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(UNCLASSIFIED TITLE)
KINETICS OF DECOMPOSITION OF HIGH ENERGY MATERIALS

LOCKHEED PROPULSION COMPANY
REDLANDS, CALIFORNIA

TECHNICAL REPORT AFRPL-TR-70-111
SEPTEMBER 1970

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FOREWORD

This is the final report issued under contract FO4611-69-C-0071 covering the period 1 May 1969 through 31 July 1970. This contract was assigned to Lockheed Propulsion Company, Redlands, California, and it was monitored by Capt. Fred Clark, Air Force Rocket Propulsion Laboratory, Edwards, California.

The technical effort under this program was conducted by Mr. Yuji Tajima (Program Manager), Dr. James Hammond (Senior Investigator) within the Chemistry Department (Dr. W. E. Baumgartner, Manager). Participating technical personnel were Leo Asaoka and W. Allan (Propellant processing and surveillance), G. Stapleton (Mass Thermal Analysis) and Dr. R. Plock (Computer Programs).

This report has been reviewed and is approved: Charles Cooke, Chief Rocket Motor Division.

ABSTRACT

The stability and the compatibility of PBEP and of PCDE were investigated by Mass Thermal Analysis (MTA), propellant surveillance tests and measurement of propellant gas generation rates. The tests served to determine which, if any, of the purification procedures produced desirable gains in propellant thermal stability and shelflife.

With PBEP the products resulting from various column and solvent treatments were evaluated, and the data show that specific purification procedures can produce a product that is suitable for use in advanced propellants. With PCDE the data imply that the presently employed treatment does not as yet produce an optimum product, and further refinements in the purification of PCDE are expected to become reflected in further gains in propellant stability and shelflife. However, propellant surveillance data show that even in its present state of purity PCDE matches PBEP as regards stability in propellants.

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ILLUSTRATIONS (Continued)

TABLES

GLOSSARY

Al	Aluminum
AlH_3	Aluminum hydride
Alon C	Aluminum oxide, submicron size, Cabot Corporation
AP	Ammonium perchlorate
ARC	Atlantic Research Corporation
BEP	1,2-bis(difluoramino)epoxy propane - Theoretical PBEP monomer unit
BEP-H	Hydrogen-terminated BEP unit
COT	Cyclooctatetraene
DBP	Dibutylphthalate
DBTDA	Dibutyltindiacetate
DPA	Diphenylacetylene
HT	1,2,6-hexanetriol
Imax	Maximum intensity of a peak
Int. Scav.	Integrated Scavenger
I.S.	Integrated Scavenger
LPC	Lockheed Propulsion Company
MTA	Mass thermal analysis
m/e	Mass to charge ratio
PBEP	Poly(1,2-bis(difluoramino)2,3-epoxy propane
PCDE	Pyridine treated PBEP
Pd/C	Palladium on carbon
R-45	Hydroxy terminated polybutadiene
Taliani	Gas evolution reactor/manometer
TDI	Tolylene diisocyanate
TVOPA	Tris-(bis-(difluoramino)vinoxy) propane

SECTION I

INTRODUCTION

(C) In an effort to increase the performance of solid propellants various attempts were made to incorporate into the propellant materials (solids, plasticizers, binders) containing the difluoramino ($-NF_2$) group as an oxidizer principle. These efforts resulted in the development and the more extensive evaluation of two materials, namely tris-(bis-(difluoramino)vinoxy) propane (TVOPA) and poly(1, 2-bis(difluoramino)2, 3-epoxy propane) (PBEP). The former material is a liquid and used as a plasticizer, while the latter material (PBEP) is a polymeric material that contains hydroxyl functionality and that can be cured with isocyanates.

(C) Both materials are prepared by adding N_2F_4 across the olefin unsaturation in a precursor. In the case of TVOPA, the precursor is trivinoxy propane which is a specialty chemical; in the case of PBEP, the precursor is dehydrohalogenated polyepichlorohydrin which is a readily available commercial product. Since the two materials energetically are closely similar, PBEP could have a potential cost advantage over TVOPA. However, this advantage is somewhat offset by difficulties that were experienced in the purification of the final product. While TVOPA is a monomeric product that can be purified by distillation and column treatments, the purity of PBEP must largely be controlled by controlling the process conditions during N_2F_4 addition to the unsaturated prepolymer. Additionally, various means of post-treatment (solvent precipitation, column treatment, adsorption) were studied in an effort to produce a chemically more uniform and a thermally more stable product. In support of these efforts Lockheed Propulsion Company applied a Mass Thermal Analysis technique for the purpose of identifying impurities and structural irregularities in the product. These efforts were conducted under Air Force Contract FO4611-68-C-0079 (Ref 1) and resulted in the conclusion that none of the methods of material purification used up to that time were as yet adequate for producing a propellant grade material. At the same time, however the data suggested that further improvements in the processing or purification steps should be capable of producing a material that would at least equal TVOPA in stability and enable better reproducibility in the cure reaction.

(U) As a result of these studies a renewed effort between Lockheed Propulsion Company and Shell Development, the manufacturer of the material, was initiated by the Air Force for the purpose of producing a material of higher purity and uniformity.

SECTION II

SUMMARY AND CONCLUSIONS

(C) PBEP samples that had been subjected to various purification procedures by the Shell Development Company were evaluated in propellants (shelflife, gas generation rates) and by a mass thermal analysis technique (compositional analysis, decomposition kinetics). In addition, a sample of PBEP that had been converted to PCDE by pyridine treatment was evaluated by the same techniques.

(C) Propellant evaluation was conducted with aluminized and aluminum hydride containing formulations using two-inch cracking cubes and elliptical tube specimens to determine the effects of the varying treatments upon propellants shelflife at 50 and 60°C. Representative samples of the various propellants were used to determine gas generation rates, and the off-gas mixtures were analyzed by mass spectrometry.

(U) The combine of data warrants the following conclusions:

(C) (1) Of the various non-destructive treatments, precipitation with hexane affords the best material for propellant usage. This treatment removes materials of comparatively low molecular weight that are produced either during the synthesis steps or during subsequent handling or storage. Mass thermal analysis (MTA) indicates that the hexane precipitate contains only a minor weight fraction of materials that can be volatilized prior to the onset of PBEP pyrolysis.

(U) Of the alternative treatment methods, molecular sieve treatment is rather ineffective, while Amberlyst and Norite treatment seem to cause some degree of material degradation.

(C) (2) The chemical treatment of PBEP with pyridine which converts the material into PCDE by dehydrofluorination of the primary NF_2 group produces a prepolymer that tends to retain methylene chloride solvent quite strongly. The MTA data moreover show that pyridine treatment will not remove some of the low molecular weight impurities, although it may render these impurities chemically rather inert. Somewhat unexpectedly the data also show that PBEP and PCDE produce comparable amounts of HF. The latter indicates that in the thermal degradation of PBEP the reaction does not proceed via the PCDE intermediate.

(C) In propellant application PCDE equals or surpasses the hexane precipitated PBEP in stability and compatibility, and further gains are likely to be achieved by hexane precipitation of the pyridine treated material.

(C) (3) Aluminized propellants containing hexane precipitated, molecular sieve treated and pyridine treated PBEP did not fail within 100 days at 60°C while early failure occurred with the Amberlyst treated PBEP. In the aluminum hydride formulation the hexane precipitated PBEP and PCDE (pyridine treated PBEP) were superior; these samples failed after 40 days at 60°C in the absence of gas scavengers, and after 75 days in the presence of scavengers. By contrast the propellant samples containing the molecular sieve and the Amberlyst treated materials failed during cure, or shortly thereafter. At 50°C the AlH_3 propellants containing the hexane precipitated PBEP and the PCDE showed no signs of cracking or swelling after 100 days, while the propellants containing molecular sieve and Amberlyst treated PBEP failed within 10-90 days. Additional test data appear necessary to determine the effectiveness of Norite treatment.

(U) The surveillance data are masked by variability in the degree of hydride surface attrition that occurs during propellant mixing, and that can produce high gassing rates during cure and during an initial 100 day storage period at 50°C.

(C) (4) The mass spectrometer analysis of the off-gases showed CO_2, CO, HCN and N_2 to be the major species with the aluminized formulations at 60°C; at 50°C, CO_2 and N_2 remain as the dominant species, however, HF now also appears in the spectra. In the aluminum hydride containing systems the dominant species at 60°C are H_2, CO, CO_2, H_2O, HF and HCN with nitrogen appearing at lower concentration. At 50°C the dominant species are CO_2, CO, nitrogen and hydrogen. Hydrogen gas scavengers (Palladium on carbon, COT) are effective in reducing hydrogen and HF concentrations at 50°C; at 60°C the scavengers may increase hydrogen, and in some cases CO_2, generation rates. Alon C can effect a significant increase in hydrogen gas generation rate at 60°C while reducing CO production rates significantly at 50°C in the PCDE containing sample. The combination of gas analysis data shows that with the AlH_3 formulations, 60°C is too high a test temperature to collect meaningful data, notably in the study of the effects of scavengers.

(C) (5) The analysis of the MTA data provides evidence that stability and compatibility problems with PBEP are associated with the existence of end-groups other than glyceryl or 2-methoxy-1,2-propylol ether groups. Chains, or chain fractions containing thermally unstable end-groups (e.g., acetol or BEP-H) end-groups tend to degrade until 2-methoxy-1,2-propanediol ether groups that are present as chain links become the new terminals. In this process the BEP units degrade into low molecular weight fluorine containing species, while the non-BEP units remain intact. As a consequence the early spectra in the MTA show a high abundance of mass species attributable to non-BEP units.

(C) The data suggest that both PBEP and PCDE might gain in apparent stability by a moderate increase in the number of 3-methoxy-1,2-propane glycol ether chain links. An increase in the number of these chain links would protect the polymer against excessive degradation in molecular weight as the initially present BEP-H type end-groups become eliminated.

SECTION III

TECHNICAL EFFORT

(U) The Shell Development Company, manufacturer of PBEP, had been investigating a number of processes for the clean-up of PBEP in an effort to improve the neat thermal stability and to achieve consistent cure. Thermal stability was checked by measuring the gas evolved in 100 hours at 80°C. Based on their results, five samples of PBEP cleaned up by various processes and including a sample of as-manufactured material (Series 11111) were selected for evaluation in a model AlH_3 propellant formulation. An Al-analog formulation was also used to obtain shelflife and gas generation data that would more directly reflect the stability of cured PBEP with least complications from propellant incompatibility.

(C) Based on these initial accelerated surveillance data, four more samples of PBEP (9851 Series) were selected for more intensive study. These samples were processed by combinations of clean-up steps that showed the most promise in the preliminary tests. This series included a sample that had been treated with pyridine to effect conversion of the primary NF_2 group into the nitrile group.

1. ANALYTICAL RESULTS

(C) The analytical results that were obtained by Shell are summarized in Tables I and II. The data show that the various treatments modify molecular weight, functionality and thermal stability as determined at 80°C. Pyridine treatment reduces the fluorine content by 30-35 percent with concurrent improvement in the 80°C thermal stability. Pyridine treatment also appears to effect a reduction in OH functionality while the reduction in molecular weight essentially reflects the loss in fluorine content.

2. PROPELLANT SURVEILLANCE TESTS

(U) The various PBEP samples were evaluated in both aluminized and aluminum hydride containing propellants whose formulations are quoted in Table III. In the aluminum hydride formulations the gas scavenger (Ref 2) composition constituted an additional variable.

(U) The initial sample series (Series 11111) was processed into propellant using a 150 cc conical-vertical Atlantic Research mixer, and the propellant was cast into standard two-inch JANAF cubes. It was subsequently found that high shear conditions in this mixer affected varying degrees of particle attrition which caused premature sample failure. Consequently the propellant for

TABLE I

ANALYTICAL DATA, SAMPLE SERIES 11111

Sample Number	11097-50	11111-149A/86A		11111-149B/86B		11111-149C/86C		11111-149D/86D	
	Master Batch, No Treatment	Molecular Sieve		Samples "A" precipitated with hexane		Samples "B" treated with charcoal		Samples "C" with COT (1%) added	
		149A	86A	149B	86B	149C Nuchar	86C Norite	149D Nuchar	86D Norite
Elemental Analysis									
% C	26.0	26.3	26.5	25.8	26.1	27.8	27.6	27.9	N/A
% H	3.1	3.8	3.3	3.4	3.2	3.2	3.0	3.3	N/A
% N	16.2	16.4	16.1	16.2	15.9	17.2	16.7	17.2	N/A
% F	39.7	38.6	40.3	38.9	39.7	36.5	35.8	35.5	N/A
% NF_2	60.1								
F/N Ratio	1.8								
Molecular Weight	3690	4240	3590	4850	4370	3900	3710	3930	N/A
OH, Equiv/100 g	0.062	0.048	0.050	0.046	0.045	0.051	0.052	0.051	N/A
Functionality	1.8	2.1	1.8	2.2	2.0	2.0	1.9	2.0	N/A
Thermal Stability, cc/g/100 hrs @ 80°C:	5.6	4.6	5.1	4.0	5.1	2.3	2.5	2.5	2.4

Table II

ANALYTICAL DATA, SAMPLE SERIES 9851

	-123A (Pyridine)	-125A (Amberlyst)	-128 (Hexane Ppt)*	-135 (Mol Sieve)
%F	26.3			
Molecular Weight	3080	3400	4560	3750
Thermal Stability, cc/g/100 hrs @ 80°C	0.1	3.9	4.5	5.6
@ 100°C	4.0			
Functionality:	1.7			
OH; Equiv/100 g	0.057			

---

* All other properties similar to previous materials prepared the same way (Shell Letter, 2 May 1969); -128 ~11111-149B, -86B; -135 ~11111-149A, -86A.

Table III

BASIC FORMULATIONS
PBEP TEST

	1	2	3	4
PBEP	18.4 wt %	18.4 wt %	18.4 wt %	18.4 wt %
DBP	13.5	13.5	13.5	13.5
TDI	2.6	2.6	2.6	2.6
HT	0.7	0.7	0.7	0.7
AP Type II	28.5	28.5	28.0	27.8
AP, 8μ	14.0	14.0	13.0	13.0
AlH_3, doped/nBA (Lot B-7)	--	22.0	22.0	22.0
DBTDA	0.3	0.3	0.3	0.3
Al, H-5	22.0	--	--	--
COT/DPA Int. Scav.	--	--	1.00	1.00
Alon C	--	--	--	0.20
COT	--	--	0.50	0.50

Integrated Scavenger:

R-45	22.26 wt %
TDI	2.59
HT	0.12
COT	30.00
DPA	10.00
Catalyst (Ref 2)	35.00
DBTDA	0.50

the subsequent tests were processed using a low shear vibrating blade mixer and cast into two-inch elliptical tube specimens (Ref 3).

(U) The specimens were stored at 50 and 60°C under inert atmosphere for periodic examination by X-ray (cracking); additionally the sample dimensions were monitored to detect the onset of swelling (porosity formation, not detectable by X-ray). Identical samples of the various propellants were used to determine gas evolution rates (Subsection 3).

a. Sample Series 11111

(1) Sample Series 11111-86

(U) The results (failure times) of a first test series are summarized in Figure 1. The samples used in this series were processed in the 150-cc ARC mixer, and the early failure of many of the samples is attributed to removal of the protective coating on the hydride as a result of high shear mix conditions.

(U) Of the aluminized systems only the specimen prepared with untreated PBEP has failed to-date (350 days). In the aluminum hydride systems the addition of gas scavengers caused a significant improvement in shelflife with the exception of PBEP sample 11111-86A which failed in four days at 50°C.

(U) Additional samples were placed into 30°C surveillance, none of these samples have failed to date.

(2) Sample Series 11111-146

(C) The results obtained with sample series 11111-146 which was processed into propellant using a low shear vibrating blade mixer are summarized in Figure 2. The low shear mixing eliminated the problem of premature sample failure; however, overall stability did not seem improved. In part this may be attributed to the omission of Alon C. Only with the samples containing the molecular sieve treated PBEP was shelflife reduced by the addition of a hydrogen gas scavenger system (Pd/C, COT); with all other samples the addition of the hydrogen gas scavenger again improved shelflife.

(U) The propellant mechanical properties are quoted in Table IV.

(3) Conclusions, Series 11111

(U) On the basis of these test data none of the various treatments can be singled out as being the most effective. At the same time it is apparent that the data are masked by variability in processing conditions (e.g., mix viscosity) and, possibly, by differences in propellant mechanical properties.

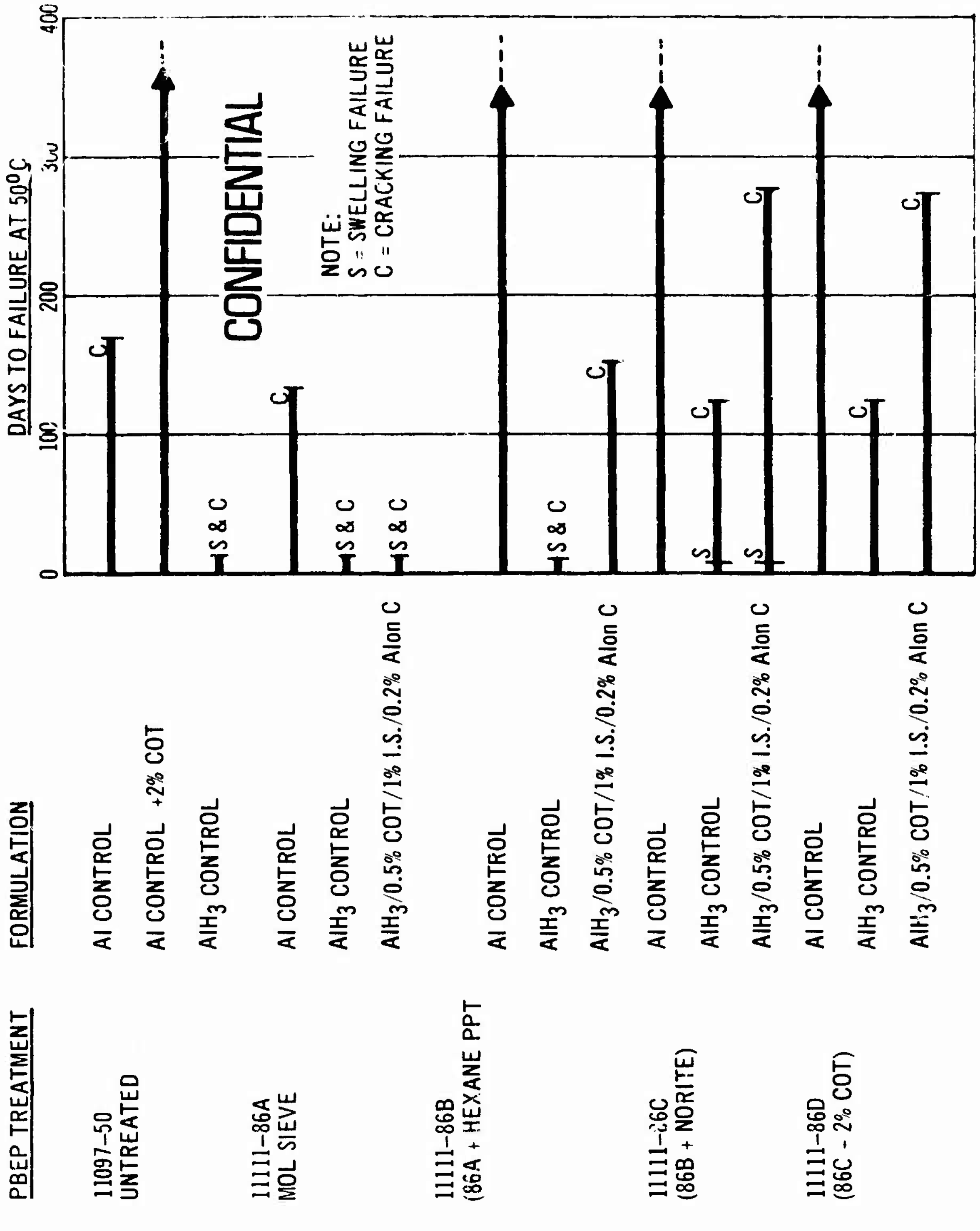

Figure 1 Two-Inch Cube Data, 50°C Surveillance High Shear ARC Mixer

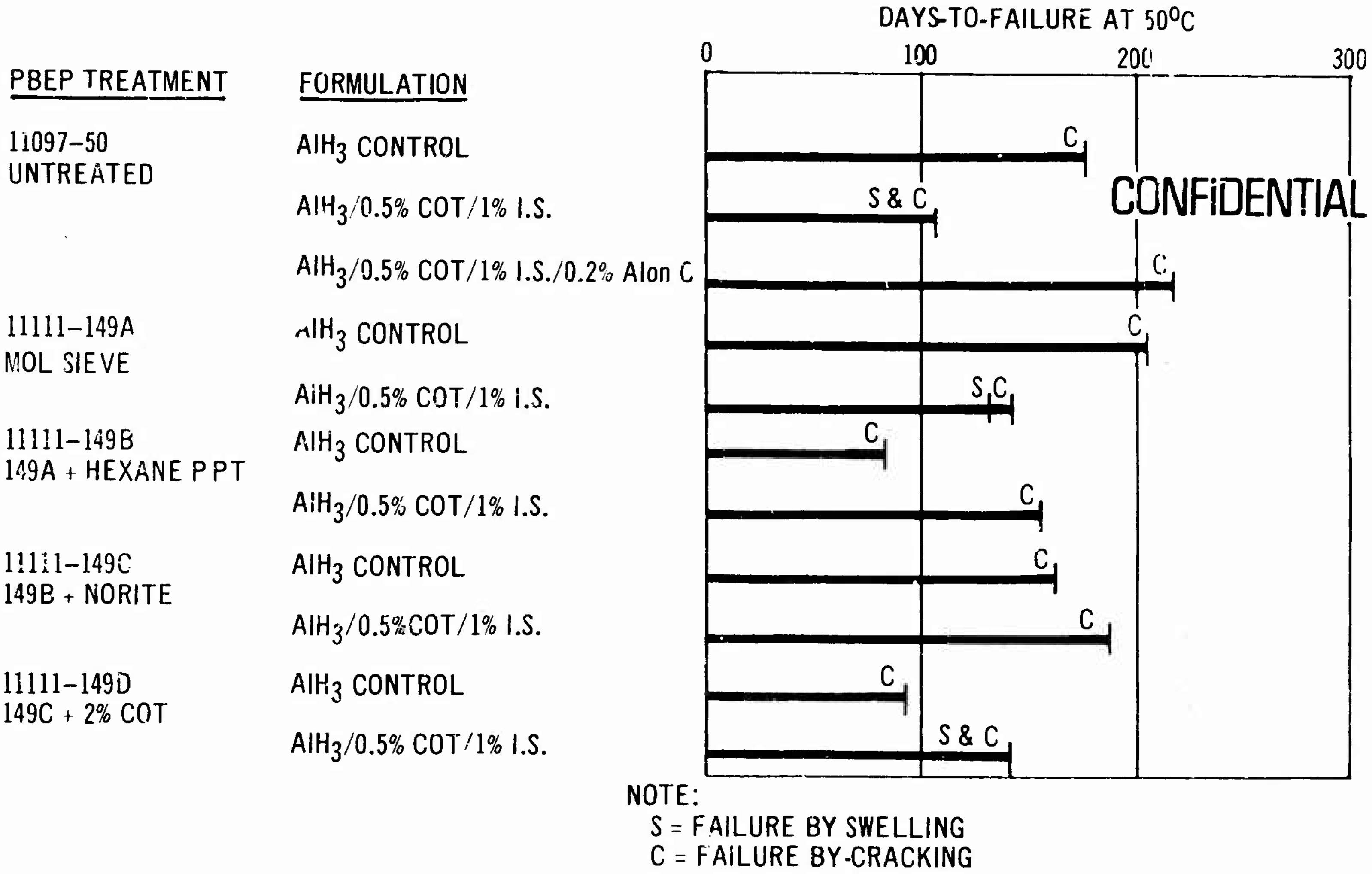

Figure 2 Two-Inch Elliptical Tube Data, 50°C Surveillance (Low Shear VB/RP Mixer)

TABLE IV

MECHANICAL PROPERTIES OF PBEP/AlH_3 PROPELLANTS

	Lot Numbers (PBEP)				
	11109-50	11111-149A	11111-149B	11111-149C	11111-149D
Stress/Strain (psi) (%)	170.2/20	182.7/21	119.0/20	132.2/20	147.0/21

Differences in propellant mechanical properties have been shown to affect shelflife and failure modes (Ref 4).

b. Series 9851 PBEP

(C) In a second test series the PBEP samples were subjected to a single treatment rather than consecutive treatments, with the exception of the pyridine treated material that was additionally passed through an Amberlyst ion exchange resin.

(C) The corresponding propellant mixes were all processed with the low shear vibrating blade mixer and cast into two-inch elliptical tubes. Sufficient additional propellant was processed to provide material for the measurement of gas evolution rates (Subsection 3). Both surveillance and gas evolution testing was conducted at 50 and 60°C.

(C) The propellant mechanical properties obtained with this series of PBEP samples are summarized in Table V.

(1) 50°C Surveillance Test Results

(C) The results (failure times) obtained in the 50°C surveillance test are summarized in Figure 3. None of the aluminized propellants have failed to date (120 days). With the AlH_3 propellants the samples containing the Amberlyst and the Molecular Sieve treated PBEP failed prior to 100 days, and gas scavenger addition, rather than improving shelflife, shortened the time to failure. The samples are being kept under surveillance.*

(2) 60°C Surveillance

(C) For the purpose of obtaining a comparison with the shelflife capability of Al/TVOPA and AlH_3/TVOPA containing propellants an additional surveillance study was conducted at 60°C. The results are summarized in Figure 4.

(C) A comparison between times-to-failure of the aluminized samples and the mechanical property data that were obtained with the AlH_3 containing systems suggests that the early failure of the samples containing the hexane precipitated and the Amberlyst treated PBEP might be attributable to poor binder strength.

(U) Addition of gas scavengers improved shelflife with the pyridine treated and the hexane precipitated samples, but had no beneficial effect with the Amberlyst treated samples. The specimens containing molecular sieve treated PBEP failed during cure. This may be attributable to adverse processing conditions.

(C) * At the issue date of this report, AlH_3 propellant samples containing the hexane precipitated PBEP and the pyridine treated PBEP have passed close to 200 days storage without evidence of failure. Subsequent surveillance test results will be quoted in the reports issued under Contract FO4611-69-C-0038.

TABLE V

MECHANICAL PROPERTIES OF PBEP-9851/AlH_3 PROPELLANTS

	9851-128	9851-125A	9851-123A	9851-135
Treatment ⟶	Hexane ppt	Amberlyst	Pyridine	Mol Sieve
5 days @ 27°C	102.1psi/22%	70.2psi/22.8%	105.3psi/21.8%	136.0psi/19.7%
10 days @ 27°C	113.1 /17.4	106.6 /16.7	142.6 /20.2	181.8 /15.5

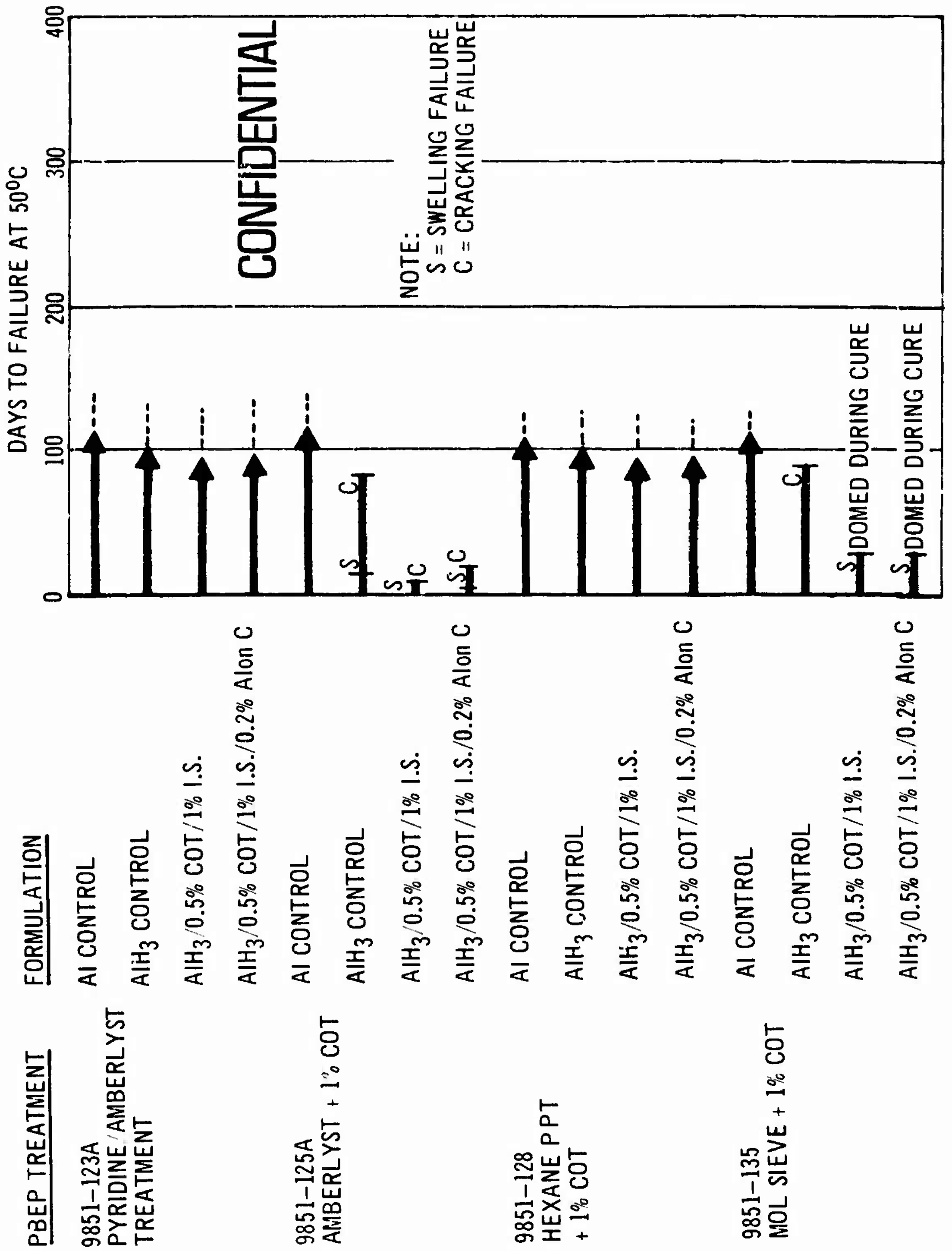

Figure 3 Two-Inch Elliptical Tube Data, 50°C Surveillance (Low Shear VB/RP Mixer)

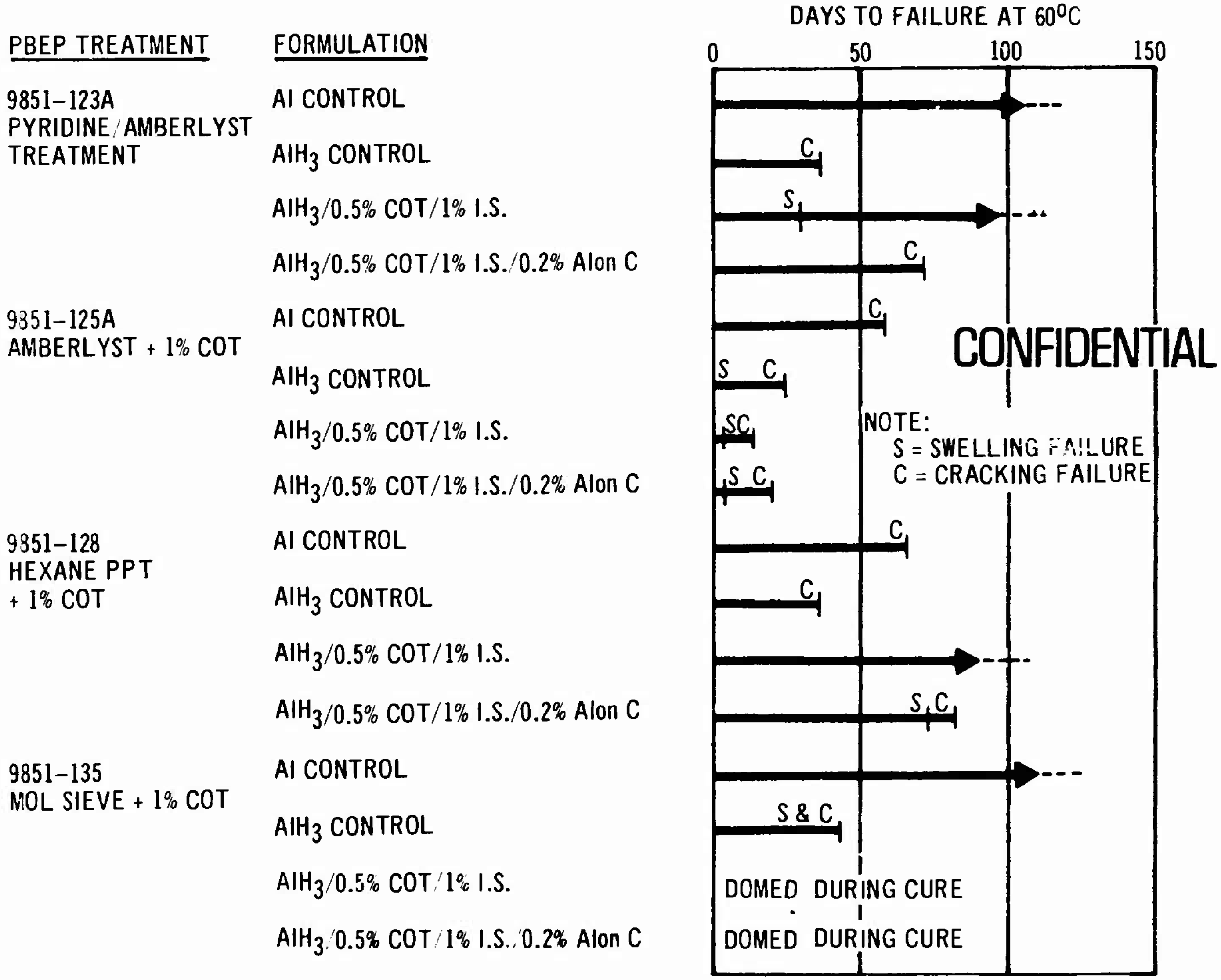

Figure 4 Two-Inch Elliptical Tube Data, 60°C Surveillance (Low Shear VB/RP Mixer)

c. Conclusions

(C) The data indicate that rather subtle changes can be effected in the PBEP structure that will affect both thermal stability of the material and compatibility with other ingredients. At the same time, rather minor changes in the degree of AlH_3 surface passivation, and related attrition effects (mixing) can affect sample stability and shelflife quite drastically; moreover, these latter effects can mask effects attributable to PBEP purity and stability.

(C) In overall stability the PBEP/Al and PBEP/AlH_3 systems compare favorably with TVOPA/Al and TVOPA/AlH_3 systems of comparable NF_2 content. This is shown in Figure 5 and 6 (60°C data).

(C) As regards treatment preference, the combination of data shows that in aluminized propellant, molecular sieve treatment and pyridine treatment produce closely similar results (failure times), while Amberlyst treatment impairs stability. In the aluminum hydride containing systems the hexane precipitated material and the pyridine treated material appear to exhibit better compatibility.

(C) Gas scavenger systems (Pd/C, Alon C) tend to improve shelflife of the AlH_3/PBEP systems quite markedly.

(U) To arrive at a more quantitative assessment it would be necessary to conduct a surveillance test program using a significantly larger number of individually processed samples to account for the numerous variables that exist. Duplicate samples from the same mix generally failed within a narrow time range (2-5 days), failure being indicated by the first indication of a sample volume change.

3. OFF GAS ANALYSES

(U) Samples of the AlH_3 propellants prepared with the 9851 PBEP series were used to determine gas evolution rates at 50 and 60°C, and for determining the time-temperature dependent changes in gas composition.

a. Gas Evolution Rates

(U) Micro-Taliani type manometers were used to determine gas evolution rates.

(C) The gas generation data for the Al-analog propellant samples are presented in Figure 7, and the data for the AlH_3 control propellants are plotted in Figure 8. The PCDE/Amberlyst-15 PBEP (9851-123A) is clearly the most stable in the Al-analog formulation. The molecular sieve/one percent COT PBEP (9851-125A) is the least stable. It is assumed that the gas generation data for the Al-analog formulation reflects the stability of the PBEP.

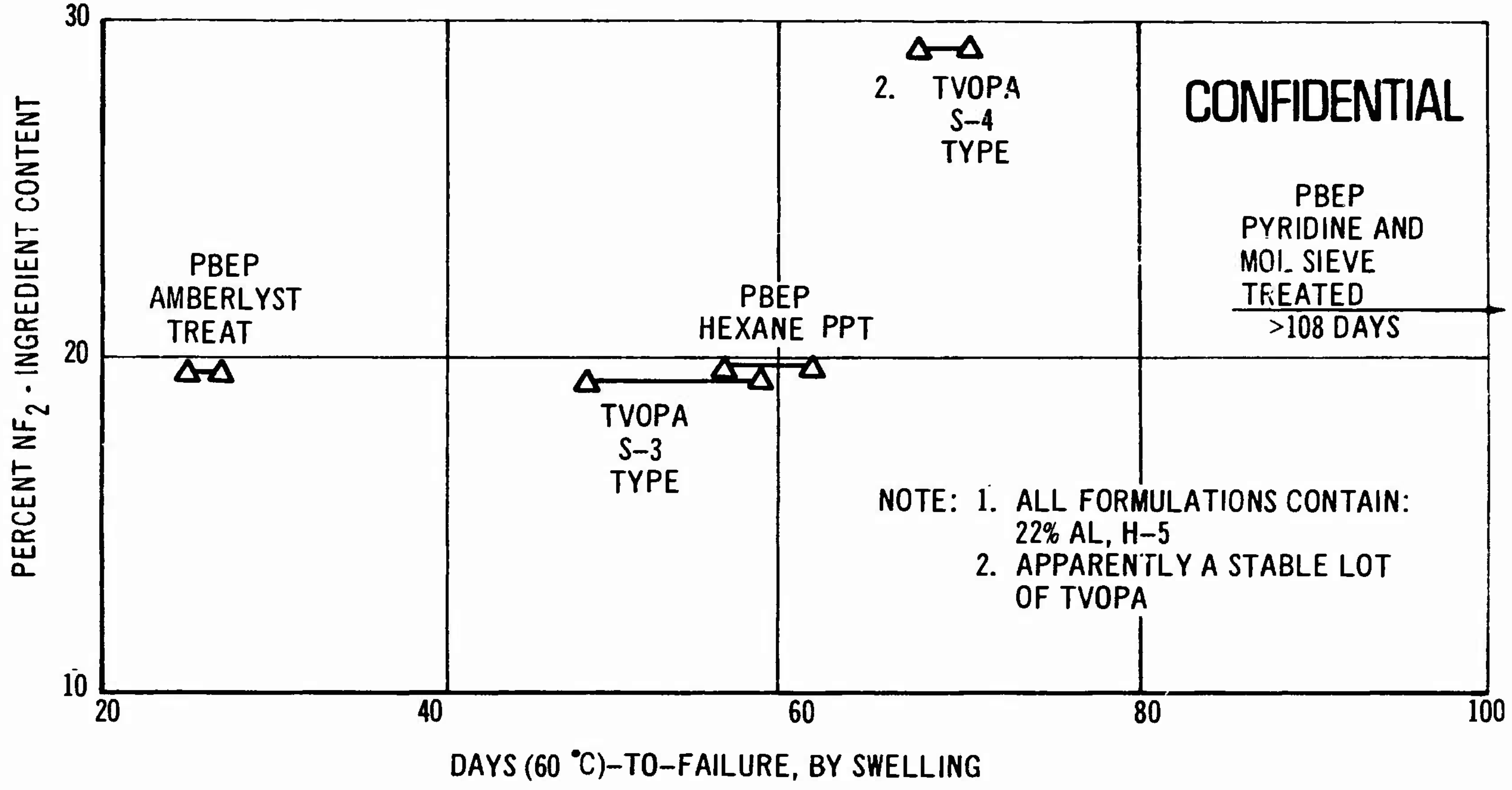

Figure 5 Comparison of PBEP and TVOPA Stability, Al Formulations, Two-Inch Elliptical Tube Data, 60°C Surveillance

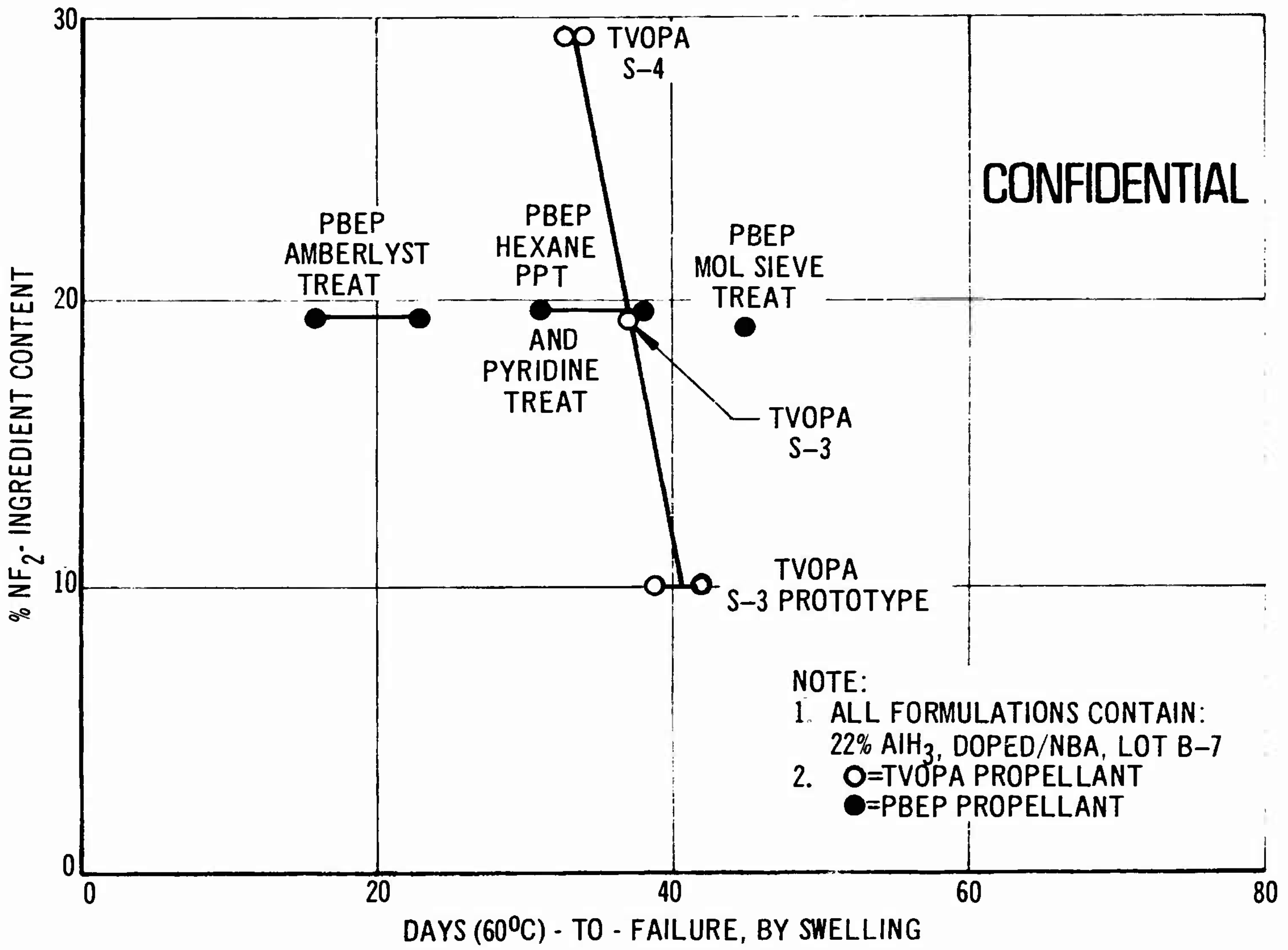

Figure 6 Comparison PBEP and TVOPA Stability, AlH_3 Formulations, Two-Inch Elliptical Tube Data, 60°C Surveillance

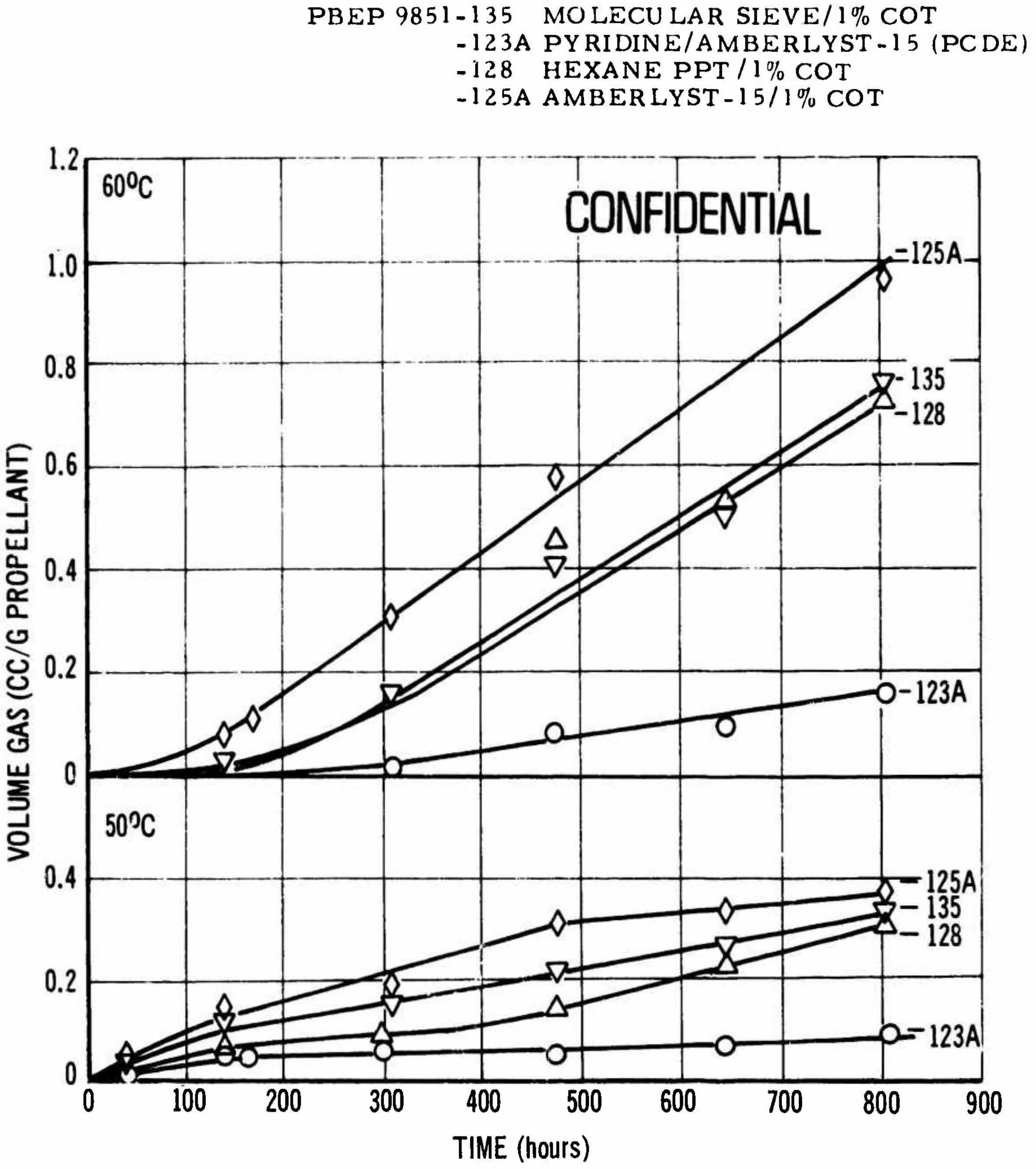

Figure 7 Gas Generation: Al-Analog Propellant

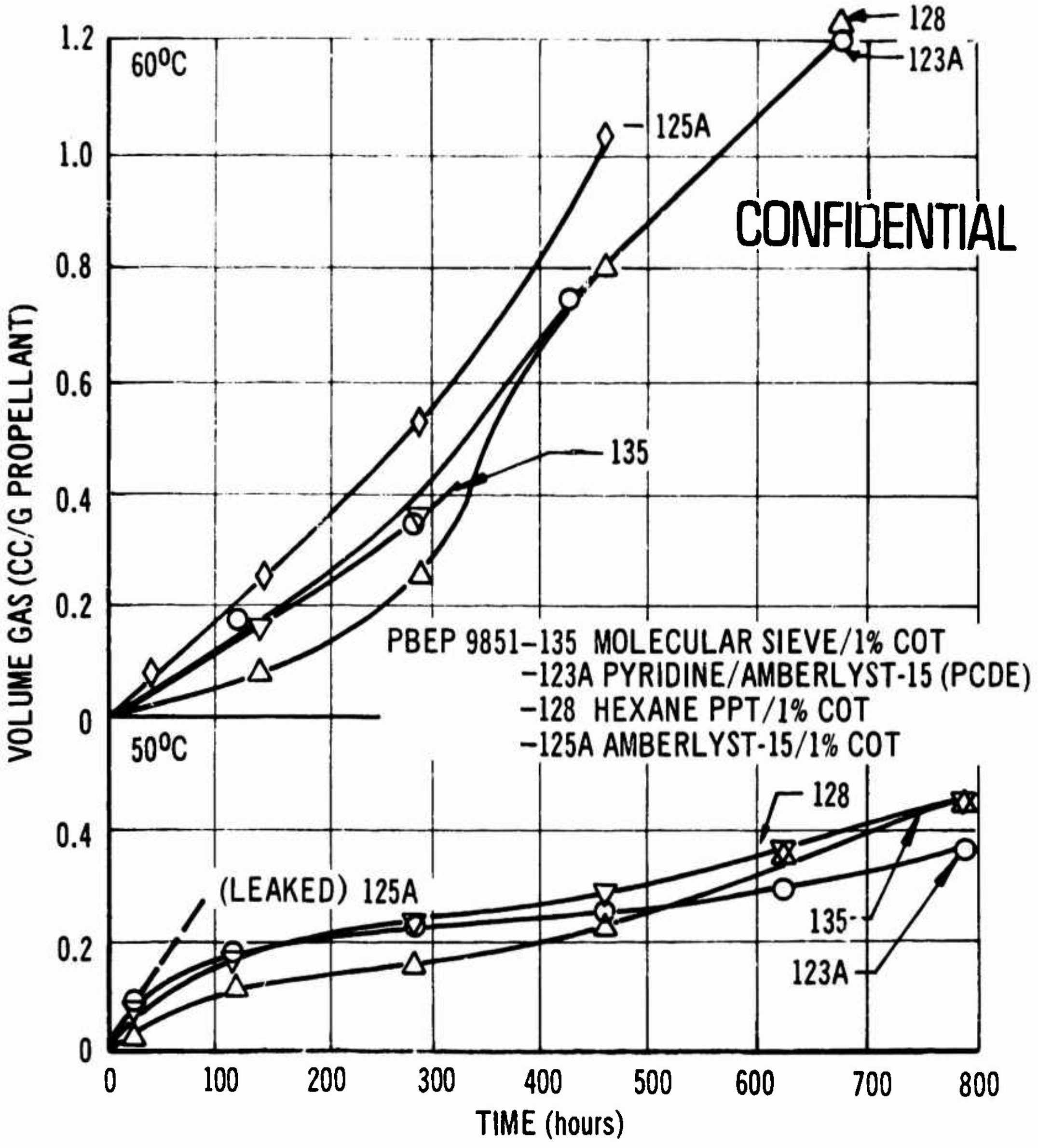

Figure 8 Gas Generation: AlH_3 Control Propellant

(C) No PBEP sample stands out with regard to gassing in the AlH_3 formulation. Possibly the Amberlyst-15/one percent COT PBEP is the least stable; the 60°C data would suggest this. The gas generation data for the AlH_3 formulation probably reflects the incompatibility among the propellant ingredients, in particular PBEP/AlH_3 interactions, rather than the stability of the PBEP per se. A detailed analysis is presented in the following section.

(U) Gas generation measurements for the AlH_3 formulation containing two scavenger compositions are presented in Figures 9 through 12. One scavenger consisted of an integrated scavenger and COT. The second scavenger was identical except for the addition of Alon C. The scavengers were found to be effective at 50°C but ineffective at 60°C. The marked negative temperature coefficient for the scavengers suggests that they will be very active under ambient storage conditions Two data points suggest that the addition of Alon C may have been beneficial. The scavenged formulation for the hexane precipitated PBEP shows a peculiar behavior that has been observed with R-18/TVOPA/AlH_3/AP propellants; the small initial volumes of evolved gas are completely absorbed by the scavenger. This pattern of activity, which is under active investigation with the TVOPA propellant, is thought to be due to an induction period associated with the hydrogenation catalyst.

b. Off Gas Analyses

(U) The gases evolved in the Taliani manometers were sampled periodically and analyzed with a Perkin Elmer Model 270 mass spectrometer.* It can be presumed that the off gases from the aluminized systems primarily reflect slow PBEP degradation (PBEP thermal stability), while the off-gases from the AlH_3 propellants reflect PBEP/AlH_3 compatibility and scavenger action.

(1) Aluminized Propellants

(U) The analytical results that were obtained on the off-gases of the aluminized propellants are summarized in Figure 13. At 60°C the dominant gaseous products are CO_2, HCN, CO and nitrogen, while at 60°C CO_2 dominates with HF, HCN, CO and N_2 being present in lesser quantities.

(C) The propellants containing the hexane precipitated and the pyridine treated PBEP had the lowest rates of gas production with respect to all species except carbon monoxide.

(U) There are significant variations in the temperature coefficients and also in the time dependence. For example, nitrogen gas generation rates vary little with temperature and with time; on the other hand, CO_2 concentrations increase both with time and temperature. This suggests that

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* The authors wish to thank Mr. Berge Goshgarian of the Air Force Rocket Propulsion Laboratory who ran a number of off-gas samples for use in the high resolution mass spectrometer and helped in the identification of species.

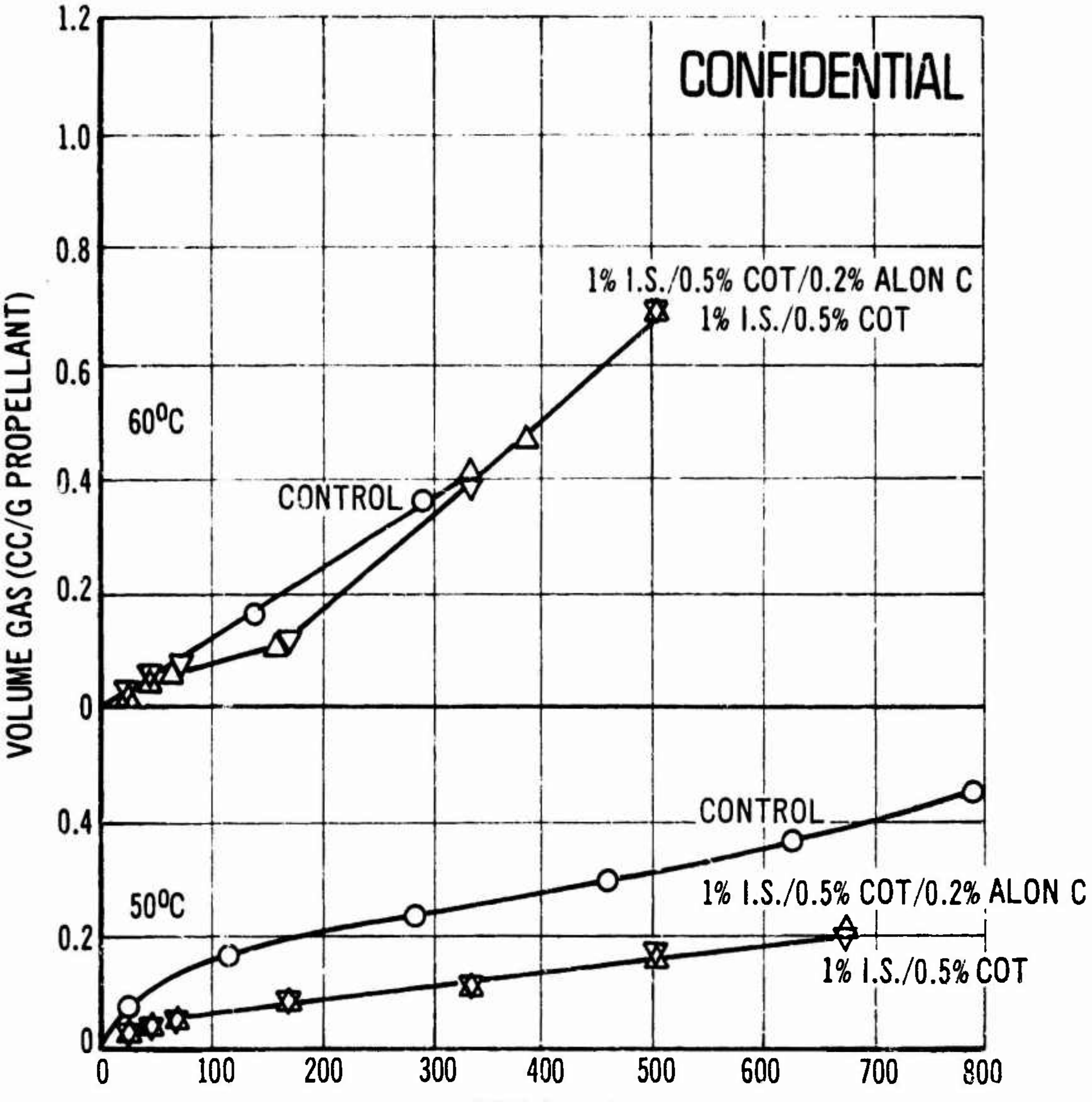


Figure 9 Gas Generation: PBEP 9851-135 (Molecular Sieved/1% COT)/Scavenger

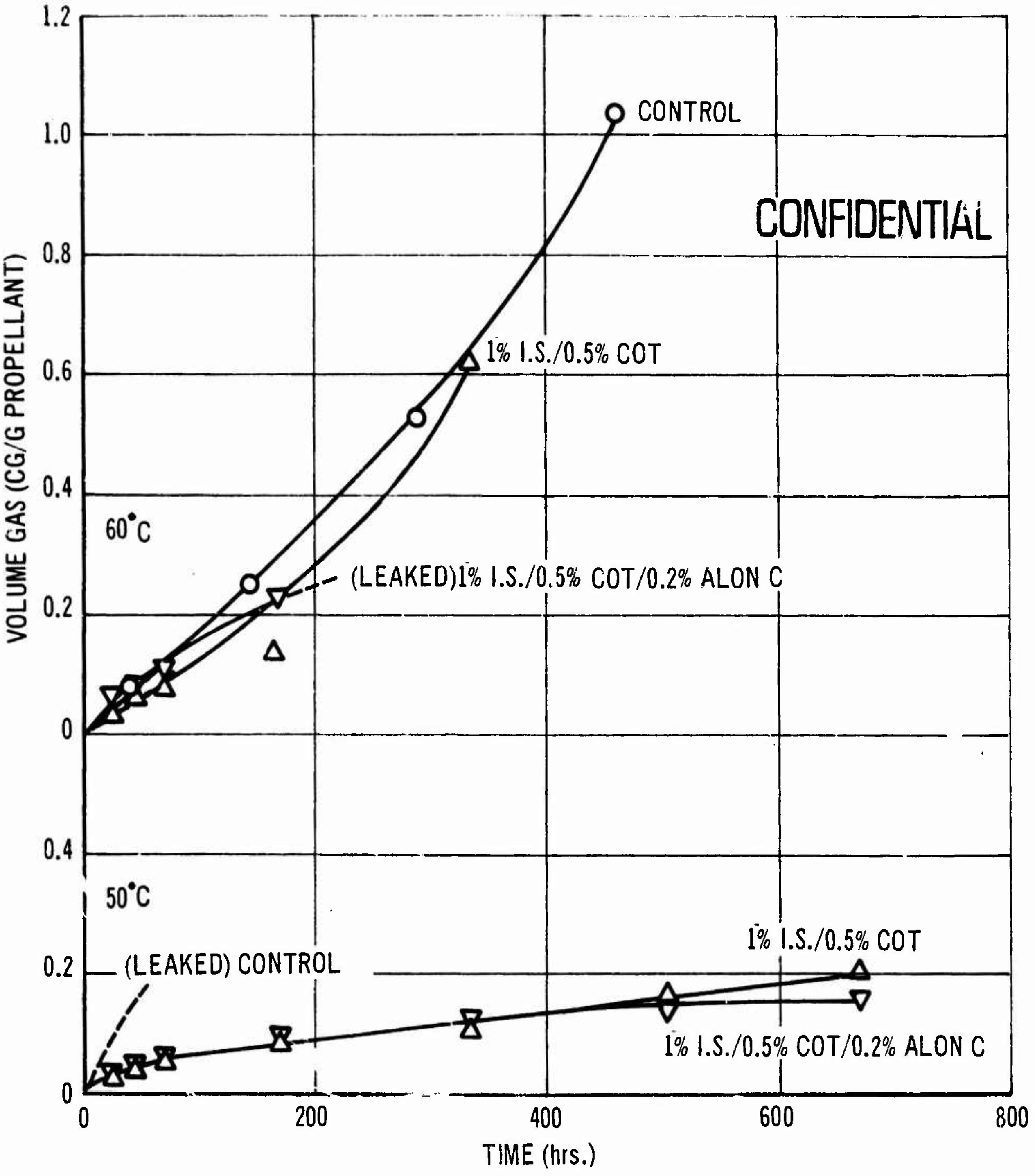


Figure 10 Gas Generation: PBEP-125A (Amberlyst-15/1% COT)/ Scavenger

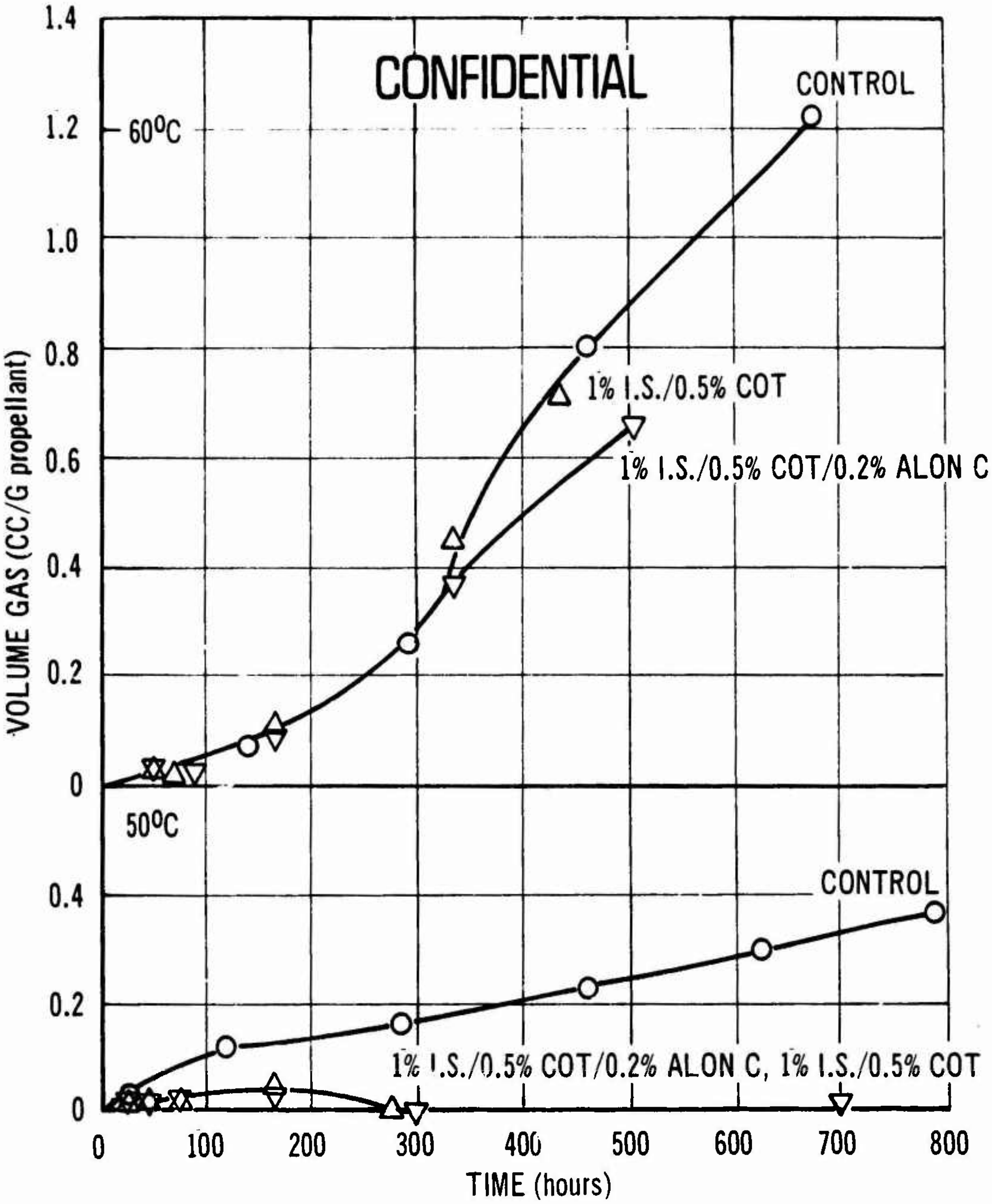


Figure 11 Gas Generation: PBEP 9851-128 (Hexane ppt/1% COT)/ Scavenger

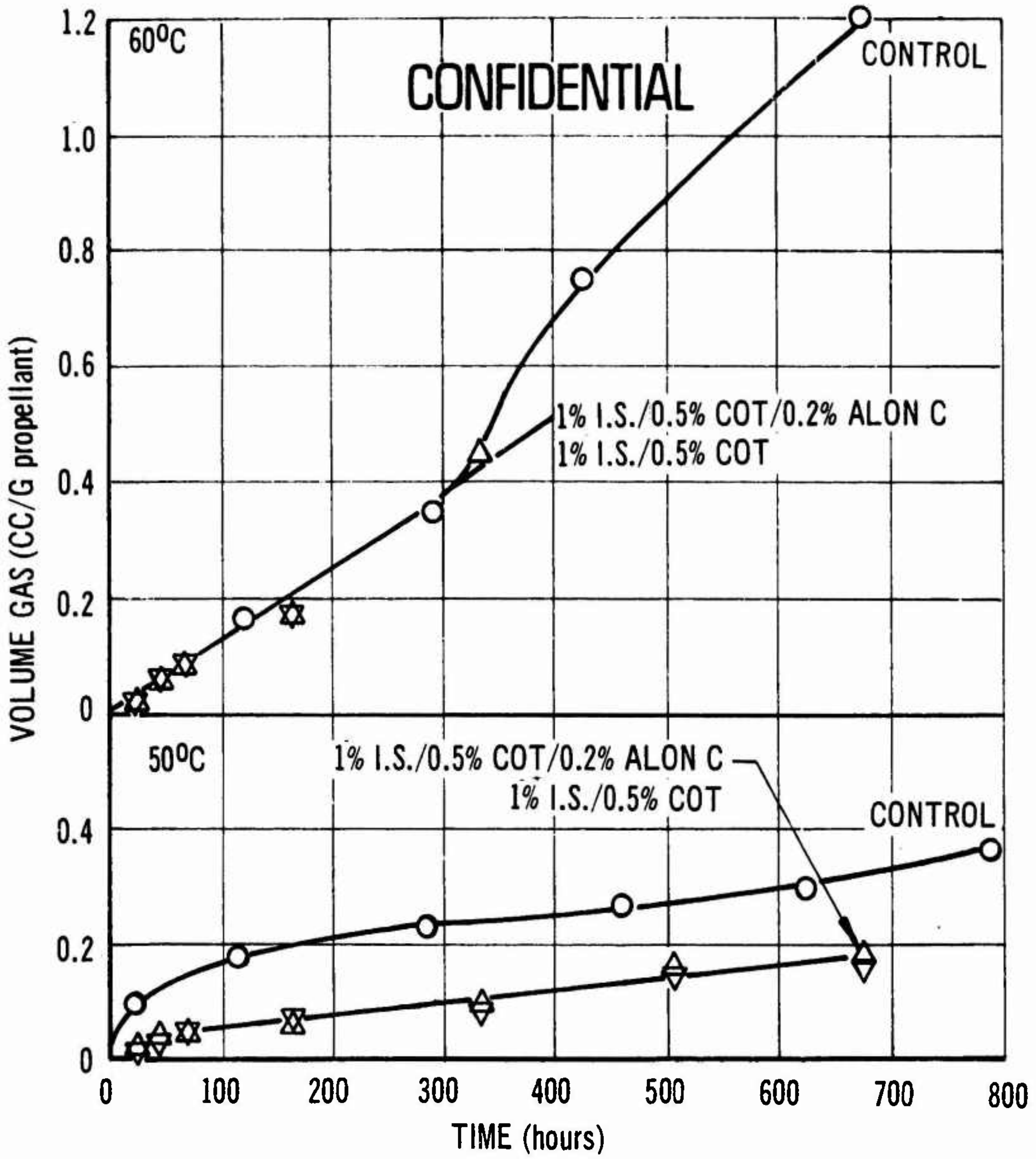


Figure 12 Gas Generation: PBEP 9851-123A (Pyridine/Amberlyst-15)/ Scavenger

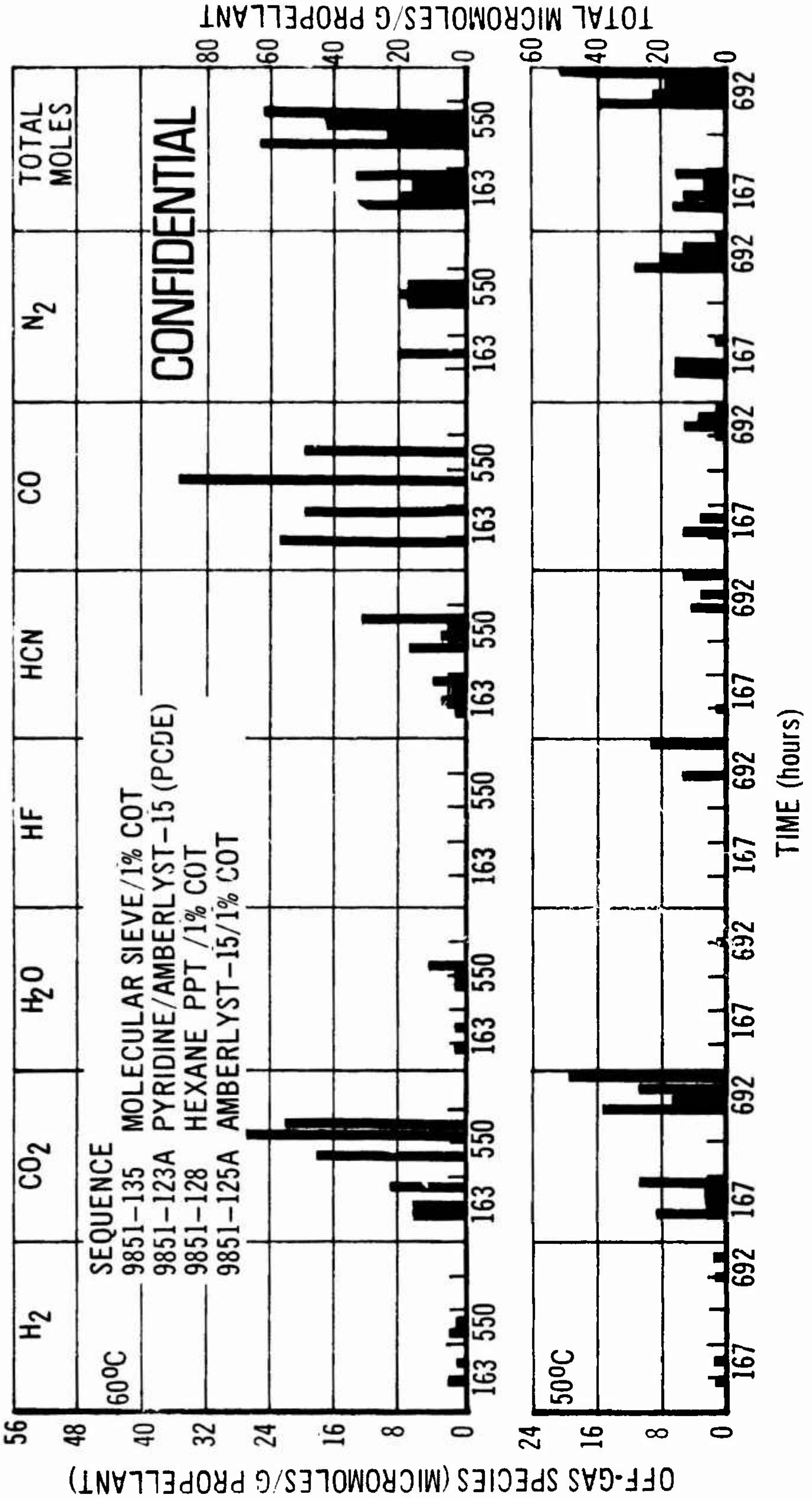


Figure 13 Off-Gas Composition: Al-Analog PBEP Propellants

different mechanisms are involved, which, in turn, could be indicative of different levels of residual impurities in all samples.

(2) Aluminum Hydride Propellants

(U) The various PBEP materials were studied both with scavenger-free and scavenger-containing formulations, and in conformance with the surveillance tests at both 50 and 60°C.

(U) The combination of the data (Figures 14 - 18) suggests that 60°C, or even 50°C, is too high a test temperature for obtaining meaningful data as the off-gas analyses reflect both stability and compatibility problems, and since the temperature coefficients for the various underlying processes seem to vary considerably.

(a) Effect of PBEP Treatment

(C) Figure 15 summarizes the data that were obtained with the scavenger-free propellant samples. At 60°C the predominant gaseous species are carbon monoxide, HF, hydrogen, CO_2 and HCN, while H_2O levels vary significantly between samples. At 50°C the dominant species is CO_2; additionally, CO is formed to a significant extent with the sample containing the molecular sieve treated material.

(C) It is noteworthy that the concentration of some gases increases very little with time (e.g., nitrogen in all samples, H_2O at 50°C), which again is indicative of residual impurities and/or changes in mechanisms. As with the aluminized propellants there is only a slight increase in the rate of nitrogen production in going from 50°C to 60°C, while the temperature coefficients for the production of HF and CO appear to be quite large notably with the samples containing the molecular sieve treated PBEP.

(b) Effect of Scavengers

(C) The scavenger systems that were evaluated are the Pd/COT hydrogen scavenger and Alon C, the latter presumably acting as an HF scavenger.

(C) The combination of data (Figures 16 - 19) shows that the hydrogen scavengers become active in condensing hydrogen gas only as the temperature is lowered; at 60°C this scavenger system appears to catalyze the decomposition of PBEP or of PBEP impurities as indicated by high rates of H_2O and CO production. High rates of hydrogen gas evolution associated with low rates of HF production, suggest HF-AlH_3 interaction. In the propellant containing the pyridine treated PBEP hydrogen gas evolution at 60°C is further enhanced by addition of Alon C.

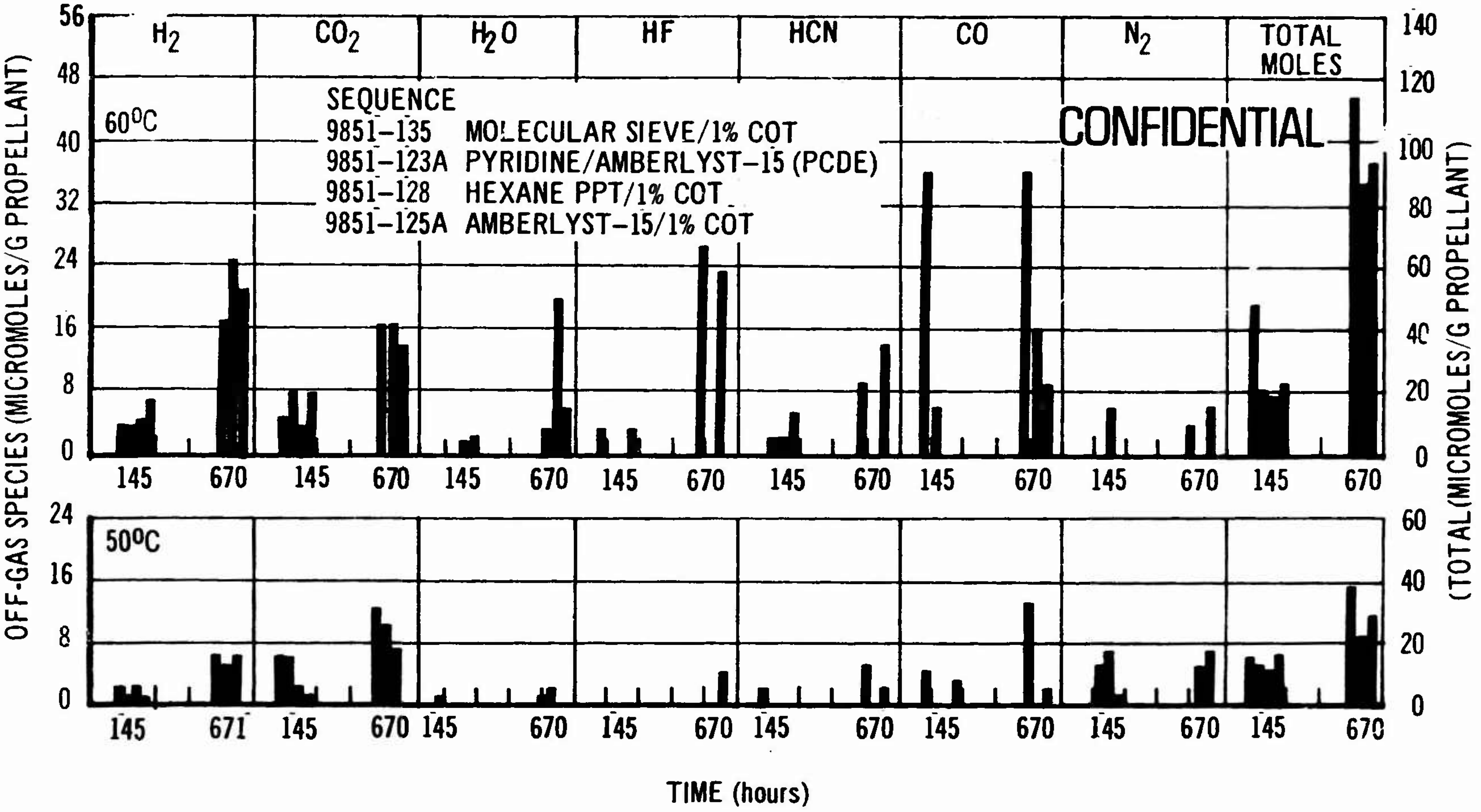


Figure 14 Off-Gas Composition: PBEP/AlH$_3$ Propellants

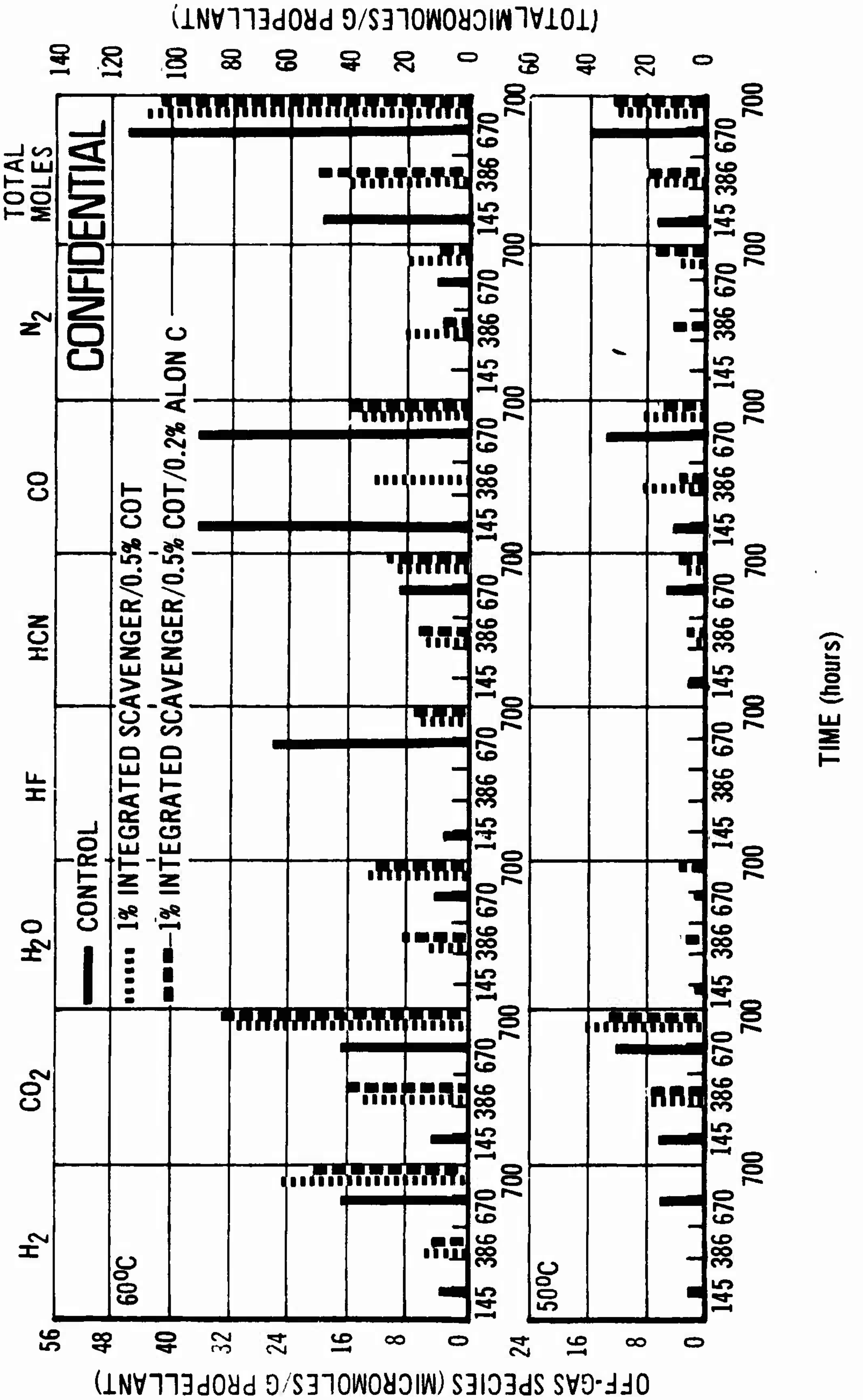


Figure 15 Off-Gas Composition: PBEP (Molecular Sieve/1% COT)/AlH$_3$ Propellant

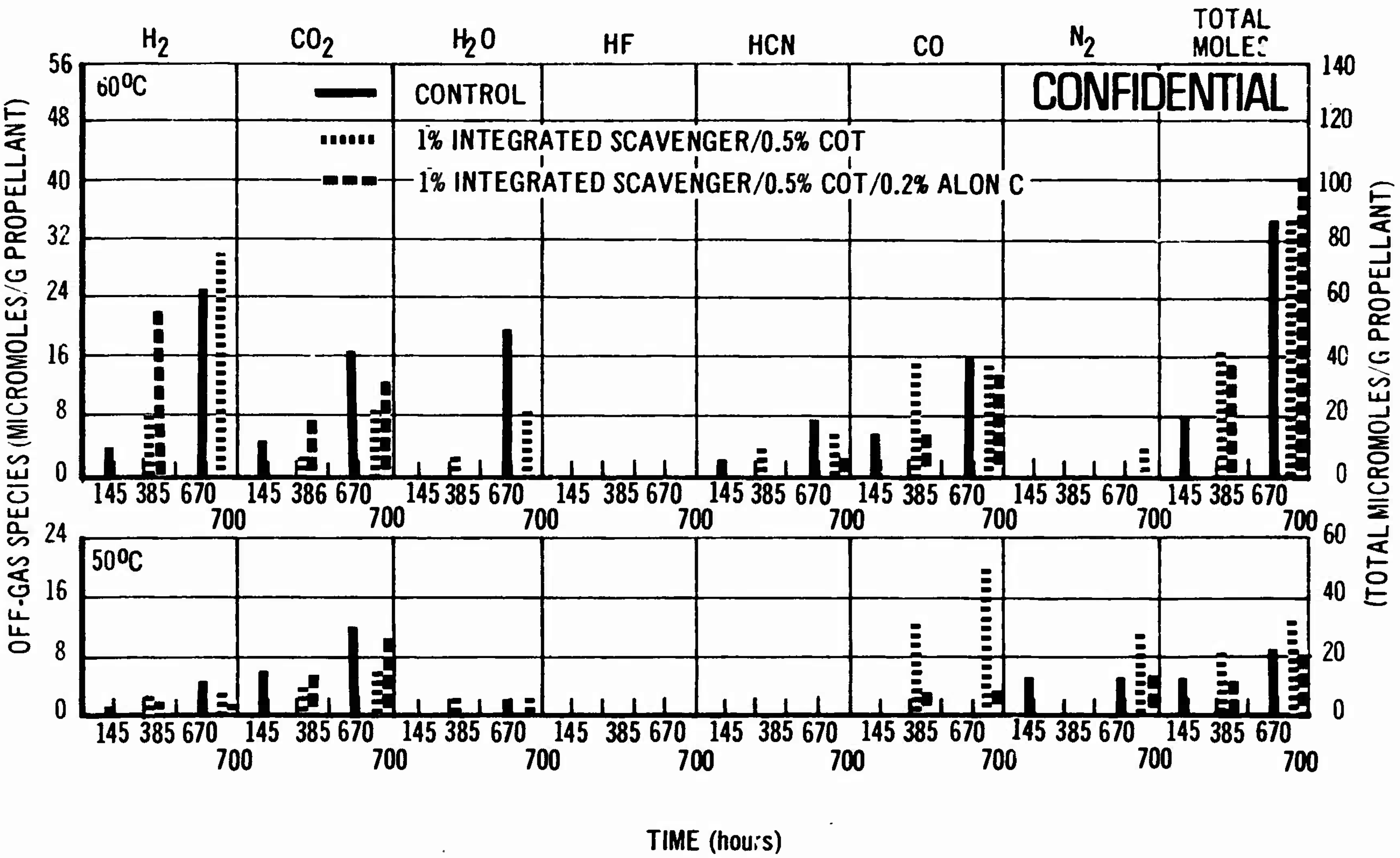


Figure 16 Off-Gas Composition: PBEP (Pyridine/Amberlyst-15; PCDE)/AlH_3 Propellants

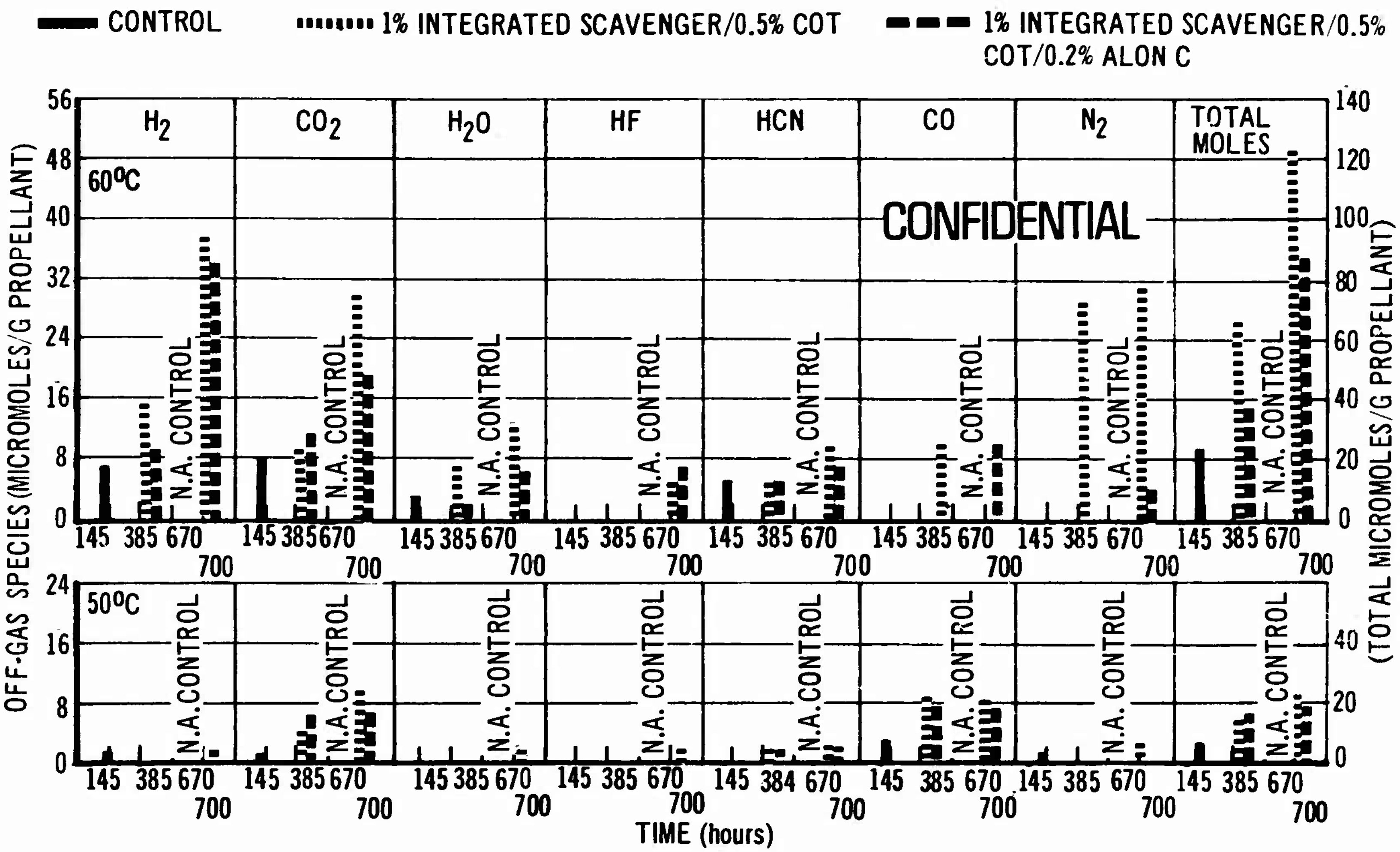


Figure 17 Off-Gas Composition: PBEP (Amberlyst-15 Treated/1% COT)/AlH3 Propellants

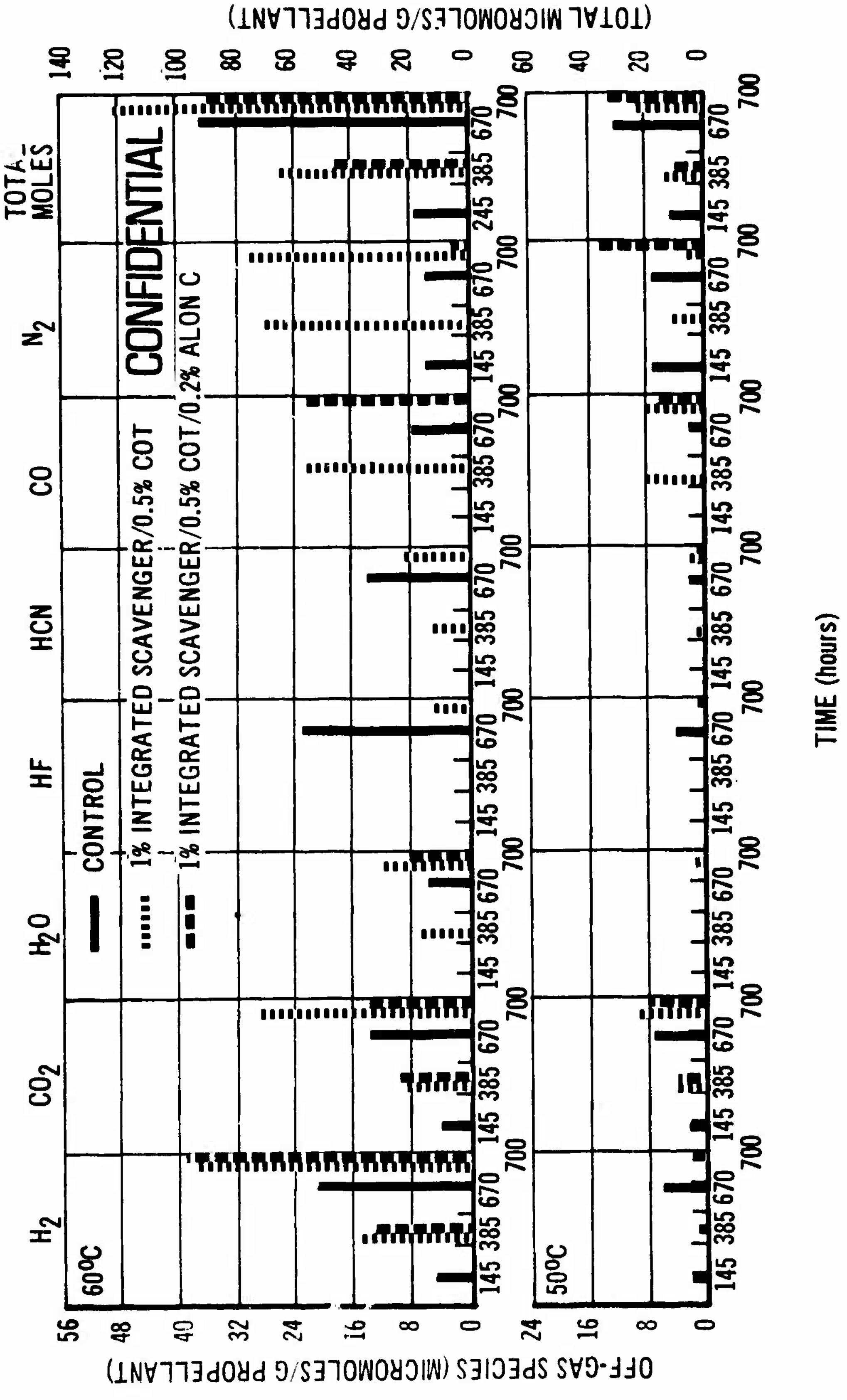


Figure 18 Off-Gas Composition: PBEP (Hexane Precipitated/1% COT)/AlH_3 Propellants

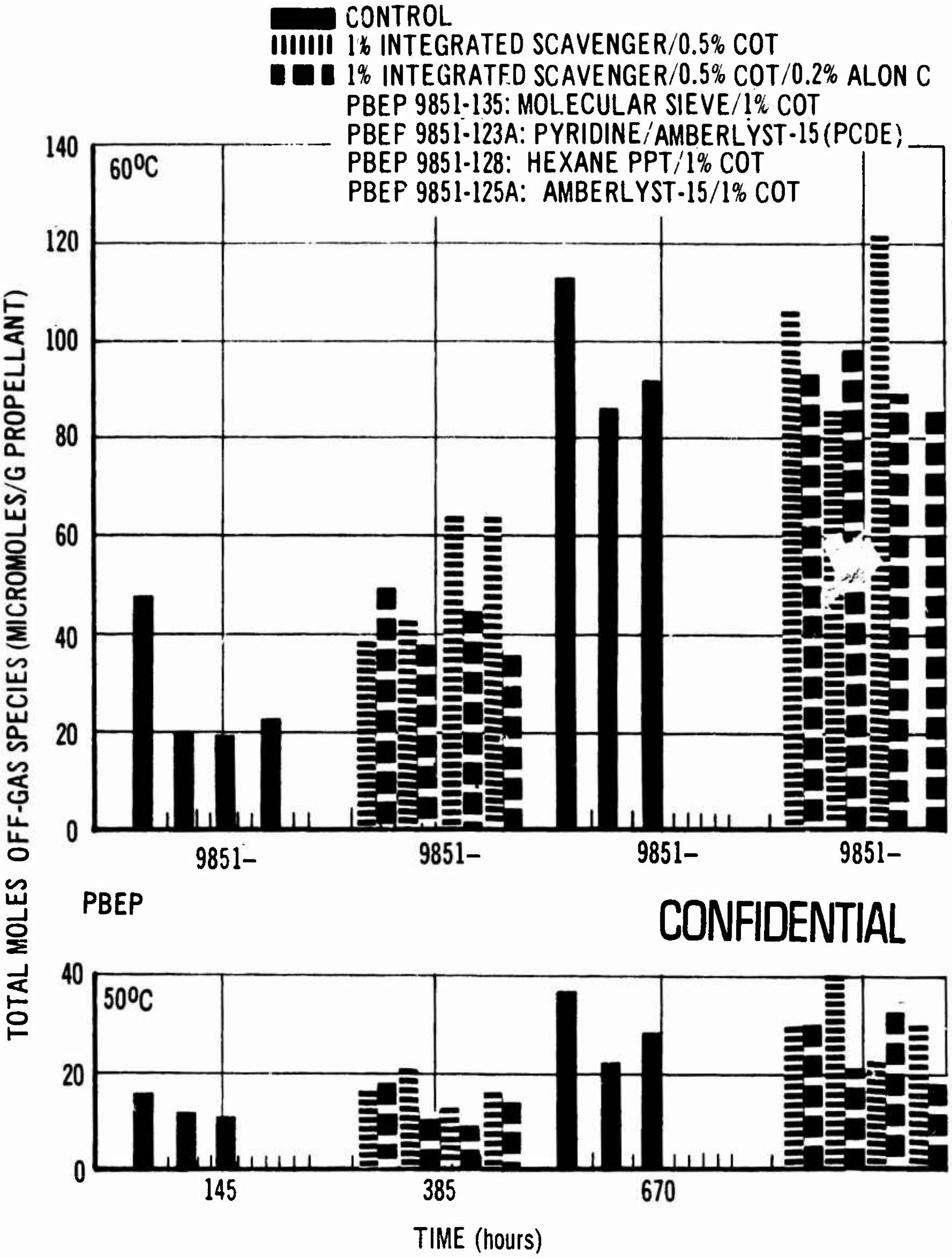


Figure 19 Effect of Scavengers and PBEP on Off-Gas Evolution: PBEP/AlH_3 Propellant

(C) Lowering the temperature to 50°C generally reduces gas generation rates quite markedly, with CO_2 and CO remaining as the dominant species in essentially all cases. In contrast to the 60°C data, Alon C addition tends to reduce gas generation rates at 50°C; this effect is particularly pronounced in the rates of CO evolution with the pyridine treated material.

(3) Conclusions

The conclusions to be drawn from these gas analyses are as follows:

- For use in aluminized formulations, the hexane precipitated and the pyridine treated PBEP appear best. With either material only the CO_2 concentration increases markedly with time, which is indicative of residual impurities that undergo slow oxidation to CO_2. It implies that further raffination of PBEP should enable use of propellant storage temperatures in excess of 60°C.
- With the aluminum hydride containing propellants a test temperature of 60°C is excessive; at this temperature the hydrogen scavengers, rather than stabilizing the system, seem to be catalyzing the decomposition of PBEP or PBEP impurities. At 50°C the scavenger systems start to become active; however, in addition to hydrogen and carbon dioxide, i.e., gases that could be scavenged, significant quantities of carbon monoxide and of nitrogen are formed, that presently cannot be scavenged.

(C) At 50°C carbon monoxide formation is most pronounced with the samples containing the pyridine treated PBEP in combination with Pd/COT; there is a marked reduction in CO production if the sample additionally contains Alon C. With the hexane precipitated material the situation is reversed.

4. MASS THERMAL ANALYSIS

(U) Off-gas analyses conducted with propellants, and by standard techniques (Taliani manometric measurements combined with MS analysis), only evidence the end-products of a complex series of chemical processes, consequently, the data may prove of limited value in associating apparent instability with the presence of specific materials or related impurities. On the subject program the emphasis was upon the evaluation of various procedures used to purify PBEP, and there was need to supplement the surveillance data and the off-gas analyses by additional test data that would more clearly identify the chemical changes brought about in the composition of the PBEP samples as a function of sample treatment. The method that was used was the Mass Thermal Analysis (MTA) technique.

a. Description of Method

(U) In the mass thermal analysis method small (microgram quantities of the materials are pyrolyzed in the immediate vicinity of the ionization region of a time-of-flight mass spectrometer, and the composition of the decomposition species is monitored by recording the full mass spectra at the rate of 200 spectra/second while concurrently monitoring sample temperature. In the present study, sample heating rates of 80-150°C/second were used.

(C) Since the sample is present as a thin film, sample heating (linear heating rate) to cause fractionation and pyrolysis is effected under vacuo, and since the operation is conducted in the immediate vicinity of the ionization beam, the technique provides information upon the primary species that are produced (volatilized) and in a manner that enables the deduction of initiating reaction kinetics. Moreover, since the spectral data acquisition rate is high, one can arrive at a description of the sequence of thermochemical events. For example, and to state some of the results at this point, in the case of "as received" PBEP, HF generation is preceded by the generation of mass m/e 45+. but paralleled by the generation of high molecular weight (m/e ~200) species. The data thereby indicate that crude material contains low molecular weight materials that have undergone partial dehydrofluorination during sample work-up or storage. In the conventional analysis techniques, by contrast, the identifiable products would in all cases be HF and HCN.

(U) The test samples were prepared by depositing the sample (14-17 micrograms) upon a platinum ribbon, the latter serving as the heating element for pyrolysis. In all cases the samples which were received in methylene chloride solution were stripped of solvent under vacuum in a rotary evaporator, applied to the ribbon in the neat state, weighed on an electrobalance (accuracy ±0.1 microgram) and inserted into the mass spectrometer. They were exposed to the high vacuum of the spectrometer for 30-40 minutes prior to pyrolysis.

(U) The data reduction method is described in detail in the reports issued under contract FO4611-68-C-0079 (Ref 1).

b. General Results

(1) Summary of Test Data

(C) The thermal decomposition of both PBEP and PCDE proceed via a series of thermal events that produce different mass species as the sample temperature is increased. This is shown schematically in Figure 20 using hexane precipitated PBEP as the example.

(U) Pyrolysis starts with the appearance of masses m/e 45, 43 at temperatures below 140°C (Frames 5-150). These mass species, in this thermal region form a shoulder without distinct peak.

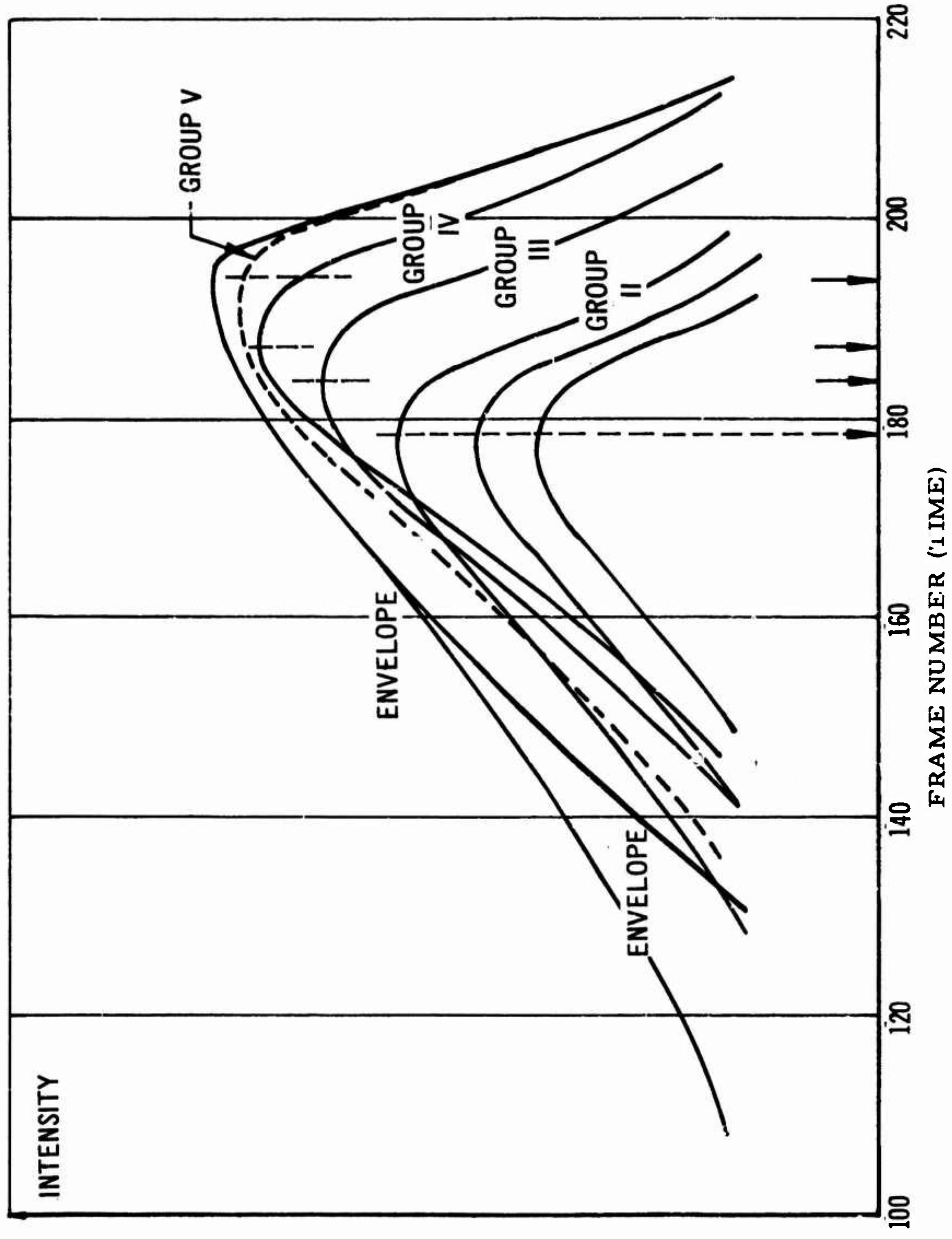


Figure 20 Sequence of Thermal Events, PBEP Pyrolysis

(U) Subsequently a first distinct peak is formed by mass species m/e 89, 143 and 196 (Group II, listed in decreasing order of intensity). These species peak at 179°C (Frames 190-100). Immediately thereafter there is a new peak that is formed at 183°C (Frames 195-205) by mass species m/e 71, 57, 59, 63, 87, 96, 103 and 105 (Group III, again listed in decreasing order of intensity). Moreover mass m/e 45 peaks within this thermal region. The subsequent peak at 187°C (Frames 205-210) is formed by mass species m/e 33, 66, 52, 43, 124, 92 and 75 (Group IV). Finally there is a rather diffuse peak at 194°C (Frames 205-215) that comprises mass species m/e 27, 47, 31, 41, 40, 54, 30, 44, 26, 39, 55, 61, 19, 82, 85 and 68. Mass species 20 and 29, which together with mass species 45 form the envelope, also peak in this region.

(C) With the PBEP samples the pyrolysis ends rather abruptly, while with the PCDE samples various mass species continue to be produced for quite some time (e.g., m/e 14, 27, 29, 30, 43, 44). Moreover, there is less of a distinction between thermal events with the PCDE; instead there are numerous "bursts" wherein series of mass species are being generated, some species showing peaks at two different temperatures.

(C) A tabulation of the observed mass species and relative intensities is given in Table VI. Also shown in this tabulation are tentative structures. Since many of the tabulated species, however, can be presumed to originate with different parents it is not possible to arrive in all cases at an unequivocal structure assignment. The tabulation shows the qualitative differences in the pyrolysis products composition between PBEP and PCDE (pyridine treated PBEP); in addition there were noticeable differences between the various PBEP samples (Molecular Sieve treated, Amberlyst treated, Hexane precipitated) that will be discussed in more detail.

(U) Table VII quotes maximum intensities for selected mass peaks normalized to m/e 71 as a reference peak.* Table VIII quotes areas under the time-intensity peaks for the same mass species, and maximum intensities as a function of sample weight.

(U) Arrhenius type plots showing the 1/T-intensity traces for major mass species for the various samples are given in Figures 21 through 24. In this data presentation the presence of impurities in the various samples is indicated by the break in the curves. For example, hexane precipitation of PBEP effects a significant increase in the apparent activation energy for the generation of mass species m/e 45, 33, 66 and 29, notably during the early stages of sample pyrolysis. The plots also suggest that even after hexane precipitation some impurities still remain in the sample.

(2) Interpretation of Data

(C) The data that were obtained can be interpreted as follows:

(C) * The selection of m/e 71 as a reference is arbitrary. This peak appears both in the PBEP and the PCDE spectra during the peak decomposition period, and it is presumed to originate with the methoxylated chain links.

TABLE VI

MASS ASSIGNMENTS

Mass Number m/e	Formula(s) Positive Ions of:	Relative Intensities PBEP	Relative Intensities PCDE
12	C	+	+
13	CH	+	+
14	CH, N	+++	+++
15	CH, NH	+++	+++
16	NH_2, O	+	+
17	NH_3, OH	nil	nil
18	OH_2	nil	nil
19	OH_3, F	++	++
20	HF	+++	+++
24	C_2	nil	nil
25	C_2H	nil	+
26	C_2H_2, CN	+++	+++
27	C_2H_3, HCN	+++	+++
28	C_2H_4, CH_2N CO, N_2	+++	+++
29	C_2H_5, CH_2NH CHO	+	+
30	CH_2NH_2, CH_2O	+	+
31	CH_2OH, CF	++	++
32	CH_3OH, CHF , O_2	+	nil
33	CH_2F, NF	+++	[illegible]
34	HNF	nil	++
38	C_3H_2, C_2N	+	++
39	C_3H_3, CHCN	+	+
40	C_3H_4, CH_2CN , C_2O	++	+++
41	C_3H_5, CH_2CNH , HCCO	++	++
42	C_3H_6, CH_2CHNH , CH_2CO	++	++
43	C_3H_7, CH_3CO , CONH	+++	++
44	$CHOCH_3$, HCONH , C_2HF	++	++
45	$HOCH_2CH_2$, CH_2OCH_3 , C_2H_2F, CNF	+++	+++
46	C_2H_3F, CHNF	+	+
47	C_2H_7O (from CH_3OCH_2R) C_2H_4F, COF	++	++
51	CHCCN , CHF_2	+	+
52	CHCHCN , NF_2	+++	+++
53	CH_2CHCN , HNF_2	+	+
54	COCN , CH_2CCO , CH_2CH_2CN	++	+++
55	CH_2CHCO	+	+
56	CH-$COCH_3$, CHCONH	+	+
57	CH_2COCH_3, $CHCHOCH_3$ CF_3	++	+
58	$CHCH_2OCH_3$	+	+

TABLE VI (Continued)

Mass Number m/e	Formula(s) Positive Ions of:	Relative Intensities	
		PBEP	PCDE
59	CH_2CNF	++	+
60	CH_2CHNF	+	+
61	CONF	+	+
62	C_2F_2	+	+
63	C_2HF_2	++	++
64	$C_2H_2F_2$	+	+
65	$C_2H_3F_2$	+	+
66	NCCCO , CH_2NF_2	+++	+++
67	NCCHCO	(+)	(+)
68	$NCCH_2CO$	+	+
69	$HCCCHOCH_3$, NC-CCF	+	+
70	$HCCCH_2OCH$, NC-CHCF	+	++
71	$H_2CCCH_2OCH_3$, $NC-C_2H_2F$	++	++
72	$CH_2CHCH_2OCH_3$	+	+
73	$OC-CH_2OCH_3$	+	+
74		(+)	(+)
75	C_3HF_2	+	+
76	$C_3H_2F_2$	(+)	(+)
77	$C_3H_3F_2$	+	+
78	$OCCF_2$	+	+
79		(+)	+
80		(+)	+
82	C_2HF_3	+	++
83	CF_2NF , $C_2H_2F_3$	(+)	(+)
84		nil	nil
85	OC-CF CN	+	+
86		(+)	(+)
87	$HOCH_2C$ $CHOCH_3$	++	+
89	$HOCH_2CH$ CH_2OCH_3 $CH-CF_2$ CN	++	(+)
90	NC-CF+NF	(+)	(+)
91		+	(+)
92		(+)	(+)
94		+	+
96	$FN+CH-CF_2$	+	+
100	C_2F_4	(+)	+
103		++	+
105		++	+
124	$CH_3OCH=CHOCH=C-CN$	++	(+)
143	$CH_3OCH=CHOCH=CF$ CN	++	-
197	$CH_3OCH=CHOCHC=NF$ $HCNF_2$	++	-

NOTE

Relative intensities:
+ = Weak
++ = Medium
+++ = Strong
- = Not present

(The reverse is blank)

TABLE VII

MASS SPECTRA OF PBEP SAMPLES

	Mol Sieve	Amberlyst	Hexane Precipitate			Pyridine Treatment		
	41-4	43-1	41-3	48-4	Ave	42-2	42-3	Ave
m/e	Imax	Imax	Imax	Imax	Imax	Imax	Imax	Imax
14	34	32	30	71	50±20*	90	75	82±7
15	44	45	43	77	60±17	145	117	131±14↑
20	165	179	260	226	243±17	200	140	170±30*↓
26	28	36	35	40	38±2	126	88	107±19*↑
27	98	118	100	125	112±12	166	138	152±14↑
28	158	208	270	212	241±19	237	203	220±17
29	168	136	130	197	163±33*	162	170	166±4
30	61	41	100	54	72±18*	33	47	40±7
31	67	74	57	88	72±16*	59	61	60±2
33	226	210	228	242	235±7	164	116	140±24*↓
40	44	63	135	65	100±35*	125	122	123±2
41	56	72	65	74	70±5	54	56	55±1
42	59	77	65	88	76±12*	136	85	110±26*
43	76	77	71	100	86±15*	128	125	126±2↑
44	67	68	41	59	50±9	96	80	88±8↑
45	222	224	238	274	256±18	196	191	194±3↓
47	100	82	86	106	96±10	64	69	66±3↓
52	160	125	160	114	137±23*	138	138	138±0
54		48	127	68	98±30*	113	125	119±6
57	48	54	57	68	62±5	31	39	35±4↓
59	45	50	54	66	60±6	26	29	27±2↓
63	40	40	114	60	87±27*	41	40	40±1
66	165	163	174	208	191±17	96	113	104±9↓
71	100.0	100.0	100.0	100.0	-	100.0	100.0	-
75	18	23	54	35	45±10*	50	44	47±3
87		29	82	43	62±20*	21	25	23±2
89	74	90	62	83	72±10	26	24	25±1↓

* Considered outside of range of instrument and reading error within duplicate runs. Direction of arrows signify direction of change of PCDE from Hexane precipitated PBEP.

TABLE VIII

AREAS UNDER TIME-INTENSITY CURVES FOR SELECTED M/E

	Mol Sieve		Amberlyst			Hexane Precipitate					Pyridine Treatment			
m/e	Area	Ratio Area/Im	Area	Ratio Area/Im	Area	Ratio Area/Im	Area	Ratio Area/Im	Area	Area	Ratio Area/Im	Area	Ratio Area/Im	Area
15	122	2.77	43	1.00	46	1.05	75	1.01	60±15	10	0.09	13	0.09	12±2
20	210	1.27	213	1.17	276	1.05	272	1.18	274±2	233	1.66	305	1.52	269±36
26	26	0.93	16	0.44	25	0.71	31	0.77	28±3	78	0.89	117	0.93	98±20
27	232	2.37	85	0.72	237	2.36	-		-	215	1.55	305	1.84	260±45
29	398	2.38	120	0.89	309	2.41	181	0.90	245±64	270	1.59	285	1.75	278±8
33	260	1.16	164	0.79	210	0.92	208	0.85	209±1	170	1.47	194	1.18	182±12
40	36	0.82	29	0.46	91	0.67	47	0.72	69±22	85	0.70	91	0.72	88±3
43	72	0.96	80	1.03	60	0.83	86	0.84	73±13	166	1.33	235	1.83	200±35
45	242	1.10	236	1.05	241	1.01	282	0.97	261±20	318	1.66	376	2.02	347±29
52	206	1.29	96	0.74	182	1.14	103	0.88	142±40	200	1.45	185	1.34	192±8
66	128	0.78	120	0.74	118	0.67	152	0.72	135±17	81	0.72	79	0.82	80±1
71	100.0	1.00	100.0	1.00	100.0	1.00	100.0	1.00		100.0	1.00	100.0	1.00	
89	80	1.08	84	0.87	72	1.18	76	0.90	74±2	20	0.83	19	0.73	20±1
Run No.	41-4		43-1		41-3		48-4			42-3		42-2		
Sample Wt, micrograms	6.4		14.4		5.9		4.4			16.4		16.4		
$I_m^{71}/10$ g	270		153		125		160			177		208		
$Area^{71}/10$ g	78		34		22		32			34		27		
Heating Rate, °C/sec	146		85		158		100			90		133		

NOTE: Im = Peak maximum intensity (height)

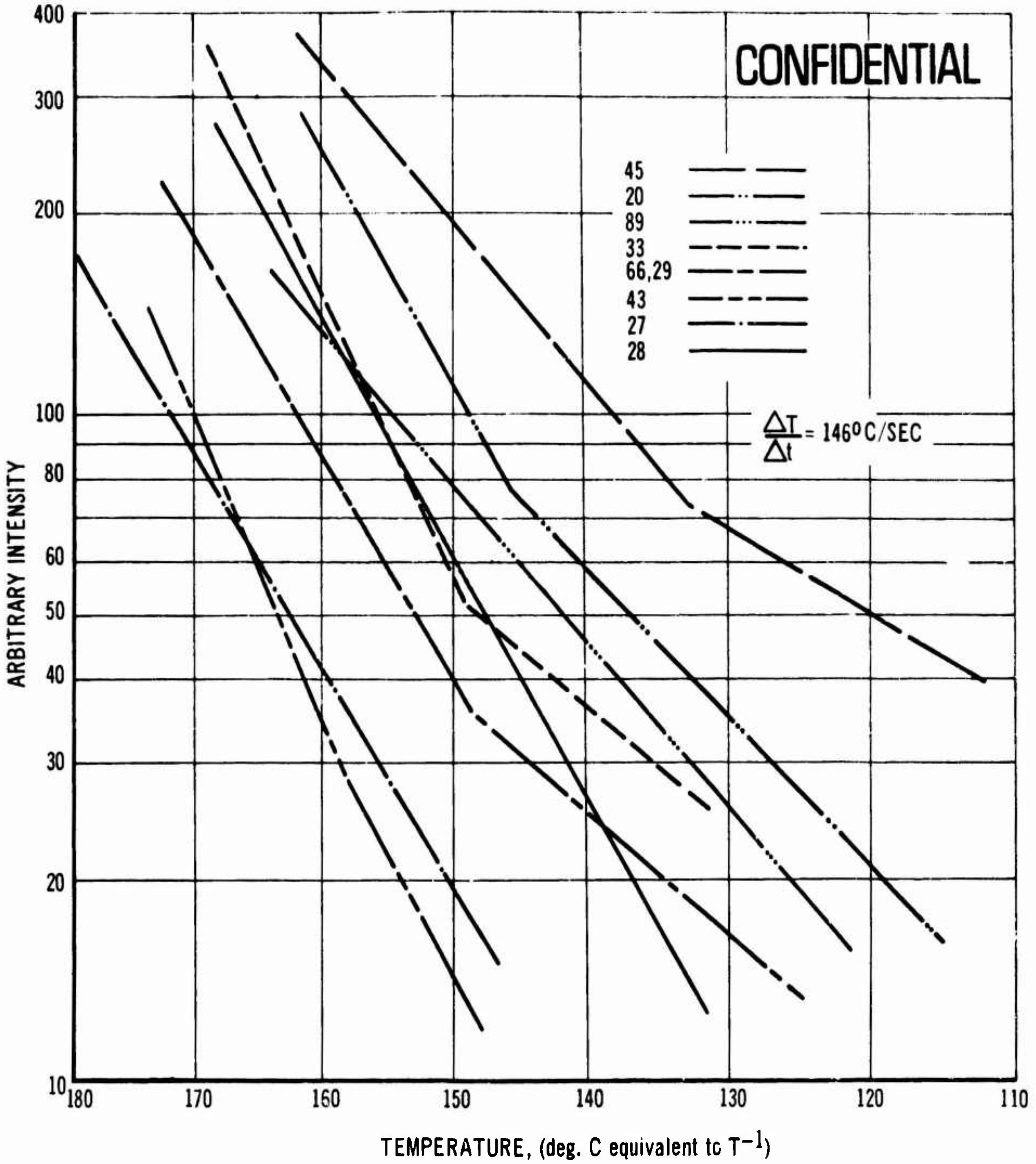


Figure 21 Arrhenius Type Plot of PBEP 9851-135 ("As Is" With Mol. Sieve)

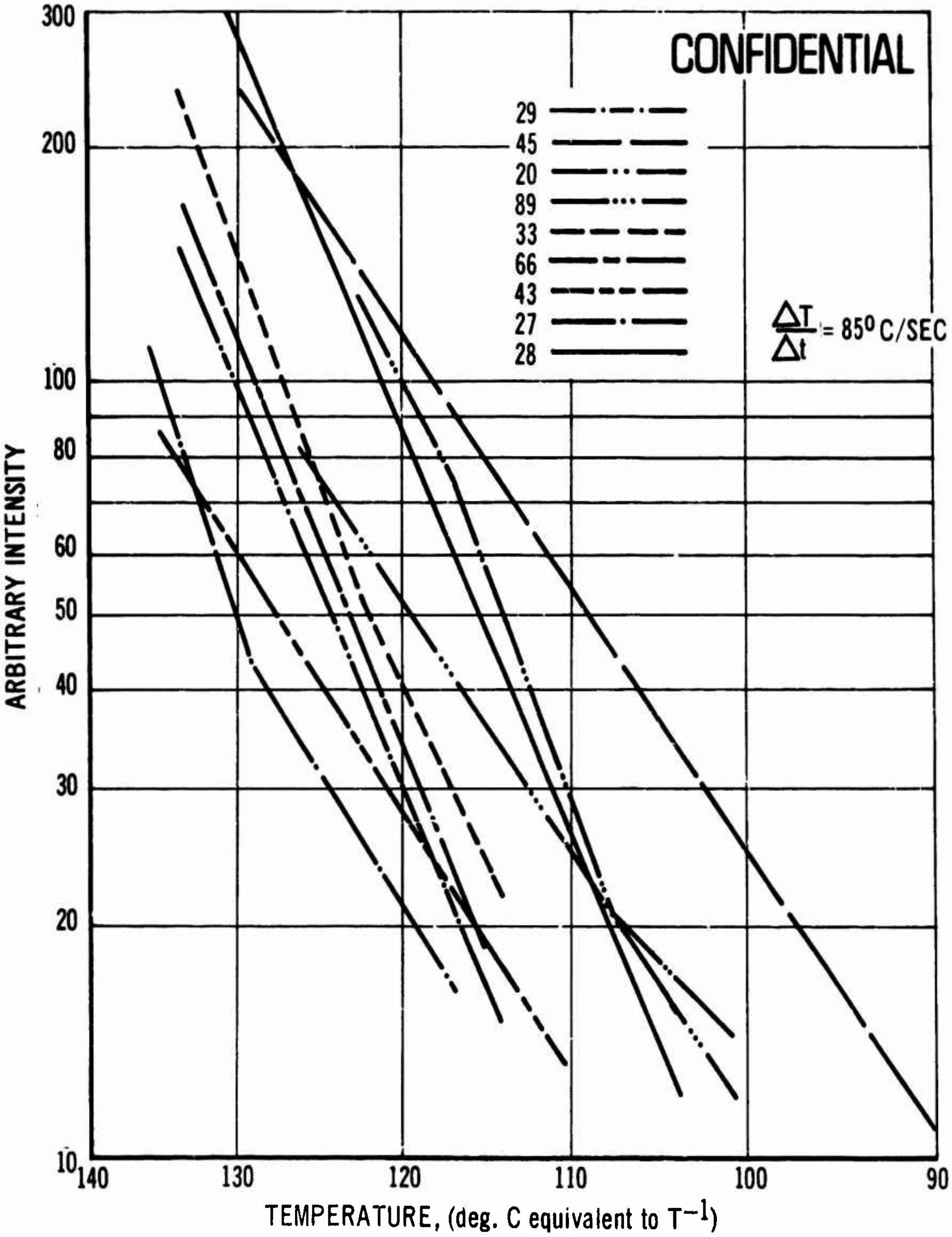


Figure 22 Arrhenius-Type Plot for PBEP 9851-125A (Amberlyst/COT Treated

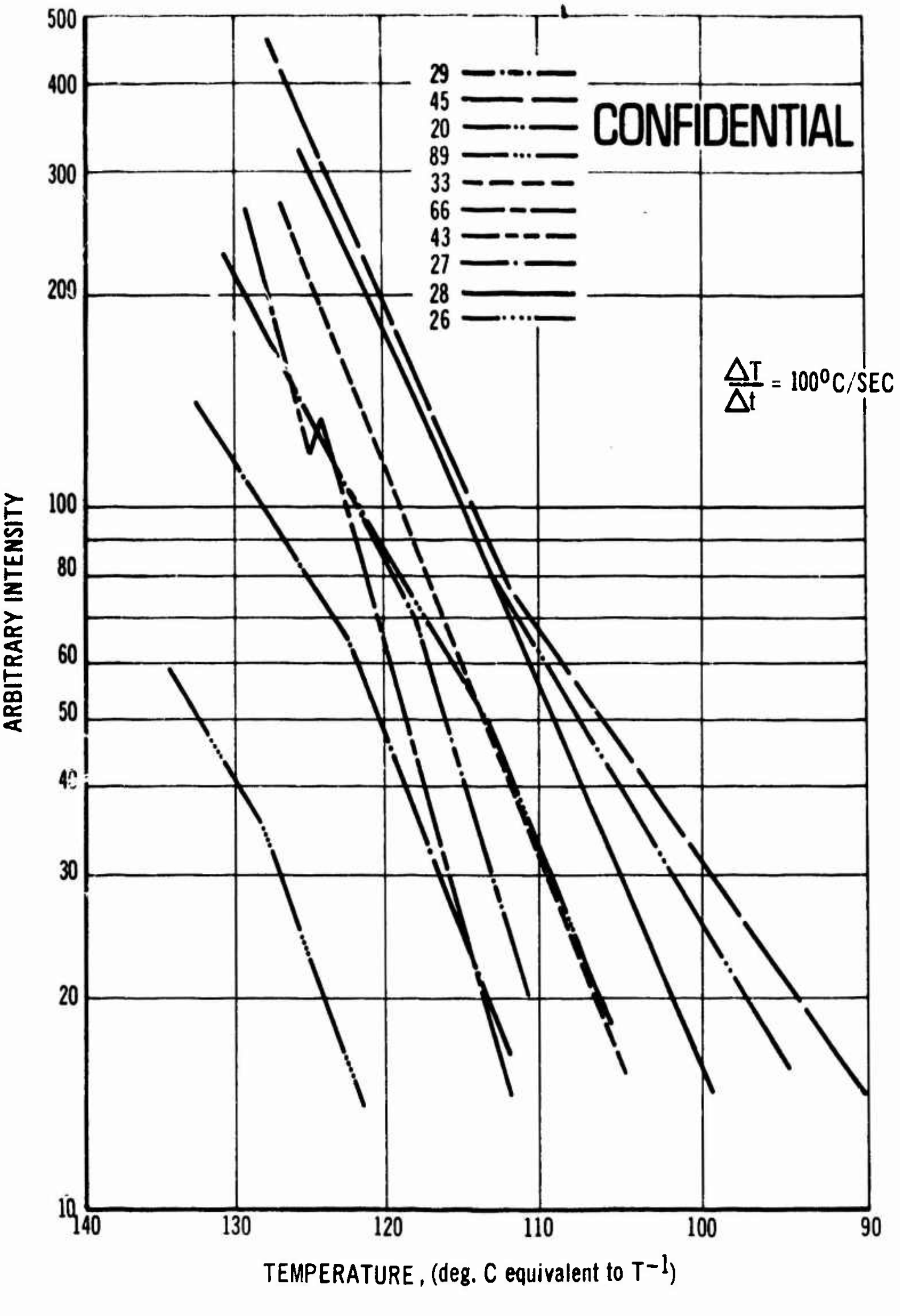


Figure 23 Arrhenius-Type Plot for PBEP 9851-128 (Hexane Precipitated)

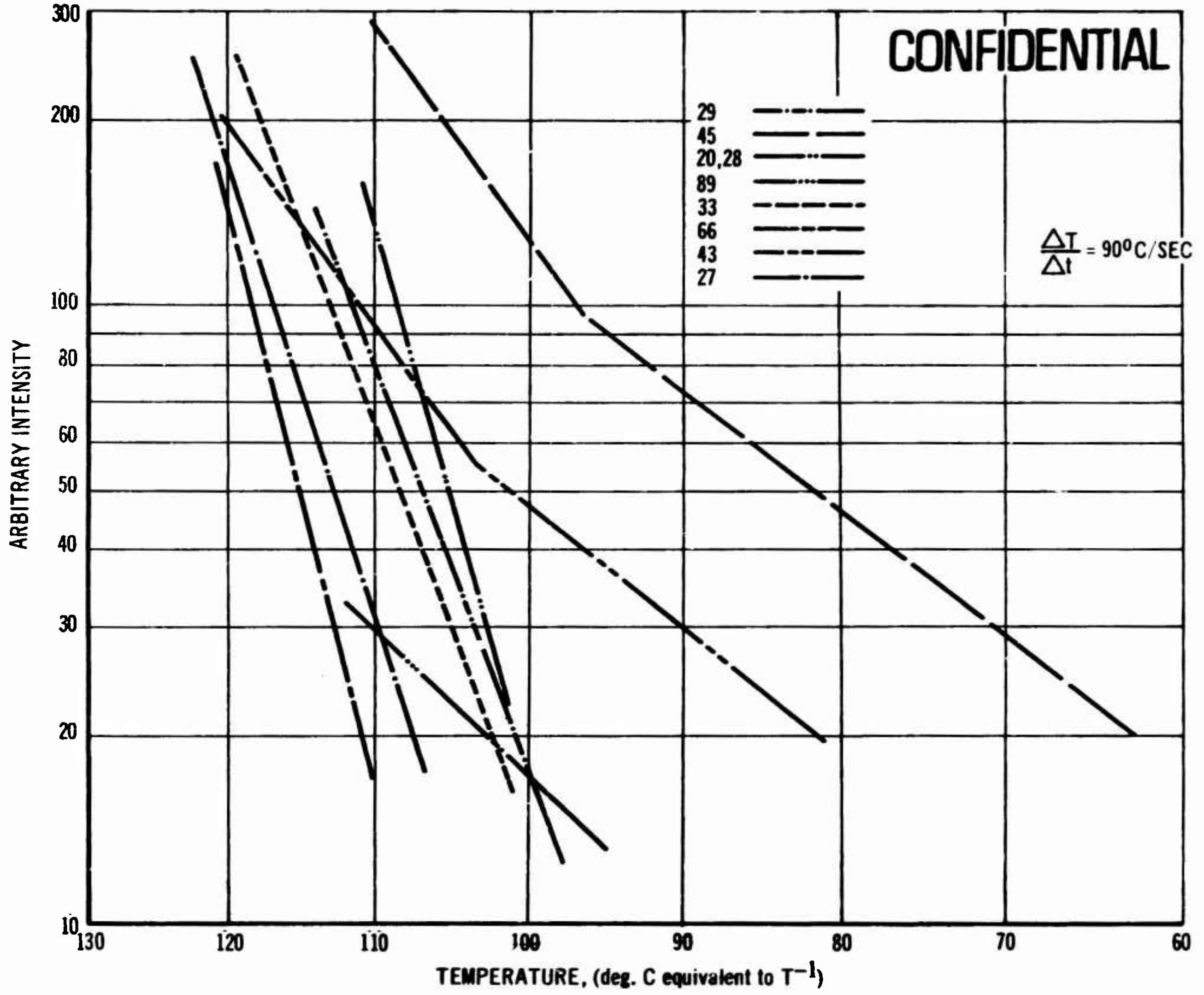


Figure 24 Arrhenius-Type Plot for PCDE 9851-123A (Pyridine/Amberlyst Treated PBEP

(C) In previous samples the decomposition initiated with the generation of HF (m/e 20) which appeared to be present in a loosely bound (adsorbed, complexed) form. With all samples of series 9851 the appearance of HF (m/e 20) was preceded by the appearance of mass species:

(C) Sample	Early Mass Species (in sequence of appearance) m/e
Molecular Sieve treated PBEP (135)	45;43;20, 89;29, 41, 71, 143;33
Amberlyst treated PBEP (125A)	45, 71, 78, 89;20;33, 43, 66;29
Hexane precipitated PBEP (128)	45;20, 33, 71, 89;52;29, 66;15, 47, 57, 59
Pyridine treated PBEP, PCDE (123A)	45;43;29, 71;35, 57;20, 27, 33, 41;31

(U) It implies that the residual impurities primarily constitute materials that have undergone degradation during the processing steps to the point of attaining some degree of thermal stability.

(C) (a) With the pyridine treated samples the reproducibility of the data (normalized peak intensities, normalized areas) is better than it is with the PBEP samples:

(C)	PBEP, hexane precipitated	PCDE (pyridine treated PBEP)
Average difference in peak intensities between duplicate runs	±17%	± 9%
Average difference in peak areas between duplicate runs	±15%	±10%
Difference in maximum intensity, m/e 71 per unit sample weight	±12%	± 8%
Difference in peak area, m/e 71 per unit sample weight	±18%	±13%

(C) The data show that the PBEP samples contain a higher percentage of material of relatively low molecular weight that is being depleted during the evacuation period.

(C) (b) If the ratio between peak area and peak intensity$_{max}$ (Table VIII) can be taken as indication of the structural uniformity of the sample, then the data would suggest that the hexane precipitated PBEP is structurally more uniform than the pyridine treated material (PCDE).

(C) (c) With regard to spectral differences, the pyridine treated material appears to produce the same amount of HF (m/e 20) as the hexane precipitated material, while producing a larger quantity of CH+ (m/e 26) and mass species m/e 43 and 45. Mass m/e 66 which is attributed to the primary NF_2 group ($CH_2NF_2^+$) appears at a reduced intensity in the pyridine treated material.

(C) According to the elemental analyses supplied by Shell, the pyridine treatment reduced the fluorine content by 32-34 percent, indicating a 66-68 percent conversion of PBEP into PCDE. This conversion of the $-CH_2NF_2$ side chain into the nitrile group is evidenced by an increase in the m/e 26/20 ratio (0.1 in PBEP, 0.36 in PCDE). On the other hand, if m/e 66 (CH_2NF_2+) is taken as an index, the data would indicate that conversion of the $-CH_2NF_2$ side chain proceeded only to the extent of approximately 40 percent, implying some loss of fluorine from the tertiary NF_2 group as a result of pyridine treatment. Finally, the data show that upon the thermal decomposition of PBEP the primary CH_2NF_2 group does not degrade by dehydrofluorination to form the nitrile intermediate.

(C) (d) The data quoted in Table IX show the strong retention of methylene chloride by PCDE. Moreover, the intensity of the mass peaks attributable to methylene chloride (m/e 49, 84, 86, 51, 47, 48) relative to the intensity of mass peak m/e 71 is surprisingly reproducible between duplicate sample runs.

(C) This suggests that methylene chloride is strongly retained by PCDE, possibly in a complexed form which renders it difficult to remove the solvent by vacuum treatment. The methylene chloride peaks also appear in the PBEP sample that was treated with Amberlyst, and to a lesser extent in the molecular sieve treated sample; they are not observed in the hexane precipitate sample.

c. Determination of Impurities

(U) To provide more detailed information upon the nature of the impurities that may be presumed to decompose or react at a comparatively low temperature, some of the samples were retested using a higher sample weight.* The results of these tests are summarized below:

(1) Molecular Sieve Treated PBEP (135)

(C) The analysis of the initial species being generated by molecular sieve treated PBEP shows a high concentration of mass species m/e 45 and 43.

---

* This causes an overload in the Mass Spectrometer output signal during the peak decomposition period, but it provides higher sensitivity during the heat-up period.

TABLE IX

METHYLENE CHLORIDE RESIDUES

Sample Run	Samples	m/e 49	m/e 84	49/84 Ratio(1)
41-4	PBEP, Molecular Sieve Treated (135)	18	trace	1.9
43-1	PBEP, Amberlyst Treated (125A)	34	18	
41-3	PBEP, Hexane Precipitated (128)	nil	nil	
48-4		nil	nil	
42-2	PCDE (Pyridine treated PBEP) (123A)	76	48	1.58
42-3		85	52	1.63

---

(1) Ratio in pure methylene chloride spectrum is 1.9.
All intensities normalized to m/e 71 = 100.0.

(U) The data are tabulated below for comparison with the maximum peak intensities:

(U)	Frame 120	Frame 140	Maximum Intensity Duplicate Run
33	absent	80	226
45	248	300	222
29	140	90	168
20	absent	90	165
66	absent	absent	165
52	absent	absent	160
71	100.0	100.0	100.0
47	absent	absent	100
27	absent	64	98
43	76	244	76
89	absent	74	74
30	80	trace	61
41	56	134	56
57	148	150	48
40	100	absent	44

(C) The data indicate that during the very early stages of pyrolysis the composition of the products differs significantly from the overall composition. Specifically, there is an abundance of mass species 57 and 40 at frame 120, and mass species 45, 43, 41 and 57 at frame 140. On the other hand, and comparing again with maximum intensities (frames 240-260), the composition of the initial products of decomposition is low in mass species 33 (NF^+), 20 (HF^+), 66 ($CH_2NF_2^+$) and 47 (possibly COF^+).

(2) Hexane Precipitated PBEP

(C) The early part of the spectral sequence for hexane precipitated PBEP is shown in Figure 25. The figure shows that only a small shoulder, formed by mass species m/e 45 remains prior to the onset of the first thermal event. The latter is evidenced by the generation of low molecular weight species that are abundant in fluorine content (m/e 20, 33, 52, 66). The data imply that the hexane precipitation has effectively removed the majority of the low molecular weight degradation products.

(3) Pyridine Treated PBEP (PCDE)

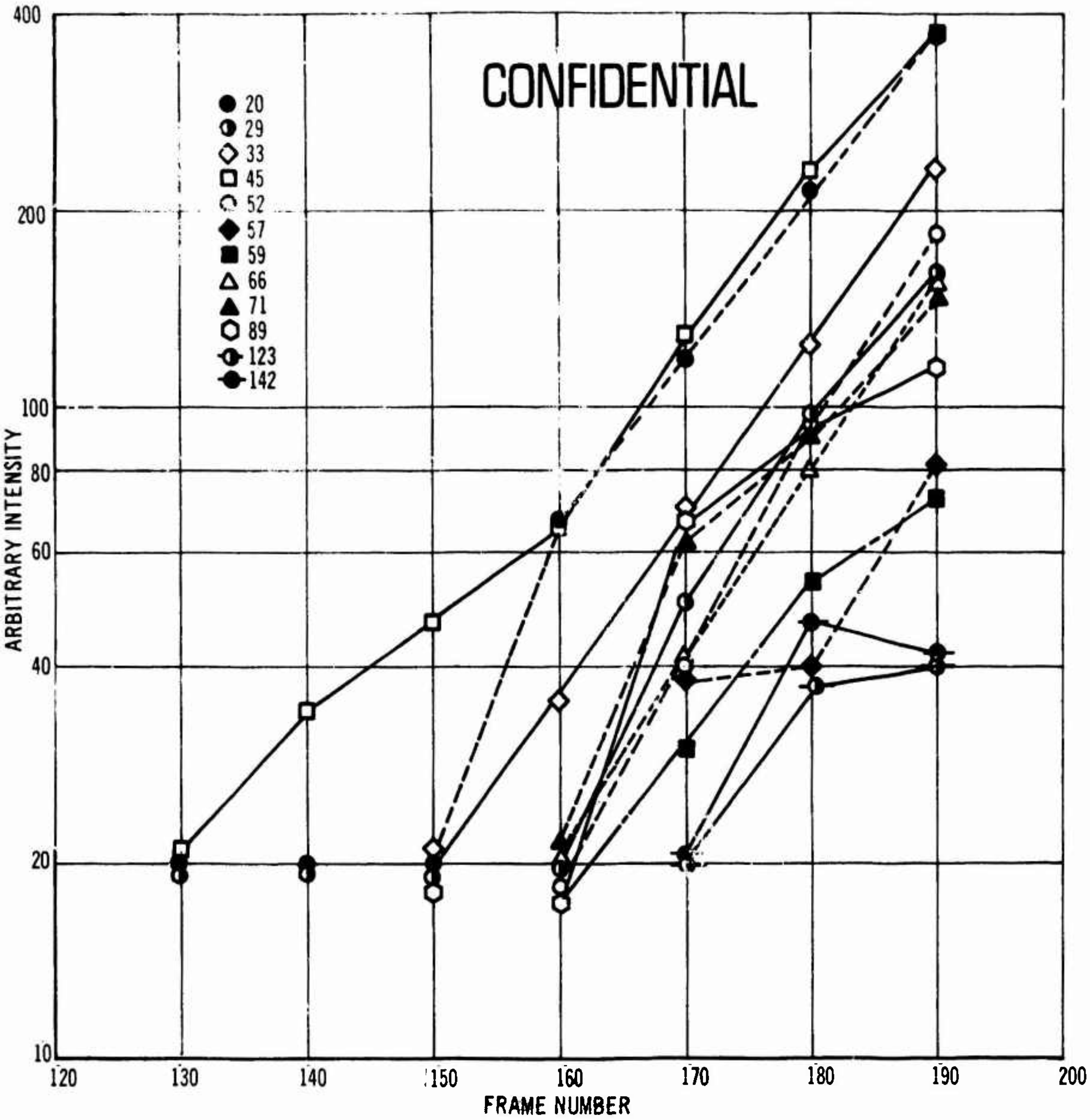


Figure 25 Mass Spectral Sequence During Early Heat-Up Period, PBEP 9851-128 (Hexane Precipitated)

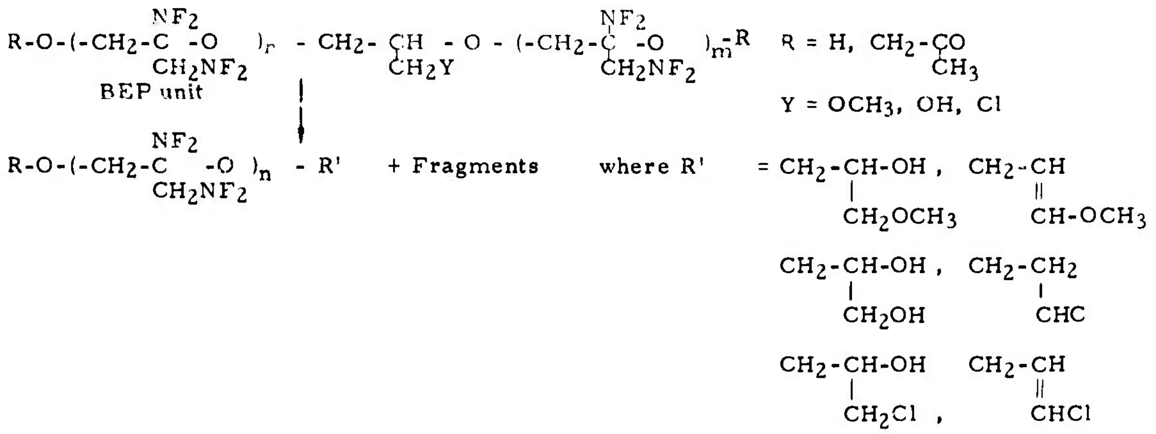
(C) The initial part of the spectral sequence for PCDE is shown in Figure 26. It shows the high abundance of mass species attributable to methylene chloride, (m/e 49, 84, 86, 51, and 47), but also the early appearance of m/e 45, 43 and 41. Gross decomposition of the material starts around frames 155-165 with the appearance of mass species (not shown) 71, 57, 52, 41, 29, 20, 27 and 33 (listed in decreasing order of intensity). The peak decomposition rate occurred within frames 221-225 (124-125°C).

(C) Another noticeable difference between the PBEP and the PCDE spectra is the absence of high molecular weight species (e.g., m/e ~200) from the PCDE spectra.

d. Discussion of Results

(1) PBEP Data

(C) It can be presumed that PBEP is stabilized thermally by virtue of carrying non-reactive chain terminals in the form of the glycerol or 3-methoxy-1,2-propylol ether groups. The introduction of other endgroups, either via synthesis (e.g., BEPH units, acetal endgroups (Figures 27-I - 27-III)) or via partial hydrolysis is likely to destabilize the polymer chain thermally. It will cause degradation along the chain until this process is interrupted by the conversion of non-BEP units into new, stable endgroups:



$$R\text{-}O\text{-}(\text{-}CH_2\text{-}\underset{CH_2NF_2}{\overset{NF_2}{C}}\text{-}O)_r\text{-}CH_2\text{-}\underset{CH_2Y}{CH}\text{-}O\text{-}(\text{-}CH_2\text{-}\underset{CH_2NF_2}{\overset{NF_2}{C}}\text{-}O)_m\text{-}R \qquad R = H,\ CH_2\text{-}\underset{CH_3}{CO}$$

BEP unit

$$Y = OCH_3,\ OH,\ Cl$$

$$\downarrow$$

$$R\text{-}O\text{-}(\text{-}CH_2\text{-}\underset{CH_2NF_2}{\overset{NF_2}{C}}\text{-}O)_n\text{-}R' \quad + \text{ Fragments} \qquad \text{where } R' = CH_2\text{-}\underset{CH_2OCH_3}{CH}\text{-}OH,\ \ CH_2\text{-}CH{=}CH\text{-}OCH_3$$

$$CH_2\text{-}\underset{CH_2OH}{CH}\text{-}OH,\ \ CH_2\text{-}\underset{CHC}{CH_2}$$

$$CH_2\text{-}\underset{CH_2Cl}{CH}\text{-}OH,\ \ CH_2\text{-}CH{=}CHCl$$

(C) During this process the original BEP units are likely to degrade into species of low molecular weight (e.g., HF, $CH_2{=}NF$, CH_2O, COF_2) that are lost during storage or solvent stripping, while the non-BEP units, which are thermally stable, accumulate. This brings about an apparent increase in the concentration of end-groups, and perhaps an increase in functionality; the former is reflected in the early mass spectra by a high abundance of mass species that can be associated with the non-BEP endgroups or chain links (e.g., m/e 57, 45, 43) while mass species reflecting the generation of species like NF_2^+, HF^+, $CH_2NF_2^+$ are initially absent.

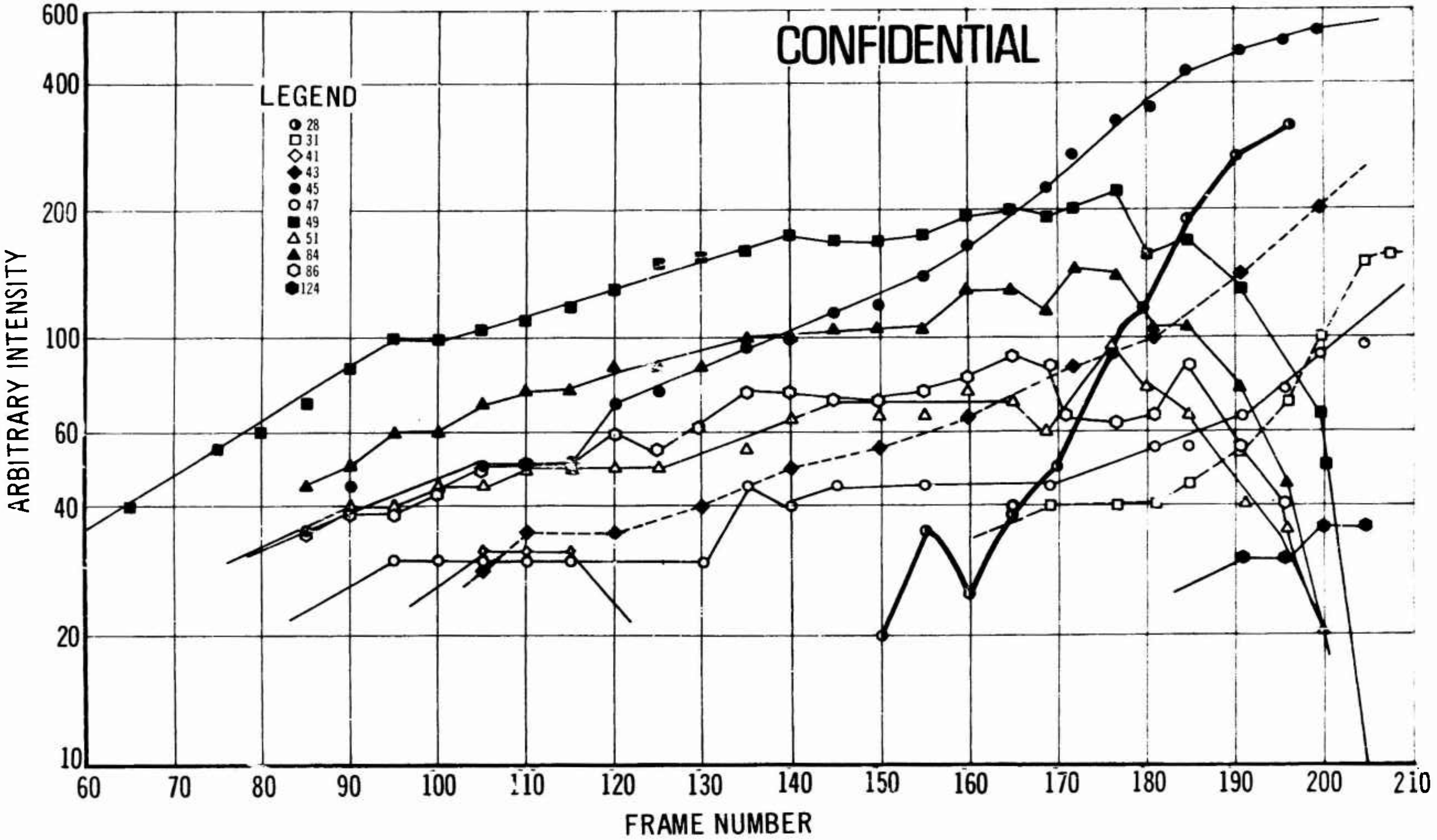


Figure 26 Mass Spectral Sequence During Early Heat-Up Period, PCDE 9851-123A (Pyridine/ Amberlyst Treated PBEP)

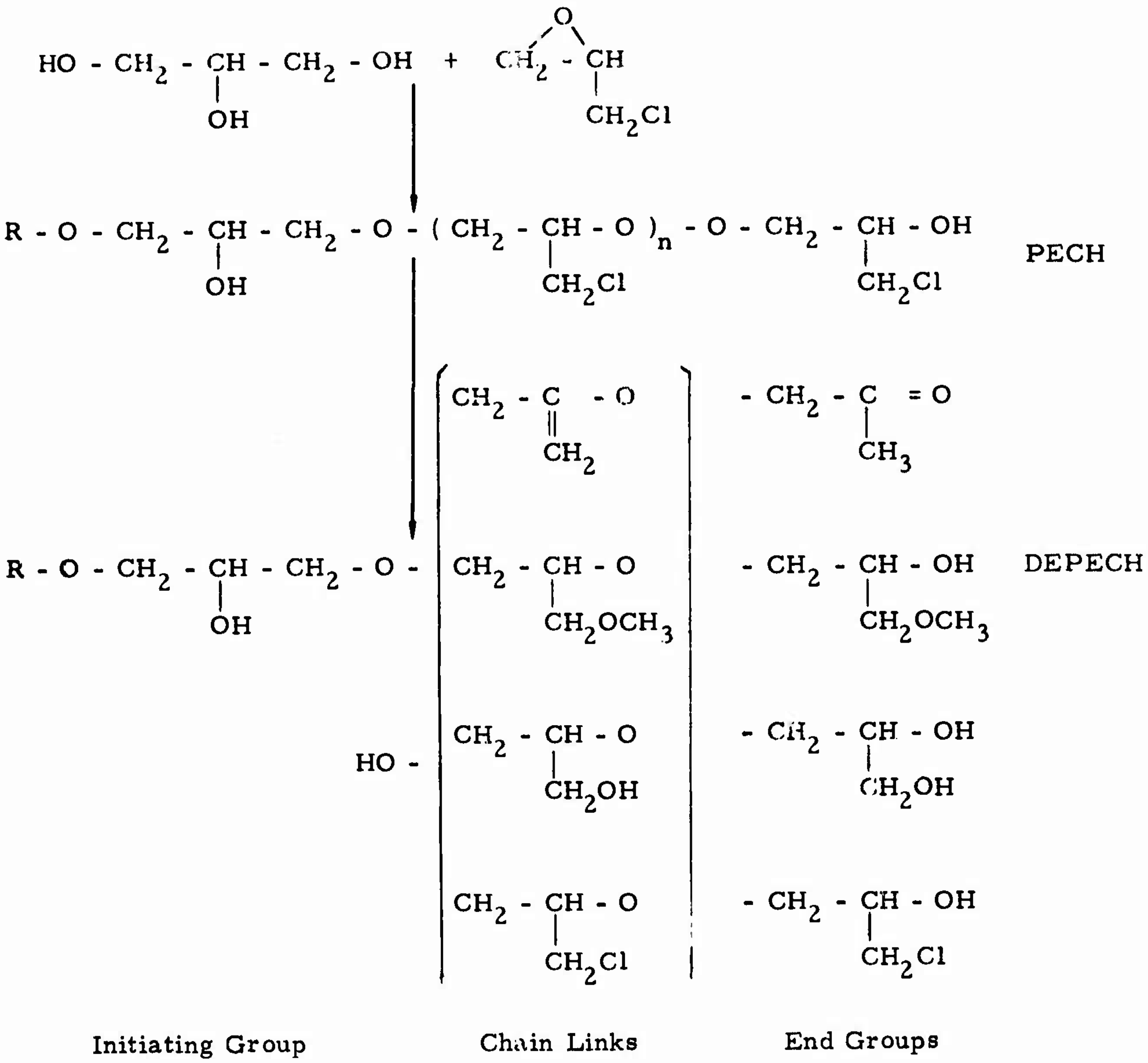
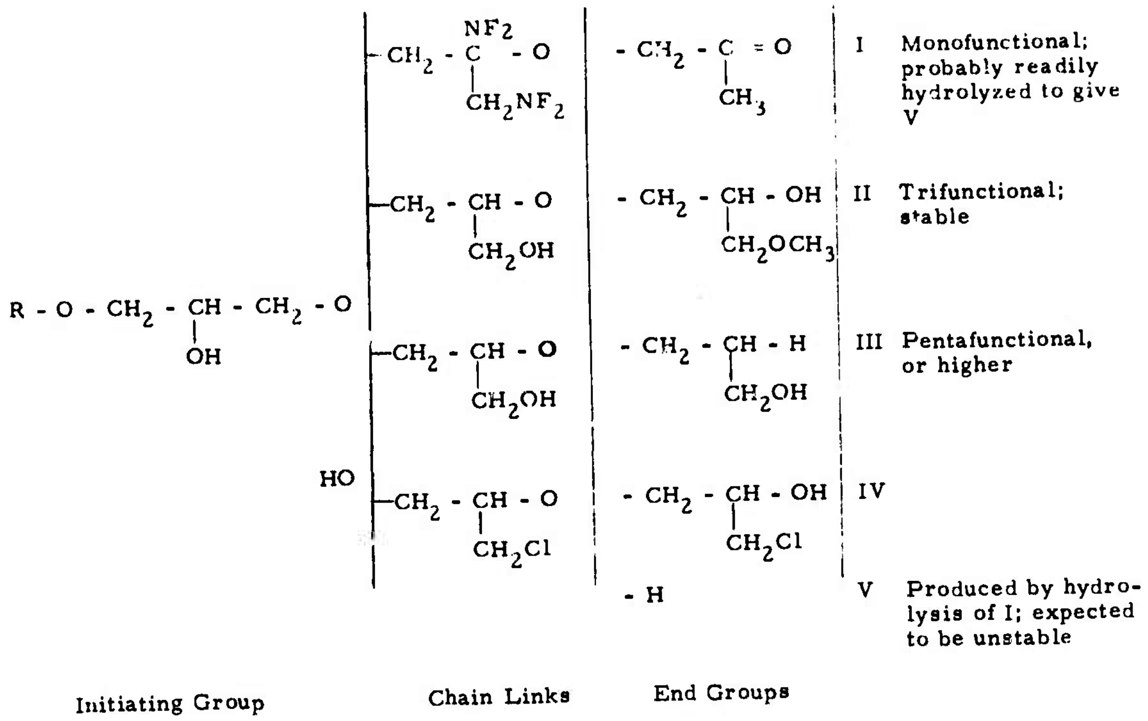
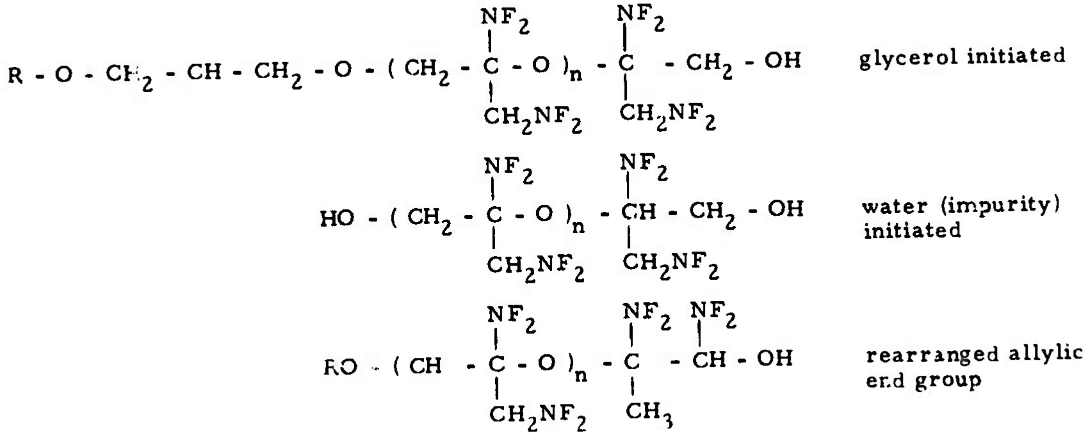


Figure 27-I Synthesis Steps, DEPECH



Additionally there could exist end groups representing a different orientation of the PECH unit:



$$R-O-CH_2-CH-CH_2-O-(CH_2-\underset{CH_2NF_2}{\overset{NF_2}{C}}-O)_n-\underset{CH_2NF_2}{\overset{NF_2}{C}}-CH_2-OH$$

glycerol initiated

$$HO-(CH_2-\underset{CH_2NF_2}{\overset{NF_2}{C}}-O)_n-\underset{CH_2NF_2}{\overset{NF_2}{CH}}-CH_2-OH$$

water (impurity) initiated

$$RO-(CH\ -\underset{CH_2NF_2}{\overset{NF_2}{C}}-O)_n-\underset{CH_3}{\overset{NF_2}{C}}-\overset{NF_2}{CH}-OH$$

rearranged allylic end group

Figure 27-II Synthesis of PBEP

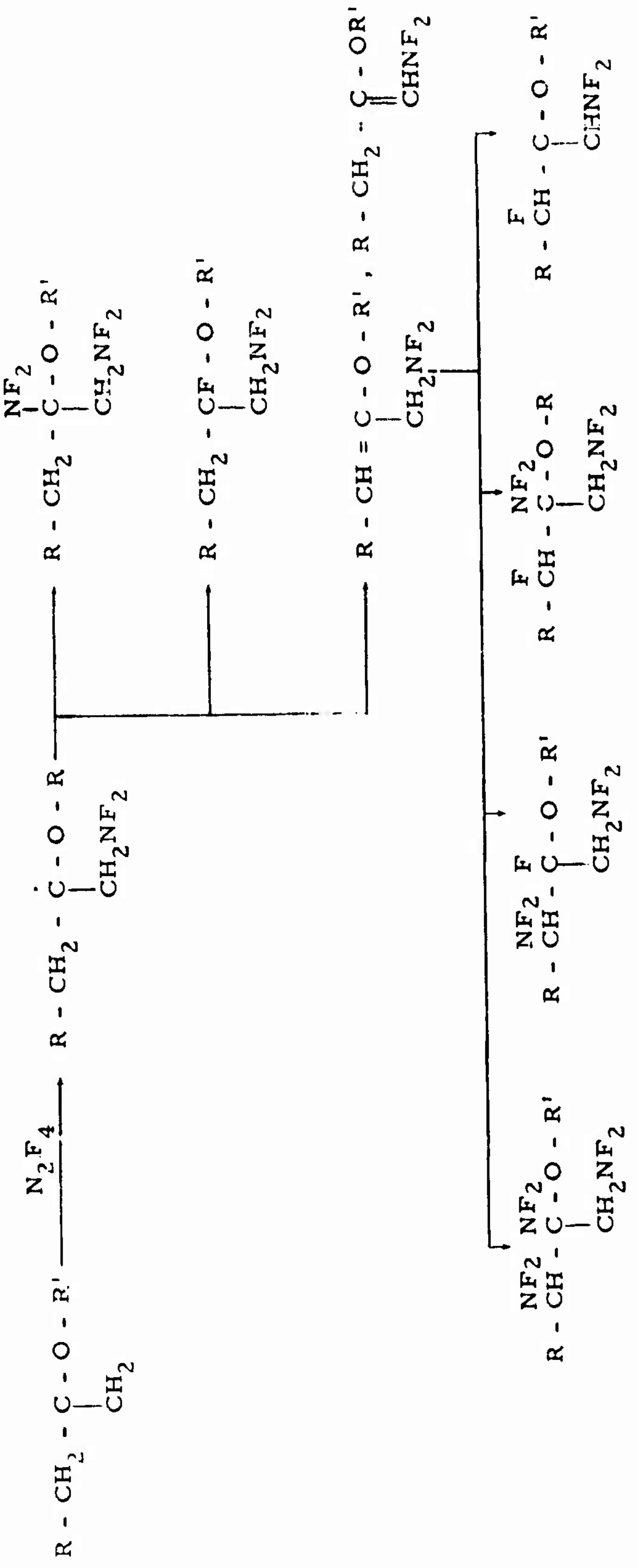


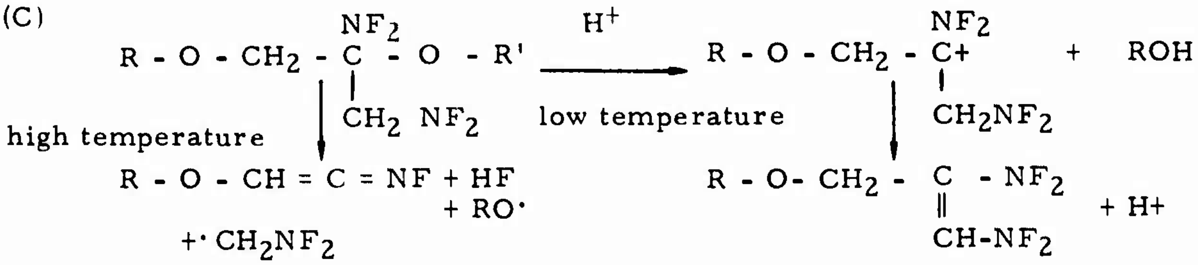
Figure 27-III Possible Side Reaction, PBEP Synthesis

(C) As the temperature of the sample increases, materials of higher molecular weight (e.g., m/e 109, 124, 143, 196) evolve that constitute fragments wherein partially degraded (e.g., hydrolyzed, reduced) BEP fragments still adhere to the non-BEP groups. At still higher sample temperatures these higher molecular weight fragments undergo degradation prior to being ejected into the gas stream.

(C) The mass species m/e 45 which appears in all PBEP and PCDE spectra at a high intensity is probably generated by both the non-BEP units (CH_2OCH_3+) and the BEP units ($CNF+$).

(C) The observation of several consecutive thermal events during pyrolysis suggests that the mechanism of decomposition changes as the temperature rises. It is conceivable that initially catalysis by residual HF (H+) plays a role in degrading the polymer chains, while at the higher temperatures a free radical type mechanism may enter into play:

(C)



(C) In either mechanism the primary NF_2 group appears to degrade without passing through the nitrilo intermediate stage. This is evidenced by the fact that both PBEP and PCDE generate comparable quantities of HF. By contrast, treatment of PBEP with a base (e.g., pyridine) generates nitrilo groups by HF elimination from the CH_2NF_2 side chain.

(C) As regards posttreatments, it is apparent that molecular sieve treatment affects little or no improvement in the materials' composition and stability. Hexane treatment by contrast is quite effective in removing the low molecular weight degradation products. The data for the Amberlyst treated material are conflicting. On the basis of mass thermal analysis data one would expect propellant prepared with Amberlyst treated material to have a better stability and shelflife than was actually observed. It is conceivable that Amberlyst treatment causes some degree of hydrolysis, thus introducing fragments of comparatively high molecular weight that will not substantially modify the sample's composition and spectra.

(C) From this interpretation of the data one can conclude that the stability and the compatibility of PBEP might be improved by:

(C) (a) moderately increasing the number of methoxylated chain links (molecular weight stabilization)

(C) (b) moderate heat treatment or acid treatment followed by thin-film vacuum treatment for removing unstable fragments of comparatively low molecular weight.

(C) (c) since all PBEP samples are likely to undergo some degree of slow decomposition during storage, propellant stability could probably be improved by a repeat precipitation with hexane immediately prior to use. Solvent precipitation of the material should always follow, but not precede, any column treatment.

(2) PCDE Data

(C) The outstanding feature in the PCDE spectra was the high concentration of species attributable to methylene chloride. In addition mass species m/e 45, 43 and 89 appear to be generated early and at low activation energies. It is conceivable that during the conversion of PBEP to PCDE some imino ether groups are formed, possibly involving the hydroxyl end-groups that, in turn, may complex with methylene chloride. However, this is speculative, and more analyses involving different samples would have to be performed to resolve the question.

(C) It is also to be noted that the PCDE sample that was analyzed was treated with Amberlyst following pyridine treatment. This sequence should be reversed, or be followed by hexane precipitation.

(3) Kinetics and Energetics of PBEP and PCDE Decomposition

(U) The kinetics of PBEP and PCDE decomposition was derived from the time versus intensity curves and heating rate data, and using a previously described (Ref 1) method.

(U) The total area under the time-intensity curve for any given species is proportional to the total quantity of the particular species produced during pyrolysis, and area fractions within small time increments yield the reaction rate constant. Moreover, since the temperature increases linearly with time, these area increments also represent different temperature increments, thus lend themselves to Arrhenius type plots to derive activation energies and frequency factors.

(U) The technique, however, requires that the time-intensity cure is closed, i.e., that the decomposition species under observation ceases to be produced within the overall time or temperature interval. With the PBEP and PCDE time resolved mass spectra this was the case with all species of interest except mass species m/e 28. The kinetic parameters for the generation of m/e 28 were therefore estimated by analogy to the rates of formation of HF (m/e 20), while assuming m/e 28 to represent predominantly CO+, applying ionization cross-section values estimated according to Otvos and Stevension (Ref 5).

(U) Table X presents the thus derived data for the major decomposition species represented by the product ions m/e 20, 26, 27, 28, 29, 33, 43, 45, 66 and 89. Their presumed structures were quoted in Table VI.

(C) This tabulation shows that treatment of PBEP with Amberlyst, precipitation with hexane and conversion (dehydrofluorination) with pyridine all tend to increase the apparent energy of activation for all quoted species except m/e 28. The energy of activation for the generation of m/e 28 was significantly lower with the pyridine treated material (PCDE).

(C) This tabulation shows that Amberlyst treatment as well as hexane precipitation of PBEP generally increases the apparent activation energy for the production of the quoted species, implying that these treatments had been effective in removing more readily decomposed impurities Of particular interest is the increase in the apparent energy of activation for the generation of HF (m/e 20); the data, in this regard show that molecular sieve treatment produces little improvement, while Amberlyst and hexane treatment appear equally effective. This, in turn, suggests that the early generation of HF is associated with the presence of a thermally unstable and reactive impurity which is either degraded by the Amberlyst treatment, or removed by the solvent precipitation.

(C) The comparatively low activation energies that are obtained for the generation of the ion species m/e 28, 43, 45 and 89 with PCDE suggest that pyridine treatment may convert impurities that are present in the original material (molecular sieve treated PBEP) into a form that no longer is capable of ready release of HF; however, the pyridine treatment is not as effective as the hexane precipitation in actually removing the impurities which are presumed to constitute materials of lower molecular weight. One might therefore expect the hexane precipitation of the pyridine treated material would tend to further improve this product.

TABLE X

KINETICS OF THE DECOMPOSITION OF PBEP - INITIAL REACTIONS

m/e	Molecular Sieve/1% COT (9851-135)	Amberlyst-15/1% COT (9851-125A)	Hexane ppte/1% COT (9851-128)	PCDE/ Amberlyst-15 (9851-123A)	Average of	
20						
$\bar{E}$ (KCAL/MOLE)	20.9	39.7	35.9	35.8	-125A	37.1
log A (sec^{-1})	10.85				-128	20.25
k, 50°C ($10^{-2}hr^{-1}$)	187				-123A	5.18
k, 60°C ($10^{-2}hr^{-1}$)	495					29.3
Q_{10}[1]	2.7					5.7
26, 27						
$\bar{E}$ (KCAL/MOLE)	27.5	48.1	49.7	50.1	-125A	48.2
log A (sec^{-1})	14.7				-128	26.72
k, 50°C ($10^{-2}hr^{-1}$)	45.4				-123A	0.475
k, 60°C ($10^{-2}hr^{-1}$)	164					4.52
Q_{10}	3.6					9.5
28						
$\bar{E}$ (KCAL/MOLE)	33.0	39.7	36.9	21.1	-135	36.5
log A (sec^{-1})				11.1	-125A	19.87
k, 50°C ($10^{-2}hr^{-1}$)				207	-128	5.49
k, 60°C ($10^{-2}hr^{-1}$)				651		30.3
Q_{10}				2.7		5.5
29						
$\bar{E}$ (KCAL/MOLE)	29.1	49.7	47.8	44.1	-125A	47.2
log A (sec^{-1})	14.78				-128	26.2
k, 50°C ($10^{-2}hr^{-1}$)	4.52				-123A	0.681
k, 60°C ($10^{-2}hr^{-1}$)	18.0					6.18
Q_{10}	4.0					9.1
33						
$\bar{E}$ (KCAL/MOLE)	24.1	54.6[2]	41.5	44.3	-128	42.9
log A (sec^{-1})	12.75	30.3			-123A	23.65
k, 50°C ($10^{-2}hr^{-1}$)	102	0.0846				1.55
k, 60°C ($10^{-2}hr^{-1}$)	313	0.109				11.5
Q_{10}	3.1	12.9				7.4
43						
$\bar{E}$ (KCAL/MOLE)	22.6	37.2	44.5	24.7	-135	23.7
log A (sec^{-1})		20.3	24.55		-123A	12.40
k, 50°C ($10^{-2}hr^{-1}$)		4.97	1.02			0.845
k, 60°C ($10^{-2}hr^{-1}$)		28.3	8.16			2.56
Q_{10}		5.7	7.8			3.0
45						
$\bar{E}$ (KCAL/MOLE)	18.6	42.6	41.2	23.2	-125A	41.9
log A (sec^{-1})	9.8			13.3	-128	23.65
k, 50°C ($10^{-2}hr^{-1}$)	598			1460		7.37
k, 60°C ($10^{-2}hr^{-1}$)	1430			4330		52.3
Q_{10}	2.4			3.0		7.1
66						
$\bar{E}$ (KCAL/MOLE)	25.2	56.3	53.3	55.2	-125A	54.9
log A (sec^{-1})	12.96				-128	30.75
k, 50°C ($10^{-2}hr^{-1}$)	29.7				-123A	0.150
k, 60°C ($10^{-2}hr^{-1}$)	96.4					1.95
Q_{10}	3.3					13.0
89						
$\bar{E}$ (KCAL/MOLE)	17.8	34.8	37.7	28.5	-125A	36.3
log A (sec^{-1})	10.13			16.9	-128	20.85
k, 50°C ($10^{-2}hr^{-1}$)	4440			1520		71.6
k, 60°C ($10^{-2}hr^{-1}$)	10200			5740		391
Q_{10}	2.3			3.8		5.5

---

1. Q10 - Temperature coefficient for ΔT = 10°C.
2. Value is probably too high, should be closer to 43 KCAL/MOLE

SECTION IV

RECOMMENDATIONS FOR FUTURE WORK

1. FURTHER STABILIZATION OF PBEP

(C) The Mass Spectrometric Thermal Analysis results indicate that hexane precipitation and Amberlyst treatment of PBEP are comparable in their effectiveness in removing what is believed to be unstable and reactive impurities of low molecular weight. The propellant surveillance data confirm the MSTA data as regards the hexane precipitated PBEP, but exhibit some discrepanices as regards the Amberlyst treated material, the latter material producing relatively early failure notably in AlH_3 formulations.

(C) Amberlyst treatment can be presumed to effect chemical changes, and the MSTA data suggest that the treatment affects primarily impurities that would otherwise give rise to low activation energies for the production of various products including HF. Amberlyst treatment, however, will not physically remove the resulting reaction products, and to effect their removal it appears desirable to follow this treatment by solvent precipitation.

(C) A noticable feature of the MSTA data is the fact that the activation energies for the production of the various ion species with both the Amberlyst treated and the hexane precipitated material appear to converge, this, in turn, suggests that either treatment produces a material that approaches optimum stability, and it implies that the achievement of batch-to-batch reproducibility is a matter of optimizing the solvent precipitation process, or a process involving a combination between Amberlyst treatment and solvent precipitation.

2. FURTHER STABILIZATION OF PCDE

(C) The MSTA data provide conclusive evidence that pyridine treatment, like Amberlyst treatment, effects chemical conversions, but that this treatment does not physically remove reaction products representing impurities. The data also indicate that dehydrofluorination does not proceed exclusively with the primary NF_2 group, and that the reaction is far from being quantitative. Since, on the other hand the surveillance data with both aluminized and aluminum hydride containing formulations show good results with PCDE in its present state of purity, there is good reason to believe that the further development of the dehydrofluorination step coupled with solvent precipitation of the product will produce a material of considerable interest.

3. ANALYTICAL METHOD REFINEMENTS

(U) On the basis of the test experience accumulated during this program the following recommendation are made regarding refinements in the analytical procedures:

(U) (a) To achieve a higher degree of reproducibility in the surveillance tests (time-to-failure, gas evolution rates) it will be desirable to resort to formulations that are comparatively low in solids loading for the purpose of minimizing mix effects. This will enable closer comparison of the effectiveness of purification processes on a relative basis.

(U) (b) In applying the MSTA technique the spectral sequence of prime interest occurs during the early sample heating period during which the impurities are driven off. To enhance the sensitivity during this critical period in the analysis larger sample weights should be used, accepting the loss in data during the peak decomposition period (overloading of the instrument). Moreover, as there could exist a significant difference in stability between materials wherein the terminal hydroxyl groups are reacted (representative of the cured state) and as received material, it may be advisable to prereact both PBEP and PCDE with monofunctional isocyanates.

(U) (c) The data produced under this program have contributed much toward associating the presence of impurities with the early appearance of specific product ions (MSTA). This in turn will enable greater economy in future studies by simplifying the data acquisition process. Rather than using a high speed motion film to record the entire spectrum, the instrument can be tuned in on selected mass species for still photography (Polaroid) of the selected m/e time-intensity traces.

SECTION V

REFERENCES

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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Lockheed Propulsion Company P.O. Box 111 Redlands, California 92373	2a. REPORT SECURITY CLASSIFICATION CONFIDENTIAL 2b. GROUP Group 4

3. REPORT TITLE

Kinetics of Decomposition of High Energy Materials (U)

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final report

5. AUTHOR(S) (First name, middle initial, last name)

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6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
1 May 1969 through 31 July 1970	72	5

8a. CONTRACT OR GRANT NO FO4611-69-C-0071	9a. ORIGINATOR'S REPORT NUMBER(S) 346-F
b. PROJECT NO.	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	AFRPL-TR-70-111

10. DISTRIBUTION STATEMENT In addition to security requirements which must be met, this document is subject to special export controls and each transmittal to foreign government or foreign nationals may be made only with prior approval of AFRPL (RPPR/STINFO), Edwards, California 93523.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY AFRPL Edwards Air Force Base, California

13. ABSTRACT

The stability and the compatibility of PBEP and of PCDE were investigated by Mass Thermal Analysis (MTA), propellant surveillance tests and measurement of propellant gas generation rates. The tests served to determine which, if any, of the purification procedures produced desirable gains in propellant thermal stability and shelflife. (U)

With PBEP the products resulting from various column and solvent treatments were evaluated, and the data show that specific purification procedures can produce a product that is suitable for use in advanced propellants. With PCDE the data imply that the presently employed treatment does not as yet produce an optimum product, and further refinements in the purification of PCDE are expected to become reflected in further gains in propellant stability and shelflife. However, propellant surveillance data show that even in its present state of purity PCDE matches PBEP as regards stability in propellants. (U)

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Scavenger						
Surveillance						
Shelflife						
Mass thermal analysis						