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PCDE PROPELLANT FOR BALLISTIC MISSILES

Morton A. Klotz, B. B. Lampert, J. P. Coughlin and R. M. Smith
Aerojet Solid Propulsion Company

Technical Report AFRPL-TR-73-28

April 1973

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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 first quarterly report issued under Contract F04611-73-C-0034, and covers the period 4 December 1972 through 28 February 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-1.

The work was performed under the supervision of Dr. L. J. Rosen, within the Propellant Development Department, Dr. C. J. Rogers, Manager. The Principal Investigator is Dr. Morton A. Klotz. Dr. B. B. Lampert, Mr. J. P. Coughlin, Dr. R. M. Smith and Miss I. T. Pierce 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 in the list of references included in this volume.

This technical report has been reviewed and is approved.

Charles R. Cooke
Chief, Solid Rocket Division
Air Force Rocket Propulsion Laboratory

UNCLASSIFIED ABSTRACT

This program is concerned with the development, characterization, and ballistic testing of propellants containing PCDE, SYFO, and FEFO. A detailed theoretical study was made of the effects of compositional variables on the predicted performance of PCDE/SYFO and PCDE/SYFO/FEFO propellants in order to select formulations for maximum range. The details are given and discussed. An impurity was found to be present in PCDE in significant concentration. It was identified and two methods were devised for its removal. The hazard characteristics of the ingredients were determined alone and in combination with each other. Potential antioxidants were screened for use in propellants. Preliminary propellant formulation studies gave propellants with mechanical properties close to the program goals and with encouraging sensitivities.

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FIGURE LIST

FIGURE LIST (Cont.)

FIGURE LIST (cont.)

TABLE LIST

TABLE LIST (cont.)

GLOSSARY

AO-2246	2,2'-Methylene-*bis*(4-methyl-6-t-butyl phenol)
AP	Ammonium perchlorate
BDNPA	*bis*(2,2-Dinitropropyl) acetal
BDNPA/F	1:1 Mixture of BDNPF and BDNPA
BDNPF	*bis*(2,2-Dinitropropyl) formal
BuMines	Bureau of Mines
DBR	4,6-Di-t-butylresorcinol
d_t	Throat diameter
DTA	Differential thermal analysis
E_o	Initial tangent modulus
FeAA	Ferric acetylacetonate
FEFO	*bis*(2-Fluoro-2,2-dinitroethyl) formal
HMX	Cyclotetramethylene tetranitramine
HT	1,2,6-Hexanetriol
I°_{sps}	Theoretical I_{sp} under standard conditions of $P_c = 1000$ psia, $P_e = 14.7$ psia, ideal expansion, adiabatic conditions, zero degree half-angle nozzle.
I_{15s}	Delivered specific impulse (predicted or measured) corrected to standard conditions of $P_c = 1000$ psia, $P_e = 14.7$ psia, 15° half-angle nozzle
I_{sp}	Specific impulse (in general)
ℓ_o	Original length (in swelling ratio)
ℓ	Swollen length (in swelling ratio)
$\dot{m}$	Mass flow rate of propellant combustion products
n	Pressure exponent
Neozone D	N-Phenyl-β-naphthylamine

GLOSSARY (cont.) (U)

	NMR	Nuclear magnetic resonance
	OFR	Ratio of total equivalents of oxidants to total equivalents of carbon and metal $(=(\bar{O} + 0.5\ F)/\bar{C} + 1.5\ Al))$
	OMOX	Condition of exact equivalence between oxygen and sum of carbon and oxidizable metals (carbon in +2 oxidation state and hydrogen inert) $(=(\bar{O} + .5\ \bar{F})/\bar{C}))$
	OR	Oxidation ratio $(=(2\bar{C} + \bar{F})/(4\bar{C} + \bar{H}))$
(C)	P-722	2,3-*bis*(Difluoramino)propyl 2,2-dinitropyl carbonate
(C)	PBEP	Poly[1,2-*bis*(difluoramino)-2,3-epoxypropane]
(C)	PCDE	Poly(1-cyano-1-difluoraminoethylene oxide)
	r	Burning rate
	Santicizer 8	N-ethyl toluenesulfononamide (o and p mixture; Monsanto Chemical Co.)
	SRI	Stanford Research Institute
(C)	SYFO	*bis*(2,2-Difluoramino-5-fluoro-5,5-dinitropentyl) formal
	T_c	Theoretical flame temperature
	TDI	Tolylene-2,4-diisocyanate
	T_e	Motor exit-plane temperature
	TMETN	Trimethylolethane trinitrate
(C)	TVOPA	1,2,3-tris[α,β-*bis*(Difluoramine)ethoxy]propane
	ΔH_f	Heat of formation
	ϵ_b	Elongation at σ_b
	ϵ_m	Elongation at σ_m
	μm	Micrometer, 10^{-6} meter (formerly micron, symbol μ)

GLOSSARY (cont.)

ρ	Propellant density
ρ_o	Reference density in Ω equation
σ_m	Maximum tensile strength
Ω	Effective specific impulse, $= I_{sp}(\rho/\rho_o)^K$

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 delivered specific impulse in the range of 259-262 lbf-sec/lbm.
- A density as high as 0.070 lb/cu in.
- A burning rate range from 0.4 to 0.5 in./sec at 1000 psia with a pressure exponent at or below 0.6. Based on preliminary system requirement analysis it is anticipated that a second-stage strategic missile will require a burning rate of about 0.4 in./sec and a third-stage burning rate of 0.4 to 0.5 in./sec at 1000 psia.
- Adequate aging stability.
- Adequate processing and cure properties.
- Safe manufacturing, handling, and use characteristics.
- Adequate liner-bond properties.
- Adequate combustion-stability characteristics.
- High reproducibility characteristics.

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,

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* 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

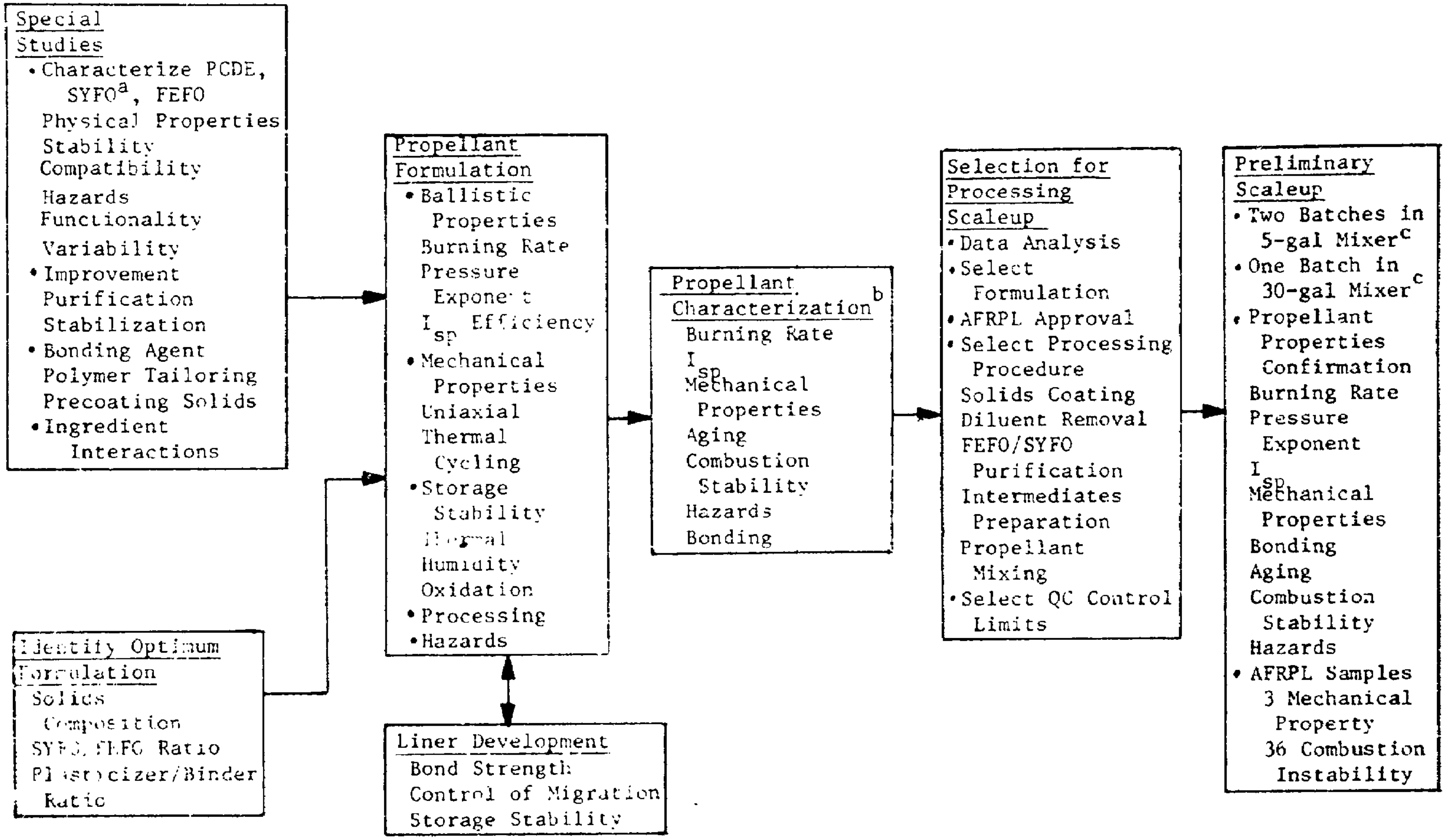

Figure 1

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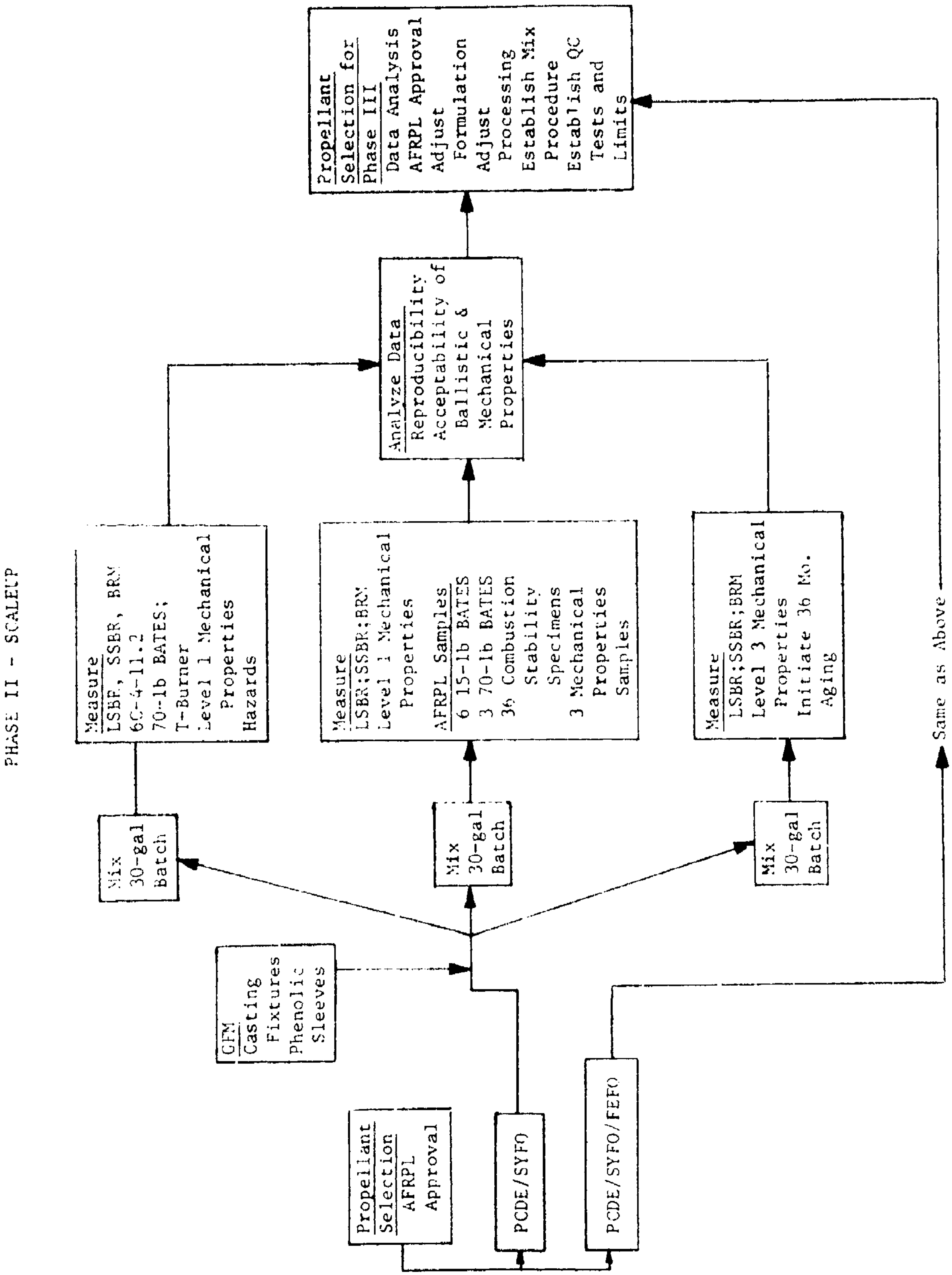
[a] Including heat of formation by subcontract to Dow.
[b] Six formulations: 3 PCDE/SYFO, 3 PCDE/SYFO/FEFO.
[c] For each of two propellants: 1 PCDE/SYFO, 1 PCDE/SYFO/FEFO.



PHASE II - SCALEUP

Figure 2

PHASE III - MOTOR DEMONSTRATION

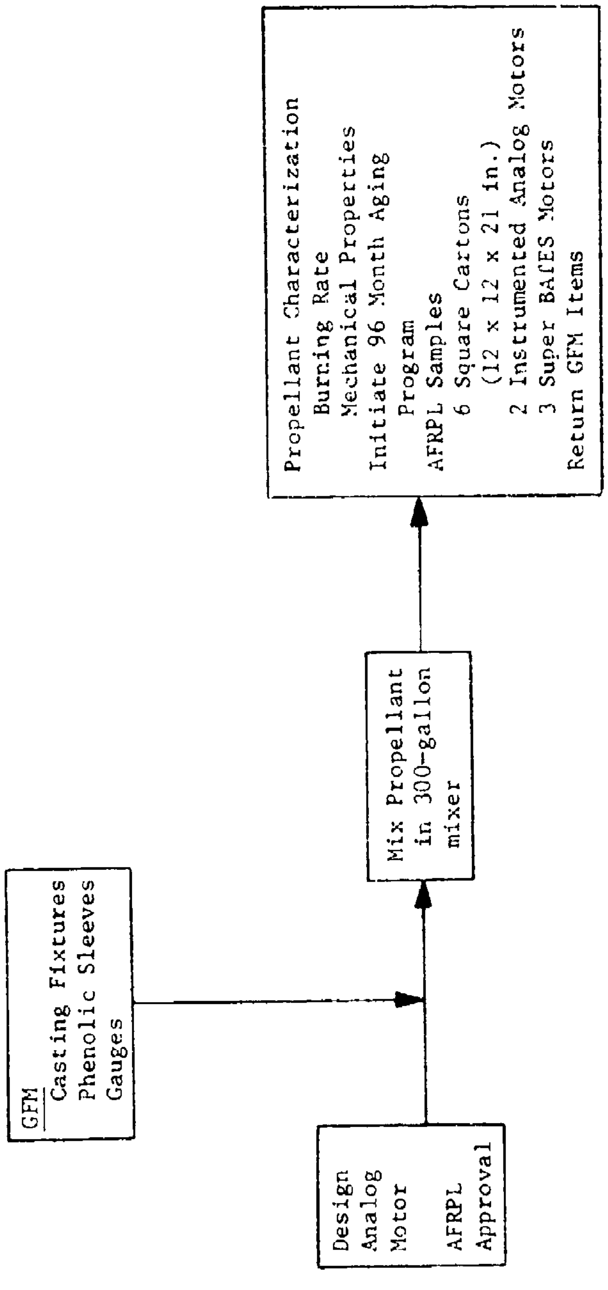


Figure 3

SECTION II

SUMMARY

(C) A. A detailed theoretical study was made of the effects of compositional variables on the predicted performance of PCDE/SYFO and PCDE/SYFO/FEFO propellants in order to select formulations for maximum range. Within the limits imposed by practical considerations such as processing, etc., only small changes in performance are found. The optimum propellant formulation will probably contain 78 to 80 wt% solids, 16 to 17 wt% aluminum, a 3/1 HMX/AP wt ratio, and a 2/1 plasticizer/polymer wt ratio. The delivered specific impulse in a large motor will probably be in the range of 262 to 264 lbf-sec/lbm, with a density of approximately 0.069 lbm/in.^{3}.

(C) B. The carbonyl band in the infrared absorption spectrum of as-received PCDE was found to be due to the presence of over 4% acetone. The impurity (C) is removable by either vacuum distillation or treatment with 13X molecular sieves, but it is not yet known which method is best.

(C) C. Neat SYFO is very sensitive to friction and moderately sensitive to impact, but is readily desensitized to either by admixture with PCDE or FEFO. Molecular sieve treatment had no effect on the sensitivity of a PCDE/FEFO mixture.

(U) D. Four potential antioxidants for use in PCDE propellants were screened by comparison of DTA data in PCDE/FEFO and PCDE/SYFO submixes. The results were inconclusive, but Neozone D was selected for current use pending more thorough evaluation.

(U) E. PCDE/SYFO and PCDE/SYFO/FEFO propellants have exhibited mechanical properties close to the program goals, with no effort at optimization. The propellant sensitivities are also encouraging.

(C) F. The results of a small-scale Company-sponsored investigation of the thermal stability of PCDE/FEFO/Al/HMX/AP propellant is reported. In 68 days at 135°F there was no exotherm, an no significant loss in weight or increase in hazard, but there was evidence of fissuring and deterioration of mechanical properties.

SECTION III

TECHNICAL PROGRESS

A. SELECTION OF FORMULATIONS FOR OPTIMUM RANGE

1. Introduction

This task was divided into two parts. The first (Section III.A.2) was a detailed study of the effect of compositional variables on the performance potential of PCDE/SYFO propellants. In this study, in addition to theoretical specific impulse, the factors affecting delivered specific impulse were considered and used in predicting propellant performance. The recommendations arrived at for formulations for initial evaluation also considered practical constraints such as processability and probable burning-rate range.

The second part (Section III.A.3) was a refinement of these calculations taking into consideration the effects of modifications of an actual baseline propellant composition.

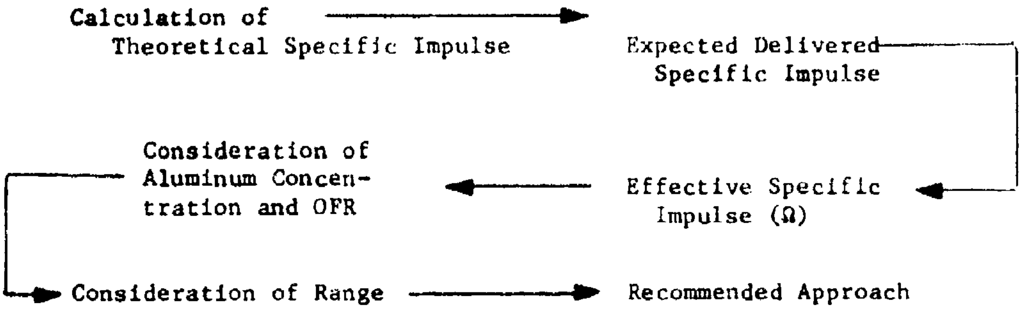
2. The Effect of Compositional Variables on Performance

a. Constraints

In order to conduct the most effective and economical program, it is desirable to establish practical formulation development limits based on optimum performance, processability, mechanical properties and aging stability. The limits set by performance must, in turn, consider not only specific impulse and density but also burning rate achievable, pressure exponent and the requirements peculiar to each stage of the ballistic missile. The processability limits are based on experience. Mechanical properties limits must exclude potential formulations with too little polymer and/or binder and must consider the possibility that, especially in an upper stage, a formulation with lower solids loading, and therefore lower performance, may provide superior mechanical properties which can be used to reduce insulation weight (no boots), and thus permit higher volumetric loading.

This section describes the process used for limiting the scope of formulation development to permit concentration on the most promising formulation range.

A roadmap of the selection process is as follows:



Throughout this analysis the following practical guidelines were used, based on the propellant target properties in Section I.A.

Propellant Goals	Guide Lines	Reasons
r and n	2/1 to 3/1 HMX/AP ratio	Ease of r and n tailoring
Mechanical Properties	≥ 22 vol % binder ≥ 8 vol % polymer (≤3/1 plasticizer/ polymer ratio)	Current technology based on similar propellants
Processing Properties	≥ 22 vol % binder ≥ 1 plasticizer/ polymer ratio	Current technology based on similar propellants
Storage Stability	≤3/1 plasticizer/ polymer	Increase stability
Hazard	≥2/1 HMX/AP ratio	Reduce friction sensitivity
	≤3/1 plasticizer/ polymer	Avoid migration or exudation

b. Propellant Performance Evaluation

Within the framework of other constraints as identified above, the propellant choice will depend upon the ideal combination of expected delivered specific impulse and density. The result of the tradeoff analysis is the effective specific impulse.

Expected delivered specific impulse is a complex function of theoretical specific impulse and all of the compositional, thermodynamic and motor-design parameters which affect specific impulse efficiency.

Chief among these are (1) total aluminum content and propellant OFR which affect aluminum combustion efficiency, (2) total propellant mass, firing duration and motor geometry, which affect heat loss, (3) total Al_2O_3 content of the exhaust products, average Al_2O_3 particle size, exhaust temperature and motor geometry, all of which play an important role in determining efficiency losses due to two-phase-flow effects, and (4) active fluorine content of the propellant, which can have a profound effect on both aluminum combustion efficiency and two-phase-flow losses. A theoretical model which utilizes these parameters for predictions of deliverable specific impulse is described below and utilized in subsequent sections for predictions of final motor performance.

In order to select optimum compositions from the many potential ingredient combinations for this application, optimization calculations of propellant performance as a function of composition were made on the basis of three-component propellant systems consisting of:

- Three binder compositions with each plasticizer, containing PCDE polymer and plasticizer (either SYFO or SYFO/FEFO mixtures) at fixed ratios of 1:1, 2:1, and 3:1, as well as the unplasticized polymer for reference.
- Six oxidizer combinations consisting of HMX and NH_4ClO_4 mixtures in ratios of 1:1, 3:2, 2:1, 3:1 and 7:1, as well as pure HMX.
- Aluminum metal as the fuel additive and third component.

Each system was then evaluated as a function of binder content (from 12 to 21* weight percent in 3% steps) and aluminum content (in 2% steps from 12% to the maximum dictated by propellant oxygen balance for each binder content). For each system, the performance parameters evaluated were:

- Theoretical Specific Impulse
- Predicted specific impulse for a typical large-motor configuration (I_{15s})
- Effective Specific Impulse based on $I_{15s}(\rho/\rho_o)^{0.3}$
- The volume fraction of binder
- The chamber flame temperature
- A detailed discussion of the results of these evaluations

is presented in the following three sections. In the first section, the effect of composition variables on the <u>theoretical specific impulse</u> is described. In the second section, the same compositions are examined in

---

*A limited number of calculations is included for 24 weight percent binder at an HMX/AP oxidizer ratio of 3/1.

terms of the expected delivered specific impulse using a prediction model for large-motor applications. Next, specific impulse-density tradeoffs are made to establish optimum formulations on the basis of effective specific impulse.

(1) Theoretical Specific Impulse (I°_{sps})

A preliminary comparison of theoretical I_{sp} data for three plasticizers (FEFO, SYFO and a 1:1 weight mixture of the two) with similar data for unplasticized PCDE polymer is shown in Figure 4. The calculations were performed for binder compositions of 2:1 plasticizer: polymer ratio (except for the unplasticized polymer) and at a constant oxidizer composition of 3/1 HMX/NH_4ClO_4 mixture. Each of the points plotted represents the composition (aluminum content) yielding the maximum theoretical I_{sp} at the particular solids loading of interest, expressed as weight percent total solids (Al + AP + HMX).

The plot shows that peak theoretical specific impulse increases with the total solids loading, and that both FEFO and SYFO plasticizers result in an improvement of theoretical I_{sp} over that of the unplasticized PCDE polymer.

The peak theoretical I_{sp} values for all the SYFO, FEFO, and mixed SYFO/FEFO plasticized PCDE binders occur at pure HMX or a high (7/1) ratio of HMX to AP, as can be observed in Figures 5 (82% solids) and 6 (79% solids). More information on the points plotted, including aluminum content, density and volume fraction binder, as well as theoretical I_{sp}, are included as grid summaries

PEAK THEORETICAL I°_{sps} VS. % TOTAL SOLIDS FOR HMX/AP/3/1 OXIDIZER AND PLASTICIZER/POLYMER = 2/1 AND NONPLASTICIZED PCDE POLYMER (U)

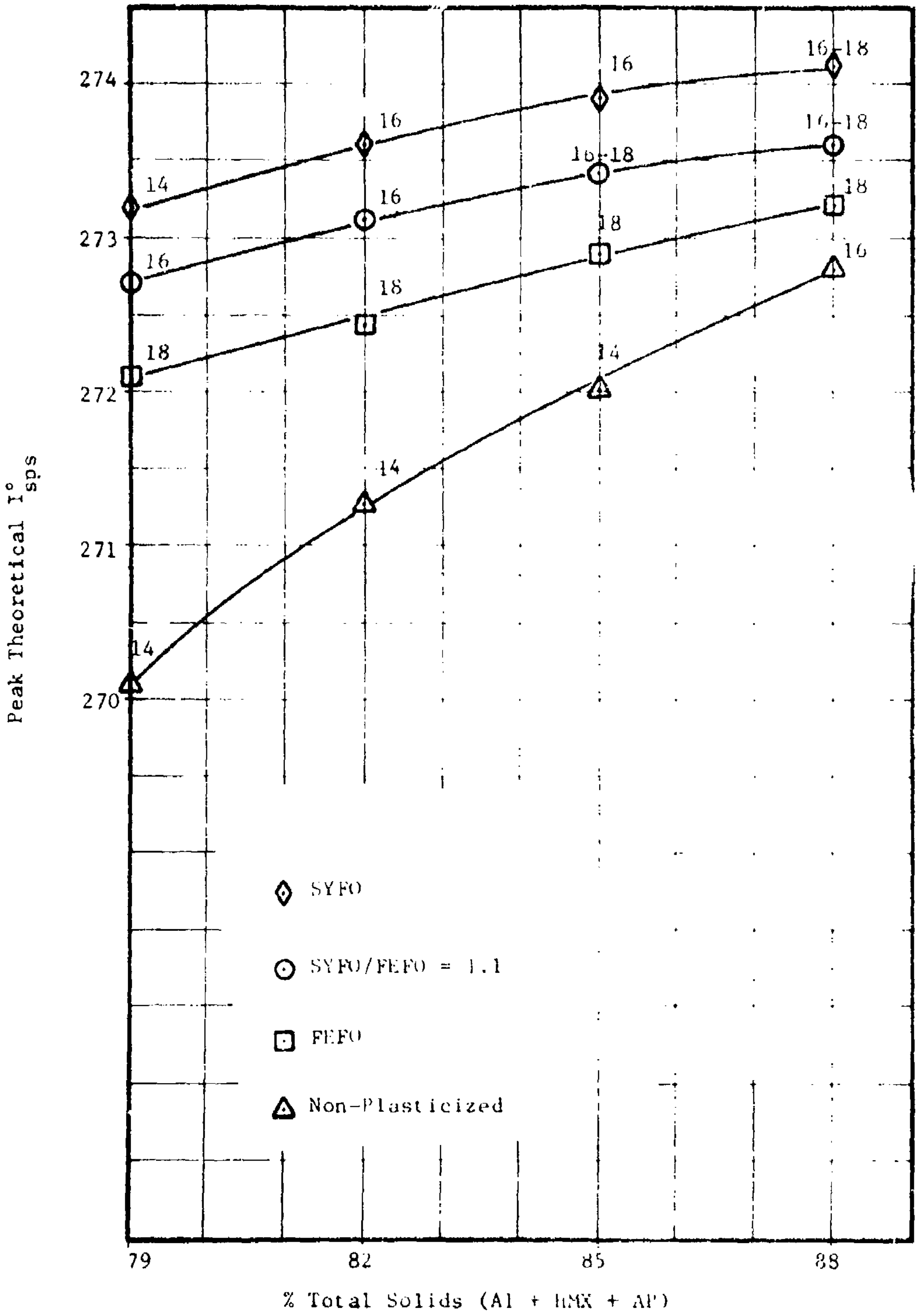


Figure 4

PEAK THEORETICAL I°_{sps} VS % HMX IN HMX/AP
OXIDIZER AT 82 WT% SOLIDS (U)

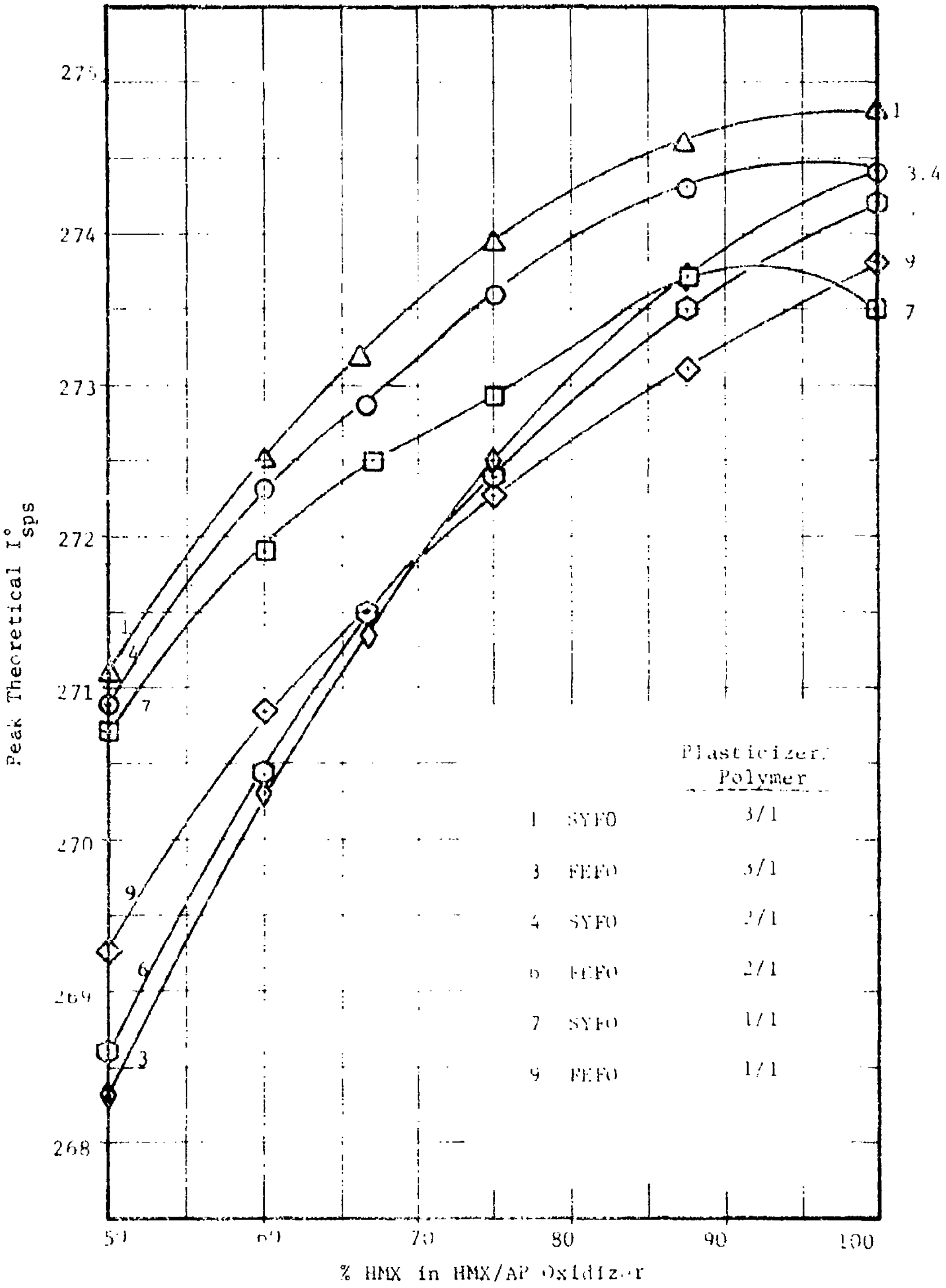


Figure 5

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PEAK THEORETICAL I°_{sps} VS % HMX IN HMX/AP
OXIDIZER AT 79 WT% SOLIDS (U)

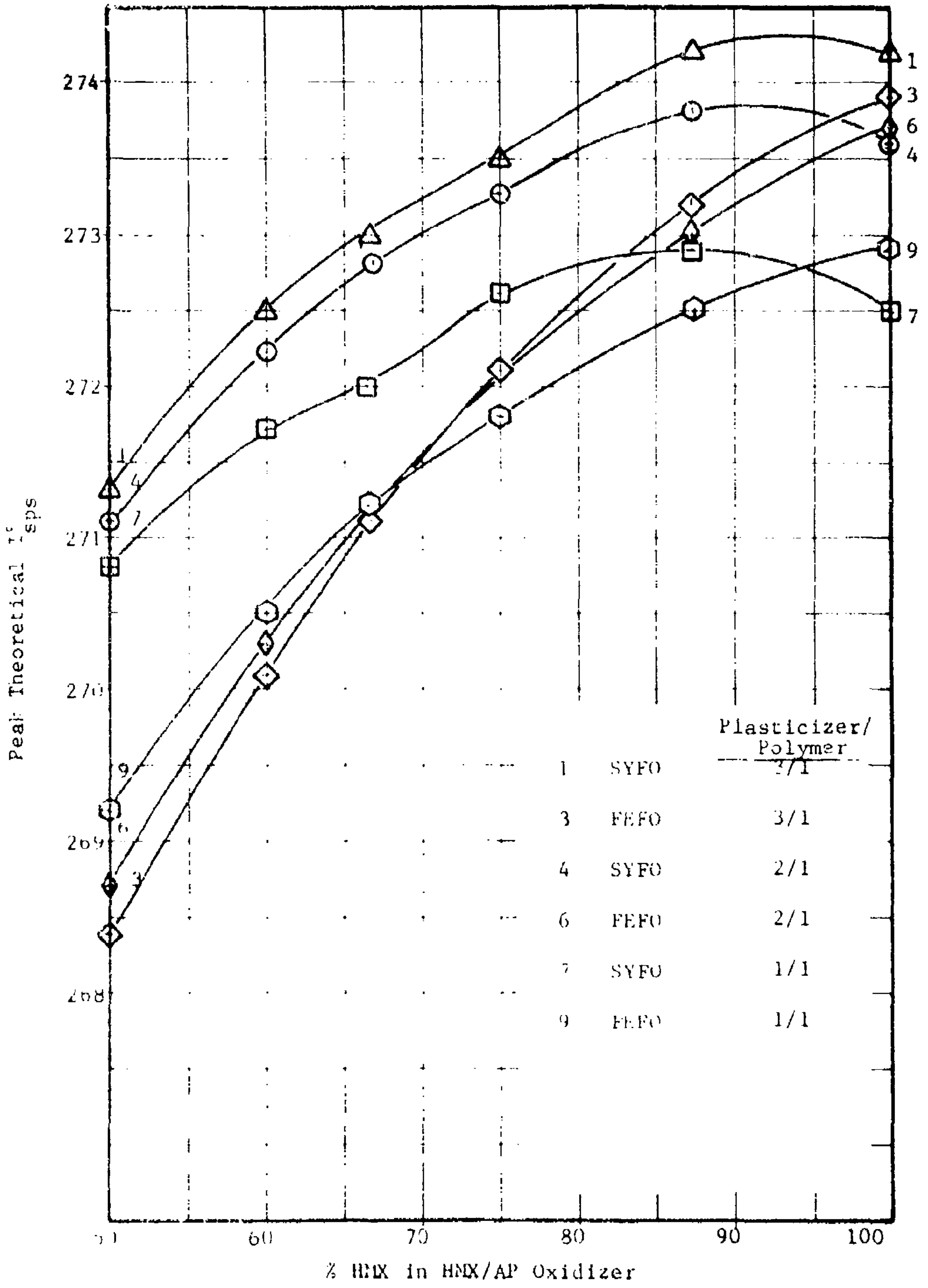

Figure 6

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in Figure 7 for the 82% solids systems and in Figure 8 for the 79% solids systems. Also included in these grids are the corresponding data for the mixed-plasticizer systems which were not plotted in Figures 5 and 6. At these peak values of theoretical I_{sp}, SYFO or the mixtures of FEFO and SYFO indicate only tenths of I_{sp} units advantage over FEFO. These specific impulses are in the expected order as regards plasticizer-to-polymer ratios i.e. 3/1 > 2/1 > 1/1.

SYFO contains more hydrogen and carbon (fuel value) and has a more positive heat of formation per unit weight than FEFO. Therefore SYFO is expected to yield higher specific impulse than FEFO with a good oxidizer such as AP. On the other hand since FEFO has a stoichiometric ratio of oxidizer (O+F) to fuel (C+H) of greater than one, it benefits from combination with a less than stoichiometric oxidizer such as HMX. Thus FEFO provides very good performance with HMX oxidizer systems.

At the more practical (less than optimum) HMX/AP ratios (3/1 or lower) which will probably be utilized to achieve burning rate and pressure exponent targets, SYFO has a more pronounced advantage over FEFO (1-2 I_{sp} units). In fact, with lower HMX/AP ratios, PCDE polymer appears better than FEFO, since there is a slight decrease of I_{sp} with increasing FEFO content. For the plasticizers of concern for this program--SYFO or the SYFO/FEFO mixtures--the I°_{sps} increases in the expected order with increasing plasticizer-to-polymer ratio.

PCDE POLYMER PROPELLANTS AT PEAK THEORETICAL I°_{sps} FOR 82% SOLIDS (U)

I°_{sps}
wt.% Al
ρ g/cc
Vol.frac.binder

	HMX/AP Weight Ratio					
Plasticizer and Ratio	1/1	3/2	2/1	3/1	7/1	100/0
SYFO = 3/1	271.1 18 1.951 .220	272.5 18 1.946 .219	273.2 16 1.932 .218	273.8 16 1.929 .217	274.6 14 1.912 .215	274.8 12 1.896 .214
SYFO/FEFO = 3/3/2	269.7 20 1.957 .223	271.4 18 1.941 .221	272.3 18 1.939 .221	273.2 18 1.936 .221	274.1 16 1.919 .219	274.9 14 1.903 [illegible]
FEFO = 3/1	268.3 18 1.941 .224	270.3 18 1.936 .223	271.3 18 1.934 .223	272.5 18 1.931 .223	273.7 18 1.926 .222	274.[illegible] 16 1.909 .220
SYFO = 2/1	270.9 18 1.947 .221	272.3 16 1.931 .219	272.9 16 1.929 .219	273.6 16 1.925 .219	274.3 14 1.909 .217	274.4 14 1.904 .216
SYFO/FEFO = 1/1/1	269.8 18 1.942 .223	271.5 18 1.938 .222	272.3 18 1.936 .222	273.1 16 1.921 .221	273.9 14 1.905 .219	274.5 14 1.900 .218
FEFO = 2/1	268.6 18 1.938 .225	270.4 20 1.945 .226	271.5 18 1.931 .224	272.4 18 1.928 .224	273.5 16 1.912 .222	274.2 14 1.895 .220
SYFO = 1/1	270.7 18 1.940 .224	271.9 16 1.924 .222	272.5 16 1.921 .222	272.9 16 1.918 .222	273.7 14 1.902 .220	273.5 12 1.885 .218
SYFO/FEFO = 1/1/2	270.0 18 1.936 .225	271.3 18 1.932 .225	272.0 18 1.929 .225	272.7 16 1.915 .223	273.5 14 1.899 .221	273.7 14 1.894 .220
FEFO - 1/1	269.2 18 1.933 .227	270.8 18 1.929 .226	271.5 18 1.926 .226	272.3 18 1.923 .226	273.1 16 1.907 .224	273.8 14 1.891 .222
Non Plasticized	269.6 16 1.907 .231	270.4 16 1.903 .231	270.8 14 1.889 .229	271.3 14 1.886 .229	271.2 12 1.870 .227	269.9 12 1.865 .226

Figure 7

I°_{sps} wt.% Al ρ g/cc Vol.frac.binder

PCDE POLYMER PROPELLANTS AT
PEAK THEORETICAL I°_{sps} FOR 79% SOLIDS (U)

	HMX/AP Weight Ratio					
Plasticizer and Ratio	1/1	3/2	2/1	3/1	7/1	100/0
SYFO = 3/1	271.3 18 1.939 .255	272.5 16 1.923 .253	273.0 16 1.921 .252	273.5 14 1.907 .251	274.2 14 1.901 .250	274.2 12 1.885 .248
SYFO/FEFO = 3/3/2	270.0 18 1.933 .257	271.4 18 1.929 .256	272.2 16 1.915 .255	273.0 16 1.912 .254	273.7 14 1.896 .252	274.3 14 1.891 [illegible]
FEFO = 3/1	268.4 18 1.927 .259	270.1 18 1.923 .259	271.1 18 1.921 .258	272.1 18 1.918 .258	273.2 18 1.913 .257	273.9 14 1.886 .254
SYFO = 2/1	271.1 16 1.923 .255	272.2 16 1.919 .254	272.8 16 1.917 .254	273.2 14 1.902 .252	273.8 14 1.897 .252	273.6 12 1.881 .249
SYFO/FEFO = 1/1/1	270.0 18 1.929 .258	271.4 18 1.925 .258	272.0 16 1.912 .256	272.7 16 1.909 .256	273.4 14 1.893 .253	273.8 14 1.888 .253
FEFO = 2/1	268.7 20 1.936 .262	270.3 18 1.920 .260	271.2 18 1.918 .259	272.1 18 1.915 .259	273.0 16 1.899 .257	273.7 14 1.883 .255
SYFO = 1/1	270.8 16 1.915 .258	271.7 16 1.911 .258	272.0 16 1.908 .257	272.6 14 1.894 .255	272.9 14 1.889 .255	272.5 12 1.873 .253
SYFO/FEFO = 1/1/2	270.1 18 1.922 .261	271.1 16 1.907 .259	271.7 16 1.905 .259	272.1 16 1.902 .258	272.9 14 1.886 .256	272.7 12 1.870 .254
FEFO = 1/1	269.2 18 1.919 .263	270.5 18 1.915 .262	271.2 18 1.912 .262	271.8 16 1.898 .260	272.5 14 1.882 .258	272.9 14 1.877 .257
Non Plasticized	269.1 16 1.890 .268	269.7 14 1.876 .266	270.1 14 1.873 .265	270.1 14 1.870 .265	269.6 12 1.855 .263	267.8 10 1.839 .260

Figure 8

At the highest HMX/AP ratios the peak I°_{sps} occurs at 14% aluminum or lower. The optimum aluminum content is, of course, dictated by the availability of oxygen, which decreases as the HMX/AP ratio increases. Even at the more practical HMX/AP ratio of 3/1, the optimum aluminum content (in terms of I°_{sps}) for these SYFO- and SYFO/FEFO-plasticized binders is never over 16% aluminum. In Figure 9 a triangular composition diagram shows lines of constant OFR=1.0 for systems containing aluminum, SYFO/PCDE polymer = 2/1 and the various oxidizers concerned. From this figure, one can determine the aluminum content corresponding to an OFR of 1.0 for a given combination of binder level and oxidizer composition. Thus, for 7/1 HMX/AP at 79% solids, the limiting aluminum content is 18%, and the peak theoretical I_{sp} occurs at an OFR of 1.14 (14% Al); similarly, for the same binder and solids loading with 2:1 HMX/AP oxidizer, the limiting aluminum content corresponding to OFR=1.0 is 22% and the peak theoretical I_{sp} occurs at 16% aluminum or an OFR of 1:21 with increasing aluminum content. With less energetic binders more aluminum is required to achieve a peak theoretical I_{sp}.

Another indication of the energy potential of these SYFO-plasticized PCDE binders is that there is only tenths of a unit of I°_{sps} advantage of the 82% solids formulations over the 79% solids propellants. Thus, if a high-volume-fraction binder is required to achieve mixing, casting, and mechanical-properties targets, there are minimal losses in theoretical performance. The advantages of high solids are, therefore,

LINES OF CONSTANT OFR = 1.0 VS. COMPOSITION FOR VARIOUS OXIDIZERS (U)

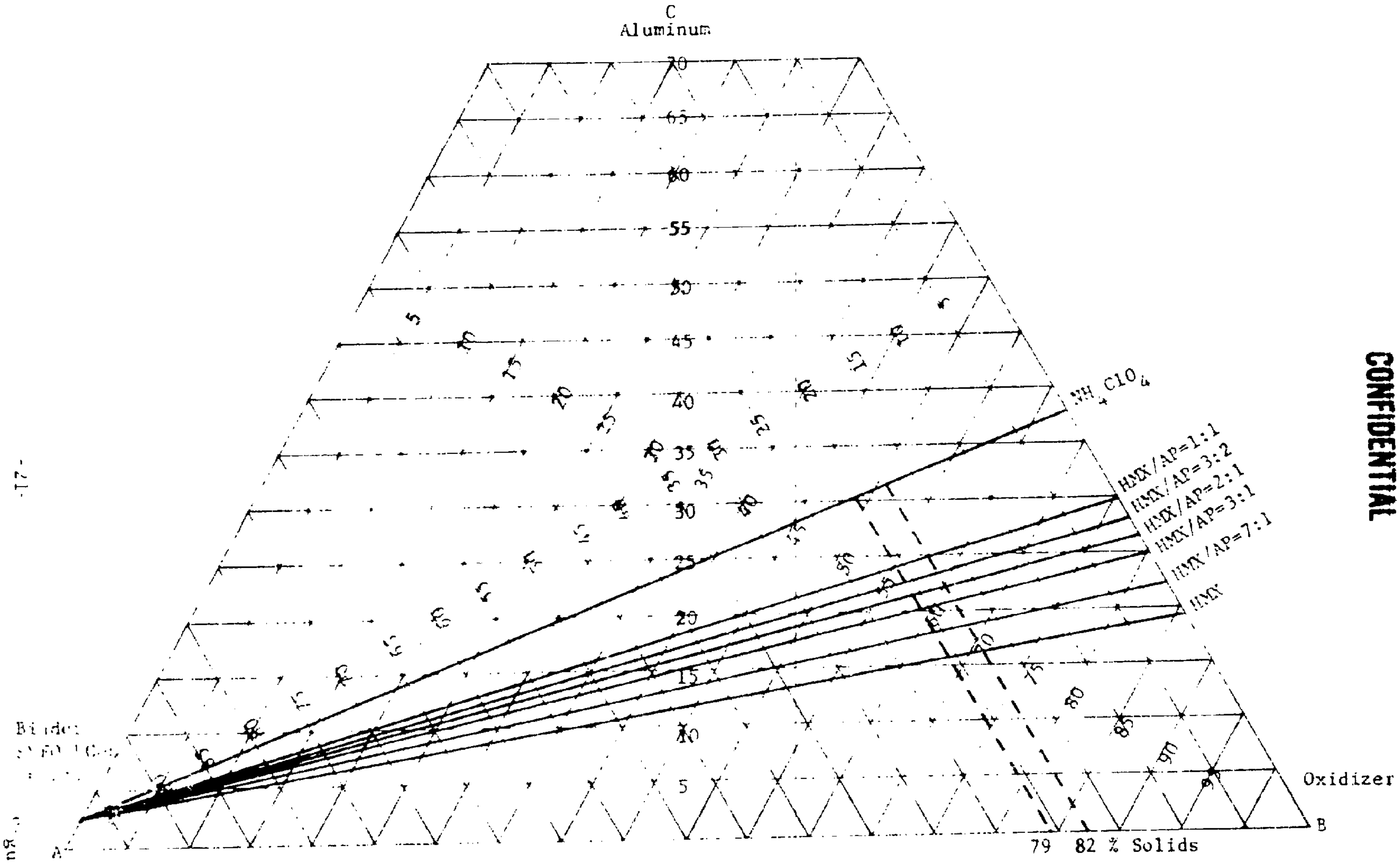

Figure 9

primarily in cost and material requirements.

(2) Expected Delivered Specific Impulse (I_{15s}) (U)

(a) Prediction Model (U)

(C) The performance prediction model developed on the P722 Program (Ref. 1,2)

$$E = 98.30 - 6.198x - 6.732\ x/(\dot{m})^{1/2} - .9428\ (A/\dot{m})^{1/2},$$

has been modified on the basis of additional experimental data to a form which explicitly accounts for the effect of active fluorine in the propellant composition (Ref. 3),

$$E = 98.62 - 15.86x - 6.092\ x/(\dot{m})^{1/2} - .5336\ (A/\dot{m})^{1/2} + .5144(x)(F),$$

where x = moles of Al_2O_3 per 100 grams of propellant combustion products,

$\dot{m}$ = propellant mass flow rate in lb/sec,

A = exposed surface area of motor inert parts, in sq. in.

F = wt% active fluorine in the propellant, and

E = specific impulse efficiency, %

(U) The first term of the equation, 98.62, represents the limiting efficiency for a propellant of all gaseous combustion products fired in a rocket motor having zero heat loss with a nozzle of 15°-half-angle exit cone. This (as well as all other equation coefficients) was derived from experimental data by a least-squares fitting technique--and agrees quite closely with the theoretical value of 98.30.

(C) The first, second and fifth terms in combination, 98.62 - 15.86x + (.5144)(x)(F), represent the limiting efficiency of aluminized propellants in general--as a function of both $Al_2 0_3$ content and active fluorine content. Thus every aluminized propellant has its own limiting asymptote of efficiency (at infinite mass flow rate) dependent on the exact $Al_2 0_3$ content of the combustion products and active fluorine content. This facet of the prediction model is in conflict with earlier prediction models, such as that of Rohm and Haas (Ref. 4), which assume that $Al_2 0_3$ particle size is a function of propellant composition and independent of motor size, but in substantial agreement with a recent Air Force Survey (Ref. 5) which showed that $Al_2 0_3$ particle size is principally a function of rocket motor size or throat diameter.

(C) The third term of the equation, $-6.092\ x/(\dot{m})^{1/2}$, represents the variation in two-phase-flow losses with motor scale-up effects. Fractional velocity lag is inversely proportional to nozzle length or nozzle throat diameter or (alternatively) inversely proportional to mass flow rate to the one-half power under conditions of constant chamber pressure comparisons. Total loss due to velocity lag is equal to fractional velocity lag multiplied by mass fraction of $Al_2 0_3$ in the combustion products.

(C) The fourth term of the efficiency equation, $-\ .5336(A/\dot{m})^{1/2}$, represents a heat-loss term, where heat loss per unit mass is directly proportional to exposed surface area of rocket-motor inert parts and to firing duration, $\frac{A \cdot t}{m}$ or $(\frac{A}{\dot{m}})$. The corresponding loss in specific impulse or specific impulse efficiency is proportional to the square root of heat loss or to $(A/\dot{m})^{1/2}$. At infinite mass flow rate the third and fourth terms drop out yielding the limiting efficiency defined by the first, second and fifth terms.

(C) The fifth term, + .5144 (x)(F), represents the improvement in specific impulse efficiency due to the presence of active fluorine in the propellant composition. The observed effect of fluorine is of necessity related to Al_2O_3 concentration as well as fluorine concentration in terms of either (a) improved combustion efficiency or (b) reduced two-phase-flow losses (or both).

(U) The experimental data upon which this efficiency equation is based are summarized in Table I. Included are 2C1.5-4.0 and 2C1.5-11.2 motor-firing data for 5 PBD propellants from an in-house study (Ref. 6), 2C1.5-4.0 and 2C1.5-11.2 data for one non-Domino reference propellant, two TVOPA propellants and five P722 propellants from the P722 Program (Ref. 1), and 2C1.5-4.0 and 2C1.5-11.2 data for 5 TVOPA propellants as well as one 6C4.8-11.4 TVOPA propellant firing from the High-Impulse, High-Density Program (Ref. 3).

(U) It would be highly desirable to extend this correlation effort to include additional classes of propellants and additional data from other motor sizes. Data which are being incorporated include:

(U) ● 15-lb and 70-lb BATES motor data for DOMINO propellants as well as conventional propellants.

(U) ● Data for smokeless (nonaluminized) formulations in all motor sizes.

Table I

COMBINED MOTOR FIRING DATA (U)

	Motor Size	Propellant Designation	Wt % Al	Wt % F	I_{sp} Efficiency	$\dot{m}$, lb/sec	Al_2O_3 Moles/100g	A Sq in.	d_t in.	Equiv. Wt % TVOPA	OFR
1	2C1.5-4.0	PBD 88-15	15	0	.8655	.4250	.2603	11.2800	.2910	.0000	1.467
2	"	PBD 90-17	17	0	.8851	.4690	.2941	11.2800	.3040	.0000	1.509
3	"	PBD 90-20	20	0	.8750	.4680	.3355	11.2800	.3050	.0000	1.315
4	"	PBD 90-23	23	0	.8642	.4800	.3684	11.2800	.3070	.0000	1.153
5	"	PBD 90-26	26	0	.8570	.4610	.3901	11.2800	.3030	.0000	1.017
6	2C1.5-11.2	PBD 88-15	15	0	.9958	1.2880	.2603	11.2800	.5290	.0000	1.467
7	"	PBD 90-17	17	0	.9150	1.4170	.2941	11.2800	.5320	.0000	1.509
8	"	PBD 90-20	20	0	.9005	1.4250	.3355	11.2800	.5380	.0000	1.315
9	"	PBD 90-23	23	0	.8935	1.4340	.3684	11.2800	.5335	.0000	1.153
10	"	PBD 90-26	26	0	.8857	1.4240	.3901	11.2800	.5260	.0000	1.017
11	2C1.5-4.0	Reference	17.72	0	.8689	.3960	.3130	11.2800	.2810	.0000	1.40
12	"	6.31 P722	18.22	1.42	.8895	.4600	.3130	11.2800	.3040	3.0000	1.40
13	2C1.5-4.0	12.62 P722	18.95	2.84	.8827	.4360	.3130	11.2800	.3060	6.0000	1.40
14	"	6 TVOPA	18.91	2.84	.8996	.4950	.3130	11.2800	.3300	6.0000	1.40
15	"	12 TVOPA	20.93	5.67	.9057	.6060	.3130	11.2800	.3560	12.0000	1.40
16	2C1.5-11.2	Reference	17.72	0	.9080	1.1700	.3130	11.2800	.4740	.0000	1.40
17	"	6.31 P722	18.22	1.42	.9126	1.3900	.3130	11.2800	.5170	3.0000	1.40
18	"	12.62 P722	18.95	2.84	.9105	1.3700	.3130	11.2800	.5110	6.0000	1.40
19	"	6 TVOPA	18.91	2.84	.9198	1.5900	.3130	11.2800	.5670	6.0000	1.40
20	"	12 TVOPA	20.93	5.67	.9253	1.8800	.3130	11.2800	.6260	12.0000	1.40
21	2C1.5-11.2	P722 No. 6	28.40	2.84	.8938	1.5900	.4100	11.2800	.5440	6.0000	1.10
22	"	P722 No. 11	19.80	2.84	.9168	1.2700	.3130	11.2800	.4900	6.0000	1.10
23	"	P722 No. 12	18.95	2.84	.9273	1.9100	.3130	11.2800	.6120	6.0000	1.40
24	2C1.5-4.0	12T	20.93	5.61	.9123	.5930	.3130	11.2800	.3540	12.0000	1.40
25	"	13.9T-2	23	6.57	.9121	1.6000	.3198	11.2800	.5680	13.9000	1.296
26	"	13.9T-3	23	6.57	.9056	1.1260	.3198	11.2800	.4700	13.9000	1.296
27	"	14T	26	6.57	.8979	.9150	.3303	11.2800	.4580	14.0000	1.076
28	"	17.2T	22.50	8.13	.9116	1.7100	.2952	11.2800	.5860	17.2000	1.270
29	2C1.5-11.2	12T	20.93	5.67	.9168	1.8530	.3130	11.2800	.6110	12.0000	1.40
30	"	13.9T-2	23	6.57	.9233	4.9800	.3198	11.2800	.9970	13.9000	1.296
31	"	13.9T-3	23	6.57	.9288	3.1100	.3198	11.2800	.8000	13.9000	1.296
32	"	14T	26	6.62	.9222	2.9440	.3303	11.2800	.7490	14.0000	1.076
33	"	17.2T	22.50	8.13	.9294	5.3300	.2952	11.2800	1.0050	17.2000	1.270
34	6C4.8-11.4	13.9T-4	23	6.57	.9206	10.5680	.3198	129.5000	1.5200	13.9000	1.296

- Large motor data for all classes of propellants.

(b) Predictions

Specific-impulse predictions were made for all of the theoretical I_{sp} calculations discussed in the previous paragraphs, based on the prediction model above and a hypothetical large motor having an exposed inert parts area (A) of 400 square inches* and a mass flow rate 400 lb/sec. For both SYFO and FEFO as well as their mixtures, the peak delivered I_{15s} predicted for each binder occurs at a high ratio of HMX/AP ($\geq$7/1), similar to the theoretical values. Figures 10 through 13 show the peak I_{15s} values along with the aluminum content, density, volume-fraction binder and oxidation-fluorination ratio $(OFR=\frac{O + .5F}{C + 1.5\ Al})$. However, the spread between SYFO and FEFO is more marked than in the theoretical I_{sp}. The active fluorine content of SYFO leads to higher efficiencies, and this, coupled with the higher theoretical I_{sp} values for SYFO-plasticized propellants, results in an even greater spread in the predicted I_{15s} (2-3 units).

At both 82 and 79% total solids the peak predicted I_{15s} occurred at the lower aluminum level (12% of the range calculated for all binders and all HMX/AP ratios. Since the two-phase-flow loss terms in the efficiency equation are dominating terms and the I_{15s} values for these

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* The A term refers to actual area of metal or graphite inerts inserts in small test motors. For large flight-weight motors the A term includes actual throat insert parts plus an equivalent metal surface area for insulated areas.

PEAK DELIVERED I_{15s} VS. % HMX IN HMX/AP
OXIDIZER 82% SOLIDS, 12% ALUMINUM (H)

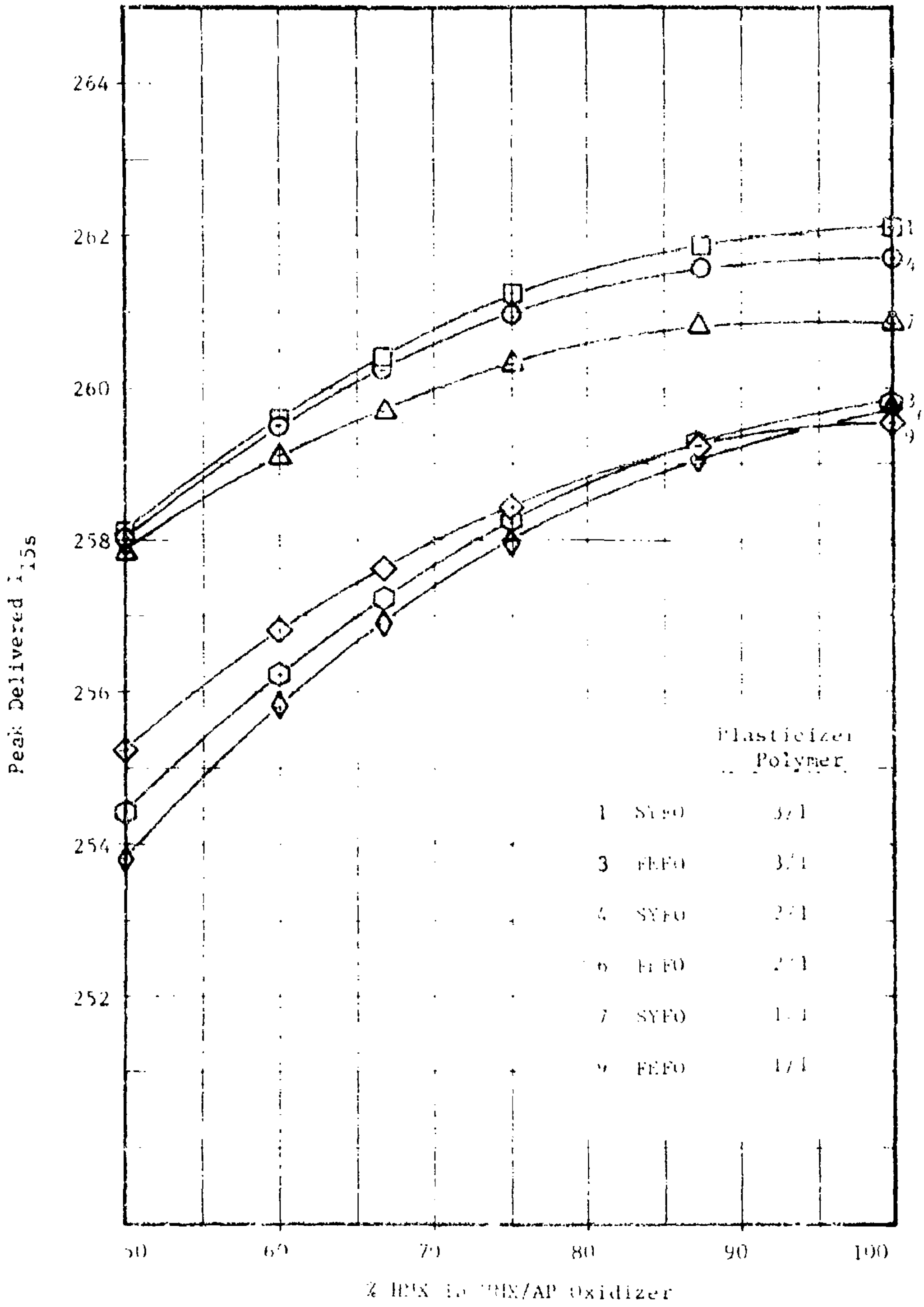

Figure 10

PEAK DELIVERED I_{15s} VS. % HMX IN HMX/AP
OXIDIZER AT 79% SOLIDS, 12% Al (U)

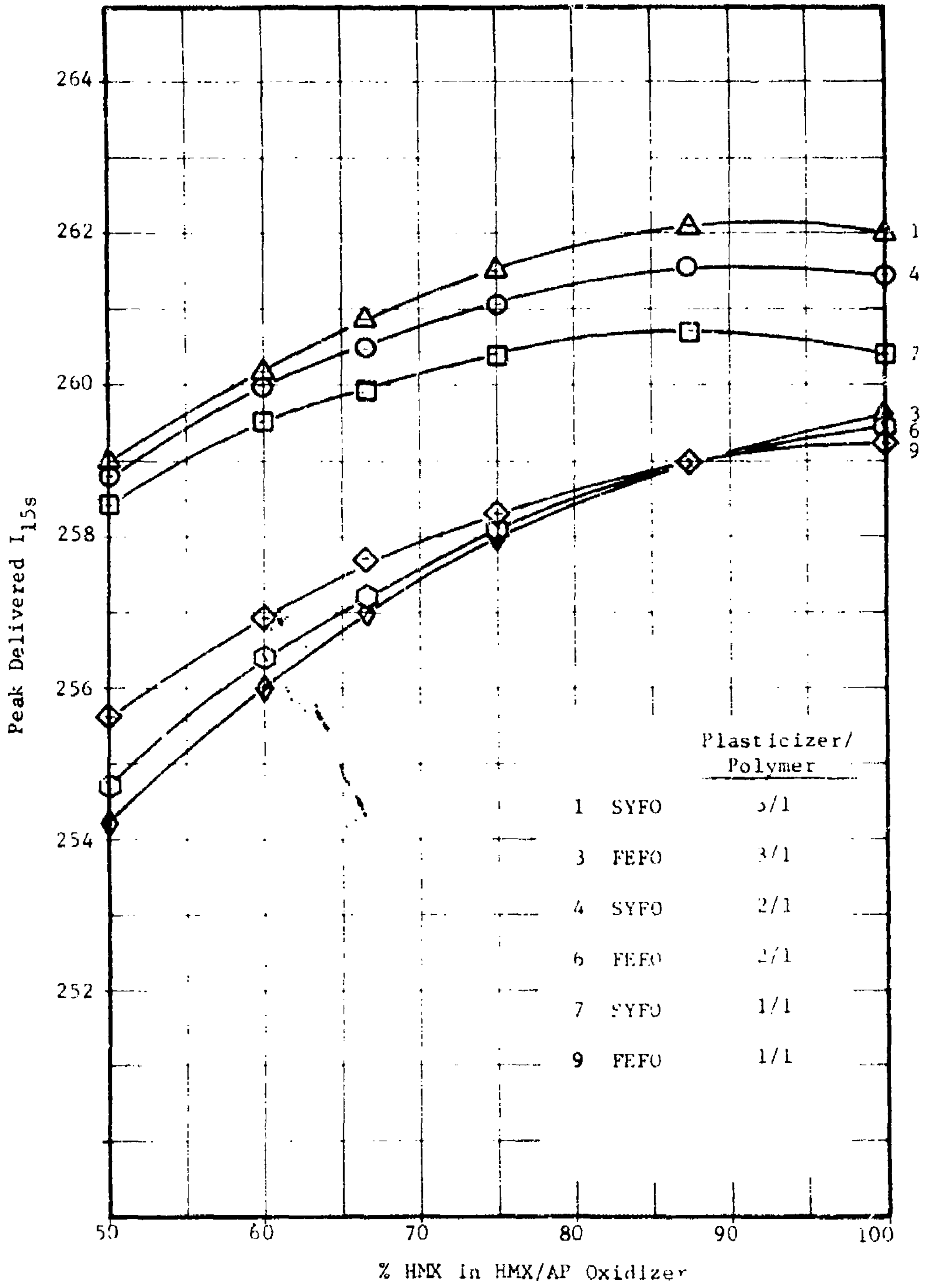

Figure 11

I_{15s}
wt.% Al
ρ g/cc
Vol.frac.binder
OFR

PEAK PREDICTED DELIVERED I_{15s} FOR PCDE PROPELLANTS WITH 82% SOLIDS (U)
(New Efficiency Equation with Fluorine Coefficient)

	HMX/AP Weight Ratio					
Plasticizer and Ratio	1/1	3/2	2/1	3/1	7/1	100/0
SYFO = 3/1	258.1 12 1.917 .216 1.688	259.6 12 1.912 .215 1.557	260.4 12 1.910 .215 1.479	261.2 12 1.906 .215 1.388	261.9 12 1.901 .214 1.267	262.1 12 1.896 .214 1.160
SYFO/FEFO = 3/3/2	256.1 12 1.912 .218 1.750	257.8 12 1.908 .217 1.615	258.7 12 1.905 .217 1.533	259.7 12 1.902 .217 1.439	260.6 12 1.896 .216 1.314	261.1 12 1.891 .216 1.204
FEFO = 3/1	253.8 12 1.907 .220 1.815	255.8 12 1.903 .219 1.674	256.9 12 1.900 .219 1.589	258.0 12 1.897 .219 1.492	259.1 12 1.892 .218 1.362	259.8 12 1.887 .217 1.247
SYFO = 2/1	258.0 12 1.913 .217 1.664	259.5 12 1.909 .217 1.536	260.2 12 1.906 .217 1.459	260.9 12 1.903 .216 1.370	261.6 12 1.897 .216 1.251	261.7 12 1.892 .215 1.146
SYFO/FEFO = 1/1/1	256.3 12 1.909 .219 1.719	257.9 12 1.905 .219 1.587	258.8 12 1.902 .218 1.507	259.6 12 1.899 .218 1.415	260.4 12 1.893 .217 1.292	260.8 1.888 .217 1.184
FEFO = 2/1	254.4 12 1.905 .221 1.775	256.2 12 1.900 .220 1.638	257.2 12 1.898 .220 1.556	258.2 12 1.894 .220 1.461	259.2 12 1.889 .219 1.334	259.7 1.884 .218 1.223
SYFO = 1/1	257.8 12 1.906 .220 1.618	259.1 12 1.902 .220 1.495	259.7 12 1.899 .219 1.421	260.3 12 1.896 .219 1.335	260.8 12 1.890 .218 1.220	260.8 12 1.885 .218 1.118
SYFO/FEFO = 1/1/2	256.5 12 1.903 .222 1.658	258.0 12 1.899 .221 1.532	258.7 12 1.896 .221 1.456	259.4 12 1.893 .220 1.368	260.1 12 1.887 .220 1.250	260.3 12 1.882 .219 1.146
FEFO = 1/1	255.2 12 1.900 .223 1.699	256.8 12 1.896 .222 1.569	257.6 12 1.893 .222 1.491	258.4 12 1.890 .222 1.461	259.2 12 1.884 .221 [illegible]	259.5 12 1.879 .220 1.174
Non Plasticized	256.7 12 1.885 .229	257.7 12 1.881 .228	258.1 12 1.878 .228	258.4 12 1.875 .228	[illegible] 12 1.870 .227	257.4 12 1.865 .226

Figure 12

PEAK PREDICTED DELIVERED I_{15s} FOR PCDE PROPELLANTS WITH 79% SOLIDS (U)
(New Efficiency Equation with Fluorine Coefficient)

I_{15s}
wt.% Al
ρ g/cc
Vol.frac.binder
OFR

	HMX/AP Weight Ratio					
Plasticizer and Ratio	1/1	3/2	2/1	3/1	7/1	100/0
SYFO = 3/1	259.0 12 1.905 .250 1.628	260.2 12 1.901 .250 1.509	260.9 12 1.898 .250 1.437	261.5 12 1.895 .249 1.354	262.1 12 1.890 .248 1.241	262.0 12 1.885 .248 1.141
SYFO/FEFO = 3/3/2	256.7 12 1.900 .253 1.698	258.2 12 1.896 .252 1.574	259.0 12 1.893 .252 1.499	259.8 12 1.890 .251 1.412	260.6 12 1.885 .251 1.295	261.0 12 1.880 .250 1.191
FEFO = 3/1	254.2 12 1.894 .255 1.771	256.0 12 1.890 .254 1.641	257.0 12 1.888 .254 1.562	258.0 12 1.885 .253 1.472	259.0 12 1.880 .253 1.350	259.[illegible] 1.875 .252 1.242
SYFO = 2/1	258.8 12 1.901 .252 1.602	260.0 12 1.897 .251 1.485	260.5 12 1.894 .251 1.415	261.1 12 1.891 .251 1.333	261.6 12 1.886 .250 1.223	261.5 12 1.881 .249 1.125
SYFO/FEFO = 1/1/1	256.8 12 1.896 .254 1.663	258.2 12 1.892 .253 1.543	259.0 12 1.890 .253 1.469	259.7 12 1.887 .253 1.385	260.4 12 1.881 .252 1.270	260.7 12 1.877 .251 1.169
FEFO = 2/1	254.7 12 1.892 .256 1.726	256.4 12 1.887 .255 1.601	257.2 12 1.885 .255 1.525	258.1 12 1.882 .255 1.437	259.0 12 1.877 .254 1.318	259.5 12 1.872 .253 1.213
SYFO = 1/1	258.4 12 1.893 .255 1.551	259.5 12 1.889 .255 1.440	259.9 12 1.886 .254 1.372	260.4 12 1.883 .254 1.294	260.7 12 1.878 .253 1.188	260.4 12 1.873 .253 1.093
SYFO/FEFO = 1/1/2	257.1 12 1.889 .257 1.596	258.3 12 1.885 .256 1.481	258.8 12 1.883 .256 1.412	259.4 12 1.880 .255 1.331	259.9 12 1.875 .255 1.222	259.9 12 1.870 .254 1.125
FEFO = 1/1	255.6 12 1.886 .258 1.641	256.9 12 1.882 .257 1.524	257.7 12 1.879 .257 1.452	258.3 12 1.876 .257 1.369	259.0 12 1.871 .256 1.257	259.2 12 1.866 .255 1.158
Non Plasticized	259.9 12 1.869 .265	257.5 12 1.865 .264	257.7 12 1.862 .264	257.8 12 1.860 .263	257.5 12 1.855 .263	256.4 10 1.839 .260

Figure 13

energetic binder system increase very slowly with aluminum content.

At the lower, practical, HMX/AP ratios (3/1 or lower) the delivered I_{15s} values for SYFO at all plasticizer levels exceeds the values for the FEFO-plasticized propellant compositions. Table 11 shows the results of an extended range of calculations (from 76 to 85 wt% total solids) made with a single oxidizer composition (3/1 HMX/AP) and the six binder compositions of primary interest (3/1, 2/1, and 1/1 plasticizer/polymer ratio with SYFO and SYFO-FEFO mixed plasticizer). In every case the predicted I_{sp} for 76% solids is equal to or greater than that for 79, 82 or 85 solids loadings. In the case of the all-SYFO-plasticized systems, the trend is quite pronounced and exactly opposite to the corresponding trend of I°_{sps} vs % solids (Figure 5), which indicates that the increase of I_{sp} efficiency with active fluorine content (from PCDE and SYFO) outweighs the effect of decreasing I°_{sps}.

In the case of the mixed SYFO-FEFO systems (with lesser amounts of active fluorine), the corresponding gain in I_{sp} efficiency with increasing binder content is in almost exact balance with decreasing I°_{sps}, resulting in virtually constant values of predicted I_{15s} over the range of solids loadings from 76 to 85 weight percent. Thus, as far as delivered I_{15s} is concerned, there is no loss indicated at the lower solids loadings. However, as described in the next section, the higher-solids formulations provide an increase in effective specific impulse due to the higher density.

TABLE II

PEAK EXPECTED I_{15s}, 12% Al, HMX/AP = 3/1 (U)

Plasticizer/Polymer	85% Solids	82% Solids	79% Solids	76% Solids
SYFO/PCDE 3/1	260.8	261.2	261.5	261.8
SYFO/PCDE 2/1	260.6	260.9	261.1	261.3
SYFO/PCDE 1/1	260.1	260.3	260.4	260.4
SYFO/FEFO/PCDE/3/3/2	259.5	259.7	259.8	259.9
SYFO/FEFO/PCDE/1/1/1	259.4	259.6	259.7	259.8
SYFO/FEFO/PCDE/1/1/2	259.3	259.4	259.4	259.3

(3) Effective Specific Impulse (Ω)

a. Theoretical

Gordon (Ref. 7) has shown that the relative effects of propellant specific impulse and density in a volume-limited vehicle may be evaluated by the equation

$$\Omega_K = I_{sp}(\rho/\rho_o)^K \qquad (1)$$

where ρ is the density of the propellant, ρ_o the density of a reference propellant, K a fraction between 0 and 1.0 calculated from the design parameters of a given vehicle, and Ω is defined as the "effective specific impulse".

The tradeoff exponent, K, was defined earlier by Geckler (Ref. 8) as minus the derivative of log I_{sp} with respect to log density at constant burnout velocity

$$K = -\left[\frac{d\ell n\ I_{sp}}{d\ell n\rho}\right]_{V_b} \qquad (2)$$

where the burnout velocity referred to here is the overall missile velocity (not the burnout-velocity increment of a single stage). Since changing the density of an upper-stage propellant affects, not only the performance of that particular stage, but also that of all lower stages, the mathematical expression for evaluation of K in the general case is rather complex and will not be covered here. For booster or single stage application, however, the expression reduces to the simple form

$$K = \frac{M_p/M_o}{\ln R} = \frac{M_p/M_o}{\ln(M_o/M_b)} \qquad (3)$$

where M_p is the propellant mass and the stage mass ratio, R, is defined as the ratio of the initial mass, M_o (or $M_p + M_b$), to the burnout mass, M_b.

To compute the gain in burnout velocity due to substitution of a propellant of specific impulse I'_{sp} and density ρ' for one of reference specific impulse I_{sp} and reference density ρ, one merely substitutes for I_{sp} in the conventional burnout velocity equation

$$\Delta V_b = I_{sp}\ g\ \ln \frac{M_p + M_b}{M_b}\ , \qquad (4)$$

the appropriate value of Ω' for the replacement propellant

$$\Delta V'_b = \Omega'\ g\ \ln \frac{M_p + M_b}{M_b}\ , \qquad (5)$$

while retaining the original mass ratio, where $\Omega' = I'_{sp}\ (\rho'/\rho_o)^K$. In even simpler terms one may write

$$\Delta V'_b = \Delta V_b\ (\Omega'/I_{sp}), \qquad (6)$$

which is exactly equivalent to the actual burnout velocity expression applied to the new propellant

$$\Delta V'_b = I'_{sp}\ g\ \ln \frac{M_p(\rho'/\rho) + M_b}{M_b} \qquad (7)$$

For a specific example, consider the case of a missile having a propellant mass of 250 lb, with $I_{sp} = 250.0$ and density - 1.80g/cc and an overall missile mass of 1000 lb. For this example M_p/M_o - 0.25, R = 1.333, K = 0.877 from Equation (3) and $\Delta V_b = (250)\ (2.174)\ (\ell n\ 1.333) = 2314$ ft/sec from Equation (4). Substitution of an equal volume of dense propellant having an I_{sp} of 248.0 and density of 1.890 yields $\Omega = 248.0\ (1.89/1.80)^{.877} = 258.84$ and $\Delta V_b = (258.84)(32.174)(\ell n(1.333)) = 2396$ ft/sec by Equation (5). For comparison, the exact calculation of ΔV_b by Equation (4) (substituting new values of I_{sp} and M_p) is $\Delta V_b = (248.0)\ (32.174)(\ell n(\frac{262.5 + 750}{750})) = 2395$ ft/sec, a difference of only 1 ft/sec.

Gordon (Ref. 7) listed the following values of K for the individual stages of an ideally staged rocket with propellant mass fractions of 0.9 in each stage and a stage ratio of 3:

First Stage	0.70
Second Stage	0.36
Third Stage	0.25
Fourth Stage	0.15

For subsequent discussions herein, this table is simplified still further by using a K value of 0.3 for upper-stage applications, as a generality.

(b) Optimization of Candidate Formulations for Upper-Stage Applications

The effective specific impulse, or $\Omega_{0.3}$, for upper stage, which includes weighing for both density and delivered specific impulse, is computed by the term $\Omega_{0.3}=I_{15s}(\rho/\rho_o)^{0.3}$. The 0.3 exponent for the density term has been found to optimize this effective specific impulse parameter at the same compositions that more detailed range calculations indicate for upper stages. These values for 79 and 82% total solids are indicated in Figures 14, 15, 16 and 17.

As was the case for the theoretical and delivered specific-impulse values, the effective, $\Omega_{0.3}$, values optimized at very high HMX/AP ratios, particularly for the FEFO-containing compositions. In addition to yielding higher specific impulse values, SYFO has a higher density than FEFO and hence the all-SYFO-plasticized systems yield higher upper-stage effective-specific-impulse values than the mixed SYFO/FEFO- or FEFO-plasticized systems. At the lower HMX/AP ratios of 3/1 the SYFO-plasticized compositions exceed the mixed-SYFO/FEFO-plasticized compositions by about 2 units. The ranking of the best candidate propellants for the SYFO and mixed-SYFO/FEFO propellants are presented in Table III. In every case, the best effective specific impulses are seen to be at high solids, high HMX/AP ratios and high plasticizer:polymer ratios, but the total variation in performance levels over a wide range of compositional variables is very small.

For the all-SYFO systems. the 20 best systems fall within the range of 7/1 to 3/2 in HMX/AP ratio, within a range of 3/1 to 1/1 in plasticizer/polymer ratio and within the range of 76 to 82% total solids. Based on $I_{15s}(\rho/1.8)^{0.3}$ as a figure of merit for performance, the maximum deviation in performance within this range of compositions is only 3.0 units.

PEAK EFFECTIVE I_{15s} (Ω=0.3) FOR UPPER STAGE VS.
% HMX IN HMX/AP OXIDIZER AT 82% SOLIDS (U)

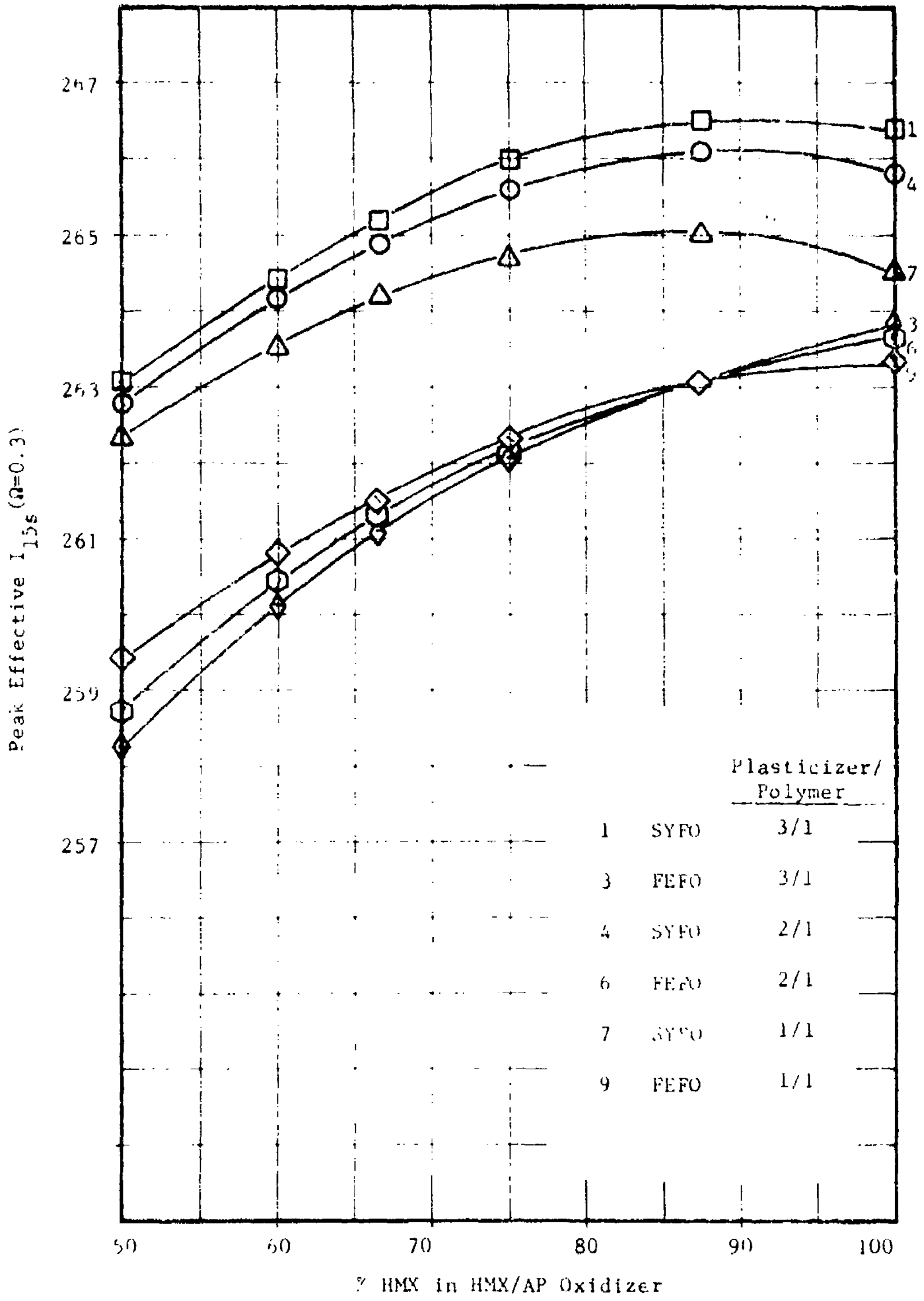

Figure 14

PEAK EFFECTIVE I_{15s} (Ω=0.3) FOR UPPER STAGE VS.
% HMX IN HMX/AP OXIDIZER AT 79% SOLIDS (U)

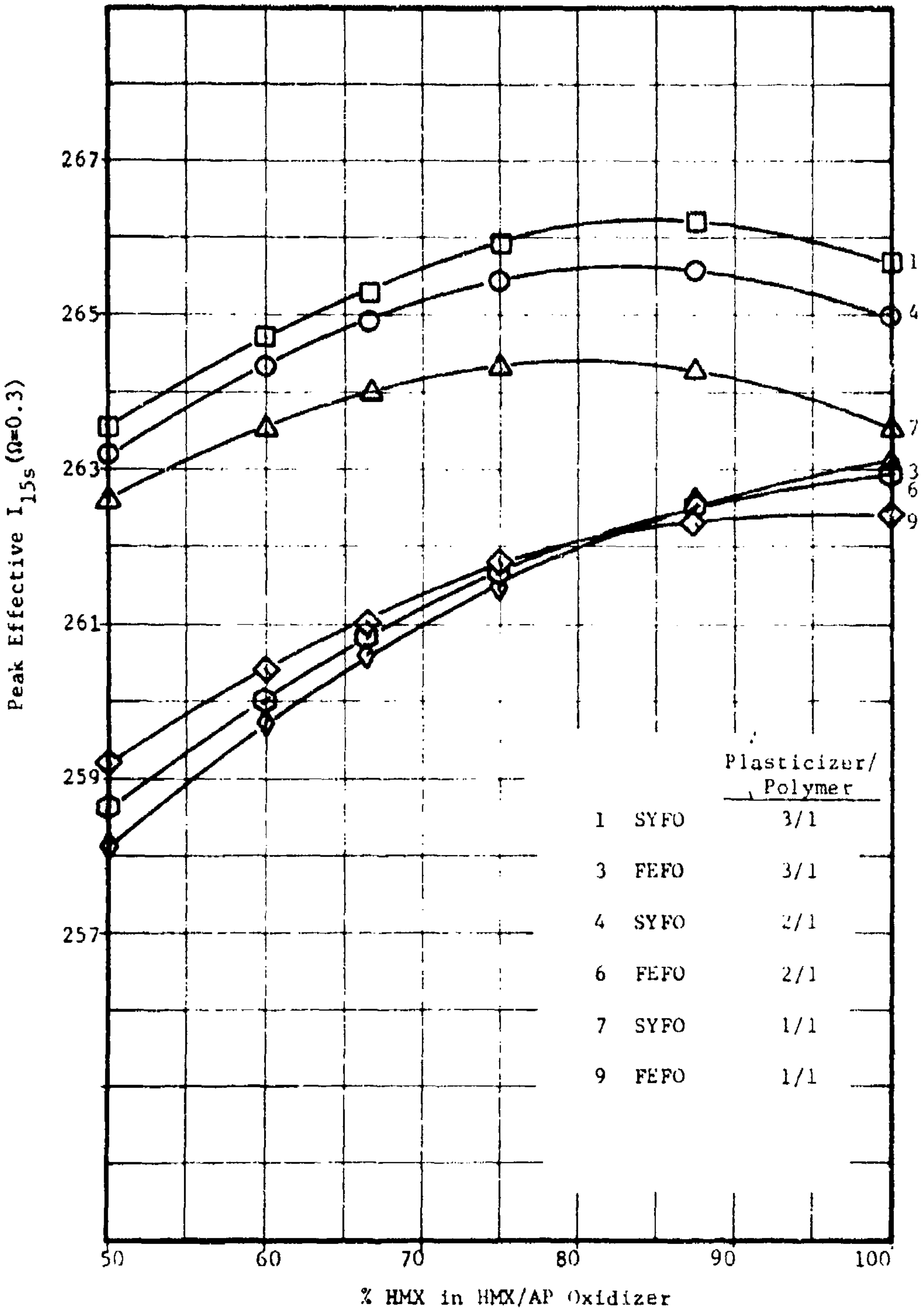

Figure 15

I_{SP} $_{0.3}$ FOR UPPER-STAGE PCDE PROPELLANTS WITH 82% SOLIDS (U)
(New Efficiency Equation with Fluorine Coefficient)

I_{SP} 0.3
wt. % Al
ρ g/cc
Vol. fr. binder
OFF

HMX/AP Weight Ratio

Plasticizer and Ratio	1/1	3/2	2/1	3/1	7/1	100/0
SYFO = 3/1	263.1 14 1.928 .217 1.547	264.4 16 1.935 .218 1.326	265.2 16 1.932 .218 1.266	266.0 14 1.918 .216 1.288	266.5 14 1.912 .215 1.181	266.4 14 1.90[illegible] .215 1.087
SYFO/FEFO = 3/3/2	260.8 12 1.912 .218 1.750	262.3 14 1.919 .219 1.488	263.2 14 1.916 .218 1.417	264.0 16 1.924 .220 1.242	265.0 14 1.906 .217 1.226	265.3 14 1.897 .217 1.128
FEFO = 3/1	258.2 12 1.907 .220 1.815	260.1 12 1.903 .219 1.674	261.1 12 1.900 .219 1.589	262.1 12 1.897 .219 1.492	263.1 16 1.914 .221 1.167	[illegible] 16 [illegible] .220 [illegible]
SYFO = 2/1	262.8 16 1.936 .220 1.403	264.2 16 1.931 .219 1.308	264.9 14 1.917 .218 1.349	265.6 14 1.914 .217 1.272	266.1 14 1.909 .217 1.167	265.8 14 1.904 .216 1.074
SYFO/FEFO = 1/1/1	260.8 12 1.909 .219 1.719	262.3 14 1.916 .220 1.463	263.1 14 1.913 .220 1.393	263.9 16 1.921 .221 1.222	264.7 14 1.905 .219 1.206	264.[illegible] 14 1.900 .218 1.109
FEFO = 2/1	258.7 12 1.905 .221 1.775	260.4 12 1.900 .220 1.638	261.3 12 1.898 .220 1.556	262.2 12 1.894 .220 1.461	263.1 16 1.912 .222 1.163	[illegible] 16 1.907 .221 1.075
SYFO = 1/1	262.3 16 1.928 .223 1.367	263.5 16 1.924 .222 1.275	264.2 14 1.910 .221 1.314	264.7 16 1.918 .222 1.153	265.0 14 1.902 .220 1.138	264.5 12 1.88[illegible] .215 1.118
SYFO/FEFO = 1/1/2	260.8 14 1.914 .223 1.522	262.2 14 1.910 .222 1.413	262.8 16 1.918 .223 1.249	263.6 14 1.904 .222 1.270	264.2 14 1.889 .221 1.166	264.0 14 1.894 .220 1.140
FEFO = 1/1	259.3 12 1.900 .223 1.699	260.8 12 1.896 .222 1.569	261.5 14 1.904 .223 1.380	262.3 16 1.912 .224 1.211	263.1 16 1.907 .224 1.117	263.3 14 1.891 .222 1.101
Non Plasticized	260.5 16 1.907 .231	261.4 14 1.892 .230	261.8 14 1.889 .229	261.9 14 1.886 .229	261.4 14 1.881 .228	260.[illegible] 12 1.865 .226

Figure 16

$\Omega_K = 0.3$
wt.% Al
ρ g/cc
Vol.frac.binder
OFR

PEAK $\Omega_{0.3}$ FOR UPPER-STAGE PCDE PROPELLANTS WITH 79% SOLIDS (U)
(New Efficiency Equation With Fluorine Coefficient)

	HMX/AP Weight Ratio					
Plasticizer and Ratio	1/1	3/2	2/1	3/1	7/1	100/0
SYFO = 3/1	263.5 16 1.927 .253 1.375	264.7 16 1.923 .253 1.287	265.3 14 1.910 .251 1.329	265.9 14 1.907 .251 1.257	266.2 14 1.901 .250 1.158	265.7 14 1.897 .249 1.070
SYFO/FEFO = 3/3/2	260.9 12 1.900 .253 1.698	262.2 16 1.918 .255 1.343	263.0 16 1.915 .255 1.286	263.8 16 1.912 .254 1.220	264.6 14 1.896 .252 1.209	264.7 14 1.891 .251 1.117
FEFO = 3/1	258.1 12 1.894 .255 1.771	259.7 12 1.890 .254 1.641	260.6 12 1.888 .254 1.562	261.5 12 1.885 .253 1.472	262.5 16 1.902 .256 1.178	263.1 16 1.897 .255 1.093
SYFO = 2/1	263.2 16 1.923 .255 1.354	264.3 16 1.919 .254 1.268	264.9 16 1.917 .254 1.214	265.4 14 1.902 .252 1.238	265.6 14 1.897 .252 1.141	265.0 12 1.881 .249 1.125
SYFO/FEFO = 1/1/1	260.9 12 1.896 .254 1.663	262.2 16 1.914 .256 1.317	262.9 16 1.912 .256 1.261	263.3 16 1.909 .256 1.197	264.2 14 1.893 .253 1.186	264.2 14 1.888 .253 1.096
FEFO = 2/1	258.6 12 1.892 .256 1.726	260.0 12 1.887 .255 1.601	260.8 12 1.885 .255 1.525	261.7 14 1.893 .256 1.335	262.5 16 1.899 .257 1.151	263.0 14 1.883 .255 1.138
SYFO = 1/1	262.6 16 1.915 .258 1.551	263.5 16 1.911 .258 1.230	264.0 14 1.897 .256 1.271	264.3 14 1.894 .255 1.202	264.3 14 1.889 .255 1.109	263.5 12 1.873 .253 1.093
SYFO/FEFO = 1/1/2	260.9 14 1.900 .258 1.596	262.0 16 1.907 .259 1.266	262.6 16 1.905 .259 1.213	263.1 16 1.901 .258 1.152	263.4 14 1.886 .256 1.141	262.9 14 1.881 .256 1.055
FEFO = 1/1	259.2 12 1.886 .258 1.641	260.4 16 1.903 .260 1.303	261.0 16 1.901 .260 1.248	261.8 14 1.887 .258 1.273	262.3 16 1.893 .259 1.098	262.4 14 1.877 .257 1.086
Non Plasticized	260.1 16 1.890 .268	260.6 14 1.876 .266	260.7 14 1.873 .265	260.6 14 1.876 .265	259.8 12 1.855 .263	258.0 10 1.893 .260

Figure 17

TABLE III

THERMODYNAMIC RANKING OF CANDIDATE FORMULATIONS FOR UPPER STAGE APPLICATION BASED ON [illegible]

BEST SYFO FORMULATIONS

Rank	$I_{15s}(\rho/1.8)^{0.3}$	HMX/AP	Plasticizer/ Polymer	% Solids	% Al	OFR	Binder Vol %	Polymer Vol %
1	266.5	7/1	3	82	14	1.181	21.5	5.80
2	266.2	7/1	3	79	14	1.158	25.0	6.73
3	266.1	7/1	2	82	14	1.167	21.7	7.72
4	266.0	5/1	3	82	14	1.288	21.6	5.82
5	265.9	3/1	3	79	14	1.257	25.1	6.75
6	265.7	3/1	3	76	14	1.227	28.5	7.67
7	265.6	3/1	2	82	14	1.272	21.7	7.74
8	265.6	7/1	2	79	14	1.141	25.2	8.95
9	265.4	3/1	2	79	14	1.238	25.2	9.00
10	265.0	7/1	1	82	14	1.138	22.0	11.54
11	265.0	3/1	2	76	14	1.206	28.6	10.2
12	264.9	2/1	2	79	16	1.214	25.4	9.05
13	264.9	2/1	2	82	14	1.349	2.18	7.76
14	264.7	3/1	1	82	16	1.153	22.2	11.64
15	264.3		2	79	16	1.268	25.4	9.05
16	264.3		2	79	14	1.141	25.5	8.95
17	264.3		2	79	14	.236	25.5	9.00
18	264.2		1	82	14	1.314	22.2	11.59
19	263.8	1/1	2	76	14	1.166	29.0	15.2
20	263.5	3/2	1	82	16	1.275	22.2	11.6

TABLE III (Cont.)

THERMODYNAMIC RANKING OF CANDIDATE FORMULATIONS FOR UPPER STAGE APPLICATION BASED ON $I_{15}(\rho/1.8)^{0.3}$ (U)

II. BEST MIXED SYFO/FEFO = 1:1 ST. CANDIDATES

Rank	$I_{15s}(\rho/1.8)^{0.3}$	HMX/AP	Plasticizer/ Polymer	% Solids	% Al	OFR	Binder Vol %	Polymer Vol %
1	265.3	100/0	3	82	14	1.097	22.0	5.77
2	265.0	7/1	3	82	14	1.226	21.7	5.74
3	264.9	100/0	2	82	14	1.109	21.8	7.69
4	264.7	7/1	2	82	14	1.206	21.9	7.71
5	264.7	100/0	3	79	14	1.137	25.1	6.69
6	264.6	7/1	3	79	14	1.209	25.2	6.71
7	264.2	7/1	1	82	14	1.166	22.1	11.46
8	264.2	7/1	2	79	14	1.186	25.3	8.94
9	264.0	3/1	3	82	16	1.242	21.9	5.33
10	263.9	3/1	2	82	16	1.222	22.1	7.71
11	263.8	3/1	3	79	16	1.220	25.4	6.77
12	263.6	3/1	1	82	14	1.270	22.7	11.55
13	263.5	3/1	3	76	16	1.199	28.9	7.69
14	263.4	3/1	2	76	14	1.260	28.9	10.2
15	263.4	7/1	1	79	14	1.141	25.6	13.35
16	263.3	3/1	2	79	16	1.197	25.6	8.98
17	263.1	3/1	1	79	16	1.152	25.8	13.47
18	263.1	2/1	2	82	14	1.393	22.0	7.74
19	262.9	2/1	2	79	16	1.261	25.6	9.02
20	262.8	2/1	1	82	16	1.249	22.3	11.64
21	262.6	3/1	1	76	14	1.205	29.1	15.2
22	262.6	2/1	1	79	16	1.213	25.9	13.49
23	262.3	3/2	2	82	14	1.463	22.0	7.74
24	262.2	3/2	1	82	14	1.413	22.2	11.6

The optimum performance in 16 of the 20 cases occurred at 14 weight percent aluminum, with the remaining 4 optimized at 16% Al.

For the mixed SYFO-FEFO plasticizer systems, 24 individual systems yielded optimum performance values based on $I_{15s}(\rho/1.8)^{.3}$ within a total range of 3.1 units. Three of the five best systems in this comparison are based on 100% HMX oxidizer, which is indicative of the higher oxygen content of the FEFO plasticizer. The higher oxygen content of these systems also shifts the optimum aluminum content to slightly higher values (9 of the 24 systems showed optimum performance values based on $I_{15s}(\rho/1.8)^{.3}$ within a total range of 3.1 units. Three of the five best systems in this comparison are based on 100% HMX oxidizer, which is indicative of the higher oxygen content of the FEFO plasticizer. The higher oxygen content of these systems also shifts the optimum aluminum content to slightly higher values (9 of the 24 systems showed optimum performance at 16% Al, while the remaining 15 optimized at 14% Al).

The data in this table illustrate the wide range of formulation variables which are available without significant variation in performance potential.

The variation of predicted performance with changes in aluminum content and OFR is considered in more detail in the following section.

(4) Effect of Aluminum Concentration and OFR

The possible use of formulations

containing 20% or more aluminum was considered, but in every case evaluated, the optimum performance level (in terms of I°_{sps}, I_{15s}, or $I_{15s}(\rho/1.8)^{.3}$) occurs at an aluminum concentration of less than 20%. For the highest performance systems, containing all-SYFO plasticizer and 7/1 or 3/1 HMX/AP oxidizer, optimum values of $I_{15s}(\rho/1.8)^{.3}$ occur at 14 to 16% aluminum and corresponding OFR values in the range of 1.288 to 1.309 (see Figures 16 and 17). For many of these same systems the OFR may drop to values less than 1.0 for formulations containing 20% or more aluminum at solids loadings of 79 to 82% (see Figure 9 for systems based on 2/1 SYFO/PCDE binder).

This effect is in direct contrast to systems based on an all-AP-oxidizer system, for which an OFR value of 1.0 corresponds to an aluminum concentration of about 30%, as also shown in Figure 9. With such systems, we would expect optimum performance to occur at aluminum concentrations of 20% or higher, particularly if the propellant is intended for use as a booster propellant or single propellant of a tactical rocket system. An example of such a system is one based on a binder of PCDE polymer/BDNPF (2:1) with aluminum and AP oxidizer, which, at a solids loading of 79% peaks at an optimum aluminum concentration of 24 to 26%, based on the same efficiency equation used here and the effective I_{sp} parameter $I_{15s}(\rho/1.8)^{0.7}$ as a figure of merit.

For the propellant of interest here, however, the optimum performance level occurs at an aluminum content of 14%, as illustrated in Figure 18 for the system consisting of 3/1 SYFO/PCDE binder, aluminum and 3/1 HMX/AF oxidizer at 79% total solids. The uppermost curve shows theoretical I_{sp} vs. % aluminum with the peak occurring at 14% aluminum, while the lowermost curve shows that the peak value of predicted I_{sp} occurs at 10 to 12% aluminum. The two intermediate curves show $I_{15s}(\rho/1.8)^{.3}$, with a peak value indicated at 14% aluminum, and $I_{15s}(\rho/1.8)^{.7}$, with a corresponding peak at 16 to 18% aluminum. Of particular interest in this highly energetic propellant system are the extremely high values of theoretical and predicted I_{sp} (as well as density) corresponding to the 0% aluminum formulation. The gain in predicted I_{sp} from 0 aluminum to the maximum value is only 2.3 units while the corresponding gain in terms of $I_{15s}(\rho/1.8)^{.3}$ is only 5.3 units.

Additional details of the calculations for this and one other system are shown in Table IV, providing additional clues to the less-than-normal increase in performance with aluminum content. Flame temperatures for these systems are very high even at zero percent aluminum, while the corresponding increase in flame temperature with aluminum is much less than with conventional systems. This is because the base system, consisting of an energetic binder and 75% HMX in the oxidizer, already provides a very high flame temperature with little need for further increases from aluminum metal fuel. Flame temperature increases very little beyond 14% aluminum because the additional aluminum goes largely to

THEORETICAL, DELIVERED, EFFECTIVE FOR UPPER AND BOOSTER STAGE SPECIFIC IMPULSES VS. WEIGHT PERCENT ALUMINUM (U)
SYFO/PCDE POL. = 3:1 AT 79% SOLIDS, HMX/AP = 3.1

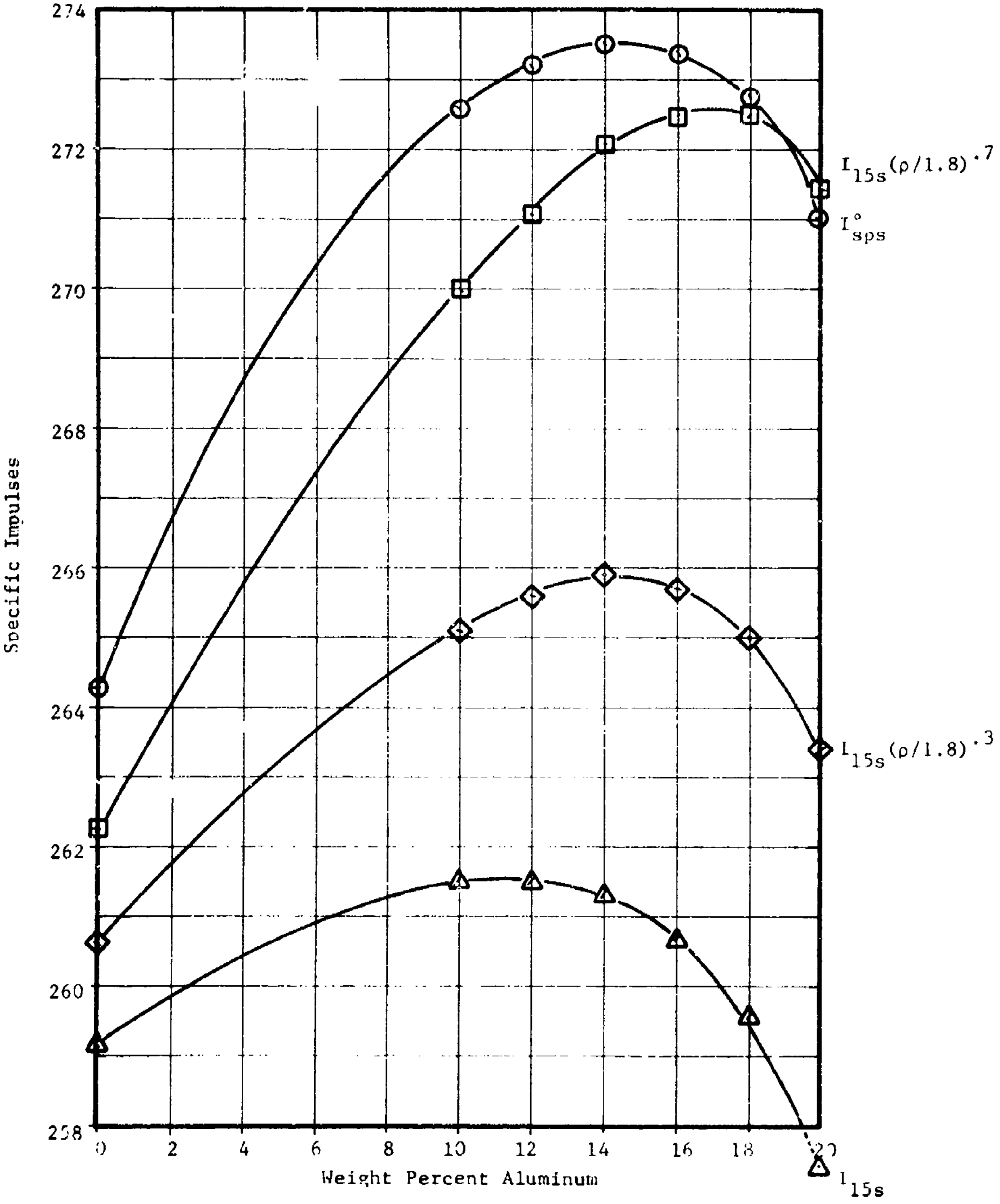

Figure 18

TABLE IV

FLAME TEMPERATURE, SPECIFIC IMPULSE, OFR, AND EFFICIENCY AS A FUNCTION OF ALUMINUM CONTENT (U)

I. SYFO/PCDE POL = 1:1, HMX/AP = 3:1, 79% Solids

Aluminum →	0.0	10	12	14	16	18	20
T_c °K	3290	3607	3658	3698	3727	3745	3745
I°_{sps}	262.4	271.6	272.4	272.6	272.1	270.9	268.7
I_{15s}	257.4	260.3	260.4	260.3	259.6	258.0	255.6
$\Omega_{0.3}$	258.2	263.3	264.0	264.3	264.1	263.0	261.0
Efficiency	.9809	.9584	.9559	.9549	.9541	.9524	.9512
OFR	2.117	1.395	1.294	1.202	1.119	1.043	0.973

II. SYFO/PCDE POL = 3:1, HMX/AP = 3:1, 79% Solids

Aluminum →	0.0	10	12	14	16	18	20
T_c °K	3319	3641	3695	3741	3776	3802	3813
I°_{sps}	264.3	272.6	273.2	273.5	273.4	272.8	271.0
I_{15s}	259.2	261.5	261.5	261.3	260.7	259.6	257.5
$\Omega_{0.3}$	260.6	265.1	265.6	265.9	265.7	265.0	263.4
Efficiency	.9807	.9593	.9572	.9554	.9535	.9516	.9502
OFR	2.279	1.461	1.354	1.257	1.169	1.089	1.016

underoxidized vapor phase species such as Al(g), aluminum suboxides and subhalides such as AlO, AlCl and AlF, with very little increase in condensed phase Al_2O_3. Since the prediction equation is based on condensed phase Al_2O_3 rather than total aluminum content, this effect is correspondingly reflected in the very slight reduction in predicted efficiency with increased aluminum above 14%. Thus, the variation is predicted I_{sp} is very flat over a wide range of compositions, and the variation between optimum and near-optimum aluminum levels amounts to only tenths of I_{sp} units.

(5) Range Calculations

A series of preliminary range calculations were made for 2% steps of aluminum content at 79% total solids in the system consisting of 2/1 SYFO/PCDE binder, 3/1 HMX/AP oxidizer and aluminum metal. The program used was the Spherical Earth Trajectory Program AIDE (Aerojet Program SJ-001) based on a three-stage missile with a nominal range of 4500 miles and containing propellant ANB-3066 in the third stage. The five SYFO propellants were then substituted for the reference third-stage propellant on the basis of equal propellant volume while maintaining equal values of chamber pressure, throat diameter, expansion ratio and inert weights. The results of these calculations are summarized below and indicate an exact correspondence between formulations yielding maximum values of range and maximum values of $I_{15s}(\rho/1.8)^{0.3}$.

(C) Propellant	% Al	I_{15s}	ρ lb/in.^{3}	Range (Miles)	$I_{15s}(\rho/.065)^{0.3}$
Reference	15	248.7	.06402	4500.1	247.5
SYFO/PCDE	10	261.1	.06792	5099.8	264.6
SYFO/PCDE	12	261.1	.06832	5113.0	265.0
SYFO/PCDE	14	261.0	.06871	$\boxed{5121.8}$	$\boxed{265.4}$
SYFO/PCDE	16	260.4	.06915	5108.0	265.2
SYFO/PCDE	18	259.1	.06955	5061.6	264.9

c. Recommended Composition Range (U)

(U) In line with the physical constraints discussed earlier, the compositional constraints for propellants for initial experimental evaluation are:

- Minimum polymer content of 6 wt%, or approximately 8 volume %
- Plasticizer:polymer ratio in the range of 3:1 to 1:1
- Total solids loadings in the range of 76 to 82 weight percent
- HMX/AP ratios in the range of 7:1 to 2:1
- Aluminum content for each system based on the maximum value of $\Omega_{0.3}$.

Table V lists predicted performance in terms of $\Omega_{0.3}$ for eight possible variations of composition within this range for each of the systems based on SYFO plasticizer and SYFO/FEFO mixed plasticizer.

(U) The eight composition options and possible reasons for final choice of each composition are shown below:

TABLE V

RECOMMENDED FORMULATION RANGE (U)

Option	Performance	Composition			Volume Percent	
	$\Omega_{.3}$	HMX/AP	Plast./Polymer	% Solids	Binder	Polymer
	SYFO Systems					
I	265.4	3/1	2/1	79	25.2	9.00
II	266.1	7/1	2/1	82	21.7	7.72
III	265.7	3/1	3/1	76	28.5	7.67
IV	265.6	3/1	2/1	82	21.7	7.74
V	265.6	7/1	2/1	79	25.2	8.95
VI	264.7	3/1	1/1	82	22.2	11.64
VII	265.0	3/1	2/1	76	28.6	10.20
VIII	264.9	2/1	2/1	79	25.4	9.05
	SYFO/FEFO SYSTEMS					
I	263.3	3/1	2/1	79	25.6	8.98
II	264.7	7/1	2/1	82	21.9	7.71
III	263.5	3/1	3/1	76	28.9	7.69
IV	263.9	3/1	2.1	82	22.1	7.71
V	264.2	7/1	2/1	79	25.3	8.94
VI	263.6	3/1	1/1	82	22.7	11.55
VII	263.4	3/1	2/1	76	28.9	10.20
VIII	262.9	2/1	2/1	79	25.6	9.02

Option I - This composition of 79% total solids, 2/1 plasticizer to polymer ratio, 3/1 HMX/AP ratio and 9 volume percent polymer represents what may be the best compromise of good processability, final mechanical properties, burning rate and pressure exponent. Performance level in terms of $\Omega_{0.3}$ is only 1.1 units below the maximum for the all-SYFO systems and 2.0 units below the maximum for the mixed plasticizer systems.

Option II - represents the highest performance of all the systems meeting the minimum guidelines noted above, as well as lower cost than Option I, but at a sacrifice of lower volume fraction binder and polymer and higher HMX/AP ratio. Performance is only 0.4 units below the maximum for the all-SYFO systems.

Option III - represents what may be the best from point of view of processing, with highest volume fraction binder and highest plasticizer/polymer ratio, and performance level 0.2 to 0.3 units better than Option I. Disadvantages include the minimum range of acceptable volume fraction polymer and highest SYFO content and material cost.

Option IV - represents a combination of higher total solids with the same plasticizer:polymer ratio and HMX/AP ratio as Option I, with slightly higher performance, lower volume fraction polymer and lower material cost.

Option V - represents a slightly higher performance level in the SYFO systems due to higher HMX/AP ratio with no other changes. In the mixed plasticizer systems the performance gain is 0.9 units. In either system this would be a good formulation if burning rate exponent fell in the acceptable range.

Option VI - is based on a higher total solids loading and lower plasticizer:polymer ratio than Option I, and is 0.7 units lower in performance for the SYFO system (0.3 units higher in the mixed plasticizer system). Although processing might present a problem with this formulation, final mechanical properties should be the best of the seven options because of highest volume fraction polymer.

Option VII - represents what may be the best combination of processing ease and final mechanical properties, based on the highest volume fraction binder and second highest volume fraction polymer. Performance is close to that of Option I, but SYFO content and material cost would be second highest among the 8 variations.

Option VIII - is based on a reduction of HMX/AP ratio compared with Option I with no other changes. Resulting performance loss is 0.5 units in the case of all SYFO systems and 0.4 units for the mixed plasticizer systems, with possible benefits of improved burning rate exponent.

The recommended range of formulations for both SYFO and mixed SYFO/FEFO formulations, therefore, is from 76 to 82% total solids, from 3/1 to 1/1 plasticizer/polymer ratio, and from 7/1 to 2/1 HMX/AP ratio. The recommended aluminum level for all systems of interest is 14 to 16 weight percent.

In order to confirm the choice of optimum compositions based on the impulse prediction model it is recommended that during the early part of the program three series of one-lb motor firings (2C-1.5-11.2 motors)

3. Modification of Baseline Formulation (U)

a. General (U)

(U) The conclusions given in Section III.A.2 were refined and extended with the aid of additional calculations using an actual PCDE binder composition. A PCDE/FEFO/Al/AP/HMX propellant composition which has actually been prepared was taken as a baseline against which to judge the effects of changes in composition. The binder and baseline propellant compositions are given in Table VI, together with some calculated properties.

(C) The thermodynamic properties of FEFO, SYFO and PCDE prepolymer are compared in Table VII. The oxygen balances as measured by the OMOX or OR ratios are in the order PCDE prepolymer < SYFO < FEFO. The oxygen balance of the binder is an important indicator as to whether simultaneous optimization at high HMX/AP ratios and high aluminum content is feasible. SYFO has a higher density and a more endothermic heat of formation per unit weight than FEFO. In addition, the higher fluorine content of SYFO relative to FEFO aids in obtaining lower two-phase flow losses via formation of volatile aluminum fluorides and may contribute to good metal combustion efficiency. Hence, in general, when SYFO is substituted for FEFO there is an increase in both delivered specific impulse and density, provided the oxygen balance is reasonably high. The lower oxygen balance of SYFO relative to FEFO, however, limits the gains expected from SYFO unless high plasticizer-to-polymer ratios or high solids loadings are employed resulting in optimization at high HMX/AP ratios (3:1 or greater).

TABLE VI

COMPOSITION AND PROPERTIES OF BASELINE PROPELLANT (U)

Composition

Ingredient	Weight %
Aluminum	16.0000
NH_4ClO_4	15.5000
HMX	46.5000
PCDE prepolymer	10.4553
FEFO	10.4553
HT	0.1209
TDI	0.8185
Neozone D	0.1000
FeAA	0.0500

HMX/AP	3:1 wt ratio
Plasticizer	47.52 wt% of binder
Total solids	78 wt%

Properties

T_c, °K	3789
T_e, °K	2319
I°_{sps}, lbf-sec/lbm	271.5
I_{15s}, lbf-sec/lbm	260.2*
OFR	1.1653
ρ, gm/cc	1.8928
ρ, lb/in.^{3}	0.0684

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* Based on ASPC efficiency equation for high mass flow motor with $\dot{m}$ = 400 lb/sec, given in the Appendix.

TABLE VII

CALCULATED THERMODYNAMIC COMPARISON OF PLASTICIZERS AND PCDE PREPOLYMER (U)

Compound	ΔH_f Kcal/100gm	ρ gm/cc	C	H	O	N	F	OMOX	OR
			gm-atoms/100 grams						
FEFO	-55.5	1.59	1.5618	1.8742	3.1236	1.2494	0.6247	2.2000	0.8461
SYFO	-44.13	1.64	1.8083	2.3015	1.6440	1.3152	1.6440	1.3637	0.5173
PCDE Prepolymer	-19.82	1.52	2.4986	1.6657	0.8328	1.6657	1.6657	0.6666	0.2857

b. Delivered Specific Impulse and Density (U)

(C) The objective of these calculations was to maximize delivered specific impulse and density up to the limits imposed by processing, mechanical properties, burning rate and pressure exponent, hazard rating, cost, etc. In this evaluation, only small excursions from the baseline variables (78% total solids, plasticizer = 47.52% of binder, HMX/AP = 3:1 weight and 16% aluminum) were checked for trend. Figures 19, 20, and 21 show the increases in delivered specific impulse to be expected from various single changes in the baseline propellant plasticized with FEFO alone, a 1:1 SYFO/FEFO mixture (by weight), and SYFO alone. A comparison of the three central formulations indicates a small increase of only 0.6 I_{sp} units between FEFO and SYFO and an increase in density, as expected.

(U) The variables which augment the specific impulse of the central formulations are different in effect for the two plasticizers and are partly functions of the oxygen balance of the plasticizers, as mentioned previously.

(C) In Figure 19, the best single change from the FEFO baseline is seen to be an increase in solids from 78 to 80%. This results in small increases of both delivered specific impulse (0.3 units) and density, but has to be weighed against losses in mechanical-property or processing potential. An increase in the HMX/AP ratio from 3/1 to 7/1 also increases specific impulse (0.3 units) but at the sacrifice of density. In addition, any increase in HMX

FEFO-PLASTICIZED PCDE PROPELLANTS (U)

Effect of Various Single Changes in Baseline Formulation on Predicted I_{15s} and Density

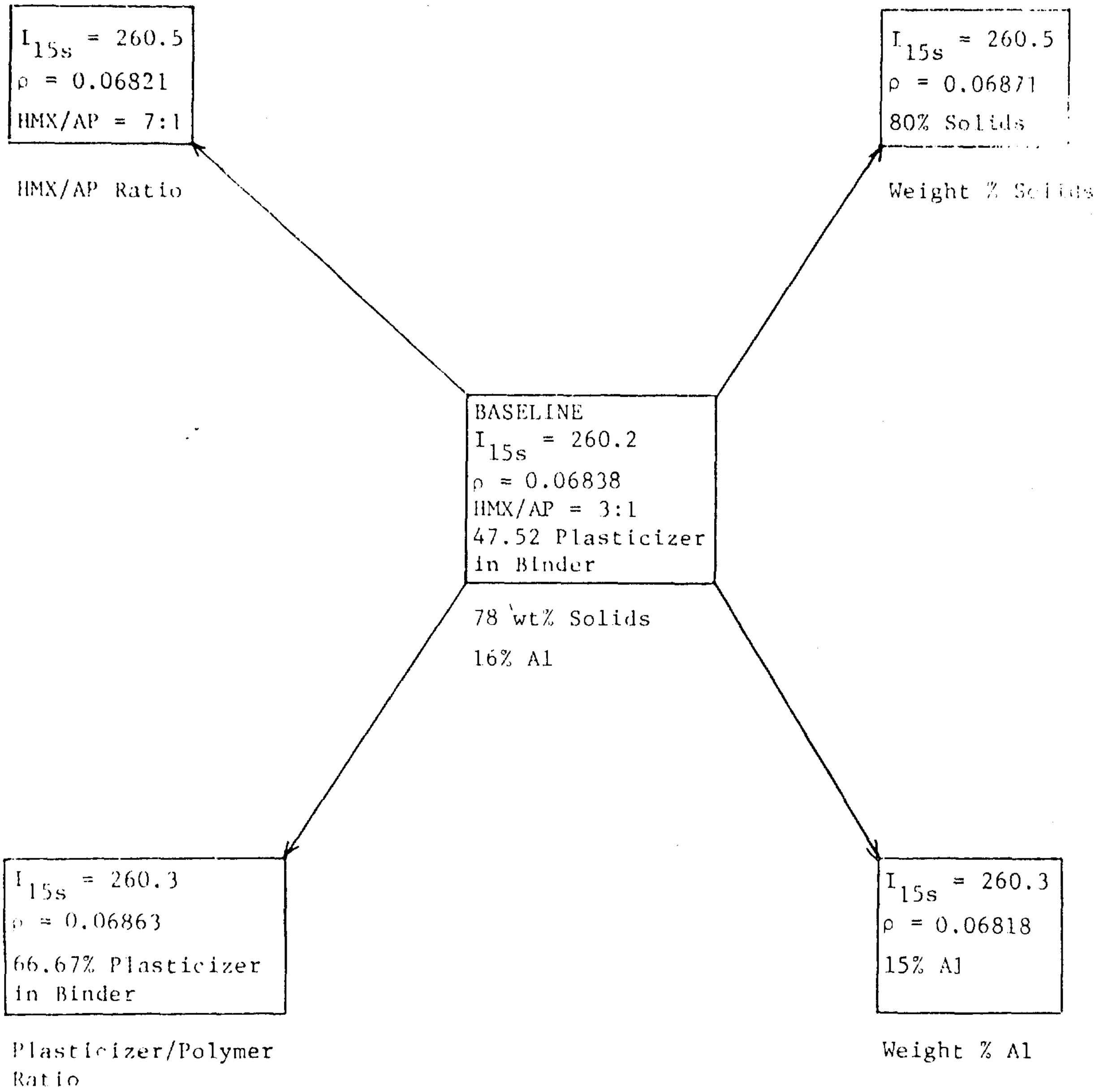


Figure 19

SYFO/FEFO (1/1) PLASTICIZED PCDE PROPELLANTS (U)

Effect of Various Single Changes in Baseline Formulation on Predicted I_{15s} and Density

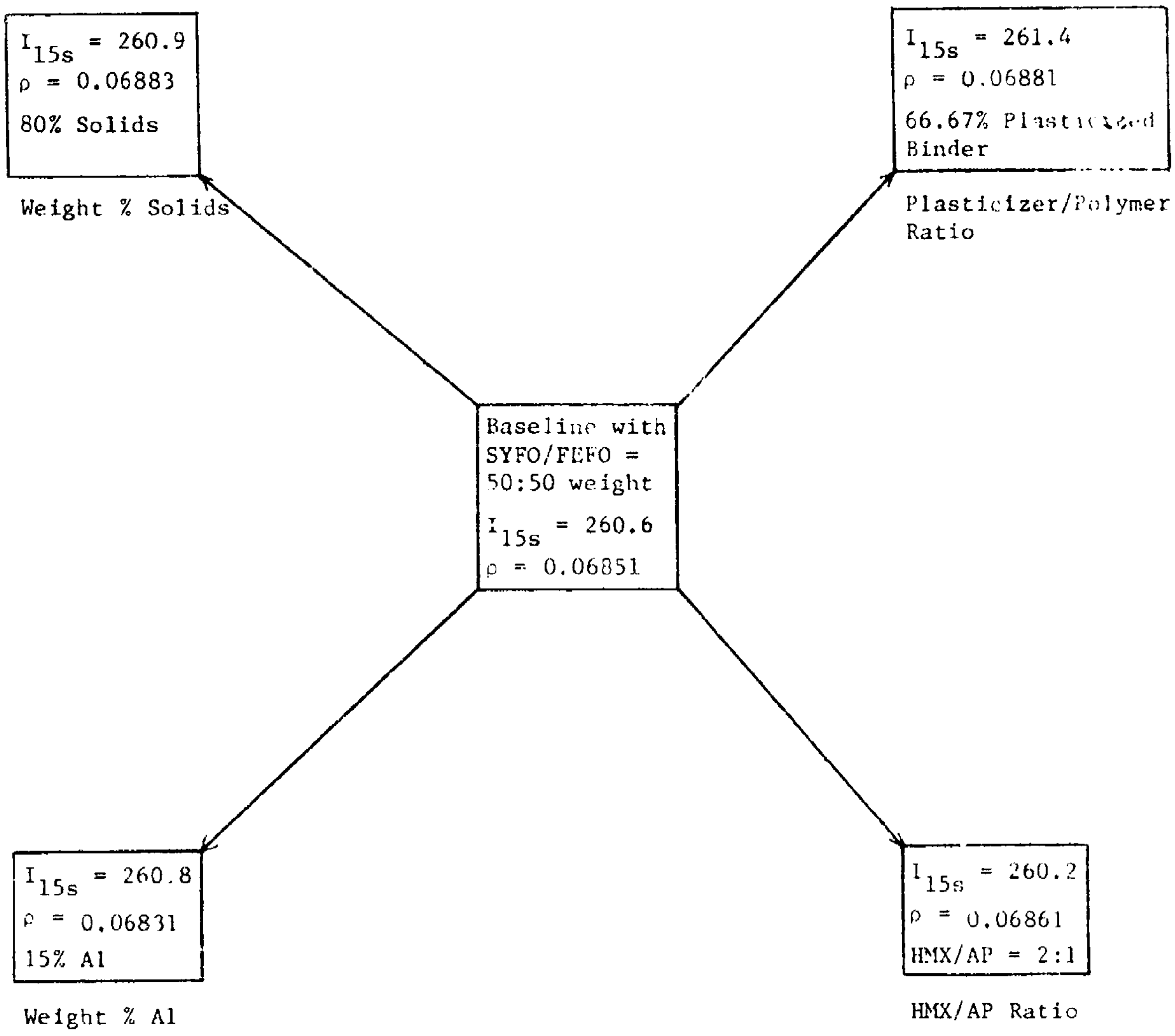


Figure 20

SYFO-PLASTICIZED PCDE PROPELLANTS (U)
Effect of Various Single Changes in Baseline Formulation on Predicted I_{15s} and Density

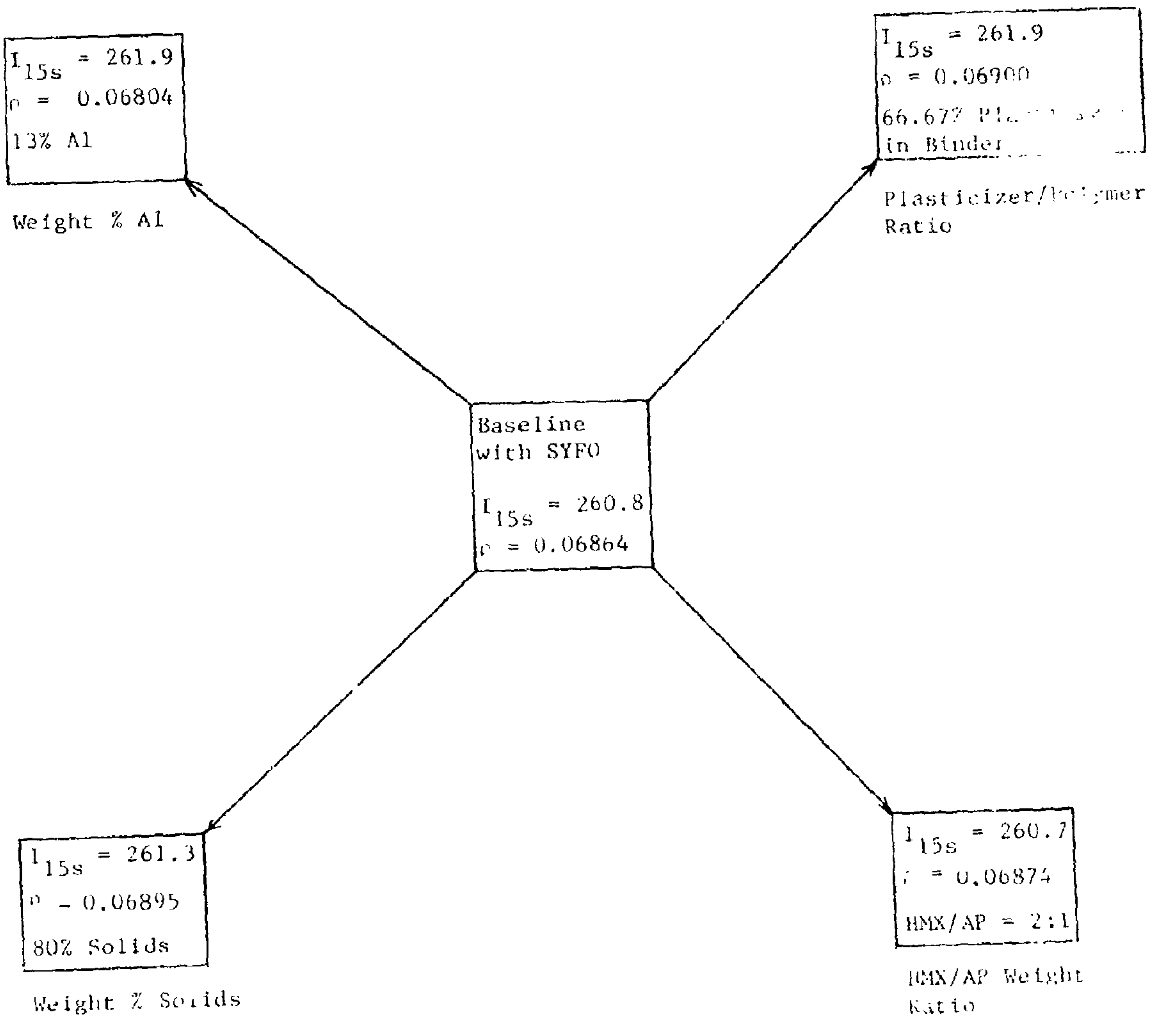


Figure 21

(C) content must be weighed against expected changes in the burning rate, pressure exponent and combustion efficiency of the propellant. Smaller increases (0.1 units) in specific impulse are obtained by increasing the plasticizer-to-polymer ratio (from 47.52% to 66.67% of the binder), which also increases density but may hurt mechanical properties. Processing should be aided by the higher plasticizer level. The slight increase in delivered specific impulse (0.1 units) obtained by lowering Al content from 16 to 15% is obtained at the sacrifice of propellant density.

(C) Figure 20 presents the results of making similar changes from the central formulation with mixed FEFO/SYFO plasticizer. The best single change is to increase the plasticizer-to-polymer ratio from 47.52% of binder to 66.67%, resulting in an increase of 0.8 I_{sp} units and an increase in density. Secondly, an increase of the total solids 80% increases I_{sp} by 0.3 units, along with an increase in density. Decreasing the aluminum content in the central formulation from 16 to 15% increases I_{sp} by 0.2 units, but at the sacrifice of density. In contrast to the all-FEFO plasticized system, increasing the HMX/AP ratio to 7:1 decreases both I_{sp} and density. Decreasing the HMX/AP ratio to 2:1 results in a smaller decrease of 0.4 I_{sp} units and an increase in density.

(C) The trends exhibited by the mixed FEFO/SYFO plasticizer are even more pronounced with the all-SYFO plasticized system, as shown in Figure 21. The best single change from the central formulation is to increase the plasticizer content of the binder from 47.52% to 66.67%, resulting in an increase of 1.1 I_{sp} units, which also results in a density increase. A change in oxidizer from 3:1 HMX/AP to 7:1 produces

(C) a large decrease in I_{sp} and density. Decreasing the HMX/AP ratio to 2:1 decreases I_{sp} only by 0.1 unit while increasing density. A slightly lower HMX/AP ratio could also lower the burning rate, pressure exponent, and cost of the propellant. Again, increases in I_{sp} are obtained by increasing solids to 80% or by decreasing aluminum content.

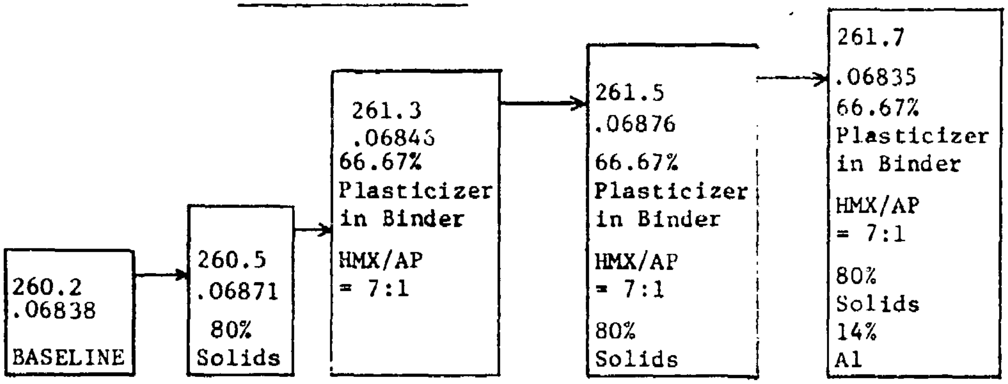
(C) Combinations of the above-mentioned single changes augment the delivered I_{sp} and density for these systems even further. Thus a combination of increased plasticizer level, higher total solids, higher HMX/AP ratio, and lower aluminum increases the delivered I_{sp} of the FEFO baseline propellant by 1.5 I_{sp} units and the SYFO baseline propellant by 1.9 I_{sp} units. These changes are presented in Figure 22 and Tables VIII through X.

c. Effective Specific Impulse (Ω) (U)

(U) Tradeoffs between delivered specific impulse and density are most conveniently evaluated by use of the Omega Function or Effective Specific Impulse, defined by the equation $\Omega = I_{15s}(\rho/\rho_o)^K$, in which ρ is the propellant density, ρ_o is a reference density, customarily taken as 1.8 gm/cc = 0.065 lb/in.^{3}, and K is dependent on the missile stage and design parameters. K is approximately 0.3 for upper-stage vehicles. Section III.A.2.b.(3) describes the derivation of this equation and justifies its use by showing that conclusions from Ω calculations agree closely with those based on actual range calculations.

SUMMARY OF GAINS IN I_{15s} AND DENSITY FROM VARIOUS CHANGES IN BASELINE FORMULATION (U)

A. FEFO Plasticizer



B. SYFO Plasticizer

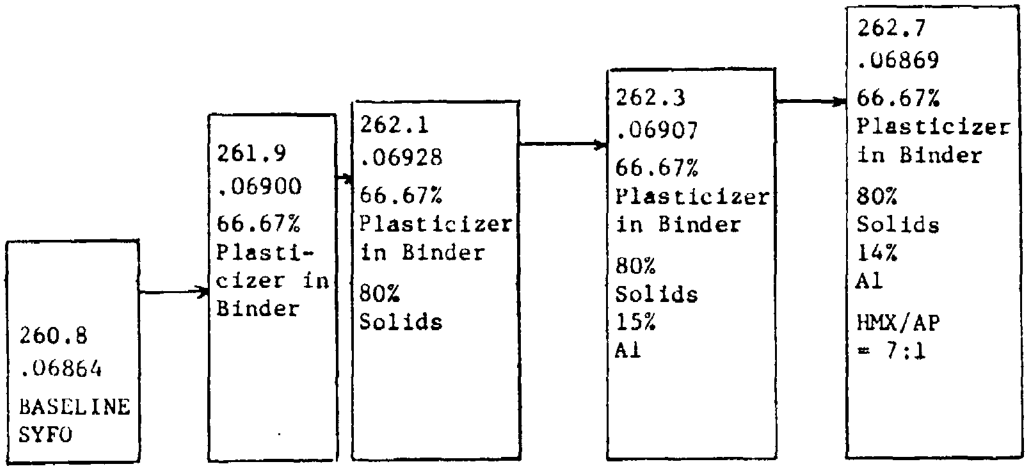


Figure 22

TABLE VIII

SUMMARY OF VARIATIONS IN BASELINE FORMULATION OFFERING INCREASES IN DELIVERED SPECIFIC IMPULSE I: FEFO PLASTICIZER (U)

	% Al	% Solids	% Plasticizer in Binder	HMX/AP	I_{15s} sec	ρ, lb/in.^{3}
BASELINE	16	78	47.52	3:1	260.2	.06838
Single Changes						
A	16	80	47.52	3:1	260.5	.06871
B	16	78	47.52	7:1	260.5	.06796
C	16	78	66.67	3:1	260.3	.06847
D	15	78	47.52	3:1	260.3	.06[illegible]8
Double Changes						
E	16	78	66.67	7:1	261.3	.06846
F	16	80	47.52	7:1	261.0	.06853
G	15	78	47.52	7:1	260.8	.06801
H	15	80	47.52	3:1	260.6	.06851
I	16	80	66.67	3:1	260.5	.06894
J	15	78	66.67	3:1	260.4	.06843
Triple Changes						
K	16	80	66.67	7:1	261.5	.06876
L	15	80	47.52	7:1	261.2	.06833
Quadruple Changes						
M	14	80	66.67	7:1	261.7	.06835
N	15	80	66.67	7:1	261.6	.06856

TABLE IX

SUMMARY OF VARIATIONS IN BASELINE FORMULATION OFFERING INCREASES IN DELIVERED SPECIFIC IMPULSE
II: SYFO/FEFO PLASTICIZER (1/1) (U)

	% Al	% Solids	% Plasticizer in Binder	HMX/AP	I_{15s} sec	ρ, lb/in.^{3}
BASELINE	16	78	47.52	3:1	260.6	.06851
Single Changes						
A	16	78	66.67	3:1	261.4	.06881
B	16	80	47.52	3:1	260.9	.06883
C	15	78	47.52	3:1	260.8	.06831
Double Changes						
D	16	78	66.67	7:1	261.7	.06864
E	16	80	66.67	3:1	261.4	.06911
F	14	80	47.52	3:1	261.2	.06843
G	15	80	47.52	3:1	261.1	.06863
H	14	78	47.52	7:1	261.1	.06794
I	16	80	47.52	7:1	261.0	.06865
Triple Changes						
J	16	80	66.67	7:1	262.1	.06893
K	15	78	66.67	7:1	262.0	.06844
L	14	78	66.67	7:1	262.0	.06823
M	15	80	66.67	3:1	261.5	.06891
N	15	80	47.52	7:1	261.4	.06845
Quadruple Changes						
O	15	80	66.67	7:1	262.2	.06873
P	14	80	66.67	7:1	262.2	.06852

TABLE X

SUMMARY OF VARIATIONS IN BASELINE FORMULATION OFFERING INCREASES IN DELIVERED SPECIFIC IMPULSE
III: SYFO PLASTICIZER (U)

	% Al	% Solids	% Plasticizer in Binder	HMX/AP Ratio	I 15s sec	ρ, lb/in.^{3}
BASELINE	16	78	47.52	3:1	260.8	.06864
Single Changes						
A	16	78	66.67	3:1	261.9	.05900
B	13	78	47.52	3:1	261.9	.06804
C	16	80	47.52	3:1	261.3	[illegible]
Double Changes						
D	14	78	66.67	3:1	262.2	.06863
E	16	80	66.67	3:1	262.1	.06928
F	15	78	66.67	3:1	262.1	.06897
G	14	80	47.52	3:1	261.6	.06855
H	15	80	47.52	3:1	261.5	.06875
I	16	78	66.67	7:1	261.4	.06882
Triple Changes						
J	14	78	66.67	7:1	262.4	.06841
K	15	80	66.67	3:1	262.3	.06907
L	16	80	66.67	7:1	262.1	.06910
M	15	78	66.67	7:1	262.1	.06862
N	14	80	47.52	7:1	261.6	.06836
O	15	80	47.52	7:1	261.3	.06857
Quadruple Changes						
P	14	80	66.67	7:1	262.7	.06869
Q	15	80	66.67	7:1	262.6	.06889

(C) The effect of excursions from the baseline formulation on Effective Specific Impulse was evaluated in the same manner as for I_{15s} in the preceding section. The variables investigated were total solids, HMX/AP weight ratio, plasticizer-to-polymer ratio, aluminum content and change of plasticizer from FEFO to SYFO. Figures 23, 24 and 25 show the effect of various single changes in the baseline formulations plasticized with FEFO, mixed FEFO/SYFO (1/1) and SYFO on Ω for upper-stage applications. An increase in solids loading generally increases both delivered I_{sp} and density and, therefore, tends to augment Ω for all systems. This change, of course, has to be evaluated in terms of the probable effect on processing and required mechanical properties. Likewise, the plasticizers have higher densities and higher oxygen balances than the PCDE polymer so that any increase in plasticizer-to-polymer ratio also tends to increase the Effective Specific Impulse. A high oxygen balance is required for simultaneous optimization at reasonably high aluminum and HMX/AP ratios. The plasticizer level is extremely important for the SYFO system since SYFO has a lower oxygen balance than FEFO. Only minor gains are realized by altering the aluminum content or HMX/AP ratio from the baseline formulation. These latter changes have opposing effects in these systems. For example, increasing aluminum content increases density but increases two-phase-flow losses (and lowers oxygen balance) lowering specific impulse efficiency. Increasing HMX/AP ratio decreases both density and oxygen balance so that increases in Effective Specific Impulse are realized only in systems already at high oxygen balance.

EFFECT OF SINGLE CHANGES IN BASELINE FORMULATION ON EFFECTIVE DELIVERED SPECIFIC IMPULSE (K = 0.3); FEFO PLASTICIZER (U)

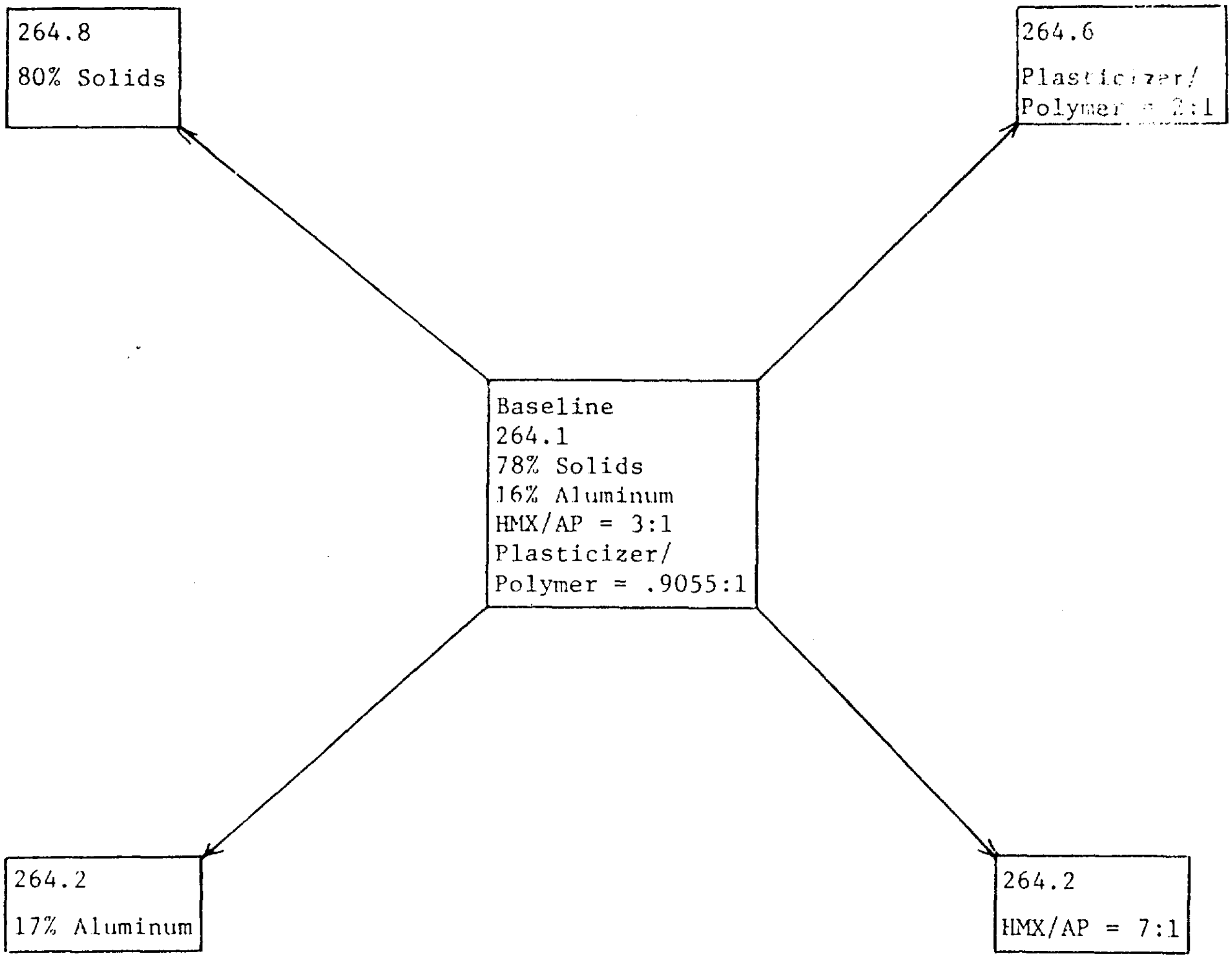


Figure 23

EFFECT OF SINGLE CHANGES IN BASELINE FORMULATION ON EFFECTIVE DELIVERED SPECIFIC IMPULSE (K = 0.3); MIXED FEFO/SYFO PLASTICIZER (U)

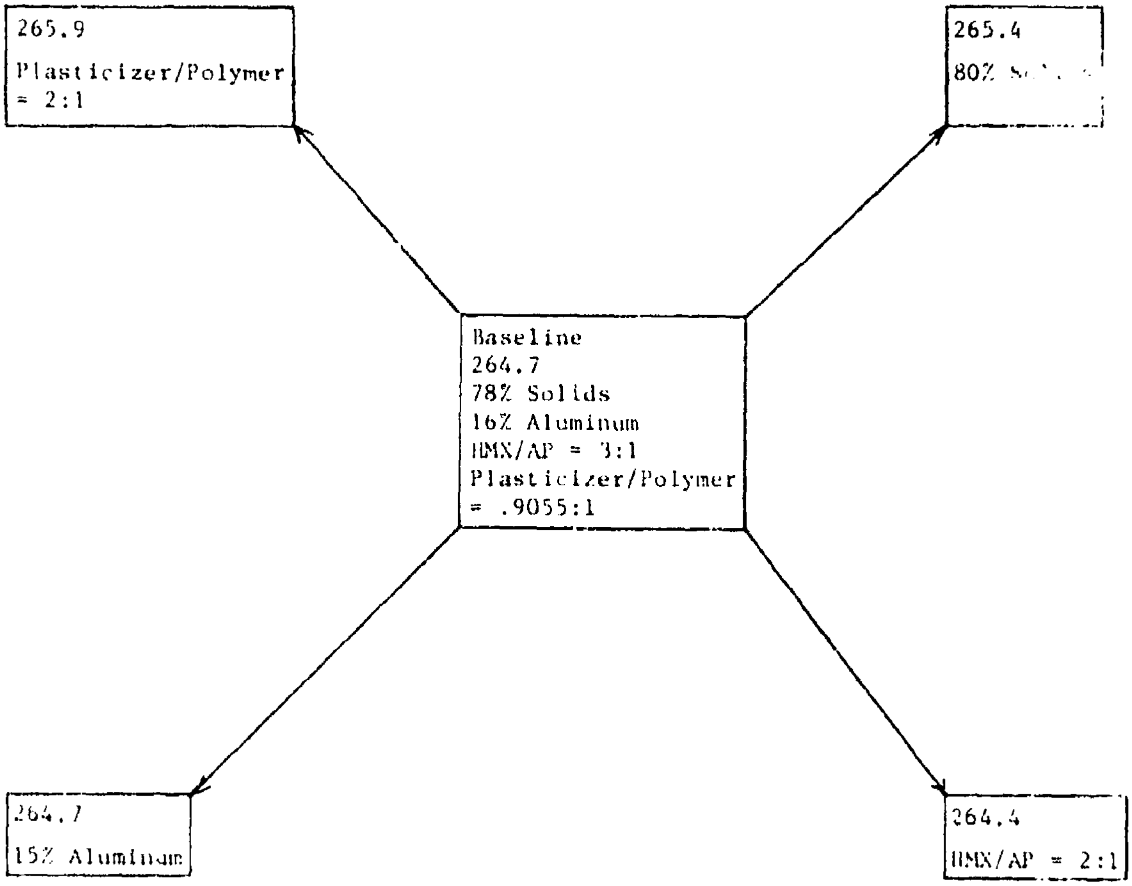


Figure 24

EFFECT OF SINGLE CHANGES IN BASELINE FORMULATION ON EFFECTIVE DELIVERED SPECIFIC IMPULSE (K = 0.3); SYFO PLASTICIZER (U)

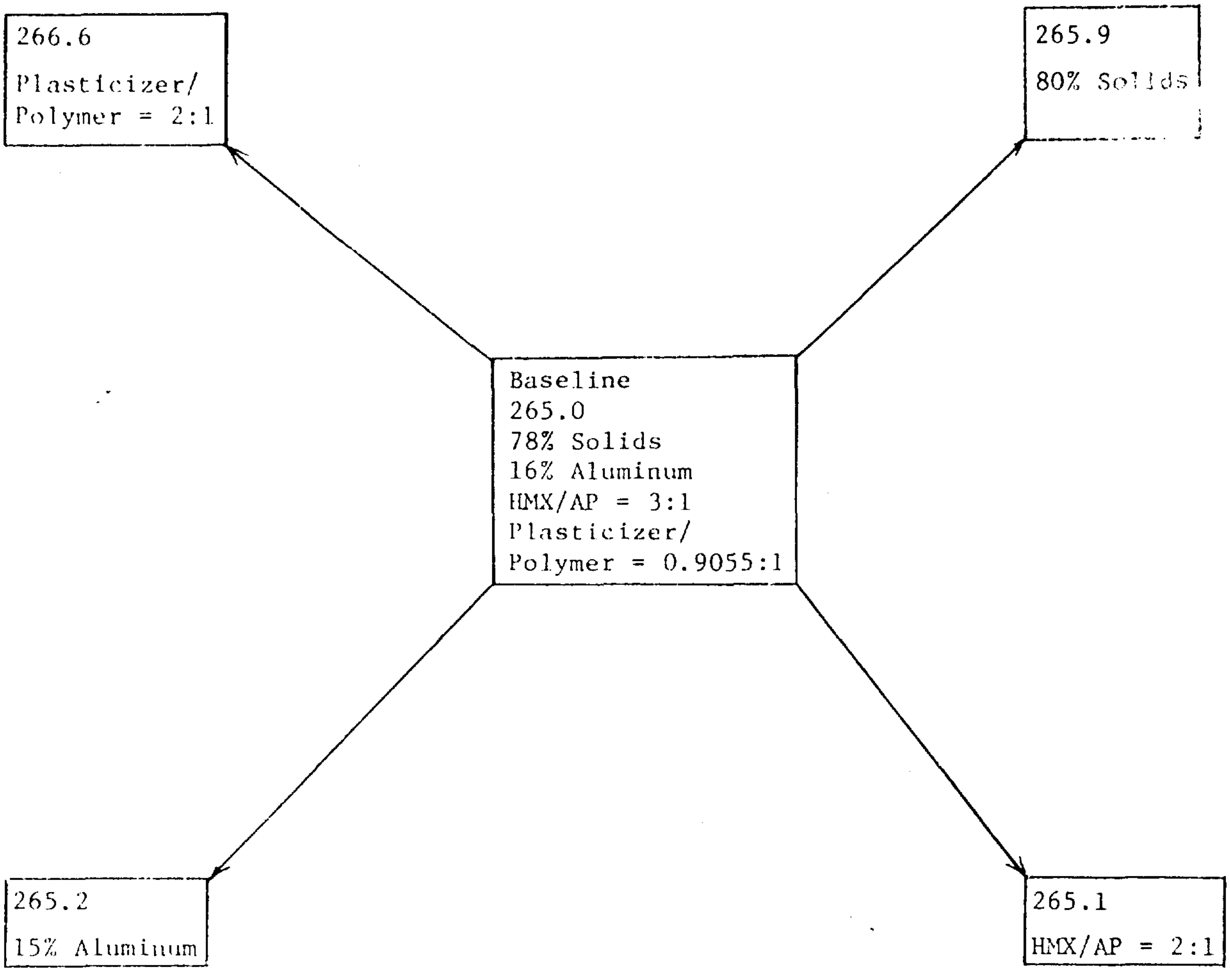


Figure 25

(C) Tables XI, XII and XIII present a summary of the gains to be realized in the Effective Specific Impulse parameter from various multiple alterations in the baseline formulations. In summary, altering all the variables, i.e., 2% increase in solids, increase of plasticizer-to-polymer ratio to 2:1, increasing the HMX/AP ratio to 7:1 and optimizing the aluminum content, results in a gain of only about 2 I_{sp} units for any of the three baseline propellants. In particular, there is an increase of only about one I_{sp} unit in both the baseline formulations and the best optimized formulations between FEFO and SYFO. This is a result of the lower oxygen balance of SYFO. The result is that the SYFO system optimizes at either lower HMX/AP ratios or lower aluminum contents than the FEFO system. For example, at 80 solids, 2:1 plasticizer/polymer ratio and HMX/AP weight ratio of 7:1, the FEFO-plasticized system optimizes at 17% Al, the mixed FEFO/SYFO-plasticized system optimizes at 16% Al and the all SYFO-plasticized system optimizes at 15% Al. At 16% aluminum the SYFO plasticized system optimizes at HMX/AP = 3:1, which has an Effective Specific Impulse equal to the value for the 7:1 HMX/AP optimized system.

(U) In conclusion, these results show that only small differences in performance can be expected by changes in composition within the limits imposed by practical considerations such as processability, etc. Furthermore, these results are based on a performance-prediction method which has not yet been shown to be applicable to the present propellant systems, which confirms the correctness of the selected approach, which is to select compositions for scale-up on the basis of actual motor-firing results.

TABLE XI

SUMMARY OF VARIATIONS IN BASELINE FORMULATION OFFERING INCREASES IN EFFECTIVE SPECIFIC IMPULSE
I: FEFO PLASTICIZER (U)

	% Al	% Solids	% Plasticizer in Binder	HMX/AP Weight Ratio	$^{\Omega}0.3$ sec
Baseline	16	78	47.52	3:1	264.1
Single Change					
A	16	80	47.52	3:1	264.8
B	16	78	66.67	3:1	264.6
C	17	78	47.52	3:1	264.2
D	16	78	47.52	7:1	264.2
Double Change					
E	16	78	66.67	7:1	265.3
F	16	80	66.67	3:1	265.1
G	16	80	47.52	7:1	265.1
H	17	80	47.52	3:1	264.9
I	17	78	66.67	3:1	264.8
J	15	78	47.52	7:1	264.3
Triple Change					
K	16	80	66.67	7:1	266.0
L	17	78	66.67	7:1	265.3
M	18	80	66.67	3:1	265.3
N	15	80	47.52	7:1	265.1
Quadruple Change					
O	17	80	66.67	7:1	266.1

TABLE XII

SUMMARY OF VARIATIONS IN BASELINE FORMULATION OFFERING INCREASES IN EFFECTIVE SPECIFIC IMPULSE
II: MIXED FEFO/SYFO PLASTICIZER (U)

	% Al	% Solids	% Plasticizer in Binder	HMX/AP Weight Ratio	$\Omega_{0.3}$ sec
Baseline	16	78	47.52	3:1	264.7
Single Change					
A	16	78	66.67	3:1	265.9
B	16	80	47.52	3:1	265.4
C	15	78	47.52	3:1	264.7
Double Change					
D	16	80	66.67	3:1	266.1
E	16	78	66.67	7:1	266.0
F	15	78	66.67	3:1	265.6
G	15	78	47.52	7:1	265.5
H	17	80	47.52	3:1	265.4
I	16	80	47.52	7:1	265.3
Triple Change					
J	16	80	66.67	7:1	266.6
K	17	80	66.67	3:1	266.3
L	15	78	66.67	7:1	266.0
M	15	80	47.52	7:1	265.4
Quadruple Change					
N	15	80	66.67	7:1	266.5

TABLE XIII

SUMMARY OF VARIATIONS IN BASELINE FORMULATION OFFERING INCREASES IN EFFECTIVE SPECIFIC IMPULSE III: SYFO PLASTICIZER (U)

	% Al	% Solids	% Plasticizer in Binder	HMX/AP Weight Ratio	“0.3 sec
Baseline	16	78	47.52	3:1	265.0
Single Change					
A	16	78	66.67	3:1	266.6
B	16	80	47.52	3:1	265.[illegible]
C	15	78	47.52	3:1	265.[illegible]
D	16	78	47.52	2:1	26[illegible].1
Double Change					
E	16	80	66.67	3:1	267.1
F	15	78	66.67	3:1	266.5
G	15	80	47.52	3:1	265.9
H	16	78	66.67	7:1	265.9
I	15	78	47.52	2:1	265.0
Triple Change					
J	15	80	66.67	3:1	267.0
K	16	80	66.67	7:1	266.9
L	15	78	66.67	7:1	266.4
M	14	80	47.52	7:1	265.5
Quadruple Change					
N	15	80	66.67	7:1	267.1

B. CHARACTERIZATION OF INGREDIENTS (U)

1. PCDE Purity and Purification (U)

a. Introduction (U)

(C) Work was begun on identifying and eliminating possible impurities in PCDE which interfere with cure. During a company-sponsored program on PCDE/FEFO propellants in 1972, pot life was found to be a major problem. This was attributed to the fact that a much larger concentration of catalyst (about 0.05 wt% FeAA) was needed to sustain polymerization than is needed in conventional polyurethane propellants. Attempts to use less catalyst often resulted in unreliable cures. A similar problem had been reported on the PCDE Propellant Studies program (Ref. 10). Since different plasticizers (TMETN and BDNPA/F) are employed on that program than on this one, it appears that the common source of difficulty may be related to the PCDE. Submixes (PCDE/TMETN) containing PCDE purified by passage over Linde 13X molecular sieves were reported to provide propellant exhibiting greater extent of cure and requiring lower FeAA concentration than for untreated PCDE (Ref. 10). Accordingly, an effort was made to investigate the advisability of pretreating PCDE to be used with SYFO and FEFO plasticizers.

b. Detection of Carbonyl Impurity (U)

(C) The as-received PCDE methylene chloride solution (2,264 gm, 18.3 wt% solution, Lot No. LR-12260-44) was passed once through 929 gm of 13X molecular sieves in a 3.75-in. diameter column. Recovery was 83% (determined by vacuum stripping of an aliquot) with no attempt to elute the column with fresh solvent. Comparison of infrared

(C) spectra (Figures 26 and 27), taken before and after treatment, is instructive. Untreated PCDE has a strong absorption band with frequency between 1700 and 1730 cm^{-1} and peaking about 1715 to 1718 cm^{-1}. This region is usually assigned to carbonyl and -C=N- absorption and thus may be considered an impurity. An infrared spectrum of the PCDE precursor PBEP taken at Aerojet in 1966, Figure 28, shows only slight absorption in the same region, but quite different from the carbonyl band in PCDE before treatment with molecular sieves. The shape of the trace for PBEP between 1700 and 1800 cm^{-1} is very similar to that for treated PCDE in the same frequency region.

c. Identification of Carbonyl Impurity (U)

(C) The source of the carbonyl absorption band was found to be acetone. Its identity was shown conclusively by isolating a 2,4-dinitrophenylhydrazone from as-received PCDE-methylene chloride solution. There did not appear to be a mixture of derivatives. After recrystallization twice from methanol-water solution, the melting point of the derivative was 124-125°C (reported m.p. 125°C). The infrared spectrum of the derivative (KBr pellet) showed no absorption attributable to nitrile, thus eliminating PCDE polymer involvement. A mixed m.p. of the derivative with the 2,4-dinitrophenylhydrazone of an authentic sample of acetone purified similarly showed no depression.

d. Purification by Vacuum Distillation (U)

(C) The concentration of acetone in as-received PCDE was found to be greater than 4%. A weighed sample of PCDE which had been stripped under vacuum at 48°C for 4.5 hours was vacuum-stripped

INFRARED SCAN OF PCDE AS RECEIVED (U)

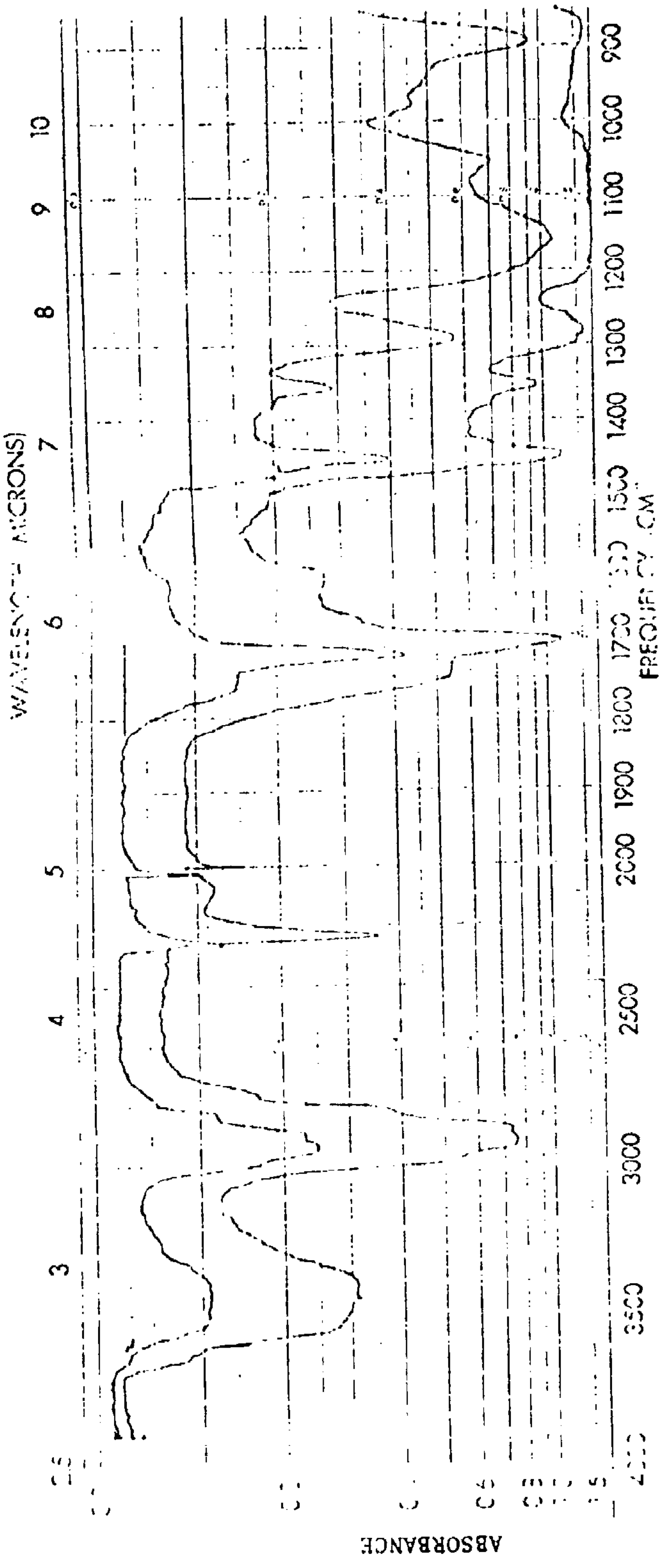


Figure 26

INFRARED SCAN OF PCDF AFTER ONE PASS THROUGH MOLECULAR SIEVE 13X (U)

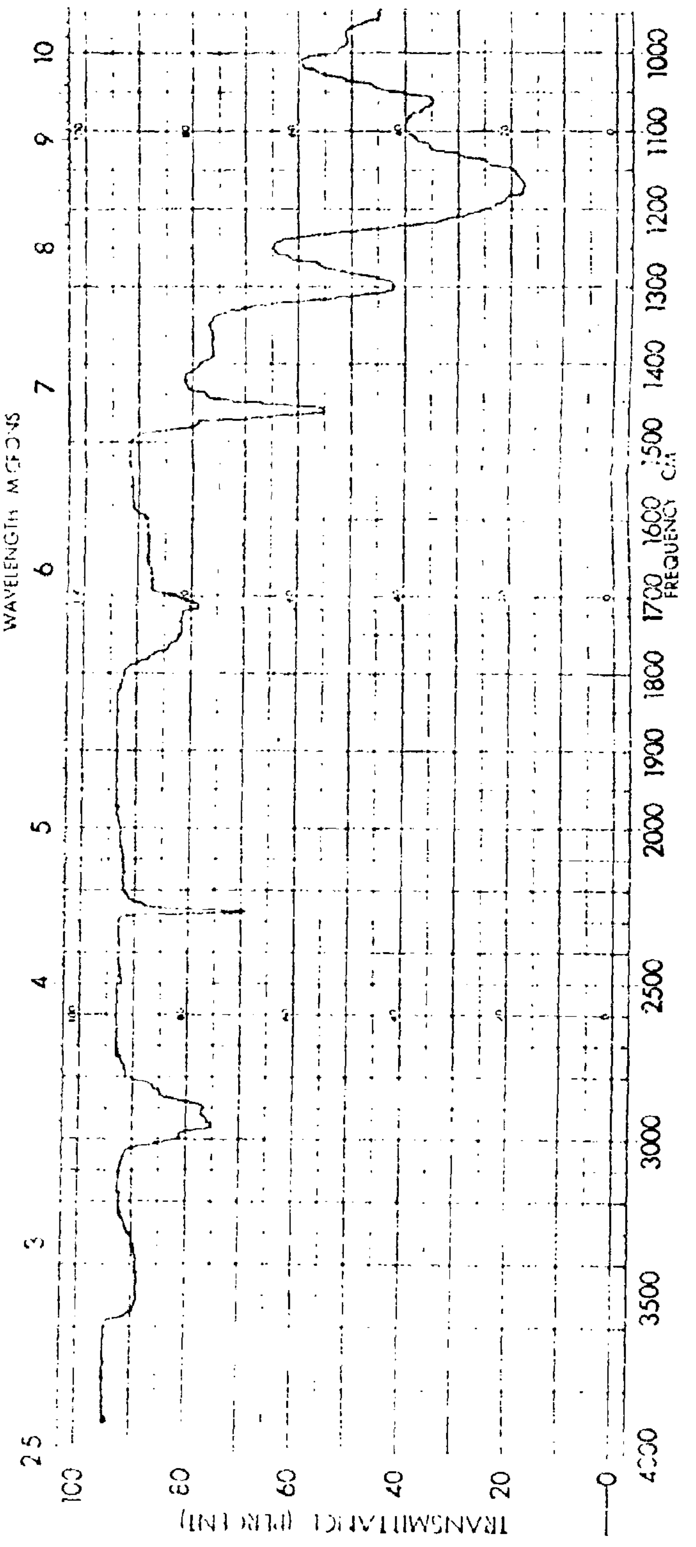
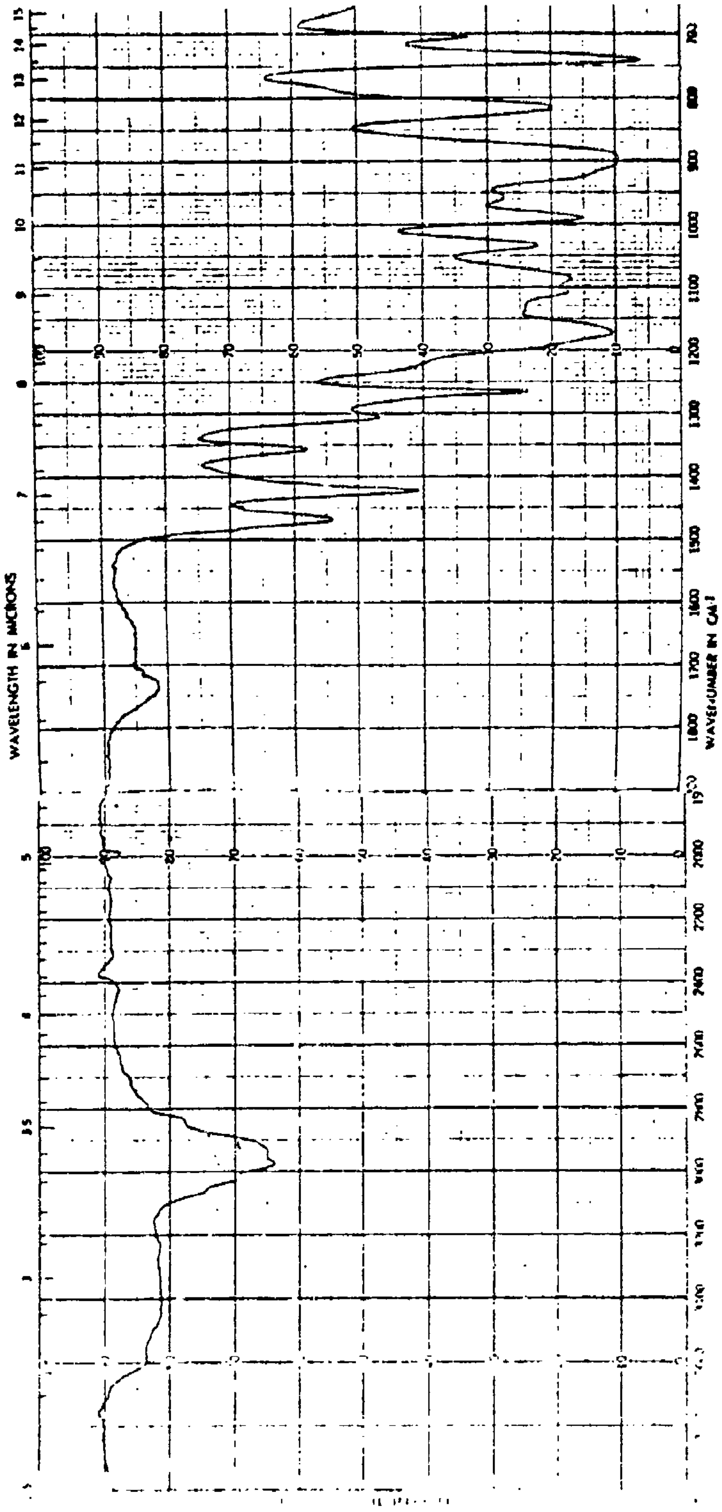


Figure 27

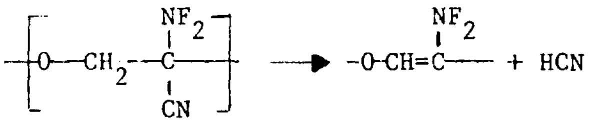


INFRARED SCAN OF PBEP (U)

Figure 2F

again at 82 to 87°C for 9.5 hours, resulting in a weight loss of 4.2% at the higher temperature.

(C) Undoubtedly some acetone was also lost during the lower-temperature stripping. Loss of acetone during stripping was accompanied by reduction of carbonyl absorption in the infrared, but some loss in nitrile absorption, as well as CH_2 band absorption, was also detected at the conclusion of the high-temperature stripping. This, as well as the detection of HCN in the atmosphere above PCDE-methylene chloride solutions, suggests the possibility of vinyl ether formation in the polymer backbone by a reaction such as



$$-\left[O-CH_2-\overset{NF_2}{\underset{CN}{C}}- \right] \longrightarrow -O-CH=\overset{NF_2}{C}- + HCN$$

Conditions favoring the loss of HCN should be explored with a view towards inhibiting this undesirable side reaction. At any rate, stripping in the presence of plasticizer at a lower temperature is expected to minimize the loss of HCN. It will be shown in Section III.B.2 that acetone is more easily removed from a SYFO-PCDE solution when the SYFO content is high and the viscosity is relatively low.

e. Purification by Molecular Sieve Treatment (U)

(U) As stated earlier, the infrared carbonyl absorption in as-received PCDE is also reduced by treatment with 13X molecular sieves, with one pass giving a recovery of 83%. A second passage of 313 gm of the one-pass PCDE solution (10.8 wt% concentration) through 125 gm of 13X molecular sieves (0.27 gm PCDE/gm sieves) in a 1.25-in. diameter column yielded 415 gm of 6.8 wt% PCDE solution, or about 84% recovery. Another 2.2 gm of PCDE (6.5 wt%) was recovered by eluting the column with additional methylene chloride. In all, 91% recovery (including washing from the column) was achieved on the second pass. Quantitative measurements of the carbonyl absorption band showed a reduction of 57% after one pass through molecular sieves and 77.5% after the second pass. It should be noted that PCDE-methylene chloride solution is shipped over 13X molecular sieves by the vendor.

If vacuum stripping alone removes all of the undesirable impurities in PCDE, this would be the preferred method of purification with respect to both economy and efficiency, because the amount of labor would be lower and because the loss of PCDE on the column would be eliminated. It reamins to be determined, however, if the molecular sieve treatment provides a superior product.

2. Spectral Studies of SYFO and FEFO (U)

a. Infrared Spectra

Spectra are presented for SYFO, FEFO, PCDE/FEFO (1/1 by weight), and PCDE/SYFO (1/1 by weight) in Figures 29 through 32. The spectra for PCDE/FEFO and PCDE/SYFO is being used to develop an infrared technique for determining the concentration of each plasticizer (singly) in PCDE submixes, by employing nitro-group absorption at approximately 1600 cm^{-1}. This would be particularly convenient since the submix is prepared from PCDE-methylene chloride solution, the concentration of which tends to vary each time a container is opened. It is less convenient to determine the concentration of individual constituents in a PCDE/SYFO/FEFO submix using infrared techniques, because SYFO and FEFO exhibit similar absorption peaks.

INFRARED SCAN OF SYFO (U)

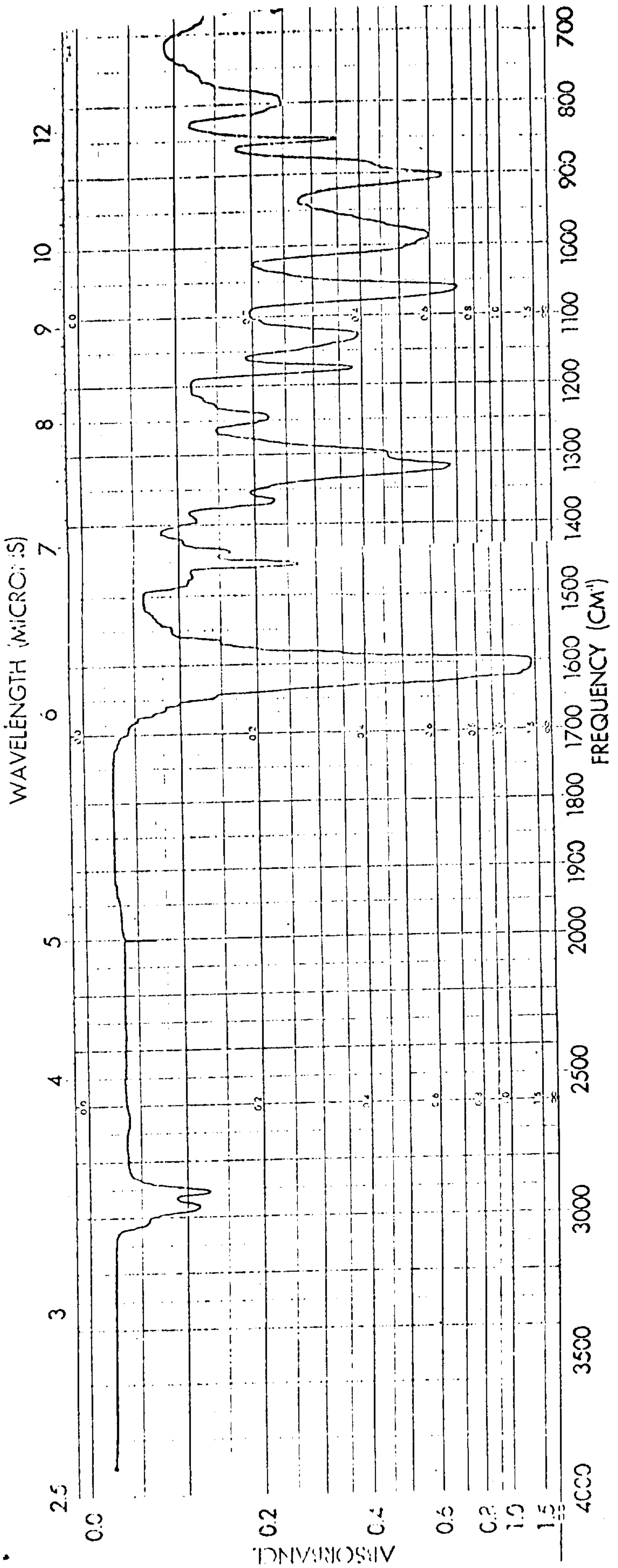


Figure 29

INFRARED SCAN OF PCDE/FEFO (1/1) (U)

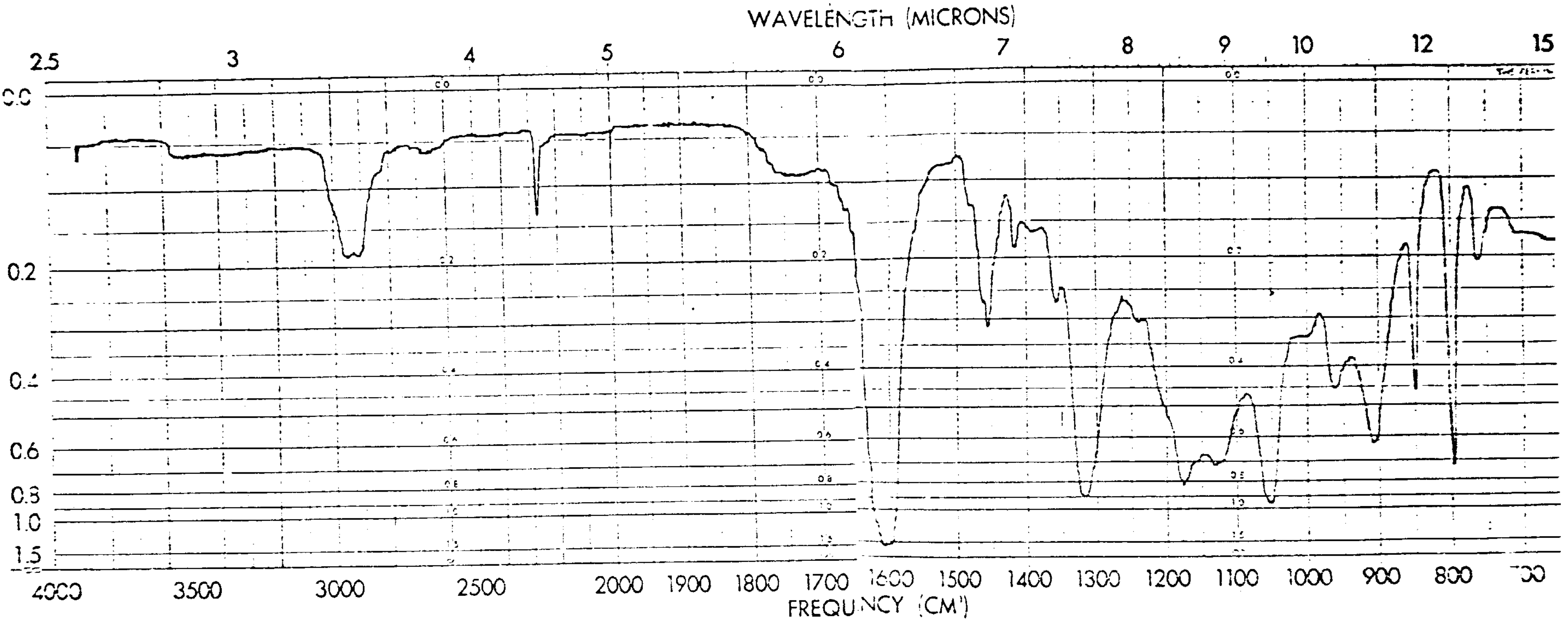


Figure 31

INFRARED SCAN OF FEFO

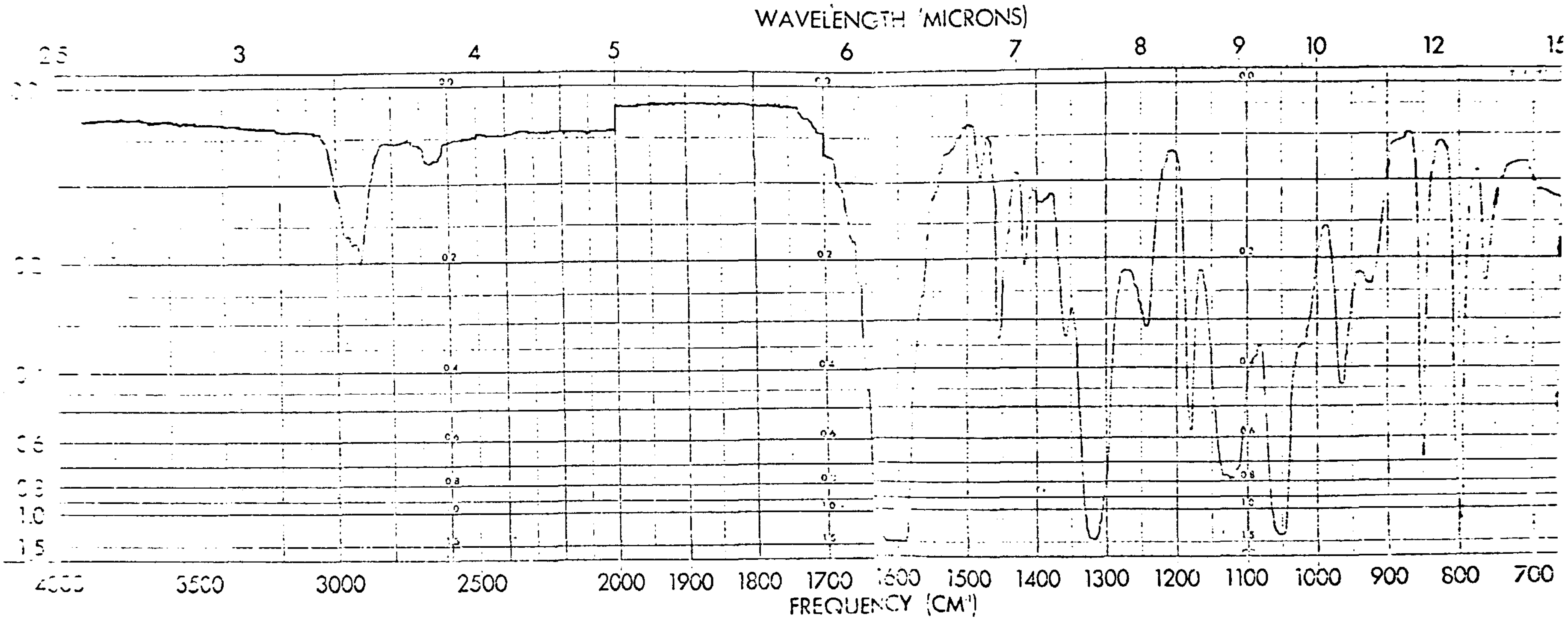


Figure 30

INFRARED SCAN OF PCDE/SYFU (1/1) (C)

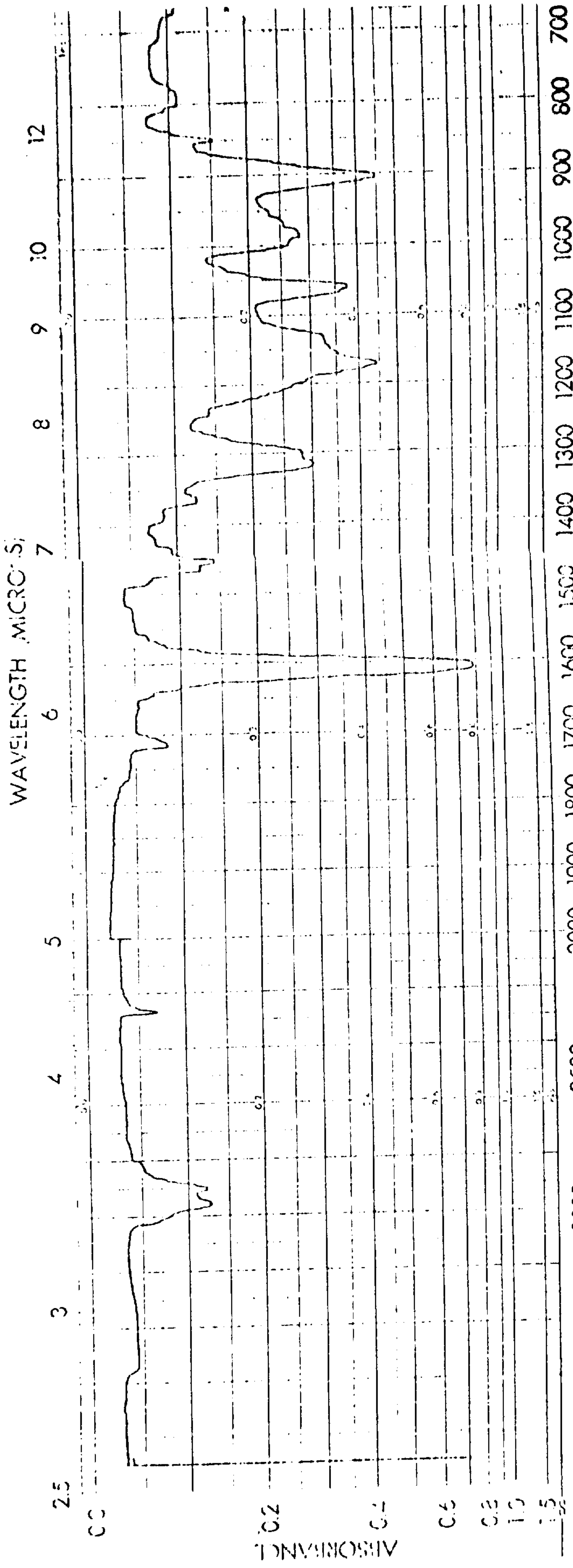


Figure 32

b. Precision of Infrared Analytical Method

The precision of the infrared method for determining the PCDE/SYFO weight ratio was tested with several submixes. The first two were made up to a weight ratio of approximately 1/1 by weighing the methylene chloride solutions, but because of the possibility of loss of some of the volatile methylene chloride before weighing, the true concentrations of PCDE and SYFO could not be determined accurately. The first submix, stripped for about 4 hours at 49°C (before acetone had been discovered in the solution) contained 51.7 and 52.0, or 51.8 average wt% SYFO. The second submix was heated under vacuum for 27 hours at 49°C, much longer than necessary to eliminate the carbonyl peak from the spectrum. The infrared analyses indicated 50.1 and 48.3, average 49.2 wt% SYFO, with no indication of loss of nitrile at this temperature. These results, particularly on the second sample, are less than satisfactory, and attempts will be made to improve the precision.

Two additional submixes demonstrated the precision of the method at other concentrations, and also showed that the ease of removal of acetone was dependent on SYFO concentration, undoubtedly because of the greater ease of diffusion of acetone through a more fluid solution. A SYFO/PCDE/CH_2Cl_2 solution made up to contain approximately a 1/3 wt ratio of SYFO to PCDE still showed carbonyl absorption in the infrared after 20 hours of vacuum stripping at 45°C. After an additional 16 hr at 55°C the carbonyl absorption was gone. The resulting submix was extremely viscous, rather like tar. Another solution was made up to contain approximately a 3/1 SYFO/PCDE ratio. This solution still showed some carbonyl absorption after 17 hours at 18°C, but only 6

(U) hours additional at 45°C was sufficient to eliminate it. The resulting submix was honey-like in viscosity--much less viscous than the 1/3 submix. Quantitative infrared analysis indicated 33.6 and 35.1, average 34.4, wt% SYFO in the first submix and 71.4 and 73.4, average 72.4, wt% SYFO in the second submix.

c. NMR Spectra of SYFO and FEFO (U)

(U) Nuclear magnetic resonance (NMR) traces for FEFO and SYFO are shown in Figures 33 and 34. Peaks (a) (s, OCH_2O) and (b) (d, CNO_2CH_2) in FEFO correspond to (d) and (c) respectively in SYFO. Although the determination of SYFO in admixture with FEFO has not yet been a problem, it is apparent from inspection of the NMR traces that it may be accomplished using this technique. The scan for this sample of SYFO correlates satisfactorily with that of a 96% pure sample reported by SRI (Ref.11).

3. Thermal Stability Studies (U)

(C) A brief investigation was made of the effect of certain stabilizers on the DTA exotherms of PCDE/FEFO (1/1) and PCDE/SYFO (1/1) submixes. The stabilizers selected were the antioxidants AO-2246, DBR, Neozone D, and Santicizer-8. The results are summarized in Table XIV. Except for AO-2246 there appears to be no marked effect of the additives on the thermal stability of the submixes. The onset of exotherm (195°F) for PCDE/FEFO (1/1) containing 2wt% AO-2246 is lower than the other values in the FEFO series. Similarly, the onset of exotherm 255°F for PCDE/SYFO (1/1) containing 2 wt% AO-2246 is also lower than for other mixtures in the series. The study is preliminary and of itself not conclusive.

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF FEFO

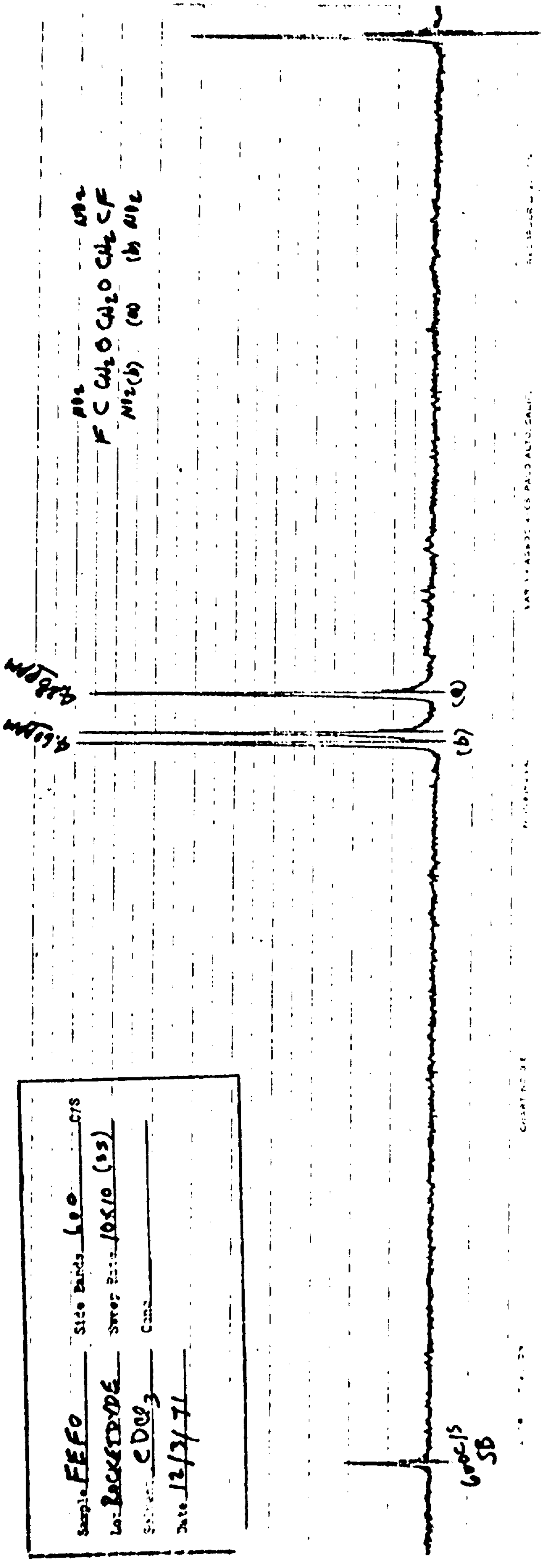


Figure 33

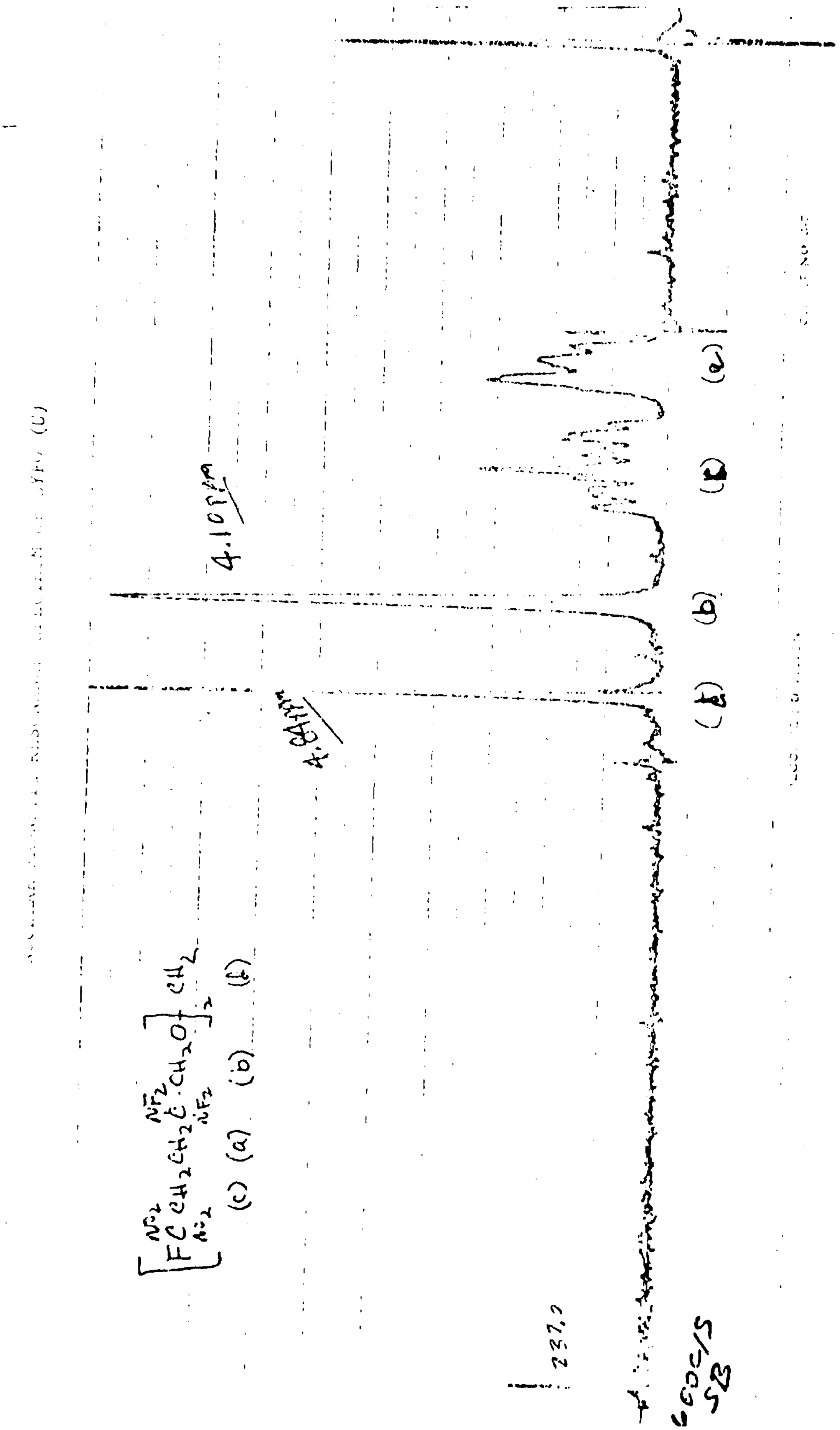

[F C(NF2)2 CH2 CH2 C(NF2)2 CH2 O]2 CH2
(c) (a) (b) (f)
4.10 ppm
4.84 ppm
(a)
(c)
(b)
(f)
237.0
60c/s
SB

Figure 34

(C) Neozone D has been selected for current use in PCDE/SYFO propellants, but the final choice of stabilizer for candidate propellants will be made after consideration of propellant aging and hazard properties.

4. Hazard Properties (U)

a. SYFO and SYFO-Containing Ingredients (U)

(C) Impact and friction sensitivities and DTA for SYFO and SYFO mixtures were measured using the first lot of pure SYFO received from SRI, and in one case, the first lot of Rocketdyne SYFO. The results are shown in Table XV, along with data for TVOPA for comparison. The friction sensitivity of neat SYFO was unusually high (for a liquid), but fortunately mixtures of SYFO with FEFO and/or PCDE are much less sensitive. Preliminary tests of neat SYFO on the sliding friction apparatus indicate high sensitivity here as well. Results will be reported at a future data when additional testing is completed. The impact sensitivity of 13 cm/2-Kg wt for neat, semi-crystalline SYFO on a bare anvil is considerably worse than for TVOPA. Under the same conditions, PCDE/SYFO (1/1) had an impact sensitivity of 97 cm/2-Kg wt, and the values for SYFO/FEFO (1/1) and PCDE/SYFO/FEFO (2/1/1) were over 100 cm/2-Kg wt in each case. Even at 2.62 SYFO/1 PCDE (72.4% SYFO), the impact and friction sensitivities were good. DTA traces were within expected limits. It is concluded that, although neat SYFO is quite sensitive, it is readily phlegmatized to a significant extent by dilution with PCDE or FEFO.

b. Effect of Molecular Sieve Treatment (U)

(U) Treatment of PCDE with 13X molecular sieves did not appear to have any effect on the hazard properties of a PCDE/FEFO

TABLE XIV

DTA EXOTHERM OF PCDE/FEFO (1/1) AND PCDE/SYFO (1/1) WITH SELECTED STABILIZERS (U)

	PCDE/FEFO (1/1)		PCDE/SYFO (1/1)	
Additive	Onset, °F	Peak, °F	Onset, °F	Peak, °F
2% AO-2246	195	305, 441	255	411, 440
2% DBR	267	398, 442	295	417, 450
2% Neozone D	307	437	314	407, 450
2% Santicizer-8	295	392	331	444
1% DBR + 1% Santicizer-8	255	434	359	416, 443
Control [no additive]	320	452	333	448

Table XV

HAZARD PROPERTIES OF SYFO AND SYFO MIXTURES (U)

	BuMines Impact, cm/2-Kg wt (50% Point	DTA Exotherm, °F		Rotary Friction, gm at 3000 rpm (50% Point)
		Onset	Peak	
SYFO	13*	319	423	485
SYFO/FEFO (1/1)	57**	300	441	>4 Kg
PCDE/SYFO (1/1)	97	333	448	>4 Kg
PCDE/SYFO (1/2.62)***	30	330	456	>4 Kg
PCDE/SYFO/FEFO (2/1/1)	38**	336	451	>4 kg
TVOPA	35	379	497	>4 Kg

---

* Semicrystalline, bare anvil.

** With No. 2 Whatman filter paper; otherwise bare anvil. (SYFO/FEFO and PCDE/SYFO/FEFO >100 cm on bare anvil, using SRI SYFO).

*** Rocketdyne SYFO, Lot 1 in this mixture. All others contain SRI SYFO.

(U) (1/1) submix as shown by Table XVI.

TABLE XVI

SENSITIVITY OF MOLECULAR SIEVE-TREATED PCDE/FEFO (1/1) (U)

(C)	Molecular Sieve-Treated	Conventional Stripping
Impact, cm/2-Kg wt (50% pt)	38	39
DTA exotherm, °F		
Onset	349	308
Peak	395	409
Rotary friction, gm @ 3000 rpm	>4000	>4000

(U) The hazard properties of propellants containing molecular sieve-treated PCDE do not appear to be any different from those of propellants containing conventionally stripped PCDE (presumably containing some acetone). (See Section III.C.)

C. PROPELLANT FORMULATION STUDIES (U)

(C) To date, only exploratory 70-gm propellant batches have been made. All contained 16 wt% Al, 46.5 wt% Al, 46.5 wt% HMX, and 15.5 wt% AP, or 78 wt% total solids, and all binders were made with PCDE/HT/TDI equivalents ratios of 70/30/105.

(U) Two batches of a PCDE/SYFO propellant were prepared with a PCDE/SYFO weight ratio of 1/1. The compositions and properties are shown in Table SVII. The castability was very poor, but the mechanical properties

(U) are quite encouraging. The difference in friction sensitivity of the two batches may be related to the difference in hardness, but this observation will require confirmation. It should be noted that these batches were prepared before acetone had been detected in the PCDE, so that the conventional stripping technique used to remove the methylene chloride shipping solvent may have left some acetone in the propellants.

(U) Four batches of propellant were made with PCDE/SYFO/FEFO weight ratios of 2/1/1. Again, these may have contained some acetone. The properties are shown in Table XVIII. The processability was poor, but better than that of the PCDE/SYFO propellants described above. All flowed well on vibration. Cures were obtained with both FeAA and dibutyltin dilaurate. The mechanical properties are encouraging for this series also, and the sensitivity tests do not indicate any serious problems at this time.

(C) Other propellant studies are being done with the PCDE/FEFO system in order to conserve SYFO when this can be done without affecting the results of the study. For example, experiments with other triols and diisocyanates are in progress. Two batches were made to compare molecular sieve-treated PCDE with conventionally stripped PCDE. Pertinent data are presented in Table XIX. Batch No. B23-36C, containing conventionally stripped PCDE (without regard for ketone content), was removed from the curing oven with a Shore A hardness of 38 after 4 days at 110°F. The propellant with molecular sieve-treated PCDE, B23-36A, had a Shore A hardness of 42 after a 2-day cure and was cut after 5 days of cure (Shore A, 44). Later work indicated that cure may extend over longer periods at the lower catalyst level employed (0.02 wt%), so that a direct

Table XVII

PROPERTIES OF PRELIMINARY PCDE-SYFO PROPELLANTS* (U)

Batch No. B-23-	31A	36D
Binder Ingredients, Wt%		
PCDE	10.47	10.47
SYFO	10.47	10.47
Hexanetriol	0.12	0.12
TDI	0.82	0.82
FeAA	0.05	0.02
Neozone D	0.10	0.10
Cure, Days at 110°F	4	3
Hardness, Shore A	74	49
Castability	Very Poor	Very Poor
Mechanical Properties (avg. of 5 minibars)		
σ_m, psi	Too Hard To Cut	99
ε_m, %		27
ε_b, %		30
E_o, psi		446
Sensitivity		
Impact, cm/2-kg wt, 50% pt (BuMines apparatus)		
Uncured	12	15
Cured	11	9
DTA, °F, Exotherm Onset		
Uncured	300	320
Cured	330	290
Ignition,		
Uncured	415	413
Cured	412	420
Rotary friction, gm at 3000 rpm		
Uncured	840	1280
Cured	400	>4000

---

* Both with 16 wt% Al (MDX-65), 30.5 wt% HMX-A (ctd), 16 wt% HMX-E, 15.5 wt% 130μm AP (ctd); 70-gm batches.

Table XVIII

PROPERTIES OF PRELIMINARY PCDE-SYFO-FEFO PROPELLANTS[*] (U)

Batch No. B-23-	31B	31C	31D	33B
Binder Ingredients, Wt%				
PCDE	10.46	10.46	10.46	10.47
SYFO	5.23	5.23	5.23	5.23
FEFO	5.23	5.23	5.23	5.23
Hexanetriol	0.12	0.12	0.12	0.12
TDI	0.82	0.82	0.82	0.82
FeAA	0.05	0.03	0.05[**]	0.02
Neozone D	0.1	0.1	0.1	0.1
Cure, Days at 110°F	3	7	7	5
Hardness, Shore A	63	52	44	55
Castability	Poor	Poor	Poor	Fair
Mechanical Properties (avg. of 5 minibars)				
σ_m, psi	116	95	86	83
ϵ_m, %	22	22	23	22
ϵ_b, %	24	24	25	24
E_o, psi	635	516	442	453
Sensitivity				
Impact, cm/2-kg wt, 50% pt (BuMines apparatus)				
Uncured	9	-	-	-
Cured	9	10	9	11
DTA, °F, Exotherm Onset,				
Uncured	300	-	-	-
Cured	310	323	313	320
Exotherm Peak				
Uncured	-	-	-	-
Cured	412	418	411	-
Ignition,				
Uncured	411	-	-	-
Cured	-	-	-	412
Rotary friction, gm at 3000 rpm				
Uncured	600	-	-	-
Cured	965	2200	1900	2100
Swelling Ratio, $(\ell/\ell_o)^3$	3.51	-	-	-

---

[*] All with 16 wt% Al (MDX-65), 30.5 wt% HMX-A (ctd), 16 wt% HMX-E, 15.5 wt% 130μm AP (ctd); 70-gm batches.

[**] Dibutyltin dilaurate

comparison of properties may not be valid. Other work which should provide this data is in progress.

D. PROPELLANT AGING STUDIES (U)

(C) In the absence of data with SYFO, a preliminary small-scale Company-sponsored aging study with PCDE/FEFO propellant is reported. this study was made to obtain an early assessment of potential problems. Definite gassing was observed in a propellant after six weeks at 135°F, Shore A hardness changed from 14 to 27, and swelling ratio increase 7.2%; there was little change in hazard characteristics.

(C) This propellant contained 0.1% Neozone D antioxidant. It seemed of interest to evaluate other promising antioxidants under development on another FEFO-propellant system. Two propellants, one containing 0.2 wt% of a resorcinol-type free-radical stabilizer, Batch No. 7696-64A, and the other 0.1 wt% free-radical stabilizer + 0.1 wt% acid scavenger (a sulfonamide), Batch No. 7696-64B, were wrapped in aluminum foil and aged 68 days at 135°F. Thermocouples were inserted in each sample and monitored for exotherm; none was detected. Neither sample lost any significant weight. Batch 64A had definite fissures, and Shore A hardness decreased from 36 to 26. Swelling ratio decreased 2.0%, and modulus decreased from 391 psi to 177 psi. Fissuring in sample 64B appeared much less severe, although Shore A hardness decreased from 51 to 36. Here, again, swelling ratio decreased 1.0%, and modulus decreased from 926 psi to 521 psi. There were no significant changes in hazard properties of the aged propellants. The pertinent data are tabulated in Table XX.

TABLE XIX

EFFECT OF MOLECULAR SIEVE-TREATED PCDE ON PROPERTIES OF PCDE/FEFO (1/1) PROPELLANTS* (U)

Batch No. B23-	Molecular Sieve-Treated PCDE** 36-A	Untreated PCDE 36-C
Shore A Hardness	44	38
Days @ 110°F	5	4
Mechanical Properties		
σ_m, psi	80	71
ϵ_m, %	21	27
ϵ_b, %	23	30
E_0, psi	453	337
Hazard Properties (cured)		
Impact, cm/2-Kg wt (50% fire pt)	8	18
Friction, gm @ 3000 rpm (50% fire pt)	1200	2000
DTA, Exotherm, °F		
Onset	280	315
Ignition	418	418

---

* HMX/AP (3/1), 78% solids, 16% Al, 0.02% FeAA

** One pass through 13X molecular sieves

TABLE XX

PCDE/FEFO PROPELLANT AGING STUDY* (U)
68 days @ 135°F

Batch No. 7696-		64A		64B	
		Control**	Aged	Control	Aged
Weight, gm	Before		54.7		54.4
	After		54.6		54.4
Appearance			Darker; fissures		Darker; incipient fissures
Shore A Hardness		36	26	51	36
Swelling Ratio $(\ell/\ell_o)^3$ % change		-2.0		-1.0	
Mechanical Properties @ 77°F					
σ_m, psi		71	39	128	90
ϵ_m, %		22	26	18	22
ϵ_b, %		25	28	20	25
E_o, psi		391	177	926	521
Hazard Properties					
Bureau of Mines Impact, cm/2 kg (50% pt)		19	21	19	14
DTA Exotherm, °F	Onset	365	357	355	357
	Peak	410	409	413	416
Rotary Friction, gm load @ 3000 rpm		>4 kg	>4 kg	>4 kg	>3750

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* Propellant Composition: PCDE/FEFO (1/1), TMP, and IDI; 78% Solids: Al 16%, HMX/AP (3/1) 64A: 0.2% free radical stabilizer; 64B: 0.1% free radical stabilizer + 0.1% scavenger.

** Control aged 68 days at ambient temperature.

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13. ABSTRACT

This program is concerned with the development, characterization, and ballistic testing of propellants containing PCDE, SYFO, and FEFO. A detailed theoretical study was made of the effects of compositional variables on the predicted performance of PCDE/SYFO and PCDE/SYFO/FEFO propellants in order to select formulations for maximum range. The details are given and discussed. An impurity was found to be present in PCDE in significant concentration. It was identified and two methods were devised for its removal. The hazard characteristics of the ingredients were determined alone and in combination with each other. Potential anti-oxidants were screened for use in propellants. Preliminary propellant formulation studies gave propellants with mechanical properties close to the program goals and with encouraging sensitivities.

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SYFO						
FEFO						
Solid Propellant						

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