiency correlations was expected to be an important part of the Phase II effort. Delivered impulses assuming both a 1- and 4-micron oxide particle are shown in Figure 11 as a function of AlH_3 loading for a constant system density of 0.0615 lb/in.^{3}. As expected from lag-loss considerations, the assumption of a 1-micron oxide particle size gives the highest predicted impulse values and optimizes at near optimum theoretical AlH_3 loadings (greater than 25 percent). Peak predicted delivered impulses in the processible range for the 1-micron oxide assumption are approximately 274 sec, in excess of the program requirements of 272 sec.

(C) The assumption of a 4-micron oxide particle and 1.2 percent miscellaneous losses gives a much flatter optimization curve with a peak delivered impulse of 270 sec predicted in the 20 to 25 percent AlH_3 range. Because the AlH_3 loading will control the upper limit or processibility and the final propellant density, it becomes necessary to determine which one of the correlation assumptions is most valid. For example, if the 1-micron

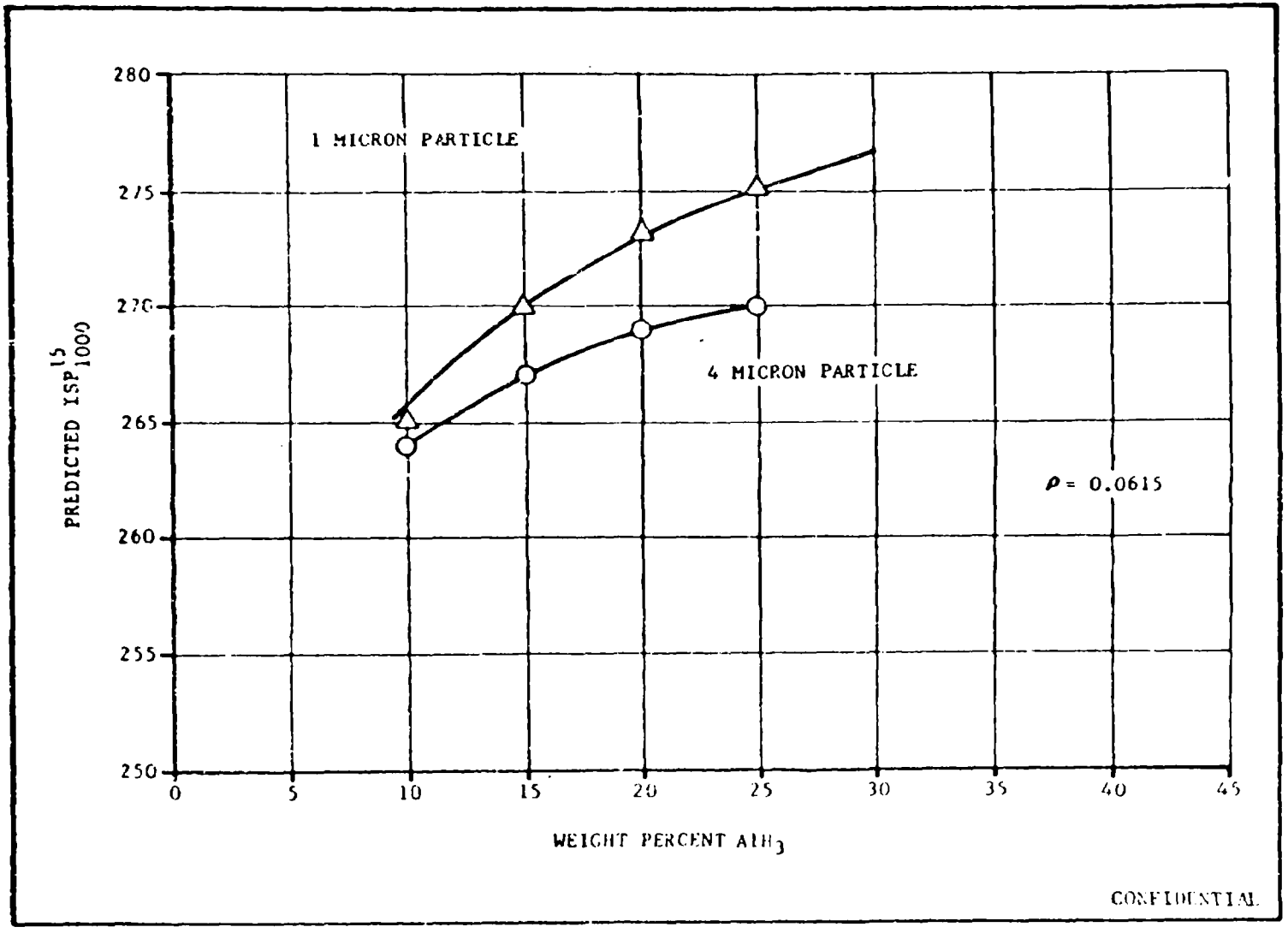

Figure 11. Effect of AlH_3 on Specific Impulse for 1 and 4 Micron Al_2O_3 for AP Systems

(C) assumption is valid, formulations should be designed with the highest AlH_3 loadings possible; however, if the 4-micron size assumption is valid, it may be more favorable to formulate at a lower AlH_3 loading and maximize AP loadings to achieve higher densities. Figures 12 and 13 show triangular plots of predicted impulse for the P-BEP/AlH_3/AP system assuming 4- and 1-micron oxide particles, respectively. Initial ballistic screening will be carried out with formulations designed to determine which of the oxide size assumptions is most valid. Formulations within the inner triangle shown in Figures 12 and 13 will be explored. Formulations in the range of 18 percent AlH_3 to the maximum obtainable (expected to be approximately 25 percent for an 0.0615 lb/in.^{3} density) will be tested. Oxide particles should be collected from micro and 5-lb motor firings in further refining the efficiency and delivered impulse predictions. Once the formulation region has been explored, an optimum formulation can be designed for maximum impulse and density within the processible region.

2. Laboratory Formulation Effort

(C) In support of the formulation effort, packing fraction measurements were determined for multimodal blends of AP and AlH_3. Blends of 600μ, 400μ, 50μ, and 15μ AP with AlH_3 were studied. Optimization of the size distribution was conducted using the Simplex method introduced by Alley and Dykes.[8] A typical response surface is shown in Figure 14. Results indicated most favorable AP distribution was a blend of approximately 30 percent -600μ, 30 percent -400μ, and 40 percent -15μ. However, based on mechanical property considerations, a blend of 65 percent 400μ and 35 percent 15μ AP was used throughout the bulk of the formulation effort.

(C) Using the above AP blend, studies were conducted to determine the effect of increasing solids loadings from 60 to approximately 70 percent. The effect of increasing solids loadings in several formulations are presented in Table XLIII. Within this grid the TVOPA content in the binder was increased from 50 to 67 percent. The NCO:OH ratio was increased to compensate for the higher TVOPA formulations. The data show that a formulation containing approximately 32-weight percent binder is processible. However, to process at this level requires the use of the higher TVOPA containing binder. Unfortunately, as shown in Table XLIII, these propellants characteristically cured more slowly and exhibited poorer mechanical properties than those made with a 1:1 P-BEP:TVOPA level.

(U) To further optimize the cure of P-BEP propellants, the following variables were explored in a series of 300-gm mixes:

[8] Refer to List of References

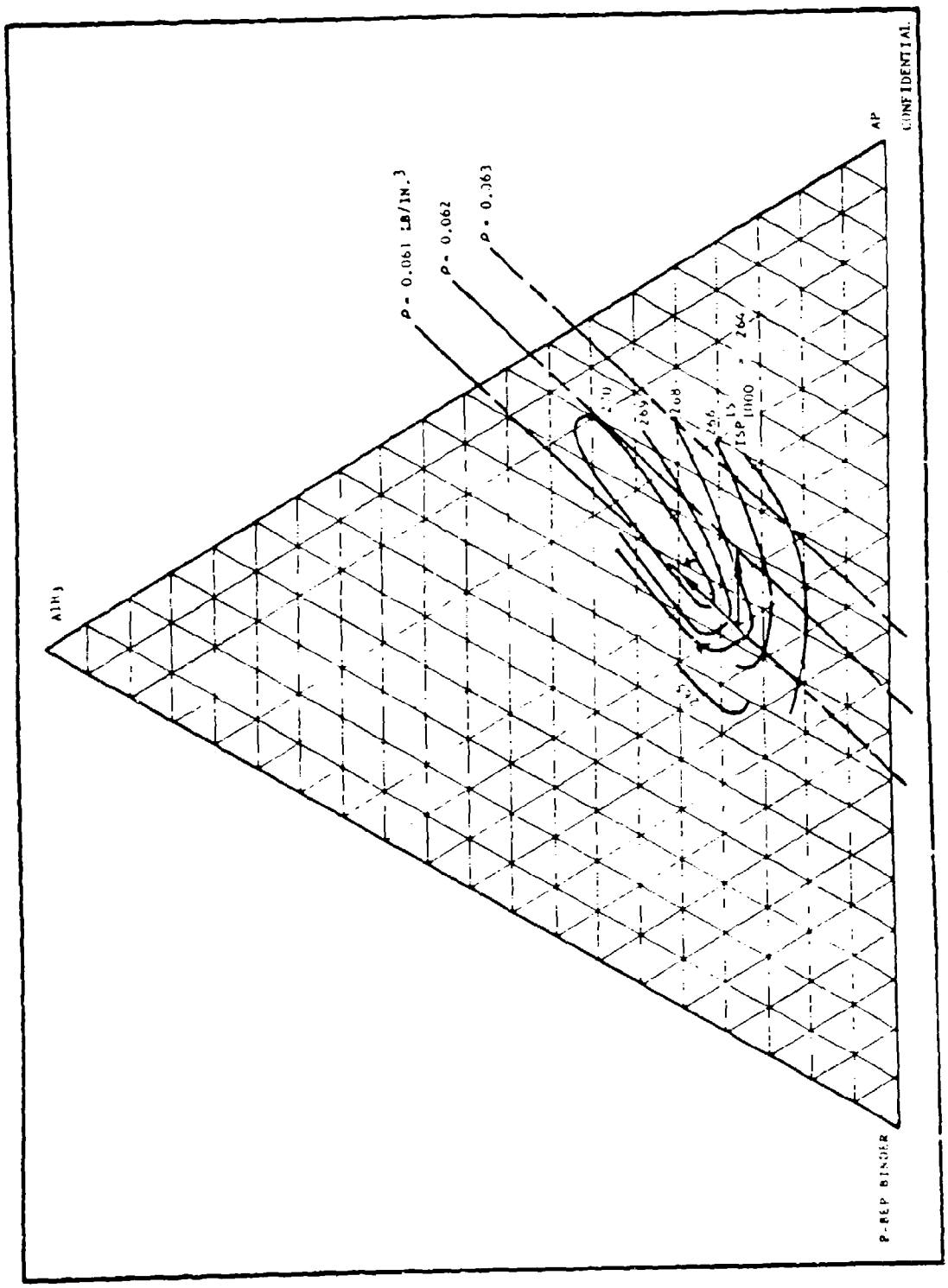

Figure 12. Predicted Performance, Isp^{15}_{1000}, for P-BEP/AlH_3/AP System Assuming 4 μ Al_2O_3

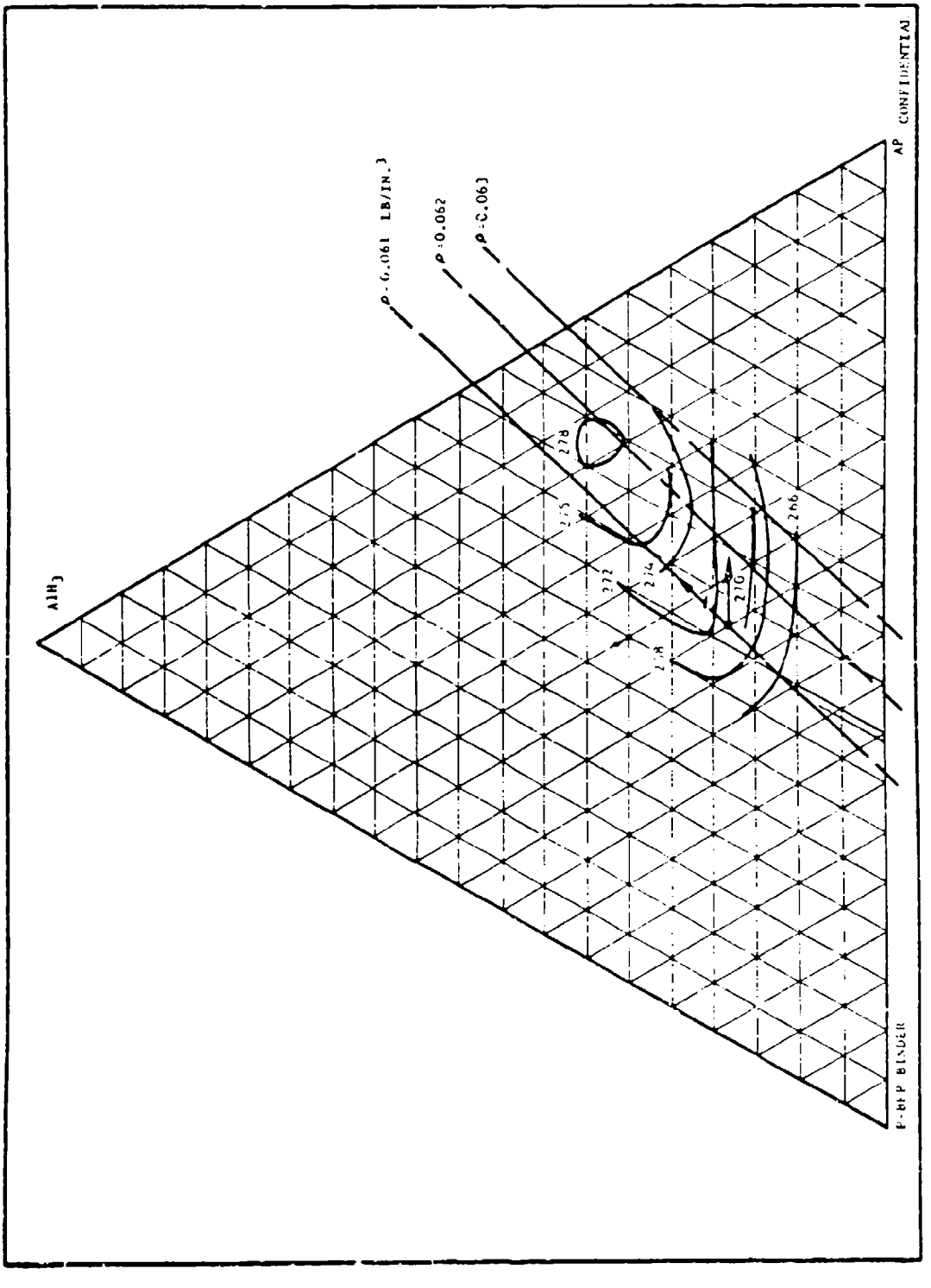

Figure 13. Predicted Performance, Isp^{15}_{1000}, for P-BEP/AlH_3/AP System Assuming 1μ Al_2O_3

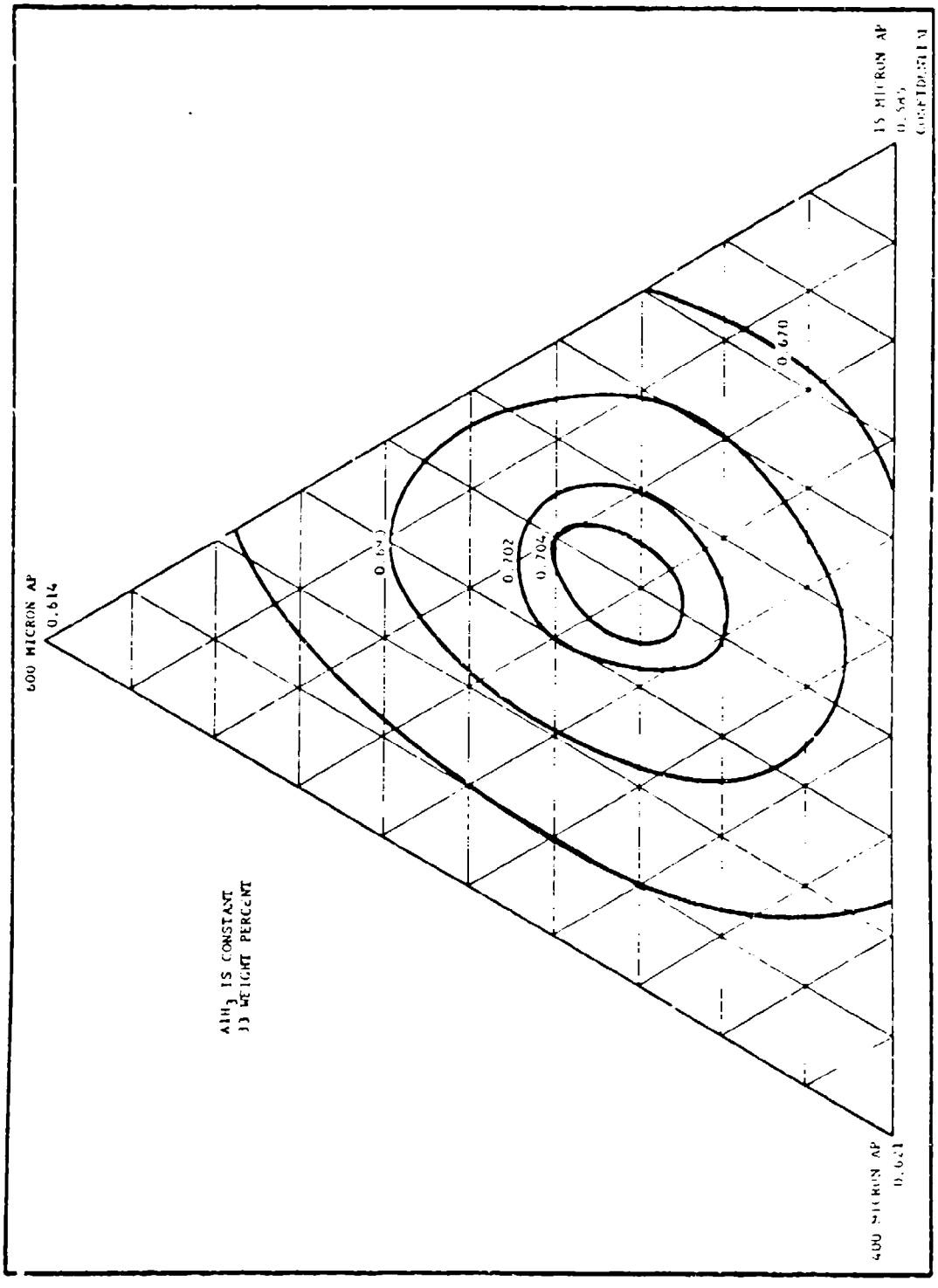

Figure 14. Packing Fraction Response Surfaces for Blends of 600μ/400μ/15μ AP, and AlH_3

TABLE XLIII

P-BEP/TVOPA FORMULATIONS FOR SOLIDS LOADING

	BC-165-19-1	BC-165-19-2	BC-165-19-3	BC-165-19-4	BC-165-19-5	BC-165-28
P-BEP	17.00	17.00	11.33	10.00	10.00	10.00
TVOPA	17.00	17.00	22.67	20.00	20.00	20.00
TCP	0.50	0.50	0.50	0.50	0.50	0.50
TPMII	1.625	1.625	1.35	1.20	1.20	1.20
CWX-105	0.20	0.20	0.20	0.20	0.20	0.20
AP	45.67	42.67	42.95	50.10	44.10	44.10
AlH_3	18.00	21.00	21.00	18.00	24.00	24.00
P-BEP/TVOPA	1/1	1/1	1/2	1/2	1/2	1/2
NCO/OH 1.6/1	1.6/1	1.6/1	2.0/1	2.0/1	2.0/1	2.0/1
Weight percent binder	36.125	36.125	35.85	31.70	31.70	31.70
Viscosity index @ °F	7.8 @ 98 (25 gm)	7.9 @ 100 (25 gm)	7.5 @100 (25 gm)	7.5 @ 100 (25 gm)	8.1 @ 104 (25 gm)	7.0 @ 115 (300 gm)
Cure properties	Cured good	Cured good	7 days soft and tacky @ 80° F. 15 days cured but poor tear strength	7 days soft and tacky @ 80° F. 15 days cured but poor tear strength	7 days soft and tacky @ 80° F. 15 days cured but poor tear strength	7 days soft and tacky @ 80° F

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(U) (a) NCO:OH ratio

(b) DBTDL catalyst level

(c) The non-HF reactive catalyst, DMTDC

(d) Al vs AlH_3

(e) Cure temperature

(f) Binder level

(g) P-BEP:TVOPA ratio

(h) TVOPA purification

(i) HF scavengers

(k) Polymer modification (triisocyanate/diisocyanate blends)

The large number of variables made a complete analysis impractical and in several cases only an initial indication of the effect of a particular variable was obtained. During the last part of the evaluation the effort was directed not only at mechanical property determinations but at reducing the CO_2 generation during cure and this effort will be discussed separately. Table XLIV shows composition of the two basic formulations explored at 40-percent binder.

(C) Two initial 1-lb mixes were made of formulation No. 1 at a catalyst level of 0.005 percent; one had an NCO:OH ratio of 1.4 and the other had an NCO:OH ratio of 1.6. Both mixes were cured at 120° F. The cure was not as complete as indicated by previous 25-gm mixes. This was shown by slight tackiness and softer than expected propellant. Physical properties of 42 psi, 36.5-percent elongation, and 170-psi modulus were obtained for the propellant cured at an NCO:OH ratio of 1.6. These data show that the propellant was not fully cured. The propellant formulation cured at 1.4 NCO:OH was not tested because of softness and solids settling during cure. As a result of the less satisfactory properties in the 1-lb mixes, the catalyst level was increased to 0.02 percent for the bulk of the remaining effort.

(C) Table XLV shows the results of a series of the Al control made at a 40 percent binder level. These results indicated that best mechanical properties were obtained at high catalyst levels and high cure temperatures. Previous 25-gm mixes had indicated the optimum NCO:OH ratio was in the range of 1.4 to 1.6. Studies over an NCO:OH ratio range of 1.4 to 2.0 indicated as expected, that the higher NCO:OH ratios gave highest tensile strengths while the lower ratios favored higher strain levels at the sacrifice of tensile strength. Decreasing the P-BEP:TVOPA ratio appeared to significantly degrade mechanical properties even when corrections were made for the TVOPA isocyanate demand. The use of the non-HF reactive catalyst dimethyltin dichloride appeared to give comparable properties to the CWX-105 catalyst system with 10 times higher catalyst levels requiring slightly longer cure times.

TABLE XLIV

FORMULATIONS FOR PHYSICAL PROPERTY
EVALUATION OF P-BEP/TPMTI BINDER AT 40 PERCENT BINDER LEVEL

	1	2
P-BEP	19.00	19.00
TVOPA	19.00	19.00
TCP	0.50	0.50
Mondur TM (TPMTI)	1.50 - 1.71	1.71
CW-X105 (10-percent DBTDL)	0.05 - 0.40	0.20
AP	45.00	42.00
Al	15.00	--
AlH_3	--	18.00

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TABLE XLV

MECHANICAL PROPERTIES OF P-BEP/Al PROPELLANTS

Mix No.	Binder Level	NCO:OH/Cat. Level	P-BEP:TVOPA	Aging Conditions*	Physical Properties Tensile/Elong/Modulus
165-20	40	1.6/.02	1:1	12/80	51/27/249
				19/80	61/19/417
				36/80	67/16/634
165-16	40	1.5/.02	1:1	12/80	53/24/287
				20/80	72/20/489
165-22	40	2.0/.02	1:1	16/80	87/18/599
				31/80	94/15/690
165-27	40	1.6/.04	1:1	8/80	64/29/298
				18/80	73/27/378
				31/80	75/25/411
				58/80	73/27/391
165-9	40	1.6/.02	1:1	8/80	
				5/120	65/25/367
165-11	40	1.6/.02	1:1	5/120	58/25/295
				10/120	78/20/519
165-21	40	1.6/.02	1:1	7/120	66/23/397
				14/120	63/23/383
				33/120	60/25/371
165-10	40	1.4/.02	1:1	9/120	69/24/401
165-23	40	1.4/.02	1:1	7/120	64/26/372
				14/120	64/26/360
				27/120	60/32/286

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TABLE XLV (Cont)

MECHANICAL PROPERTIES OF P-BEP/Al PROPELLANTS

Mix No.	Binder Level	NCO:OH/Cat. Level	P-BEP:TVOPA	Aging Conditions*	Physical Properties Tensile/Elong/Modulus
165-46	40	1.7/.02	1:1.25	13/80	42/29/206
				26/80	61/20/428
				41/80	65/19/508
				70/80	61/18/467
165-39	40	1.8/.02	1:1.5	10/80 + 3/120	26/48/78
				10/80 + 10/120	45/26/231
				36/80	50/24/282
				51/80	53/22/334
165-65	40	1.6/.2 (DMTDC)		17/80	53/28/259
				45/80	55/23/291

*Days/temperature (°F)

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(C) Table XLVI shows results of extension of the binder optimization studies to AlH_3. As shown between mixes 165-20 (Table XLV) and 165-20 (Table XLVI) there did not appear to be any significant difference between the ultimate properties of Al and AlH_3 propellants. However, the cure rates were noticeably slower for the Al propellants. The use of a purified TVOPA (no isocyanate demand) appeared comparable to increasing the NCO:OH ratio (mix 165-25, Table XLV vs mix 165-53, Table XLVI). (See also mixes 165-60 and 165-87, Table XLVI.) Decreasing the binder decreased elongation but did not significantly effect the tensile strength. The use of a blend of TPMTI and TDI (mix 165-86) appeared to give better properties than TPMTI alone (at a lower NCO:OH ratio, mix 165-75). One interesting anomaly occurred recently in duplicating the pilot plant mix cycle in the laboratory (mix 165-60). This particular sample was mixed much longer than usual prior to catalyst addition and gave a significantly higher tensile strength than normal. However, strain capability was not improved.

(C) Another interesting phenomenon occurred with the use of calcium tetraborate (CTB). In one experiment the CTB was added to the P-BEP/TVOPA solution prior to solvent stripping. After solvent stripping for 24 hr the free HF in the solution was reduced from 900 μg/gm to 140 μg/gm. This premix was used to make a 500-gm VKQ propellant mix. However, immediately after addition of the normal 0.02 percent DBTDL catalyst the mix set up in the mix bowl. These results confirmed that CTB is effective in removing large quantities of free HF, improving the catalyst efficiency. This same phenomenon has been observed in pilot plant mixes where an extra day of stripping has significantly reduced pot life. An additional mix was made with the CTB treated premix (mix 165-84) with no catalyst. This mix cured reasonably well at 90° F indicating CTB may also be an effective P-BEP cure catalyst.

(C) In summary, results of the binder optimization effort indicated mechanical properties of 70 psi tensile strength and 15 percent elongation could reasonably be expected at binder levels of 35 to 40 percent, a P-BEP:TVOPA ratio of 1:1, a DBTDL catalyst level of 0.02, with a room temperature cure. At lower binder levels, where increased TVOPA levels are necessary, properties are significantly poorer.

(U) It is recognized that improved properties could be obtained from P-BEP propellants through the addition of polyols. However, this approach significantly lowers energy and density levels and makes the use of P-BEP as a binder less attractive.

(U) Based on the above studies, a NCO:OH ratio of 1.6:1 and a CWX-105 catalyst level of 0.2 (0.02 percent DBTDL) was selected for additional scaleup mixes.

3. P-BEP Scaleup Mixes

(U) A total of 13 large P-BEP mixes were made using the TPMTI/CWX-105 cure and catalyst system. Table XLVII shows details of the five formulations which were scaled up. Table XLVIII summarizes details of the mixes made. All mixes were made by the inert diluent process in a 10-quart

TABLE XLVI

MECHANICAL PROPERTIES OF P-BEP/AlH_3 PROPELLANTS

Mix No.	Binder Level	NCO:OH/Cat. Level	P-BEP:TVOPA	Aging Conditions*	Physical Properties Tensile/Elong/Modulus
165-5	40	1.6/.02	1:1	19/80	60/17/572
165-51	40	1.6/.02	1:1	16/80	65/17/625
				32/80	66/15/696
				60/80	64/15/622
165-53	40	1.6/.02	1:1 (Purified)	28/80	95/10/1390
				57/80	95/10/1380
165-75	40	1.3/.02	1:1	26/80	42/22/290
165-89	40	1.6/0.2 (DMTDC)	1:1	7/90	
				1/80	63/15/536
165-33	37	1.6/.02	1:1	27/120	65/18/497
				49/?	67/16/654
165-36	33	1.6/.02	1:1	14/80	48/18/370
				20/80	67/13/777
				34/80	66/13/681
165-57	35	1.6/.01	1:1	23/80	74/12/874
				28/80	77/11/1100
165-60	35	1.8/.04	1:1.5	19/80	55/10/723
				27/80	57/11/793
165-28	32	2.0/.02	1.2	14/80	
				3/120	25/13/237
165-88	30	1.1/.02	1:1 (Purified)	7/90	
				3/80	55/12/719

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TABLE XLVI (Cont)

MECHANICAL PROPERTIES OF P-BEP/AlH_3 PROPELLANT

Mix No.	Binder Level	NCO:OH/Cat. Level	P-BEP:TVOPA	Aging Conditions*	Physical Properties Tensile/Elong/Modulus
165-87	35	1.1/.02	1:1.5 (Purified)	7/90 3/80	41/11/475
165-84	35	1.3/0 (0.5% CTB)	1:1	7/90 4/80	43/20/286
165-86	35	1.3/.02 (75 TPMTI/ 25 TDI)	1:1	7/90 4/80	63/17/475

*Days/temperature (°F)

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TABLE XLVII

P-BEP SCALEUP FORMULATIONS

Formulation	VKN	VKO	VKP	VKQ	VKR
P-BEP	17.6	19.0	19.0	16.5	16.5
TVOPA	17.6	19.0	19.0	16.5	16.5
TPMTI	1.7	1.82	1.82	--	1.58
AP	62.7	36.9	42.0	47.0	44.0
AlH_3	--	23.0	18.0	18.0	21.0
TCP	0.5	0.5	0.5	0.5	0.5
CWX-105	0.2	0.2	0.2	0.2	0.2
Theoretical Performance					
Isp (1000/14.7)	263.8	281.4	282	283	
ρ (lb/in.^{3})	0.0647	0.0602	0.0609	0.0615	
Tc (^{o}K)	3259	3202	3260	3415	
Oxidation Ratio	3.54	0.997	1.22	1.34	
Weight % Conds.	--	23.0	17.8	20.4	

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TABLE XLVIII

P-BEP PILOT PLANT MIX SUMMARY

Mix No.	Propellant	Size (lb)	Stripping Time (days)	Cure Time to Disassembly	Grains Cast	Remarks
1 thru 4	VKN	~10	1	3-6 days @ 115° F	Aging Samples	All nonporous
5 thru 8	VKO	~10	1	10 days @ 80	Aging Samples	3 nonporous, 1 grain contained a few small voids to 1/16 in.
9	VKP	11	1	13 @ 80	S-813	Disassembly cracks in top
				13 @ 80	S-814	Disassembly cracks top and bottom-machined out
10	VKQ	5.5	2	5 @ 80	S-818	Three small voids 3/32 in. near grain bottom
11	VKQ	11.5	1	11 @ 80	S-819	Eleven small voids throughout grain
				11 @ 80	S-820	Numerous voids to 1/4 in. throughout grain
12	VKP	5.5	2	5 @ 80	S-821	Twelve voids to 1/2 in. throughout grain
13	VKR	5.75	2	10 @ 80	S-815	Six large voids to 7/16 in. throughout grain

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(U) Hobart mixer. The first eight mixes shown were made under Contract F01611-68-C-0039 to supply AFRPL aging samples. These mixes were cast into either 5-in. cubes, 2-in. cubes, or Saylock tensile molds. The VKN propellant has a very slow cure rate at 80° F, but cured well within 3 to 6 days at 120° F. The VKO propellant also cured slower than in the smaller mixer but was well cured in 9 days at 80° F. The comparative cure characteristics were the same as observed for 1-pint Baker Perkins mixes made in the laboratory, i.e., addition of AlH_3, or more specifically, nBA-treated AlH_3 catalyzed the isocyanate cure.

(C) The remaining 5 mixes were cast into 5PC grains, as described in the following paragraphs. Mix No. 9 was an 11-lb mix of VKP propellant, and was cast into two 5PC molds. The propellant contained 0.02 percent DBTDL catalyst and also cured slower than laboratory mixes. The grains were cured 13 days before mold disassembly. Both grains were slightly damaged during disassembly by propellant fractures caused by propellant adhering to the polyethylene mold plates. The propellant fractures were removed by machining, and both grains fired.

(C) Mix No. 10 was a 5.5-lb mix of VKQ propellant and was cast into one 5PC mold. To study the effect of stripping efficiency on propellant cure rate, the P-BEP:TVOPA solvent was stripped for an extra day prior to completing this mix. This grain cured approximately twice as fast as previous mixes made using a 1-day stripping cycle The pot life was also noticeably shorter for this mix. The grain obtained from this mix was of good quality and fired.

(U) Mix No. 11 was an 11.5-lb mix of VKQ propellant and was cast in a dual grain 5PC mold. This mix was made with the normal one day stripping cycle. Again, this grain exhibited the slower cure rate. X-ray inspection showed that top grain contained some porosity while the bottom grain contained numerous voids to a 1/4 in. diameter. The top grain was subsequently fired successfully. The cause of the porosity in this grain was not readily apparent.

(U) To confirm the faster cure rate with the longer stripping cycle, an additional 5.5-lb mix (mix No. 12) of VKP propellant was made with a 2-day stripping cycle. Again, the pot life was much shorter and the cure rate faster than with the shorter stripping cycle. Radiographic inspection showed several large voids throughout this grain which were felt to be due to poor consolidation resulting from the short pot life.

(C) One final mix (mix No. 13) was made of the VKR formulation in which modifications were made to reduce gas generation and improve pot life. Ammonium perchlorate was vacuum dried several days at 140° F to lower residual moisture to a minimum. In addition, the TPMTI was reduced so as to provide a 1.3 NCO:OH ratio. Previous mixes were made with a 1.6 NCO:OH ratio. These steps were designed to reduce the potential for the production of CO_2. The P-BEP/TVOPA mixture was vacuum stripped for 2 days. The CWX-105 catalyst level was reduced from 0.2 to 0.1 percent. The mix temperature was kept below 100° F. This grain was cured at 90° F and was disassembled after 5-days cure. X-ray examination of each grain showed ten voids, two were about 3/8 in. in diameter, and four had cracks associated with them.

(C) The results of this casting indicated the porosity problem is associated with a rheology problem during casting and consolidation. It is known that the reduction in the free HF level during the stripping cycle significantly reduces pot life. This factor, coupled with the higher solids loaded formulations may have led to poor grain consolidation on the latter mixes. A solution to this problem appeared to require a good deal of additional effort, including reformulation at higher TVCPA levels to get a more fluid mix, and prior elimination of HF to get a more reproducible pot life. This effort did not appear warranted in light of the short P-BEP/AlH_3 shelf lives and no additional P-BEP mixes were made. (Refer to Section V, paragraph 5.) Further scaleup was accomplished with the R-18 binder.

4. Ballistic Evaluation

a. Micro-Motor Firings

(C) A limited number of micro-motor firings were made of P-BEP propellants to determine initial burning rate characteristics to size nozzles for the larger motors. The basic micro-motor design is the same as the Rohm & Haas 75C.50-1.5 motor design and contained approximately 10-gm of propellant. Initial firings were made with an igniter composed of an M-105 Atlas match with 200 mg of NNP-503 powder with VKP propellant. However, a rather severe ignition saddle was experienced with this system. Additional firings were made with a wide variety of igniter materials in an attempt to obtain more neutral traces. Magnesium-teflon was found to provide the most desirable ignition characteristics and a series of firings were conducted using various weights and combinations of magnesium-teflon powder and quartered 3M magnesium-teflon pellets. All firings were conducted at 1000 psia design pressure. A bag igniter composed of an M-105 Atlas match and 400 mg of magnesium-teflon powder gave the most acceptable pressure-time trace. A typical trace is shown in Figure 15. Discharge coefficients of 0.0063 sec^{-1} were obtained for all firings using 300 to 400 mg of magnesium-teflon material.

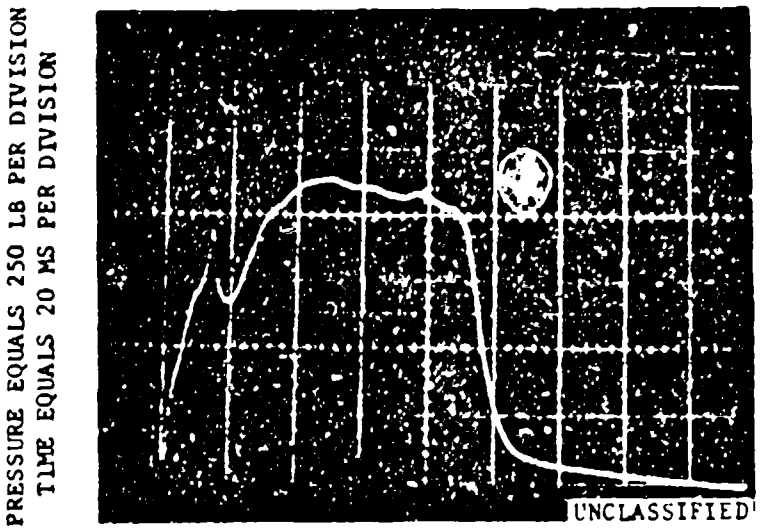

Figure 15. Pressure-Time Trace for Micro Motor Grain No. 165-12-4, Propellant Composition BC-165-12

(C) Using -bove ignition system, P-K-r data was obtained on VKP propellant over a pressure range of 500 to 1500 psia. There were no indications of any ballistic anomalies over this pressure range. The P-K-r data from these firings is shown in Figure 16. Also shown in Figure 16 are the results of strand burning tests of this propellant. Good agreement with the micro-motor data is evident. The burning rate of the VKP propellant was 1.4 in./sec at 1000 psia with a pressure exponent of 0.67.

b. Five Pound Motor Firings

(U) Four 5-lb motor firings of the P-BEP/AlH_3 propellant, produced from the scaleup mixes, were made. Two firings of each of VKP and VKQ propellants were made. Details of these firings are presented in Table XLIX and typical pressure and thrust-time curves are shown in Figure 17.

(C) The first firing was of VKP grain S-814. Apparently, the beaker split during initial pressurization due to a more rapid than usual pressure rise for this propellant. The increased surface caused a peak pressure of about 2400 lb, overloading both pressure and thrust data acquisition systems. Reliable ballistic data was thus not obtained from this firing. Succeeding firings were made with a modification in motor loading to permit faster pressurization behind the grain inhibitor. The second VKP firing gave a delivered Isp^{15}_{1000} of 258.9 sec for an efficiency of 91.9 percent. The two VKQ firings gave an average delivered Isp^{5}_{1000} of 265.3 sec for an efficiency of 94.1 percent. The average mass flow rate for the VKQ firings was 8.4 lb/sec. The high efficiency and high delivered impulse of the VKQ propellant at this mass flow rate confirmed the expected high performance of DOMINO/AlH_3 propellants. Additional analysis of this data is given in Paragraph 8.4

5. Shelf Life Studies of P-BEP Propellant

a. Posttreatment Studies

(C) Previously reported efforts showed significant improvements in stability of neat AlH_3 could be obtained with the NBA passivation. This initial effort indicated a 7 day/60°C cycle was near optimum from the standpoint of early gas formation and oxygen uptake (purity decrease). Further-optimization studies were conducted to optimize the treatment cycle based on long-term stability in P-BEP propellant. In this study, a determination was made of the off-gases evolved from P-BEP/TVOPA/AlH_3 propellants as a function of passivation time at 60° C. The samples were contained in stainless steel tubes coupled to a modified GC column for separation and quantization of the gases. Figure 18 shows a summary of total gases determined from complete P-BEP/AlH_3 propellants containing "as received," 7-day, and 14-day nBA created AlH_3, respectively. Figure 19 shows the same plot for hydrogen only. These samples were prepared in the laboratory (25-gm mixes) and placed in the off-gas analyzer immediately after mixing, i.e., prior to cure. The off-gas results on 25-gm mixes after 21-day testing at 60°C is shown in the following tabulation

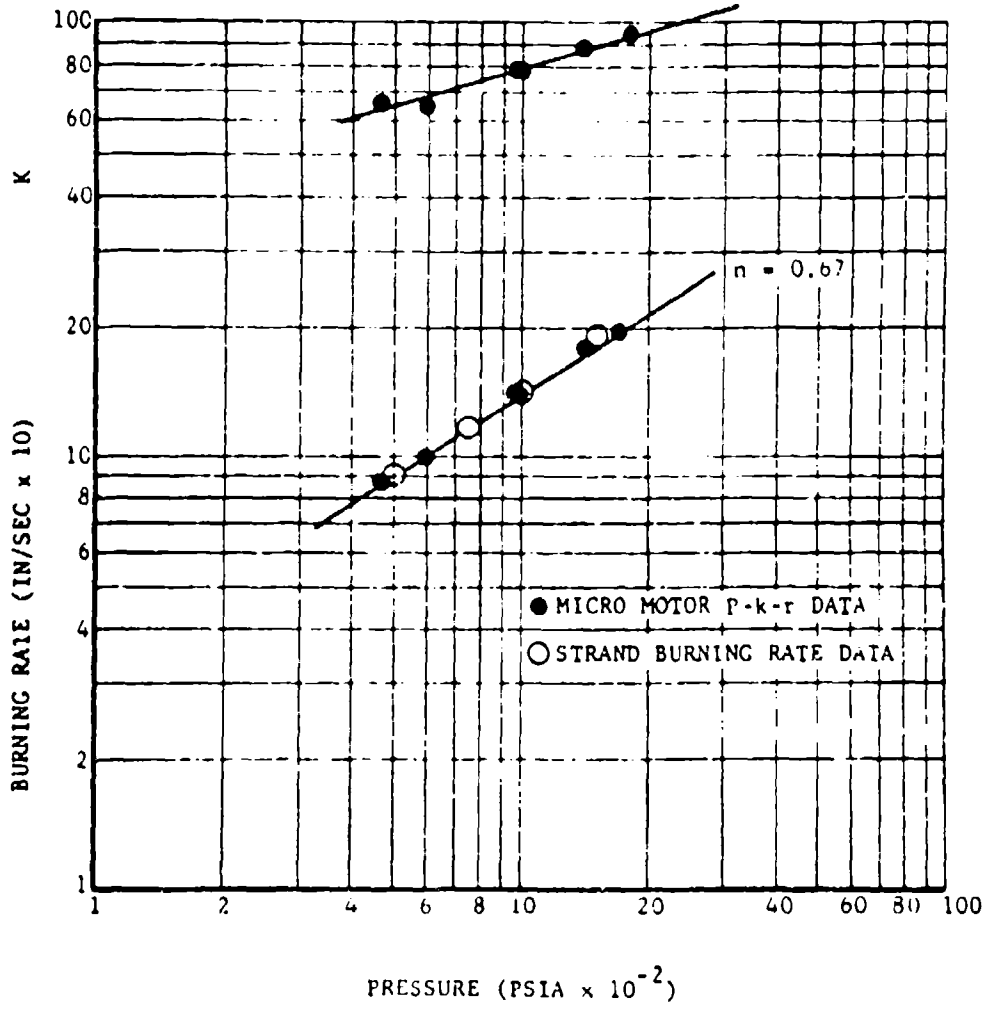

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Figure 16. P-k-r Data for VKP Propellant

TABLE XLIX

MOTOR FIRING SUMMARY

Formulation	VKP	VKP	VKQ	VKQ	
Motor Design	5PC	5PC	5PC	5PC	
Firing Date	4/30/69	4/18/69	4/30/69	5/7/69	
Crain No.	S-813AH	S-814AH	S-818AH	S-819AH	
Firing No.	DOM-1	DOM-2	DOM-3	DOM-4	
Propellant Wtg.	4.90	4.74	4.78	5.38	
$K-S/A_t$	61.68	*	70.40	67.99	
t_a-sec	1.006	*	0.582	0.637	
t_b-sec	0.945	*	0.555	0.590	
$\bar{P}_a$-psia	606	*	1208	1060	
$\bar{P}_b$-psia	628	*	1240	1098	
$\bar{P}$max-psia	701	*	1350	1178	
$\bar{P}$amb-psia	12.22	*	12.22	12.29	
$\bar{r}$-in./sec	1.007	*	1.701	1.607	
$\dot{m}$-lb/sec	4.87	*	8.21	8.45	
C_d-sec^{-1}	0.00588	*	0.00576	0.00585	
$\epsilon-A_e/A_t$	6.250	6.285	7.257	6.231	
$\bar{F}_a$-lb_f	1216	*	2223	2230	
Isp del.-$\frac{lb_f\text{-sec}}{lbm}$	249.9	*	271.0	264.7	
Theoretic l Isp at Firing Conditions	271.9	*	287.0	283.6	
Efficiency, Eff	91.91	*	94.42	93.68	
Isp^{15}_{1000}	258.9	*	267.0	264.9	

Notes:

*Not considered valid because of beaker split at initial pressurization.

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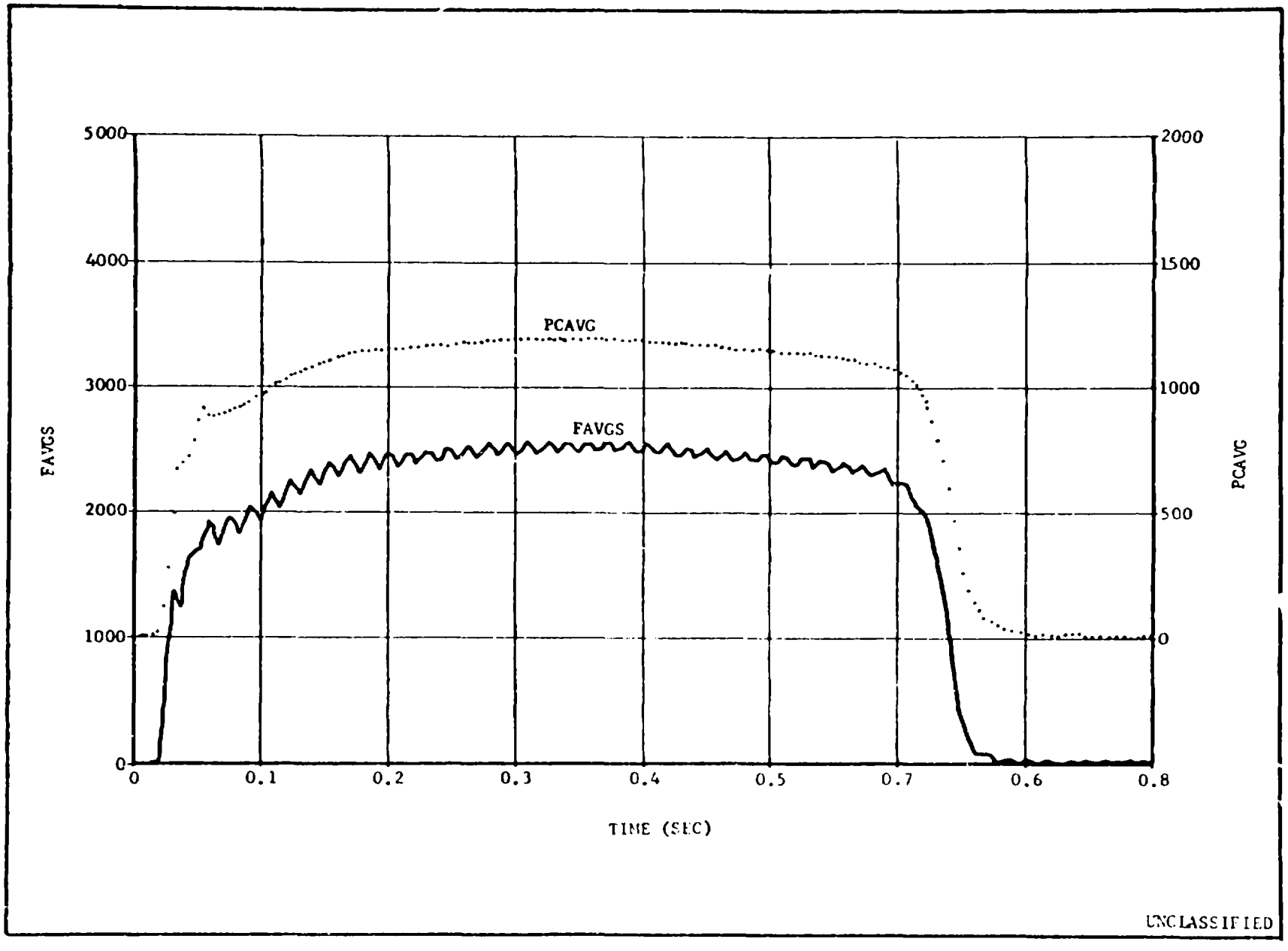

Figure 17. FAVGS and PCAVG Versus Time (5-Lb DOM 4, Range Round 9105, Date Fired 05-07-69)

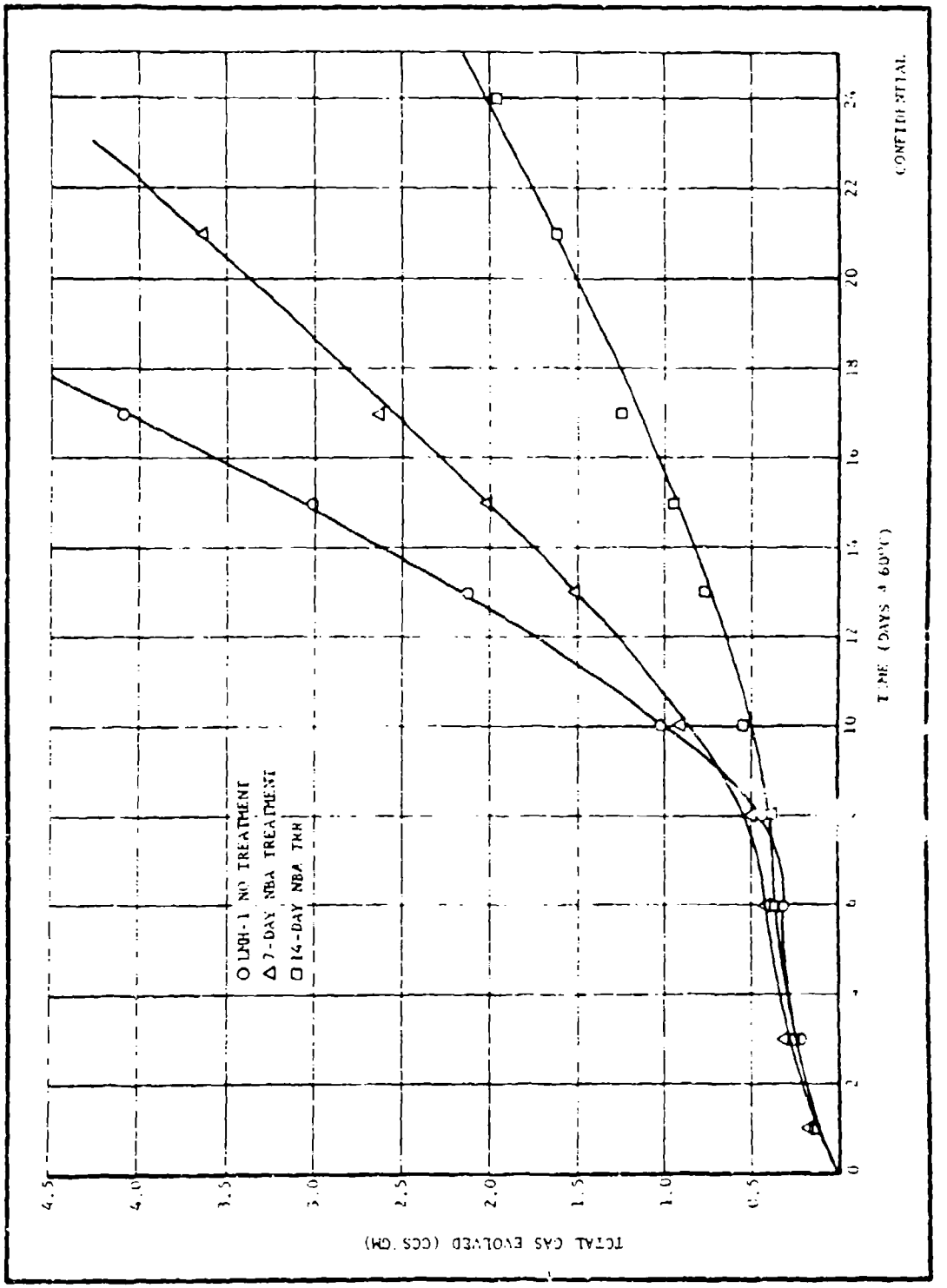

Figure 18. Gas Generation of P-HIP/TVOPA Propellants (Total Gases)

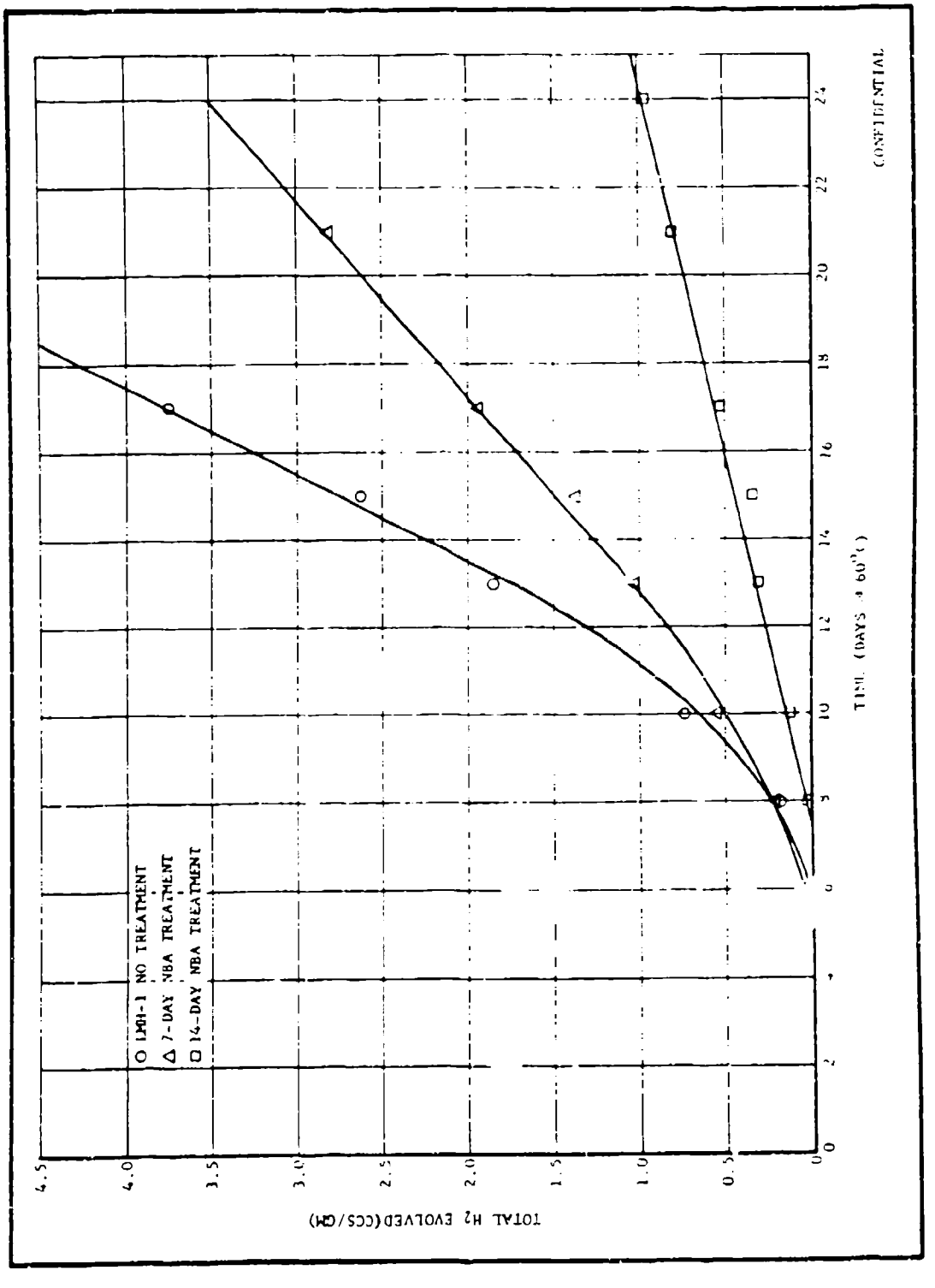

Figure 19. Gas Generation of P-BEP/TVOPA Propellants (Hydrogen)

(C)

AlH_3 Treatment cc's Gas/Gram	"As Received"	7-Day NBA	14-Day NBA
H_2	5.54	2.80	0.78
CO_2	0.28	0.49	0.54
HCN	0.04	0.37	0.30
Total	5.86	3.66	1.62

These data show that significant improvements were obtained in the stability of AlH_3 by the n-butylamine treatment. Also of importance is the increase in the amount of CO_2 and HCN with the NBA-treated material, indicating a possibility of an interaction between the P-BEP binder and the NBA-treated AlH_3. Off-gas data for a repeat run with 14-day NBA AlH_3 taken from a large pilot plant mix after 20 days at 60° C is tabulated as follows:

AlH_3 Treatment cc's Gas/Gram	14-Day NBA
H_2	1.17
CO_2	0.25
HCN	0.12
Total	1.54

These data show less CO_2 and HCN, possibly due to better stripping in the pilot plant over the 25-gm mixer. However, the HCN level is still higher than the "laboratory" "as received" AlH_3 sample.

b. Stability Studies

(C) To obtain gas generation rate results that would be directly relatable to cracking cube results, several 2-in. cubes of both P-BEP/Al and P-BEP/AlH_3 propellants were made. (Refer to Table XLVII for details of the formulations used in this study.) These cubes were cured at 80° F and samples of the cubes placed in the off-gas analyzer just prior to placing the cubes in surveillance. Results of off-gas testing with these samples at 60°C are presented in Table L. Of major significance is the fact that the induction period to the onset of AlH_3 decomposition observed in the tests conducted with curing propellant has apparently been used up so that hydrogen was detected immediately. In addition, a much higher initial CO_2 peak was observed with the P-BEP/Al propellant. This high peak may be the result of a poorer cure of the Al propellant, leaving residual isocyanate to react with moisture contamination. Again, as with the previous tests, the NBA-treated AlH_3 sample gave larger quantities of HCN.

TABLE L

GAS EVOLUTION DATA FOR CURED P-BEP/TVOPA PROPELLANTS

Sample	Days @ 60° C	Gas Evolved Since Previous Test, cc/gm/Propellant					
		H_2	Air	CO_2	N_2O	HCN	Freon 113
No AlH_3	1	nd*	0.80	0.13	trace	trace	0.03
AlH_3	1	0.03	nd*	0.06	trace	trace	0.01
No AlH_3	2	nd*	0.19	0.03	trace	0.004	0.02
AlH_3	2	0.03	nd*	0.05	trace	0.007	0.01
No AlH_3	3	nd*	nd*	0.03	trace	0.004	0.02
AlH_3	3	0.02	nd*	0.03	trace	0.005	0.01
No AlH_3	4	nd*	nd*	0.01	trace	0.01	0.02
AlH_3	4	0.02	nd*	0.02	trace	0.008	0.01
No AlH_3	7	nd*	nd*	0.03	trace	0.019	trace (<0.01)
AlH_3	7	0.06	nd*	0.03	trace	0.023	0.01
Total Gas 7 Days, cc/gm of Propellant		H_2	Air	CO_2	HCN	Freon 113	Total
No AlH_3		nd*	0.99	0.23	0.037	0.09	1.35
AlH_3		0.16	nd*	0.19	0.046	0.04	0.44

*none detected

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(C) The 2-in. cubes of both Al and AlH_3 propellants were stored at 80°, 100°, 120°, and 140° F. The AlH_3 propellant was also stored at 167° F (75° C). At 167° and 140° F, the AlH_3 propellants cracked within 2 days storage. At 120° F, the AlH_3 propellant cracked between 2 and 5 days. At 100° and 80° F, there was an initial indication of some porosity formation after 9 and 14 days, respectively. However, no additional changes were apparent after 57 days in these samples. This initial failure indication is probably due to a high initial gassing rate which decreases after several days allowing the gas to diffuse out from the sample as rapidly as it is formed.

(C) The P-BEP/Al samples failed between 5 and 9 days at 140° F and between 21 and 34 days at 120° F. No signs of failure were apparent in the samples stored at 100° and 80° F after 57 days. It was felt that the 2-in. cubes were below the critical cube thickness for these temperatures and the tests were terminated. Figure 20 summarizes the cracking results graphically.

(C) The short time to fissuring of the P-BEP/Al propellants at 140° and 120° F was disappointing and indicative of a potentially serious long term aging problem for the binder. For example, it has been shown that 2-in. cubes of the EAAA/TVOPA/Al propellants will survive for several months at 80° C.

(C) Based on the off-gas analysis testing at 140° F (60° C), the failure of P-BEP/Al cubes at 140° F can be attributed to CO_2 generation during cure and elevated temperature storage. This can be deduced from the CO_2 solubility data and the propellant mechanical properties using Henry's law and the Lawson failure criteria (Refer to Section V, paragraph B for a discussion of the method of predicting failure.) For the P-BEP/Al propellant, the critical CO_2 concentration was calculated as approximately 0.22 cc's/gm propellant. As presented in Table L, this concentration is achieved in approximately 7 days when grain rupture would be expected. As discussed, actual grain failure occurred between 5 and 9 days. For the P-BEP/AlH_3 propellant, both hydrogen and CO_2 pressure would contribute to an earlier failure as was observed.

(U) To further define the shelf life for both P-BEP/Al and P-BEP/AlH_3 propellants, additional gas generation rate studies were conducted at 100° F.

(C) Propellant taken from the surveillance cubes was stored at 100° F and used in these tests. The following tabulation presents data obtained to date:

Sample	Days @ 100° F	cc's/g H_2	cc's/g CO_2
No AlH_3	3	ND	0.050
AlH_3	3	0.05	0.24
No AlH_3	4	ND	0.020
AlH_3	4	0.007	0.030
No AlH_3	5	ND	0.004
AlH_3	5	0.001	0.011
No AlH_3	6	ND	0.004
AlH_3	6	0.001	0.010
No AlH_3	11	ND	0.013
AlH_3	11	0.011	0.038

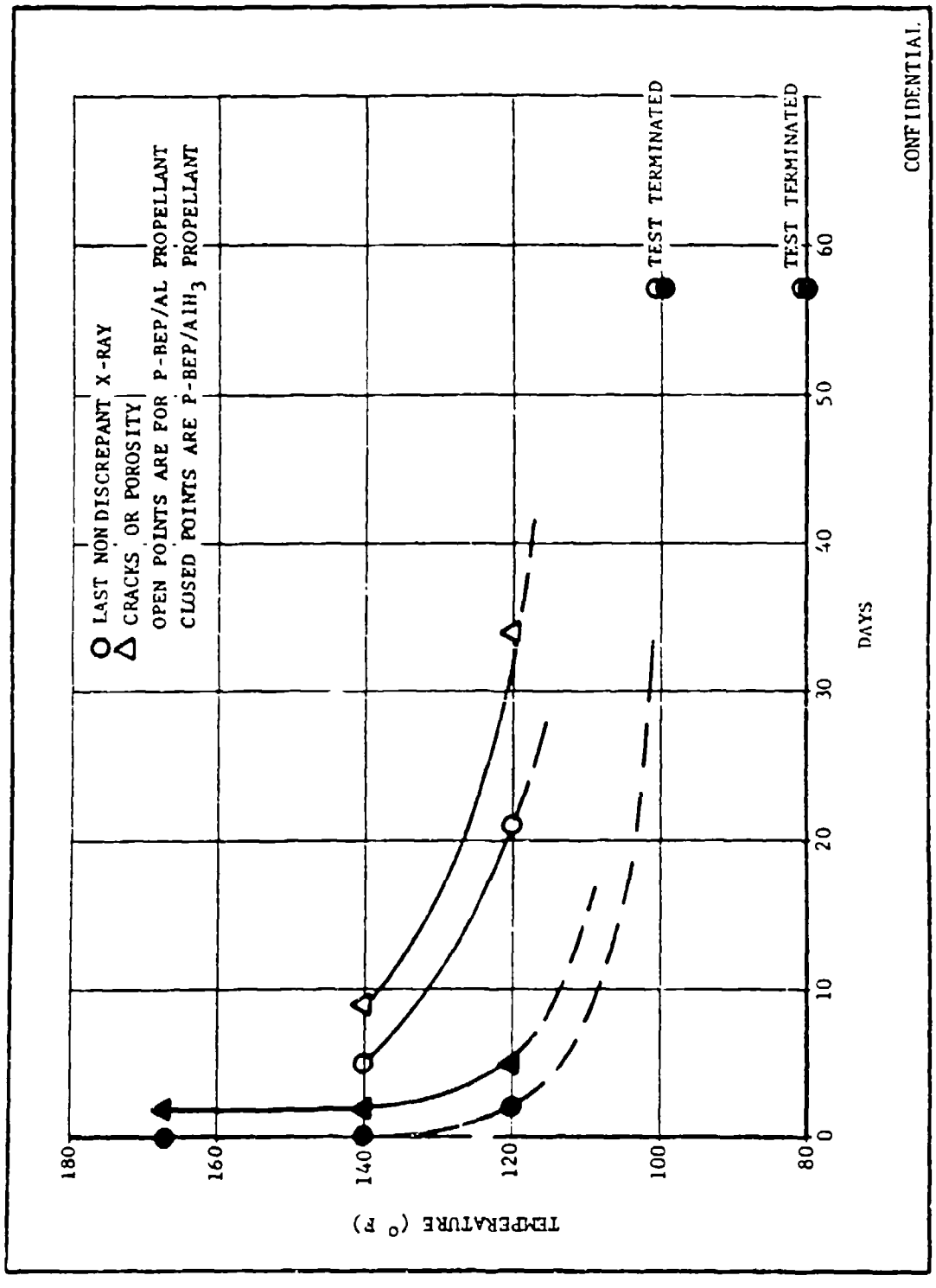

Figure 20. Failure Envelope for P-BEP Propellants Based on 2-Inch Cubes

(C) Of major significance was the rapid initial CO_2 and H_2 gas generation for the P-BEP/AlH_3 propellant so that early failure might be expected. However, once past this initial high generation period, diffusion processes could control the shelf life. As discussed previously, this appeared to be the case with the 2-in. cubes stored at 100° F. For the P-BEP/Al sample, early failures would not be anticipated from the lower CO_2 generation rate shown at 100° F.

(C) Further analysis of the CO_2 generation in both P-BEP/Al and P-BEP/AlH_3 propellants is shown at 140° and 100° F in Figures 21 and 22, respectively. These data show that both propellant systems are in the same population at 140° F. In addition, it appears that the initial gas generation is roughly twice the final generation rate, and may be due to a residual isocyanate-water reaction or an incompatibility with these impurities. In contrast, Figure 22 indicates the P-BEP/Al and P-BEP/AlH_3 propellants are of different populations at 100° F and AlH_3 is catalyzing CO_2 generation.

(C) Several attempts were made to reduce the CO_2 generation from P-BEP/AlH_3 propellants and included the use of HF scavengers, varying the cure stoichiometry, and strictor moisture controls.

(C) Non of these techniques substantially reduced the gassing problems. Based on these efforts, the following conclusions were made regarding the use of AlH_3 in a P-BEP binder.

(a) The use of the catalyst loaded molecular sieves assured that firm cures could be consistently obtained, however, cure rates and consequently pot life varied with stripping efficiency as a result with mix size. This problem could possibly be resolved by pretreating the P-BEP to remove HF.

(b) Mechanical properties in a ballistically optimized propellant are marginal with the use of the triisocyanate cure system. Improvements could probably be made with the use of reinforcing polyols, but this approach dilutes the energy and density advantages of the P-BEP binder.

(c) Shelf lives of both P-BEP/Al and P-BEP/AlH_3 propellants are very short at 120° F in small webs and probably short in large webs at temperatures as low as 100° F. There is also indication of a compatibility problem between AlH_3 and the P-BEP binder. This problem may be due to residual NBA left on the AlH_3 catalyzing decomposition of the P-BEP binder, catalysis of the competitive water-isocyanate reaction or catalysis of urethane hydrolysis all of which could give CO_2 during storage. The presence of more HCN gas during storage for P-BEP/AlH_3 propellants is indicative that at least some additional P-BEP degradation is occurring.

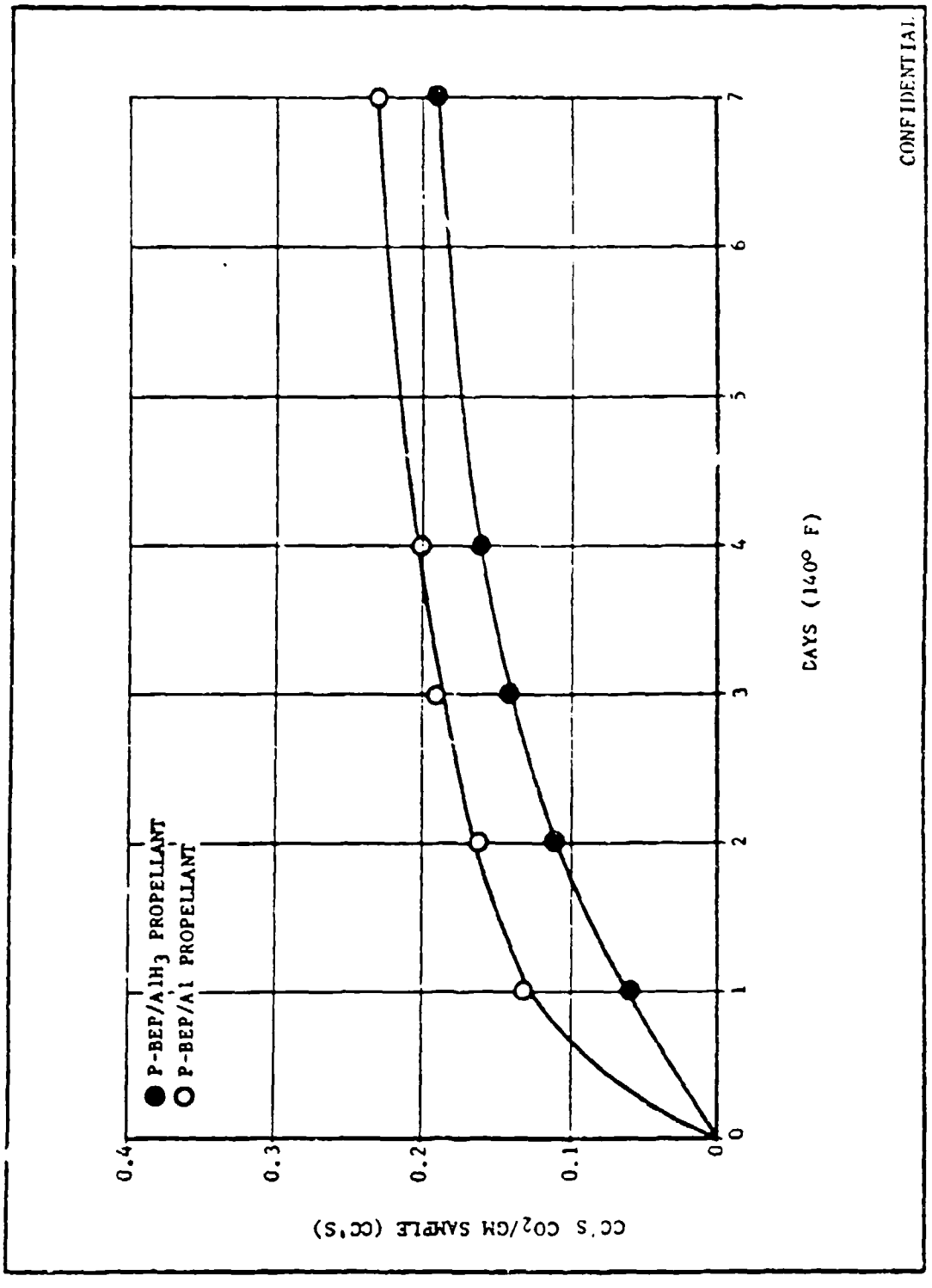

Figure 21. Comparison of CO_2 Generation for P-BEP/AlH_3 and P-BEP/Al Propellants at 140° F

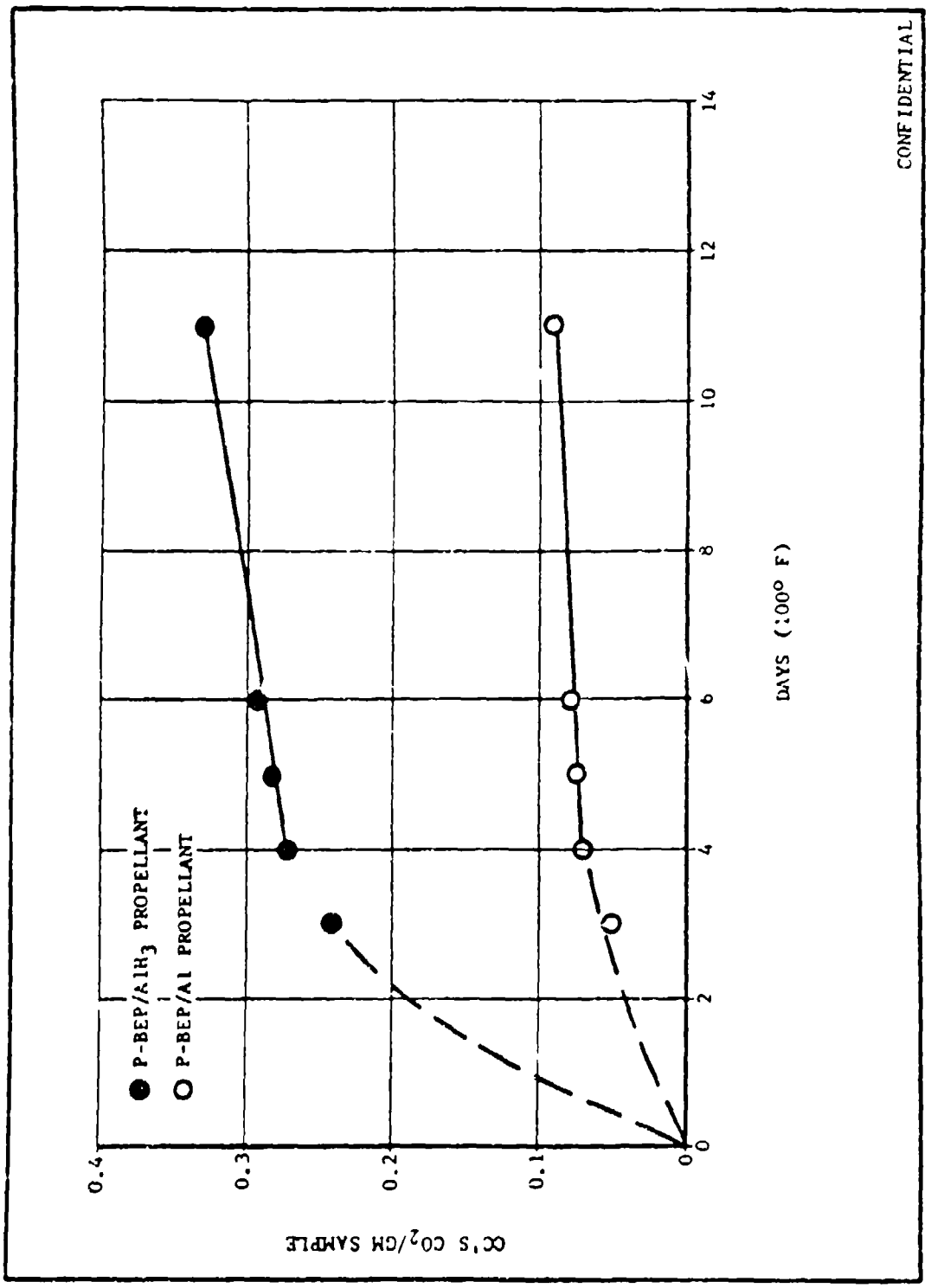

Figure 22. Comparison of CO_2 Generation for P-BEP/AlH_3 and P-BEP/Al Propellants at 100° F

(C) The above problems led to the belief that the scaleup of P-BEP/AlH_3 propellants was not attractive without a good deal of additional effort directed towards purification of P-BEP and development of a cleaner P-BEP cure. Further compatibility studies with AlH_3 in the P-BEP binder were also considered a necessity. As a result, it was recommended that further P-BEP scaleup efforts be eliminated in favor of the alternate binder approach.

B. ALTERNATE BINDER SCALEUP

1. Selection of Candidate Propellants

(C) A series of theoretical specific impulse calculations were made with the R-18 binder to aid in the selection of propellants to be fired in 5-lb motors. These calculations (Table LI and Figure 23) indicate that the theoretical impulse begins to level off above 22 percent aluminum hydride, so there is little advantage to attempt to use larger quantities. Addition of HMX has little effect on the theoretical impulse, lowering it slightly on the AlH_3 system, and raising the impulse on systems containing less hydride. The two compositions that were selected for testing (VKU and VKW) are presented in Table LII.

2. Scaleup Experience

(C) Process hazards studies indicated the AlH_3/TVOPA propellants could be safely handled in the Bacchus 1 pint and 10 quart Hobart mixers without substantial equipment or procedural modifications. However, in scaling up to 70-lb mixes in the 5-gal J. H. Day mixer, hazards analysis indicated that several steps were required which had inadequate safety margins.

(C) Based on extensive hazards tests on the AlH_3/DOMINO propellants, Hercules feels that an inert diluent process is highly desirable for scale up above the 1-gal Hobart Mixer. Both impact and friction sensitivity of these propellants are well below the sensitivity of non-AlH_3 propellants normally processed in larger mixers. Recent tests of combinations of individual ingredients that could occur during mixing indicate that even more sensitive combinations are possible than the complete green slurry. The most probable source of initiation during mixing is due to friction, and the results of friction tests with these combinations are shown in Figure 24. The shaded area is the force level that is achievable in manual operations. The AlH_3 propellant (in the green slurry) falls well within this force region, whereas high energy double-base propellants do not penetrate this region. Two combinations of AlH_3, with AP and with TVOPA, are much more sensitive even than the uncured slurry propellant. The TVOPA/AlH_3 combination can even be initiated without any force being applied to the wheel in the friction apparatus. (See Figure 25.) A sample of TVOPA/AlH_3 placed on the anvil will initate with a clearance of 1/16 in. between the wheel and the anvil at speeds of 6 ft/sec or above. Thus, the only friction forces developed in this test are from the propellant ingredients themselves since there was no metal-to-metal contact. Therefore, the mix procedure should be such that there is no chance of forming these sensitive binary combinations at any time during the mix cycle.

TABLE LI

THEORETICAL IMPULSE CALCULATIONS

AlH_3*	AP	HMX	Isp	ρ	Tc	OI	Te	Omox
25	45		286.2	1.66	3385	.218	2205	1.09
22	48		285.6	1.67	3441	.313	2225	1.24
20	50		284.5	1.68	3467	.363	2209	1.36
18	52		283.0	1.69	3486	.416	2185	1.49
15	55		280.3	1.71	3500	.499	2147	1.72
22	43	5	285.6	1.67	3394	.274	2169	1.18
22	38	10	285.2	1.67	3342	.236	2107	1.12
22	33	15	284.2	1.67	3284	.198	2039	1.06
18	47	5	283.3	1.69	3448	.376	2132	1.41
18	42	10	283.5	1.69	3408	.336	2078	1.33
18	37	15	283.5	1.69	3363	.296	2027	1.26

*The remainder of the propellant composition is 3.9% R-18 binder and 26.1% TVOPA.

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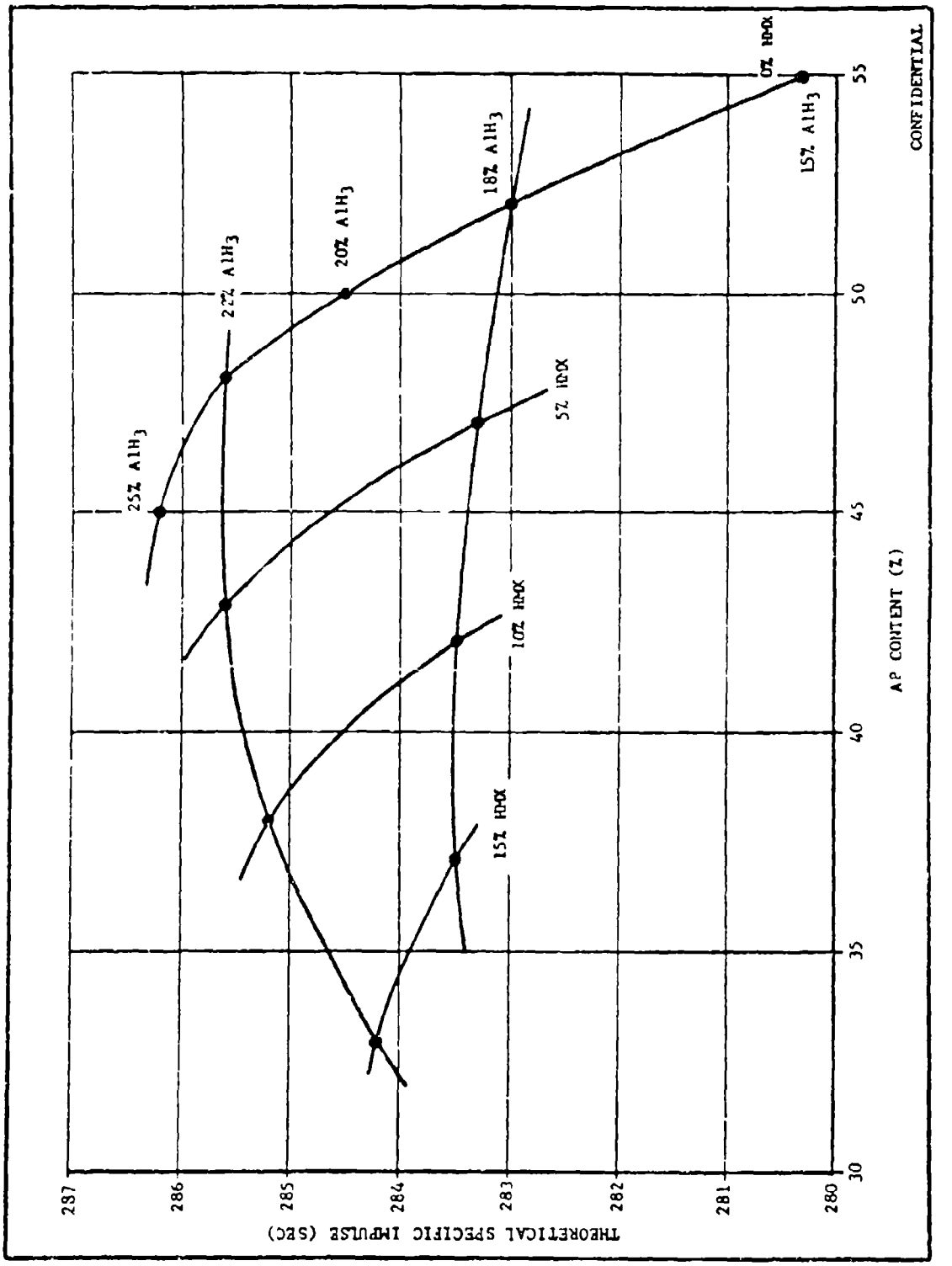

Figure 23. Theoretical Isp Calculations

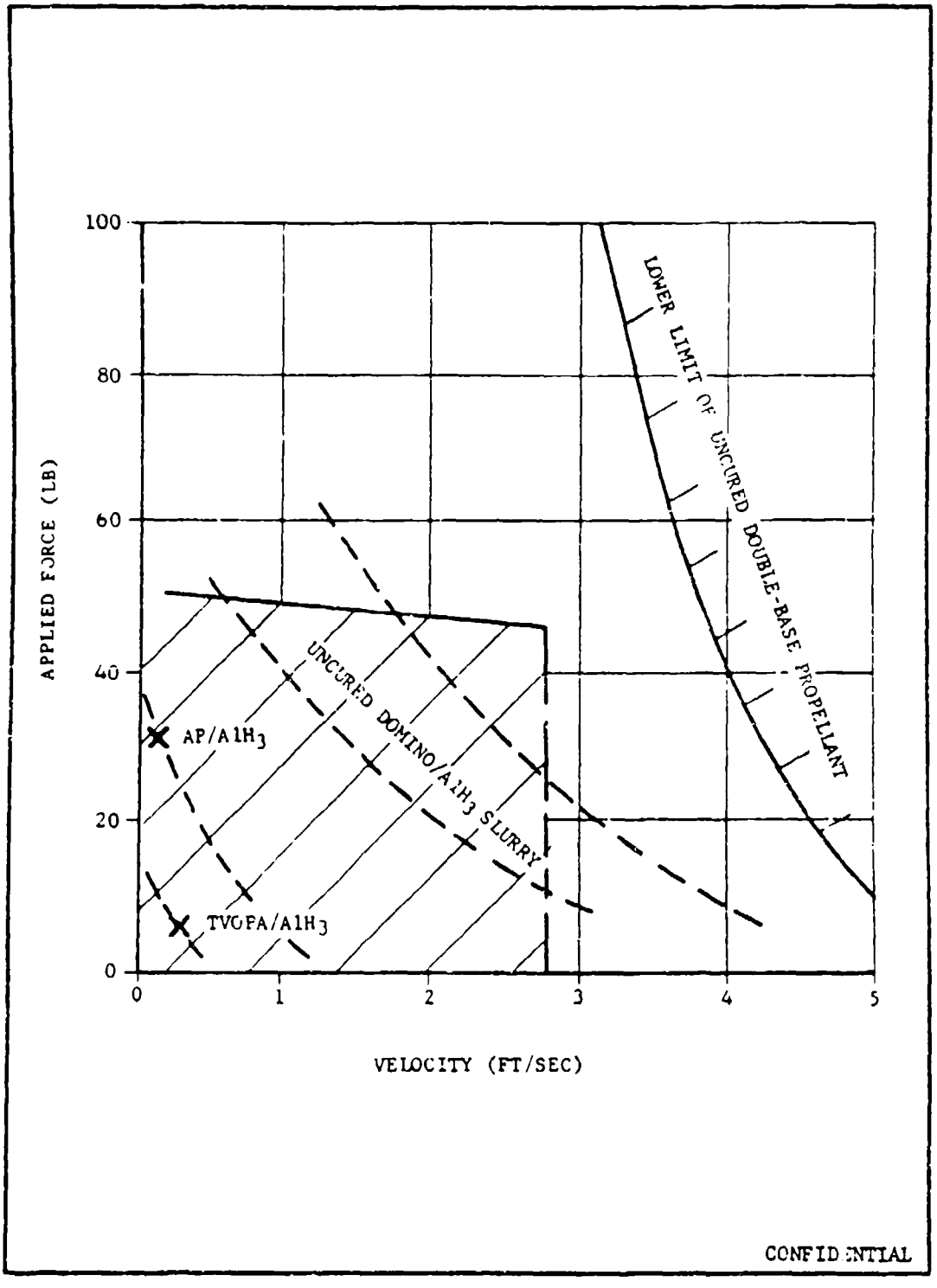

Figure 24. Friction Sensitivity of Ingredient Combinations

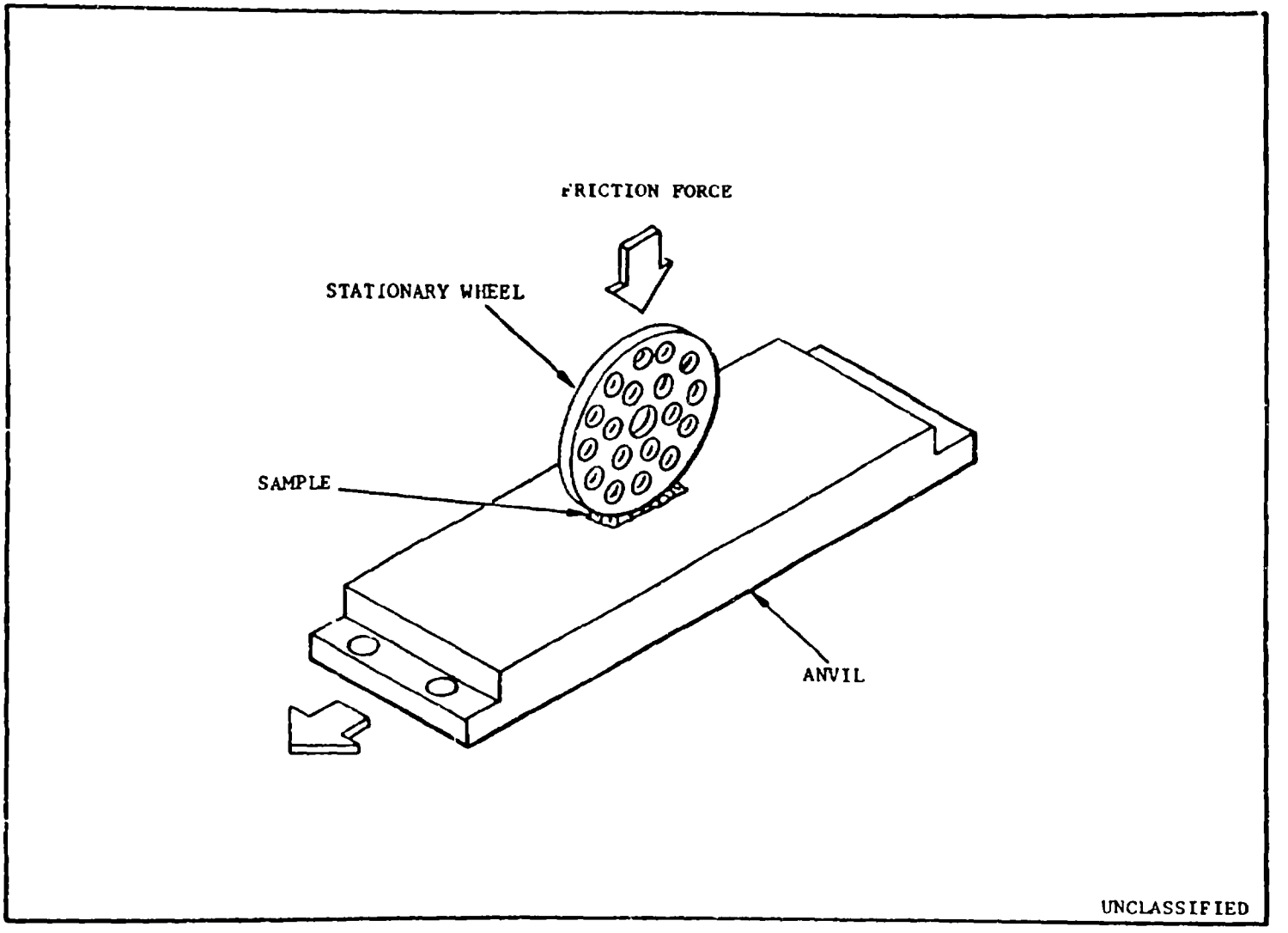

Figure 25. Operating Principal of Friction Test Apparatus

TABLE LII

COMPOSITIONS FOR SCALEUP

Propellant Designation	VKU	VKW
Composition		
R-18 Binder	3.9	3.9
TVOPA	26.1	26.1
AP	48	42
HMX	--	10
AlH_3	22	18
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(C) An analysis of the heat generation during mixing is presented in Appendix C. Insignificant heat generation is obtained during normal operation of the 5-gal J. H. Day mixer.

(U) The addition of inert diluent to the mix procedure can reduce the hazards in a number of ways:

(a) The possibility of forming binary mixtures of the most sensitive combinations will be reduced.

(b) The chances of initiation of the mix through accidental application of abnormal forces will be reduced.

(c) The possibility of an initiation propagating to the whole mix will be reduced.

3. Inert Diluent Process

(C) Considerable difficulty was encountered in designing an inert diluent process that would cure. A summary of the R-18 inert diluent mixes made under this program is given in Table LIII. The following three basic procedures were tested:

(a) The dry solids were added to a TVOPA/diluent mixture from the remote addition hoppers. This procedure required that the solid be added at ambient pressure to prevent premature diluent stripping whereas they are normally added under vacuum. It was found, however, that ambient addition of the solids caused the generation of large

TABLE LIII

INERT DILUENT MIXES

Mix Number	Propellant Type	Mix Procedure[a]	Cure Time	Properties	Remarks
BC 172-94	VKW	4	3	good	Control
BC 172-95	VKW	1	11	soft	Dusting problem.
BC 172-97	VKU	4	4	good	Repeat of Mix 94
BC 172-99	VKW	1	-	very soft	Dusting and stress crack
BC 172-100	VKW	4	5	good	Iso/OH ratio of 1.15
BC 138-57	VKU	2	5	good	Crosslinkers mixes at 145° F prior to adding catalyst
12 lb Hobart mix	VKU	2	2	soft	Porous
BC 138-67	VKU	3	-	soft	TDI in mix while Freon was removed (16 hr)
BC 138-72	VKU	3	-	skin cure	90 minute mix cycle
BC 138-75	VKU	3	-	soft	Iso/OH = 1.0, 0.1% carbon black added
BC 138-77	VKU	3	2	good	CWX 105B used in this mix *
BC 138-80	VKU	3	6	good	Repeat of 77 to get pot life (3 hr)
1st 70 lb Day mix	VKW	3	2	fair	Several casting voids
2nd 70 lb Day mix	VKW	3	2	soft	Porous, stress cracks
BC 138-89	VKW	3	-	didn't cure	
BC 138-90	VKW	4	-	didn't cure	Gassed, stress cracks
NOTE: Mixes 77, 80, 89, and 90 had the same lots of AlH_3 and TVOPA					
BC 138-96	VKW	4	12	good	Slow cure but no porosity
BC 138-97	VKW	3	-	no cure	Ingredients used in 2nd Day mix
BC 138-98	VKU	4		poor	Different lot of TVOPA from 96, stress cracks
BC 138-99	VKW	4	4	good	TVOPA stored over silica gel
BC 165-2	VKW	4	slow	soft	Blend of TVOPA lots
BC 165-3	VKW	3	4	soft	CWX 105C. Fast cure but low modulus propellant

[a] No. 1, 2, and 3 refer to inert diluent procedures, and No. 4 refers to the non-inert diluent mix procedure.

*CWX 105B used in this and subsequent mixes.

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(C) quantities of dust which is a serious safety hazard. A slow cure was also evident with this procedure (see mix No. BC-172-95 and -99). Therefore, this approach was abandoned.

(b) In the second process, the mix was performed without inert diluent until after the solids were added. Diluent was then added to aid in solids dispersion and to remove any agglomerates on the mix blades. After removal of the diluent, the catalyst was added and the mix completed under vacuum. This procedure was tested in the 1-pint Baker-Perkins mixer and resulted in a high quality propellant which cured in 5 days at 100° F (BC-138-57). However, when tried in the Hobart mixer (12 lb) the propellant cured very slowly resulting in a soft porous propellant. Analysis of this mix revealed that sufficient isocyanate and hydroxyl groups were available to react, so the blame must fall on the catalyst. The catalytic activity is reduced by the procedure, probably due to incomplete dispersion of the catalyst. The fact that the Baker-Perkins mix (which has better mixing action) cured, whereas the Hobart mix did not cure, supports this explanation.

(c) The order of solids addition was reversed in the third procedure to remove all possibility of dusting and solids caking on the blades. Dry AlH_3 was added to the mixer bowl followed by the TVOPA/diluent/R-18 mixture. Then, a slurry of oxidizer in freon was added by hand to the bowl and the freon was carefully removed to avoid splashing. After complete removal, the crosslinker (HT) and TDI were added and dispersed in the mix, followed by the catalyst. The mix was then vacuum mixed and cast. Poor cures were also obtained with this procedure even with a final mix cycle of 90 min.

(C) Each inert diluent process has one thing in common, catalyst is added after the solids are incorporated in the mix and the inert diluent is removed. It appears that the small amount of liquid DBTDA catalyst (0.005 percent) does not get dispersed when added after all of the solids are in the mix. To overcome this problem the catalyst was placed on molecular sieves. The sieves not only aid in the dispersal of the catalyst but also allow the use of larger quantities of catalyst while maintaining an adequate pot life. For example, 0.2 percent of sieves containing 20 percent DBTDL (CWX 105B from Linde Division of Union Carbide) gave adequate pot life and good cure whereas 0.01 percent of DBTDA (liquid) resulted in insufficient pot life. The sieves are designed to protect the catalyst so that it is not available for catalytic activity until it is displaced from the sieves by either heat or by another molecule (in this case probably by water and/or HF).

(U) Using the third inert diluent procedure with the catalyst on sieves, two 1-lb Baker-Perkins mixes were made successfully (mix No. BC-138-77 and -80). Also, a 70-lb mix was made in the Day mixer, using a 1-hr mix cycle after addition of the catalyst, resulting in a soft rubbery propellant after a 2-day cure at 100° F. The propellant was nonporous, except that several casting voids were present in one of the 15-lb motors.

(U) To improve castability in the second 70-lb mix the procedure was modified by cutting the mix cycle to 30 min after catalyst addition. This mix did not cure properly. A very soft porous propellant resulted after 2 days at 100° F. The soft propellant and slow cure was caused by impurities in the TVOPA as was discussed in Section III, paragraph 5. Purification of TVOPA resolved the problem. (Refer to Appendix B.)

(U) One characteristic that is common to all inert diluent propellants is a marked decrease in mix viscosity over propellants made without inert diluent. The explanation for this reduced viscosity is believed to be an improved wetting of the solids by the binder ingredients, plasticizer, and binder. Residual diluent is not responsible for the improved viscosity, since analysis has shown the amount of diluent to be less than 0.01 percent in the propellant at the end of the mix cycle.

4. Ballistic Results

(C) The burn rate of VKU and VKW propellants was tested by strand and micromotors. The effect of varying the AP particle size and the adding of HMX to VKU were also tested. The results (Figure 26) indicate that replacing 5μ AP with 15μ AP lowers the burn rate approximately 8 percent, whereas adding 10 percent HMX lowers the rate an additional 20 percent. Micro-motor P-K-r firing results of VKW propellant are shown in Figure 27. A burn rate of 1.3 in./sec at 1000 psi at a slope of 0.60 was achieved. The results agree closely with strand data. In addition, the burn rates of the 5-lb motor firings are plotted on the same graph showing that close agreement was achieved.

(C) Both VKU and VKW propellants were fired for impulse measurements in micro motors and 5-lb motors. VKW was also fired in a 15-lb motor. The results of these firings are summarized in Table LIV. Details of the large motor firings and firing traces are presented in Table LV and Figures 28 through 32. The results of the micro motor and 5-lb motor firings clearly indicated that the impulse efficiency of the 18 percent AlH_3 VKW is higher than the 22 percent AlH_3 VKU, thus giving equivalent delivered impulse from the two propellants. Since VKW has a higher density, it was chosen for scaleup to the 15-lb motor. The delivered impulse I_{1000}^{15} of 267 with an efficiency of 94.69 is impressive for a 15-lb motor firing.

(C) The results demonstrate that very high efficiencies are achievable from AlH_3 propellants through the use of a DOMINO binder; thus, the NF ingredients increase the efficiency of AlH_3-fueled propellants as well as Al-fueled propellants. A comparison of the impulse efficiency of aluminum versus AlH_3 propellants is shown in Figure 33 in which the effect

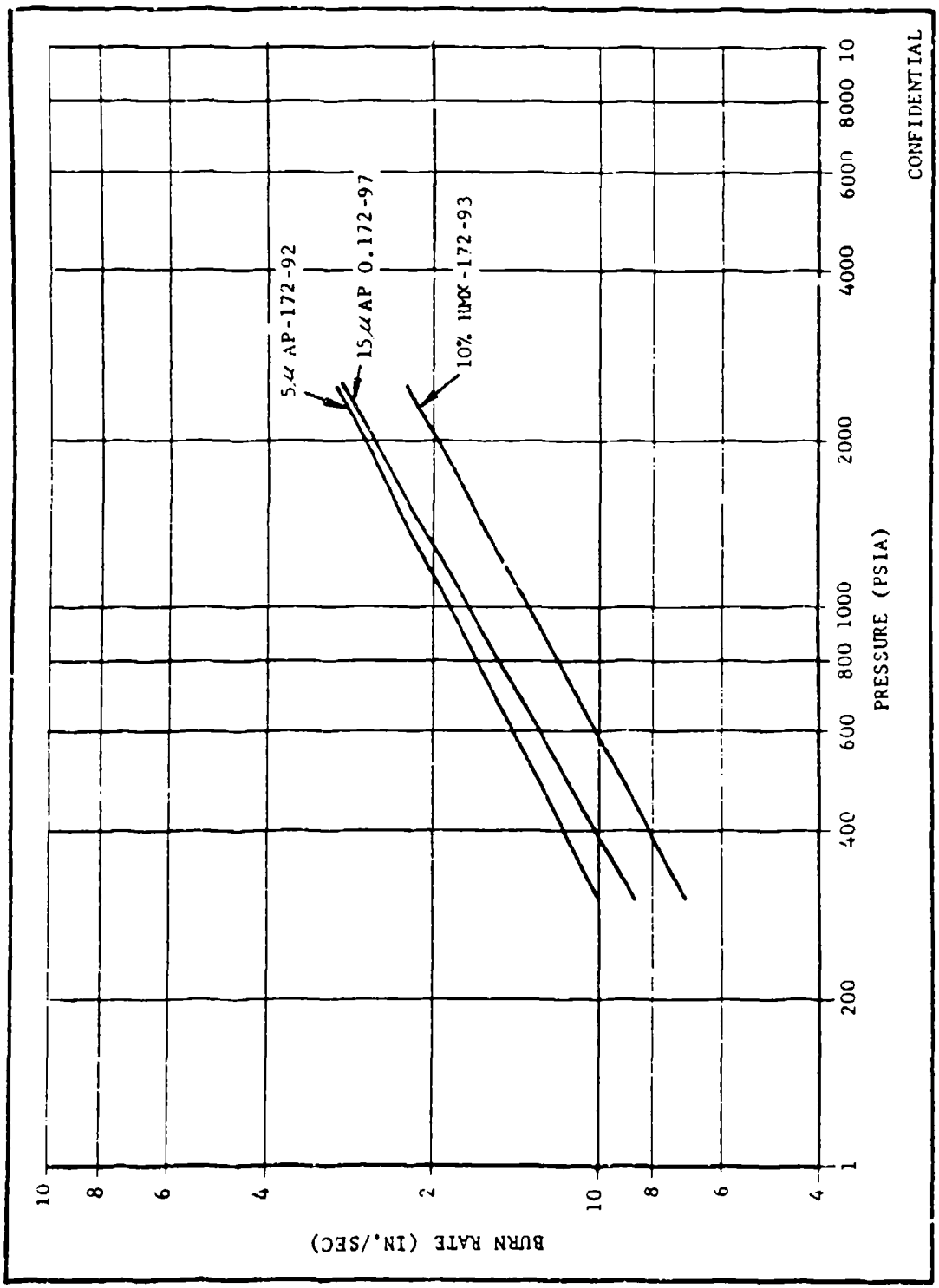

Figure 26. Strand Data of VKU Propellant

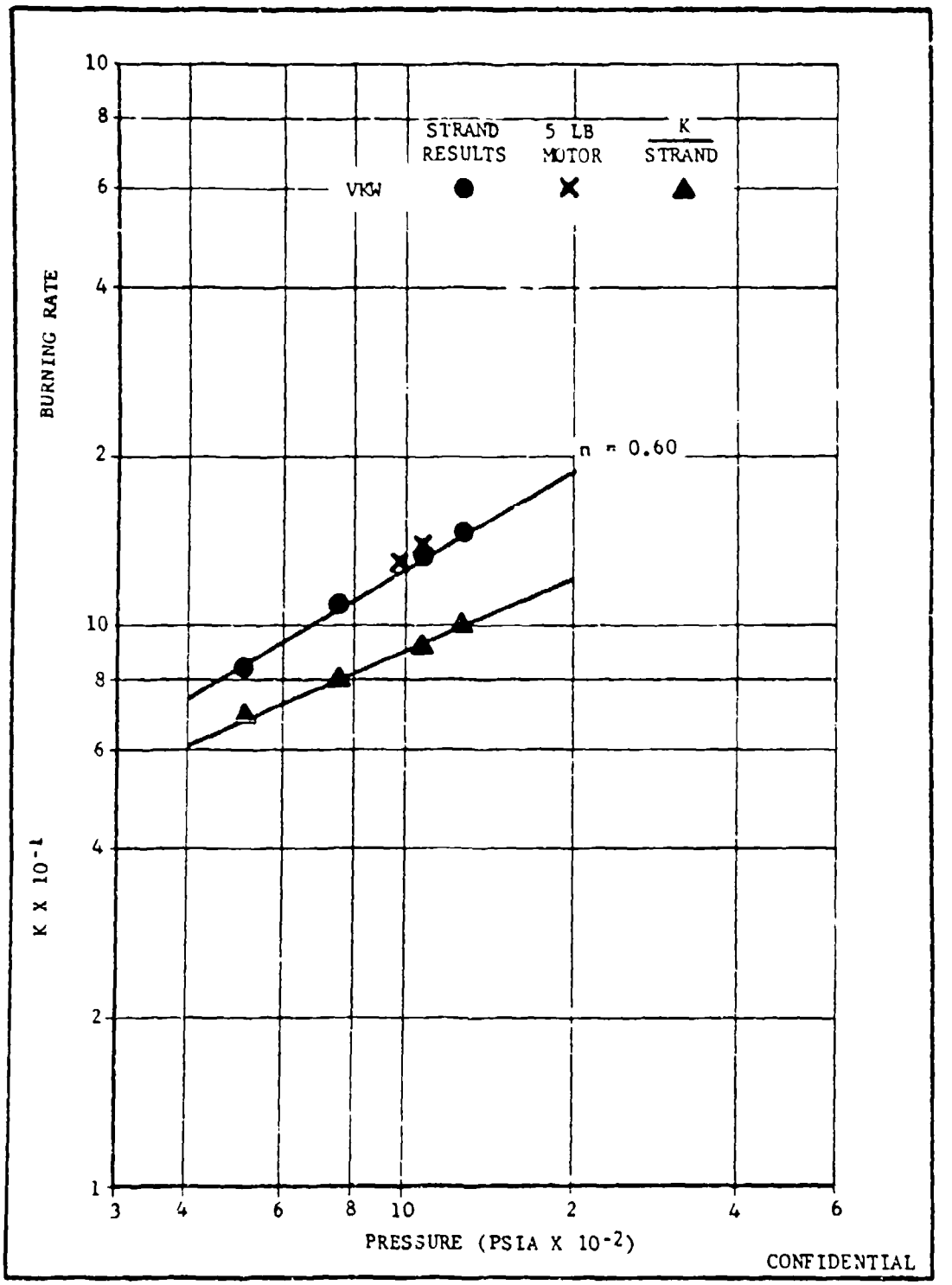

Figure 27. Micro Motor P-k-r Data for VKW Propellant

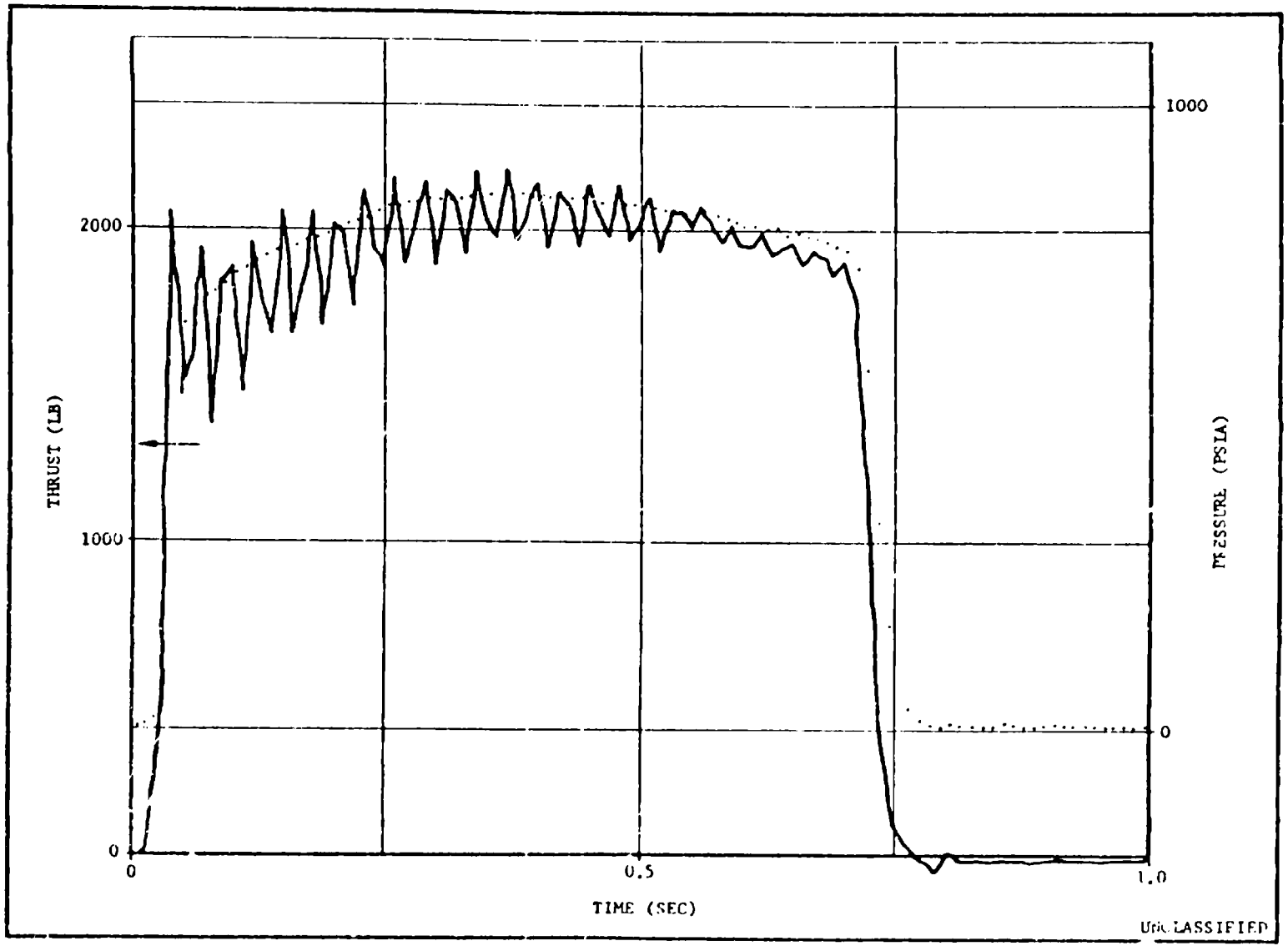

Figure 28. 5-Lb Motor Firing of VKU, Firing No. DOM-5

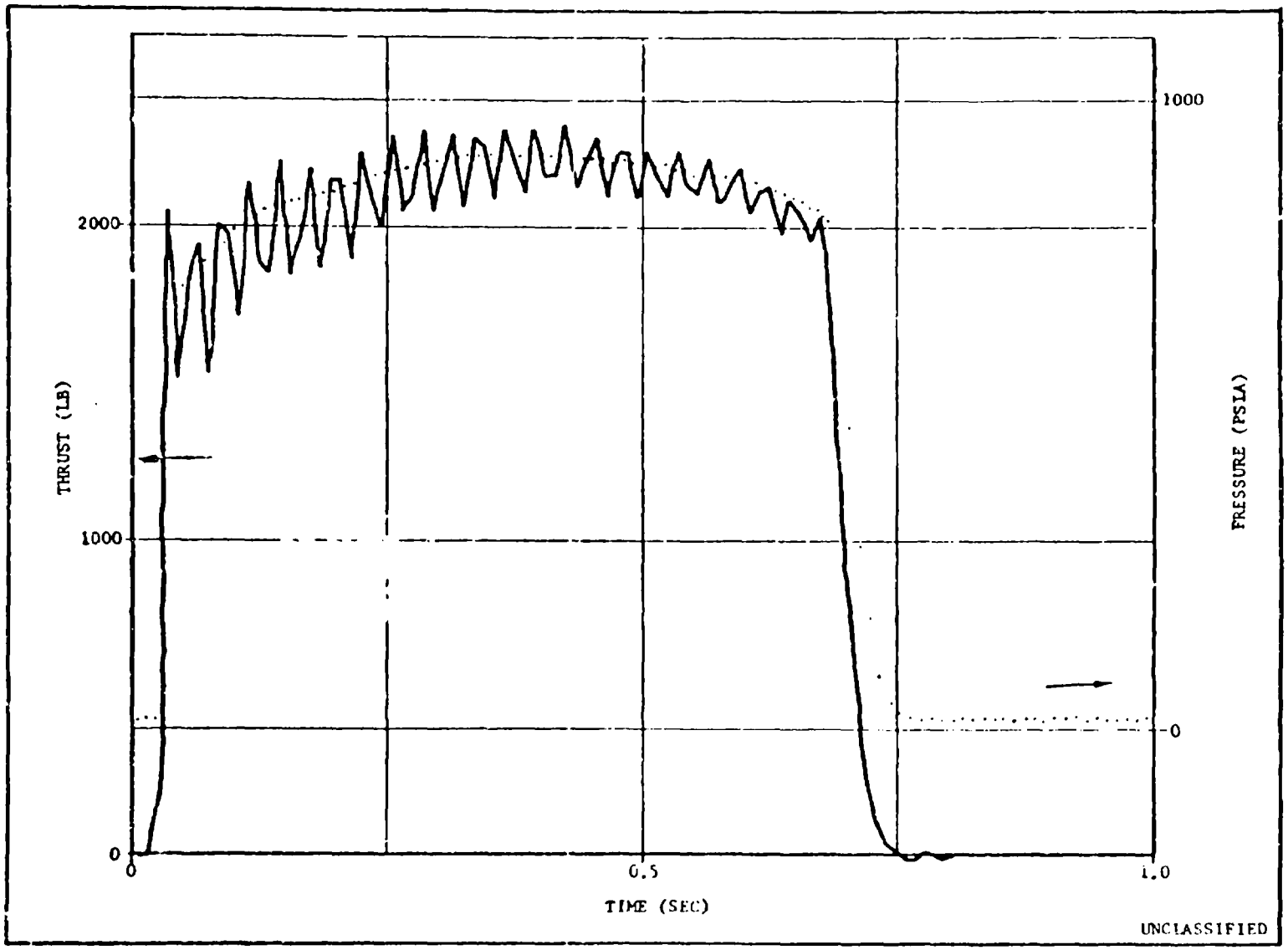

Figure 29. 5-Lb Motor Firing of VKU, Firing No. DOM-6

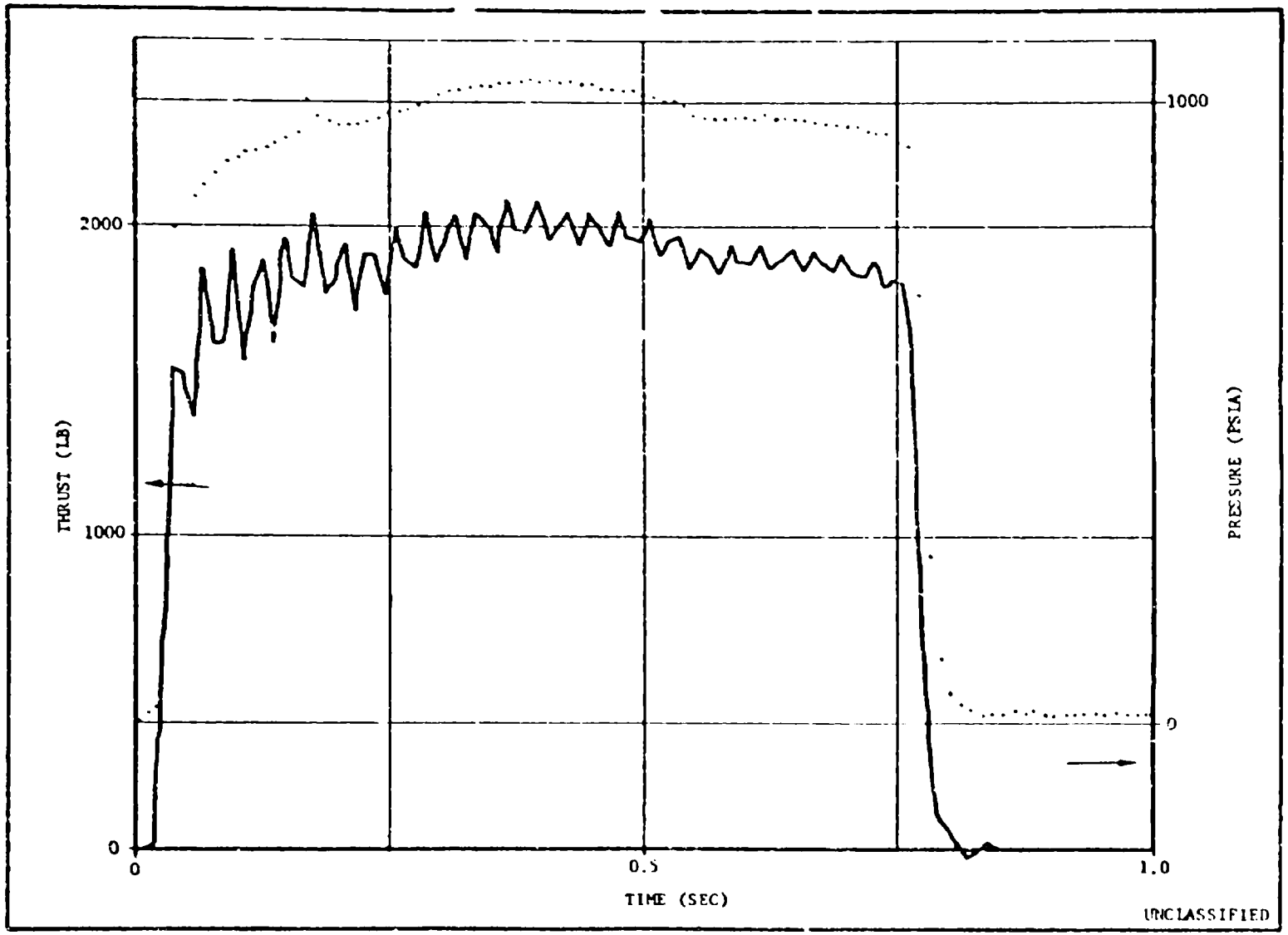

Figure 30. 5-Lb Motor Firing of VKW, Firing No. DOM-7

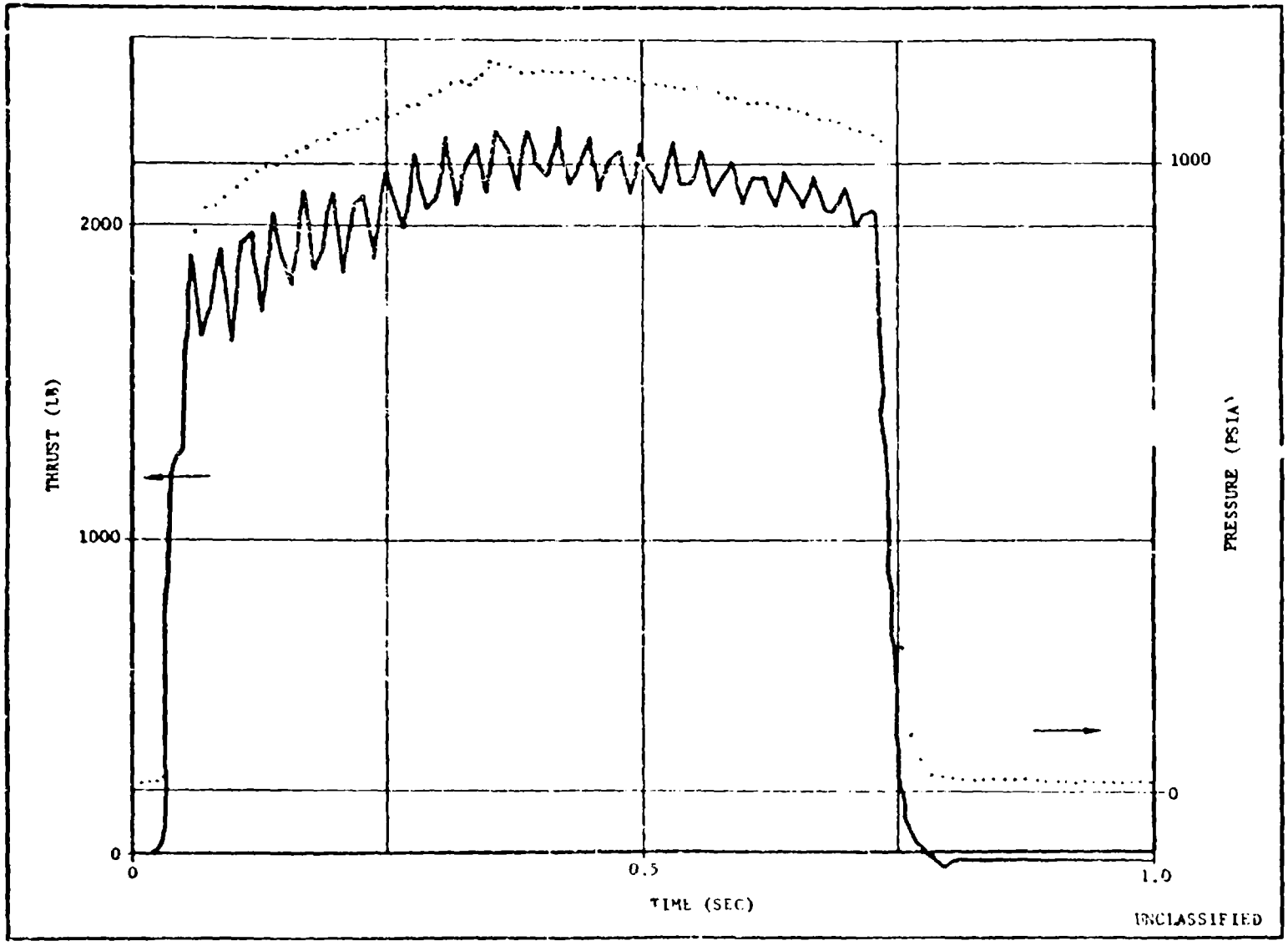

Figure 31. 5-Lb Motor Firing of VKW, Firing No. DON-8

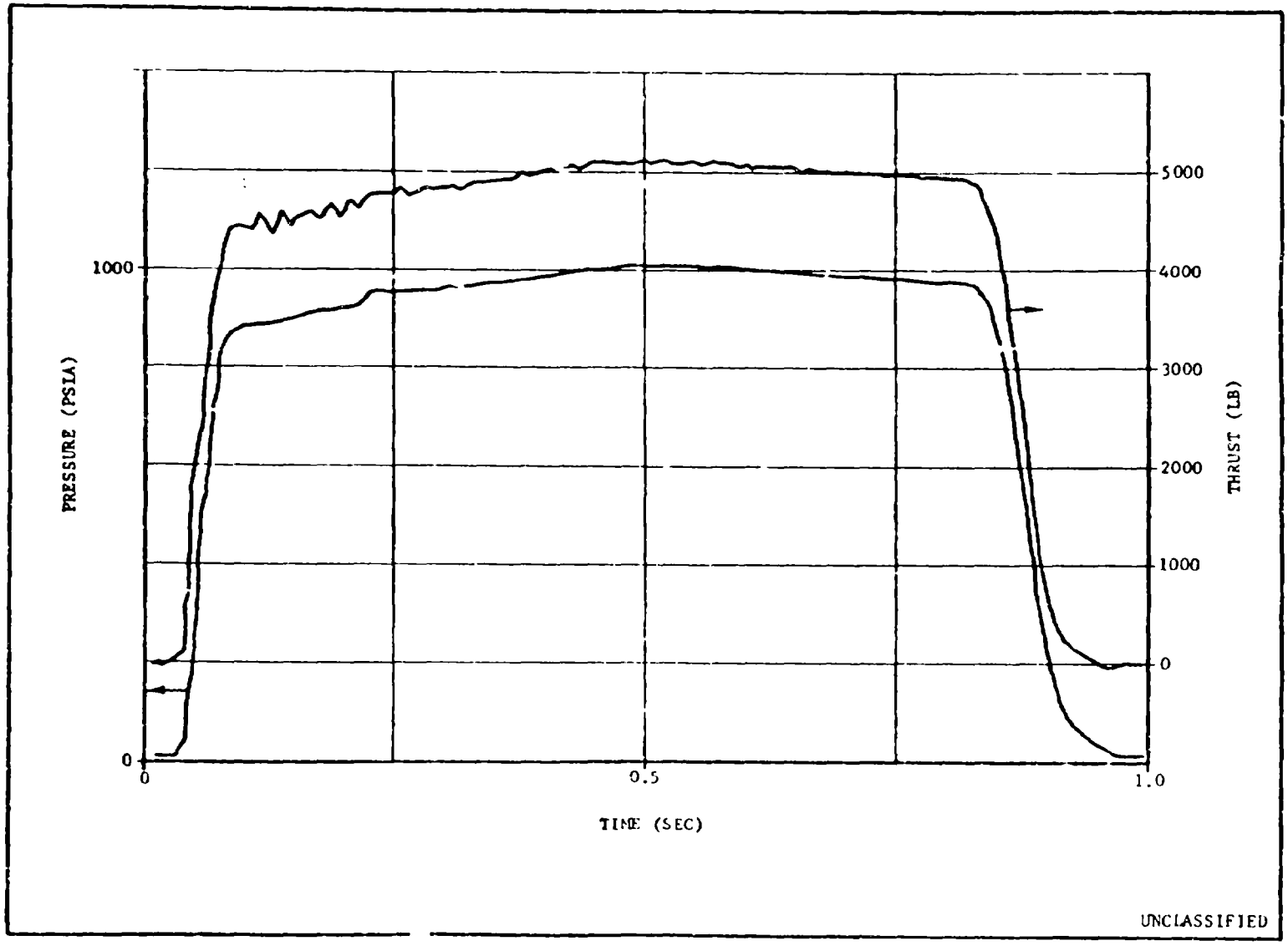

Figure 32. 15-Lb Motor Firing of VKW, Firing No. DOM-10

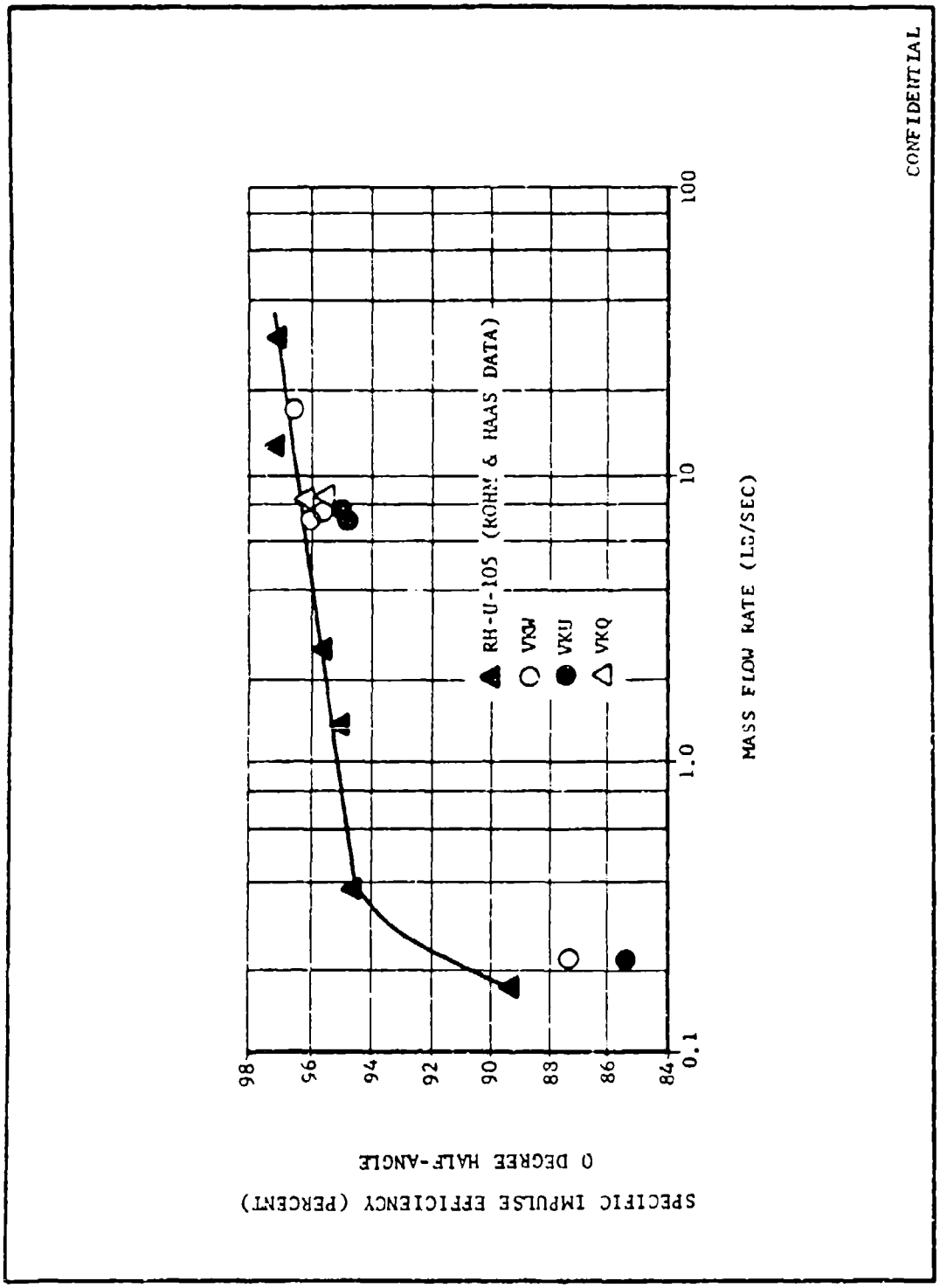

Figure 33. Mass Flow Rate Versus Specific Impulse Efficiency

(C) of mass flow rate on impulse efficiency is given for both fuels. The data for aluminized propellant is taken from Rohm & Haas reports for their well characterized RH-U-105 propellant. At higher flow rates the two fuels give the same efficiency, whereas at lower flow rates the AlH_3 propellants may be less efficient which could be caused by combustion losses at the shorter residence times.

TABLE LIV

SUMMARY OF MOTOR FIRINGS

Propellant Type	VKU	VKW
Theoretical Performance		
Isp (1000/14.7	285	283
ζ (lb/in.^{3})	0.0607	0.0612
Tc (^{o}K)	3410	3392
Oxidation Ratio	1.24	1.32
Weight % Condensibl	27.2	23.1
Delivered Performance		
Isps*/Efficiency		
20-gm motor	238/83.5	242/85.5
5-lb motor	265.3/93.3	265.3/94.0
15-lb motor	--	267.0/94.6
*15 degree half angle		
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TABLE LV

MOTOR FIRING DETAILS

Formulation	VKU	VKU	VKW	VKW	VKW
Motor Design	5PC	5PC	5PC	5PC	15PC
Firing Date	11/14/69	11/14/69	11/14/69	11/14/69	12/8/69
Grain No.	S-828AH-1	S-828AH-2	S-829AH-1	S-829AH-2	S-237AH
Firing No.	DOM-5	DOM-6	DOM-7	DOM-8	DOM-10
Propellant Wt	5.260	5.42	5.28	5.51	15.05
$K-S/A_t$	57.38	58.94	72.68	75.91	75.55
t_a-sec	0.719	0.697	0.761	0.723	0.874
t_b-sec	0.679	0.651	0.732	0.697	0.804
$\bar{P}_a$-psia	780	826	948	1042	921
$\bar{P}_b$-psia	804	856	968	1063	958
$\bar{P}$max-psia	864	910	1034	1137	1011
$\bar{P}$amb-psia	12.44	12.41	12.44	12.57	12.23
$\bar{r}$-in./sec	1.385	1.461	1.287	1.361	1.249
$\dot{m}$-lb/sec	7.32	7.78	6.94	7.62	17.23
C_d-sec^{-1}	0.00581	0.00582	0.00533	0.00578	0.00579
$\epsilon-A_e/A_t$	5.303	5.293	6.771	6.733	8.774
$\bar{F}_a$-lb_f	1883	2010	1839	2019	4621
Isp del.-$\frac{lb_f\text{-sec}}{lbm}$	257.6	258.8	265.4	265.2	268.7
Theoretical Isp at Firing Conditions	276.32	277.25	281.61	282.90	284.12
Efficiency, Eff	93.23	93.35	94.24	93.74	94.57
Isp_{1000}^{15}	265.1	265.5	266.0	264.6	267.0

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SECTION V

SHELF LIFE STUDIES

A. STABILITY TESTING

(C) Testing of the stability of n-BA-treated AlH_3 was performed in both EAAA and R-18 TVOPA plasticized binders. Results of this testing is summarized in Figure 34 and compared to the stability of AlH_3 in the P-BEP binder. As shown, the stability of AlH_3 in all three binder systems appears to be approximately the same with times required to reach 0.1 percent AlH_3 decomposition varying from 8 to 11 days.

(C) Additional studies were also conducted to compare the 14-day/60° C n-BA treatment cycle with a 5-day/80° C treatment cycle recently recommended by Dow Chemical. The new procedure consisted of refluxing the n-BA (78° C) for 5 days followed by the normal washing procedure and then drying for 3 hr at 60° C rather than the 1 hr at 100° C which was used in the old procedure. A comparison of the resultant AlH_3 from the new procedure by off-gas analysis indicated that no improvement of the stability in VKW propellant was achieved over the passivation procedure used previously. (See Figure 35.) However, this treatment has a definite advantage in the shorter cycle required.

(C) It should be noted that during the course of the n-BA treatment of one 7.5-lb batch of AlH_3 an incident occurred which resulted in the loss of the complete batch. This was the standard 14-day/60° C cycle which had been repeated without incident several times. Passivation appeared normal for the first 13 days. However, when inspected on the 14th day it was obvious that an abnormal reaction had occurred. The temperature had increased to 75° C, the level of the hydride had risen approximately 1-1/2 in. in the flask, and the top portion of the hydride was dry and caked. In fact, the top part of the hydride had a polymeric texture, being hard and rubbery. The odor of n-BA was evident in the room.

(U) In searching for a solvent to quench the hydride it was found that the resulting mixture was extremely reactive. Small samples reacted violently when added to acetone, n-BA, or Freon MF. It was also noted that the teflon stirring blades were distorted, as if partly melted. The mixture was finally covered with heptane and safely disposed of in the burning grounds.

(C) One possible explanation for this incident is that the water in the n-BA could have been used up during treatment thus causing a reaction between the AlH_3 and n-BA to begin. This could have produced sufficient heat to drive the remaining n-BA through the condenser thus causing the odor in the room. Analysis of the top (polymeric) portion of the AlH_3 revealed that it contained 12.7 percent carbon and 2.7 percent nitrogen. Extraction with methylene chloride revealed that part of the organic

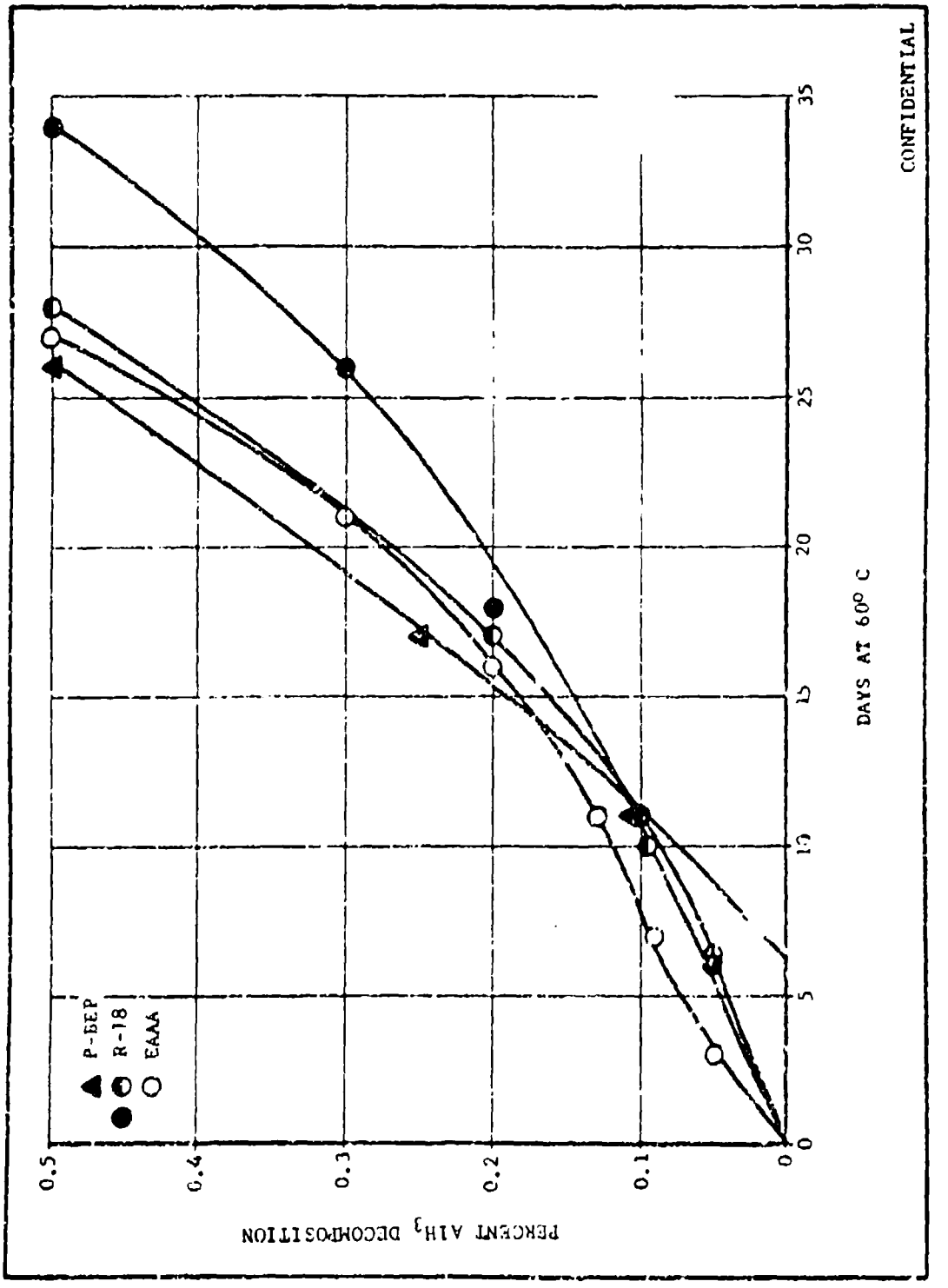

Figure 34. Comparison of AlH_3 Decomposition in Various Propellants at 60° C

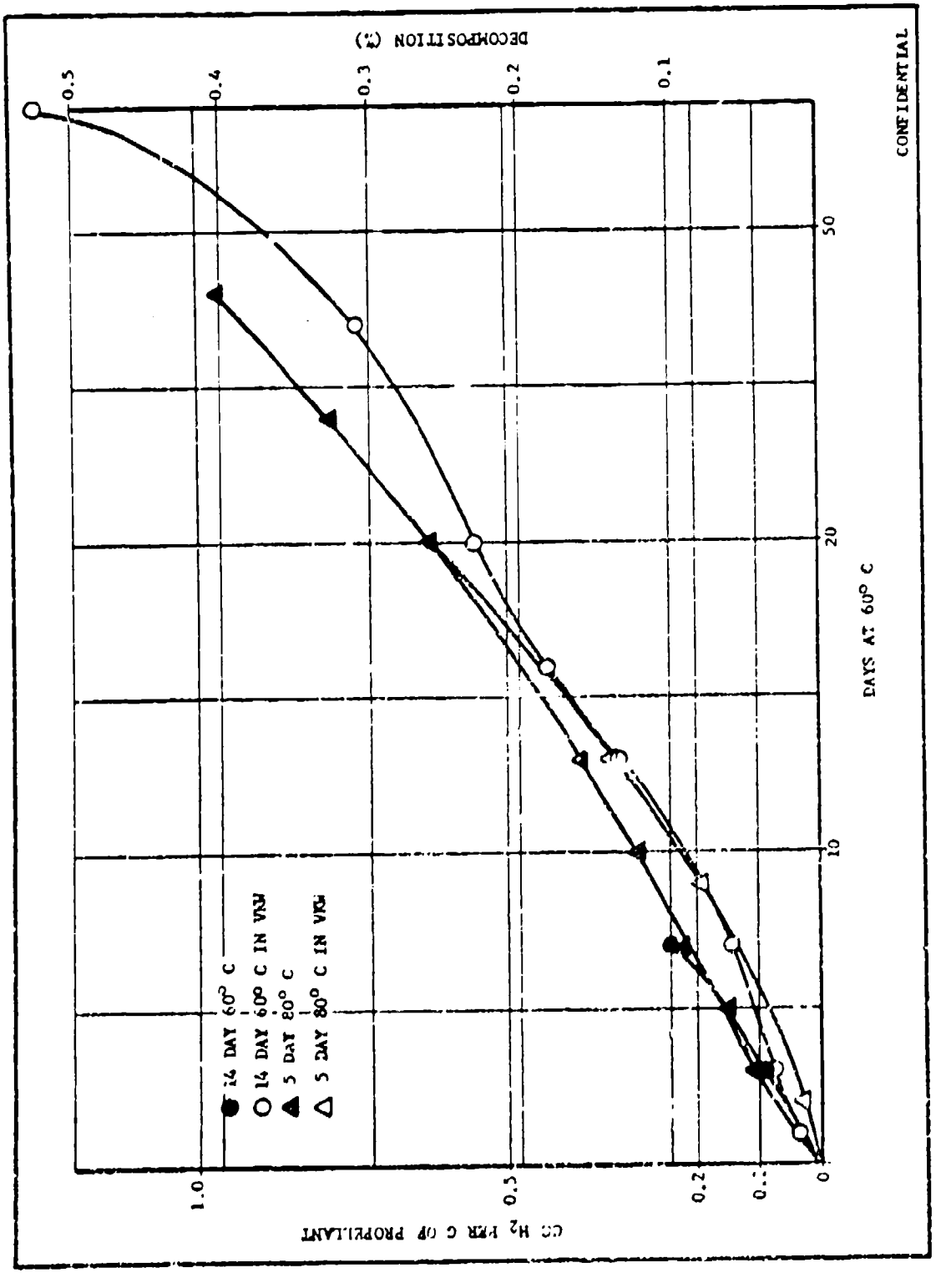

Figure 35. Comparison of Passivation Procedure

(C) portion is diphenyl acetylene thus accounting for the disparity between the nitrogen and carbon analysis from that expected for n-BA. The remainder is believed to be a reaction product of AlH_3 with n-BA in which the amine hydrogen reacts with AlH_3 or with nascent Al forming an H compound. $Al{:}N(C_4H_9)$

(U) Two additional 7.5-lb batches of the AlH_3 blend were treated using the 14 day/60° C n-BA treatment in which the n-BA level was doubled. The water level was monitored throughout the passivations using two analytical techniques. Both the Karl Fischer method and a gas chromatographic method for water analysis (Table LVI) were used to analyze the water. The two methods agreed closely, showing that the water level gradually lowered until a water content of approximately 0.79 was reached at the end of treatment.

(U) The above incident points out that the AlH_3 water hydrolysis treatments are not only sensitive to process variations but to lot-to-lot (probably initial stability) variations as well.

B. SHELF LIFE TESTING

(C) To obtain a preliminary assessment of the shelf life of the R-18/TVOPA/AlH_3 propellant, cracking cubes of various sizes were made from the first 70-lb Day mix of VKW propellant. These cubes were tested at 40°, 50°, 60°, and 75° C. Cubes of VKU propellant were also made in the 1-pint Baker-Perkins mixer and tested at 60° and 40° C. To support this analysis, off-gas data were obtained from propellant obtained in the 70-lb mix. Results of the cube fissuring tests are presented in Table LVII and the off-gas data are shown in Figure 36 The cracking cubes from VKU, which were made prior to the cure difficulties that were encountered during the scaleup portion of this program (Section IV) lasted much longer (35 to 42 days at 60° C) than could be predicted from hydrogen off-gas measurements. Cubes with purified TVOPA lasted longer than as received, probably due to the higher modulus of purified TVOPA propellants. Based on these results, most cubes from VKW were tested at 60° C to give data within a reasonable time period. Unfortunately, VKW cubes had a much shorter life (< 5 days at 60° C and 76 to 90 days at 40° C) than VKU cubes, limiting the usefulness of the results. The off-gas data obtained from the VKW samples indicate that these cubes failed at 60° and 40° C due to CO_2 evolution rather than hydrogen. As previously discussed, propellant from this mix cured somewhat slower than previous mixes. These results, coupled with the soft cure obtained on the second large mix, indicated the necessity for purifying the TVOPA to obtain a clean and consistent cure. Further shelf life studies should be based on the use of the purified TVOPA to obtain as clean and reproducible cure as possible prior to placing samples into surveillance.

(U) A 5-gal mix was made to obtain larger surveillance samples using purified TVOPA. Due to an error during casting, no usable samples were obtained. By the time this mix could be repeated, interest in surveillance of this propellant was reduced; therefore, a 40-lb grain was made of a

TABLE LVI

MOISTURE ANALYSIS DURING PASSIVATION

First Batch	Water Content, %	
n-BA Lots 101 and 102	Karl Fischer	Gas Chromatograph
0	1.70	1.50
3 days	1.19	0.78
6	--	1.13
10	1.10	0.82
14	0.64	--
Second Batch		
n-BA Lots 103 and 104		
0	--	2.00
4	1.10	0.91
7	1.02	0.68
11	0.84	0.73
13	0.72	0.68

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TABLE LVII

CRACKING CUBE DATA

Propellant Designation	Binder	Temp (°C)	Time to Failure (days) Cube Size (in.) 1	2	4.3
VKU	R-18	60		35-42	
		40		>140	
VKU-P Purified TVOPA	R-18	60		49-56	
		40		>140	
VKW (from 70-lb mix)	R-18	60		<5	
		40		76-90	
		60	20-28		
		60			2-7
		50		<5	
		75	<2		
		75		<2	

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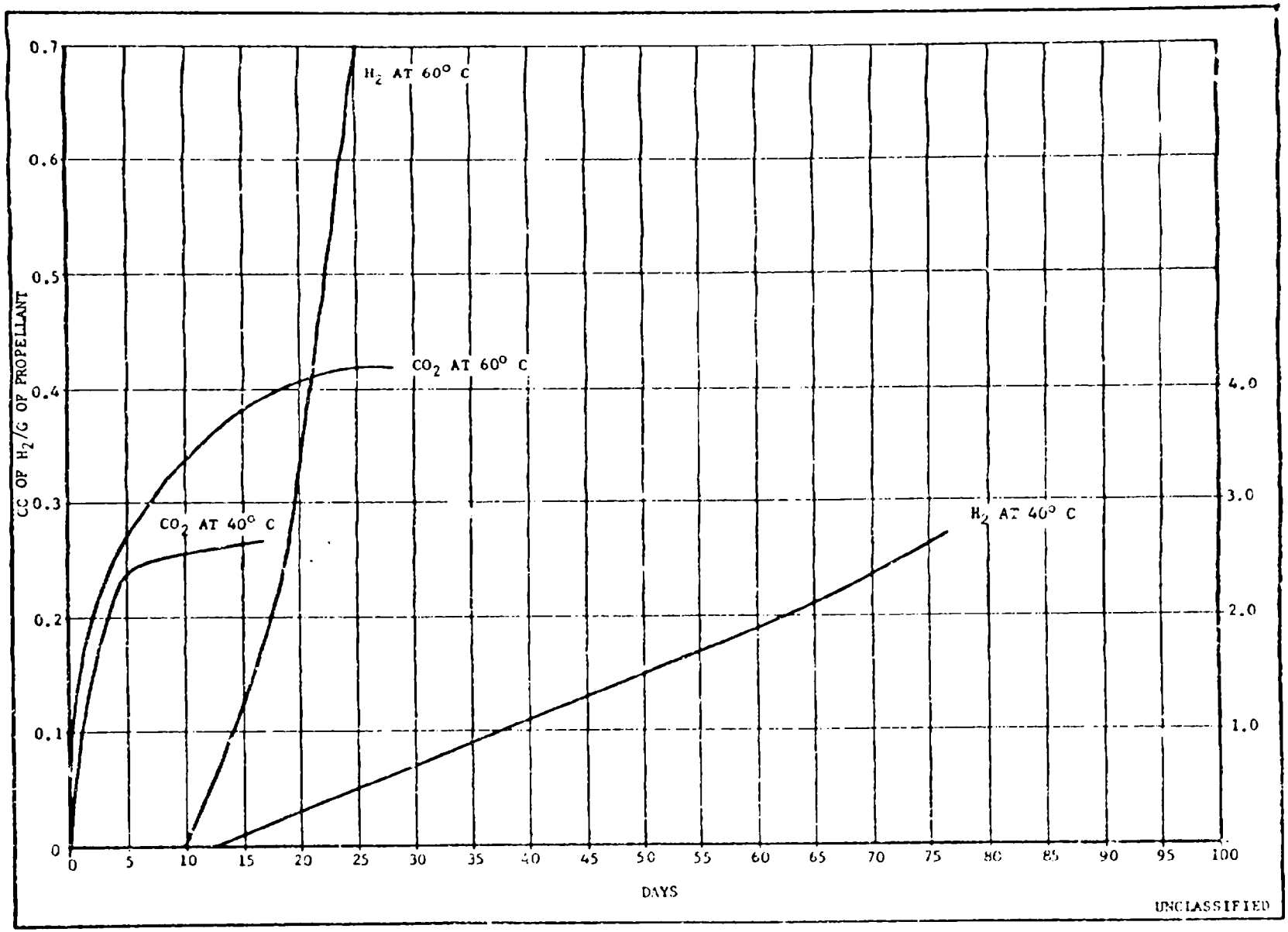

Figure 36. Gas Evolved from VKW Propellant During Storage at 40° and 60° C

(U) propellant (VKL) developed on the follow-on Contract F04611-700-0067. This grain will be fired on the follow-on contract.

C. SHELF LIFE PREDICTIONS

(C) Although a reproducible scaleup cure was later demonstrated with the use of purified TVOPA, sufficient time was not available to evaluate the shelf life of propellant made by this process. Until this can be done, rigorous shelf life predictions should not be made. However, an estimate of the contribution of AlH_3 decomposition to shelf life can be made. To make this estimate, a limited study of the kinetics of the decomposition of AlH_3 was performed.

(C) Based on the success that Dow Chemical reported in applying the Avrami equation, $-kt = \ln (1-\alpha)^{1/2}$, where α = fraction decomposed - to the decomposition of neat AlH_3, the decomposition of AlH_3 in propellant was analyzed using the same approach.

(C) The results shown in Figure 37 were taken from the decomposition of AlH_3 at 60° and 40° C in the R-18/TVOPA propellant and indicate fair agreement with this equation. Calculation of the activation energy from this data using the Arrhenuis equation gave the following results:

Neat AlH_3 (n-BA treated)	19K cal/mol
VKU	17K cal/mol
VKV	22K cal/mol

(U) Dow Chemical reported an average activation energy of 23K cal/mol. Using the rate constants calculated from the above data, a ratio of reactivities of the propellants at various temperatures can be calculated. The ratios are as follows:

60° C - 40° C = 8

60° C - 25° C = 48

40° C - 25° C = 6

(C) These ratios can be used to predict fissuring times of cracking cubes at low temperatures from higher temperature results, giving a conservative estimate since diffusional losses are neglected. Applying these ratios to the results from the VKU cubes (which failed from H_2 generation) a fissuring life of between 280 and 336 days at 40° C and between 1680 and 2000 days or approximately 5 yr at 25° C is predicted for 2-in. cubes. The fact that the 40° C cubes of VKU have not failed in 140 days lends support to this prediction scheme. Since initial diffusion from the 2-in. VKU cubes was ignored, this estimate cannot be applied directly to larger samples. In addition, the contribution of other gases has not been rigorously considered. However, these results do indicate that long shelf life can be projected for AlH_3 propellants in thin webs. For larger samples, some additional improvements in stability or the use of a scavenger technique appear necessary.

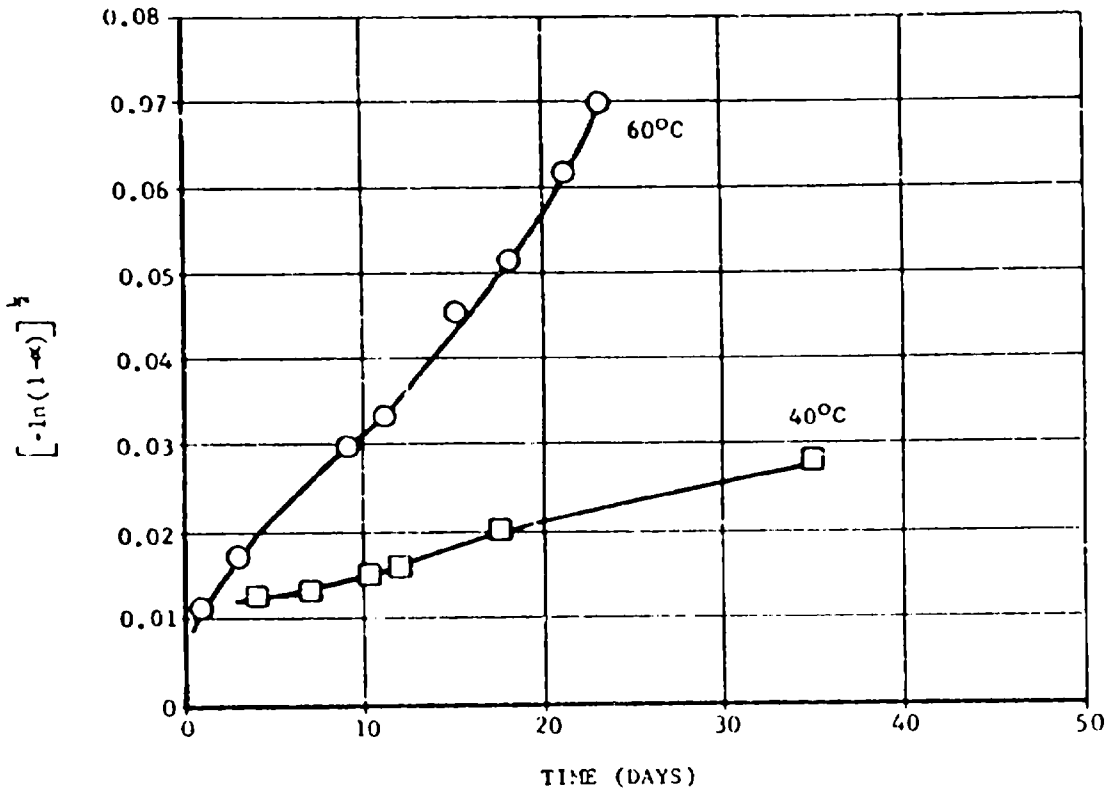

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Figure 37. Gas Generation Data (Avrami Equation Correlation) for R-18/TVOPA/AlH_3 Propellant

D. SHELF LIFE PREDICTION OF BATES MOTOR

(C) An analysis of the properties of the VKW propellant was made and a prediction of its shelf life in a 70-lb Bates motor has been made. Two major sources of gas exist in VKW propellant. AlH_3 slowly decomposes to release hydrogen, and carbon dioxide is released from the isocyanate during cure. Small amounts of CO_2 also may evolve from the reaction of TVOFA impurities with traces of water. The rate of release of these gases has been measured in the off-gas analyzer. The solubility and diffusion rate of these gases has also been measured in the propellant binder. This data permitted the calculation of the gas concentration in the propellant at any time by comparing the gas generation rate versus the diffusion rate.

(U) The 70-lb Bates rocket motor grain configuration is shown in Figure 38. The Bates grain has a free surface at both the inner bore and cylinder ends. The grain also has a slight taper. Gas diffusion out of the Bates grain is, therefore, two-dimensional.

(U) Hydrogen and carbon dioxide gas concentrations in the Bates grain for a constant gas generation rate were calculated with the Hercules HETRAN computer program. This program numerically solves the diffusion equation. The location in the Bates grain (Figure 38), having the maximum gas concentration, was then determined. The gas concentrations as a function of time at this location (for a constant gas generation rate), along with the actual time-dependent gas generation rate, were used in the Hercules Linear Response computer program. Numerically evaluating the convolutional integral, this program calculated the gas concentrations in the Bates grain (at the location shown in Figure 38) for the time-dependent gas generation rates.

(U) The diffusion calculations were all made with the assumptions that the gas concentration at the grain-free surface is effectively zero and that the motor case is impermeable to hydrogen. These are reasonably good assumptions.

(U) The grain internal pressure (pressure exerted by the dissolved gas) was calculated from Henry's Law:

$$\text{Pressure} = \frac{\text{gas concentration}}{\text{gas solubility at 1 atm}}$$

This pressure was then compared with the allowable pressure calculated from the following equation:

$$P_{\text{allowable}} = \frac{2E\epsilon}{1+2\epsilon}$$

where

E is the propellant modulus

ϵ is the propellant elongation

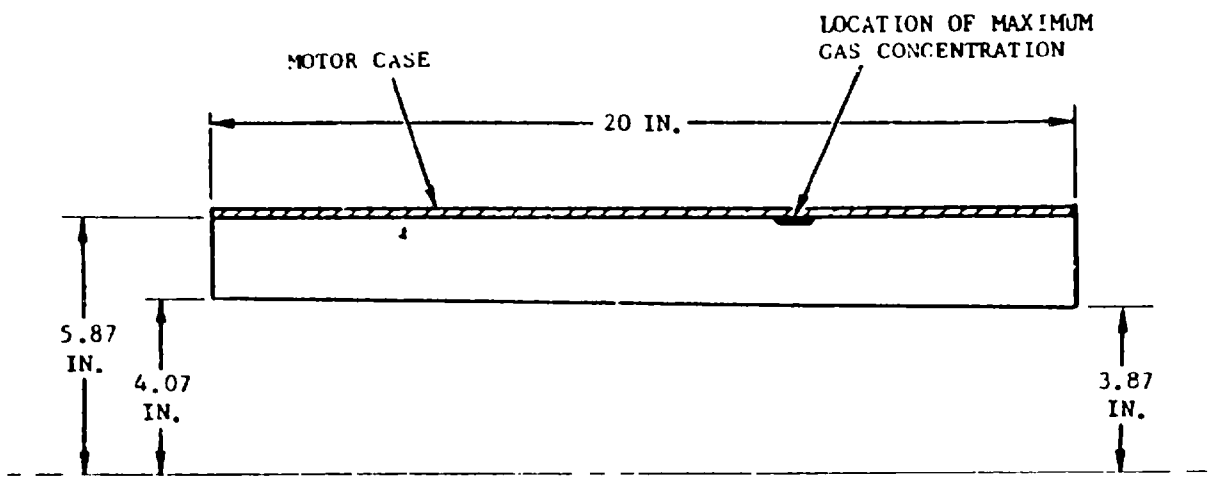

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Figure 3[illegible]. Configuration of 70-Lb Bates Motor Grain

(U) The amounts of hydrogen and carbon dioxide gas evolved at storage temperatures of 40° and 60° C are given in Figure 36. These curves of total evolved gas versus storage time were numerically differentiated to give the instantaneous gas evolution rates at 40° and 60° C. These were then extrapolated to obtain the gas generation rates at 25° C. The extrapolation was performed by plotting the logarithm of the gas generation rate against the absolute temperature. The resulting gas generation rates at 25° C for hydrogen and carbon dioxide are given in Figures 39 and 40, respectively.

(U) The diffusivity and solubility data for hydrogen and carbon dioxide in VKW propellant at 25° C are presented in Table LVIII. The mechanical property data for VKW propellant are summarized in Table LIX.

(C) The hydrogen gas concentration in the 70-lb Bates motor as a function of time at 25° C is given in Figure 41. The maximum gas concentration occurs at 18-days storage time. This is approximately 5 days after the evolution of hydrogen was assumed to begin. The maximum hydrogen concentration reaches 2.7×10^{-4} cc (STP) per gram propellant.

(C) The carbon dioxide concentration in the 70-lb Bates motor at 25° C as a function of time is given in Figure 42. The maximum carbon dioxide concentration of 0.127 cc (STP) per gram propellant occurs at 4 days storage time.

(C) The internal pressure in the Bates motor resulting from each evolved gas was calculated using Henry's Law. The total internal pressure as a function of storage time at 25° C is presented in Figure 43. The maximum internal pressure of 6.6 atm at 4 days is caused entirely by the evolved carbon dioxide. The pressure developed by the evolved hydrogen is negligible in comparison to the carbon dioxide pressure. The maximum hydrogen pressure is 0.2 atm at 18 days storage time.

(C) The maximum allowable pressure based on the 6 day mechanical property measurements is 7.55 atm. Since the maximum internal pressure, 6.6 atm, is less than the allowable pressure, the Bates motor grain will not crack.

(C) The maximum internal pressure in the Bates grain occurs at 4 days storage time and is due primarily to evolved carbon dioxide. This maximum internal pressure is slightly less than the maximum allowable internal pressure, but uncertainties in the data used make the structural integrity of the grain marginal. Softening of the propellant or slow cure resulting in a low modulus after 4 days would be expected to result in porosity.

(C) The pressure resulting from the evolved hydrogen is negligible in comparison to the carbon dioxide pressure. The evolved hydrogen does not affect the grain structural integrity. Unfortunately, the gas generation rate measurements could not be carried out long enough to see the accelerating rate that is normally seen in AlH_3 decompositions. Therefore, the conclusion can be made that if the propellant survives the first week it will not fail until the hydrogen generation becomes accelerating or the propellant softens significantly due to binder degradation.

TABLE LVIII

DIFFUSIVITY AND SOLUBILITY DATA
H_2 AND CO_2 IN VKW PROPELLANT AT 25° C

Gas	Diffusivity	Solubility
	(cm^2/sec)	(cc/g-binder)
Hydrogen	2.2×10^{-5}	4.4×10^{-3}
Carbon Dioxide	1.5×10^{-5}	64.0×10^{-3}

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TABLE LIX

VKW PROPELLANT MECHANICAL PROPERTIES
(Batch BC-138-57)

Cure Time at 100° F (days)	Crosshead Speed (in./min)	Temp (°F)	Maximum Tensile Strength (psi)	Elongation at Max Stress (%)	Tensile Modulus (psi)
6	2	77	67	31	290
120	2	77	83	23	430
120	0.02	77	54	23	260

NOTE: JANNAF tensile specimens were used.

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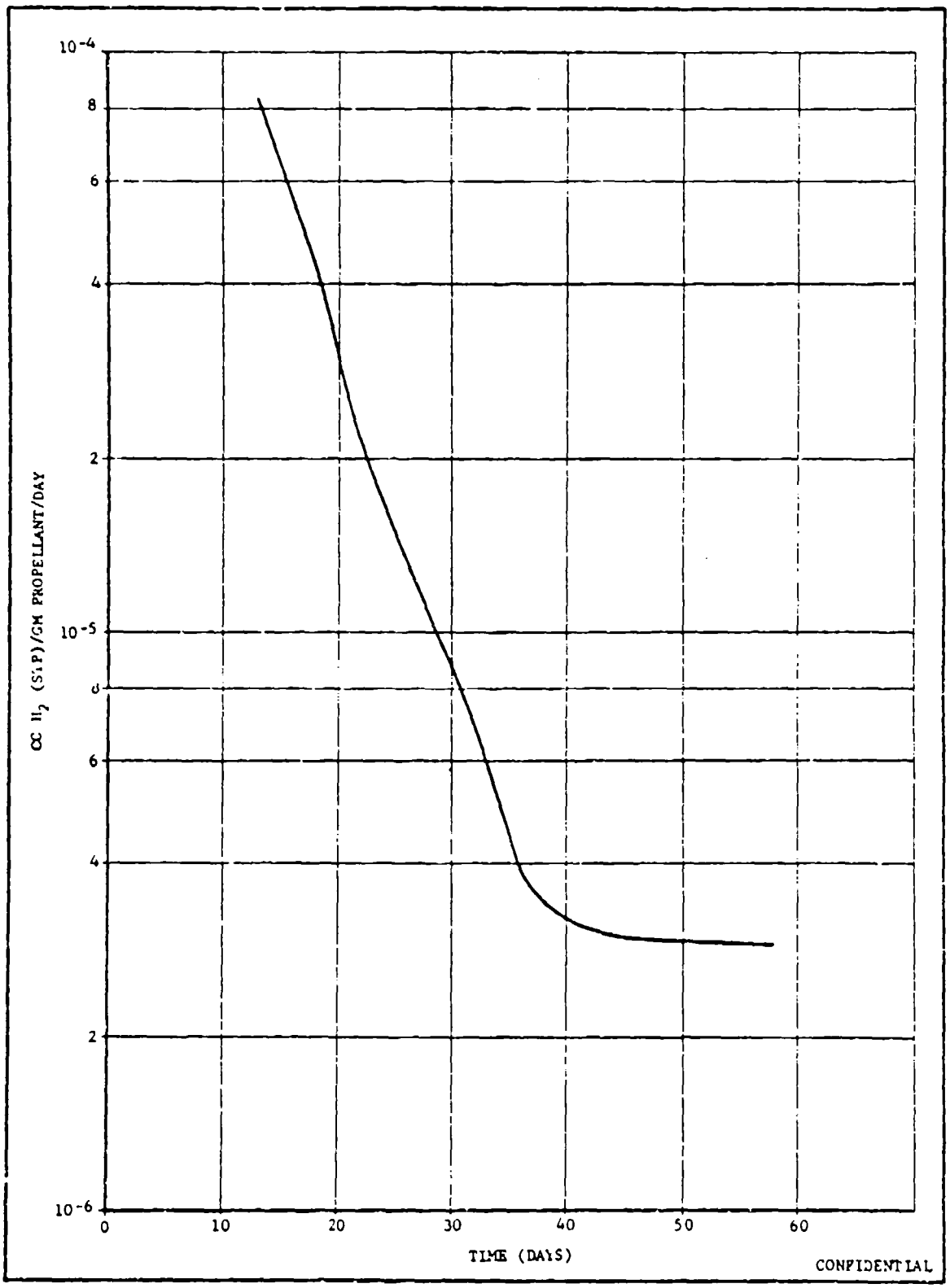

Figure 39. Hydrogen Generation Rate in VKW Propellant at 25° C

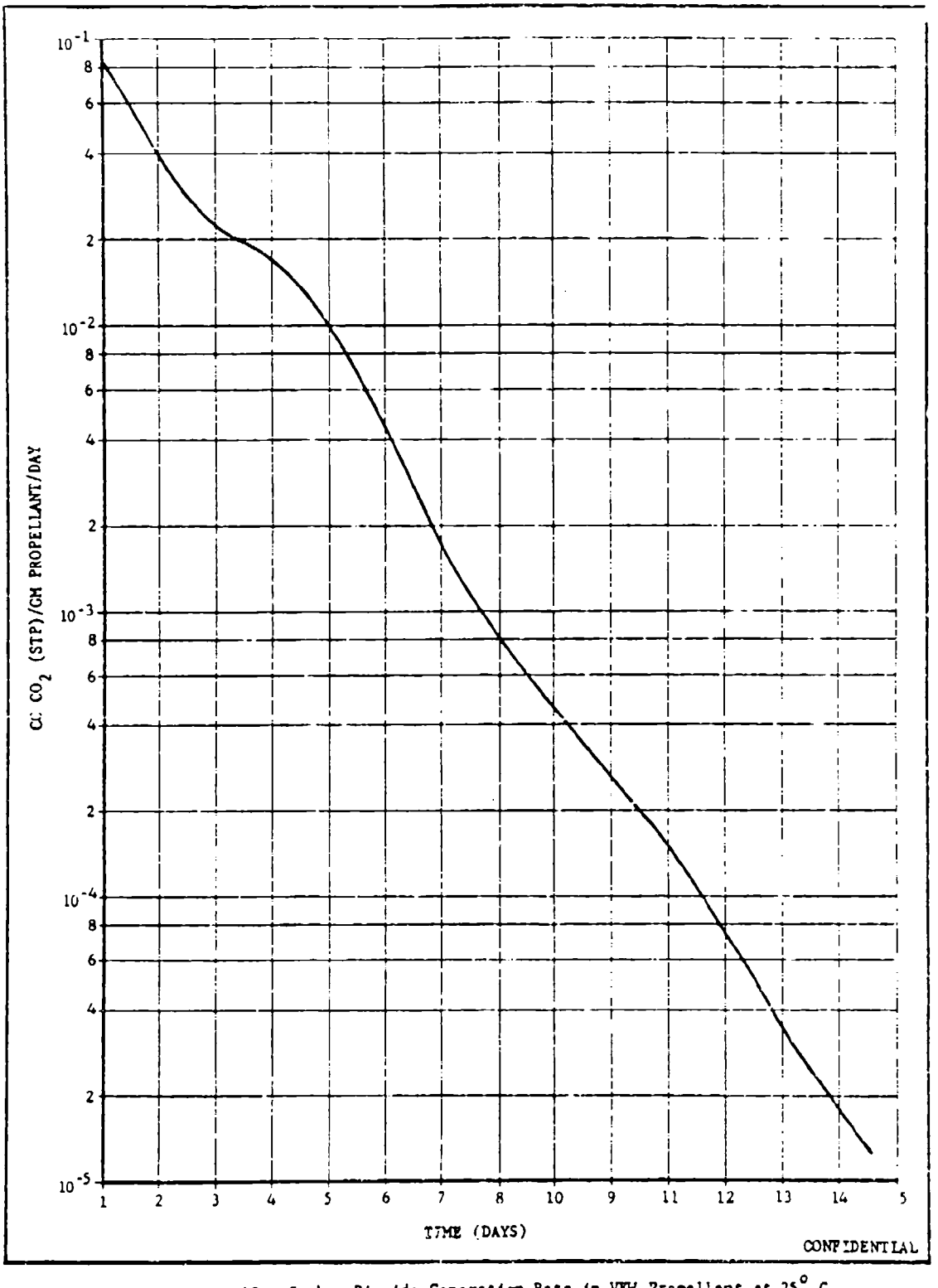

Figure 40. Carbon Dioxide Generation Rate in VKW Propellant at 25° C

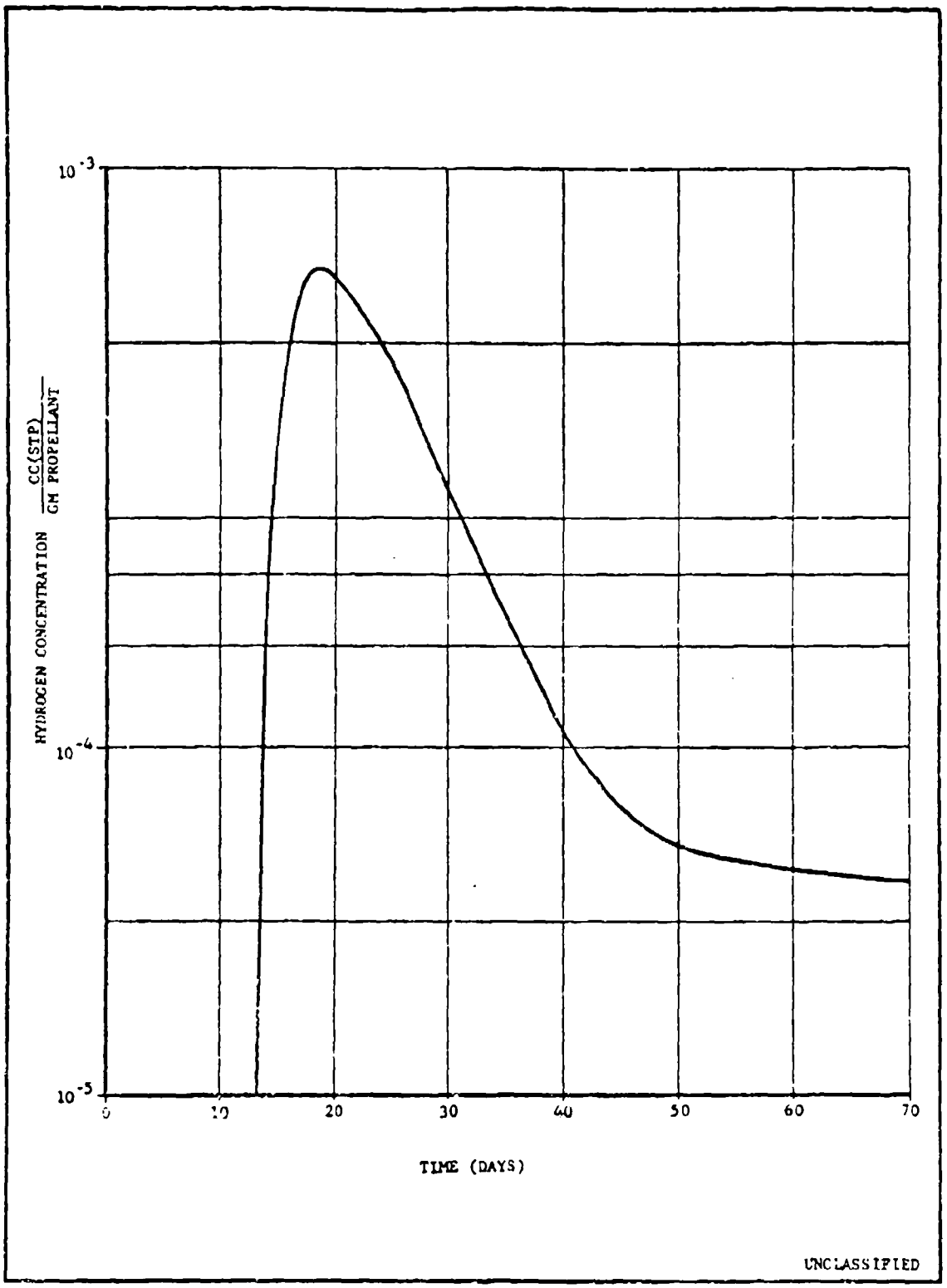

Figure 41. Hydrogen Concentration Versus Time at Location of Maximum Gas Concentration in 70-Lb Bates Motor

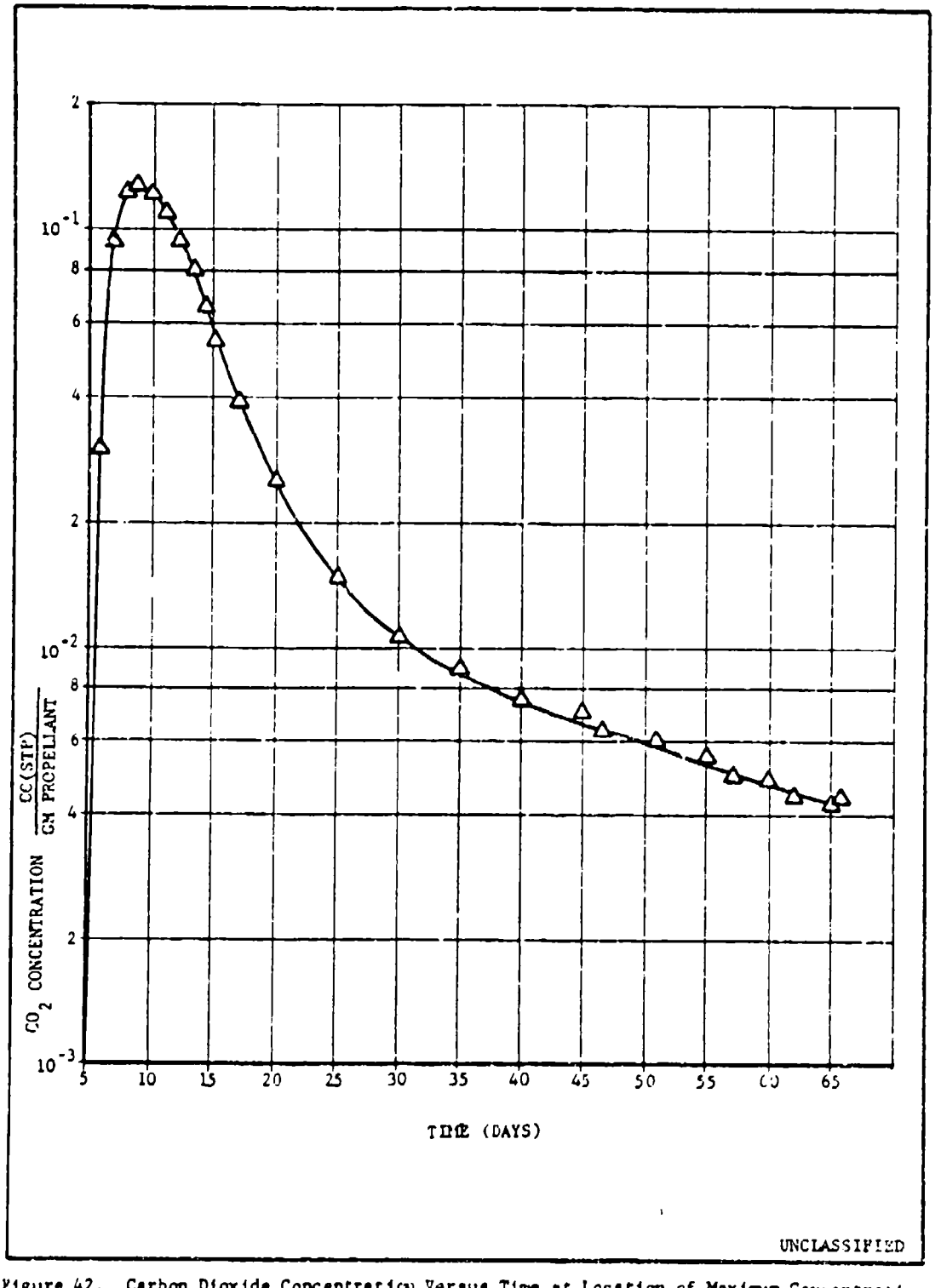

Figure 42. Carbon Dioxide Concentration Versus Time at Location of Maximum Concentration in 70-Lb Bates Motor

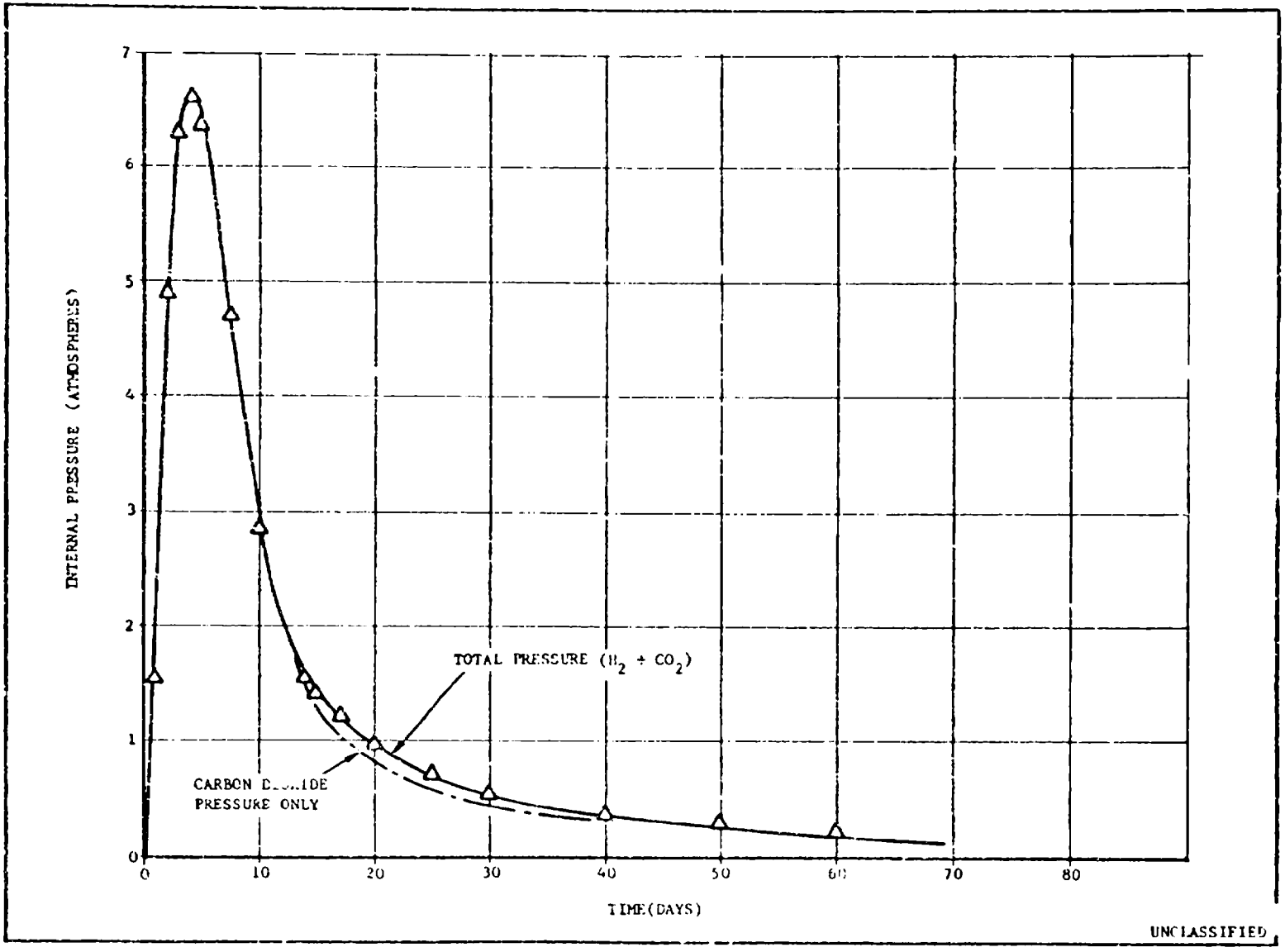

Figure 43. Internal Pressure in the 70-Lb Bates Motor at 25° C Caused by Hydrogen and Carbon Dioxide Evolution

SECTION VI

CONCLUSIONS AND RECOMMENDATIONS

(C) The following conclusions have been reached from the results of this program:

(1) Hydroxyl ammonium perchlorate (HAP) is not usable with the DOMINO binder due to poor stability.

(2) The P-BEP-TVOPA binder has a very short shelf life and it does not give any performance advantages over the highly plasticized low energy polymers which are more easily developed.

(3) Two alternate binders gave promising results:

(a) EAAA needs a lower temperature cure to be usable with AlH_3.

(b) Multron R-18 gives a good low temperature cure and mechanical properties, especially when the TVOPA is purified to remove the isocyanate reactive impurity.

(4) DOMINO/AlH_3 propellants give the same high impulse efficiency as the DOMINO/Al propellants. In a 15-pound motor the TVOPA/R-18/AlH_3/AP/HMX propellant gave an impulse (I^{15}_{1000}) of 267 sec and an impulse efficiency of 94.5 percent.

(5) Small web motors (1 inch) would be expected to survive 5 years at 25° C if they survive cure. However, increased stability of the AlH_3 or the use of stabilizers or scavengers will be needed for larger web motors.

(6) A rapid low temperature cure is required to prevent porosity formation from CO_2 gassing during cure.

(7) Removal of the HMX and lowering the TVOPA/polymer ratio (VML vs VKW) did not markedly reduce the sensitivity of the uncured propellant. Thus the TVOPA/AlH_3 propellants remain much more sensitive to initiation by impact and friction than conventional non-AlH_3 propellants.

(C) The following areas for further investigations are recommended:

(1) An extensive binder comparison should be made to compare the EAAA binder with R-18 in a TVOPA/AlH_3 propellant. The EAAA binder requires a low temperature cure catalyst. The R-18 binder requires optimization of the cure stoichiometry and mechanical properties.

(C) (2) In-process and in-use studies should be made to determine the safety margins involved with scaling this propellant to large motors. Efforts to reduce these hazards should be studied both by reducing the sensitivity of the propellant and also by modifying the processing procedures to ensure larger safety margins.

(3) Means should be sought to increase the shelf life of the AlH_3 propellant by increasing the stability of the neat AlH_3 and through the use of stabilizers and/or scavengers in the propellant.

(4) Extensive accelerated aging studies should be made to determine the effect of processing conditions on shelf life.

(5) The effect of compositional changes on ballistic and mechanical properties should be determined and the TVOPA/AlH_3 propellant should be scaled up to 40-pound motor firings to determine the impulse efficiency.

(U) Each of these recommendations have been carried out in other Air Force sponsored programs.

(C) Based on this program and related Air Force sponsored programs by Hercules,[9] DOW,[10] LPC,[11,12] Rocketdyne,[13] and ARC[14] it is concluded that the AlH_3 based propellants are inherently sensitive and subject to poor shelf life due to the basic nature of the AlH_3 itself.

(C) Extensive studies to determine the fundamental reasons for the extreme sensitivity of AlH_3 containing compositions were not encouraging. Attempts to reduce the sensitivity of AlH_3 propellants by lowering the energy or by incorporating additives were equally discouraging. It is believed that the extreme sensitivity of AlH_3 propellants is an inherent property which must be accepted when working with these propellants. Process procedures, such as the inert diluent developed in this program, reduce the in-process hazards. However, the system must still be considered a high risk propellant during processing. After cure the propellant is less sensitive than in the uncured state, but even when cured, the propellant is initiated by impact and frictional forces more easily than non-AlH_3 containing propellants.

(C) The shelf life of AlH_3 propellants also continues to be a problem area. Efforts to passivate the surface of AlH_3 have improved the stability markedly, but the improvement was not sufficient to predict long shelf life for large web motors. Scavengers have been demonstrated that will effectively remove the hydrogen as it is produced from the decomposition of AlH_3, but the scavengers degrade the binder thus negating their potential advantage.

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9 through 14 Refer to List of References

(C) The TVOPA-AlH_3 propellants have a relatively high burn rate which limits their potential use in ballistic missiles. The burn rate can be lowered by adding HMX and/or by lowering the TVOPA level, but burn rates normally desired in ballistic missiles have yet to be demonstrated. If the TVOPA-AlH_3 propellants are to be considered for future Air Force missions, which may require their high impulse performance, the burn rate must be reduced, along with improvement in the process hazards and the shelf life.

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APPENDIX A

EFFECT OF HF AND MOISTURE IN CURE CATALYSTS

A. HF REACTIONS

(U) Work under this effort had shown that "as received" P-BEP contained a volatile fluorine compound, most probably HF. A strong acid such as HF could be detrimental to a urethane cure in several ways; it could react directly with isocyanate to either deplete it or to form more or less reactive intermediates, and HF could react with the catalyst. Since previous P-BEP formulation efforts have been hampered by incomplete propellant cures, a study was performed to determine the effects of HF on propellant curatives and catalysts.

i. Reaction of HF with Isocyanates (BC-153-63)

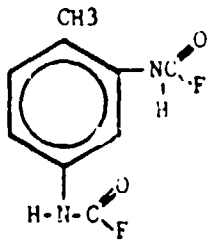
(U) Hydrogen fluoride could react in a variety of ways with isocyanates. Some workers[1] thought the following series of reactions was possible:

$$(1)\quad RN = C = O + HF \longrightarrow RN(H)C(=O) - F$$

$$(2)\quad RN(H)C(=O) - F + HF \longrightarrow RNH_2 + COF_2 \uparrow$$

$$(3)\quad RNH_2 + RN = C = O \longrightarrow RN(H) - C(=O) - NR(H)$$

(U) Thus, isocyanate would react with HF in much the same manner as water, undergoing a loss of a carbonyl group with the eventual formation of a substituted urea. This above postulation conflicted with an earlier report of Buckley, et.al.[2] who reacted a variety of isocyanates, including aromatic diisocyanates with excess HF to obtain in every case the carbamyl fluoride derivatives of the respective isocyanates. To check this, 2,4-toluene diisocyanate was reacted with an excess of HF. The reaction was carried out at room temperature by bubbling anhydrous HF into a stirring methylene chloride solution of TDI. Midway through the reaction (with respect to bubbling time) a white precipitate began to appear. Once formed, the precipitate was filtered and washed. The spectrum of this compound was obtained and is presented in Figure A-1. In this scan the isocyanate functionality at 2268 cm^{-1} virtually disappeared with the formation of a new band near 1810 cm^{-1}. This compound was base-hydrolyzed and analyzed for percent fluorine by the lanthanum (III) titration. The analysis indicated that this compound was composed of 17 percent fluorine which compares favorably with the following compound:



(U) This compound, 2,4-toluene dicarbamyl fluoride, had a melting point of 155 to 157° C. The compound was sparingly soluble in benzene and soluble in dioxane as reported for similar compounds by Buckley, et.al.[8]

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1 and 2 Refer to References at End of Appendix

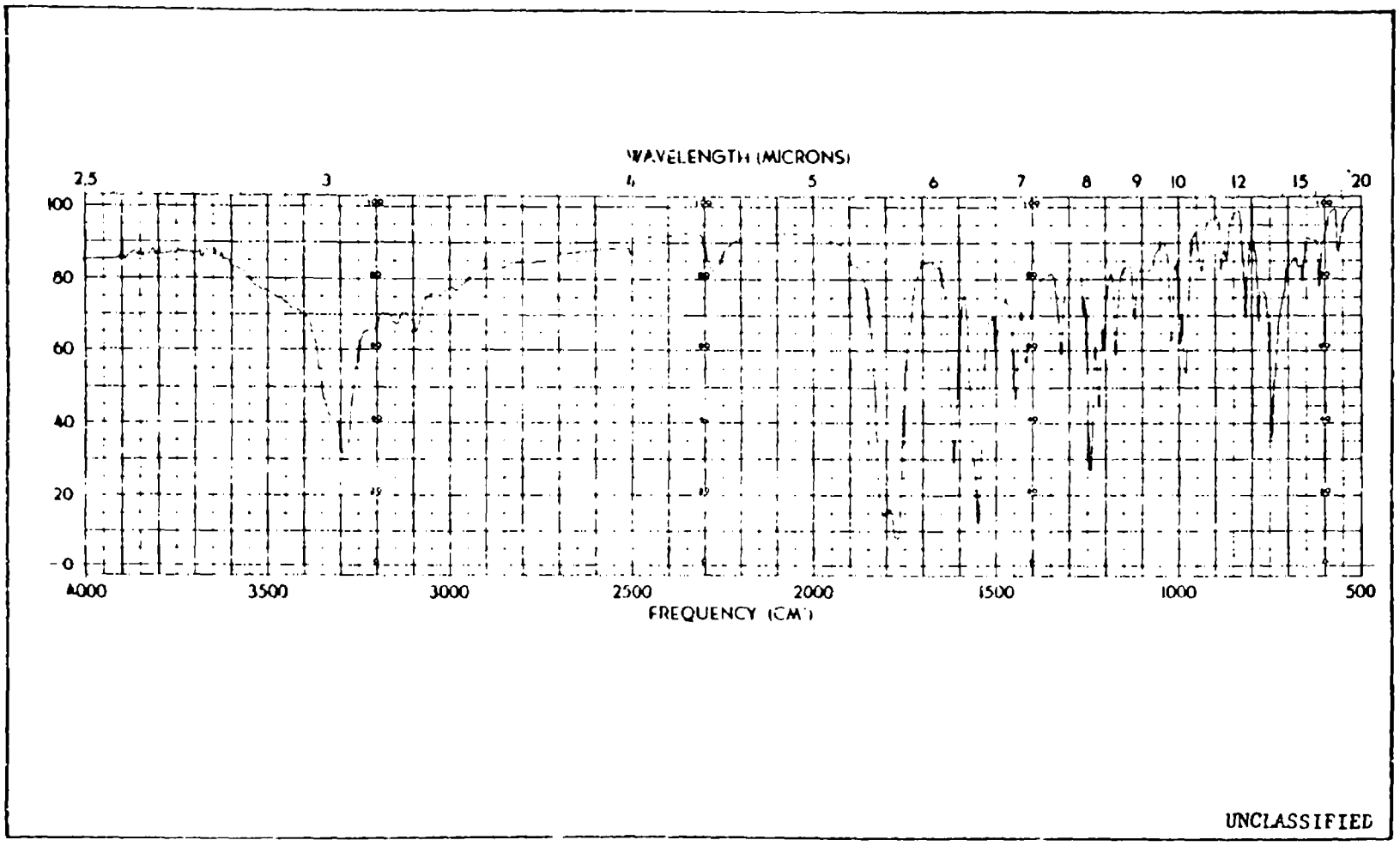

Figure A-1. Intrared Scan of 2,4 Toluene Dicarbamyl Fluoride

(U) The mono-carbamyl fluoride was also prepared for further reaction studies. This compound was somewhat less pure, having a melting point range of 109° to 118° C. The IR spectrum of this compound (Figure A-2) displayed major absorbances at 2268 and 1810 cm^{-1}, indicating the presence of both isocyanate and carbamyl fluoride with probably both ortho and para isomers being present.

(U) From these preperations, it is felt that only reaction 1 above, occurs in an anhydrous HF system.

(C) The carbamyl fluoride absorbance at 1810 cm^{-1} was used diagnostically in further HF-urethane cure studies to determine the presence or absence of that functional group. Reasonable quantities of HF (such as would be expected under normal P-BEP-urethane cures) were added to uncatalyzed TDI-polypropyleneglycol (PPG-2025) systems directly and in methylene chloride. The carbamyl fluoride absorbance was not observed in measurable amounts in any of these systems even after extended exposures.

(U) Although the carbamyl fluoride functionality was not observed in the above reactions, a possibility existed in which the carbamyl fluoride could be an unstable intermediate. Thus, at any one time during a reaction, the carbamyl fluoride functional group could form and react rapidly enough to produce virtually no characteristic IR absorbance. To check this, an attempt was made to react the prepared derivatives with PPG-2025 and glycerol systems. The carbamyl fluoride functional groups did not react at all with the hydroxyl groups of these alcohols. Only in one case where dimethyl sulfoxide (DMSO) was used as a solvent did we find the carbamyl fluoride group to react. The DMSO was later found to decompose the carbamyl fluoride to the parent functional groups, expelling HF and producing NCO.

(C) Thus, these studies indicated that although excess quantities of HF did react with isocyanates to produce carbamyl fluorides, smaller concentrations of HF would not react at all. This was especially true for the amounts of hydrogen fluoride detected to date in P-BEP systems. In one diagnostic experiment, small quantities of HF were added to several uncatalyzed curing urethane reactions. Although the presence of HF was detected in IR spectra, no noticeable effects of HF were observed in either the spectra or in the reaction rates of the systems. Similar reactions, carried out in methylene chloride, produced the same results.

(U) To check the effect of catalysis on the possible isocyanate-HF reaction, four reactions were carried out over a 5-hr period at 80° C in the following manner:

(C) A TPMTI-methylene chloride solution was prepared such that 1 mm contained 8 meq/ml of NCO. This concentration was amenable to an IR measurement of the NCO absorbance of 2268 cm^{-1} without dilution. An HF-methylene chloride solution was prepared containing 0.010 meq HF/ml and,

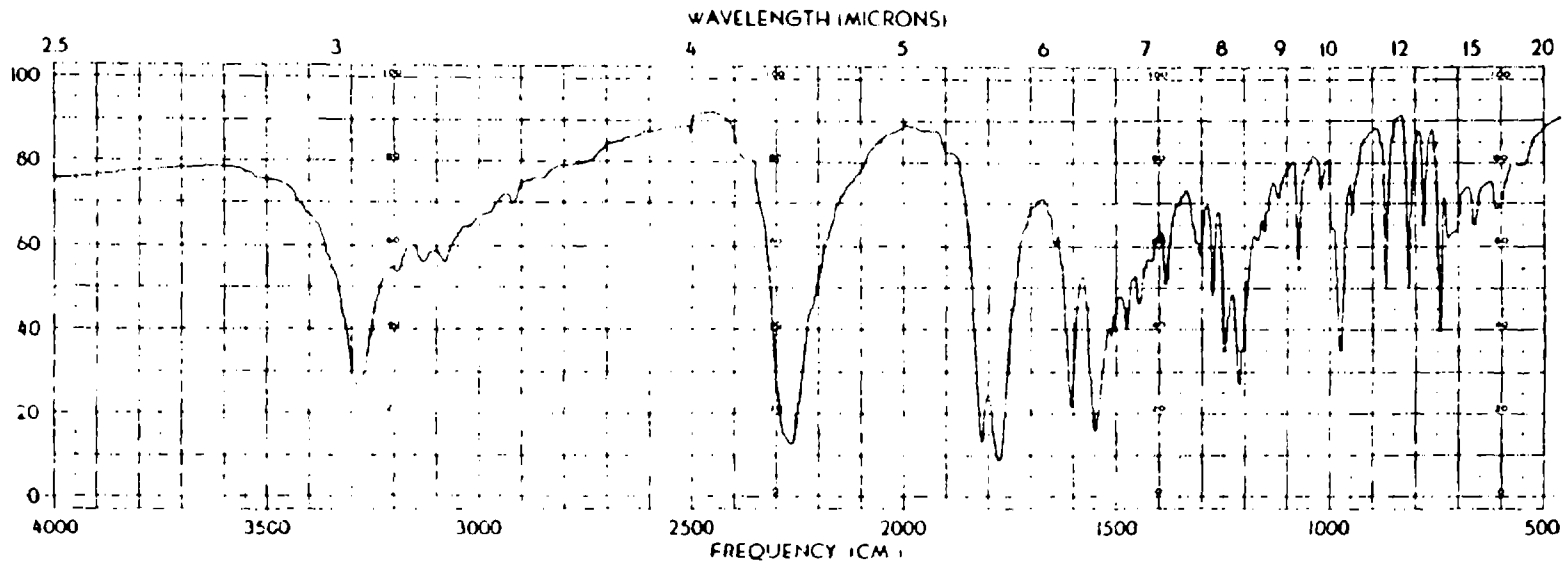

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Figure A-2. Infrared Scan of Monocarbamyl Fluoride Derivative of 2,4-Toluene Diisocyanate

(C) where indicated, DMTDC catalyst was added in equivalent concentrations to previously-described gumstock systems. The following mixtures were prepared:

Run	TPMTI Solution Added	CH_2Cl_2 Added	$HF-CH_2Cl_2$ Added	$(CH_3)_2SnCl_2$ Catalyst Added
1	1 part	1 part	--	--
2	1 part	1 part	--	Yes
3	1 part	--	1 part	--
4	1 part	--	1 part	Yes

Infrared isocyanate measurements over a 5-hr period at 80° C indicated that all four mixtures contained identical NCO concentrations which were equal to the starting concentration. Thus, it appears that HF in dilute solutions does not react with NCO even under catalysis.

2. Effect of HF on Reaction Rates of Uncatalyzed and Catalyzed Urethane Cures

(U) To determine the potential of HF to poison urethane catalysts, a series of model compound studies were performed.

(U) The first system to be studied contained 0.1 percent dibutyltin dilaurate catalyst in 1:1 equivalent mixture of PPG-2025 and TDI. This was compared to a similar system to which a small amount of gaseous HF had been added. A white precipitate was formed in the system containing HF. The mixture containing added HF cured about 75 percent slower than the control sample in the first hour. This mixture remained liquid after 18 hr while the control sample was cured to a tacky solid.

(C) The above experiment along with propellant cure studies indicated that the organo-tin catalysts were being deactivated by HF in the P-BEP. To verify the possibility of this reaction, a dilute solution of HF in methylene chloride was prepared. This was added to a small amount of the dibutyltin dilaurate catalyst. A white precipitate was immediately formed. This material was purified by ether washing and an IR scan obtained. (See Figure A-) The melting point of this solid was 149° C. The fluorine content of [illegible] compound was 13.3 percent. The solid was identified as dibutyltin d[illegible] monohydrate. A similar reaction product was obtained from dibutyltin di[illegible]te. The catalytic strength of the material was expected to be lower [illegible] the original catalyst due to its low solubility.

(U) To verify the catalytic effect of the white precipitate formed by the addition of HF to the dibutyltin dilaurate catalyst, the cure rate with this material was determined by adding an amount equivalent to 0.1 percent d[illegible]yltin dialaurate to the system. This was heated to 50° C and the isocyanate reaction rate was compared to a PPG-2025-TDI system containing no catalyst. The HF reacted catalyst had only a very slight catalytic effect on the curing of the PPG-2025-TDI system.

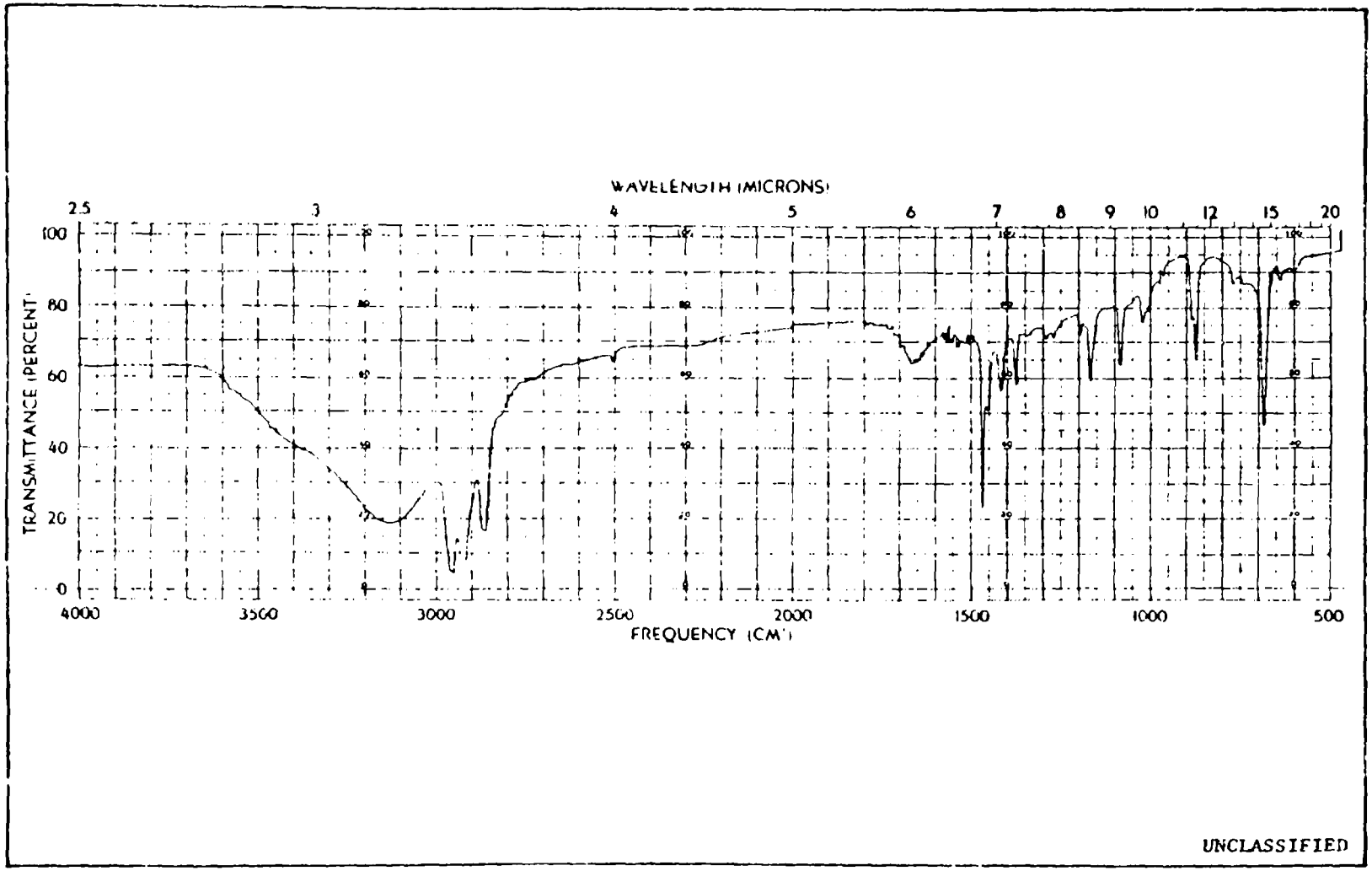

Figure A-5. Infrared Scan of Reaction Product of Dibutyltin Dilaurate and HF (BC-157-12)

[illegible] confirm the suspected catalyst deactivation by HF. These results coupled with the negative [illegible] reactivity with isocyanates and results of the stripping study, showing the difficulty in removing HF from P-BEP indicated a primary cause for P-BEP cure problems was catalyst deactivation by HF. Scaleup cure problems could be aggravated by poorer stripping efficiency as the mix size increases. Possible solutions to alleviate this problem included better stripping efficiency, HF scavengers, and alternate catalyst systems not susceptible to HF attack. These approaches were explored as the formulation effort progressed.

(C) The first approach used in the formulation efforts to remedy the HF-poisoning problem consisted of using chemically-loaded molecular sieves for catalysis. The sieve used was obtained from Linde, a subsidiary of Union Carbide, under the designation CW-X105. This material was their 13X (10A pore size) sieve, loaded 10 percent with dibutyltin dilaurate. Linde[3] reported that the sieve would "store" the loaded compound until the system was heated or until the loaded compound was replaced by a more strongly-adsorbed material like water (and HF). Thus, conceivably, the use of this type of catalyst could achieve at least a temporary scrubbing effect during cure, and a gradual release of the DBTDL as water and HF were adsorbed would mean delayed catalysis and a longer pot-life.

(C) To study the catalyst poisoning reactions in more detail, an IR technique was used to monitor the NCO concentration during the cure of the model systems. One-to-one mixtures of NCO and alcohol, together with the appropriate catalyst, called gumstock preparations, were cured at 120° F. Intermittently, samples were removed, diluted with 1,2-dichloroethane and placed in 0.2mm CaF_2 cells. The NCO absorbances were then measured at 2268 cm^{-1}. The resultant data were treated by kinetics as second order reactions. Figure A-4 presents two second order plots of 2,4-toluene diisocyanate (TDI)/polypropylene glycol-2025 (PPG) reactions catalyzed by 0.2 percent DBTDL and 0.2 percent CW-X105 (10% in DBTDL, thus adding 0.02% DBTDL). Several interesting facts can be noted from these curves. The 0.2% DBTDL reaction clearly demonstrated the reaction of both ortho and para isocyanate functional groups - the initial slope resulting from the reaction of both - and the final slope, called the rate-determining reaction, that of the ortho NCO. The slopes of these reactions are actually the reaction rate constants - the initial slope being the summation of $K_1 + K_2$ and the final slope K_2. In comparing the rates of both catalysts, one can see that the 0.2 percent CW-X105 sieve catalyzed the reaction much more than the 0.2 percent DBTDL alone, despite the fact that the CW-X105 sieve reaction contained only one-tenth the amount of DBTDL (the sieve by itself is a noncatalyst). This type of synergism has been noted before in urethane catalysis by Wolfe.[4] Also, the CW-X105 cure showed a significant change in reaction rate after the first hour. This change in rate was observed in all catalyzed systems studied and was verified by another reliable analytical technique. Tentatively we attributed this increase in rate to product catalysis, i.e , the urethane formed catalyzed the reaction which changed the rate as the product increased in concentration. This topic was recently reviewed by Smith.[5]

[3,4,5] Refer to References at End of Appendix

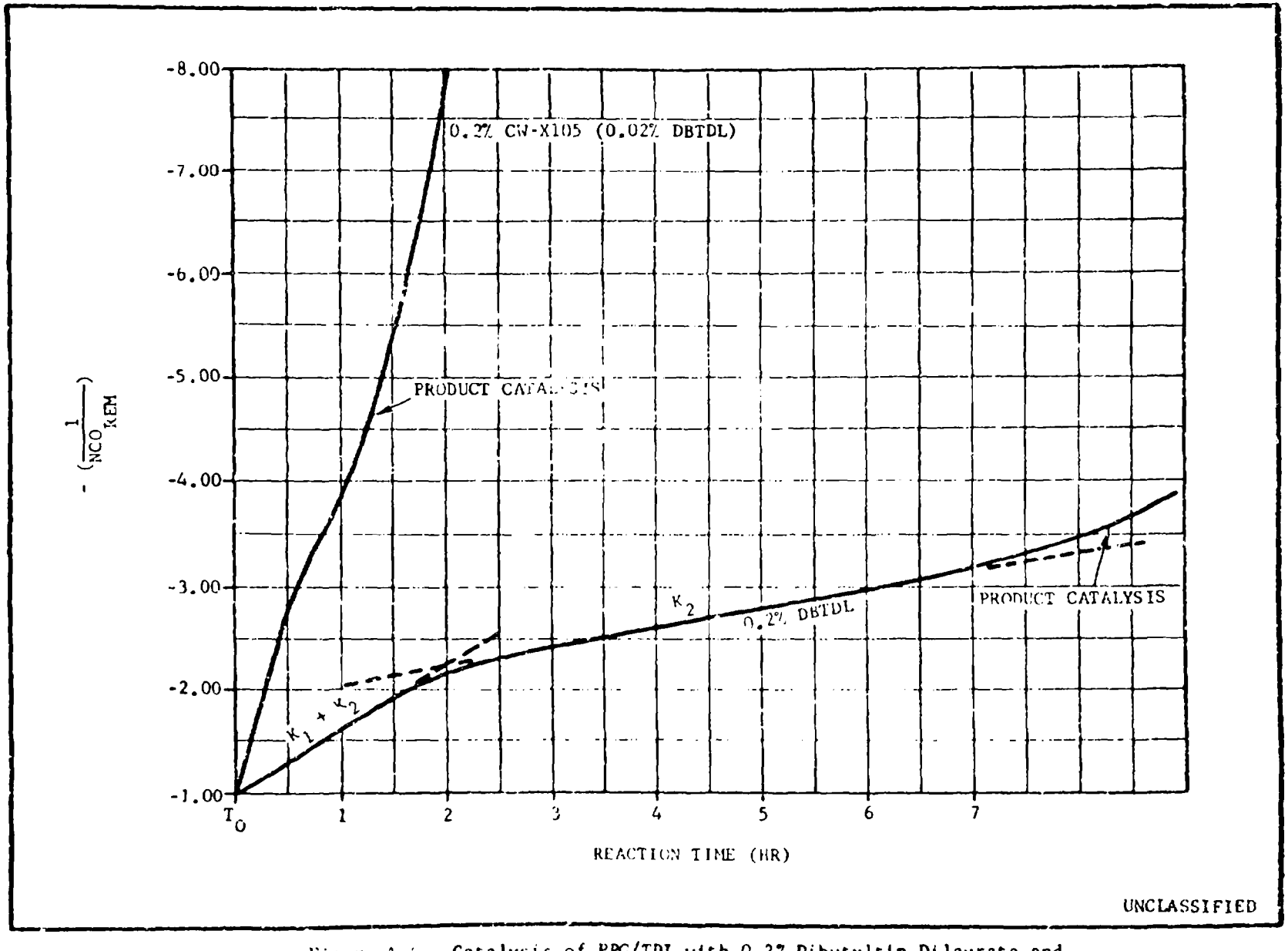

Figure A-4. Catalysis of PPG/TDI with 0.2% Dibutyltin Dilaurate and 0.2% CW-X105 (Loaded Sieve) (U)

(C) The use of the CW-X105 catalyst throughout most of the 1969 DOMINO program provided fair propellant cures. The exact mechanism of the catalysis was open to conjecture. Several limited data points, however, indicated that catalysis might actually occur on the loaded sieve. This we believe because we have found that dibutyltin compounds will actually pull fluoride away from molecular sieve to form the insoluble dibutyltin difluoride salt. Also, we have found that HF reacted with loaded sieves to coat the sieve particles with a white precipitate. Infrared spectra of the product indicated that dibutyltin difluoride was present, and from all indications still on the molecular sieve. Finally, since the loaded sieve presented a synergistic increase in reaction rate a release mechanism would tend to show an initial, very slow reaction rate which would increase throughout the cure. This was not the case even with the currently used P-BEP/TPMTI system. Initial cures always displayed initial synergistic catalytic activities and the rate would remain constant through most of the cure until product catalysis occurred.

(C) The effect HF had on DBTDL and CW-X105 sieve was studied by following the cure of inert gumstocks, with and without HF. Again, TDI/PPG was used as described previously; however, for reactions containing HF, that gas was bubbled through a portion of the PPG in an amount equal to six percent of the hydroxyl group equivalency. Thus, a substantial amount was present and in large excess with respect to the catalyst concentration. The effect HF had on these reactions is demonstrated in Figure A-5. The poisoning of DBTDL by HF is evident as the NCO concentration hardly changed at all. The effect of two different concentrations of HF on the CW-X105-catalyzed reaction is evidenced by a decrease in the reaction rate with increased HF. The fact that catalysis occurred at all with the CW-X105 catalyst in the presence of the large quantity of HF is perhaps the basis for the reasonable success experienced with P-BEP propellant cures.

(C) An additional effort was made to study an alternate catalyst which would be a non-poisoning/non-sieve compound. Previously, our work with tin-catalyzed P-BEP/NCO systems indicated that catalyst poisoning might well be a function of how soluble the resultant alkyltin fluoride was in the curing matrix. Thus, a precipitate would indicate poisoning, which was the criterion used by other workers.[6] Pursuing this further, the solubility of these alkyltin fluorides appeared to be a direct function of the size of the alkyltin cation (assuming some degree of hydrolysis). Thus, one would expect dibutyltin dilaurate and diacetate to behave identically, which was in fact, the case. On the other hand, n-butyltin or dimethyltin compounds should form generally more soluble fluoride salts. Available data on physical constants of these compounds was in agreement with these observations. Consequently, dimethyltin dichloride (DMTDC) and n-butyltin trichloride were chosen for further work. From a compatibility standpoint DMTDC was the most favorable, indicating no problem existed by warchglass, Fisher Johns Autoignition, and Modified Taliani testing. (The latter compound showed a >200mm pressure rise on the Taliani and was thereby the less favorable of the two.)

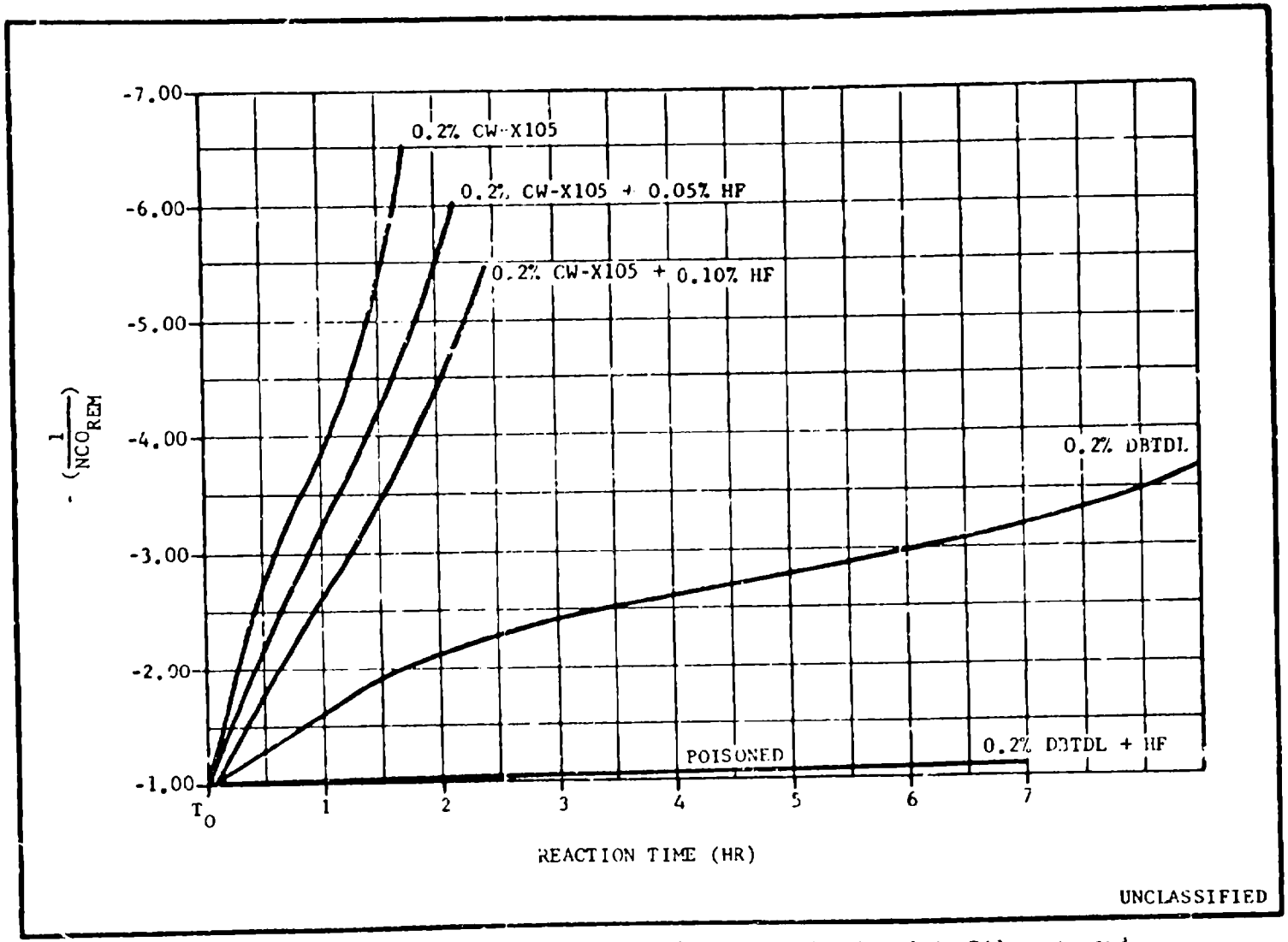

Figure A-5. Catalysis of PPG/TDI at 120°F with 0.2% Dibutyltin Dilaurate and 0.2% CW-X105 (Loaded Sieve) in the Presence and Absence of HF (U)

(C) Kinetic studies, similar to those previously described were begun using DMTDC. To determine the effect of HF on DMTDC catalysis, kinetic studies were also performed with the inert TDI/PPG system in the presence and absence of HF, as described before. Again the reactions were followed in the IR kinetic plots were made. This data is presented in Figure A-6 can be seen, the same quantity of HF that completely poisoned 0.2% DBTDL or slightly decreased the reaction rate of the same quantity of DMTDC. According to Saunders[7], strong acids do tend to function in this manner, "neutralizing portion of the catalyst." Since the concentration of HF exceeded the equivalent concentration of catalyst by a factor of six we can assume that cures with more realistic concentrations of HF from P-BEP would be practically unaffected and should thereby cure.

(C) A concentration of 0.2% CW-X105 sieves was found to provide an adequate potlife in the cure of P-BEP/TPMTI propellants. To determine what concentration of DMTDC would provide an analogous cure, several cures were made with varied DMTDC concentrations. For all practical purposes 0.1 percent DMTDC would cure at a similar rate to the current system. A comparison of the two P-BEP/TPMTI cures with these catalysts is presented in Figure A-7.

(C) From these studies we felt that at least a back up catalyst was available which probably would function in a more predictable fashion than the chemically-loaded molecular sieve. An effort was made to study DMTDC, loaded on Linde 13X sieve according to their "Waring Blender" method.[8] The catalyst was loaded 10 percent by weight and cure studies were performed with both the inert and P-BEP gumstock systems. The resultant kinetic plots of the data indicated the DMTDC-loaded sieve to be catalytically identical to the CW-X105 even in response to HF. Only the rate was slightly slower which could have been due to a number of variables, including moisture.

B. CATALYSIS AND INGREDIENT MOISTURE

(C) All DOMINO propellants formulated with the CW-X105 catalyst showed a vigorous reaction between the TPMTI and residual moisture. This was evidenced by the fact that very high NCO/OH ratios were necessary to maximize propellant mechanical properties and also by off-gas analyses where large quantities of CO_2 were measured during and after the cure cycle. Since ingredient moistures were as low as was practically possible (as all precautions were taken to operate with a dry system) we decided that, rather than attempt to cure with an ultra-dry system, perhaps it would be more realistic to selectively control the alcohol/NCO and water/NCO reactions by proper choice of catalyst.

(C) According to Saunders,[7] tin catalysts were especially good for promoting the reaction between NCO and moisture, preferring alcohols over moisture in a ratio of only 1.5 to 1. On the other hand, zinc compounds were listed as good promoters of the NCO/alcohol reaction and were not listed as promoters of the NCO/water-foam reaction. Zinc naphthenate was readily available and was studied from both the aspects of susceptibility to HF poisoning and also NCO/moisture catalysis. This catalyst was subjected to the same TDI/PPG/HF studies as mentioned before. A kinetic treatment of this data is presented in Figure A-8. As can be seen, this catalyst was not completely deactivated by HF but the rate was decreased. It probably is worth noting that the decrease was more severe than in the case of DMTDC, however.

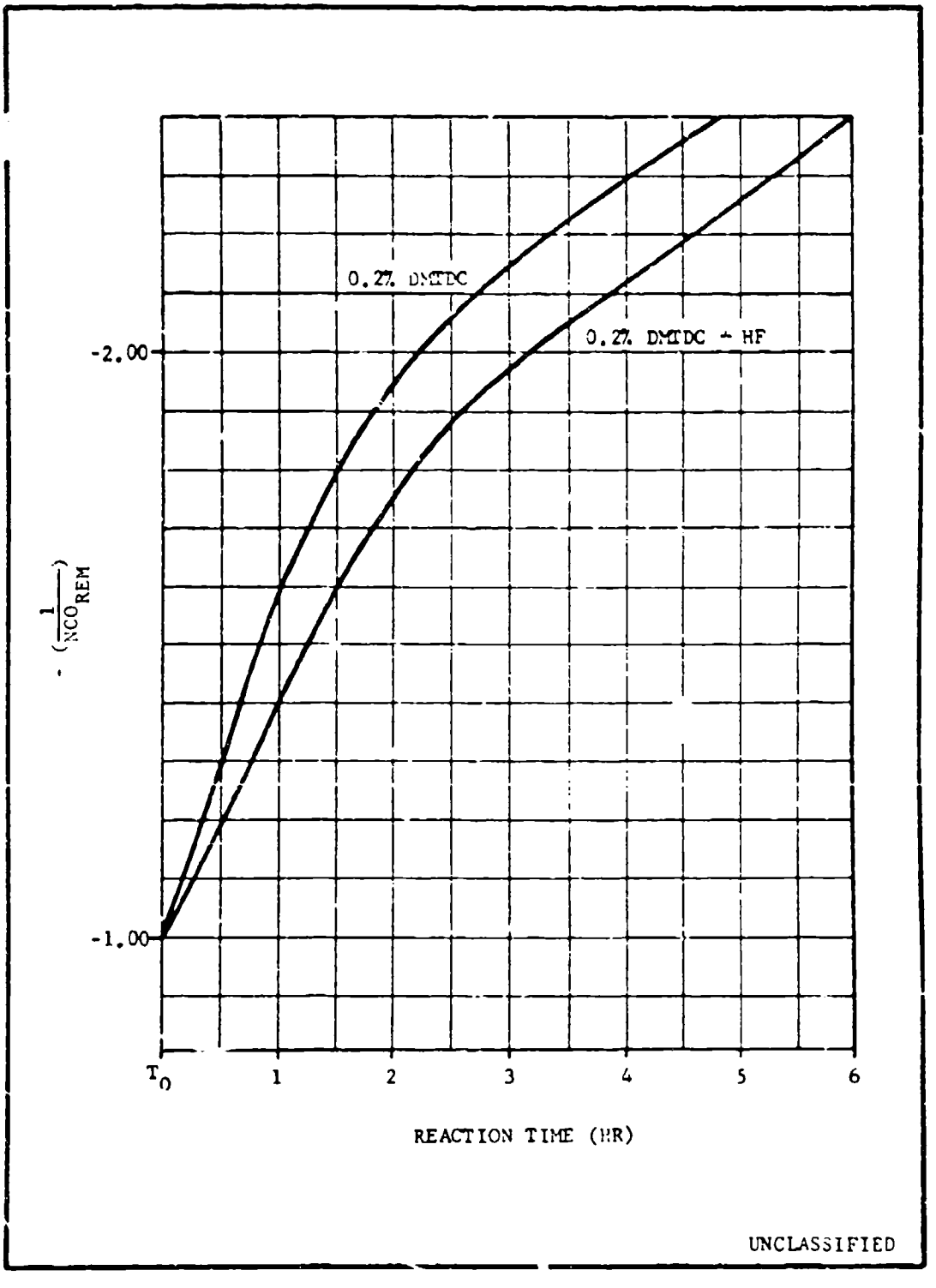

Figure A-6. Catalysis of PPG/TDI at 120°F with 0.2% Dimethyltin Dichloride in the Presence and Absence of HF (U)

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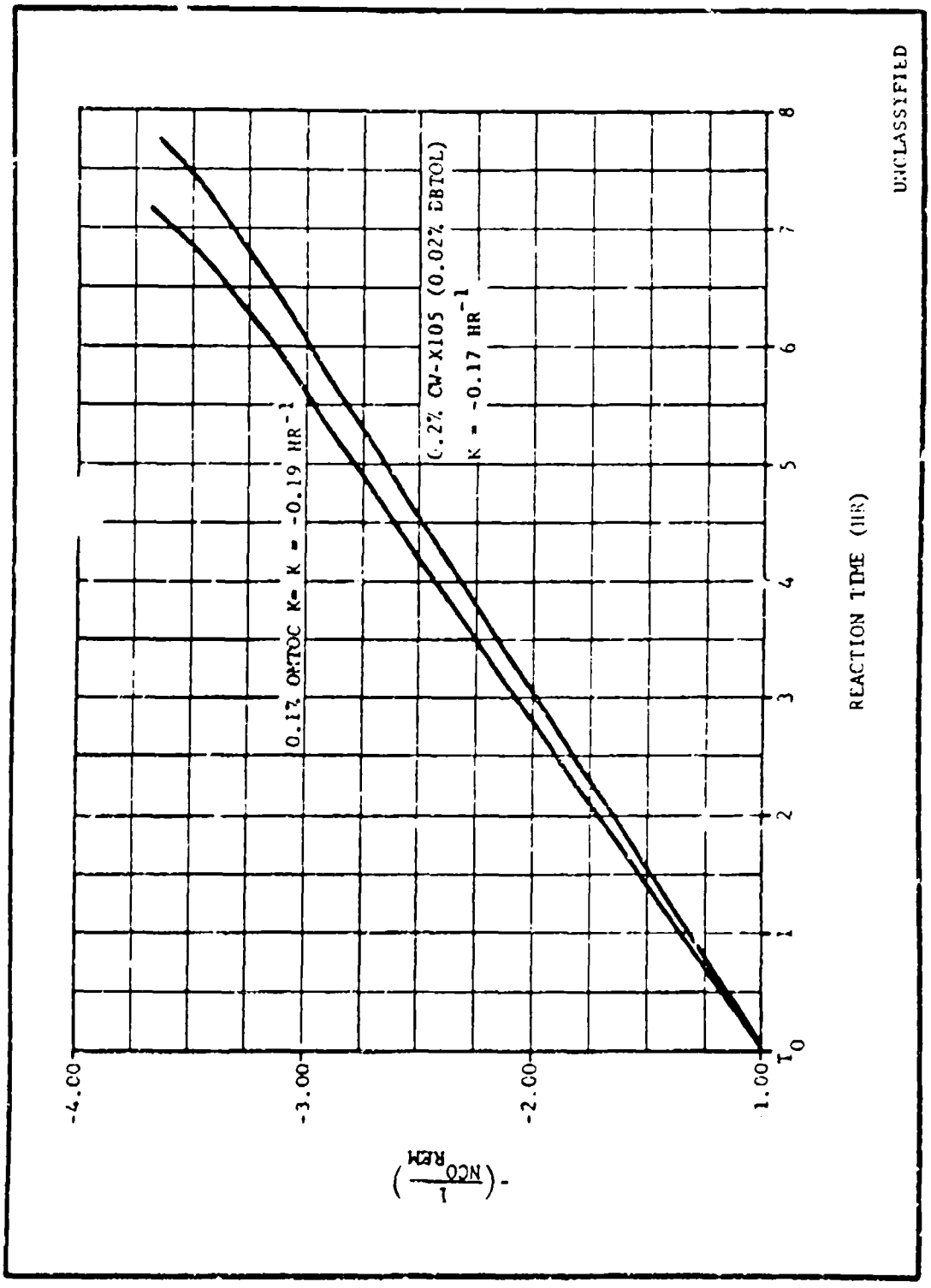

Figure A-7. Catalysis of P-BEP/1PMTI at 120°F with two HF-Impervious Catalysts, DMTDC and CW-X105 (Loaded Sieve) (U)

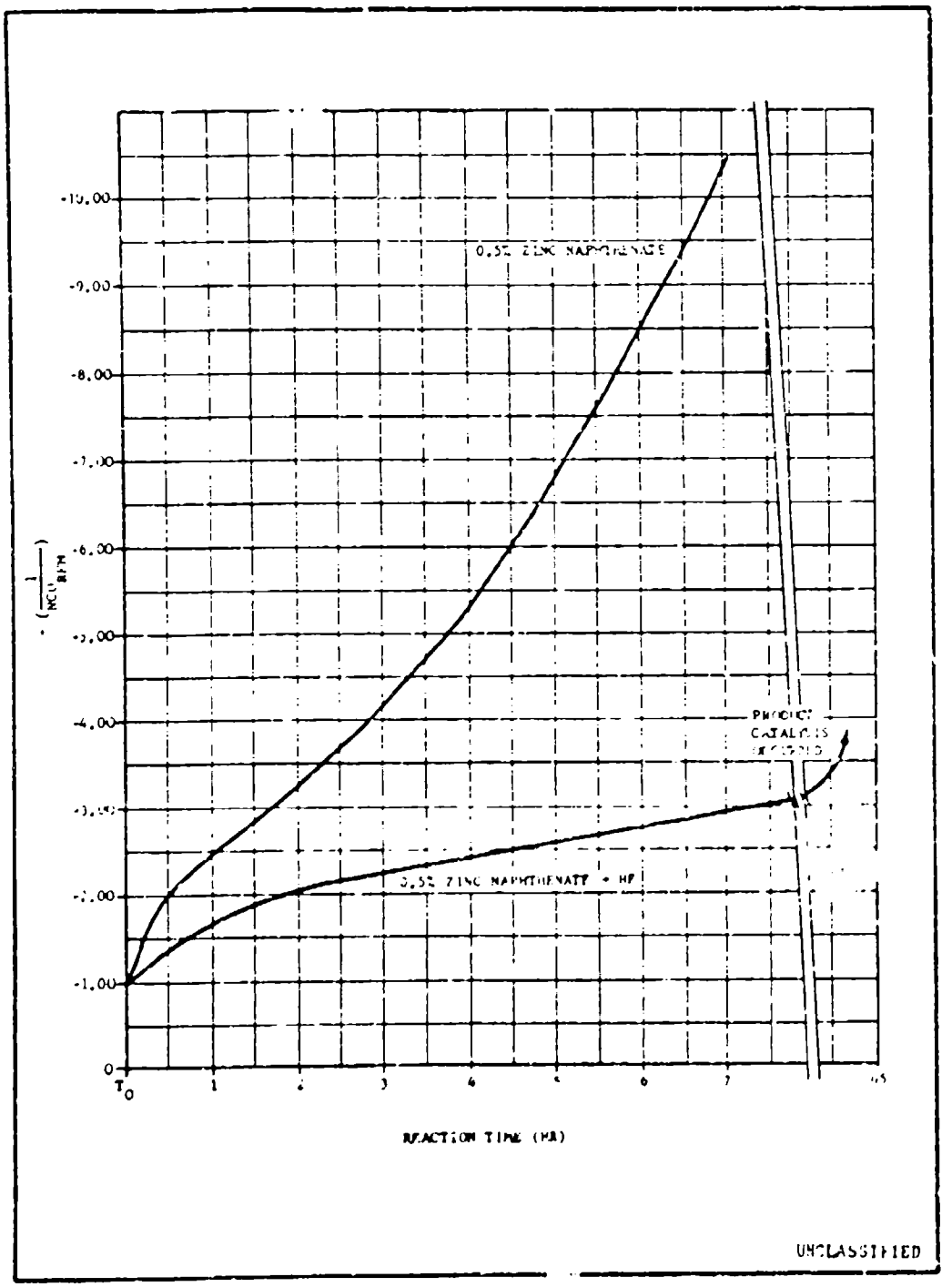

Figure A-8. Catalysis of PPG/TDI at 120° F with Zinc Naphthenate in the Presence and Absence of HF

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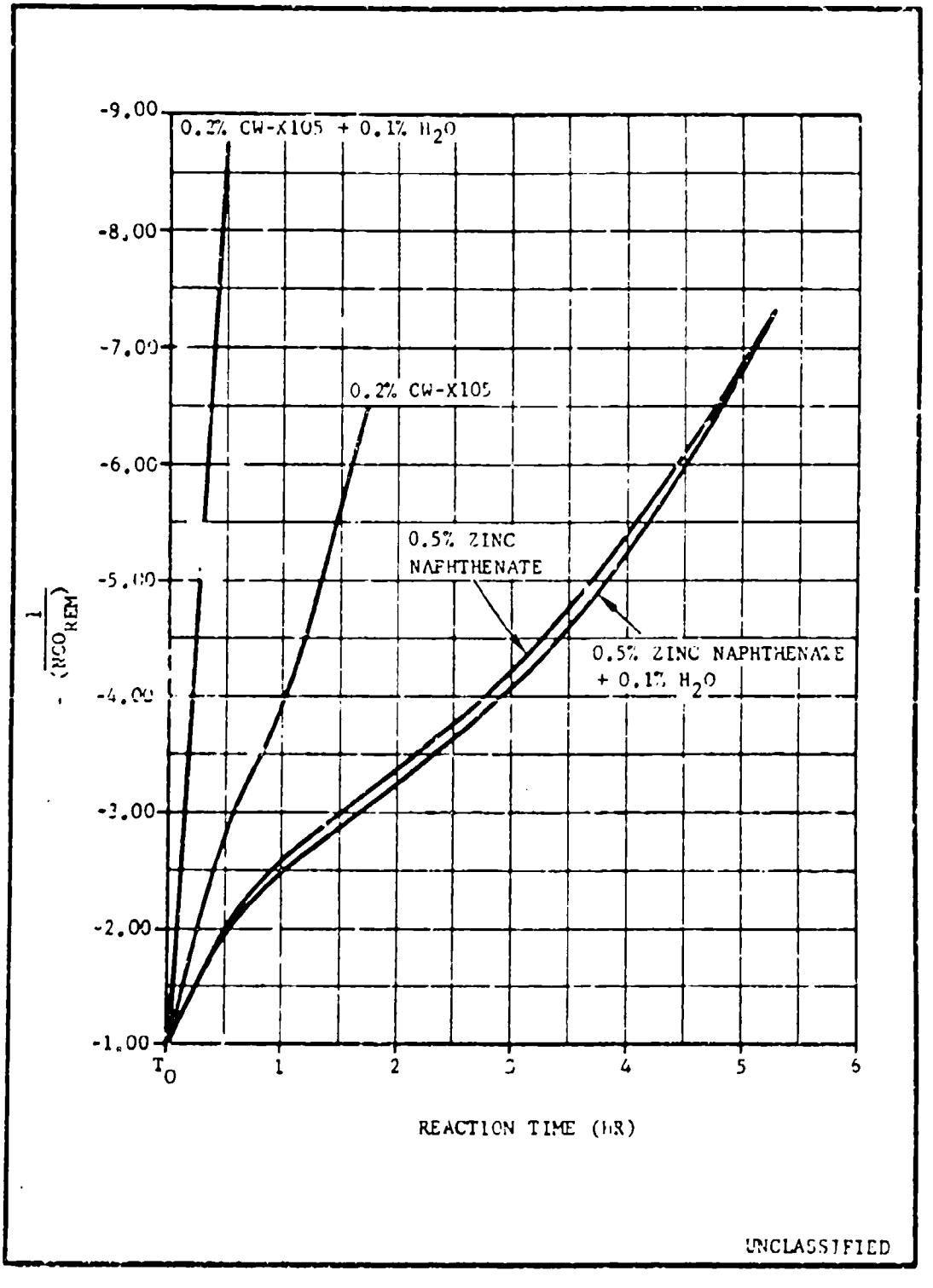

Figure A-9. Catalysis of PPG/TDI at 120°F with CW-X105 (Loaded Sieve) and Zinc Naphthenate with and Without Added Moisture (U)

(U) A comparison of both CW-X105 and zinc naphthenate with respect to water catalysis was then made using the TDI/PPG system with and without added water. The moisture content was equivalent to the added HF in previous studies and approximated a gumstock ingredient moisture of 0.1%. Figure A-9 presents second order kinetic plots of this data. As can be seen the CW-X105 reaction demonstrated a vigorous reaction with water while the zinc naphthenate reaction showed essentially no difference.

(C) To determine whether or not zinc naphthenate could actually eliminate the NCO reaction with water in the P-BEP/TPMTI system, a similar study was performed using 1.0 percent zinc naphthenate with and without added water. Figure A-10 presents kinetic plots of this data. As can be seen water did not react with TPMTI with zinc naphthenate catalysis.

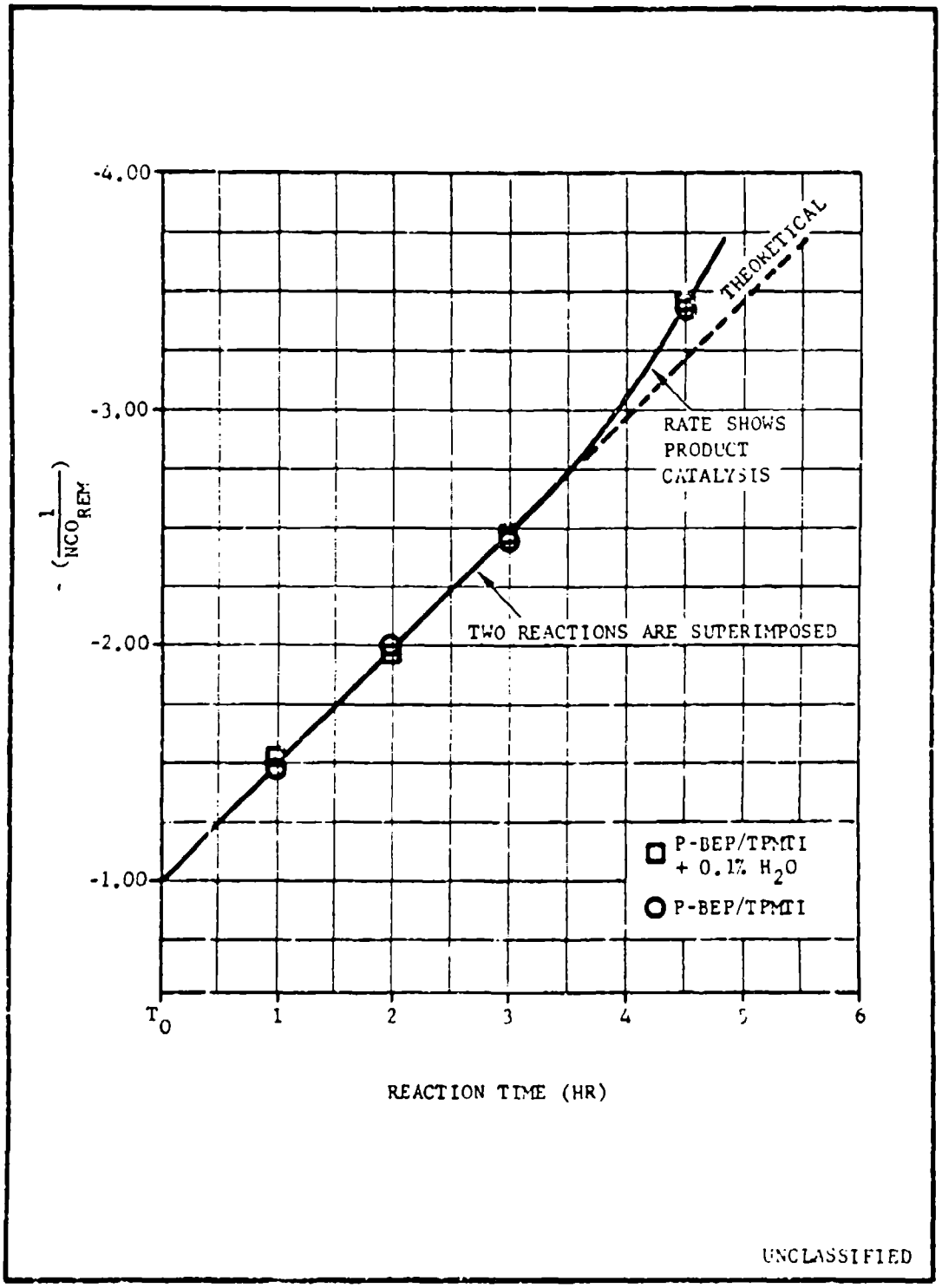

Figure A-10. Catalysis of P-BEP/TPMTI at 120°F with Zinc Naphthenate with and Without Added Water (U)

(U)

APPENDIX A
REFERENCES

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6. United Technology Center, "Evaluation of a High Energy Binder," Technical Report AFRPL-TR-68-113, Sunnyvale, California, May 1968.

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APPENDIX B

TVOPA PURIFICATION

(C) Three methods for purifying TVOPA have been tested, all based on the use of silica gel. They are as follows:

(1) Slurry process in with the TVOPA solution was slurried with silica gel for a short period of time and filtered. This procedure required a 4/1 ratio of TVOPA-to-silica gel to achieve purification, and the recovery of TVOPA was only 85 percent.

(2) Storage of the TVOPA solution over a small amount of silica gel appeared to be a promising procedure. One pound of silica gel removed the isocyanate demand from 1 gal of TVOPA-Freon solution in 1 month. However, after storage of the TVOPA solution over silica gel for 3 months, the solution turned black indicating extensive decomposition. Therefore, it is evident that storage of TVOPA over silica gel is unacceptable and precautions must be taken to ensure that all silica gel is removed from the TVOPA after purification.

(3) Column purification of TVOPA has proven to be the most satisfactory method of purification. Extensive studies with small columns showed that with the TVOPA in the original shipping solvent (Freon 113) a ratio of four parts silica gel to one part TVOPA is needed for removal of the isocyanate demand. However, replacement of the Freon with methylene chloride gave purified TVOPA at a 2/1 silica gel/TVOPA ratio. This reduction is important to keep the size of the column at a reasonable level during scale up as well as to reduce the amount of silica gel needed. The silica gel used is chromatographic grade which costs approximately $5/lb. Other cheaper grades of silica gel were tried with limited success. Scale up to 20-lb batches of TVOPA have been made successfully. Table B-I shows the analysis before and after purification.

(C) Model binder reaction studies indicate that the purified TVOPA does not interfere with the reaction between R-18 and TDI. The use of a 1/1 isocyanate/hydroxyl ratio resulted in nearly complete disappearance of the isocyanate in 24 hr at 100° F, and binder gel to gummy solid. (See Figure B-1.) In contrast, the nonpurified TVOPA increased the rate of isocyanate disappearance, indicating that the TVOPA impurities react with TDI more readily than the R-18. Also, the binder failed to gel in the nonpurified TVOPA even though excess isocyanate was added to account for the isocyanate demand of the TVOPA. Gel did not occur in 7 days at 100° F. Thus, the purification technique appears to have eliminated interference in the cure reaction by the TVOPA.

TABLE B-I

TVOPA PURIFICATION

Analysis	Nonpurified	Purified
Isocyanate demand, mg/me	9360	190,000
IR Analysis		
OH	0.116	Nil
Carbonyl	0.257	0.071
1660μ	Unchanged	Unchanged
1620μ	Unchanged	Unchanged
1518μ	Unchanged	Unchanged
Thin Layer Chromatography	3 bands	1 band
DTA		
Initial, °C	250	250
Peak, °C	250	260

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(U) The column purification of TVOPA was scaled to the 1-lb level using the column shown in Figure B-2.

(U) The TVOPA in the original shipping solvent was stripped by sparging and made up to a 50-percent solution with methylene chloride. This solution was placed on a methylene chloride wet silica gel column and eluted from the column with additional methylene chloride. Twenty-one cuts were made and tested by the thin layer chromatographic technique.

(U) All cuts of pure TVOPA were combined resulting in a 95-percent recovery. This product had an isocyanate demand of over 100,000 gm/equivalent and behaved in the cure study as did the TVOPA purified on small columns. A comparison of the infrared of purified with "as received" TVOPA is shown in Figure B-3 and Table B-II. The effect of purifying TVOPA on the mechanical properties of R-18 propellants is shown in Table B-III. Markedly higher tensile strength and modulus is obtained when using purified TVOPA at the same NCO/OH ratio, with a corresponding drop in elongation. Proper adjustment of the binder stoichiometry should permit the formulation of more elastic propellants should this be desirable. Thus, the use of purified TVOPA increases the range of mechanical properties that are attainable.

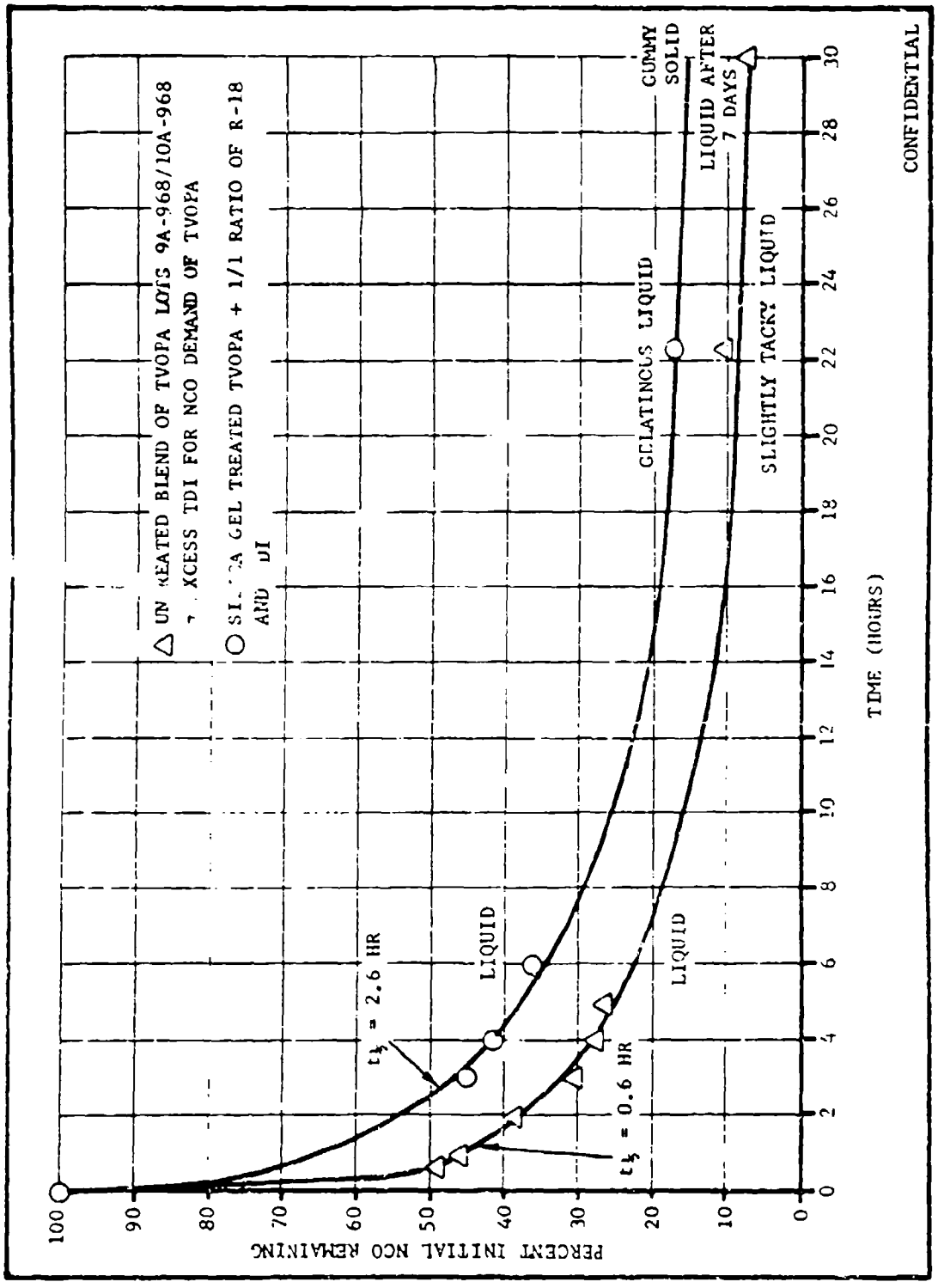

Figure B-1. Reaction of R-18 with TDI at 100° F

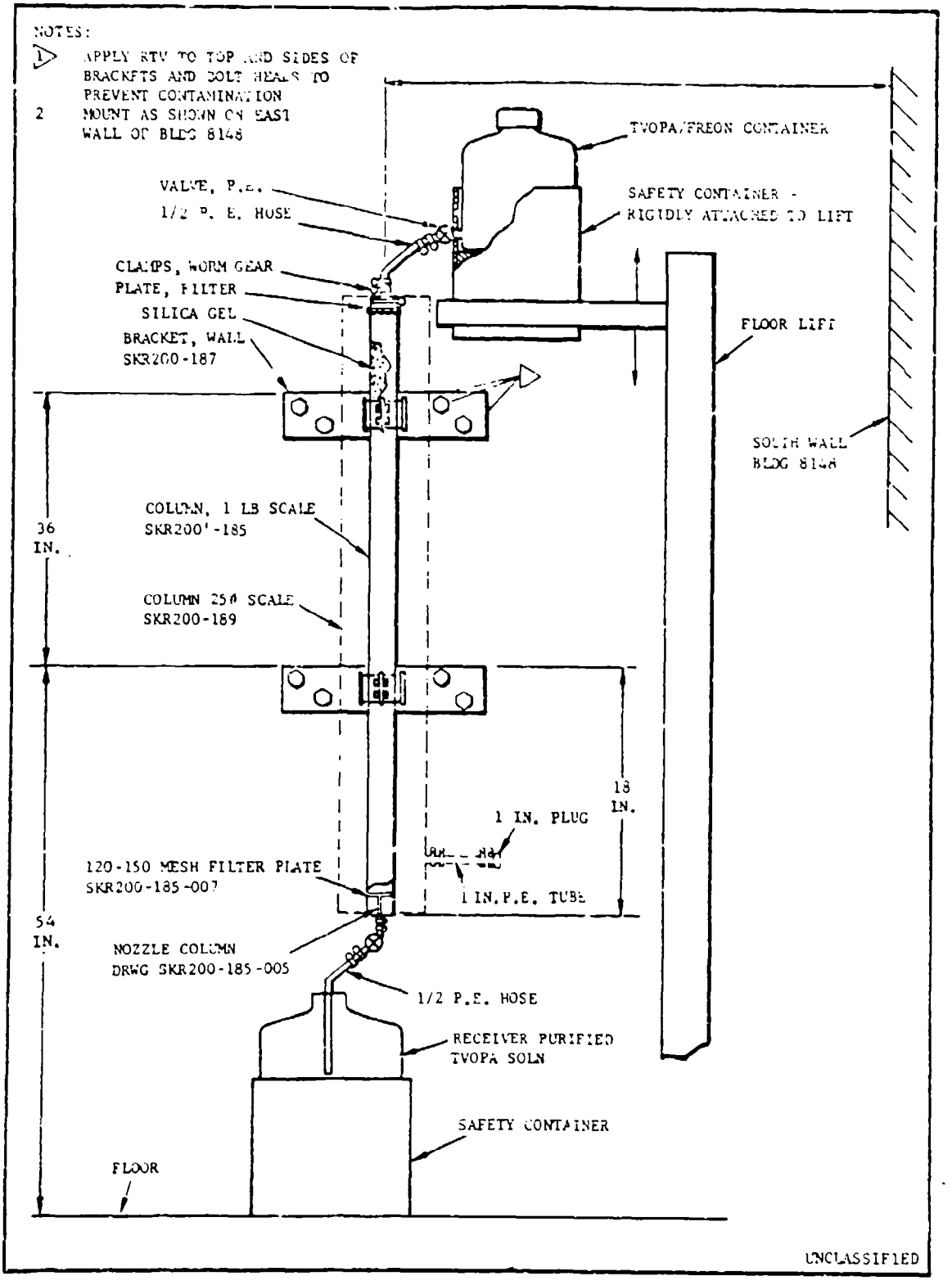

Figure B-2. Schematic TVOPA Purification Process, SKR200-186

TABLE B-1I

INFRARED COMPARISON OF "AS RECEIVED" AND PURIFIED TVOPA[1]

Frequency cm^{-1}	Interpretation	Absorbance Units[2]	
		"As Received" TVOPA	Purified TVOPA
3610	Hydroxyl	0.116	nil
1731	Carbonyl	0.257	0.071
1680	Fluorimino Carbonate	nil	nil
1660	--	0.194	0.206
1619	Vinoxy	0.032	0.038
1605	Fluorimino Nitrile	nil	nil
1518	N-Fluoro Azoxy	0.106	0.097

[1]9A-968, 10A-968 blend

[2]After correction for absorbance of Rohm & Haas good quality TVOPA

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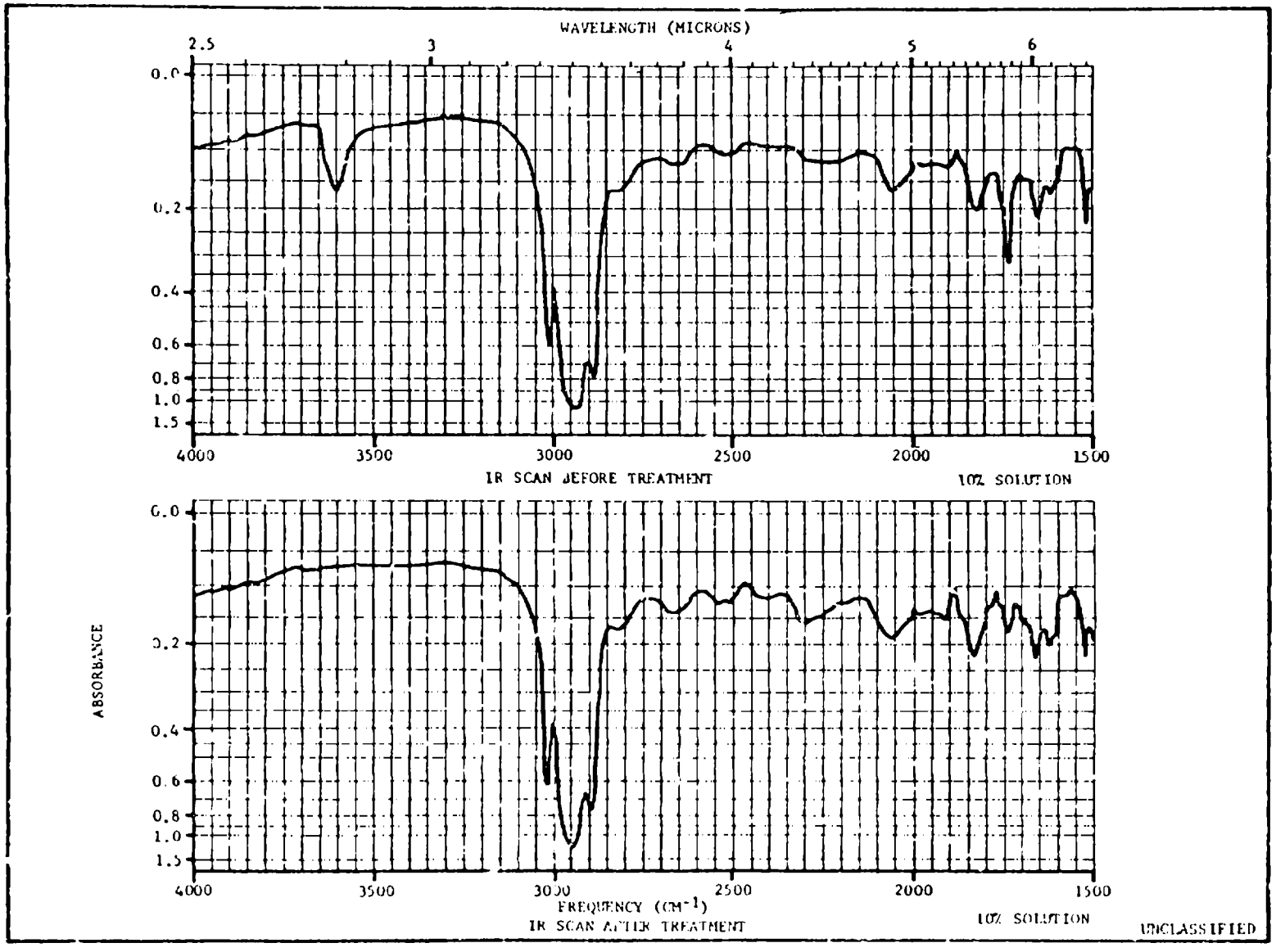

Figure B-3. Effect of Silica Gel Treatment of Infrared Spectrum

TABLE B-III

MECHANICAL PROPERTIES OF R-18 BINDER PROPELLANTS

Composition	As Received TVOPA	As Received TVOPA	Pure TVOPA
AP	48	42	48
HMX	--	10	--
AlH_3	22	18	22
Mechanical Properties			
Tensile, psi	67	68	95
Elongation, %	24	26	20
Modulus, psi	370	290	560
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(C) Additional advantages from purifying the TVOPA are as follows:

(1) The cure reactions will be much cleaner and, therefore, more reproducible since there will not be competition for the isocyanate between the TVOPA impurities and the binder hydroxyls.

(2) The isocyanate level will not have to be adjusted for each different lot of TVOPA.

(3) The chances of poisoning the cure catalyst (as observed in P-BEP studies) will be reduced.

(4) The stability of the resulting propellant should be increased.

Based on these results, Hercules recommends that all TVOPA should be purified especially when used in a urethane binder.

APPENDIX C

VISCOUS SHEAR HEATING

A. GENERAL APPROACH

(C) Significant heat generation (viscous shear heating) occurs when a viscous liquid is subjected to high shear stresses. This condition exists in the region of close clearance between the tip of the mixer blade and the mixer wall. The high shear stress results from the large velocity gradient between the tip of the blade and the stationary mixer wall. This is particularly a serious problem with propellant systems such as PVEP/HAP where thermal initiation levels are significantly lower than with conventional propellants.

(U) The propellant mixture is a power law (non-Newtonian) liquid with temperature dependent viscosity. The interrelated effects of shear rate, temperature, and viscosity make viscous heating a complex, nonlinear phenomenon.

(U) Besides the complex nature of the liquid, the geometry and motion of the mixer add further complexities to the problem. The mixer is a vertical kettle with three intermeshing helical blades that operate in a planetary motion. This geometry and motion create flow patterns within the liquid which are extremely difficult to treat analytically. During one cycle of the mixing blades the liquid in the clearance between the mixer blade tip and the kettle wall may be subjected to pulsing heat generation; laminar and turbulent flow; velocities from zero to several ft/sec; and heat transfer by conduction and convection. In order to determine upper limits of the temperature and obtain a reasonable approximation to the actual conditions, various approaches to the problem have been considered. Three approaches which were pursued are outlined below.

1. <u>One-Dimensional Solution for Steady-State, Laminar Flow, Simplified Geometry with Temperature and Shear Rate-Dependent Viscosity</u>

(U) Viscometry, lubrication, and extrusion are important applications where viscous heating is a problem. A brief review of the literature indicated that several investigators have worked to solve equations of motion and energy for viscous flow to obtain velocity and temperature profiles. Kordig at Hercules [1] presented a closed form solution to the subject problem. However, Kordig's solution assumed a Newtonian liquid, a linear velocity profile, and a constant ratio of blade velocity to clearance between the blade tip and the kettle wall. Gavis and Laurence in recent articles [2, 3] presented solutions to equations of motion and energy for plane and circular flow of both Newtonian and non-Newtonian liquids with exponential dependence of viscosity on temperature. These solutions will be used to determine upper limits of the temperature in mixing operations of Domino propellants. These solutions will yield an upper limit because they assume a continuous mixer blade and do not allow for convective heat removal from the clearance region.

[1,2,3] Refer to References at End of Appendix

(U) The solution of Gavis and Laurence for plane flow between isothermal walls is presented below. This solution provides temperature and velocity profiles of a non-Newtonian (power law) liquid between infinite, parallel, plane walls, one of which is moving with a constant velocity. The nomenclature used is defined below.

Nomenclature

$Br_1^{(n)}$ = Brinkman number for power-law liquid, $\frac{h^{1-n} V_o^{1+n} m_o}{kT_o}$

h = Distance between blade tip and kettle wall, cm

k = Thermal conductivity of liquid, g cm/sec^3 ^oK

m = Liquid consistency, g/cm sec^n

n = Power-law index, dimensionless

p = Integration constant, dimensionless

v = Local velocity, cm/sec

V_o = Velocity of moving blade, cm/sec

T = Temperature, ^oK

T_m = Maximum temperature, at ξ = 1/2, ^oK

y = Coordinate in direction of flow, cm

z = Position coordinate, cm

α = Temperature coefficient for n, dimensionless

β = Temperature coefficient for m, dimensionless

ξ = Reduced position coordinate, z/h, dimensionless

θ = Reduced temperature $(\beta/n)(T - T_o)/T_o$, dimensionless

θ_m = Maximum reduced temperature, at ξ = 1/2, dimensionless

λ_1 = Constant, dimensionless, defined by Equation 13

μ_{eff} = Effective viscosity, g/cm sec

ρ = Density, g/cm^3

(U)

τ_{zy} = Shear stress, dynes/sq cm

o = (subscript) value of a quantity at blade tip or kettle wall

(U) The liquid is one for which the shear stress-rate of shear relationship is of the form

$$\tau_{zy} = - m \left| \frac{dv}{dz} \right|^{n-1} \frac{dv}{dz} \qquad (1)$$

The consistency, m, and the power law index, n, are functions of temperature. Previous investigation[4] has shown that m is much more sensitive to temperature than is n and can be represented by

$$m = m_o \exp - \beta (T - T_o)/T_o \qquad (2)$$

The variation of n is of the form

$$n = n_o + \alpha (T - T_o)/T_o \qquad (3)$$

but α has been found to be small and temperature variations of n are neglected in this problem.

(U) The problem is considered for plane shear flow only because of the narrow clearance gap between the mixer blades and the kettle wall. Flow in narrow gaps may be approximated as plane flow.

The equation of motion,

$$\frac{d}{dz} (\tau_{zy}) = 0 \qquad (4)$$

becomes, with Equation 1, for a power-law liquid

$$\tau_{zy} = -m \left| \frac{dv}{dz} \right|^{n-1} \frac{dv}{dz} = \tau_o \text{ (constant)} \qquad (5)$$

Then Equation 5 may be integrated subject to boundary conditions

$$v(0) = 0; \; v(h) = V_o \qquad (6)$$

---

[4] Refer to References at End of Appendix

(U)

to give, since n is considered constant,

$$v = -\tau_o^{1/n} \int_0^z \frac{dz}{m^{1/n}} \tag{7}$$

with

$$\tau_o = -\left[V_o \Big/ \int_0^h \frac{dz}{m^{1/n}}\right]^n \tag{8}$$

The energy equation

$$k \frac{d^2T}{dz^2} + m \left|\frac{dv}{dz}\right|^{n-1} \left(\frac{dv}{dz}\right)^2 = 0 \tag{9}$$

becomes, with Equations 2 and 5,

$$\frac{d^2T}{dz^2} + \frac{\tau_o^{\frac{n+1}{n}}}{km_o^{1/n}} \exp\left[\frac{E}{n}\left(\frac{T - T_o}{T_o}\right)\right] = 0 \tag{10}$$

Boundary conditions are

$$T(0) = T(h) = T_o \tag{11}$$

for isothermal walls.

Introduction of the dimensionless variables

$$\theta = \left(\frac{E}{n}\right) \frac{T - T_o}{T_o}$$

and

$$\zeta = z/h$$

(U)

gives the following boundary value problems for temperature and velocity fields

$$\frac{d^2\theta}{d\zeta^2} + \lambda_1 e^{\theta} = 0 \tag{12}$$

$$\lambda_1 = \frac{\beta h^2 \tau_o^{\frac{n+1}{n}}}{knT_o m_o^{1/n}} = \frac{\frac{\beta}{n} Br_1^{(n)}}{\left[\int_o^1 e^{\theta}\, d\zeta\right]^{n+1}} \tag{13}$$

$$Br_1^{(n)} = \frac{h^{1-n} V_o^{1+n} m_o}{kT_o} \quad \text{Brinkman number for power-law liquid} \tag{14}$$

$$\theta(0) = \theta(1) = 0 \tag{15}$$

or

$$\left.\frac{d\theta}{d\zeta}\right|_{\zeta = 0} = 0;\ \theta(1) = 0 \tag{16}$$

and

$$\frac{v}{V_o} = \frac{\int_o^{\zeta} e^{\theta} d\xi}{\int_o^1 e^{\theta} d\zeta} \tag{17}$$

(U) Multiplication of Equation 12 by $2(d\theta/d\zeta)$ and integration yields

$$\frac{d\theta}{d\zeta} = \pm (2\lambda_1)^{\frac{1}{2}} (p - e^{\theta})^{\frac{1}{2}} \tag{18}$$

where p is an integration constant. The $\theta(\zeta)$ curve has a maximum at ln p. To the left of the maximum $d\theta/d\zeta$ is positive; the plus sign must then be used for integration of Equation 18 between 0 and ln p. To the right of the maximum $d\theta/d\zeta$ is negative and the negative sign is to be used between ln p and 1.

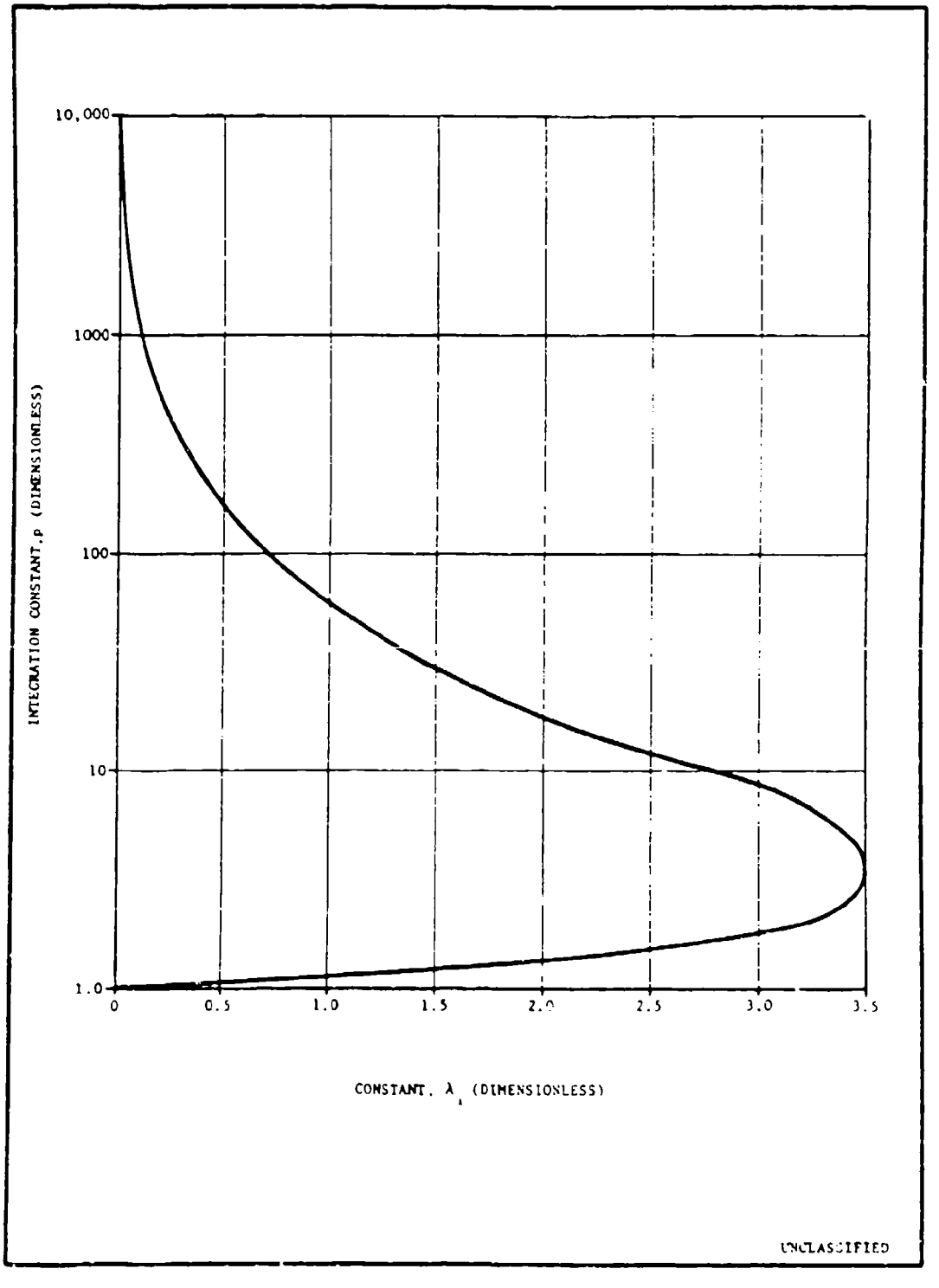

Figure C-1. Plot of Integration Constant, p, as a Function of Constant λ_1

(U) Equation 18 may be integrated subject to boundary conditions of Equation 15 to give

$$(2\lambda_1)^{\frac{1}{2}}\zeta = \int_0^{\ln p} \frac{d\theta}{(p - e^{\theta})^{\frac{1}{2}}} - \int_{\ln p}^{\theta} \frac{d\theta}{(p - e^{\theta})^{\frac{1}{2}}} \tag{19}$$

or when integrations are performed and resulting expressions are rearranged and simplified

$$\theta = \ln\left\{p \operatorname{sech}^2\left[\left(\frac{\lambda_1}{8}\right)^{\frac{1}{2}} (2\zeta - 1)\right]\right\} \tag{20}$$

with p given as the solution of

$$p = \cosh^2\left(\frac{\lambda_1 p}{8}\right)^{\frac{1}{2}} \tag{21}$$

(U) Direct computation shows that there are two values of p for each λ_1 when $\lambda_1 < 3.5138$, one value at $\lambda_1 = 3.5138$, and no real values of p when $\lambda_1 > 3.5138$. This is illustrated in Figure C-1, when p is plotted against λ_1.

(U) There are thus two different temperature profiles for each value of λ_1 for $\lambda_1 < 3.5138$. The profile is unique only when $\lambda_1 = 3.5138$. There are no solutions to the problem for $\lambda_1 > 3.5138$. Temperature profiles are illustrated in Figure C-2 for several values of λ_1. Note that the maximum temperature, θ_m, occurs at $p = 1/2$.

(U) Velocity profiles may be determined when the temperature profile, Equation 20, is inserted into Equation 17. After integration, rearrangement, and simplification, there results

$$\frac{v}{V_o} = \frac{1}{2}\left\{\frac{1 + \tanh\left[\left(\frac{\lambda_1 p}{8}\right)^{\frac{1}{2}} (2\zeta - 1)\right]}{\tanh\left(\frac{\lambda_1 p}{8}\right)^{\frac{1}{2}}}\right\} \tag{22}$$

There are, of course, two different velocity profiles for each λ_1 when $\lambda_1 < 3.5138$, and one when $\lambda_1 = 3.5138$. These are plotted in Figure C-3 for several values of λ_1.

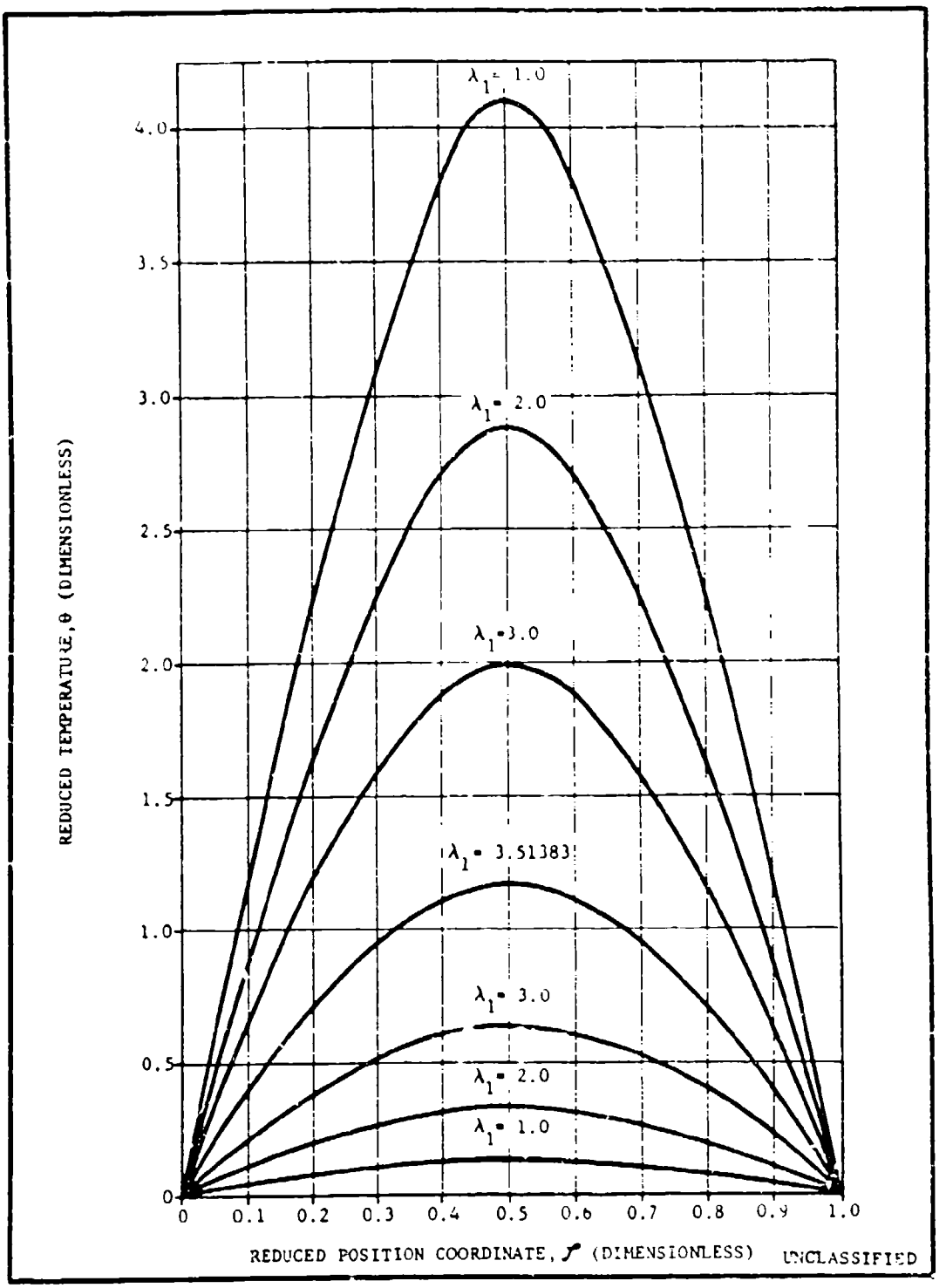

Figure C-2. Temperature Profiles - Reduced Temperatures, θ as a Function of Reduced Position Coordinate, ζ

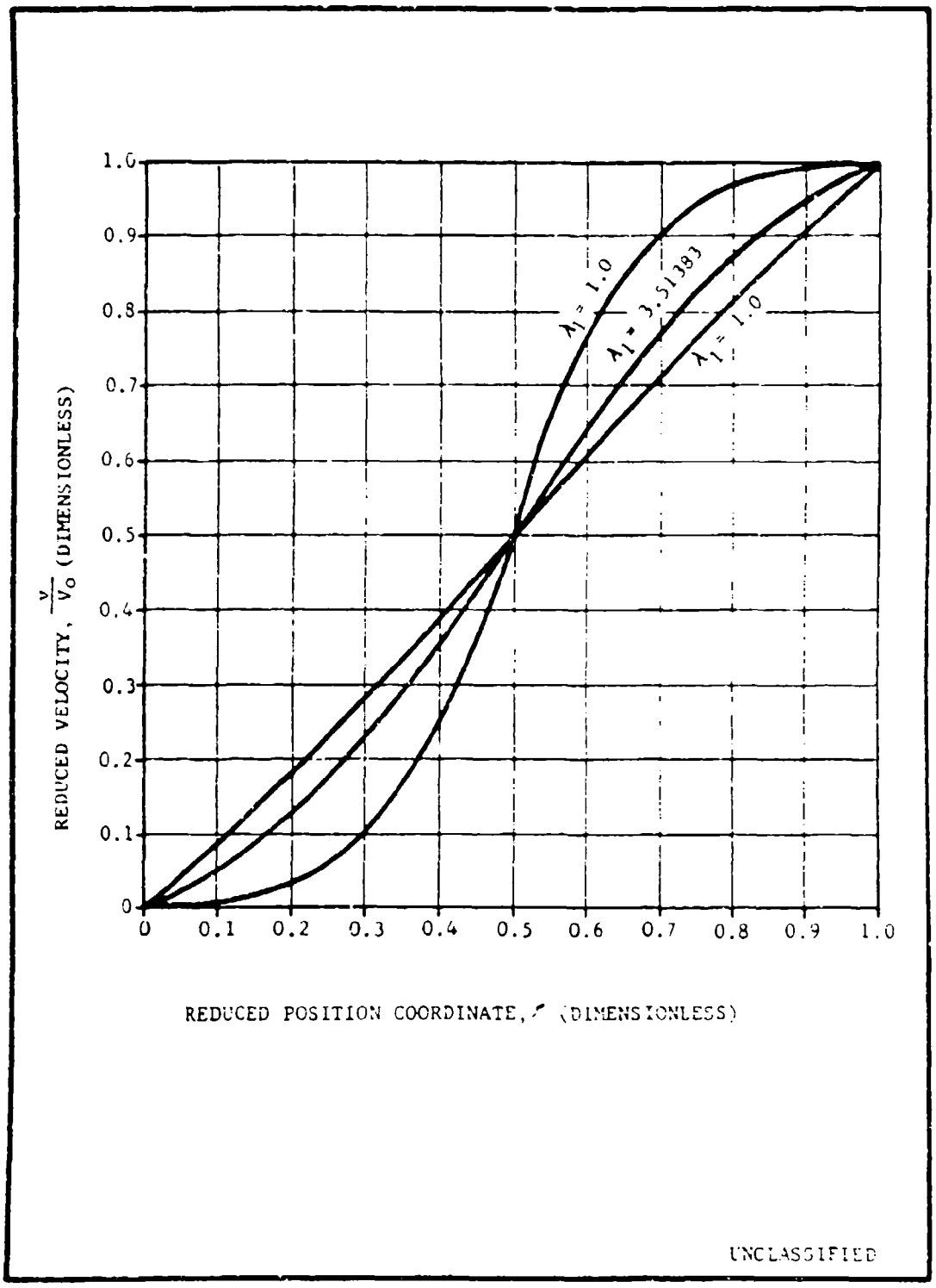

Figure C-3. Velocity Profiles - Reduced Velocity, $\frac{v}{V_o}$ as a Function of Reduced Position Coordinate, ζ

(U) There is a maximum shear stress which can be applied. This is, from Equation 13,

$$(\tau_o)_{max} = 1.5^{n}15 \left(k\, T_o m_o^{\frac{1}{n}} / \epsilon h^{n+1}\right)^{\frac{1}{2}} \qquad (23)$$

Furthermore, for each shear stress below this value there are two possible temperature and velocity profiles. Physically, however, this presents no problem, since the ambiguity is resolved when the Brinkman number is fixed through the magnitude of V_o. By Equation 13 every value of Brinkman number determines a value of λ_1 in the range of allowable values and fixes one of the allowable solutions for that λ_1. Thus, the temperature and velocity profiles are unique in the Brinkman number. Figure C-4 shows a plot of

$\frac{\beta}{n} Br_1^{(n)}$ against λ_1 for three values of n: for a shear-thinning liquid (n = 1/2), a Newtonian liquid (n = 1), and a shear thickening liquid (n = 2).

(U) The parametric curves shown in Figures C-2 and C-3 illustrate typical results from this closed form solution. The temperature and velocity profile for a particular mixing problem can be estimated by determining values of λ_1 and $Br_1^{(n)}$ from Equations (13) and (14) and reading values from Figures 7 and 8 or by evaluating Equations (20) and (22). Additional parametric curves will be computed after the ranges of β, h, n, m_o, k, V_o and T_o are established for various mixing conditions of Domino propellants.

2. <u>Determination of Local (Between the Blade Tip and Kettle Wall) Heating Effects from Pulsing Heat Generation Using Steady-State Bulk Temperature as Initial Condition</u>

(U) In this approach to the problem, a steady-state bulk temperature must be determined. This is the equilibrium temperature of the liquid mass which will be predicted analytically by an energy balance method and also experimentally by monitoring the temperature during mixing. The simplified model is expressed as follows:

heat generated = heat stored + heat out

or

$$Q_{gen} = Q_{stored} + Q_{out}$$

When the temperature of the system reaches equilibrium, then the heat stored term goes to zero and

when $Q_{stored} = 0$

$$Q_{gen} = Q_{out}$$

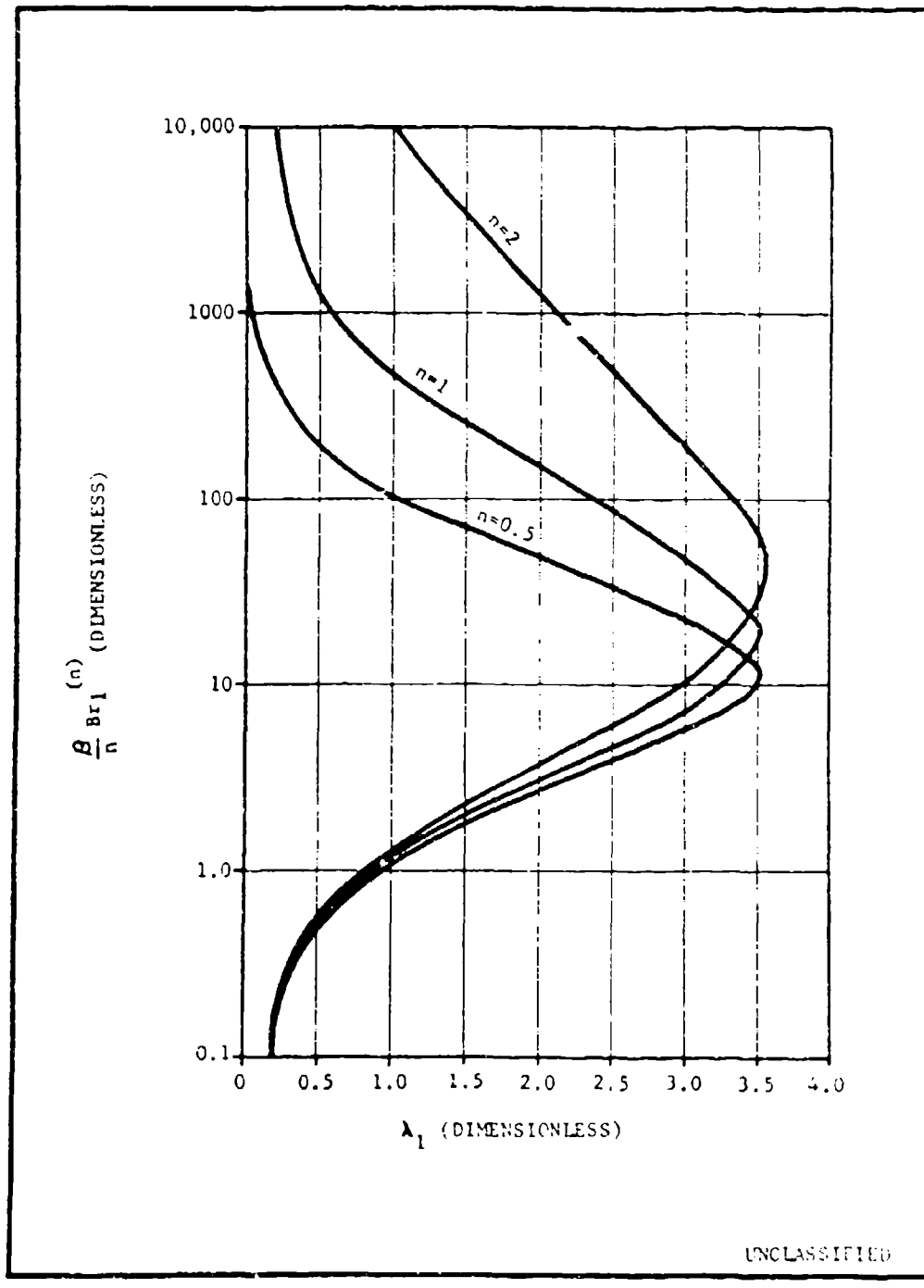

Figure C-4. Plot of $(\frac{\beta}{n})Br_1^{(n)}$ as a Function of the Constant λ_1 for Power Law Liquids

(U)

The heat generation term will be determined by evaluating the temperature time-history of the mixer system and the propellant mass. Alternate methods of determining the quantity of heat generated are: (1) Assuming all power used in driving the mixer is converted to heat and (2) monitoring the temperature and flow rates of the water in the water cooling jacket of the mixer.

(U) The next step will be to create a finite-element model of the region between the mixer blade tip and the kettle wall. The finite-element model will be used to determine temperature profiles using the bulk equilibrium temperature as an initial condition and allowing the heat generation term to be active for a time interval equal to one pass of the mixer blade.

(U) This model would probably also yield conservative results if all heat generation (power consumption) is assumed to occur in the blade tip region.

3. Determination of Transient Thermal Profiles by Modeling Pulsed Heat Generation, Two-Dimensional Heat Transfer, with Temperature and Shear Rate-Dependent Viscosity

(U) This model is the most complex and will provide transient temperature profiles from the start of mixing to thermal equilibrium. The model will be developed around a two-dimensional heat transfer computer program with special provisions to account for the pulsing heat generation (due to the cyclic movements of the mixer blades) and convective heat transfer to simulate the mass flow of liquid within the mixer.

(U) The consistency of the liquid will be exponentially temperature dependent

$$m = m_o \exp -\beta (T - T_o)/T_o$$

and also will follow a power-law model where

$$\tau_{zy} = -m \left|\frac{dv}{dz}\right|^{n-1} \frac{dv}{dz} = \mu_{eff} \frac{dv}{dz}$$

(U) These considerations will be used in the solution of the transient, differential energy equation

Heat stored = Heat Conduction + Heat Convection + Heat Generation

$$\overbrace{\rho c \frac{\partial T}{\partial t}} = \overbrace{k \frac{\partial^2 T}{\partial z^2} + k \frac{\partial^2 T}{\partial y^2}} + \overbrace{Q} + \overbrace{\mu_{eff}\left(\frac{\partial v}{\partial z}\right)^2}$$

(U) to determine how temperature, T, will increase with time, t. This model requires extensive computer program development which is not justifiable if satisfactory results are obtained from the previously described models.

B. VISCOUS SHEAR HEATING

(U) During the previous discussion the subject of viscous shear heating was treated generally, and three approaches to determining temperature bounds were discussed in detail. A more specific solution was considered to estimate the upper temperature limits in the actual scale-up process equipment, a J. H. Day Company 5-gal regal mixer. (See Figures C-5 and C-6.)

1. General Approach

(U) A finite element heat transfer model of the loaded mixer was prepared and thermal profiles within the propellant mixer were obtained. The model was especially constructed to predict the upper bound of temperatures in the clearance gap between the mixer agitators and the inside wall of the mixing bowl.

(U) The analysis used consists of the following elements and assumptions:

(a) The geometry of the mixer was established.

(b) Power input to the propellant mix was determined from calculations based on pressure drop across the hydraulic motor under loaded and nonloaded conditions.

(c) All power input to the mixer was utilized in heating the propellant between the mixer blade tips and the mixer wall. An overall heat transfer coefficient of 100 BTU/hr-ft^2-$^\circ$F was assumed for the mix bowl wall and base.

(d) It was assumed no heat was transferred to the main mass of propellant that was not between the blade tips and bowl wall.

(e) The temperature rise in the propellant is compared to DTA data to see if the temperature rise would initiate exothermic reactions in the propellant.

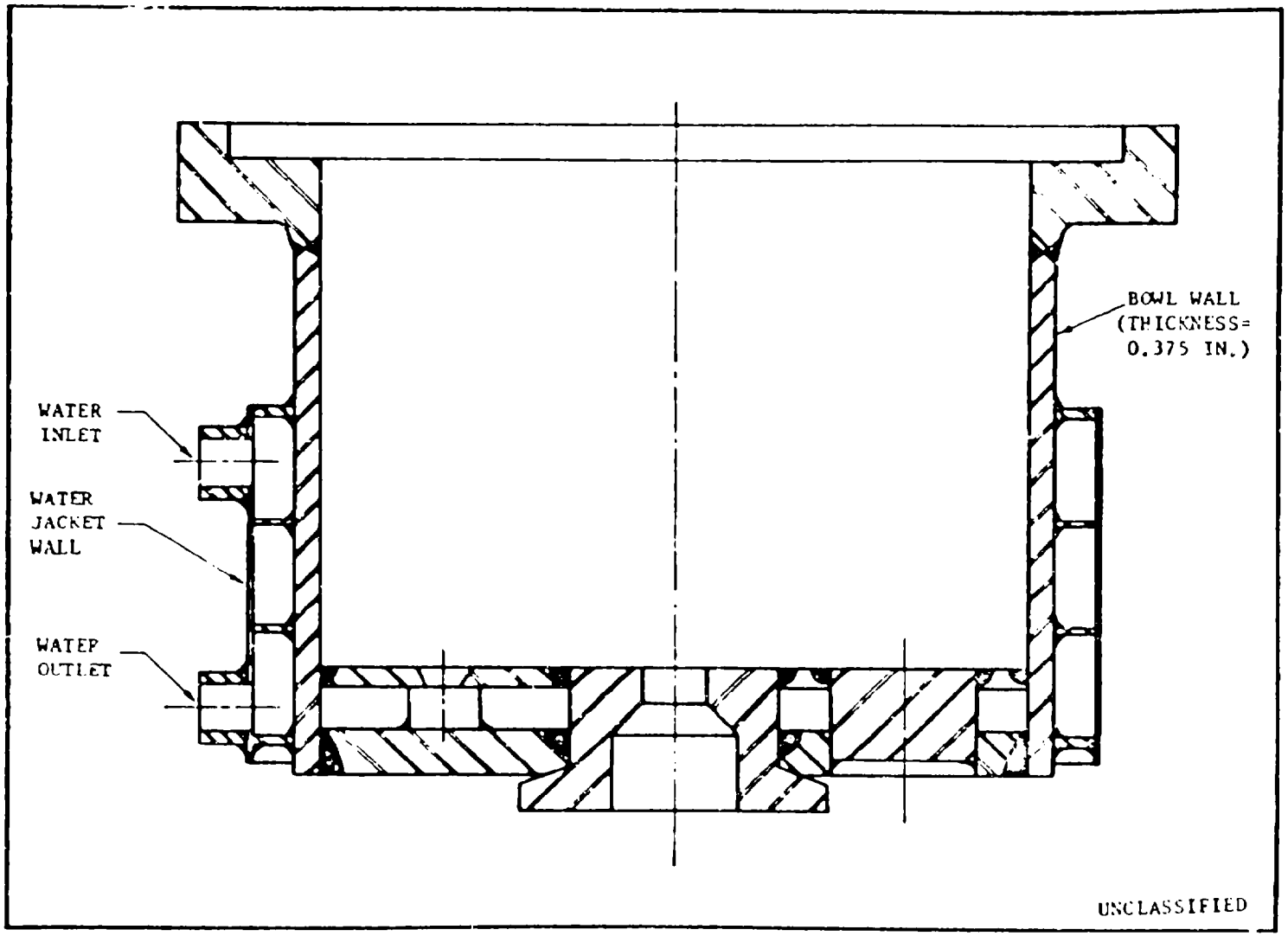

Figure C-5. Cross-Sectional View of Day 5-Gallon Regal Mixer Bowl

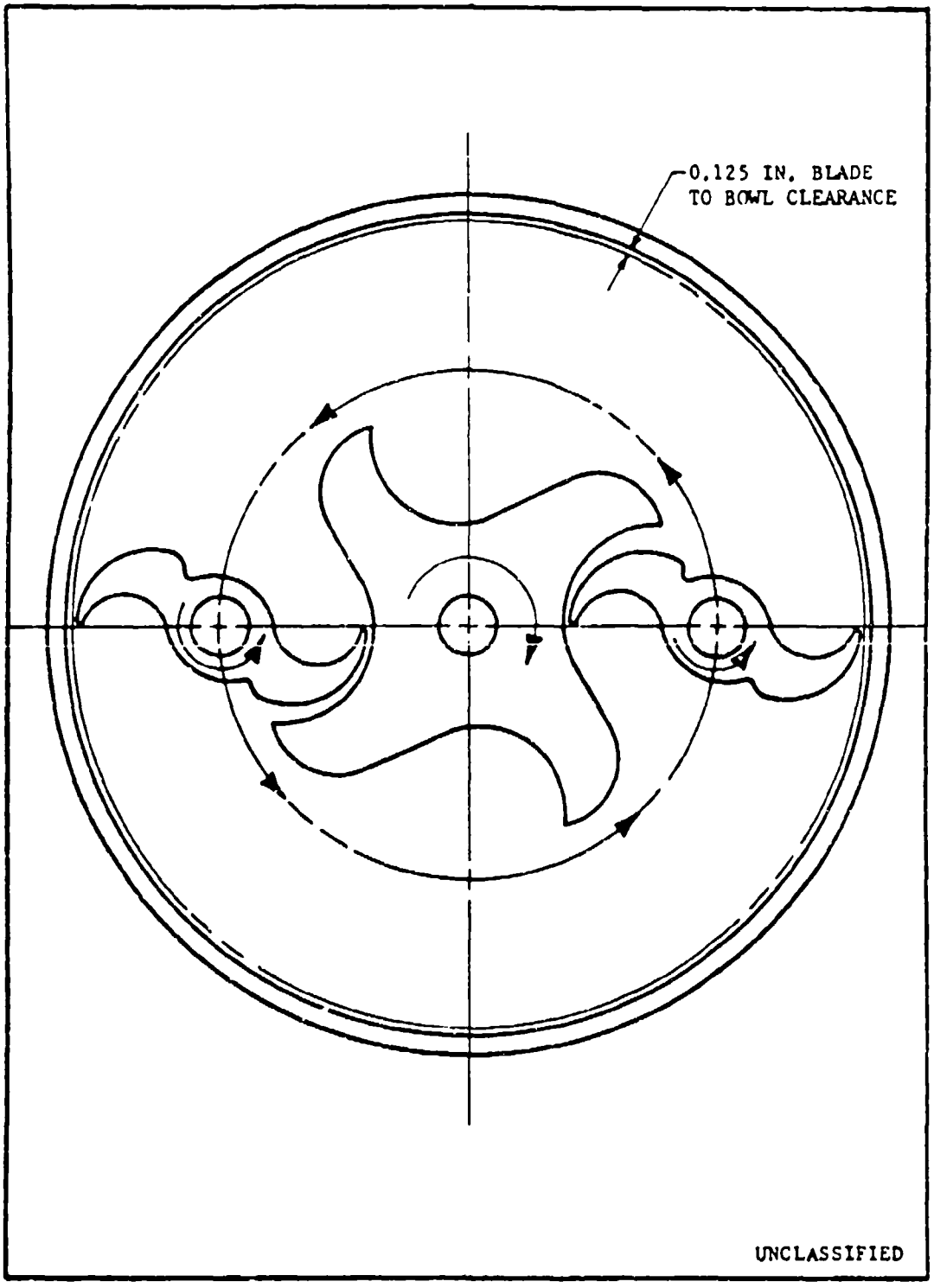

Figure C-6. Motion of Three Agitators in the Day 5-Gallon Regal Mixer (Top View)

(U) It should be noted that the heat generated by viscous shearing of the propellant mixture is a function of several parameters including the viscosity of the mixture. The viscosity is generally both temperature and shear-rate dependent. These aspects make the heat generation problem difficult and considerable experimental work must be accomplished to determine the temperature and shear-rate dependent viscosities. In the simplified analysis used, the heat generation was not related to viscosity, but was equated to power consumed during mixing. While this approach did not provide exact values of temperature increases resulting from viscous shearing, upper bounds of the temperature increases were obtained.

2. Power Consumption

(U) The mixer is driven by a hydraulic motor. The hydraulic motor is powered by a hydraulic pump which is driven by a 7.5 hp electric motor.[5] The electrical motor, however, could be overloaded to as much as 11.25 hp.[6] The power output by the hydraulic motor is related to the pressure differential (ΔP) across the motor and the flow rate (Q) of the hydraulic fluid by Equations (24) and (25):

$$hp = K\Delta PQ \tag{24}$$

(U) When ΔP is expressed in lb/sq in. (psi) and Q in gal/min, $K = 5.83 \times 10^{-4}$. The flow rate, Q, is related to the net rpm (combined planetary and rotary) of the outside blades as shown in Figure C-7.[5] The horsepower delivered to the mixer blades is limited by shear pins which are designed to fail when $\Delta P = 1500$ psi.[5, 6] Therefore, the maximum horsepower delivered to the mixer blades, assuming 100-percent efficiency (efficiencies of hydraulic motors are generally less than 90 percent)[7] of the hydraulic motor is:

$$hp_{max\ to\ blades} = (5.83 \times 10^{-4})(1500\ psi)\ Q \tag{25}$$

(U) Maximum horsepower to the blades as a function of rpm is presented in Figure C-8. Pressure differential (ΔP) measurements (Table C-I) have been made with the mixer running empty at different speeds. These measurements have been converted to horsepower using Equation (24) and Figure C-7 and are also plotted in Figure C-8. The difference between the maximum horsepower and the horsepower to run the mixer empty would be the maximum horsepower available for heat generation, which is also shown in Figure C-8. This amount of power would be available only if the pressure differential across the motor is at maximum (1500 psi). In the mixing of propellants to date, the pressure differential rarely exceeded 900 psi.[8] Thus, assuming maximum power (differential pressure of 1500 psi) will be used at each rpm level should be another factor to make this analysis quite conservative.

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5 thru 8 Refer to References at End of Appendix

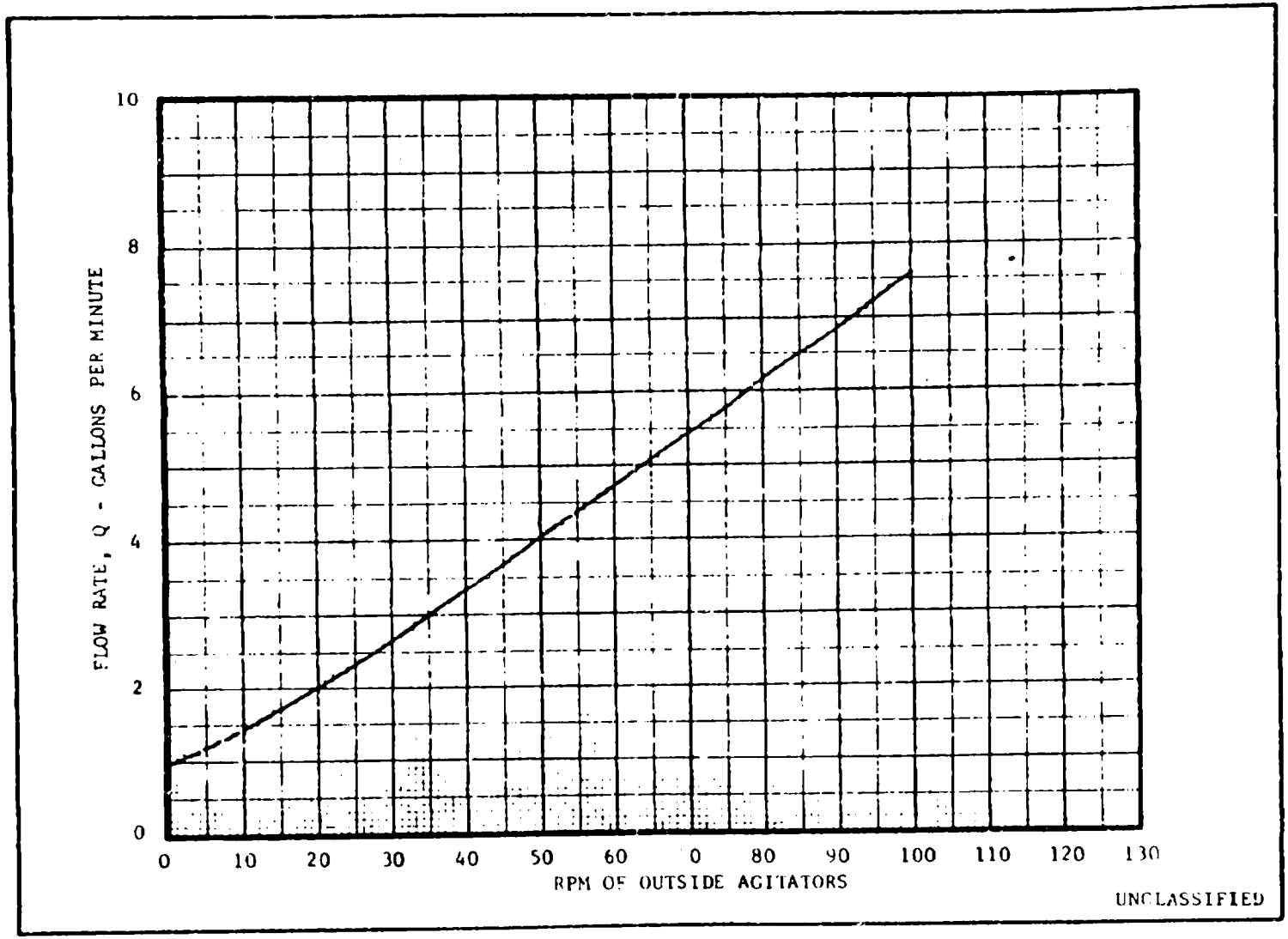

Figure C-7. Hydraulic Fluid Flow Rate, F, as a Function of rpm of the Outside Agitators of the Day 5-Gallon Regal Mixer

TABLE C-I

DIFFERENTIAL PRESSURE (ΔP) MEASUREMENTS AT DIFFERENT RPM OF THE OUTSIDE AGITATOR OF THE DAY 5-GALLON REGAL MIXER WHEN EMPTY

	Test 1		Test 2		
RPM	ΔP (psi) ↓	ΔP (psi) ↑	ΔP (psi) ↓	ΔP (psi) ↑	ΔP AVE (psi)
10	240	250			245.0
20	270	260	260	270	265.0
30	310	270	280	280	285.0
40	360	300	310	300	317.5
50	390	340	350	330	352.5
60	410	370	380	360	380.0
70	430	400	410	400	410.0
80	460	430	440	430	440.0
90	470	470	[illegible]0	450	462.5
92	470		[illegible]0		465.0

Notes: Tests were performed starting with the mixer at rest and going up to 92 rpm and back to zero rpm. Rpm is combined rotation and orbit motion.

The arrows indicate the direction of rpm change. ↓ indicates rpm increasing and ↑ indicates rpm decreasing.

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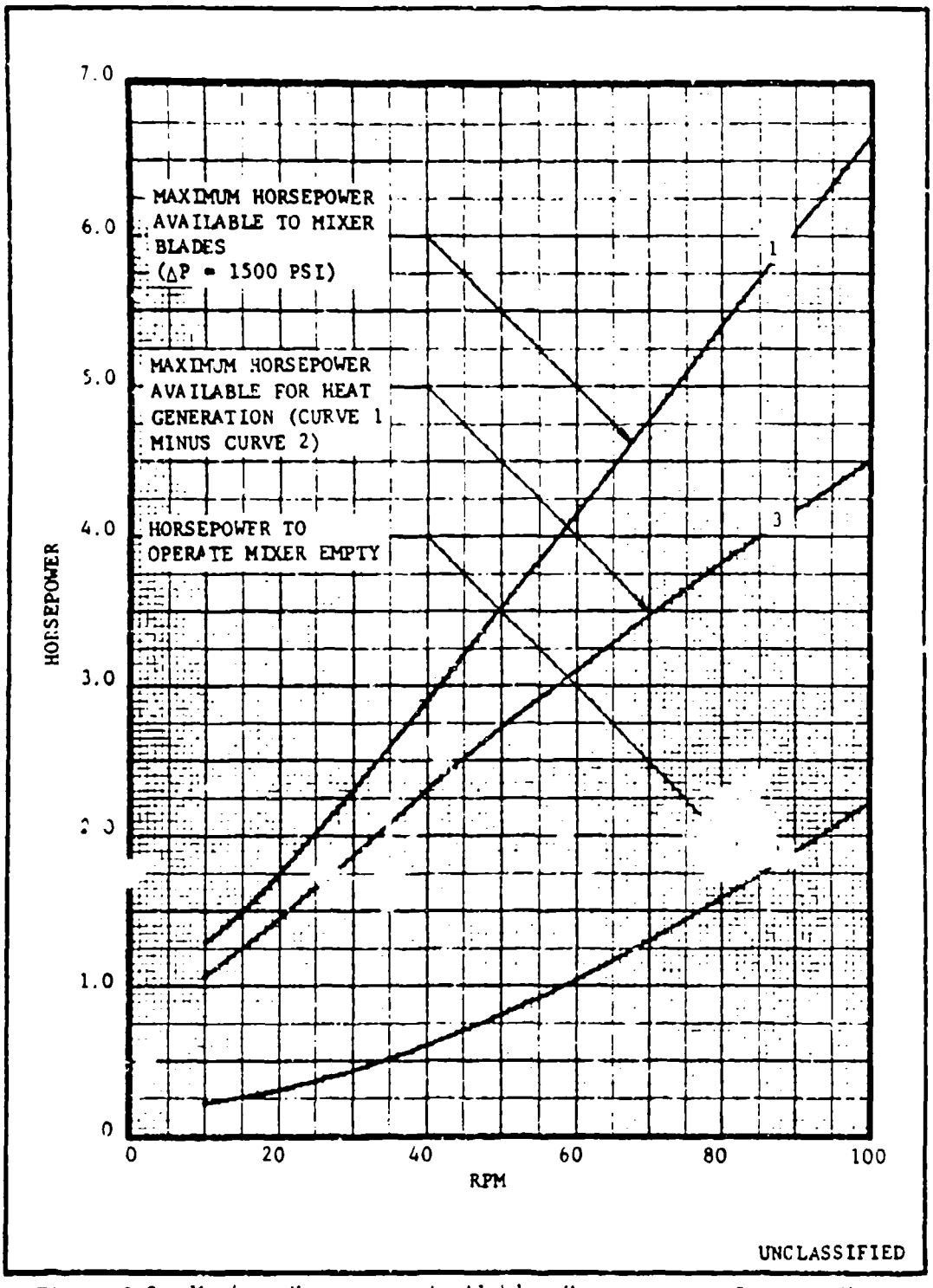

Figure C-8. Maximum Horsepower Available, Horsepower to Operate Mixer Empty and Horsepower Available for Heat Generation as a Function of rpm of the Day 5-Gallon Regal Mixer

3. Heat Transfer Model

(U) The grid network, boundary conditions, and material properties of the heat transfer model are illustrated in Figure C-9. Hercules computer program No. 61004 (Hetran II) was used in this analysis. The heat transfer model is a heat balance where the heat generated by viscous shearing is equated to heat transferred out of the propellant plus heat stored in the propellant. Convective heat transfer within the propellant mass was not modeled; thus, all the heat generated either remains in the propellant or is transferred to the bowl wall by conduction. A uniform initial temperature equivalent to the temperature of the water flowing through the water jacket was assumed for the entire body.

(U) The mixer blades were not modeled and the blades were assumed to be replaced with propellant. Also, the bowl wall and the water jacket were not modeled in the grid network, but an overall heat transfer coefficient was used at the boundary of the propellant and bowl wall to simulate the heat transfer characteristics. This heat transfer coefficient ($h_{overall}$) was determined from the following relationship:

$$\frac{1}{h_{overall}} = \frac{1}{h_{ss}} + \frac{1}{h_{scale}} \qquad (26)$$

(U) The terms on the right side of Equation (26) represent the resistance to heat conduction by the stainless steel wall and the water scale deposits on the water jacket side of the wall. The heat transfer coefficient of the stainless steel wall (h_{ss}) was calculated from the thermal conductivity of the stainless stell (k_{ss}) and the wall thickness (t).

$$h_{ss} = \frac{k_{ss}}{t} = \frac{8.5 \text{ Btu/hr-ft}^2\text{-}^\circ\text{F/ft}}{0.03125 \text{ ft}} = 272 \text{ Btu/hr-ft}^2\text{-}^\circ\text{F}$$

(U) The heat transfer coefficient for the water scale deposits (h_{scale} = 500 Btu/hr-ft^2-$^\circ$F) was taken from Reference 9. Using the above values for h_{ss} and h_{scale}, a value of $h_{overall}$ = 176 Btu/hr-ft^2-$^\circ$F was obtained. A conservative value of $h_{overall}$ = 100 Btu/hr-ft^2-$^\circ$F was used in the analysis.

(U) It was assumed that all of the power available for heat generation (Figure C-8) is consumed in the 0.125-in. clearance between the blade tip and the bowl wall. Heat generated by viscous shearing is a function of shear rate ($\frac{dV}{dX}$) and viscosity. Heat generated is higher for higher shear rates and higher viscosities; however, the relationship is complicated by the fact that viscosity is shear rate and temperature dependent. Propellant mixtures are shear thinning, i.e., the effective viscosity decreases with increasing shear rate. The viscosity also decreases with increasing temperature. These phenomena make it difficult to make

[9] Refer to References at End of Appendix

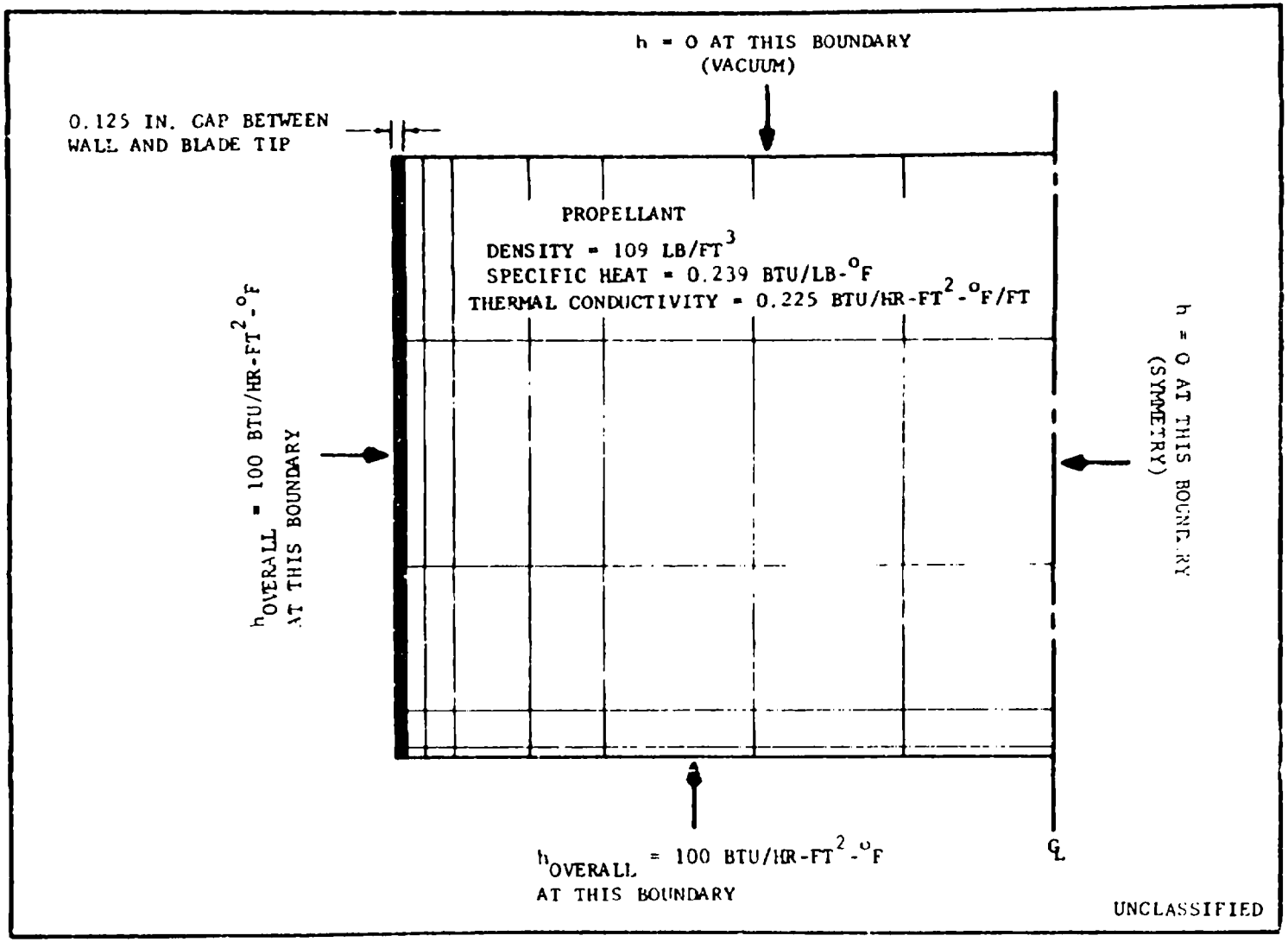

Figure C-9. Grid Network, Boundary Conditions and Material Properties of Heat Transfer Model of Day 5-Gallon Regal Mixer

(U)

a valid distribution of the power consumption across the clearance. Figure C-10 shows typical velocity profiles across a clearance between one stationary surface (the bowl wall) and one moving surface (the mixer blades). The velocity profiles depend on the clearnace, blade velocity, temperature, and viscosity. This analysis is directed towards an upper bound of temperatures and a distribution of the heat generation which allows maximum heat generation at the blade tip side of the clearance gap will produce the most severe temperatures. Therefore, in this model the heat generation (from Figure C-8) was distributed according to shear rate ($\frac{dV}{dX}$) as calculated from the lower curve of Figure C-10.[10]

4. Results

(U) Analyses were performed for 20, 40, 60, 80, and 100 rpm of the outside blades. These speeds correspond to the power or heating rates presented in Table C-II.

(U) The results are summarized in Figures C-11 and C-12. Figure C-11 shows the maximum temperature increase (ΔT_{max}) adjacent to the mixer blade tip as a function of time for the different rpm levels. The numerical solutions show ΔT_{max} values approaching a limit asymptotically. Thermal equilibrium (no change in ΔT_{max}) will be attained when the heat being removed at the boundaries is equal to the heat generated. The solutions were continued until the change in ΔT_{max} was less than 0.1° F/min. Figure C-12 illustrates the final temperature profiles between the blade tip and the bowl wall for the different rpm levels.

TABLE C-II

POWER AVAILABLE FOR HEAT GENERATION FOR VARIOUS RPM OF THE OUTSIDE AGITATORS OF THE DAY 5-GALLON REGAL MIXER*

RPM* of Outside Agitator	Horsepower For Heat Generation	Heat Rate (Btu/hr)
20	1.44	3660
40	2.30	5850
60	3.12	7930
80	3.82	9700
100	4.50	11420

*This rpm is combined rotation and orbit motion. UNCLASSIFIED

10 thru 12 Refer to References at End of Appendix

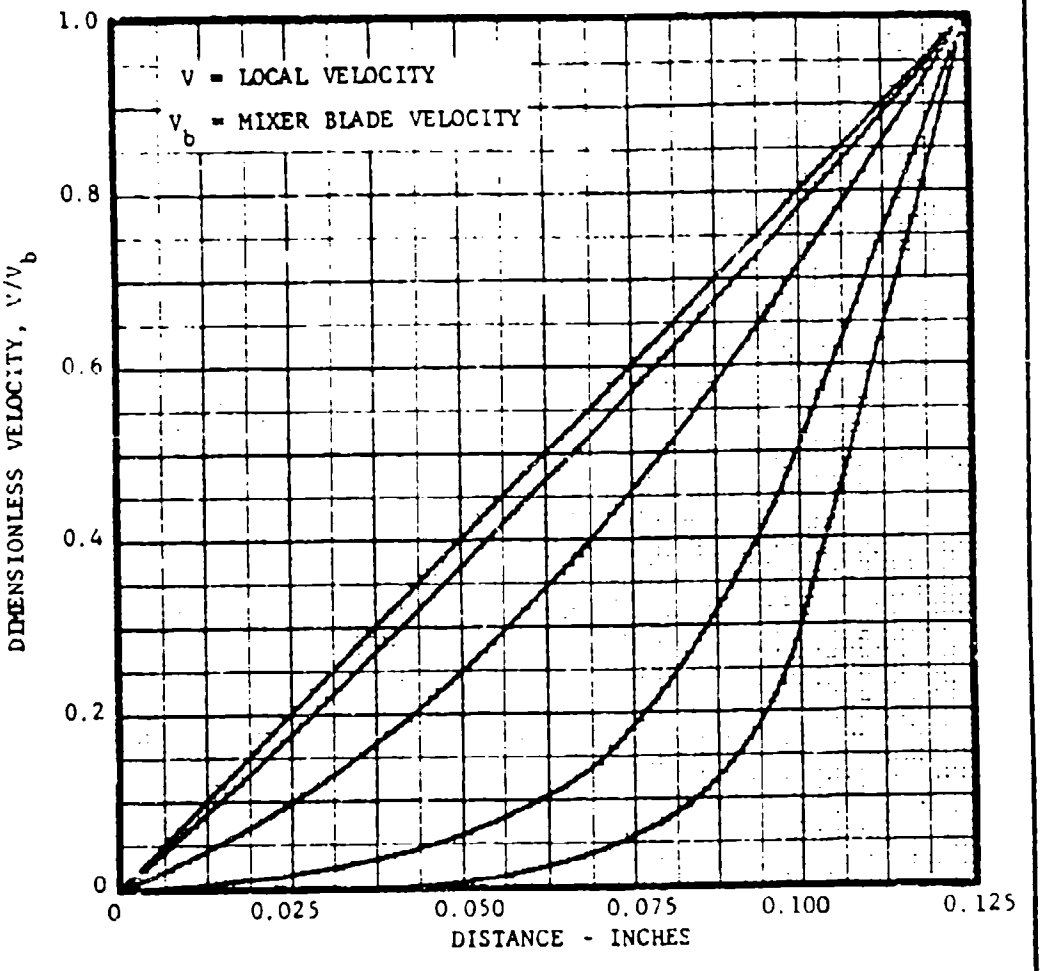

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Figure C-10. Typical Velocity Profiles Across Clearance Between Bowl Wall and Blade Tip - Dimensionless Velocity as a Function of Distance from the Bowl Wall

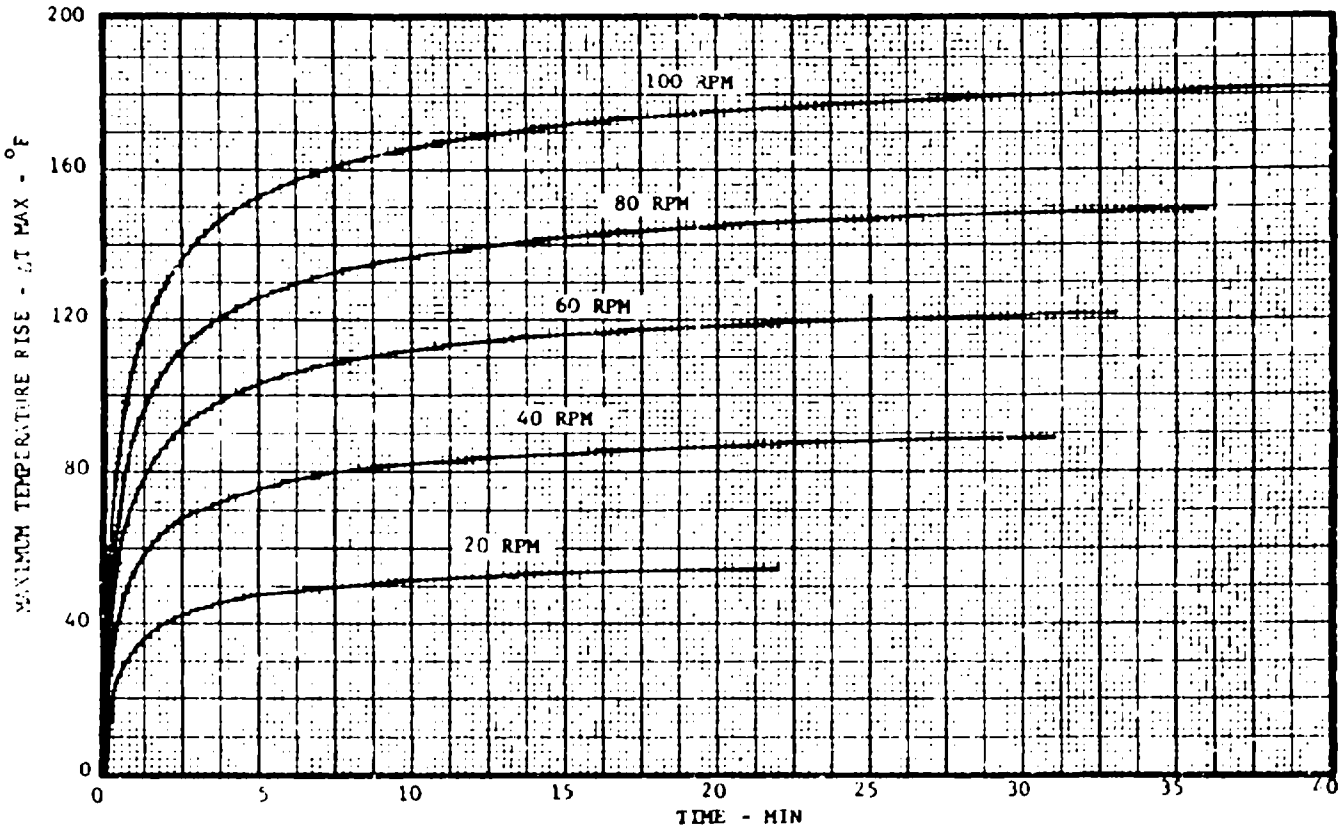

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Figure C-11. Maximum Temperature Rise (Adjacent to Outside Blade Tip) as a Function of Time in the Day 5-Gallon Regal Mixer

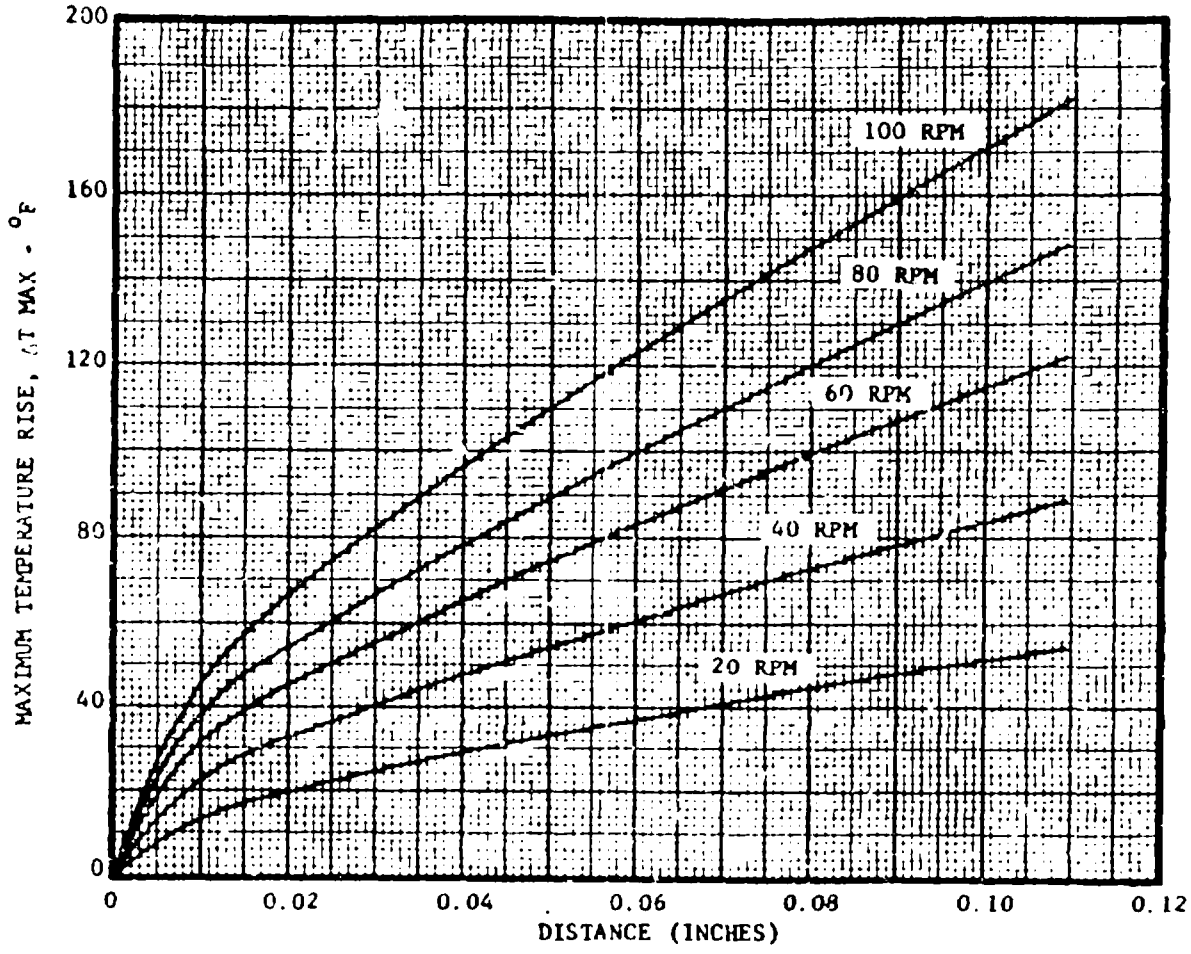

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Figure C-12. Maximum Temperature Rise as a Function of Distance from the Bowl Wall in the Day 5-Gallon Regal Mixer

(C) In order to use Figures C-11 and C-12 to determine if viscous shear heating is a hazard in mixing a propellant, experimental data on temperature levels and temperature rise rates must be available. The lowest exotherm temperature for various DOMINO systems is 120° C (248° F)). The calculated maximum temperature rise (Figure C-10) is 182° F at 100 rpm. If the mix starting temperature was 70° F, the maximum temperature predicted by this conservative analysis would be 252° F. Therefore, at any rpm less than 100 and with the initial temperature of the system and the temperature of the water jacket at 70° F, the exotherm temperature at a 5° C/min rise rate would not be attained. Experimental data on the exotherms at other temperature rise rates and also at temperatures maintained for longer time periods are not currently available. These data will be obtained as necessary later in the experimental work of this program.

(C) However, based on the conservative approach used in this analysis, it is concluded that the 5-gal mixer will not generate a viscous shear heating problem if the DTA exotherm temperature is 120° C or greater. Care should be exercised in designing mix cycles, however, since elevated temperature mixing will further reduce safety margins.

(U)

APPENDIX C
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13. ABSTRACT

(C) This program was designed to demonstrate a practical high energy propellant containing a difluoroamino binder, AlH_3, and the advanced oxidizer hydroxylammonium perchlorate (HAP).

(C) There were several problems which had to be solved before the attractive specific impulse and density of this advanced system could be realized in a practical propellant. The program was designed to further explore problems of in-process hazards, system compatibility and stability, and obtaining optimum and reproducible cures. The program included: (1) A comparison of the TVOPA plasticized P-BEP and lower energy polyester binders, (2) scale-up of TVOPA/AlH_3 propellants, and (3) an evaluation of difluoroamino binders with HAP.

(C) A high impulse TVOPA-AlH_3 propellant (VKW) was developed and successfully scaled to 70-lb mixes and 15PC motor firings. The propellant had a delivered impulse (I_{1000}^{15}) of 267 sec and a density of 0.0612 lb/in.^{3} The binder consisted of TVOPA plasticized polyester R-13. The mechanical properties were good, but the in-process hazards are high and the predicted shelf life is low. The propellants based on P-BEP were found to be unstable and, therefore, were not recommended for scale-up past 5PC motors. HAP was determined to be incompatible with the other propellant ingredients and was, therefore, dropped from the program.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT

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[redacted]

HERCULES INCORPORATED
INDUSTRIAL SYSTEMS DEPARTMENT · SYSTEMS GROUP
P.O BOX 98, MAGNA, UTAH 84044 · TELEPHONE 297-5911

28 April 1973

In Reply Refer To:
0067/10/9-2289

Air Force Rocket Propulsion Laboratory
Air Force Systems Command
Edwards Air Force Base
Edwards, California 93523

Attention: Captain A. M. Crelier (MKPA)

Subject: Development and Test of a Highly Energetic Domino Propellant (U), Report No. AFRPL-TR-73-25, dated April 1973

Reference: Contract F04611-C-68-0081, Sequence No. B005

Gentlemen:

In accordance with Contract F04611-C-68-0081, three copies of the subject report are hereby submitted.

Very truly yours,

A. H. Nielson, Superintendent
Contract Administration

AHN/AFeurer/hyr

Enclosure: Copies 1 thru 3 of subject report

cc: AFFTC
Edwards, California 93523
Attn: Lt. R. W. Norman (RTMKR-3) (letter only)

[redacted]

Regraded UNCLASSIFIED when separated from classified enclosures.