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(Unclassified Title)

PCDE PROPELLANT FOR BALLISTIC MISSILES

Morton A. Klotz, B. B. Lampert, L. J. Rosen and R. L. Lou
Aerojet Solid Propulsion Company

Technical Report AFRPL-TR-73-90

October 1973

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Unauthorized Disclosure Subject to Criminal Sanctions

Air Force Rocket Propulsion Laboratory
Director of Science and Technology
Air Force Systems Command
Edwards Air Force Base, California 93523

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FOREWORD

This is the third quarterly report issued under Contract F04611-73-C-0034, and covers the period 1 June through 31 August 1973. This contract is monitored by the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California. The Air Force Project Officer is Dr. F. Q. Roberto (MKPA).

This report is Aerojet Solid Propulsion Company Report No. 1024-26Q-3.

The work was performed under the supervision of Dr. L. J. Rosen, within the Advanced Propellants Section, under Dr. R. L. Lou, of the Propellant Development Department, Dr. C. J. Rogers, Manager. The Principal Investigator is Dr. Morton A. Klotz. Dr. B. B. Lampert, Dr. A. E. Oberth, Miss I. T. Pierce, Mr. H. A. Price, and Mr. D. E. Johns were major contributors to the studies reported.

This report contains classified information obtained from classified reports. All such reports and their classification are specifically identified.

This technical report has been reviewed and is approved.

FOR THE COMMANDER

CHARLES R. COOKE
Chief, Solid Rocket Division
Air Force Rocket Propulsion Laboratory

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PCDE	Ballistic Properties
SYFO	HMX
FEFO	Pressure Exponent
Solid Propellant	Specific Impulse

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This program is concerned with the development, characterization and ballistic testing of solid propellants containing PCDE, SYFO and FEFO. The formulations under study were changed to reflect new program performance goals established during this report period. The new propellants were significantly less sensitive, but were poorer in processability and mechanical properties than the earlier propellants. Pressure exponents from strands were higher than the program goal, but motor exponents are expected to meet the goal.

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Other formulation work is also described. Two small-scale motor firings are reported. Work was begun on screening aging stabilizers and on evaluation of new lots of PCDE.

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GLOSSARY (U)

AFRPL	Air Force Rocket Propulsion Laboratory
AP	Ammonium perchlorate
ASPC	Aerojet Solid Propulsion Company
BATES	Ballistic Test and Evaluation System
BRM	Burning Rate Motor
C*	Computer printout for c*, characteristic exhaust velocity
CD	Computer printout for C_D, mass discharge coefficient
Cu 0202	Copper chromite
DBR	4,6-Di-t-butylresorcinol
Dexsil	A proprietary silyl carborane (Olin Matheison Co.)
DOA	Dioctyl azelate
DTA	Differential thermal analysis
E_o	Initial tangent modulus
FeAA	Ferric acetylacetonate
FEFO	bis(2-Fluoro-2,2-dinitroethyl) formal
GFM	Government-furnished material
HDI	Hexane-1,6-diisocyanate
HMX	Cyclotetramethylene tetranitramine
HT	1,2,6-Hexanetriol
I_{sp}	Specific impulse (in general)
I°_{sps}	Theoretical specific impulse under standard conditions of P_c = 1000 psia, P_e = 14.7 psia, ideal expansion, adiabatic conditions, zero degree half-angle nozzle.
JANNAF	Joint Army-Navy-NASA-Air Force Committee
LSBR	Liquid strand burning rate

GLOSSARY (Cont.) (U)

	MA	Mikroatomized AP, ∿6μ dia.
	MPDA	m-Phenylenediamine
	MPDA-HMX	Adduct of MPDA and HMX, 1/1 mole ratio
	n	Pressure exponent
	NHC	n-Hexylcarborane
(C)	PCDE	Poly(1-cyano-1-difluoraminoethylene oxide)
	PCP-0200	A caprolactone-based diol, av. m.w. = 530 (Union Carbide Corp.)
	PCP-0301	A caprolactone-based triol, av. m.w. = 300 (Union Carbide Corp.)
	PEG-4000	Polyethylene glycol, m.w. = approx. 4000
	r_x	Burning rate at x psia pressure
	Santicizer 8	N-ethyl toluenesulfonamide (o and p mixture; Monsanto Chemical Co.)
	SSBR	Solid strand burning rate
(C)	SYFO	bis(2,2-Difluoramino-5-fluoro-5,5-dinitropentyl) formal
	TDI	Tolylene-2,4-diisocyanate
	T_g	Glass transition point
	TLT-64	tris(C5 fluoroalkyl)phosphate (duPont)
	UFAP	Ultrafine AP (<5 microns)
	ϵ_b	Elongation at σ_b
	ϵ_m	Elongation at σ_m
	μ	Microns, 10^{-6} meter
	σ_b	Tensile strength at break
	σ_m	Maximum tensile strength

SECTION I

INTRODUCTION

A. OBJECTIVE (U)

(C) The overall objective of this program is the development of a high-performance solid propellant for ballistic missiles based on the PCDE* prepolymer plasticized with SYFO or a combination of SYFO and FEFO, and the demonstration of this propellant in large-scale motor firings.

(C) The propellant property goals are:

- A theoretical specific impulse of 273 lbf-sec/lbm or higher.
- A density of 0.068 lb/cu in. or higher.
- A burning rate range from 0.4 to 0.5 in./sec at 1000 psia with a pressure exponent at or below 0.65.
- Better than the minimum target uniaxial mechanical properties (σ_m = 100 psi and ε_m = 30%).
- Adequate aging stability.
- Safe manufacturing, handling and use characteristics.
- Adequate liner-bond properties.
- Adequate combustion stability.
- High reproducibility.

(C) The propellant performance and density goals given above were changed during this report period and are different from those listed in previous quarterly reports. The reasons for the changes are discussed in Section III.A.

B. SCOPE (U)

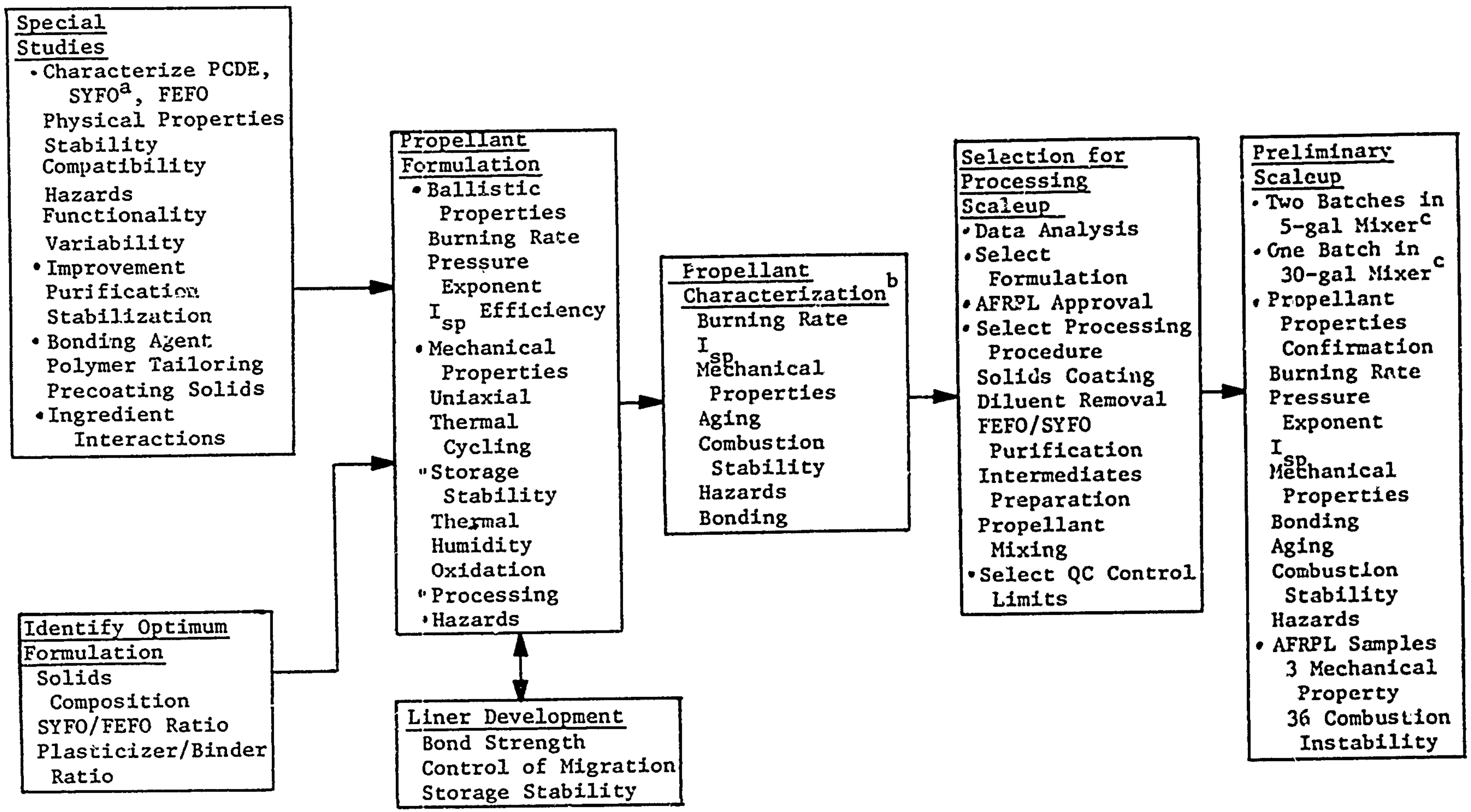
(C) The program is divided into three phases. The major objectives of Phase I - Formulation and Characterization - are the in-depth characterization of the prepolymer and plasticizers, and of a series of propellant formulations, culminating in the selection and preliminary scale-up of two formulations,

* See Glossary

(C) one with PCDE/SYFO and one with PCDE/SYFO/FEFO. The objectives of Phase II - Scale-up - are the further detailed characterization of the two formulations, including process studies in intermediate-scale mixes, systematic evaluation of mechanical properties, hazard evaluation, combustion instability studies, firings of 10- and 70-lb motors and delivery to AFRPL of 15- and 70-lb BATES motors together with other propellant samples. The objectives of Phase III - Super BATES motors - include the scaling up of one of the two propellant formulations to full production-size batches for preparation of three Super BATES motors, instrumented analog motors and test samples to be delivered to AFRPL or tested at ASPC.

(U) The approach being used to attain these objectives is illustrated by the program flow charts in Figures 1, 2 and 3.

PHASE I - FORMULATION AND CHARACTERIZATION



[a]Including heat of formation by subcontract to Dow.
[b]Six formulations: 3 PCDE/SYFO, 3 PCDE/SYFO/FEFO.
[c]For each of two propellants: 1 PCDE/SYFO, 1 PCDE/SYFO/FEFO.

Figure 1

PHASE II - SCALE-UP

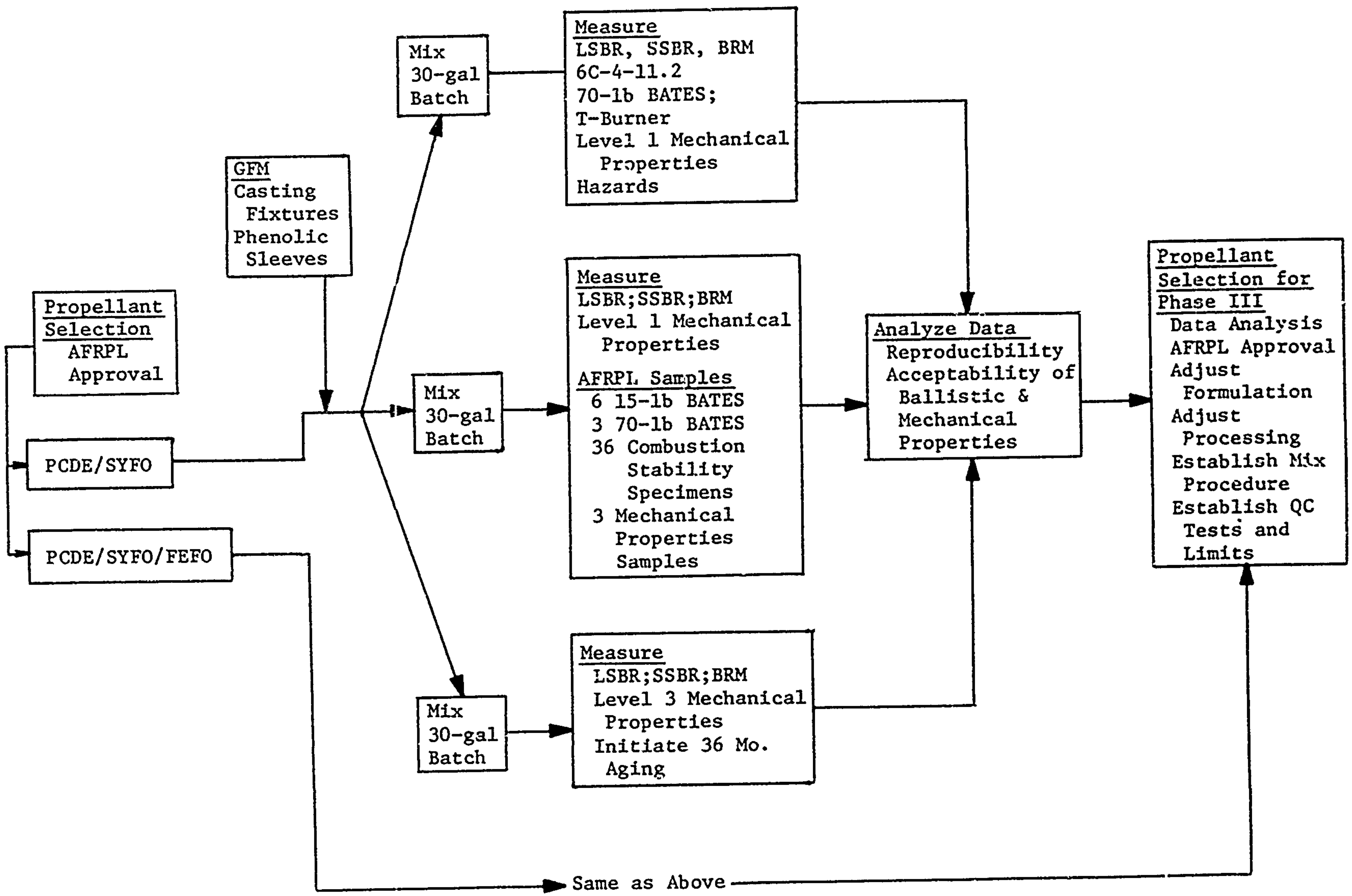


Figure 2

PHASE III - MOTOR DEMONSTRATION

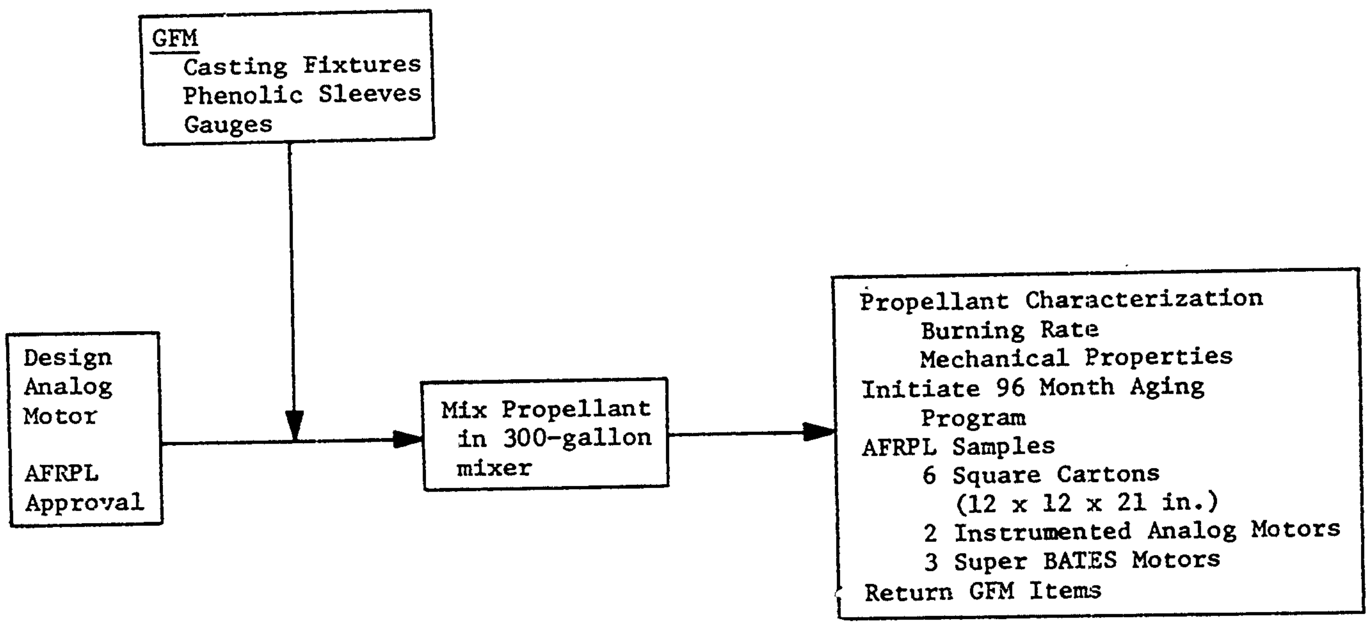


Figure 3

SECTION II

SUMMARY

(C) A. The propellant performance goals were changed during this report period to provide the highest possible theoretical specific impulse at a density no lower than 0.068 lb/cu in. Compositions meeting these goals were selected for evaluation, and are listed together with their calculated performance parameters.

(C) B. Compositions meeting the new goals were prepared and are being tested. Most contain 79 wt% solids and either a 7/1 HMX/AP ratio or HMX alone. The major effort was focused on this composition region, in which maximum theoretical specific impulse occurs at the lowest aluminum content. The conclusions regarding burning rates, processability, mechanical properties, and sensitivity are summarized below.

(C) 1. Increasing the HMX content above the previously used level lowers the burning rates at 1000 psia, but increases the pressure exponents as determined from solid strands. While propellants containing the 3/1 HMX/AP ratio generally have exponents below 0.69, those containing the 7/1 HMX/AP ratio have exponents between 0.7 and 0.8, and those with no AP have exponents above 0.8. The plasticizer composition (SYFO/FEFO or SYFO alone) and concentration have little or no effect on burning behavior. The incorporation of small amounts of UFAP or other additives produces no reduction in pressure exponent.

(C) 2. The processability of PCDE/SYFO propellants is significantly poorer than that of PCDE/SYFO/FEFO propellants. Replacement of as little as 25% of the SYFO by FEFO produces a marked improvement in processability.

(U) 3. As with previously reported propellants, the tensile properties become poorer as the plasticizer concentration increases.

(U) 4. The present propellants are generally much less sensitive than those containing 3/1 HMX/AP, particularly to friction. They appear to be less sensitive to impact as well, particularly those containing no AP.

(U) C. The performance goals can also be met at HMX/AP ratios of 5/1 or 6/1. The use of coated solids lowers the I°_{sps} slightly if the coating is considered as replacing oxidizer, and negligibly if the coating is considered as replacing binder.

(U) D. A wide variety of formulations meeting the program performance goals was prepared in batch sizes from 150-gm to 1-lb. In general, the pressure exponents derived from solid strands were significantly lower than those from corresponding liquid strands. Since pressure exponents are generally even lower in motors, it is expected that the exponent goal (0.65) will be achieved.

(C) E. Two 2C1.5-4 motors were fired. The propellant contained a PCDE/SYFO/FEFO (1/1/1) binder, 3/1 HMX/AP, 16 wt% Al, and 78 wt% total solids. The measured specific impulse efficiencies were 91.7 and 92.2%. Additional small motors (2C1.5-4 size) are being prepared with several formulations meeting the current program performance goals to determine burning rates and pressure exponents, and to test the effects of several formulation variables on performance efficiency, to the extent that this can be done in such motors.

(C) F. Propellants containing 78 wt% solids, a 3/1 HMX/AP ratio and a 1/2 PCDE/plasticizer ratio processed better but had poorer mechanical properties than propellants with a 1/1 PCDE/plasticizer ratio.

(C) G. Propellants containing 79 and 80 wt% solids, a 3/1 HMX/AP ratio and a 1/1/1 PCDE/SYFO/FEFO ratio had satisfactory processability, poor mechanical properties, and relatively high sensitivity to friction.

(U) H. A program was initiated for the screening of aging stabilizers known to be effective in FEFO-containing propellants.

(U) I. Characterization, evaluation and qualification studies were begun on PCDE manufactured by Hercules.

SECTION III

TECHNICAL DISCUSSION

A. REVISED FORMULATION RANGE (U)

(C) In the quarterly program review meeting of 14 June 1973, the Air Force Project officer, Dr. F. Q. Roberto, requested that the propellant performance goals be changed to provide the highest possible theoretical specific impulse at a density of at least 0.068 $lb/in.^3$. (The goals listed in Section I.A. have been changed accordingly.) It was agreed that the aluminum content should be kept low in order to increase the specific impulse efficiency, and that compositions with high HMX/AP ratios should be explored because these provide the highest theoretical specific impulses. (The highest HMX/AP ratio used previously on this program was 3/1.) Because increasing the HMX content generally results in higher pressure exponents, it was also agreed that a pressure exponent as high as 0.65 would be acceptable.

(C) The compositions selected for initial evaluation all contain 79 wt% solids, of which 12 to 14 wt% is Al and the remainder is either HMX alone or an HMX/AP mixture at a 7/1 wt ratio. These compositions and their calculated performance parameters are listed in Table 1 along with the values for previously investigated propellants containing a 3/1 HMX/AP ratio, and are shown, at the points marked by small squares, on the correspondingly numbered Figures 4 through 15. It may be seen from these figures that increasing the solids loading from 79 to 80 wt% would provide only small increases in specific impulse, less than 0.5 sec, and would lower the binder content to near or even below 24 volume percent, which might make processing quite difficult.

(C) All of the formulations in Table 1 have been prepared and evaluated. As described in Section III.B.1., the propellants containing no AP had excessively high pressure exponents, while the propellants containing the 7/1 HMX/AP ratio appeared to be marginal in this respect. Compositions with lower HMX/AP ratios were, therefore, examined. The compositions

TABLE 1

COMPOSITION AND THEORETICAL PERFORMANCE OF SELECTED PCDE/SYFO/FEFO PROPELLANTS (U)

No.	HMX/AP wt. ratio	Plasticizer/Polymer Ratio			Total Solids, %	Al %	Volume Percent Binder	Density, lb/cu in.	I°_{sps} lbf-sec/lbm
		SYFO	FEFO	PCDE					
1	All HMX	1	1	1	79	14	25.3	0.0682	273.8
2	7/1	1	1	1	79	14	25.3	0.0684	273.4
3	3/1	1	1	1	79	14	25.4	0.0686	272.5
4	All HMX	3	3	2	79	14	25.0	0.0683	274.3
5	7/1	3	3	2	79	14	25.2	0.0685	273.7
6	3/1	3	3	2	79	16	25.4	0.0691	273.0
7	All HMX	2	0	1	79	12	24.9	0.0680	273.6
8	7/1	2	0	1	79	14	25.2	0.0685	273.8
9	3/1	2	0	1	79	14	25.2	0.0687	273.2
10	All HMX	3	0	1	79	12	24.8	0.0681	274.2
11	7/1	3	0	1	79	14	25.0	0.0687	274.2
12	3/1	3	0	1	79	14	25.1	0.0689	273.5

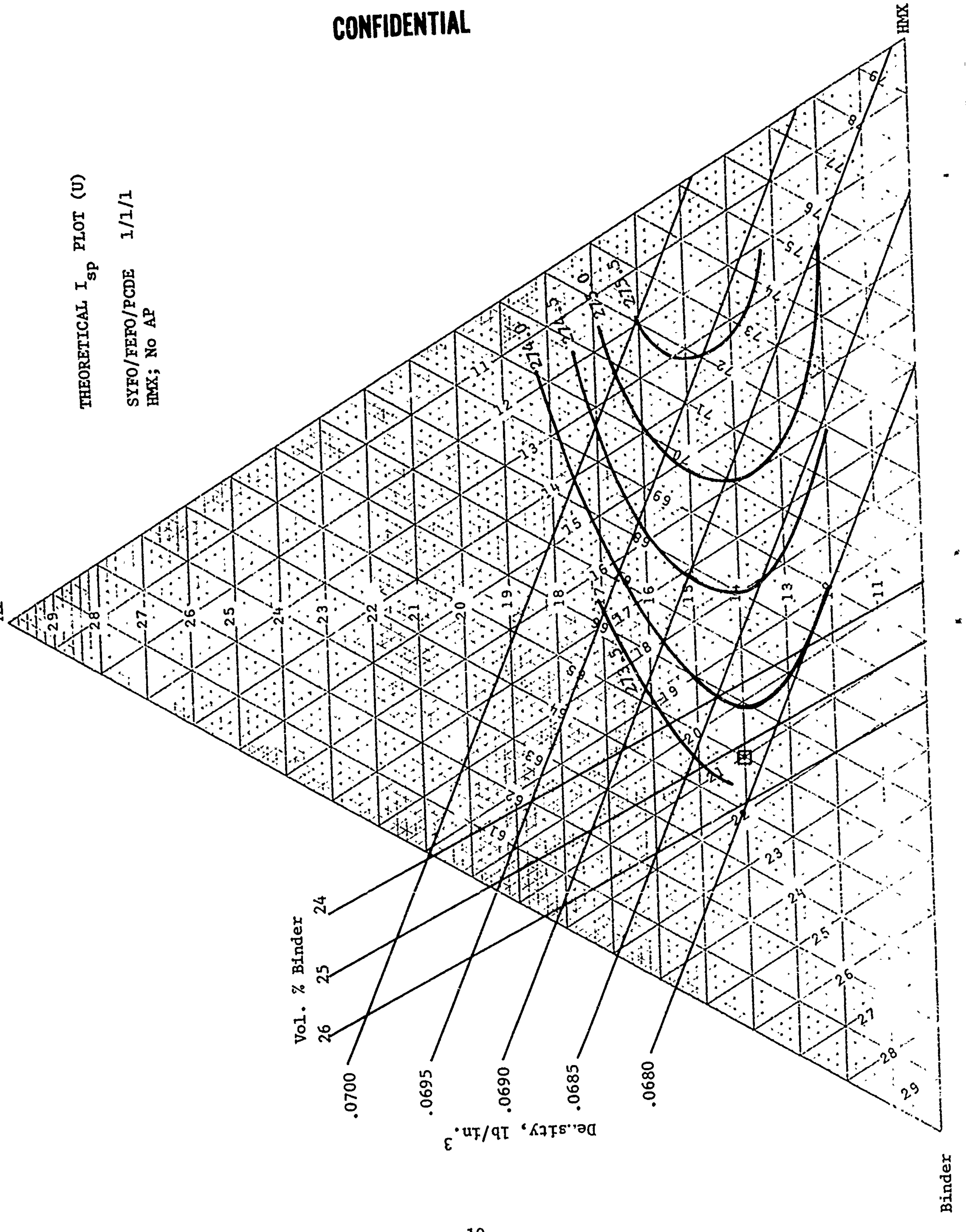
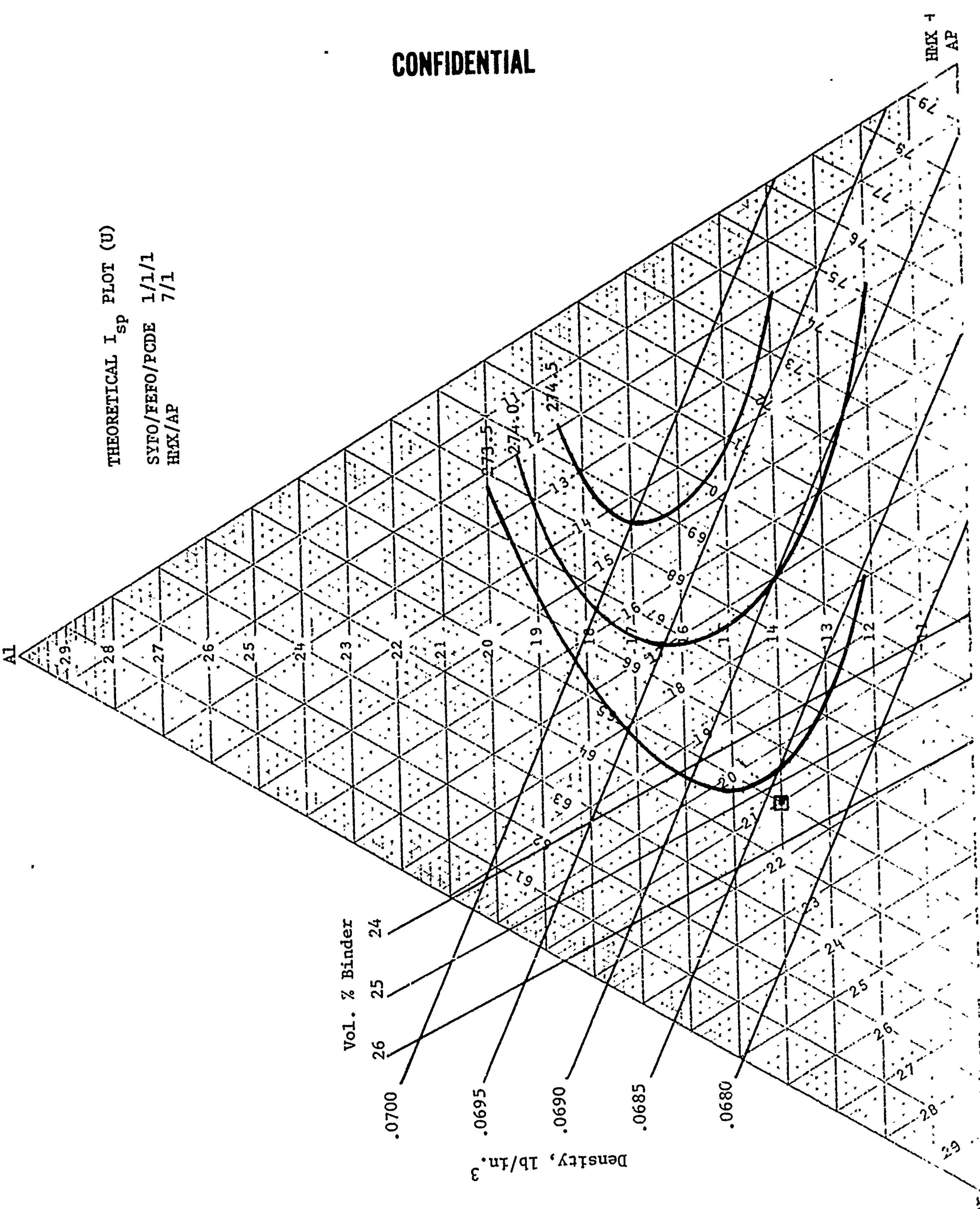

THEORETICAL I_{sp} PLOT (U)
SYFO/FEFO/PCDE 1/1/1
HMX; No AP
Al
HMX
Binder
Vol. % Binder
24
25
26
.0700
.0695
.0690
.0685
.0680
Density, lb/in.^{3}

Figure 4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SYFO/FEFO/PCDE 1/1/1
HMX/AP 7/1
Al
HMX + AP
Vol. % Binder
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25
26
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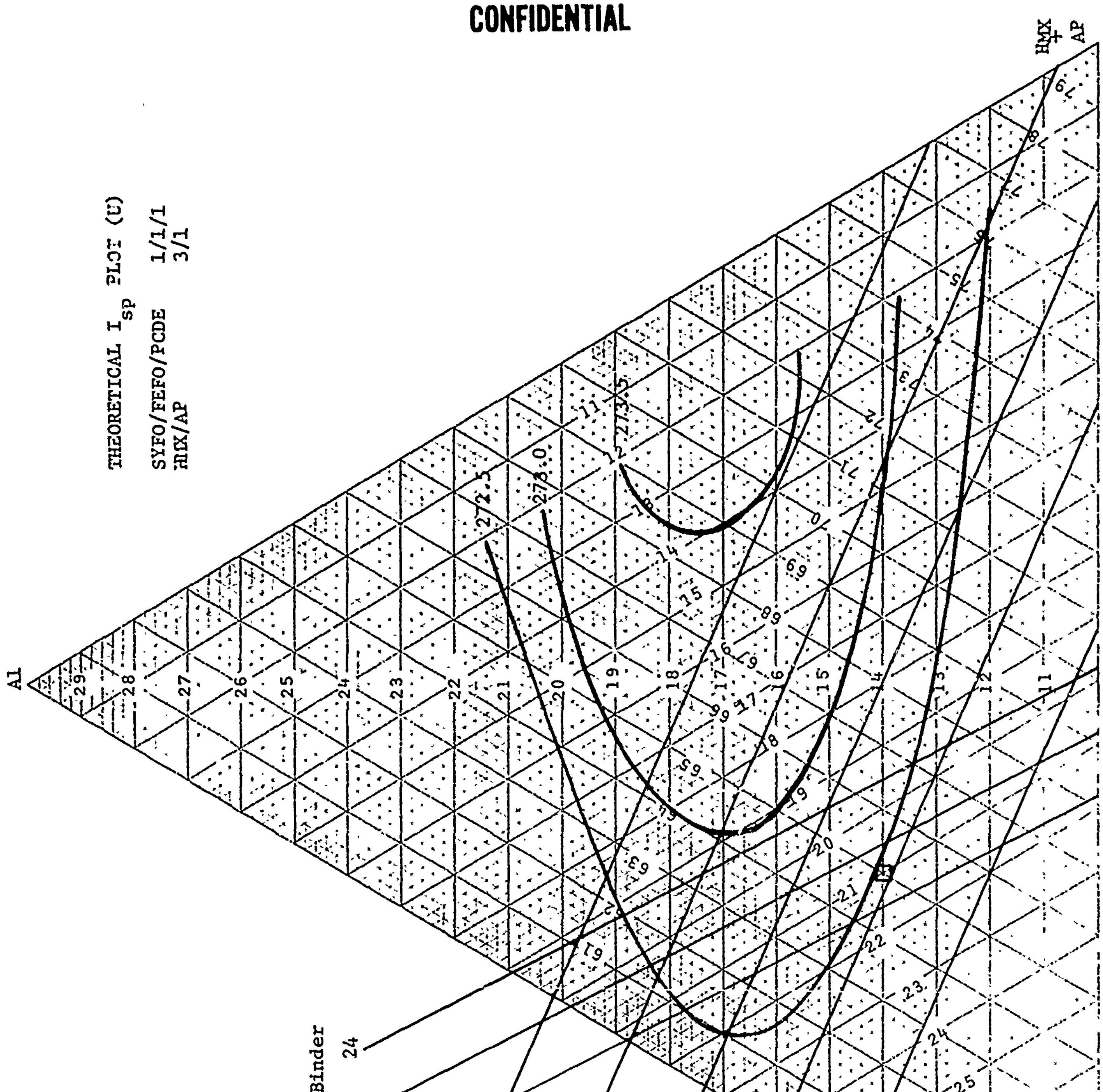
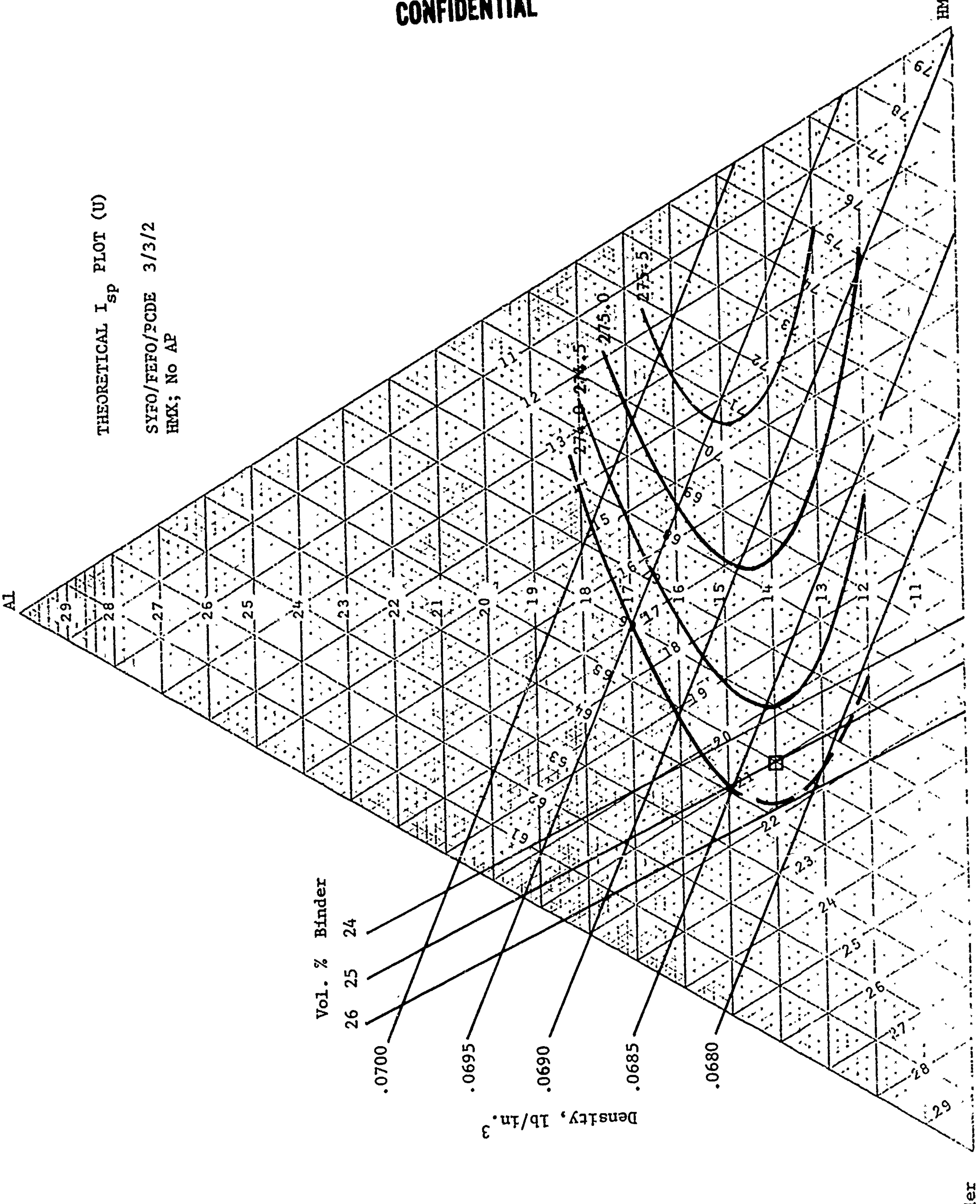
.0695
.0690
.0685
.0680
Density, lb/in.3
273.5
274.0
274.5

Figure 5



THEORETICAL I_{sp} PLOT (U)
SYFO/FEFO/PCDE 1/1/1
HMX/AP 3/1
Al
HMX + AP
Binder
Vol. % Binder
24
25
26
.0700
.0695
.0690
.0685
.0680
Density, lb/in.^{3}
272.5
273.0
273.5

Figure 6


THEORETICAL I_sp PLOT (U)
SYFO/FEFO/PCDE 3/3/2
HMX; No AP
Al
HMX
Binder
Vol. % Binder
24
25
26
Density, lb/in.^3
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.0695
.0690
.0685
.0680
274.0
274.5
275.0
275.5

Figure 7

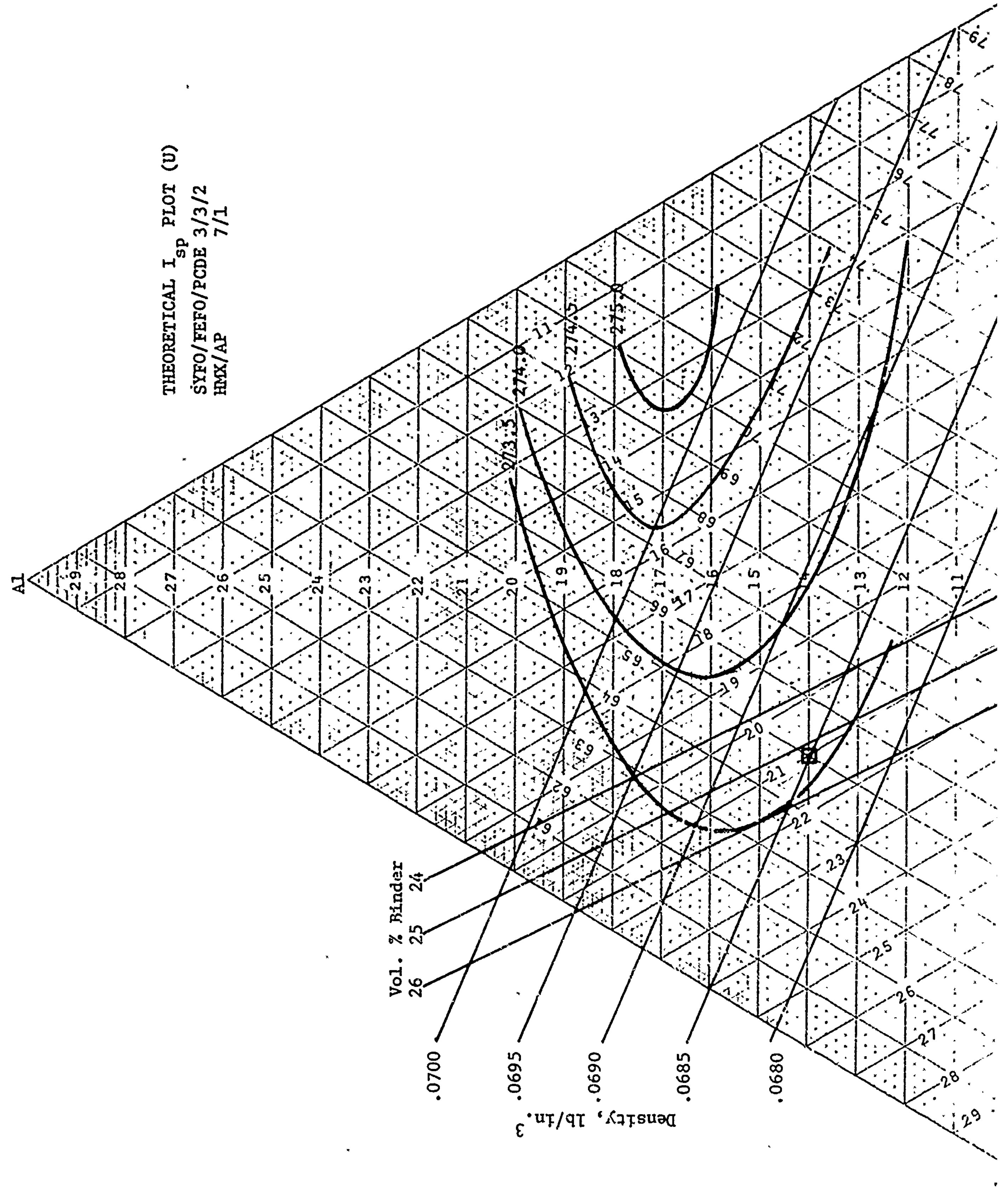

THEORETICAL I_sp PLOT (U)
SYFO/FEFO/PCDE 3/3/2
HMX/AP 7/1
Al
HMX + AP
Vol. % Binder
24
25
26
.0700
.0695
.0690
.0685
.0680
Density, lb/in.³
273.5
274.0
274.5
275.0

Figure 8

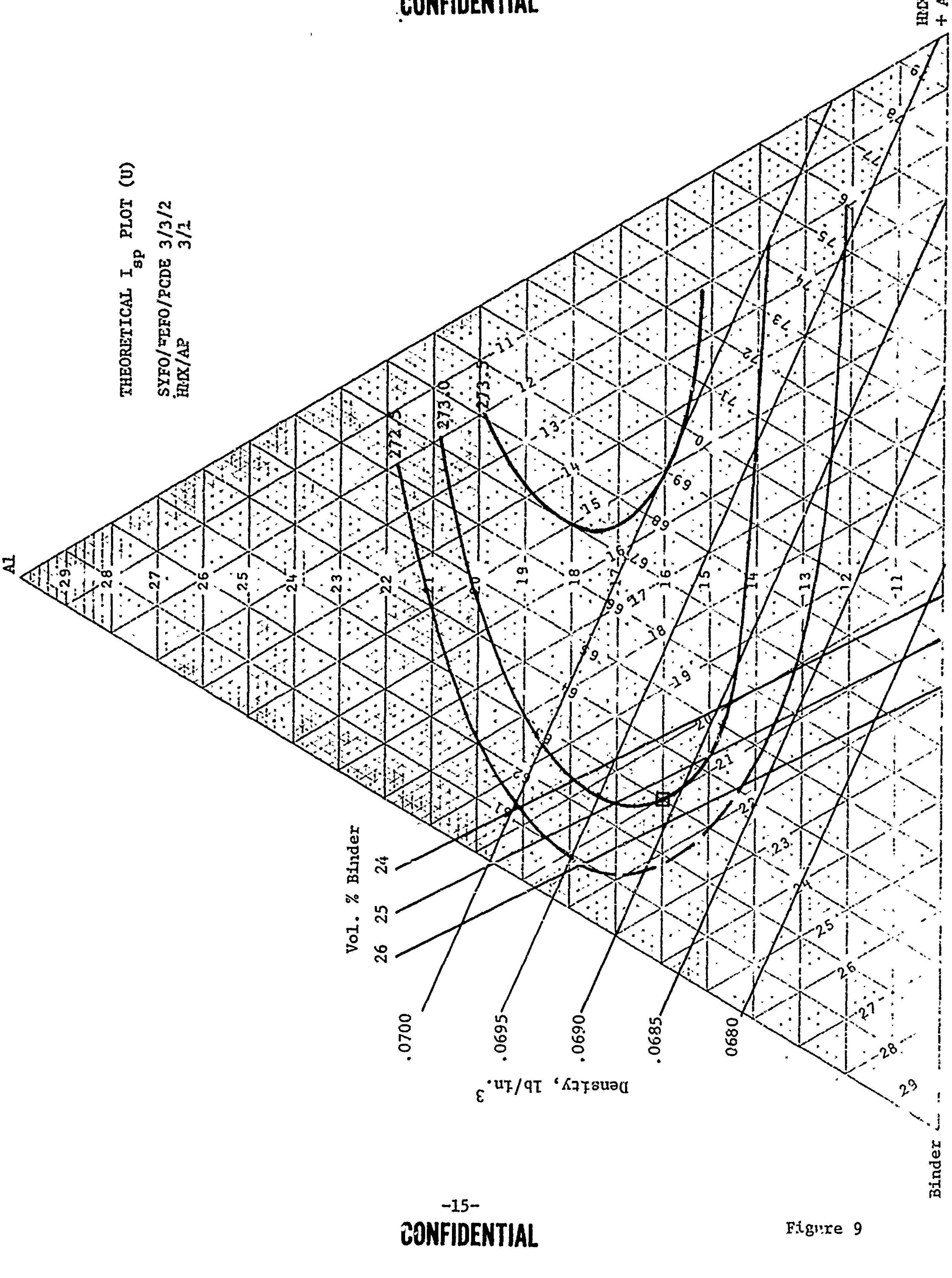
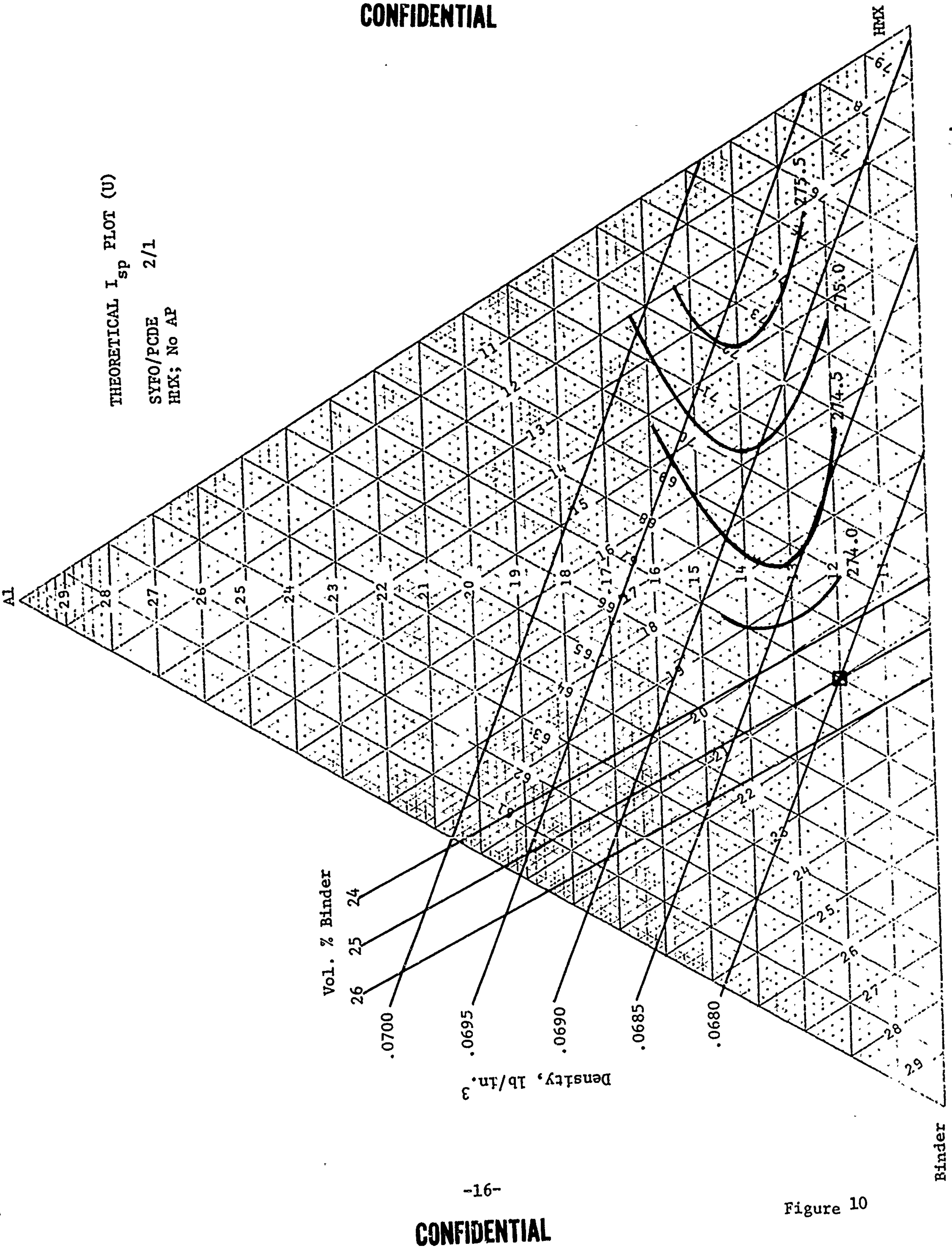

THEORETICAL I_{sp} PLOT (U)
SYFO/TEFO/PCDE 3/3/2
HMX/AP 3/1
Al
HMX + AP
Binder
Vol. % Binder
24
25
26
Density, lb/in.^{3}
.0700
.0695
.0690
.0685
.0680
272.5
273.0
273.5

Figure 9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SYFO/PCDE 2/1
HMX; No AP
Al
HMX
Binder
Vol. % Binder
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25
26
.0700
.0695
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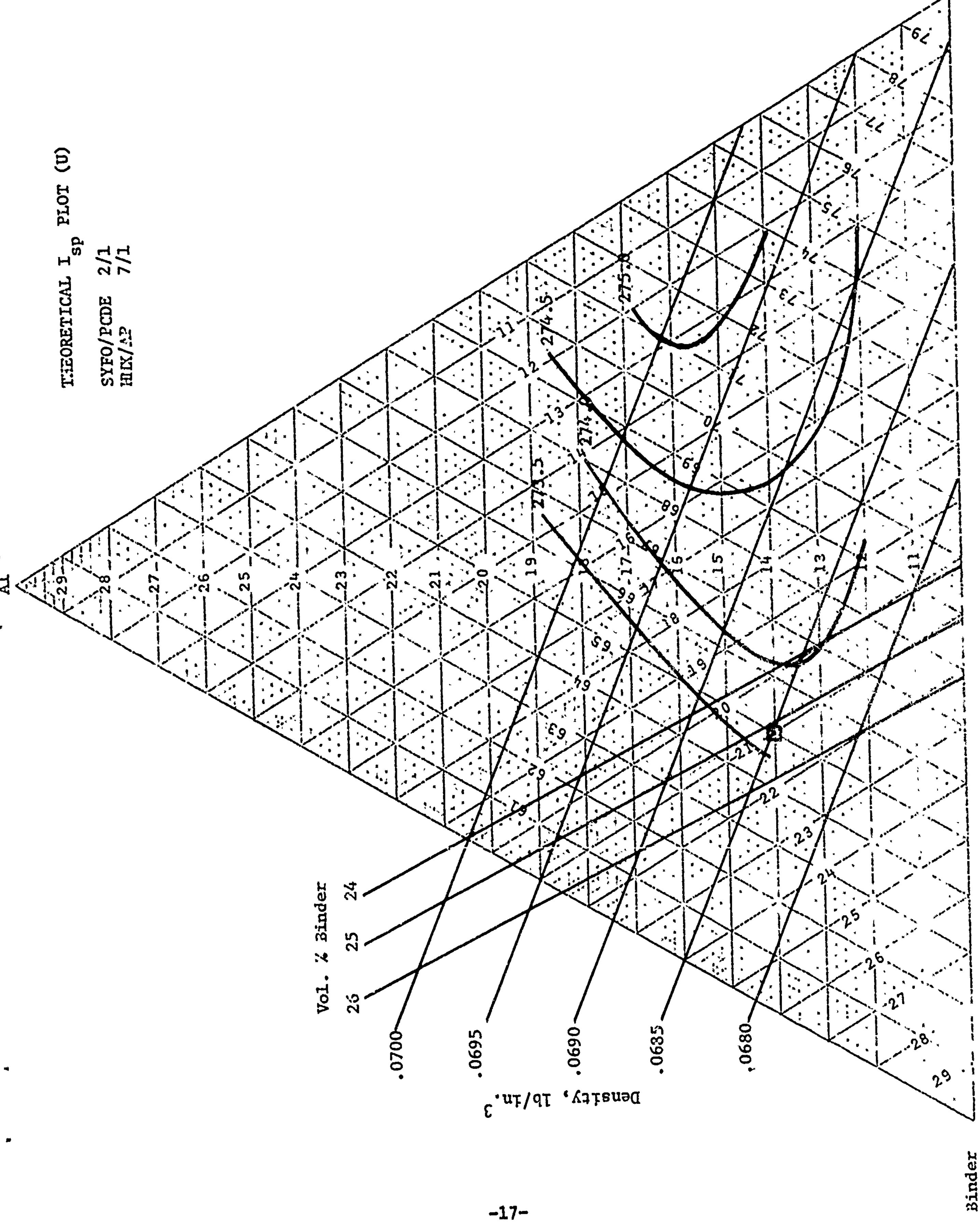
.0685
.0680
Density, lb/in.^{3}
275.5
275.0
274.5
274.0

Figure 10


THEORETICAL I sp PLOT (U)
SYFO/PCDE 2/1
HMX/AP 7/1
Al
HMX AP
Binder
Vol. % Binder
24
25
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Density, lb/in.3
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.0690
.0685
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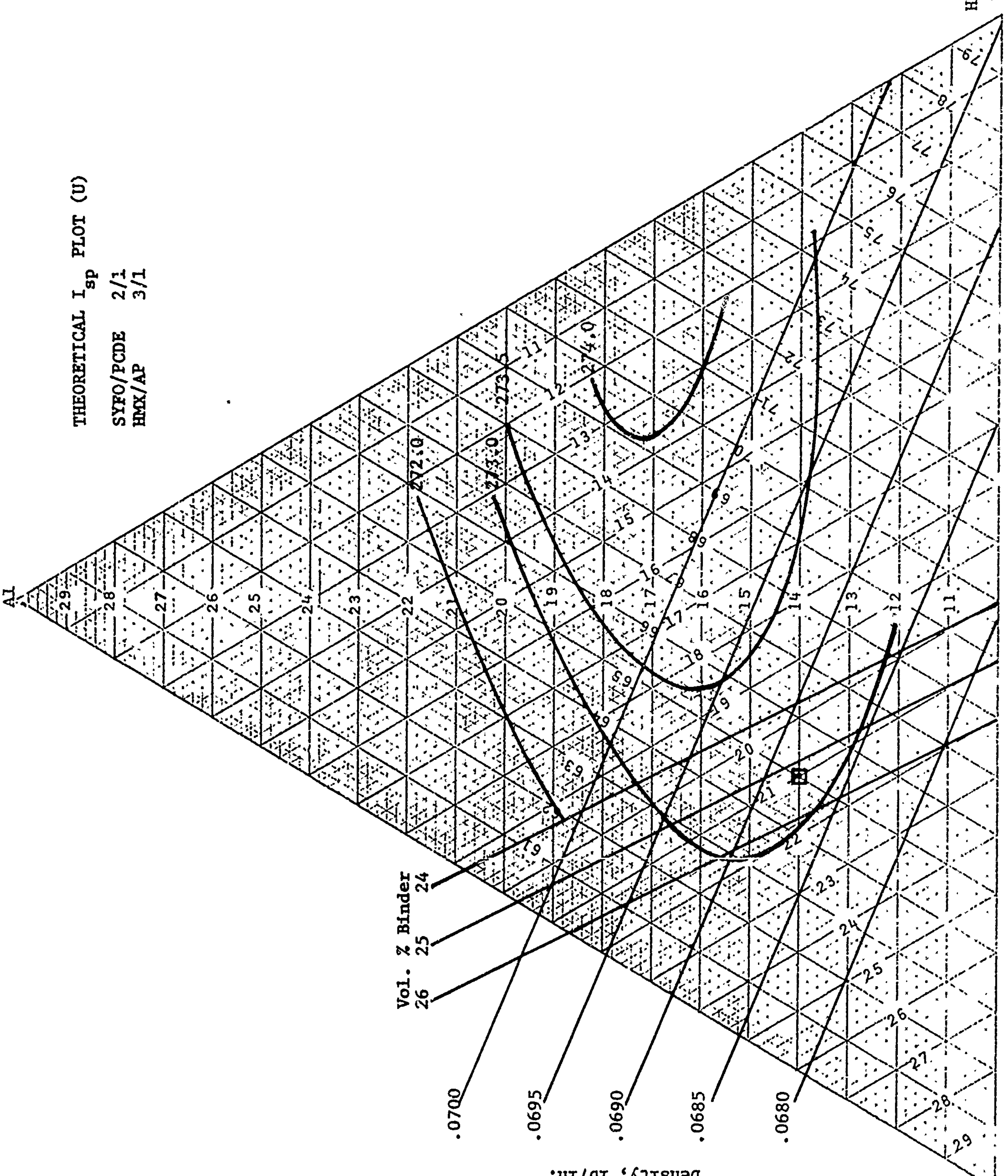
275.0
274.5
274.0
273.5

Figure 11



THEORETICAL I_{sp} PLOT (U)
SYFO/PCDE 2/1
HMX/AP 3/1
Al
HMX + AP
Binder
272.0
272.5
273.0
273.5
274.0
Vol. % Binder
24
25
26
.0700
.0695
.0690
.0685
.0680
Density, lb/in.³

Figure 12

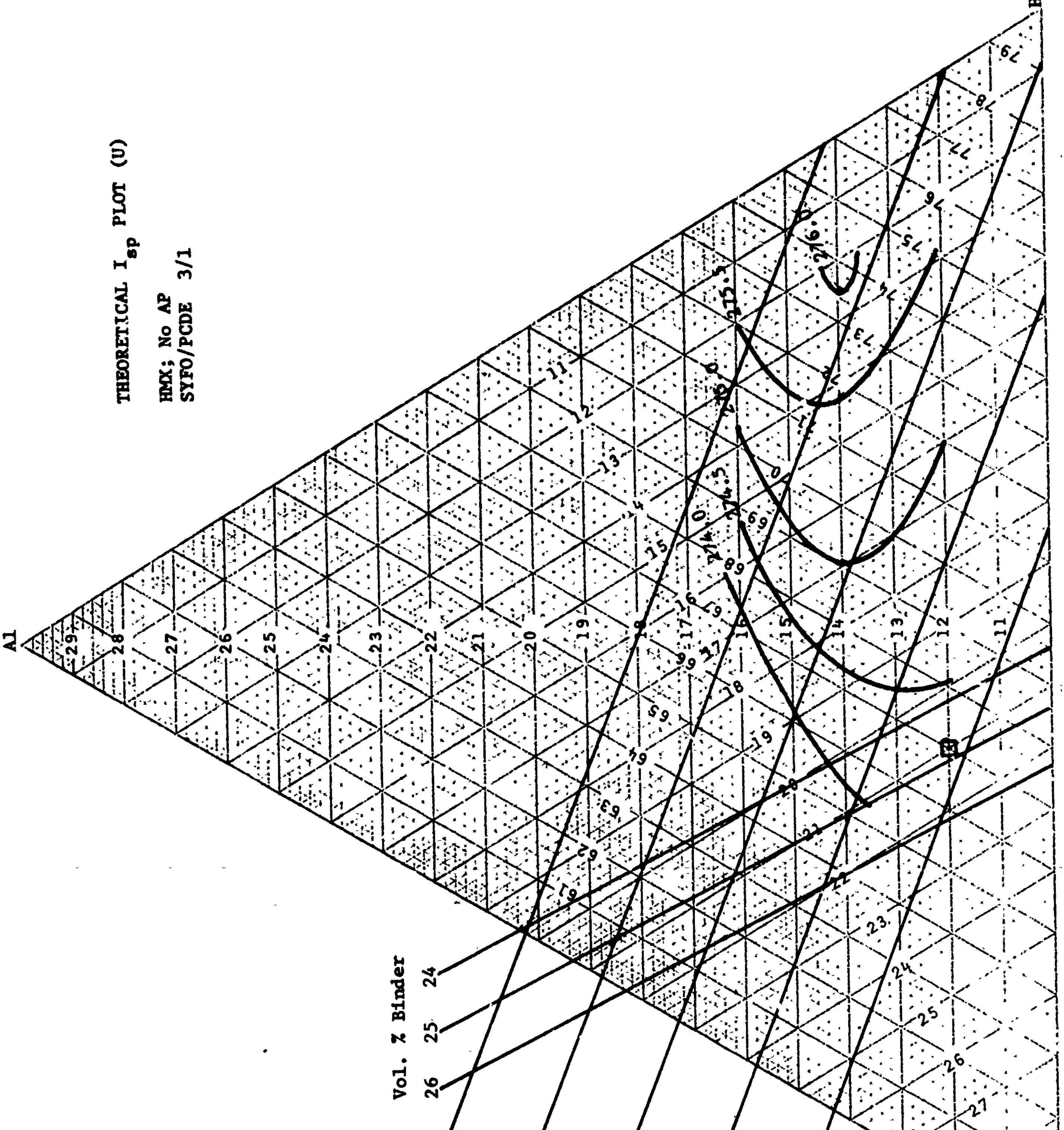

THEORETICAL I_{sp} PLOT (U)
HMX; No AP
SYFO/PCDE 3/1
Al
HMX
Binder
Vol. % Binder
24
25
26
Density, lb/in.^{3}
.0700
.0695
.0690
.0685
.0680

Figure 13

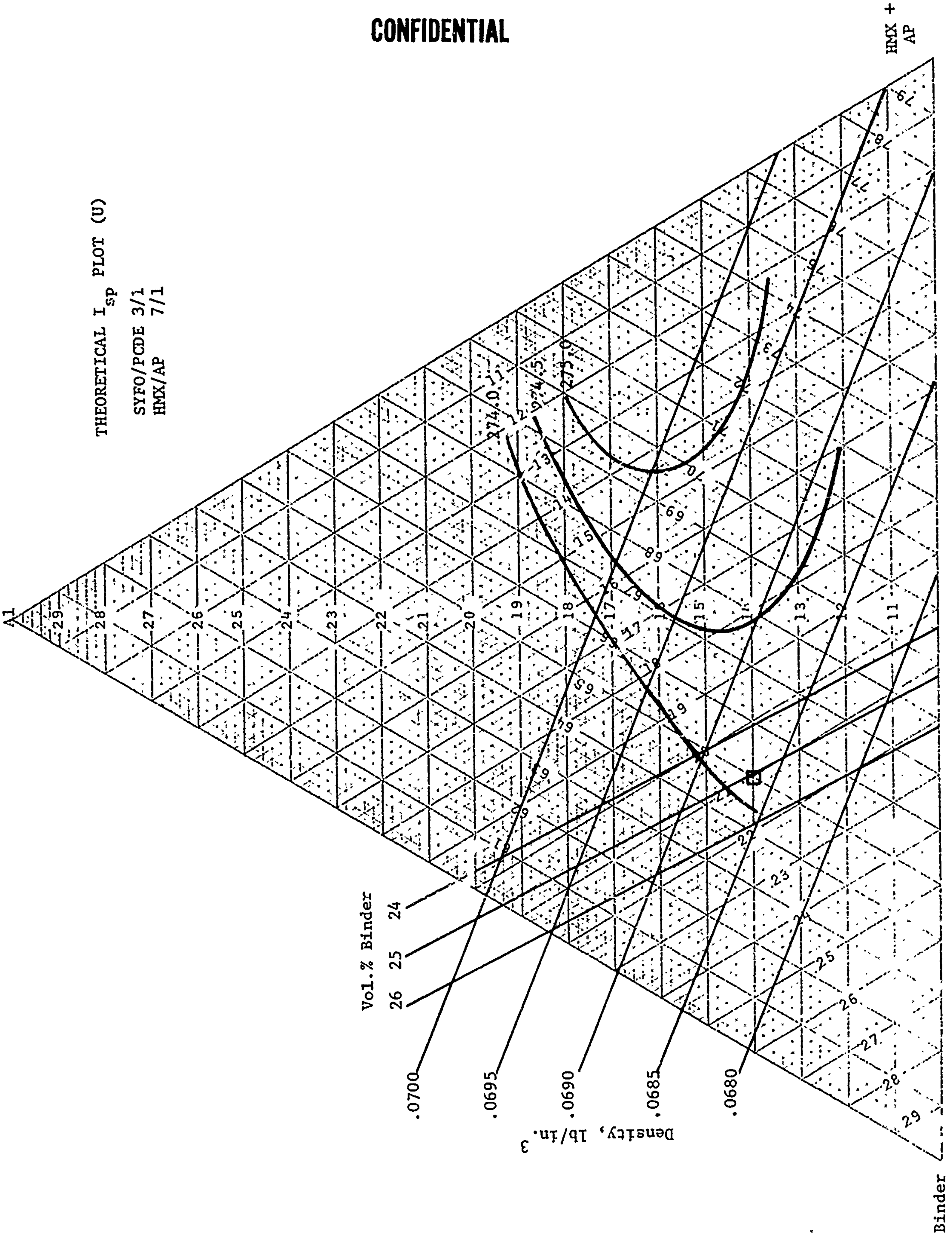

THEORETICAL I_{sp} PLOT (U)
SYFO/PCDE 3/1
HMX/AP 7/1
Al
HMX + AP
Binder
Vol.% Binder
24
25
26
.0700
.0695
.0690
.0685
.0680
Density, lb/in.^{3}
274.0
274.5
275.0

Figure 14

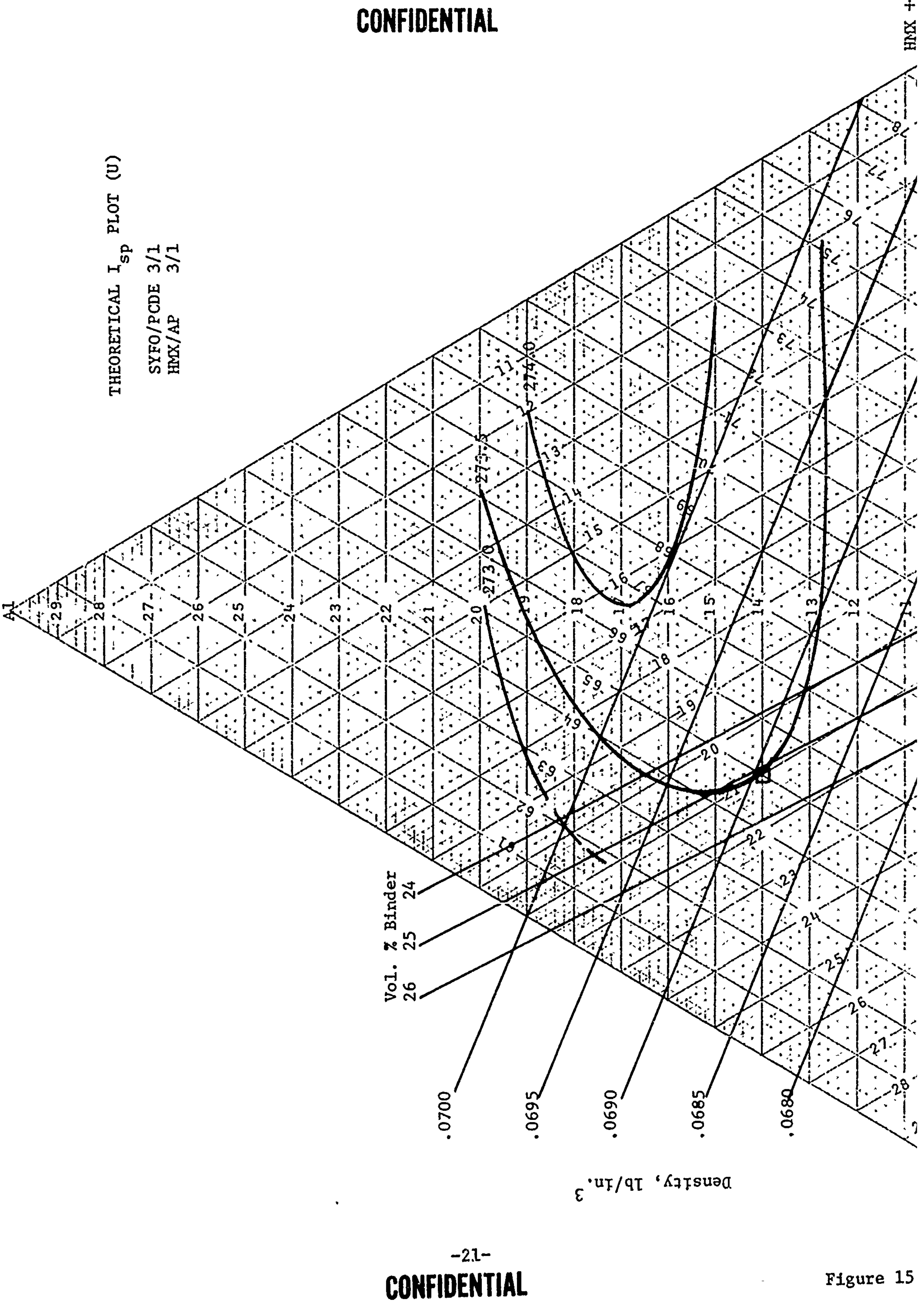

THEORETICAL I_sp PLOT (U)
SYFO/PCDE 3/1
HMX/AP 3/1
HMX +
Al
273.0
273.5
274.0
Vol. % Binder
24
25
26
.0700
.0695
.0690
.0685
.0680
Density, lb/in.3

Figure 15

(C) and performance parameters of propellants containing 5/1 and 6/1 HMX/AP ratios are given in Table 2, for propellants with a 2/1 plasticizer/polymer ratio, and in Table 3, for propellants with a 3/1 plasticizer/polymer ratio. Table 3 also contains the results of calculations with coated solids.* It may be seen that (1) the program performance goals can be met at 79 or 80 wt% solids and with either a 5/1 or 6/1 HMX/AP ratio, (2) the all-SYFO propellants permit the goals to be met at lower aluminum contents, (3) the coatings on the HMX and AP lower the specific impulse slightly if the coating is considered as replacing oxidizer, but negligibly if considered as replacing binder, and (4) compositions containing 81 wt% solids probably contain too little binder to be processable.

(C) Table 4 shows the relationship between calculated performance parameters and NF_2 or F content of a number of propellant compositions, all at 79 wt% solids. The NF_2 and F contents were calculated taking the polymer composition as that of the PCDE repeating unit: $-CNF_2(CN)CH_2O-$, which contains 43.32% NF_2 and 31.65% F. It may be seen that the highest NF_2 content is provided by the binder with the least amount of plasticizer, and that dilution with FEFO drastically reduces the NF_2 content. If it is true that the performance efficiency is a function of the NF_2 content, then the plasticizer content, especially the FEFO content, should be minimized. On the other hand, the theoretical specific impulse and the density increase with increasing SYFO content. These two mutually opposing factors--efficiency and theoretical specific impulse as functions of SYFO content--may tend to minimize the differences in delivered specific impulse among these formulations. Several formulations were selected, therefore, to test the effects of propellant composition on performance efficiency (to the extent that this can be done in small motors) as well as on burning rates and pressure exponent. These will be discussed in Section III.E.

* Assuming HMX and AP contain the coatings cited in Table 2.

TABLE 2

SYFO/FEFO-PLASTICIZED PCDE PROPELLANTS (U)

(2/1 Plasticizer/PCDE Ratio)

		Uncoated Solids				
SYFO/FEFO Per PCDE	HMX/AP Wt Ratio	Total Solids Wt %	Al Wt %	I°_{sps} lbf-sec/lbm	Density lb/cu in.	Vol. Fraction Binder
1/1	5/1	79	15	272.9	0.0688	0.255
1/1	5/1	80	14	273.0	0.0688	0.243
1/1	5/1	81	15	273.2	0.0691	0.232
1/1	6/1	79	14	273.0	0.068	0.254
1/1	6/1	80	14	273.1	0.0688	0.243
1/1	6/1	81	14	273.3	0.0689	0.231
2/0	5/1	79	13	273.4	0.0686	0.252
2/0	5/1	80	14	273.5	0.0689	0.241
2/0	5/1	81	13	273.6	0.0689	0.229
2/0	6/1	79	13	273.5	0.0686	0.252
2/0	6/1	80	13	273.6	0.0687	0.240
2/0	6/1	81	14	273.8	0.0690	0.229

TABLE 3

SYFO/FEFO-PLASTICIZED PCDE PROPELLANTS (U)

(3/1 Plasticizer/PCDE Ratio)

			Uncoated Solids				Coated Solids*			
SYFO/FEFO Per PCDE	HMX/AP Wt Ratio	Total Solids Wt %	Al Wt %	I°_{sps} lbf-sec/lbm	Density lb/cu in.	Vol. Fraction Binder	Al Wt %	I°_{sps} lbf-sec/lbm	Density lb/cu in.	Vol. Fraction Binder
1.5/1.5	5/1	79	15	273.1	0.0690	0.254				
1.5/1.5	5/1	80	16	273.3	0.0693	0.243				
1.5/1.5	5/1	81	16	273.4	0.0694	0.231				
1.5/1.5	6/1	79	15	273.3	0.0689	0.254				
1.5/1.5	6/1	80	15	273.4	0.0691	0.242				
1.5/1.5	6/1	81	15	273.5	0.0692	0.230				
2/1	5/1	79	14	273.3	0.0688	0.252	13	273.1	0.0685	0.251
2/1	5/1	80	14	273.4	0.0690	0.241	15	273.3	0.0690	0.241
2/1	5/1	81	15	273.6	0.0693	0.230	15	273.4	0.0692	0.229
2/1	6/1	79	14	273.4	0.0688	0.252	14	273.3	0.0686	0.252
2/1	6/1	80	14	273.6	0.0689	0.241	14	273.4	0.0688	0.240
2/1	6/1	81	14	273.7	0.0691	0.229	15	273.5	0.0692	0.229
3/0	5/1	79	13	273.7	0.0688	0.250	13	273.5	0.0686	0.250
3/0	5/1	80	13	273.8	0.0689	0.239	13	273.6	0.0688	0.238
3/0	5/1	81	13	273.9	0.0690	0.227	13	273.7	0.0689	0.227
3/0	6/1	79	13	273.8	0.0687	0.250	13	273.6	0.0686	0.250
3/0	6/1	80	13	273.9	0.0689	0.239	13	273.7	0.0687	0.238
3/0	6/1	81	14	274.1	0.0692	0.228	14	273.9	0.0690	0.227

* On average, 0.5 wt% polymer and 0.23 wt% DOA on HMX; 0.1 wt% polymer on AP.

TABLE 4

NF_2 AND F CONTENTS OF SELECTED SYFO/FEFO-PLASTICIZED PCDE PROPELLANTS (U)

SYFO/FEFO/PCDE Wt Ratio			HMX/AP Wt Ratio	Total Solids* Wt %	Aluminum Wt %	I^*_{sps} lbf-sec/lbm	Density lb/cu in.	Vol. Fraction Binder	$-NF_2$ % in Prop.	$-F$ % in Prop.
1	1	1	3/1	79	16	272.7	0.0690	0.256	5.43	5.24
1	1	1	5/1	79	15	272.9	0.0688	0.255	5.43	5.24
1	1	1	6/1	79	14	273.0	0.0686	0.254	5.43	5.24
1	1	1	7/1	79	14	273.4	0.0684	0.253	5.43	5.24
1	1	1	∞	79	14	273.8	0.0682	0.253	5.43	5.24
2	0	1	3/1	79	14	273.2	0.0687	0.252	7.82	6.60
2	0	1	5/1	79	13	273.4	0.0686	0.252	7.82	6.60
2	0	1	6/1	79	13	273.5	0.0686	0.252	7.82	6.60
2	0	1	7/1	79	13	273.8	0.0685	0.252	7.82	6.60
2	0	1	∞	79	12	273.6	0.0680	0.249	7.82	6.60
1.5	1.5	1	3/1	79	16	273.0	0.0691	0.254	4.96	5.06
1.5	1.5	1	5/1	79	15	273.1	0.0690	0.254	4.96	5.06
1.5	1.5	1	6/1	79	15	273.3	0.0689	0.254	4.96	5.06
1.5	1.5	1	7/1	79	14	273.7	0.0685	0.252	4.96	5.06
1.5	1.5	1	∞	79	14	274.3	0.0683	0.250	4.96	5.06
2	1	1	5/1	79	14	273.3	0.0688	0.252	5.86	5.56
2	1	1	6/1	79	14	273.4	0.0688	0.252	5.86	5.56
3	0	1	3/1	79	14	273.5	0.0689	0.251	7.66	6.58
3	0	1	5/1	79	13	273.7	0.0688	0.250	7.66	6.58
3	0	1	6/1	79	13	273.8	0.0687	0.250	7.66	6.58
3	0	1	7/1	79	13	274.2	0.0687	0.250	7.66	6.58
3	0	1	∞	79	12	274.2	0.0681	0.248	7.66	6.58

* Uncoated

B. FORMULATION STUDIES AT 78-80 WT% SOLIDS (U)

1. At 78 Wt% Solids (U)

(C) Work on PCDE/plasticizer (1/2) propellants at 78 wt% solids and an HMX/AP ratio of 3/1 was completed. The theoretical specific impulse for the SYFO-plasticized system is 272.8 lbf-sec/lbm and the density is 0.0690 lb/cu in. The corresponding values for the SYFO/FEFO (1/1) plasticized system are 272.6 lbf-sec/lbm and 0.0688 lb/cu in. The compositions and properties of a series of PCDE/SYFO (1/2) propellants are presented in Table 5 and of PCDE/SYFO/FEFO (1/1/1) propellants, in Table 6. Although both of these series processed better than the PCDE/plasticizer (1/1) series at 78 wt% solids, the mechanical properties were not as good. It may be seen from the tables that it was difficult to exceed 22% elongation and still maintain an initial modulus of approximately 500 psi. Several batches, for example, 26C, 27D, 29D, 30B and 32B exhibited such properties with tensile strengths of 82 psi or greater.

(U) A PCDE/SYFO/FEFO (1/1/1) propellant similar to 29C and 32A was scaled up to the 400-gm batch size and successfully vacuum-cast into two 1/4-lb motors. The results of the motor firings are given in Section III.F.

(C) The burning rate of the PCDE/SYFO/FEFO (1/1/1) propellant was approximately 0.52 in./sec at 1000 psia, as determined from 2-in. solid strands. This was somewhat lower than the burning rate of 0.57 in./sec reported last month for PCDE/SYFO (1/2) propellants. The pressure exponents were similar--approximately 0.66.

2. PCDE/SYFO/FEFO (1/1/1) Propellants at 79 and 80 wt% Solids (U)

(C) Before beginning an investigation of PCDE propellant systems containing HMX/AP ratios greater than 3/1, a number of PCDE/SYFO/FEFO (1/1/1) propellants with an HMX/AP ratio of 3/1 and 79 and 80 wt% total solids were processed. The theoretical specific impulse values for these are 272.5 and 272.7 lbf-sec/lbm and densities are 0.0694 and 0.0691 lb/cu in., respectively. The compositions and properties of these propellants are presented in Tables 7 and 8.

(C) Although these propellants were less fluid than those at 78 wt% solids, the processability was satisfactory. Again, acceptable tensile strengths and moduli were achieved, but the elongations were less than 20%.

TABLE 5

PROPERTIES OF PCDE/SYFO (1/2) PROPELLANTS* (U)
(78 wt% Solids, 150-gm batches)

Batch No. B64-	25A	25C	26D	27A	27C	29A	29B
Submix No. B64-	44	44	44	44	44	19A-C	19A-C
Polymer Ingredients, equivalents							
PCDE**	68	63	68	63	64	68	63
HT		32	32	31			
PCP-0301	32	32				32	32
PCP-0200		5		5	5		5
PEG-4000							
FeAA, wt%	.005	.005	.005	.005	.005	.01	.0[illegible]
Cure, Days at 110°F	7	7	10	10	10	7	7
Hardness, Shore A	31	35	36	35	36	50	50
Mechanical Properties at 77°F (Avg. of 2 JANNAF bars)							
σ_m, psi	48	59	64	62	73	91	98
ϵ_m, %	27	27	27	27	26	20	18
ϵ_b, %	33	32	34	32	28	21	19
E_o, psi	246	288	319	303	347	568	624

*Composition: 16 wt% Al (MDX-65), 30.5 wt% HMX-A (lot C0420 coat 1), 16 wt% HMX-E, 15.5 wt% AP (130μ, lot 1-13 coated); 0.1 wt% Santicizer 8, 105 equivalents HDI.

**PCDE Lot No. LR-12260-44 (Shell).

TABLE 6

PROPERTIES OF PCDE/SYFO/FEFO (1/1/1) PROPELLANTS[a] (U)

Batch No. B64-	24C	24D	25B	25D	26A	26B	26C	27D	29C	29D	30A	30B	32A'	32B	32C[b]
Submix No. B64-	43	43	43	43	43	43	42 & 43	19B	19B	281	281	281	281	281	281
Polymer Ingredients, equiv.															
PCDE[c]	64	68	63	69	69	68	64	63	63	68	63	67	63	66	66
HT				31	31	31	31			32	32	32		32	32
PCP-0301	31	32	32					32	32				32		
PCP-0200	5		5				5	5	5		5		5		
PEG-4000						1						1		2	2
FeAA, wt%	.01	.005	.005	.01	.01	.01	.01	.01	.01	.01	.01	.01	.01	.01	.01
Cure, days at 110°F	7	7	7	7	7	7	7	6	6	7	7	7	7	7	7
Hardness, Shore A	37	38	42	43	45	44	50	50	40	49	50	48	38	45	48
Mechanical Properties at 77°F (Avg. of 2 JANNAF bars)															
σ_m, psi	64	58	63	78	77	78	85	32	62	85	87	85	74	82	84
ϵ_m, %	25	24	24	22	23	26	22	22	17	21	20	22	21	22	21
ϵ_b, %	27	28	25	24	26	28	23	23	17	22	21	23	22	24	21
E_o, psi	361	328	310	453	429	383	475	510	531	510	547	473	448	470	490
Sensitivity															
Impact, cm/2 kg wt-uncured (50% fire pt, BuMines app.)									15		10	12	11	13	13
- cured				5	8	8	9	7	5	7	6	7			
DTA, °F Exotherm, onset-uncured									300		353	317	309	316	309
- cured				301	290	308	318	309	310	353	294	298			
ignition - uncured									403		407	402	405	406	402
cured				405	403	403	403	407	403	398	401	400			
Rotary Friction, gm at 3000 rpm - uncured									200		>4000	>4000	500	526	300
cured				1720	1730	1570	1600	1840	1800	1840	1740	1600			
Burning rate at 1000 psia, in./sec[d]	0.51	0.52	0.51	0.54	0.53	0.53	0.52	0.51	0.50	0.52	0.51	0.51			
Pressure Exponent	0.64	0.66	0.65	0.66	0.67	0.65	0.62	0.66	0.67	0.66	0.65	0.66			

(a) Composition: 16 wt% Al (MDX-65), 30.5 wt% HMX-A (lot C0420 coated), 16 wt% HMX-E, 15.5 wt% AP (130μ, lot 1-13 coated); 0.1 wt% Santicizer 8, 105 equivalents HDI.
(b) Batch 32C, HMX-A coated and HMX-C coated each 15.25 wt%.
(c) PCDE lot No. LR-12260-44 (Shell).
(d) 2-in. solid strands.

TABLE 7

PROPERTIES OF PCDE/SYFO/FEFO (1/1/1) PROPELLANTS[a] (U)
(79 wt% solids, 150-gm batches)

Batch No. B64-	30C	31A	31C	32D
Submix No. B64-	281	281	281	281
Polymer Ingredients, equivalents				
PCDE[b]	66	63	68	66
HT	32	32	32	32
PCP-0200		5		
PEG-4000				2
Cure, days at 110°F	7	7	7	7
Hardness, Shore A	50	56	49	46
Mechanical Properties at 77°F (Avg. of 2 JANNAF bars)				
σ_m, psi	86	98	80	78
ε_m, %	17	18	18	19
ε_b, %	18	19	19	20
E_o, psi	591	640	523	477
Sensitivity				
Impact, cm/2 kg wt - uncured	11	12	10	15
(50% fire pt, BuMines app) - cured	6	8	9	
DTA, °F, Exotherm, onset-uncured	293	297	295	293
-cured	296	316	353	
ignition - uncured	401	399	405	398
- cured	400	398	398	
Rotary Friction, gm at 3000 rpm-uncured	484	450	228 @ 125°F	680
-cured	1600	1240	1970	
Burning Rate at 1000 psia, in./sec[c]	0.51	0.51	0.53	
Pressure Exponent	0.66	0.66	0.66	

(a) Composition: 18 wt% Al (MDX-65), 15.25 wt% AP (130μ lot 1-13 coated), 15.25 wt% HMX-E, 30.50 wt% HMX-A (lot C0420 coated) for batches 30C and 31A 15.25 wt% each HMX-A and HMX-C (coated) for batches 31C and 32D; 0.1 wt% Santicizer 8, 0.01 wt% FeAA, 105 equivalents HDI.
(b) PCDE lot No. LR-12260-44 (Shell).
(c) 2-in. solid strands.

TABLE 8

PROPERTIES OF PCDE/SYFO/FEFO (1/1/1) PROPELLANTS[a] (U)
(80 wt% solids, 150-gm batches)

	30D	31B	31D	33A	33B	33C	33D	34A	34B	34C	34D
Batch No. B64-	30D	31B	31D	33A	33B	33C	33D	34A	34B	34C	34D
Submix No. B64-	281	281	281	281	281	281	281	281	281	281	281
Polymer Ingredients, equivalents											
PCDE[b]	68	63	63	66	62	65	66	66	62	65	66
HT	32	32	32	32	33	33	33				
PCP-0301								32	33	33	33
PCP-0200		5	5		5				5		
PEG-4000				2		2	1			2	1
Cure, days at 110°F	7	9	9	7	7	7	7	7	7	7	7
Hardness, Shore A	57	57	49	51	55	49	54	44	49	50	49
Mechanical Properties at 77°F (Avg. of 2 JANNAF bars)											
σ_m, psi	99	104	90	85	83	83	85	78	79	73	73
ϵ_m, %	17	18	16	17	13	16	16	17	16	15	15
ϵ_b, %	17	19	17	17	13	17	16	18	17	16	16
E_o, psi	706	726	662	602	697	620	646	565	532	556	567
Sensitivity											
Impact, cm/2 kg wt - uncured	11	11	11					12	9	9	11
(50% fire pt, BuMines app) -cured	8										
DTA, °F, Exotherm, onset-uncured	298	292	307								
-cured	308										
ignition-uncured	408	401	399								
-cured	400										
Rotary Friction, gm at 3000 rpm- -uncured	377	125 @ 125°F	159 @ 125°F	350	240	482	350	439	350	300	470
-cured	3600										
Burning Rate at 1000 psia, in./sec[c]	0.51										
Pressure Exponent	0.65										

(a) Composition: 17.5 wt% Al (MDX-65), 15.625 wt% AP (130μ lot 1-13 coated), 15.625 wt% HMX-E, 31.25 wt% HMX-A lot CO420 coated) for batches 30D and 31B - others HMX-A coated are HMX-C coated each 15.625 wt%; 0.1 wt% Santicizer-8, 0.01 wt% FeAA, 105 equivalents HDI.

(b) PCDE lot No. LR-12260-44 (Shell).

(c) 2-in. solid strands.

(C) In addition, at 80 wt% solids the rotary friction values were consistently below 500 gm at 3000 rpm. Increasing the solids did not appear to affect the burning rate or pressure exponent significantly.

C. PCDE/SYFO (1/2 and 1/3) PROPELLANTS AT 79 WT% SOLIDS (U)

(C) Several batches of propellant were prepared at 79 wt% solids which contained 1/2 and 1/3 PCDE/SYFO ratios and 14 wt% aluminum. The processabilities were considerably poorer than with the mixed plasticizer system, so that good mechanical-property specimens were not obtained. Qualitatively, no difference in processability between the 1/2- and 1/3-plasticized systems could be seen. The sensitivities were similar to those of the mixed-plasticizer propellants of the preceding section. Some improvement in the processability of the 1/2-plasticized system resulted from replacing 25% of the SYFO with FEFO and from replacing the HMX-A (approximately 150μ dia) with 340μ HMX. Mechanical properties are not yet available; sensitivity characteristics were not significantly affected.

D. FORMULATIONS CONTAINING HIGH HMX/AP RATIOS (U)

(C) All of the formulations listed in Table 1 were prepared. In addition, in the case of the PCDE/SYFO/FEFO binder system, ratios other than 1/1/1 were explored in order to approach the NF_2 content of the PCDE/SYFO binder system while retaining the beneficial effect of FEFO on the processability.

(U) In the following sections, the compositional variables, processability, and mechanical properties are discussed for each of the binder systems separately, followed by a summary of the sensitivity characteristics of all of the formulations, and a summary discussion of the burning-rate behavior of these propellants.

1. Compositions, Processability and Mechanical Properties (U)

a. PCDE/SYFO/FEFO (1/1/1) Propellants (U)

(C) The compositions and properties of a series of PCDE/SYFO/FEFO (1/1/1) propellants with HMX/AP ratios of 7.1/1 and 1/0 are presented in Tables 9 and 10. The compositions in Table 9 were prepared to explore the effects of polymer ingredient changes on mechanical properties; burning rates

TABLE 9

EFFECT OF POLYMER COMPOSITION ON MECHANICAL PROPERTIES (U)

PCDE/SYFO/FEFO (1/1/1) Propellants*; HMX/AP, 7.1/1
(150-gm batches)

Batch No. B64-	39A	40C	40D	41A	41D	42A	43A	43D	44A
Polymer Ingredients, Equiv.									
PCDE	68	67	66	65	67	66	67	66	65
HT	31	32	32	32	33	33			
PCP-0301							33	33	33
PCP-0200				2					
PEG-4000	1	1	2	1		1		1	2
Cure, days at 110°F	7	8	8	8	7	7	7	7	7
Hardness, Shore A	47	51	43	50	53	49	44	48	47
Mech. Properties at 77°F (Avg. of 2 JANNAF bars)									
σ_m, psi	80	83	81	86	84	80	74	75	76
ε_m, %	20	19	19	19	17	18	19	19	20
ε_b, %	22	20	19	19	18	19	20	20	20
E_o, psi	525	539	543	576	596	550	481	506	492

* Composition: 14 wt% Al (MDX-65), 8 wt% AP (130μ lot 1-13 coated), 20 wt% HMX-E, 37 wt% HMX-A (lot C0420 coated); 0.1 wt% Santicizer 8, 0.01 wt% FeAA, 105 equivalents HDI. PCDE lot no. LR-12260-44 (Shell). Submix batch no. B64-19D.

TABLE 10

PROPERTIES OF PCDE/SYFO/FEFO (1/1/1) PROPELLANTS* (U)
(HMX/AP, 7.1/1 and 1/0) (150-gm batches)

Batch No. B64-	25A	23B	23C	23D	26A	26B	44B	44C	44D	45B	45C
Polymer Ingredients, Equiv.											
PCDE	64	64	64	64	64	64	66	66	66	66	66
HT	31	31	31	31	31	31	33	33	33	33	33
PCP-0200	5	5	5	5	5	5					
PEG-4000							1	1	1	1	1
Solids, wt%											
HMX-A	49.66	24.83	24.83	24.83	24.83	24.83	37.0	45.0	45.0	40.0	40.0
HMX-C	-	24.83	24.83	20.00	17.50	20.00					
HMX-E	7.37	7.37	15.34	12.20	14.70	20.17	20	12	12	25	25
Al (MDX-65)	14	14	14	14	14	14	14	14	14	14	14
AP (μ)	7.97 (26μ)	7.97 (26μ)	0	7.97 (26μ)	7.97 (26μ)	0	8 (130μ)	8 (6μ)	8 (6μ)	0	0
Other							0.5 Fe_2O_3		0.5 Fe_2O_3		0.5 Fe_2O_3
Cure, days at 110°F	6	6	6	6	6	6	6	6	6	7	7
Hardness, Shore A	51	48	51	46	49	52	48	49	53		
Mechanical Properties at 77°F (Avg of 2 JANNAF bars)											
σ_m, psi	84	71	73	73	71	78	80	83	84	80	82
ϵ_m, %	16	16	15	18	17	17	18	16	17	16	15
ϵ_b, %	17	17	15	18	17	17	19	16	18	16	15
E_o, psi	662	536	596	497	503	556	574	622	618	611	631
Sensitivity											
Impact, cm/2-Kg wt - uncured	20	18	15	14	15	14	15				
(50% fire pt, Bruceton app) - cured	18	17	21								
DTA °F Exotherm, onset - uncured				7/1	290	359	229				
- cured	317	319	330								
ignition - uncured				398	398	498	407				
- cured	400	401	498								
Rotary Friction, - uncured	>4000	>4000	>4000	>4000	>4000	>4000	>4000				
gm at 3000 rpm - cured	2390	>4000	>4000								
Burning Rate at 1000 psia											
Solid strands, in./sec	0.31	0.53	0.38	0.52	0.52	0.38	0.44	0.60	0.60	0.38	0.38
Pressure Exponent	0.80	0.77	0.81	0.73	0.74	0.84	0.71	0.83	0.82	0.82	0.80

* Composition: 0.1 wt% Santicizer 8, .01 wt% FeAA, 105 equivalents of HDI; HMX-A (lot C0420) and HMX-C lots coated, AP 130μ, lot 1-13 coated, PCDE lot no. LR-12260-44 (Shell). Submix batch no. B64-19D.

(C) were not measured. In this study, the triol PCP-0301 and the diols PCP-0200 and PEG-4000 were used in an attempt to enhance processability. At similar equivalents ratios it appears that neither PCP-0200 nor PEG-4000 has a marked effect on mechanical properties. The use of PCP-0301 instead of HT (at the same equivalents ratio) does, however, appear to reduce the tensile strength without a corresponding increase in elongation. The compositions in Table 10 were prepared primarily to explore the effects of changes in solids particle sizes on the various properties including burning rates, which will be discussed further in Section III.B.3. It may also be seen that incorporation of HMX-C (∿340μ) reduces the tensile strength and modulus with little or no effect on elongation. The mechanical properties of the propellants containing the 7/1 HMX/AP ratio were similar to those of propellants prepared from the same submix at 78 wt% solids and an HMX/AP ratio of 3/1 as reported last month: tensile strength, 80 psi; elongation, 20%; and initial modulus, 500 psi. Elongations for the all HMX propellants were generally slightly lower, 15-17%. The processability of most of the batches was suitable for scale-up to the 1-lb batch size.

b. PCDE/SYFO/FEFO (2/3/3 and 1/2/1) Propellants (U)

(C) The compositions and properties of PCDE/SYFO/FEFO (2/3/3 and 1/2/1) propellants with HMX/AP ratios of 3/1 to 1/0 are presented in Tables 11 and 12. The maximum tensile strengths and initial moduli of these propellants were lower than the corresponding values for PCDE/SYFO/FEFO (1/1/1) propellants: σ_m 50-60 vs 70-80 psi and E_o 300-400 vs 500-600 psi. As noted previously, it is not unexpected for mechanical properties to deteriorate as the plasticizer concentration in the binder increases from 50 to 66-2/3 to 75%. Much of the data has been accumulated as a result of screening processes; the task of improving mechanical properties will become more effective after the plasticizer concentration and HMX/AP ratio have been selected on the basis of performance, burning rate, and safety characteristics.

TABLE 11

PROPERTIES OF PCDE/SYFO/FEFO (2/3/3) PROPELLANTS* (U) (HMX/AP, 3/1, 7.1/1, and 1/0) (150-g batches)

Batch No. B64-	36C	36D	37A	37B	37C	37D	39B	41C	42D
Polymer Ingredients, Equiv.									
PCDE	62	62	62	62	62	62	68	67	67
HT	33	33	33	33	33	33	31	33	
PCP-0301									33
PCP-0200	5	5	5	5	5	5			
PEG-4000							1		
HMX/AP	7.1/1	7.1/1	1/0	1/0	3/1	7.1/1	7.1/1	7.1/1	7.1/1
Solids, wt%									
HMX-A	49.66	40.00	49.66	40.00	30.50	37.00	37.00	37.00	37.00
HMX-E	7.37	17.03	15.34	25.00	16.70	20.00	20.00	20.00	20.00
Al(MDX-65)	14.00	14.00	14.00	14.00	16.00	14.00	14.00	14.00	14.00
AP(μ)	7.97 (26)	7.97 (26)	0	0	15.75 (130)	8 (26)	8 (26)	8 (26)	8 (26)
Cure, days at 110°F	6	6	6	6	9	9	7		
Hardness, Shore A	39	36	42	42	40	37	27	37	27
Mechanical Properties at 77°F (Avg of 2 JANNAF bars)									
σ_m, psi	57	59	64	69	66	61	54	58	48
ε_m, %	17	21	18	21	19	22	23	20	24
ε_b, %	18	22	19	22	21	23	24	22	26
E_o, psi	413	334	407	400	444	339	387	374	242
Sensitivity - Uncured									
Impact, cm/2-Kg wt	19	17	22	24	12				
DTA, °F Exotherm, onset	299	293	373	361					
ignition	395	398	498	487					
Rotary Friction, gm at 3000 rpm	>4000	>4000	>4000	>4000	178				
Burning Rate at 1000 psia									
Solid strands, in./sec	0.54	0.51	0.38	0.45					
Pressure Exponent	0.84	0.76	0.82	0.89					

* Composition: 0.1 wt% Santicizer 8, 0.1 wt% FeAA, 105 equivalents of HDI; HMX-A (Lot C0420 coated), AP-130μ, (Lot 1-13 coated), PCDE lot no. LR-12260-44 (Shell). Submix batch no. B64-283.

TABLE 12

PROPERTIES OF PCDE/SYFO/FEFO (1/2/1) PROPELLANTS* (U)
(150-g batches)

Batch No. B64-	38C	38D	39C	39D	40A	40B	41B	42B	42C	43B	43C	47B	47C	47D	48A
Polymer Ingredients, Equiv.															
PCDE	68	68	62	67	66	65	67	67	67	66	64	65	65	65	65
HT	31	31	33	32	32	32	33					34	34	34	34
PCP-0301								33	34	33	34				
PCP-0200			5			2									
PEG-4000	1	1		1	2	1				1	2	1	1	1	1
Solids, wt%															
HMX-A	37	40	37	37	37	37	37	37	37	37	37	40	40	40	40
HMX-E	20	25	20	20	20	20	20	20	20	20	20	24	24	22	24
Al(MDX-65)	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14
AP(μ)	8	0	8	8	8	8	8	8	8	8	8	1	1	3	1
	(130)		(130)	(130)	(130)	(130)	(130)	(130)	(130)	(130)	(130)	(1)	(0.5)	(1)	(1)
Other															.5 Fe_2O_3
Cure, days at 110°F	7	7	7	7	6										
Hardness, Shore	30	35	38	33	32	31	38	29	26	30	27	34	32	34	33
Mechanical Properties at 77°F (Avg of 2 JANNAF bars)															
σ_m, psi	54	60	64	55	53	58	56	48	47	52	50	56	54	58	56
ϵ_m, %	24	24	20	21	23	26	21	22	23	27	27	25	25	24	25
ϵ_b, %	27	26	21	22	25	28	22	26	25	28	29	26	28	25	27
E_o, psi	292	330	387	303	297	270	361	267	262	255	232	292	273	302	280
Sensitivity - Uncured															
Impact, cm/2-Kg wt	9	22												18	
DTA°F Exotherm, onset	313	275												300	
ignition	409	489												404	
Rotary Friction	>4000	>4000												>4000	
Burning Rate at 1000 psia															
Solid strands, in./sec												0.42	0.42	0.48	0.43
Pressure Exponent												0.82	0.83	0.92	0.82

* Composition: 0.1 wt% Santicizer 8, 0.01 wt% FeAA, 105 equivalents of HDI; HMX-A (lot C0420 coated), AP-130μ (lot 1-13 coated). PCDE lot no. LR-12260-44 (Shell). Submix batch No. B64-19AC.

c. PCDE/SYFO Propellants (U)

(C) The compositions and properties of PCDE/SYFO (1/2 and 1/3) propellants with HMX/AP ratios of 7/1 and 1/0 are given in Table 13. All of these had fair to poor processability, even at the higher plasticizer-to-polymer ratio. The tensile strengths of the 1/3 propellants were lower in every case than those of the corresponding 1/2 propellants, although there was little difference in elongation. In contrast to the FEFO-containing propellants of the preceding sections, use of PCP-0301 did not result in lower tensile strengths or moduli than HT.*

(C) Batches 79A-D and 80-A,B constitute a 2 x 3 factorial experiment using three HMX-A/HMX-E wt ratios and two NCO/OH equivalents ratios. The processability was poor in all cases. Analysis of variance of the mechanical-property data showed no significant effects of the HMX-A/HMX-E ratio on tensile strength or modulus, but a moderately significant effect (97.5%) on elongation. The NCO/OH ratio appeared to have no significant effect on tensile strength, a highly significant (99.5%) effect on elongation and a moderately significant effect (97.5%) on modulus. Because of the small batch size and the lack of batch replication, these results should not be given much weight, but they suggest that the NCO/OH ratio used in most of the batches to date, 1.05, may not be quite optimum for this lot of PCDE in this type of formulation. Because this lot of PCDE is nearly exhausted, no effort will be made to redetermine the optimum NCO/OH ratio.

(C) The propellants of Table 14 were prepared to further explore the effects of small amounts of FEFO on the propellant properties. In this case, the SYFO/FEFO ratio was 3/1 rather than 2/1 as in Table 12. All of these batches had noticeably better processability than those in Table 13. With one exception, the elongations were all low. The exception, Batch 75C, also had appreciably better processability than the others, but there is no obvious reason for these differences.

* Probably because the equivalents ratio was adjusted to give approximately equal crosslink densities.

TABLE 13

PROPERTIES OF PCDE/SYFO (1/2 AND 1/3) PROPELLANTS* (U)
(HMX/AP, 7/1 and 1/0) (150-gm batches)

Batch No. 7571-	70A	70B	76A	76B	76C	76D	79A	79B	79C	79D	80A	80B
Submix No.	B60-6A,B	B60-6A,B	B76-2A	B76-2A	B76-2B	B76-2B	B76-2B	B76-2B	B76-2B	B76-2B	B76-2B	B76-2B
Polymer Ingredients, Equiv.												
PCDE	55	60	50	40	50	40	55	55**	55**	55**	55	55
HT	45	40	0	0	0	0	45	45	45	45	45	45
PCP-0301	0	0	50	60	50	60	0	0	0	0	0	0
PCDE/SYFO wt ratio	1/3	1/2	1/2	1/2	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3
Solids, wt%												
HMX-A	41.90	41.90	36.20	36.20	36.20	36.20	39.00	35.00	39.00	37.00	37.00	35.00
HMX-E	14.98	14.98	30.80	30.80	30.80	30.80	28.00	32.00	28.00	30.00	30.00	32.00
Al (MDX-65)	14.00	14.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00
AP(μ)	8.12 (130)	8.12 (130)	0	0	0	0	0	0	0	0	0	0
Cure, days at 110°F	7	7	4	4	4	4	6	6	7	7	7	7
Hardness, Shore A	58	72	83	83	70	75	50	66	61	60	44	48
Mechanical Properties at 77°F (Minibars)												
σ_m, psi	66	114	100	95	81	90	62	69	56	52	49	51
ϵ_m, %	11	12	7	7	10	9	12	11	11	12	13	14
ϵ_b, %	11	12	7	7	10	9	13	11	11	12	14	15
E_o, psi	630	1077	1474	1512	849	1063	563	709	577	481	421	395
Sensitivity												
Impact, cm/2-Kg wt - uncured	10	11	16	21	19	20	23	22	-	-	-	-
(50% fire pt, BuMines app) - cured	10	10	19	19	27	25	32	26	32	30	28	28
DTA°F Exotherm, onset - uncured	273	319	297	283	313	313	269	282	-	-	-	-
- cured	319	321	325	370	372	371	300	284	370	271	289	363
ignition - uncured	409	413	494	494	493	493	495	495	-	-	-	-
- cured	419	419	501	495	495	497	499	499	499	499	503	500
Rotary Friction - uncured	450	472	>4000	>4000	>4000	>4000	>4000	>4000	-	-	-	-
gm at 3000 rpm - cured	>4000	>4000	>4000	>4000	>4000	>4000	>4000	>4000	>4000	>4000	>3725	>4000
Burning Rate at 1000 psia												
Solid strands, in./sec	.53	.52	.41	.40	.42	.41	.42	.42	.42	.42	.42	.42
Pressure Exponent	.73	.74	.82	.84	.84	.85	.85	.87	.85	.84	.84	.85

* Composition: 0.1 wt% Santicizer 8, .02 wt% FeAA, 105 equivalents of TDI; HMX-A (lot C0420) coated, AP 130μ, lot 1-13 coated, PCDE lot no. LR-12260-44 (Shell).

** 110 equivalents of TDI in these compositions only.

TABLE 14

PROPERTIES OF PCDE/SYFO PROPELLANTS CONTAINING SMALL AMOUNTS OF FEFO* (U)

(PCDE/SYFO/FEFO, 1/1.5/.5 and 1/2.25/.75; HMX/AP, 7/1 and 1/0)
150-gm batches)

Batch No. 7571-	70C	70D	74A	74D	75A	75B	75C	75D
Submix No.	B60-6A,B	B60-6A,B	B60-6A,B	B60-6A,B				
Polymer Ingredients, Equiv.								
PCDE	55	60	60	60	60	70	60	70
HT	45	50	0	0	0	0	0	0
PCP-0301	0	0	40	40	40	30	40	30
PCDE/SYFO/FEFO wt. ratio	1/2.25/.75	1/1.5/.5	1/1.5/.5	1/1.5/.5	1/1.5/.5	1/1.5/.5	1/1.5/.5	1/1.5/.5
Solids, wt%								
HMX-A	41.90	41.90	41.90	41.90	50.36	50.36	36.20	36.20
HMX-E	14.98	14.98	14.98	14.98	16.64	16.64	30.80	30.80
Al (MDX-65)	14.00	14.00	14.00	14.00	12.00	12.00	12.00	12.00
AP(μ)	8.125 (130)	8.125 (130)	8.125 (130)	3.125 (130) +5.000 (2.5)	0	0	0	0
Cure, days at 110°F	6	6	5	5	7	7	7	7
Hardness, Shore A	48	72	66	68	73	67	74	40
Mechanical Properties at 77°F (Minibars)								
σ_m, psi	67	87	99	96	90	106	35	92
ϵ_m, %	13	11	13	14	11	14	24	10
ϵ_b, %	13	11	13	14	11	14	25	10
E_o, psi	565	835	830	772	865	874	428	981
Sensitivity								
Impact, cm/2-Kg wt - uncured	9	8	11	13	22	22	22	21
(50%, fire pt, BuMines app) - cured	11	10	9	10	25	23	24	23
DTA°F Exotherm, onset - uncured	309	305	290	264	308	309	315	318
- cured	305	313	289	296	320	308	285	301
ignition - uncured	409	403	408	398	494	497	490	491
- cured	413	417	411	398	498	498	493	495
Rotary Friction - uncured	500	460	>4000	>4000	>4000	>4000	>4000	>4000
gm at 3000 rpm - cured	>4000	>4000	>4000	>4000	>4000	>4000	>4000	>4000
Burning Rate at 1000 psia								
Solid strands, in./sec	.55	.54	.47	.60	.41	.41	.40	.42
Pressure Exponent	.76	.58(?)	.74	.81	.85	.84	.81	.80

* Composition: 0.1 wt% Santicizer 8, .01 wt% FeAA, 105 equivalents of TDI; HMX-A (lot C0420) coated, AP 130μ, lot 1-13 coated, PCDE lot no. LR-12260-44 (Shell).

2. Sensitivity of High-HMX Propellants (U)

(C) Comparison of the sensitivity data in Tables 9 through 14 with the data in Tables 6 through 8, as well as those reported previously for similar propellants with a 3/1 HMX/AP ratio, shows that the present propellants are generally much less sensitive, particularly to friction. They also appear to be less sensitive to impact, especially those compositions without AP. The DTA behavior of the propellants containing only HMX is also different from those containing AP. Both systems exhibit an endotherm at approximately 330-340°F which is attributable to the phase change of β HMX to δ HMX. (The reported endotherm of transition for the pure crystal is near 369°F,* while the equilibrium temperature for the two polymorphs is reported to be 316°F.**) In the presence of AP further heating (at 9°F/min) of the propellant results in ignition at approximately 400°F. In the absence of AP there is a second broader endotherm peaking at approximately 460-470°F which is attributable to the melting of β HMX (reported melting point 471-475°F). This is followed by ignition at approximately 498°F, about 100°F higher than the propellant containing AP.

3. Burning Characteristics (U)

(C) As with other energetic binder systems, the pressure exponent of these PCDE propellants increases with increasing concentration of HMX, according to Crawford-bomb solid-strand burning-rate data. The binder composition appears to have little effect. Thus, for the all-HMX propellants, the burning rates at 1000 psia were as low as 0.38 in./sec, but generally in the .4 to .5 region, and the pressure exponent was always 0.8 or greater. For the HMX/AP (7/1) propellants, the burning rates at 1000 psia were approximately 0.5 in./sec, and the pressure exponents were generally 0.7 to 0.8. In PCDE/SYFO/FEFO (1/2/1) propellants, the pressure exponents were over 0.8 when UFAP was employed in HMX/AP ratios of 21/1 and 64/1, and in a PCDE/SYFO/FEFO (1/1.5/.5) propellant with 7/1 HMX/AP, both burning rate and pressure exponent increased when part of the coarse AP was replaced by UFAP.

* W. Selig, Explosivstoffe, 4, 79 (1969)
** A. Teetsov and W. McCrone, Micros. Cryst. Front, 15(1), 13-29 (1965).

4. Reduction of Pressure Exponents (U)

(C) There is an abundance of literature concerning the catalysis of AP decomposition and methods for effective control of propellant burning rate and pressure exponent. Unfortunately, useful information for similar control of HMX propellants is meager. Indeed, a practical solution to this problem would be an extremely important contribution to solid propellant technology. At this stage of the program, the high pressure exponent of highly loaded HMX propellants is the single most important obstacle preventing attainment of a suitable PCDE propellant with the highest possible theoretical performance. Current practice is to introduce increasing concentrations of AP to reduce the pressure exponent of HMX propellants, but performance is sacrificed in following this approach.

(U) Recognizing that a major effort would be required to thoroughly investigate all the parameters influencing the burning rate of HMX propellants, a brief study was undertaken to elicit gross effects of certain additives in affecting pressure exponent. In order to obtain rapid results, the technique of burning 2-in. liquid strands (uncured propellant) was employed. Although previous experience had indicated that liquid-strand burning-rate values were generally higher than corresponding solid-strand data, it seemed desirable to determine whether useful trends and guidelines could be established. Duplic measurements were made at 500, 1000, and 1500 psia.

(C) Table 15 presents the additives employed and summarizes the burning rates and pressure exponents found in each case. The submix was PCDE/SYFO/FEFO (1/2/1), and the solids level was 79 wt% with 14 wt% Al. Three different particle sizes of AP were used: 0.5, 1.0 and 130μ at several different concentrations. When Mg or Zr powder was used, it was substituted for Al in the formulation. Other substances, however, were added at 0.5-3.0 wt% on the basic formulation. (Although 3 wt% of an "inert" additive would be prohibitive with respect to optimum performance,

TABLE 15

LIQUID STRAND BURNING RATES OF PCDE/SYFO/FEFO (1/2/1) PROPELLANTS[a] (U)
(100-gm batches)

HMX/AP (dia, μ)	gm[b]	wt%	Burning Rate, 80°F, in./sec r,500	r,1000	r,1500	n
5.1/1 (130)		15.0 Al	0.31	0.51	0.68	0.70
6/1 (130)		15.5 Al	0.29	0.50	0.68	0.77
7.1/1 (0.5)		14.0 Al	0.39	0.74	1.07	0.91
(0.5)	CUO_2O_2, 0.5	14.0 Al	0.42	0.78	1.12	0.89
(0.5)	Fe_2O_3, 0.5	14.0 Al	0.41	0.74	1.06	0.87
12/1 (0.5)		14.0 Al	0.29	0.58	0.85	0.97
(0.5)	Dexsil,[c] 0.75	14.0 Al	0.32	0.63	0.93	0.93
(1.0)		14.0 Al	0.30	0.58	0.86	0.94
20.7/1 (0.5)		14.0 Al	0.25	0.48	0.70	0.93
(0.5)	NHC,[d] 1.0	14.0 Al	0.25	0.49	0.72	0.95
(0.5)		13 Al + 1.0 Zr	0.25	0.47	0.67	0.91
(0.5)		13 Al + 1.0 Mg	0.26	0.52	0.77	0.98
100/0		13.0 Al + 1.0 Zr	0.23	0.41	0.47	0.81
		13.0 Al + 1.0 Mg	0.23	0.42	0.60	0.89
		11 Al + 3.0 Zr	0.21	0.41	0.60	0.94
	LiF, 3.0	14.0 Al	0.20	0.36	0.51	0.84
	MPDA-HMX,[e] 2.0	14.0 Al	0.23	0.42	0.60	0.88
	TLT-64,[f] 3.0	14.0 Al	0.18	0.33	0.46	0.83
	Salicylate, 3.0	14.0 Al	0.24	0.43	0.60	0.82

(a) Composition: PCDE/HT/PEG-4000, 65/34/1 equivalents, 105 equivalents HDI, 0.1 wt% Santicizer 8, 0.05 wt% FeAA.
(b) Used in addition to basic formulation.
(c) Dexsil, a proprietary silyl carborane.
(d) NHC, n-Hexylcarborane
(e) MPDA-HMX, adduct m-phenylenediamine/HMX, 1/1 mole ratio
(f) TLT-64, tris(C5 Fluoroalkyl)phosphate, (duPont)

(C) the experiments were designed to reveal gross effects.) The most effective ingredient for reducing pressure exponent was AP. At an HMX/AP ratio of 5.1/1, the exponent was 0.70. Values greater than 0.80 were common with HMX/AP ratios of 7/1 or higher. UFAP (0.5 to 1μ diameter) appeared to increase the burning rate proportionately at the three pressures investigated, instead of having a greater effect at the lower pressures, as desired. Introducing UFAP at increasing concentrations merely resulted in parallel burning-rate curves. The effects of 0.5 wt% Fe_2O_3 or Cu 0202 in a 7.1/1 HMX/AP system with 0.5μ UFAP were negligible. Dexsil (a proprietary silyl carborane) at 0.75 wt% increased the burning rate at the three pressures investigated, but the pressure exponent was still greater than 0.9. The effect of NHC (n-hexylcarborane) at 1.0 wt% in the presence of UFAP (0.5μ) likewise was not encouraging. Lithium fluoride and lead salicylate are additives referred to in double-base literature for manipulation of pressure exponent. Zinc and Mg powder have also previously been investigated for the same purpose. None of these appeared to be sufficiently effective under the conditions employed. TLT-64, a tris(C_5 fluoroalkyl) phosphate, appeared to have a depressing effect on burning rate, but the pressure exponent was not improved.

(U) The use of MPDA-HMX, a 1:1 molar adduct of m-phenylenediamine with HMX, to affect the burning characteristics of HMX propellants represents a new approach. Briefly, it was an attempt to exploit the observation by Selig* that certain phenylamino, naphthylamino and hydroxyl compounds form stable adducts with HMX which have DTA exotherms well below that of HMX itself. This indicated a possible catalyzing effect of the adduct-forming compounds on the decomposition of HMX. No significant effect on burning rate was observed at the concentration employed (2 wt%), although there was a definite lowering in the DTA onset of exotherm. No further work is contemplated along these lines. However, it appears to be a good starting point for an investigation of catalysis of HMX burning.

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* op. cit.

(U) Since AP is the only effective material presently available to reduce the pressure exponent of highly loaded HMX propellants to a useful range, subsequent effort was designed to determine the most practical HMX/AP ratio consistent with optimum theoretical performance.

E. FORMULATION STUDIES FOR MOTOR FIRINGS (U)

1. Formulations Selected for Small-Scale Motor Firings (U)

(U) Table 16 lists five formulations selected for testing in small motors on the basis of data in this report. The rationale behind this selection is as follows.

(U) Formulations A and B:

a. Burning rates and pressure exponents as functions of HMX/AP ratio.

b. Efficiency to be expected in this size (2C1.5-4) motor.

(U) Formulations C and D:

a. Burning rates and pressure exponents as functions of HMX/AP ratio.

b. Efficiency of an all-HMX composition.

(U) Formulations B and D, and C and E:

a. Efficiency as a function of NF_2 or F content over widest possible range.

b. Burning rates and pressure exponents as functions of NF_2 content and HMX/AP ratio.

(U) All of these formulations will indicate whether, as expected from other work, pressure exponents are significantly lower in motors than in solid strands. It should also be noted that all of these formulations were selected for highest I°_{sps} values, lowest Al content, widest NF_2 content range and widest feasible SYFO range. The following sections describe work aimed primarily at preparing and evaluating these formulations.

TABLE 16

PCDE PROPELLANTS SELECTED FOR SMALL-SCALE MOTOR FIRINGS (U)

(All 79 Wt% Solids)

Formulation	SYFO/FEFO/PCDE Wt Ratio			HMX/AP Wt Ratio	Al Wt %	Wt% in Propellant $-NF_2$	Wt% in Propellant F	I°_{sps} lbf-sec/lbm
A	3	0	1	10/1	13	7.66	6.58	~274.2
B	3	0	1	6/1	13	7.66	6.58	273.8
C	2	1	1	∞	13	5.86	5.56	$\geq$274
D	2	1	1	6/1	14	5.86	5.56	273.4
E	0	2	1	∞	14	3.03	3.88	273.7

2. Liquid- vs Solid-Strand Burning Rates (U)

(C) As stated earlier, burning rates were obtained on liquid strands (uncured propellant) for convenience and because results could be obtained rapidly. However, the results were occasionally erratic and difficult to correlate with solid-strand burning rates. Table 17 summarizes liquid- and solid-strand burning rates obtained with PCDE/SYFO/FEFO (1/2/1) propellants at HMX/AP ratios 5/1, 6/1 and 7/1. The pressure exponents appear to be consistently lower for solid strands. Since previous experience with other systems indicates that values obtained from motor firings should be lower than those for solid strands, the results shown in Table 17 are encouraging. The burning rates at 1000 psia were in the range of 0.47 to 0.58 in./sec, and the solid-strand pressure exponents were in the range of 0.66 to 0.76. In view of these results, the major effort currently is concerned with establishing solid blends to provide propellant suitable for processing on the 1-lb scale. A 1-lb batch will provide three 2C1.5-4 motors for confirmation of burning rate and pressure exponent. To a great extent, the pressure exponent will dictate the propellant selection for eventual scale-up.

3. Formulations Containing No AP (U)

(U) In Table 18 are presented properties of several all-HMX PCDE propellants employing as plasticizer SYFO alone and a 2/1 SYFO/FEFO ratio. The theoretical specific impulse for these systems is approximately 274 lbf-sec/lbm. As expected, the pressure exponents obtained from Crawford-bomb burning of solid strands were over 0.8. Batch B113-9A was scaled up to the 1-lb batch size and two 2C1.5-4 motors were cast. In general, the processability of the all-HMX propellants was poorer than that of formulations containing some AP, although no real effort was made to study the effect of blends. Similarly, no attempt was made to improve mechanical properties.

TABLE 17

CRAWFORD-BOMB BURNING RATES OF PCDE/SYFO/FEFO (1/2/1) PROPELLANTS (U)

Batch No. B113-	3B	3C	3D	4A	4B	4C	4D	5A	5B	5C	5D	6A
HMX/AP, wt ratio	7/1	7/1	7/1	7/1	6/1	6/1	6/1	6/1	5/1	5/1	5/1	5/1
<u>Solids, wt%</u>												
Al, 5μ	14	14	14	14	14.5	14.5	14.5	14.5	15	15	15	15
HMX-A (ctd)	50	35	25	17.5	50	35	25	17.5	45	35	22.5	17.5
HMX-C (ctd)	-	-	25	17.5	-	-	25	17.5	-	-	22.5	17.5
HMX-E	7	22	7	22	5.25	20.25	5.25	20.25	8.5	18.5	8.5	18.5
AP, 130μ (ctd)	8	8	8	8	9.25	9.25	9.25	9.25	10.5	10.5	10.5	10.5
Castability	Poor	Satisf.	Good	Good	Poor	Satisf.	Good	Good	Fair	Satisf.	Good	Good
<u>Burning rate at 80°F, in./sec**</u>												
r_{500}	***	.28/.28	.32/.31	.27/.29	***/.30	.29/.29	.31/.32	.29/.30	.33/.31	.31/.30	.33/.33	***/.31
r_{1000}		.49/.47	.54/.51	.47/.47	/.51	.50/.48	.55/.53	.50/.48	.55/.52	.56/.50	.58/.52	/.51
r_{1500}		.67/.63	.72/.68	.65/.62	/.70	.68/.64	.77/.72	.68/.63	.74/.69	.79/.66	.82/.69	/.68
Pressure exponent		.79/.73	.74/.71	.78/.69	/.76	.78/.72	.83/.75	.77/.66	.75/.72	.87/.71	.83/.68	/.70

* PCDE/HT/PEG 4000, 65/34/1 equivalents; 0.1 wt% Santicizer 8; 0.01 wt% FeAA; Submix No. B64-19A1; PCDE Lot No. LR-12260-44 (Shell).
** Shown as: liquid value/solid value.
*** Erratic data.

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TABLE 18

PROPERTIES OF PCDE PROPELLANTS CONTAINING NO AP* (U)

(79 wt% Solids, 150-gm batches)

	6B	7B	7C	7D	8D	9A	9D**
Batch No. B113-	6B	7B	7C	7D	8D	9A	9D**
Submix No. B64-	463	463	463	19AC	19AC	19AC	19AC
PCDE/SYFO/FEFO	1/3/0	1/3/0	1/3/0	1/2/1	1/2/1	1/2/1	1/2/1
Solids, wt%							
HMX-A (ctd)	40	50	20	40	45	20	20
HMX-C (ctd)			20			20	20
HMX-E	27	17	27	26	21	26	26
Al, 5μ	12	12	12	13	13	13	13
Cure, days at 110°F	7	7	7	8	8	6	6
Hardness, Shore A	46	49	45	45	45	40	40
Mechanical Properties at 77°F (Avg of 2 JANNAF bars)							
σ_m, psi	84	76	69	[illegible]	66	59	55
ε_m, %	17	17	17	19	19	18	19
ε_b, %	17	18	18	20	20	19	21
E_o, psi	598	574	503	453	444	400	350
Burning rate at 1000 psia							
Solid strands, in./sec		0.42	0.41	0.40			0.40
Pressure exponent		0.87	0.85	0.81			0.85

* Polymer Ingredients: PCDE/HT/HDI, 65/35/105 equivalents; 0.1 wt% Santicizer 8; 0.01 wt% FeAA; PCDE Lot No. LR-12260-44 (Shell).

** 1-lb batch size

4. Effects of Particle-Size Blends on Processability and Burning Rates (U)

(C) In order to provide suitable processability for PCDE/SYFO propellants formulated with the highest theoretical specific impulse at 79 wt% solids loading, it is necessary to employ a plasticizer/PCDE weight ratio of approximately 3/1. Because optimum performance in these systems increases with increasing HMX/AP ratio, a series of batches was mixed to determine the effect of HMX and AP particle sizes blends at several HMX/AP ratios on processability as well as on pressure exponent. As suggested earlier, the latter will probably be the determining factor in choosing an HMX/AP ratio for scale-up. Table 19 presents the data for propellants containing a 1/3 PCDE/SYFO submix, and Table 20 presents the data for propellants containing a 1/2/1 PCDE/SYFO/FEFO submix. In order to preclude introduction of binder variables, a single submix was used for all the 1/3 PCDE/SYFO propellants, and two similar submixes were used in the 1/2/1 PCDE/SYFO/FEFO propellants. The same crosslinker (HT) concentration was used throughout.

(C) In general, inclusion of UFAP (0.5μ) markedly improves the processability; in the range of 2 to 6 wt% of UFAP, processability improved with increasing concentration. However, there are indications that the pressure exponent may also increase prohibitively with fine AP. In one instance, batch 10A, containing 9.5 wt% of MA (6-9μ) AP, the pressure exponent was 0.95. When the MA was replaced by 26μ AP (batch 93), the exponent was 0.71. It is apparent that the effect of particle size and blend on burning rate and pressure exponent ultimately will need to be confirmed by small motor firings. The composition used in batch B113-12B was successfully scaled up to the 500-gm batch size.

(C) Unfortunately, at the high plasticization level employed, the propellants were softer and had lower moduli than desired. It also appeared that propellants containing UFAP were especially soft, particularly in comparison with those containing all HMX (see Table 18). A possible explanation is solution of some AP in the highly polar binder. Work in progress indicates that some improvement may be achieved by increasing the catalyst concentration to 0.015 wt%.

TABLE 19

PROPERTIES OF PCDE/SYFO (1/3) PROPELLANTS WITH SEVERAL HMX/AP RATIOS*(U)

Batch No. B113-	6C	6D	7A	8A	8B	8C	9B	9C	10A	10B	10C	11B	11C	12B
Solids, wt%														
HMX-A (ctd)	35	35	35	20	20	20	20	20	29.5	20	20	45	45	41.57
HMX-C (ctd)				20	20	20	20	20	20	20	20			
HMX-E	22	20.25	18.5	17.75	16.5	16.5	16.5	16.5	7	16.5	16.5	16	15	15
AP 180μ														3.43
AP 130μ (ctd)	8	9.25	10.5	8.25	9.5	11		7.5		6.5	4.5			
AP 26μ							9.5							
AP 7μ									9.5					
AP 0.5μ								2		3	5	5	6	6
Al, 5μ	14	14.5	15	13	13	13	13	13	13	13	13	13	13	13
HMX/AP	7/1	6/1	5/1	7/1	6/1	5/1	6/1	6/1	6/1	6/1	6/1	12/1	10/1	6/1
Cure, days at 110°F	7	7	7	8	8	8	7	7	7	7	7	7	7	7
Hardness, Shore A	44	42	40	41	41	37	40	35	35	33	32	37	32	30
Mechanical Properties at 77°F (Avg of 2 JANNAF bars)														
σ_m, psi	74	69	69	59	62	61	59	54	53	50	51	53	51	49
ϵ_m, %	20	19	20	20	20	21	19	21	18	21	22	21	21	20
ϵ_b, %	22	21	22	22	22	23	21	24	20	24	25	24	25	22
E_o, psi	440	455	446	378	374	372	380	310	376	312	299	310	297	310
Burning rate at 1000 psia														
in./sec					0.55		0.68	0.64	0.90	0.69	0.81	0.68	0.74	0.77
exponent					0.74		0.71	0.83	0.95	0.81	0.97	0.94	0.96	0.93

* Polymer ingredients: Submix No. E64-463; PCDE/HT/HDI, 65/35/105 equivalents; 0.1 wt% Santicizer 8; 0.01 wt% FeAA; PCDE Lot No. LR-12260-44 (Shell).

** Impact, uncured (50% fire pt, Bu Mines app) - 13 cm/2-Kg wt
Rotary Friction, uncured - 760 gm at 3000 rpm

TABLE 20

PROPERTIES OF PCDE/SYFO/FEFO (1/2/1) PROPELLANTS
WITH SEVERAL HMX/AP RATIOS* (U)

(79 wt% Solids, 150-gm batches)

Batch No. B113-	10D	11A	11D	12C	12D	13A
Submix No. B64-	19AC	19AC	19AC	285	285	285
Solids, wt%						
HMX-A (ctd)	45	45	45	41.57	41.57	41.57
HMX-E	16	16	15	15	15	15
AP 180μ				3.43	4.72	7.43
AP 7μ		5			4.71	
AP 0.5μ	5		6	6		2
Al, 5μ	13	13	13	13	13	13
HMX/AP	12/1	12/1	10/1	6/1	6/1	6/1
Cure, days at 110°F	7	7	7	7	7	7
Hardness, Shore A	33	34	34	30	36	37
Mechanical Properties at 77°F (Avg of 2 JANNAF bars)						
σ_m, psi	53	49	50	49	57	57
ϵ_m, %	22	22	21	20	21	21
ϵ_b, %	23	25	22	22	24	23
E_o, psi	295	275	288	310	328	328

* Polymer Ingredients: PCDE/HT/HDI, 65/35/105 equivalents; 0.1 wt% Santicizer 8; 0.01 wt% FeAA; PCDE Lot No. LR-12260-44 (Shell).

F. MOTOR FIRINGS (U)

(C) Two 0.32-lb grains of PCDE/SYFO/FEFO (1/1/1) propellant with a 3/1 HMX/AP ratio, 16 wt% Al and 78 wt% solids were fired successfully in 2C1.5-4 motors using Micarta sleeves. As shown on the computer printouts in Tables 21 and 22, the measured specific impulses extrapolated to standard conditions were 249.5 and 250.9 lbf-sec/lbm. The specific impulse efficiencies based on prefired propellant weight were 91.7 and 92.2%, respectively. The theoretical specific impulse, 272.1 lbf-sec/lbm, was calculated without taking into account the coating on HMX-A (~0.5 wt%) and AP (~0.1 wt%), so that the true efficiency should be slightly higher. These results agree well, within experimental error, with the efficiency-mass flow rate relationship for this size motor developed under the P-722 program,* although the mass flow rates were slightly higher than any measured under that program in the 2C1.5-4 motor.

G. SCREENING OF AGING STABILIZERS (U)

(U) A number of additives are being tested as aging stabilizers for PCDE/SYFO and PCDE/SYFO/FEFO propellants. The first additives selected for testing were those found to be the best for analogous propellants under another Aerojet program. These are Santicizer 8, which has been used previously in this program, and which is a scavenger for nitric oxide; DBR, a free-radical inhibitor, to stop free-radical chain reactions which are believed to produce nitric oxide from FEFO submixes under some conditions; and sulfur, to scavenge FeAA cure catalyst, which is believed to accelerate FEFO decomposition. A discussion of the evidence for these statements will be presented when the results of the aging tests are available. The formulation in which these stabilizers are being tested contains the PCDE/SYFO/FEFO binder system at a nominal 1/1/1 wt ratio, 79 wt% total solids and a 7/1 HMX/AP ratio. The additives are being tested alone and in combination with each other at 0.1 and 0.3 wt% of the propellant. In the case of DBR, which reacts with isocyanate, the formulations were adjusted to provide the same theoretical

* AFRPL-TR-71-43, "Combustion Efficiency of P722 Plasticizer"(U), April 1971, Contract F04611-70-C-0027, p. 134. (Confidential)

TABLE 21

PCDE/SYFO/FEFO MOTOR DATA (U)

FØRMULATIØN	PCDE CL7
BATCH NØ.	64-29C
GRAIN NØ.	01
DATE FIRED	7-12-73
TIME FIRED, HØURS	1100
MØTØR SIZE	2C1.5-4
PRØPELLANT WEIGHT, GRAMS*	144.0900
THRØAT DIAMETER, IN.	
BEFØRE FIRING	.360
AFTER FIRING	.355
AVERAGE	.358
AVERAGE NØZZLE EXPANSIØN RATIO	9.126
ACTIØN TIME, SEC	.4480
WEB BURNING TIME, SEC	.3905
AVERAGE PRESSURE, PSIA	
ØVER ACTIØN TIME	1192
ØVER WEB BURNING TIME	1281
WEB TIME/ACTIØN TIME	.872
WEB P INTEGRAL/ACTIØN P INTEGRAL	.937
WEB P INTEGRAL/TØTAL P INTEGRAL	.937
ACTIØN P INTEGRAL/TØTAL P INTEGRAL	1.000
CD, LBM/LBF-SEC	
THEØRETICAL	.00599
EXPERIMENTAL	.00591
C*, FT/SEC	
THEØRETICAL	5374
EXPERIMENTAL	5440
C* EFFICIENCY, PERCENT	101.24
MASS FLØW RATE, LBM/SEC	.709
WEB BURNING RATE, IN./SEC	.615
AVERAGE THRUST, LBF	180
THEØRETICAL SPECIFIC IMPULSE, LBF-SEC/LBM	
WITH SØLIDIFICATIØN ØF ØXIDES	272.1
WITH SUPERCØØLING ØF ØXIDES	272.1
EXPERIMENTAL SPECIFIC IMPULSE, LBF-SEC/LBM	
MØTØR CØNDITIØNS, 15 DEG. HALF-ANGLE	254.3
STANDARD CØNDITIØNS (CF EXTRAPØLATIØN)	250.9
SPECIFIC IMPULSE EFFICIENCY, PERCENT	
BASED ØN SØLIDIFICATIØN ØF ØXIDES	92.19
BASED ØN SUPERCØØLING ØF ØXIDES	92.19

* PRE-FIRED PROPELLANT WEIGHT

TABLE 22

PCDE/SYFO/FEFO MOTOR DATA (U)

FORMULATION	PCDE-C7
BATCH NO.	64-29C
GRAIN NO.	02
DATE FIRED	7-13-73
TIME FIRED, HOURS	13:20
MOTOR SIZE	2C1.5-4
PROPELLANT WEIGHT, GRAMS*	146.1700
THROAT DIAMETER, IN.	
BEFORE FIRING	.370
AFTER FIRING	.365
AVERAGE	.367
AVERAGE NOZZLE EXPANSION RATIO	9.123
ACTION TIME, SEC	.4665
WEB BURNING TIME, SEC	.4155
AVERAGE PRESSURE, PSIA	
OVER ACTION TIME	1110
OVER WEB BURNING TIME	1178
WEB TIME/ACTION TIME	.891
WEB P INTEGRAL/ACTION P INTEGRAL	.946
WEB P INTEGRAL/TOTAL P INTEGRAL	.942
ACTION P INTEGRAL/TOTAL P INTEGRAL	.997
CD, LBM/LBF-SEC	
THEORETICAL	.00599
EXPERIMENTAL	.00586
C*, FT/SEC	
THEORETICAL	5370
EXPERIMENTAL	5494
C* EFFICIENCY, PERCENT	102.31
MASS FLOW RATE, LBM/SEC	.691
WEB BURNING RATE, IN./SEC	.578
AVERAGE THRUST, LBF	173
THEORETICAL SPECIFIC IMPULSE, LBF-SEC/LBM	
WITH SOLIDIFICATION OF OXIDES	272.1
WITH SUPERCOOLING OF OXIDES	272.1
EXPERIMENTAL SPECIFIC IMPULSE, LBF-SEC/LBM	
MOTOR CONDITIONS, 15 DEG. HALF-ANGLE	251.6
STANDARD CONDITIONS (CF EXTRAPOLATION)	249.5
SPECIFIC IMPULSE EFFICIENCY, PERCENT	
BASED ON SOLIDIFICATION OF OXIDES	91.70
BASED ON SUPERCOOLING OF OXIDES	91.70

* PRE-FIRED PROPELLANT WEIGHT

crosslink density, assuming that the DBR reacts completely as a diol. After cure and measurement of initial minibar mechanical properties, the samples will be aged at an elevated temperature for at least six weeks before further testing.

H. CHARACTERIZATION AND EVALUATION OF PCDE LOTS (U)

(U) Work was begun on characterizing and evaluating various lots of PCDE manufactured by Hercules. Experience with many polyurethane propellant systems indicates that the optimum combining ratio (NCO/OH) is best determined from binder or propellant properties, as the analytical data are frequently unreliable. In addition, the optimum PCDE/triol ratio can only be determined from propellant properties. Lot qualification of this type is currently being done on the "PCDE Propellant Studies" program, Contract F04611-72-C-0046. While it would be desirable to characterize each individual lot in this way in order to learn as much as possible about the effects of manufacturing conditions and PCDE properties on propellant properties, the size of some lots is disappointingly small and the number of lots being supplied is dismayingly large. Therefore, to expedite the work and minimize the effort to be devoted to this task, the larger lots are being combined in those cases where the analytical data indicate that the properties are similar. Those lots specifically designated as experimental are being studied individually.

(U) Table 23 presents the analytical data for the lots currently being tested. Additional lots, including two experimental lots, were received on August 28, near the end of this reporting period; these will also be characterized and will be discussed in the next quarterly report. Lot 1A1 was not provided to this program, but is being included because of the unusually high reported functionality.

In order to obtain some preliminary comparative data on the behavior in propellants, a formulation was selected which has given reasonably good results with the Shell prepolymer, and propellants were prepared at the

TABLE 23

PCDE LOTS BEING EVALUATED[a]

Lot No.	Molecular Wt	Equivalent Wt	Functionality
Hercules 11	2940	1630	1.8
Hercules 12	2980	1762	1.7
Hercules 13[b]	3260	1934	1.69
Hercules 1A1[c]	2960	1223	2.4
Shell LR-12260-44[d]	3080	1667	1.84

a Analytical data provided by Hercules
b Experimental lot
c Obtained from "PCDE Propellant Studies" Program
d Shown for comparison purposes

same calculated crosslink density using lots 1A1, 13, and a 1/3 blend of lots 11 and 12 (the ratio of the weights of each received). After curing, the differential scanning calorimeter will be used to seek a second order transition, possibly the glass transition point, T_g. The mechanical properties will then be measured at temperatures on both sides of this transition, as well as at room temperature. Results are not yet available.

Each lot of PCDE is also being studied with respect to reaction with a diisocyanate in solution, an approach which provides equivalent weight and functionality values under conditions more like those in propellant than do the ordinary analytical methods. If, as expected, the results are confirmed in propellant studies, this method will offer considerable savings of time and effort in propellant preparation and testing.

END

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