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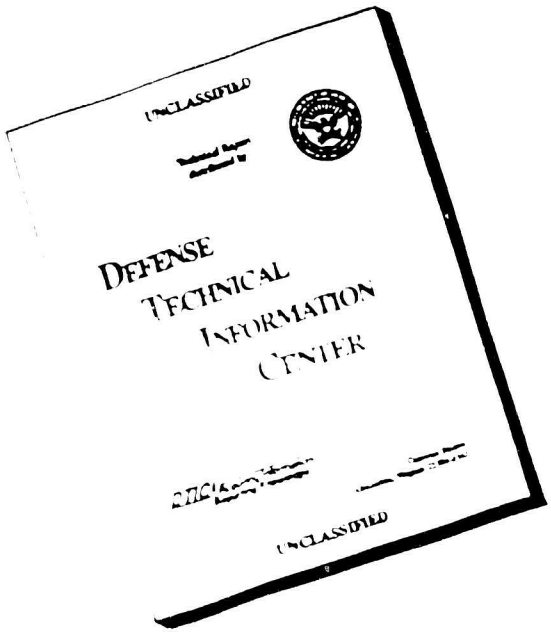

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AFRPL-TR-66-257

THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER FOR HIGH ENERGY SOLID PROPELLANTS (U)

by

D. E. Johnson and A. J. DiMilo
Aerojet-General Corporation
Solid Propellant Operations
Sacramento, California

October 1966

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AFRPL-TR-66-257

(U) THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER FOR HIGH ENERGY SOLID PROPELLANTS

By

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AFRPL-TR-66-257

FOREWORD

This technical report was prepared under Contract No. AF 04(611)-11419 as partial fulfillment of the requirements of Project 3418 of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. The work reported was done in the Advanced Propellants Department of the Aerojet-General Corporation, Sacramento, California. This report was designated Aerojet-General Corporation Report 1030-81Q-2 and covers the results of work done during the interval 14 June to 13 September 1966. The project was a follow-on to the project completed under Contract AF 04(611)-10386, the results of which are reported in Report No. AFRPL-TR-66-40. This project was monitored by Mr. Robert Corley.

Acknowledgement is made to the following persons who have contributed materially to the work performed during this period: A. J. Di Milo, Chemistry Supervisor; D. E. Johnson, Chemistry Specialist; R. H. Quacchia, Research Chemist A; J. L. Humphreys, Associate Chemist; A. H. Swift, Chemist; R. J. Farris, Physicist; and at The General Tire and Rubber Company, to: R. G. Chase, Technical Assistant to the Technical Coordinator, Research and Development.

This technical report has been reviewed and is approved.

Prepared By:

A. J. Di Milo
Program Manager

D. E. Johnson
Principal Investigator

Approved By:

L. J. Rosen, Manager
Advanced Propellants Department
Research & Technology Operations

ABSTRACT (C)

The investigation and characterization of the saturated hydrocarbon binder developed under Contract AF 04(611)-10386 for use in solid rocket propellants were continued. Forty-five pounds of a secondary hydroxy terminated Telagen S were delivered to Aerojet and characterized. Functionality determined from the crosslink density of a binder (1.9) is higher than that determined from the molecular weight to equivalent weight ratio (1.65). The difference may be due to nonfunctional units in the prepolymer. Aluminum metal does not interfere with cure stoichiometry of "workhorse" propellants, but the interference of certain plasticizers was further demonstrated. Binders were made from the Telagen S prepolymers and characterized by uniaxial tensile behavior at 77°F, stress relaxation at 77° and 150°F, compression after swelling in toluene, gel and sol fractions, and Mooney-Rivlin constants. Linear relations were demonstrated between the gel fraction, the Mooney-Rivlin C_1 constant, the crosslink density, and the logarithm of the initial uniaxial tensile modulus. Swelling studies in a large number of solvents indicate a C.E.D. value of about 80 for the binder. Propellants were made on a 400-gm scale and were characterized. The pressure exponent for burning rate was 0.7 for these propellants (88 wt% solids). The relative viscosity of NH_4ClO_4-Oronite 6 slurries was at a minimum for an oxidizer blend of 35.80%, 32.10% and 32.10% by weight of particles averaging 6, 148, and 419μ, respectively. This blend was selected to prepare a high solids loaded propellant.

Compatibility studies were extended to include epoxide and aziridine curing agents as well as isocyanates and the oxidizer hydroxylamine perchlorate. Hydroxy and olefinic functional groups are compatible with "as received" LMH-1 and -2 and chrome coated Be, but carboxy groups were not. All these functional groups were compatible with hydroxylamine perchlorate. Isocyanate was the only curing agent which is practical in the hydroxylamine perchlorate system.

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GLOSSARY OF TERMS

Ansul Ether 181	Tetraethylene glycol dimethyl ether
Armeel OD	Oleylnitrile, product of the Armour and Company
Be	Beryllium
BISA	2-Ethylaziridine adduct of sebacic acid
b.p.	Boiling point
C-1	N,N-di-(2-cyanoethyl)-2,3-dihydroxy-propylamine
C_1 and C_2	Mooney-Rivlin Constants
Carbowax 6000 Carbowax 20M	Solid poly(ethylene glycol), product of the Union Carbide Company
CED	Cohesive Energy Density
CoAA	Cobalt acetylacetonate
c.p.	Centipoise
CTI	Triisocyanate, proprietary item of the Aerojet-General Corporation
DC 705	Silicon oil, product of Dow Chemical Company
DEA	Diethanolamine
Diatoport S	Diatomaceous earth used for chromatograph support, product of F & M Scientific Corporation
DOS	Dioctyl sebacate
DOZ	Dioctyl azelate
E_o	Initial uniaxial tensile modulus
FeAA	Ferric acetylacetonate
GLC	Gas-liquid chromatography
HAA	Acetylacetone

GLOSSARY OF TERMS (CONT)

HDI	Hexamethylene diisocyanate
IDP	Isodecyl Pelargonate, product of Emery Industries, Inc.
Light Circo Oil	General purpose naphthenic type softener for neoprene and natural rubber, product of the Sun Oil Company
MAPO	2,4,6-Tri-(2-methyl-1-aziridinyl)phosphine oxide
meq	Milliequivalents
mm	Millimeters
mm/gm	Millimoles per gram
MS	Molecular sieve, 4A, product of the Linde Co.
NEMNC	2-Nitratoethyl N-nitro-N-methylcarbamate
Niax D-22	Dibutyltin dilaurate, product of the Union Carbide Co.
Nujol	Mineral oil (registered trade name), product of Plough, Inc.
Oronite-6	Liquid polyisobutylene, product of the California Chemical Co.
PhNCO	Phenyl isocyanate
psi	Pounds per square inch
S-141	Octyl diphenyl phosphate, product of the Monsanto Chemical Co.
S_{mb}	Nominal uniaxial break tensile stress
S_{mm}	Nominal maximum uniaxial tensile stress
Telagen S	Functionally-terminated hydrogenated polybutadiene, product of The General Tire and Rubber Co.
TMETN	Trimethylolethane trinitrate, 1,1,1-tri-(nitratomethyl)-ethane

GLOSSARY OF TERMS (CONT)

v_g	Gel fraction
VPO	Vapor phase osmometer
X_D	Crosslink density
γ_b	Uniaxial strain at break
γ_e	Maximum uniaxial strain
η	Viscosity, specifically for slurries
η_o	Viscosity, specifically for liquids
η_r	Relative viscosity, ratio of η to η_o
μ	Micron
ϕ	Volume fraction
ϕ_f	Maximum volume fraction

AFRPL-TR-66-257

THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER FOR HIGH ENERGY SOLID PROPELLANTS

I. INTRODUCTION

This is the second Quarterly Technical Report submitted in partial fulfillment of the requirements of Contract AF 04(611)-11419. The report covers the period 14 June through 13 September 1966.

II. OBJECTIVE

The objective of this program is to further develop and evaluate a solid propellant binder system specifically to meet the most rigid demands of advanced, high performance solid rocket motors. The solid propellant binder system consists of an isocyanate-cured, saturated hydrocarbon prepolymer developed and evaluated under Contract AF 04(611)-10386. Further development and evaluation will involve propellant optimization, maximizing solids loading, adaptation to advanced oxidizers and fuels, and study of the environmental stability of the propellant.

III. SUMMARY

A. Forty-five pounds of a secondary-hydroxy terminated Telagen S were prepared by The General Tire and Rubber Company and delivered to Aerojet-General Corporation. The unsaturated analog (5 lb) and a carboxy-terminated polybutadiene (5 lb) with similar carbon backbone were made available for study. These were characterized.

B. CTI (1.2 kg) was made, but some of it had a low NCO assay and will require recrystallization.

C. The functionality of the Telagen S was not resolved. The expected functionality (molecular weight to equivalent weight ratio) was about 1.7 and lower than the effective functionality (from crosslink density of binders) which is 1.9. Evidence was obtained that the difference was the result of non-functional units.

D. Aluminum metal did not cause a loss of isocyanate functionality when in contact with HDI. This indicated little or no interference of aluminum with the cure stoichiometry of Telagen S propellants.

E. The cure interference index of a plasticizer was defined as [1-(isocyanate remaining in a standard test solution/isocyanate remaining in a control solution)] x 100.

F. The cure interference index of squalene was lowered appreciably (from 60 to 9) by vacuum distillation. A redistilled IDP (Emery Industries) which inhibited the cure of a Telagen S binder had a measured cure interference index of 40. Armeel CD, oleyl nitrile, seriously interfered with the curing of Telagen S-isocyanate binders, but the cure interference was reduced by passing the plasticizer through a column of silica gel.

G. Armeel CD showed interference with curing of aziridine-cured binders. This indicated that the problem of cure interference was a general one that had gone unnoticed because the effects of the interference had been confused with plasticizing action.

H. A considerable number of binders was prepared and characterized by uniaxial tensile behavior at 77°F, stress relaxation, compression after swelling, gel and sol fractions and Mooney-Rivlin constants.

I. Linear correlations were demonstrated between the gel fraction and the Mooney-Rivlin C_1 constant, between the gel fraction and the crosslink density, and between the Mooney-Rivlin C_1 constant and the crosslink density. The crosslink densities derived from binder stress relaxation and from compression of toluene swollen binders were not the same but were related in an approximately linear manner. The log E_o (E_o = initial uniaxial tensile modulus) was linearly related to the gel fraction of plasticized binder.

J. The swelling of Telagen S-isocyanate binders was studied in 12 additional solvents. The scatter of the data prevented exact deductions, but the binder CED value was in the vicinity of 80.

K. Propellants were studied at the 400-gm batch size. Hydrocarbon plasticizers in propellants led to higher initial moduli than did ester type plasticizers. For the propellants, an NCO to OH ratio of 1.0 and an HDI to TDI ratio of 4.0 were best.

L. Although propellants were processed at 125°F and cured at 135°F, some were successfully processed at 110°F. When C-1 was used as a bonding agent, CoAA was not as satisfactory a catalyst as when DEA was used. Potlife was a problem at 125°F but not at 110°F.

M. Preliminary burning rate studies with 88% solids loaded propellant showed a pressure exponent of 0.7. This was a usable pressure exponent, but on the high side.

N. The effect of fillers on the relative viscosities of NH_4ClO_4-Cronite 6 slurries was determined for some bi- and trimodal NH_4ClO_4 particle blends. A blend consisting of 35.80%, 32.10% and 32.10% by weight of particles averaging 6, 148, and 419μ, respectively was selected to be used for a high solids propellant.

O. Compatibility studies were extended to include epoxide and aziridine curing agents as well as isocyanates and the oxidizer hydroxylamine perchlorate. For this purpose the model compounds, n-butyl isocyanate, 1,2-epoxycyclohexane, 1-benzoyl-2-ethylaziridine, propionic acid, and hexanoic acid were utilized.

P. Compatibility studies made with the model compounds for the prepolymer indicated little or no interference of unsaturation or hydroxy functions with "as received" LMH-1, LMH-2, or chrome-coated beryllium. However, all these fuels cause the loss of carboxy groups.

Q. Model compounds with hydroxy, carboxy or unsaturated functional groups were stable in the presence of hydroxylamine perchlorate, but further studies with combinations of functional groups were begun.

R. Aziridines and epoxy model compounds were compatible with LMH-1, LMH-2 and chrome-coated beryllium, but both were incompatible with HAP.

S. The compatibility of a model isocyanate curing system was studied with beryllium, LMH-2, HAP and mixtures of HAP and the advanced fuels. HAP was a catalyst for urethane formation. Less urethane product was detected in the presence of HAP and 1-butyl isocyanate was lost to side reactions in the presence of beryllium and LMH-2.

T. Isocyanates show considerable loss of functionality with both the advanced fuels and oxidizers. Small amounts of water present in Be and LMH-2 were the cause of isocyanate loss through side reaction.

U. Small samples of propellant were prepared using the candidate binder and advanced fuels.

IV. TECHNICAL PROGRESS

A. MATERIALS

1. Saturated Hydrocarbon Prepolymer

The work reported in this Quarterly Progress Report was done with the prepolymer developed under Contract AF 04(611)-10356. The prepolymer was made by The General Tire and Rubber Company according to the tentative requirements in Table I.[1]

Table I

CHARACTERISTICS OF CANDIDATE PREPOLYMER (TELAGEN S)

Backbone	Saturated polybutadiene with about 35% 1,2-addition
Functional Groups	Secondary-OH
Molecular Weight	About 1500
Functionality	As close to 2 as possible
Viscosity	Less than 100 poises at 50°C

[1] D. E. Johnson and A. J. Di Milo, "The Development and Evaluation of a Hydrocarbon Binder for High Energy Solid Propellants", Report No. AFRPL-TR-66-40, Aerojet-General Corporation, Sacramento, California, Contract AF 04(611)-10386, February 1966.

Twenty pounds of this candidate prepolymer were prepared under Contract AF 04(611)-10386, and forty-five pounds were prepared and delivered under the present contract. These materials have been used in the work reported here. The properties of these prepolymers are shown in Table II.

Additional saturated prepolymers, both with carboxy and hydroxy functional groups, have been ordered for this project. The General Tire and Rubber Company is now supplying these prepolymers commercially under the registered trade name Telagen S.

Table II

PROPERTIES OF HYDROXY-TERMINATED TELAGEN S PREPOLYMER

	Batch No.		
	8507-I-47.1[a]		242AW-148AH[b]
	Unsaturated	Saturated	
Molecular Weight			
Theoretical	1766	-	-
Solution Viscosity	1180	-	-
VPO	1620	1676[d]	1750[c]
Hydroxyl, meq/g	1.049	1.020	0.91
Functionality[e]	1.70	1.71	1.62[f]
Unsaturation, mm/g	17.1	0.28	0.78
cis	27.6	-	39.7[c]
trans	38.3	-	27.3[c]
vinyl	34.1	-	33.0[c]
Ash, %	-	0.03	0.015
Antioxidant 2246, %	0.5	-	-
Brookfield Viscosity, Poise at 25°C	28	190	169
Volatiles, %			

[a] Twenty-two pound batch
[b] Forty-five pound batch
[c] Before hydrogenation
[d] Estimated from VPO molecular weight of the prepolymer and change in unsaturation.
[e] Ratio of VPO molecular weight to equivalent weight.
[f] Assuming a hydrogenated polymer of 1780 molecular weight.

2. Unsaturated Prepolymers

In addition to Telagen S, two unsaturated polybutadienes, acid and hydroxy terminated, were received from The General Tire and Rubber Company. The two materials are unsaturated analogs of the Telagen S Binders, and will be used to make unsaturated binders comparable to those being studied on this program. The properties of these prepolymers are shown in Table III.

Batch 142AM of Table II is a hydrogenation product of Batch 148A.

Table III

PROPERTIES OF POLYBUTADIENE PREPOLYMERS

	Batch No. 242AM-	
	148A	148D
Functional Group	e-OH	COOH
Molecular Weight (VPO)	1750	1600
Equivalent Weight	962	1017
Functionality	1.78	1.72
Unsaturation		
trans, %	27.3	29.2
cis, %	39.7	40.9
vinyl, %	33.0	29.9
Ash, %	0.004	0.0035
Antioxidant, %	-	2.09
Brookfield Viscosity, Poises at 25°C	29	2
Water, %	0.04	0.01
Volatiles, %	0.77	0.45

3. CTI

Additional batches of the triisocyanate, CTI, were prepared and data concerning them are shown in Table IV. Batch No. 8 turned out poorly, and will require recrystallization. With the exception of Batch No. 8, the purities of these materials range from 96 to 97%.

Table IV

EQUIVALENT WEIGHTS OF NEW BATCHES OF CTI

Batch No.	Weight, g	Equivalent[a] Weight
6	200	71
7	260	72
8	560	88
9	200	71

[a]Theoretical value 69.

B. PHASE I

1. Introduction

Phase I involves a study of the exact cure stoichiometry of the prepolymer, the effects of various plasticizers on propellant properties, and the maximum achievable solids loading with NH_4ClO_4 and aluminum. The propellant with the highest specific impulse will be completely characterized with respect to mechanical behavior and will be evaluated ballistically at the 1-lb level. The specifications of the prepolymer will be established.

2. Prepolymer

a. Functionality

The functionality of a prepolymer has always been of utmost importance and functionality determinations by various methods have given widely varying results. It is necessary to know the functionality because it is perhaps the most important single factor which determines the nature of the polymer network in binders and propellants.

The expected functionality of Prepolymer 07-147.1 from molecular weight (vapor phase osmometry) divided by equivalent weight (end-group titration) was 1.65. Theoretically a binder of this prepolymer reacted with a 4 to 1 equivalents mixture of HDI and CTI should not cure but actually well cured binders were obtained (Table 6, Binders 5 and 27). Using the crosslink densities determined from compression moduli of the swollen Binders 5 and 20 (Table VI), and the equation for crosslink density

$$X_D = \sum_{i=1}^{i=n} \frac{(f_i - 2)W_i}{f_i E_i} \quad \text{(moles of crosslinks/gm of binder)}$$

where i = the binder ingredient
n = the number of binder ingredients
f = the functionality of the ingredient
W = the weight fraction of the ingredient
E = the equivalent weight of the ingredient

one derived an effective functionality of 1.90. This agreed well with the effective functionality of 1.88 determined for the same prepolymer from the equilibrium moduli during the previous program (Contract AF 04(611)-10386).

Two binders with a calculated crosslink density of zero were prepared from Prepolymer 4507-I-47.1. One was based on the expected functionality of 1.65 (Binder 44, Table VI) and the other on the effective functionality of 1.88 (Binder 45, Table VI). Both of the binders were swollen in toluene; the gel fractions of Binders 44 and 45 were 0.1808 and 0.0721, respectively. This favors the effective functionality value in the range 1.85 to 1.90; especially, inasmuch as the gel fraction of Binder 45 was nearer to zero.

In these experiments, the amounts of extractables were similar. This may indicate the presence of nonfunctional material or low molecular weight prepolymer which was not tied into either of the networks.

The HDI to CTI ratio used in these binders also indicates a prepolymer functionality of approximately 1.90. A prepolymer with a functionality of 1.5, requires a trifunctional curing agent to achieve initial crosslinking, while a prepolymer with a functionality of 2.00 requires only a trace of trifunctional curing agent to achieve crosslinking. At a functionality of 1.65, 70 parts of the trifunctional curing agent and 30 parts of the difunctional curing agent are needed, and at a functionality of 1.90, 20 parts of the tri- and 80 parts of the difunctional agent are required for crosslinking. In these experiments, a 4 to 1 ratio of HDI to CTI was used to achieve a soft (low crosslink density) binder. At an HDI to CTI ratio of 30 to 70, one obtains a very hard (high crosslink density) binder.

On the basis that the extractable materials were mainly nonfunctional and the prepolymer tied into the network contained all of the -OH groups, a calculation predicted a functionality of about 2.1 for the functional units. This was an encouraging result when the approximations involved were considered.

For the formulation of binders and propellants, the effective functionality was more useful than the expected functionality. The differences between the two can be explained by the presence of nonfunctional material in the prepolymer. While association of chains, hydrogen bonding, entanglements, etc., will effect the value of functionality determined from the mechanical behavior of a binder, these effects were minimized by making measurements on a swollen binder.

b. Comparison of Prepolymers

Two lots of prepolymer were used for the experiments reported here. Their properties are summarized in Table II. Lot 242AM-148AH,

the largest (45 lb) and most recent batch of Telagen S delivered to Aerojet to date, was more reddish and cured faster than the older Lot 4507-I-47.1. One binder made with Lot 2h2AM-1h8AH, containing Light Circo Oil, cured within 7 days without additional catalyst; however, it had a soft surface. The propellants made with these prepolymers were similar. Further characterization is being done.

3. Effect of Aluminum Metal on Isocyanate Curing Agents

The loss of isocyanate functionality was measured for toluene solutions of HDI (0.5 gm in 5 gm) both in the absence and presence of aluminum powder (1 gm in 5 gm of solution). With aluminum (30-40μ spherical particles) present, solutions both with and without FeAA catalyst did not show greater loss of isocyanate than when the metal was absent. This demonstrated that aluminum had little or no effect upon the cure stoichiometry of Telagen S propellants.

4. Plasticizer Studies

a. Effect of Plasticizers on Curing Agents

The effect of the plasticizers on the curing agents was determined from solutions containing a plasticizer (5 gm), HDI or phenyl isocyanate (0.5 gm) and a drop of catalyst (Niax D-22 or 0.5 gm FeAA in 10 ml toluene). The disappearance of the isocyanate was followed by conventional titration methods. A summary of the results was shown in a previous report.[1] The quantity [1-(isocyanate remaining in test solution/isocyanate remaining in control solution)] x 100 was designated the cure interference index, but it must be noted that this index was not adopted in the report just cited. This index or the isocyanate remaining for each plasticizer was correlated with the mechanical behavior of binders and propellants containing the plasticizer.

b. Cure-Interference Index for Purified Squalene

Squalene was purified and the loss of isocyanate dissolved in it determined. One portion of the squalene was purified by passage through a column of silica gel and another portion was redistilled under vacuum. These results shown in Table V indicated that impurities in the squalene were affecting the isocyanates. These impurities were not further identified.

It was shown that purifying the plasticizers generally gives better binder properties. The use of vacuum redistilled squalene improved the binder properties (Table VI, Nos. 11 and 32) but squalene-plasticized binders still had poorer properties than other hydrocarbon plasticized binders.

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[1] D. E. Johnson and A. J. Di Milo, "The Development and Evaluation of a Hydrocarbon Binder for High Energy Solid Propellants (U)", First Quarterly Report No. AFRPL-TR-66-159, Aerojet-General Corporation, Sacramento, California, July 1966 (Confidential).

Table V

EFFECT OF PURIFIED SQUALENE ON ISOCYANATES[a]

Purification	Isocyanate[b]	Isocyanate Remaining, %	Cure Interference Index[d]
None	HDI	37	60
	PhNCO	50	
Through Silica Gel	HDI	76	18
	PhNCO	60	
Redistilled, Vacuum	HDI	84	9.3
	PhNCO	82	

[a] FeAA added as a catalyst
[b] Hexamethylene diisocyanate and phenyl isocyanate
[c] Four days at ambient temperature
[d] [1-(Isocyanate Remaining/92.8)] x 100

c. Cure-Interference of Redistilled IDP

A sample of redistilled IDP (Emery Industries) caused a rapid loss in the isocyanate when tested with HDI. This plasticiser was used in Binder 32 (Table VI) and the poor cure confirmed that it did interfere with the cure reaction. Obviously the distillation served to concentrate rather than to remove the offending contaminants. These results also demonstrated the effectiveness of the test to predict at least qualitatively the mechanical behavior of binders containing the plasticiser.

d. Cure Interference of Armeed OD

Armeel OD, oleyl nitrile, was investigated as a plasticizer for Telagen S binders. The binder (Table VI, No. 40) did not cure in 24 days at 135°F. Armeel OD had been used in other programs with propellants containing MAPO and BISA (aziridine) curing agents. These propellants had poorer mechanical properties and aging stability than propellants containing the plasticizer IDP. Passing Armeel OD through a column of silica gel improved the propellant properties which, however, were still inferior to those IDP plasticized binders. These results demonstrated that problems of plasticizer interference with curing reactions might be common to all curing systems and had gone unnoticed because the interference had been confused with plasticizing action.

5. Binder Studies

a. Introduction

Binders were prepared to study plasticizers and their effects on the mechanical properties and cure stoichiometry. All of the current results are shown in Table VI, which includes binders prepared from two batches of Telagen S (8407-1-47.1 and 242AM-148AH) and an unsaturated prepolymer (Lot 242AM-148A) of approximately the same equivalent weight. The table presents crosslink densities by compression moduli of swollen binders and by equilibrium moduli, gel fraction, sol fractions, uniaxial mechanical properties at 77°F and the Mooney-Rivlin constants. The mechanical properties of the binders containing equal volumes of plasticizer are in Table VII.

b. Effect of Plasticizers on Binder Properties

The hydrocarbon oils, Light Circo Oil, Nujol and Oronite-6 have shown the least amount of interference with cure both in tests with HDI and in binders. The plasticizers S-141, Ansul Ether 181, Undecyl Cyanide and Arneel OD have shown the most interference. The esters DOZ, IDP, and DOS are intermediate in this respect. The n-undecyl cyanide and the Ansul Ether 181 were not improved by passage through a column of silica gel, although other purification techniques were not tried.

While vacuum distillation improved the squalene, the improvement has not been sufficient to make the squalene as inert a plasticiser for Telagen S binders as the hydrocarbon, Nujol and Light Circo Oil.

c. Compatibility of Plasticizers with Telagen S Binders

Some visual observations of plasticizer compatibility with the Telagen S-CTI-HDI binders were made. The binders contained 26 vol % of plasticizer. S-141-plasticized binders tended to exude; the exudate was presumed to be plasticizer. The binder containing Oronite-6 was cloudy, whereas the binders with Nujol and Circo Oil were slightly hazy. The clearest binder was one with IDP.

d. Correlation of Crosslink Density Measurements

Mooney-Rivlin C_1 constants, crosslink densities from the compression moduli of toluene swollen binders and the gel fraction, v_g, are related by line functions (Figures 1 to 3). The crosslink densities from compression moduli of toluene swollen binders and the crosslink densities from stress relaxation measurements at 150°F are compared in Figure 4. The stress relaxation data at 150°F gave lower crosslink densities than those at 77°F. The binders may not have reached complete equilibrium relaxation at 77°F and may not at 150°F either because crosslink densities from relaxation data are higher than those from compression moduli studies. Swelling of the binders for the compression moduli determination eliminated the effects of crystallinity and hydrogen bonding and minimized the effect of entanglements.

Table [illegible]

EFFECT OF PLASTICIZERS AND STOICHIOMETRY ON THE MECHANICAL BEHAVIOR OF TELAGEN S BINDERS[a] CURED AT 135°F

Part A, Esters

Reference No.	Plasticizer	% Weight	Plasticizer Treatment[b]	Cure Time, Days	NCO/OH	Mechanical Properties S_m psi	ϵ_m %	ϵ_b %	E_0 psi	Mooney-Rivlin C_1 kg/cm²	C_2 kg/cm²	Crosslink Density[c] Mole Chains/cc×10[4] A	B	C	Gel Fraction v_e	Sol Fraction[d]
44[h]	None	0.0	None	6	1.00	-	-	-	-	-	-	-	-	-	0.1808	-
5	None	0.0	None	6	1.00	74	478	478	69	0.23	0.57	1.90	3.37	2.33	0.079	0.341
27	None	0.0	None	6	1.00	96	425	425	64	0.34	0.70	-	-	-	0.0972	-
45[h]	None	0.0	None	6	1.00	-	-	-	-	-	-	-	-	-	0.0718	-
1	None	0.0	None	7	1.05	65	358	358	72	0.28	0.57	1.72	-	2.62	0.0908	0.220
28	IDP	10.0	SiO_2	6	1.00	63	380	380	56	0.263	0.412	-	-	-	0.0871	-
8	IDP	20.0	None	6	1.00	30	520	e	20	0.10	0.13	1.025	-	-	0.0544	0.282
6	IDP	20.4	SiO_2	6	1.00	43	536	537	22	0.14	0.16	1.285	-	1.74	0.0613	0.268
29	IDP	20.0	SiO_2	6	1.00	41	355	355	36	0.225	0.200	-	-	-	0.0697	-
17a	IDP	25.0	SiO_2	0.75	1.00	24	480	e	34	0.095	0.093	0.753	-	-	0.0558	0.346
17b	IDP	25.0	SiO_2	2	1.00	29	440	440	36	0.104	0.096	1.125	-	-	0.0583	0.251
17c	IDP	25.0	SiO_2	5	1.00	26	450	450	19	0.109	0.108	0.992	-	-	0.0598	0.241
17d	IDP	25.0	SiO_2	14	1.00	30	476	476	19	0.115	0.112	1.10	-	-	0.0602	-
39[f]	IDP	25.0	SiO_2	6	1.00	Data not available.									0.0657	-
40[f]	IDP	25.0	SiO_2	6	1.00	Data not available.									0.046	-
47[g]	IDP	25.0	SiO_2	7	1.00	Data not available.									0.0475	-
31	IDP	25.0	Red.	6	1.30	Sample did not cure completely					-	-	-	-	-	-
30	IDP	30.0	SiO_2	6	1.00	36	435	435	23	0.157	0.111	-	-	-	0.0653	-
2	IDP	10.0	SiO_2	7	1.05	37	385	385	41	0.22	0.26	1.60	3.2	2.53	0.0809	0.257
3	IDP	20.0	SiO_2	7	1.05	32	37[illegible]	375	23	0.25	0.17	1.17	2.04	1.75	0.0668	0.234
46-3	IDP	25.0	None	-	1.35	34	460	462	22	0.24	0.13	1.25	1.60	1.58	0.0654	-
4	IDP	30.0	SiO_2	7	1.05	30	386	385	16	0.20	0.10	1.185	1.35	1.39	0.0566	0.352
18A	DOZ	26.3	None	3	1.00	23	540	540	12	0.079	0.074	0.585	-	-	0.0502	0.370
18	DOZ	26.3	None	5	1.00	23	511	512	13	0.084	0.070	0.750	-	-	0.0499	0.264
19	DOZ	26.3	SiO_2	5	1.00	28	454	454	20	0.109	0.106	1.164	-	-	0.0603	0.284
17-2	DOZ	25.0	MS	10	1.05	46	472	472	24	0.16	0.17	1.41	2.23	1.96	0.0608	0.345
37	DOZ	26.2	None	6	1.00	Data not available.									0.0579	-

[a] Secondary hydroxy-terminated saturated hydrocarbon prepolymer (Lot 8507-I-47.1) cured with a 1 to 4 equivalents ratio of . and HDI; HDI to CTI ratio = 0.94 for No. 44, 4.25 for No. 45, and 1.0 for No. 39.

[b] MS = contacted with Linde Molecular Sieves; SiO_2 = passed through column of silica gel; red. = redistilled in vacuum.

[c] A = from compression moduli of swollen samples; B & C = from equilibrium moduli by stress relaxation at 77 and 150°, respectively.

[d] (weight of extractables - weight of plasticizer)/(weight of sample - weight of plasticizer).

[e] Bond failure or no break.

[f] Prepolymer Lot 8424M-148M.

[g] Unsaturated Prepolymer Lot 8424M-148.

[h] No cure catalyst added.

Table III, Part A Continued

Reference No.	Plasticizer	% Weight	% Stiffener, % Amount[b]	Cure Time, Days	NCO/OH	Mechanical Properties S_m psi	ϵ_m %	ϵ_b %	E_0 psi	Hyper-Elastic C_1 lb/in²	C_2 lb/in²	Crosslink Density[c] Main Chain/cc x10 A	B	C	Gel Fraction V_e	Sol Fraction[d]
23	S-141	39.5	None	6	1.00	17	779	803	6	0.033	0.0[illegible]	0.283	-	-	0.027	-
9	S-141	25.0	[illegible]	6	1.00	25	510	*	13	0.06	0.11	0.647	-	-	0.0408	-
10	S-141	25.0	SiO_2	6	1.00	20	510	*	16	0.07	0.11	0.821	-	-	0.0498	-
17-3	S-141	25.0	[illegible]	10	1.05	30	506	506	26	0.13	0.16	1.26	1.02	1.70	0.0609	-
						Part B, Hydrocarbon Oils										
37	None	0.0	None	6	1.00	56	425	425	64	0.34	0.70	-	-	-	0.0977	-
40	Oronite "6"	24.6	[illegible]	6	1.00	-	-	-	-	-	-	-	-	-	0.0738	-
22	Oronite "6"	24.5	SiO_2	6	1.00	25	764	764	17	0.088	0.160	0.361	-	-	0.0596	-
17-1	Oronite "6"	25.0	[illegible]	10	1.05	40	400	400	34	0.20	0.24	1.88	2.60	2.45	0.076	0.180
24	Light Circo Oil	9.1	[illegible]	5	1.00	65	406	406	60	0.25	0.485	-	-	-	0.089	-
25	Light Circo Oil	18.2	[illegible]	5	1.00	44	372	372	48	0.203	0.318	-	-	-	0.076	-
20	Light Circo Oil	22.9	[illegible]	5	1.00	42	566	566	31	0.130	0.194	1.40	-	-	0.0673	0.719
40B	Light Circo Oil	22.9	[illegible]	5	1.00	No data available.									-	-
40A[h]	Light Circo Oil	22.9	[illegible]	7	1.00	No data available									0.0593	-
26	Light Circo Oil	27.7	[illegible]	5	1.00	34	430	430	29	0.246	0.175	-	-	-	0.0636	-
17-4	Light Circo Oil	25.0	None	10	1.05	52	404	404	38	0.204	0.250	2.38	3.38	2.73	0.0728	0.271
41	Squalane	25.0	Red.	6	1.00	-	-	-	-	-	-	-	-	-	0.0674	-
10-8	Nujol	25.0	[illegible]	10	1.05	43	354	355	34	0.20	0.21	1.05	2.11	2.45	0.0809	-
43	Nujol	25.2	[illegible]	6	1.00	-	-	-	-	-	-	-	-	-	0.0777	-
11	Squalane	25.0	None	6	1.00	13	690	*	8	-	-	-	-	-	0.0[illegible]	-
37	Squalane	24.9	Red. B	6	1.00	40	775	775	18	-	-	-	-	-	0.0437	-
38	Squalane	24.9	Red. A	6	1.00	-	-	-	-	-	-	-	-	-	0.0283	-
16-1	Squalane	25.0	[illegible]	10	1.05	18	498	*	11	0.08	0.07	0.449	0.71	0.68	0.0424	-
7	Squalane	25.0	SiO_2	6	1.05	15	500	*	25	0.07	0.12	0.61	0.90	0.90	0.044	0.373
						Part C, Miscellaneous										
24	Amyl Ether 181	25.0	None	6	1.00	Dissolved in toluene and trichloroethylene										
15	n-Undecyl Cyanide	25.0	None	3	1.00	29	425	425	22	0.122	0.130	0.95	-	-	0.0586	-
16	n-Undecyl Cyanide	25.0	SiO_2	3	1.00	30	500	500	18	0.105	0.173	0.904	-	-	0.0564	-
21	n-Undecyl Cyanide	24.8	SiO_2	6	1.00	25	482	482	19	0.085	0.095	0.884	-	-	0.0518	-
36	Armeel-3D	25.0	SiO_2	14	1.00	Did not cure.										

For footnotes see Part A, first page.

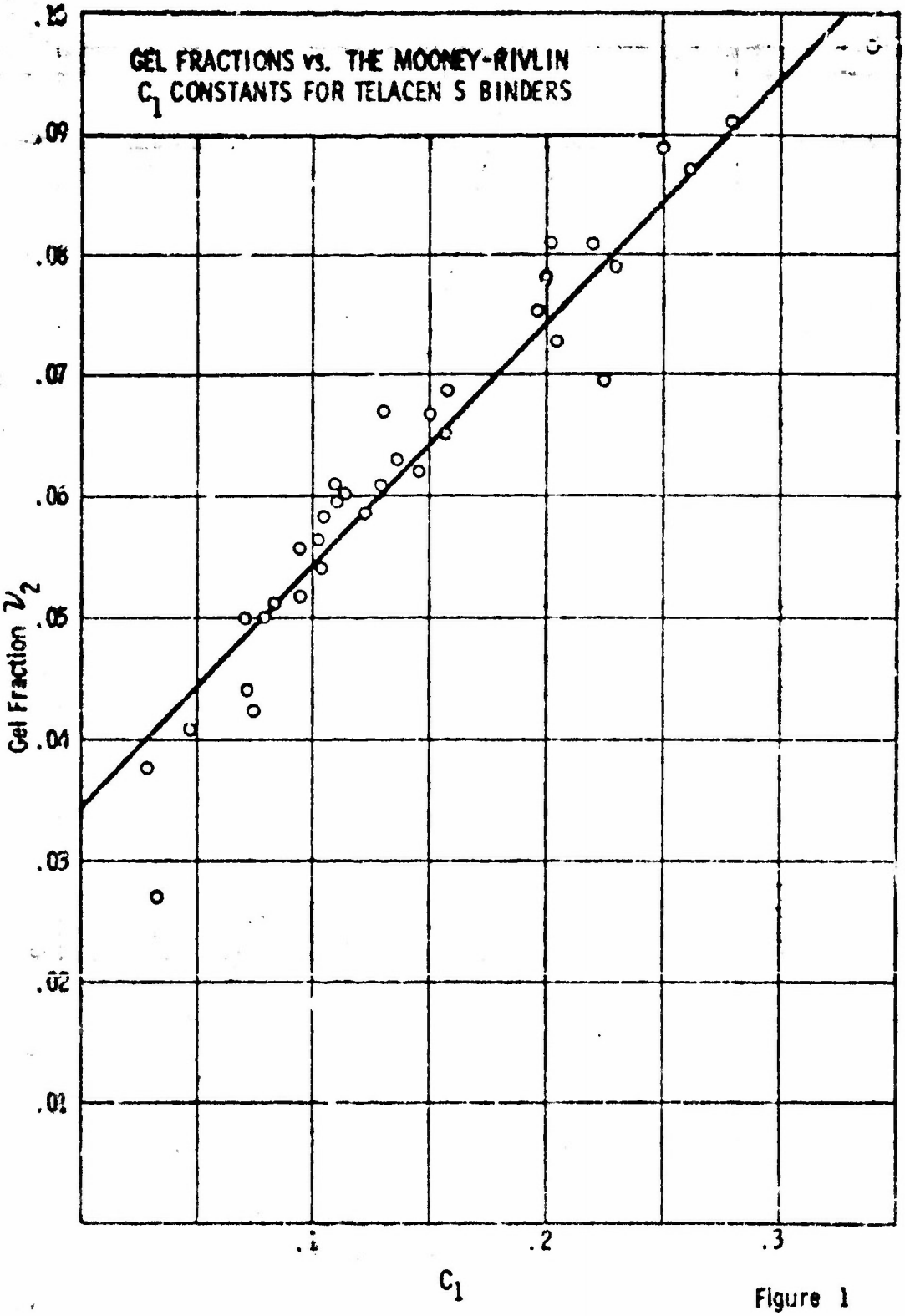
GEL FRACTIONS vs. THE MOONEY-RIVLIN
C1 CONSTANTS FOR TELACEN S BINDERS
Gel Fraction ν2
.09
.08
.07
.06
.05
.04
.03
.02
.01
.1
.2
.3
C1

Figure 1

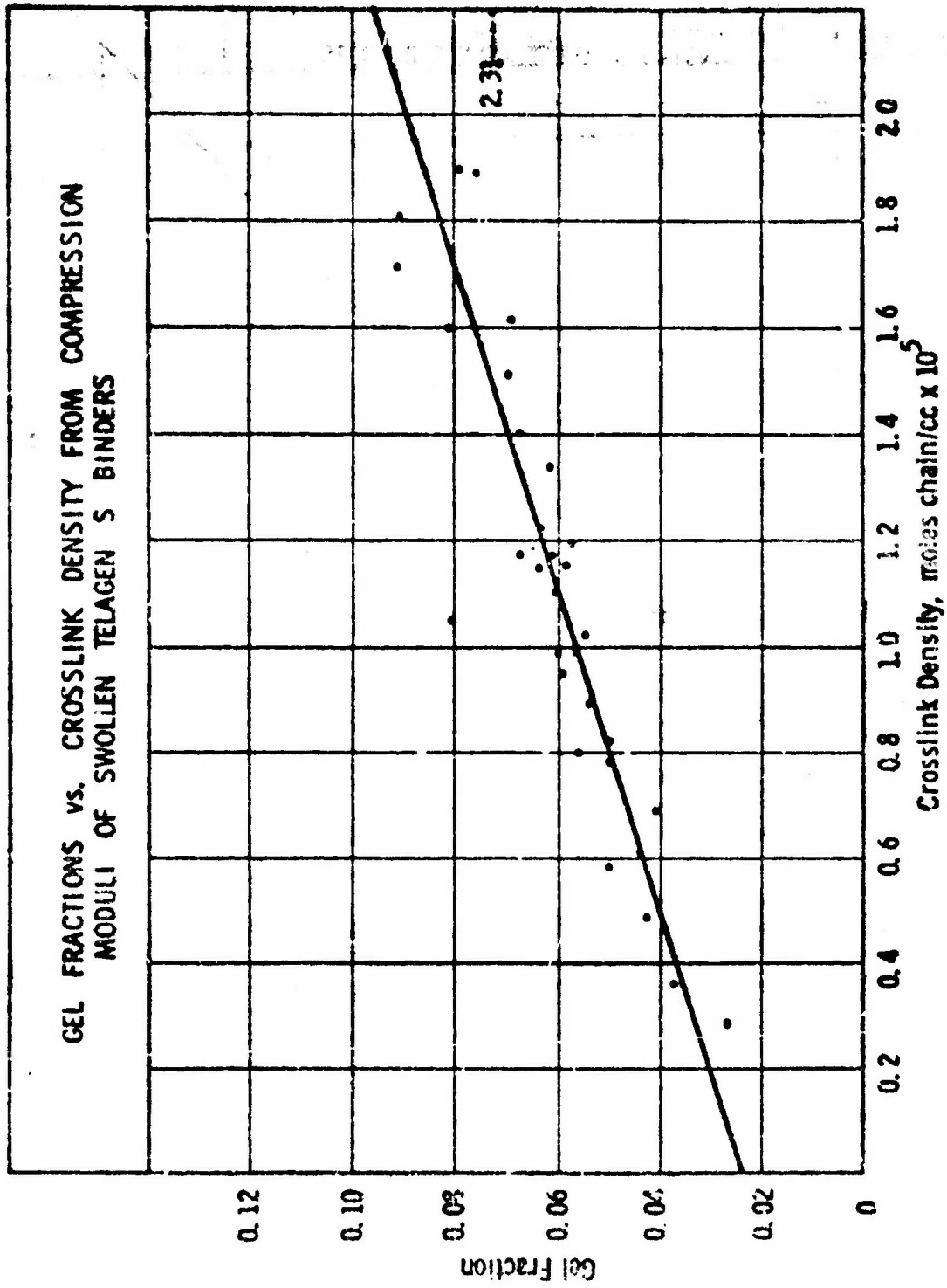
GEL FRACTIONS vs. CROSSLINK DENSITY FROM COMPRESSION MODULI OF SWOLLEN TELAGEN S BINDERS
2.31
Gel Fraction
0.12
0.10
0.08
0.06
0.04
0.02
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Crosslink Density, moles chain/cc x 10^5

Figure 2

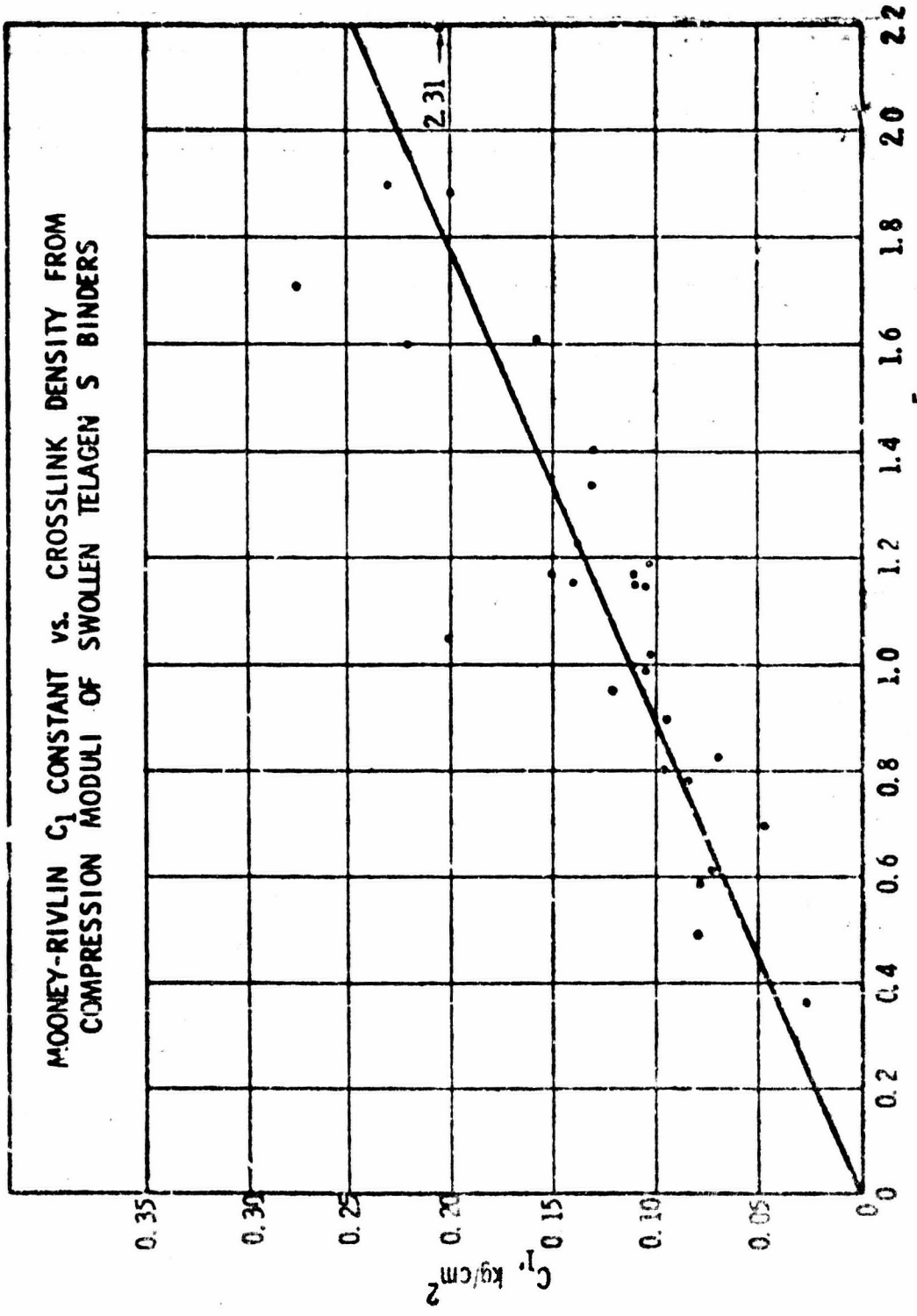
MOONEY-RIVLIN C_1 CONSTANT vs. CROSSLINK DENSITY FROM COMPRESSION MODULI OF SWOLLEN TELAGEN S BINDERS
2.31
C_1, kg/cm^2
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Crosslink Density, moles chain/cc x 10^5

Figure 3

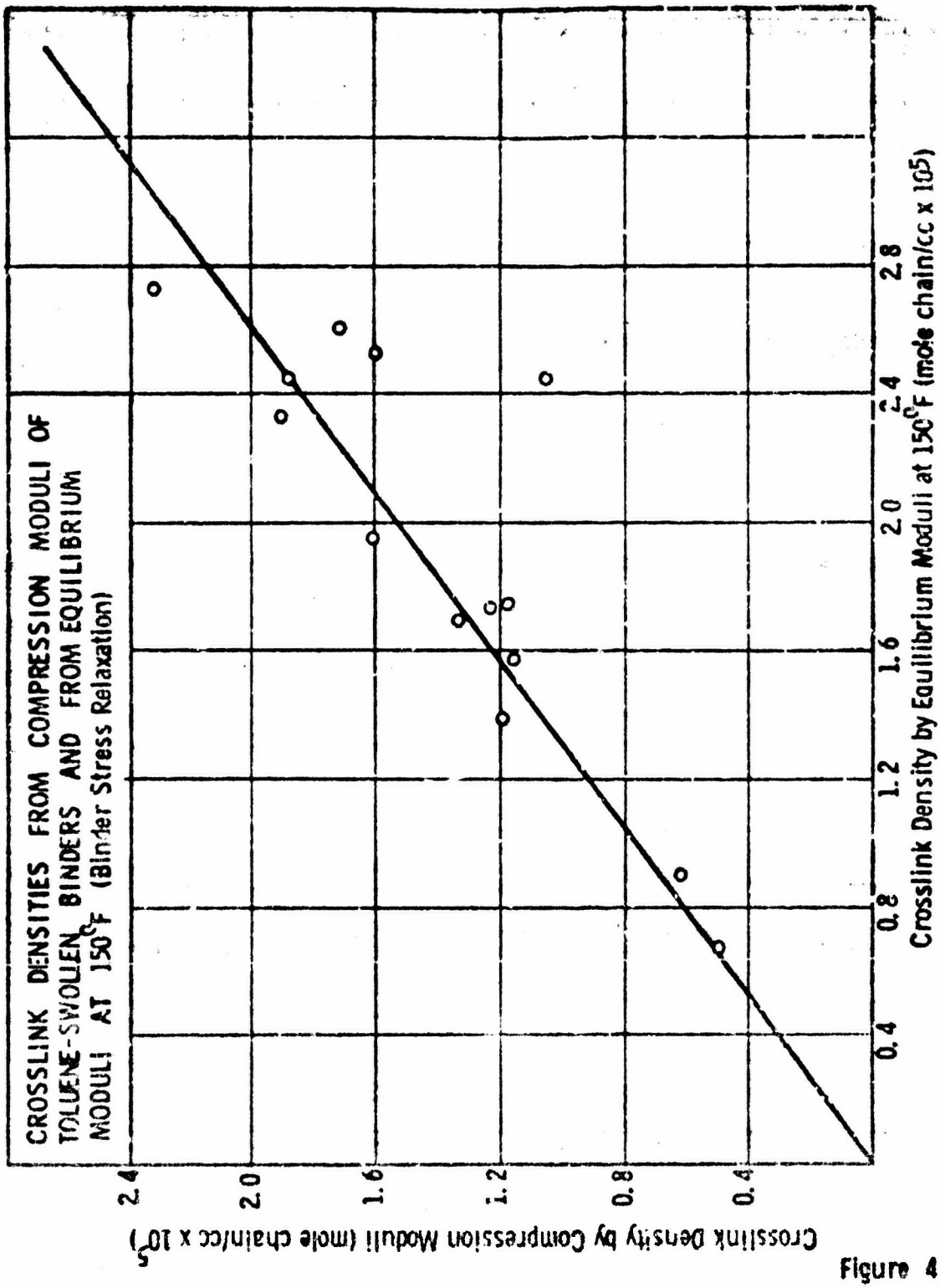
CROSSLINK DENSITIES FROM COMPRESSION MODULI OF TOLUENE-SWOLLEN BINDERS AND FROM EQUILIBRIUM MODULI AT 150°F (Binder Stress Relaxation)
Crosslink Density by Compression Moduli (mole chain/cc x 10⁵)
2.4
2.0
1.6
1.2
0.8
0.4
0.4
0.8
1.2
1.6
2.0
2.4
2.8
Crosslink Density by Equilibrium Moduli at 150°F (mole chain/cc x 10⁵)

Figure 4

Table VII

GEL FRACTION, UNIAXIAL TENSILE BEHAVIOR OF PLASTICIZED TELAGEN S-CTI-HDI BINDERS[a]

Reference No.	Plasticizer	Cure Interference Index	S_{ss} psi	γ_{ss} %	E_o psi	Gel Fraction x 10^2
43	Nujol	0.3	-	-	-	7.3
42	Cronite-6	4	-	-	-	7.3
20	Light Circo Oil	6	48	566	31	7.4
21	n-Undecyl Cyanide	9	25	482	19	5.2
32	Squalene	9	40	775	18	4.4
17C	IDP	18	26	450	19	6.0
19	DOZ	19	28	454	20	6.2
22	S-141	26	17	779	6	2.7

[a] Plasticizer content 26 vol %; binder composition, Table VI.

e. Initial Tensile Modulus and Gel Fraction of Binders

The plot log E_o (initial uniaxial tensile modulus) vs. v_s was apparently a straight line (Figures 5 and 6), indicating the relationship $v_s = a + n \log E_o$. For hydrocarbon oils (n = 14.8) n was slightly less than for the esters (n = 17.4). Tensile stress data fitted this general relationship, but the points were more scattered because the measured tensile stresses were more dependent upon random binder flaws.

Two series of binders were prepared using IDP (purified with SiO_2) and Circo Oil as representatives of the two main classes of plasticizers. Plotting either initial tensile moduli, E_o, or the gel fractions, v_s, vs. the volume fraction of plasticiser, one found the Circo Oil interfered less with the cure reactions (Figures 7 and 8).

In general, hydrocarbon plasticizers interfered less with the cure reaction in binders than did the ester plasticisers. This was consistent with the results obtained from isocyanate loss of HDI-plasticiser mixtures. Preliminary binder studies indicated that prepolymer 242AM-148AH gave binder with lower crosslink densities than those of prepolymer 8507-I-47.1 binders

f. Swelling of Binders

Swelling of binder samples with the cyanide-type plasticizers gave erroneously high gel fractions because the extracted plasticiser was

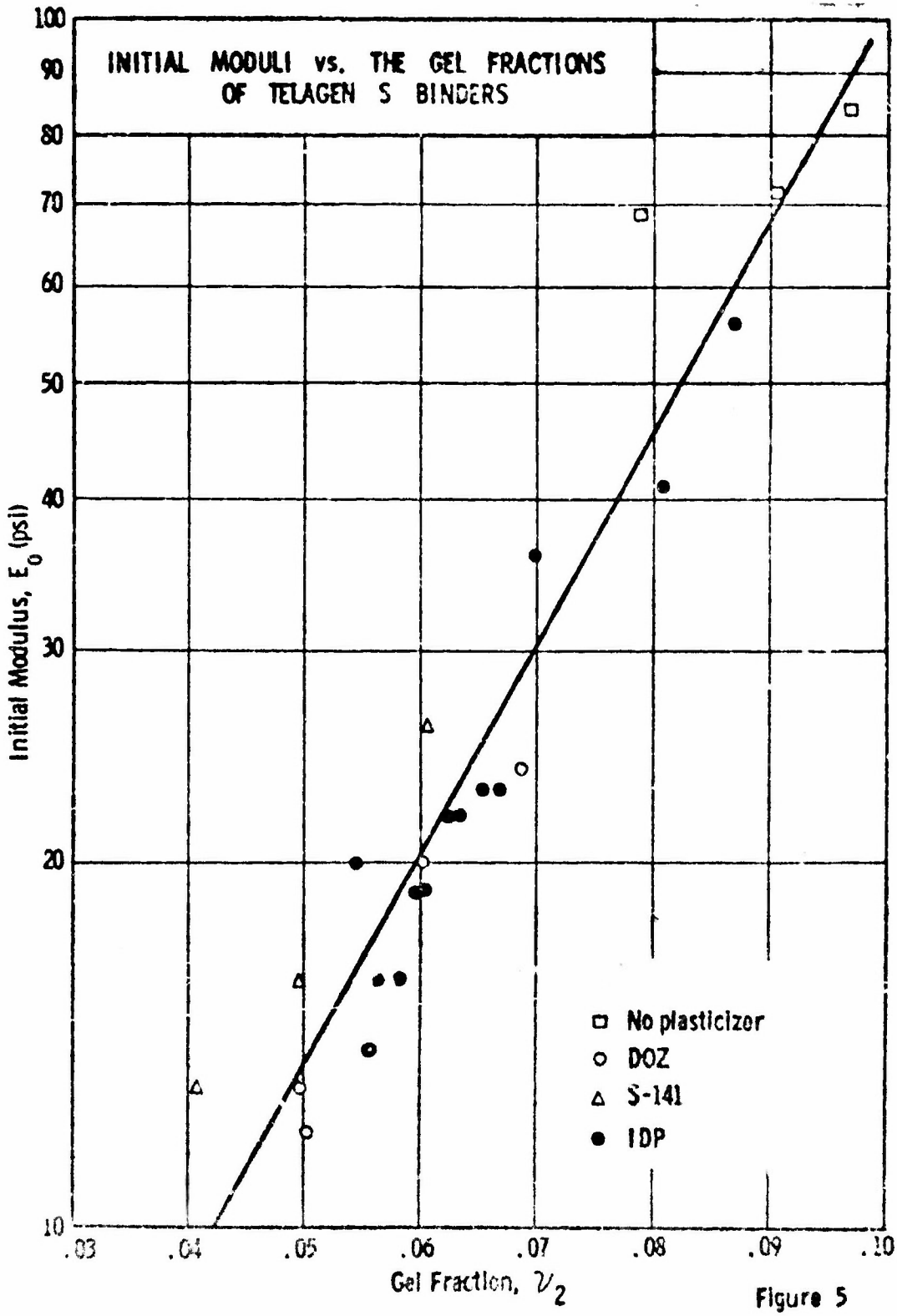
INITIAL MODULI vs. THE GEL FRACTIONS OF TELAGEN S BINDERS
Initial Modulus, E_0 (psi)
100
90
80
70
60
50
40
30
20
10
.03
.04
.05
.06
.07
.08
.09
.10
Gel Fraction, ν_2
No plasticizor
DOZ
S-141
IDP

Figure 5

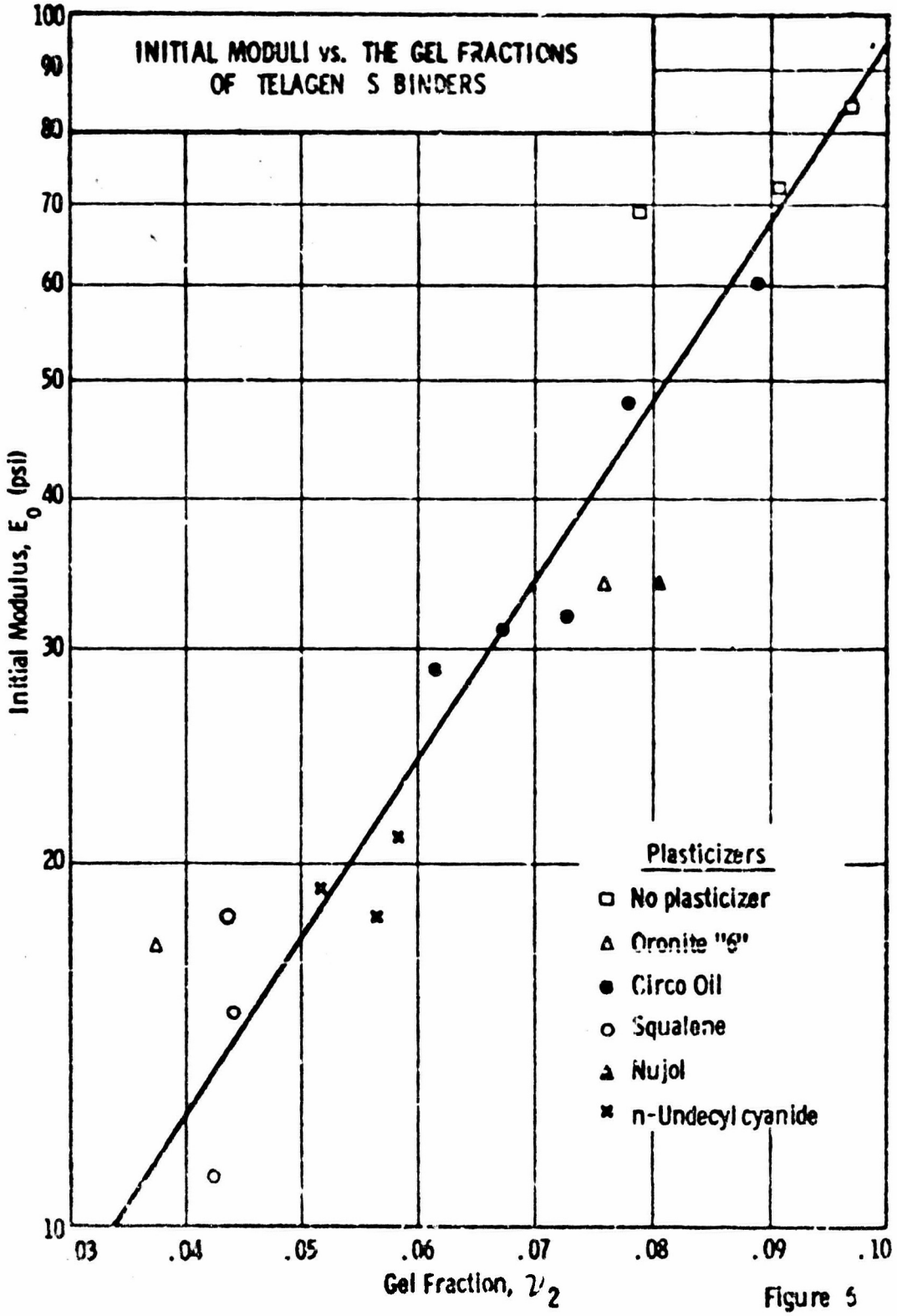
INITIAL MODULI vs. THE GEL FRACTIONS
OF TELAGEN S BINDERS
Initial Modulus, E_o (psi)
100
90
80
70
60
50
40
30
20
10
.03
.04
.05
.06
.07
.08
.09
.10
Gel Fraction, ν_2
Plasticizers
No plasticizer
Oronite "6"
Circo Oil
Squalene
Nujol
n-Undecyl cyanide

Figure 5

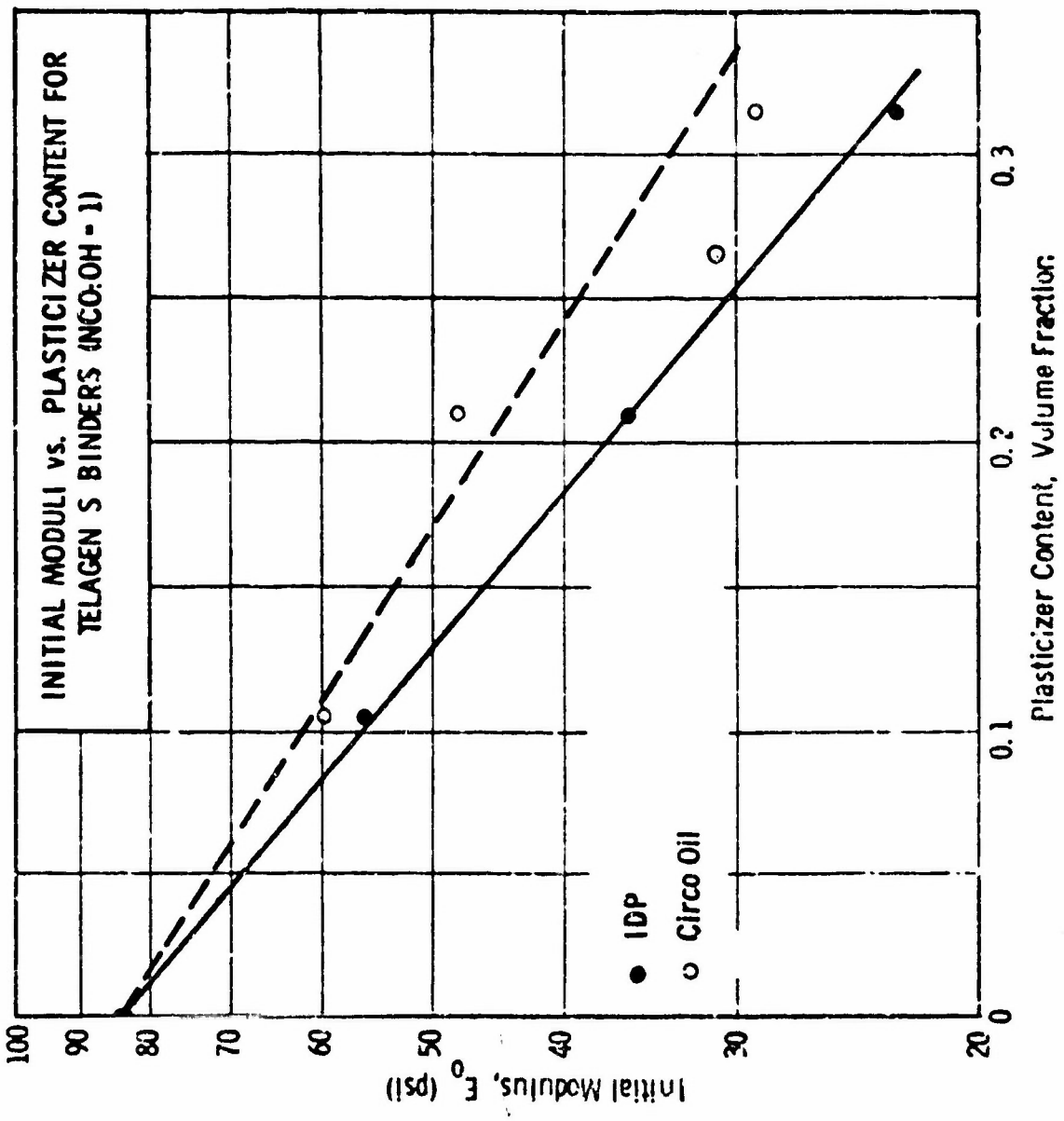
INITIAL MODULI vs. PLASTICIZER CONTENT FOR
TELAGEN S BINDERS (NCO:OH - 1)
IDP
Circo Oil
Initial Modulus, E_o (psi)
Plasticizer Content, Volume Fraction
100
90
80
70
60
50
40
30
20
0
0.1
0.2
0.3

Figure 7

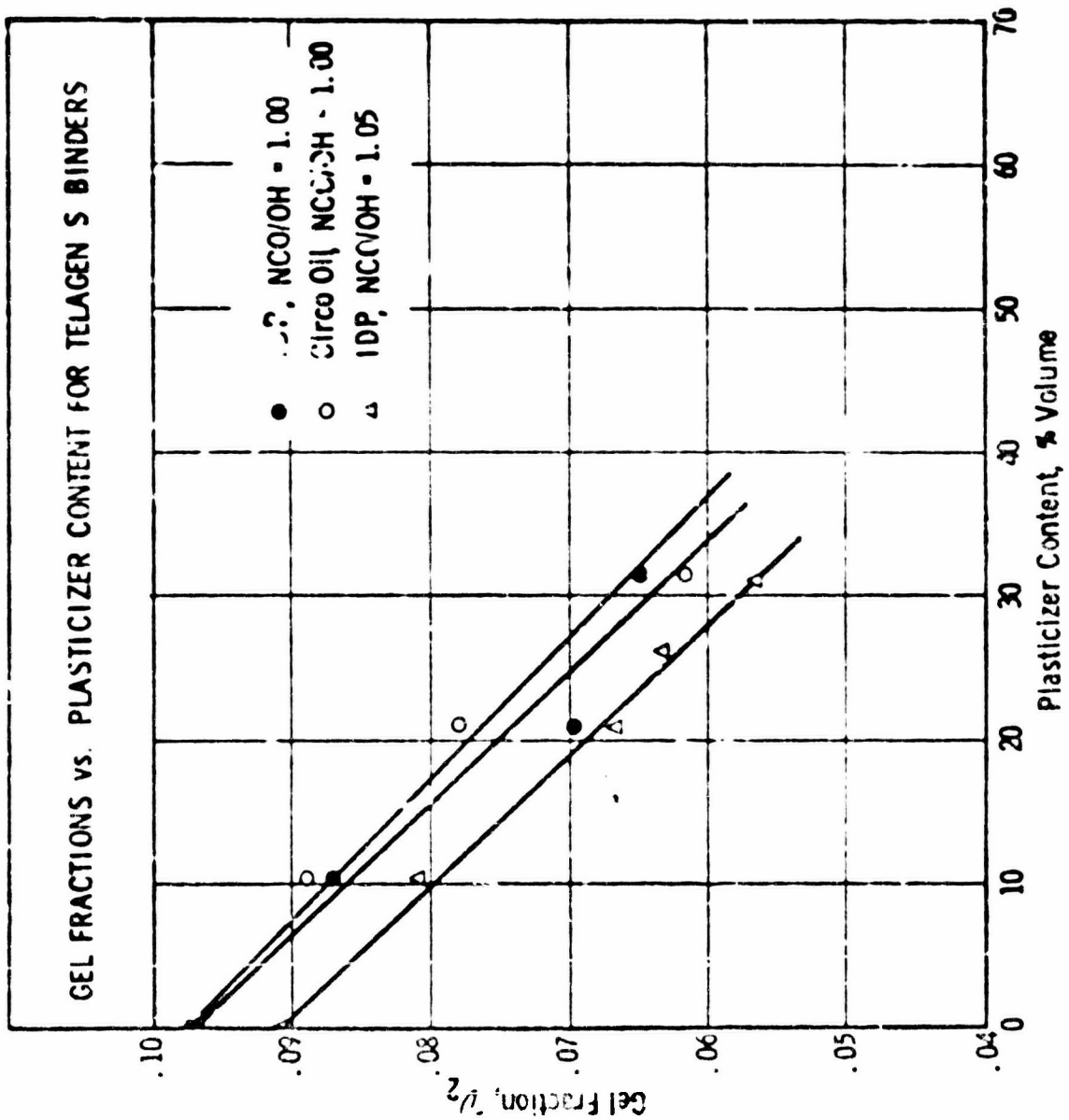
GEL FRACTIONS vs. PLASTICIZER CONTENT FOR TELAGEN S BINDERS
●, NCO/OH = 1.00
○ Circo Oil, NCO/OH = 1.00
△ IDP, NCO/OH = 1.05
Gel Fraction, y_2
.10
.09
.08
.07
.06
.05
.04
0
10
20
30
40
50
60
70
Plasticizer Content, % Volume

Figure 8

evaporating with the swelling solvent (toluene) during isolation of the extractables. The weight of extractables was therefore determined from the difference in the weights of the original sample and the deswollen sample (solvent removed in vacuo). This method gave more reliable values for the extractables in the cyanide-plasticised binders. Several of the swollen binders with other types of plasticisers were deswollen and the amounts of extractables determined by this method. In most cases, the amount of extractables by this method agreed within 5% or less with that determined by weight of non-volatiles in the swelling solvents.

Samples of a non plasticised binder of known crosslink density were placed in several plasticisers and their swelling characteristics are currently being determined. Of these plasticisers IDP, n-undecyl cyanide and squalene cause the more rapid swelling; the other plasticizers being studied include, DOS, Light Circo Oil, Oronite-6 and Nujol. The data from the experiment will be used to calculate the Flory-Huggins interaction parameter for the plasticizer.

Telagen S-CTI-HDI binders were swollen in a large number of solvents (see previous Quarterly Report) of which tetrahydrofuran and carbon tetrachloride were the best. A plot of maximum swelling vs the cohesive energy density of the swelling solvent showed two peaks, at CED = 73.6 and 86.8, with a minimum at about CED = 81.6. Some additional solvents were studied, and the swelling data are reported in Table VIIa along with data from the previous quarter.

The data were very inconsistant and the idea of a twin maximum in the maximum swelling - CED curve was difficult to substantiate. There was definitely a peak CED = 70 to 90, but the data did not locate it more exactly.

g. Catalysts

The recently acquired prepolymer, Telagen S Lot 1148AH, is being used to determine the efficiency of the isocyanate cure catalysts, CoAA, FeAA, Niax D-22, and FeAA and Niax D-22 in combination with added acetylacetone. CoAA was slower than the other catalysts and produced a binder with a tacky surface. The binders are being swollen to determine the extent of the cures.

6. Propellant Studies

Propellants (50 gm) were made to study the effects of CTI to HDI ratio, NCO to OH ratio, plasticizers and catalyst levels, and replacement of DBA by C-1. The best formulations were used to make 1-lb batches. The data are summarized in Table VIII. All propellants contained 88 wt% solids.

Both the new prepolymer and the old prepolymer were tested. Some general observations are presented below.

a. Use of DOS and IDP gave about the same properties in these formulations.

Table VII.

MAXIMUM SWELLING AND THE COHESIVE ENERGY DENSITIES OF SOLVENTS

Solvent	CED	Maximum Swelling ml solvent/g binder
Methanol	209	0.062
Nitromethane	159	0.11
Dimethylformamide	147	0.149
Acetonitrile	139	0.05
Isopropanol	132	0.178
Pyridine	112.5	0.678
Nitrobenzene	108.3	0.261
Ethylene Dichloride	98.1	0.92
Methylene Chloride	97.6	1.62
Dioxane	94.6	0.85
Acetone	93.3	0.168
Chlorobenzene	90.2	2.91
Tetrahydrofuran	86.8	4.70
Chloroform	85.3	3.36
Benzene	83.6	3.42
Methyl Ethyl Ketone	81.7	0.55
Ethyl Acetate	81.6	0.50
Toluene	79.3	4.12
Mesitylene	77.4	3.06
Xylene	77.4	2.86
Carbon Tetrachloride	73.6	4.68
Cyclohexane	66.8	3.68
Ethyl Ether	59.8	1.52
n-Heptane	55.0	2.38
n-Hexane	52.4	2.32

Table XXX

[illegible] BEHAVIOR OF [illegible] PROPELLANTS[a] AT 77°F

Reference No.	Prepolymer	Plasticizer	Treatment[b]	[illegible]	NCO/OH	Catalyst[c]	%	Castability[d] at 135°F Reading	Time Taken	Cure Time, Days, 135°F	Hardness[e] Top	Bottom	Initial	Mechanical Properties at 77°F σm psi	σb psi	εm %	εb %	E0 psi
1.	47.3	IDP	SiO_2	3.5	1.05	FeAA AAA	0.002 0.006	18	1.5	4	76	80	71	174	165	31	33	800
2.	47.3	PNB	None	3.5	1.05	FeAA AAA	0.002 0.006	22	0.5	4	80	46	45	188	184	30.5	37	775
3.	47.3	IDP	SiO_2	3.5	1.00	FeAA AAA	0.002 0.006	20	0.0	6	68	63	72	197	190	29.5	31	990
4.	47.3	IDP	SiO_2	4.0	1.05	FeAA AAA	0.002 0.006	21.5	0.0	6	73	73	75	181	173	34	40	640
5.	47.3	Light Circo Oil	MS	3.5	1.05	FeAA AAA	0.002 0.006	20	0.0	6	82	84	82	225	225	34.5	35	1290
7.	47.3	DOB	None	3.5	1.05	FeAA AAA	0.002 0.006	22	0.5	6	70	69	75	169	164	30	31.5	685
8.	47.3	DOB	None	3.5	1.05	FeAA AAA	0.002 0.006	22	0.5	6	78	70	79	163	161	30	32	825
9.	47.3	DOB	None	3.5	1.05	CoAA	0.01	13.5	0.5	6	69	76	81	171	119	32	33.5	910
10.	[illegible]	IDP	SiO_2	3.5	1.00	FeAA AAA	0.002 0.006	22	0.25	6	64	66	66	186	180	28	29	1065
11.	[illegible]	DOB	None	3.5	1.00	FeAA AAA	0.002 0.006	20	0.75	6	66	67	64	192	186	27.5	28.5	1205
12.	[illegible]	IDP	SiO_2	3.5	1.05	FeAA AAA	0.002 0.006	22.5	0.0	6	76	79	77	178	176	25.5	26.5	1085[e]
13.	[illegible]	DOB	None	3.5	1.05	FeAA AAA	0.002 0.006	23	0.0	6	68	67	71	176	172	26	27	1036

[a]All propellants were [illegible] batches and contained 75.6 vol % solids, Telagen A, C-1 (0.25), HDI and OPI; plasticizer = 25 wt% of binder. All were processed at 135°F except 7 and 10-13 which were mixed at 110°F.

[b]SiO_2 = passed through silica gel; MS = dried over molecular sieves.

[c]FeAA = ferric acetylacetonate; CoAA = cobaltic acetylacetonate; AAA = acetylacetone.

[d]10 sec. plastimeter reading taken at the indicated hours after casting; > 21 = excellent, 20-21 = good, 19-20 = fair, 16-19 = poor, and < 16 = not castable.

[e]15 sec.

b. Light Circo Oil gave a higher modulus propellant at the same HDI to CTI ratio than obtained with either DOS or IDP.

c. Propellants with the NCO to OH ratio of 1.00 had higher maximum or break tensiles and initial moduli than those at a ratio of 1.05. This reflected the highly stoichiometric nature of the cure reactions even in the propellant.

d. The HDI to CTI ratio of 4.0 appeared to give propellants of lower initial moduli and greater maximum elongation than those at a ratio of 3.5. This greater elongation was desirable.

e. The stress-strain curves showed that the τ_m and the τ_b values were nearly the same; hence, oxidizer dewetting was minimal.

f. These propellants could be mixed at 110°F, and possibly they could be made at lower temperatures. Although these propellants were cured at 135°F, small samples have been cured at 110°F.

g. CoAA was not as satisfactory as the other catalysts in the formulations which contained C-1 as the bonding agent.

The pot life was relatively short with propellants processed at 125°F, but was extended by processing at 110°F. A propellant similar to No. 10 (Table VIII) but containing 0.0013% FeAA and 0.007% HAA, was divided and samples were cured at 110°F and 135°F. Plastimeter readings for the samples taken over a period of seven hours are shown in Table IX.

Table IX

PLASTIMETER READINGS OF PROPELLANT CURING AT 110°F AND 135°F

	Time (hours) After Casting				
Temperature	0.25	1	3.25	4.5	6.75
110°F	23	23.5	20	18.5	16.5
135°F		21.5	15		

While there was considerably more potlife at the lower temperature, both propellants cured normally.

7. Propellant Burning Rates

A preliminary strand burning rate study was made for an NH_4ClO_4-Al propellant (88 wt% solids) similar to No. 4 in Table VIII. The burning rates at 400 and 700 psia were 0.20 and 0.27 in./sec, respectively at 80°F. Over the range 400 to 1500 psia, the pressure exponent of burning was 0.70. The pressure exponent was high compared to unsaturated hydrocarbon binders with the same solids, and would require further study to lower it

when required. The burning studies are summarized in Figure 9.

8. Maximum Solids Loaded Propellant

a. Solids Loading and Packing

1) Ratio of Solids to Binder Volumes

One of the advantages of a propellant binder with a highly efficient network structure is its ability to retain good mechanical properties when loaded with a greater amount of ballistic solids. Notwithstanding this advantage, the problem of achieving a higher solids loading without loss of mechanical properties is a difficult one. This is demonstrated by the ratio of the solids volume to the binder volume (including the plasticizer) and the volume fraction of solids for a number of actual and projected systems with a saturated hydrocarbon binder (Table X).

As the solids loading increases beyond the state-of-art value of 88 wt%, the ratio of the solids volume to binder volume increases greatly. This ratio becomes even greater at low temperature since the volume of the binder decreases more rapidly than that of the filler.

Table X

THE RATIO OF SOLIDS TO BINDER VOLUMES AND VOLUME FRACTION OF SOLIDS FOR VARIOUS PROPELLANT SYSTEMS

Propellant	Wt% Solids	Volume Fraction of Solids	Volume of Solids / Volume of Binder
Polaris	75	62.4	1.6
Minuteman Wing II (2nd Stage)	82.2	69.0	2.2
Tartar (sustainer)	82	70.0	2.3
Minuteman Wing VI (2nd Stage)	88	75.6	3.3
System 1[a]	90	80.2	4.1
System 2[a]	92	84.0	5.2

[a] System 1: 80% NH_4ClO_4, 10% Al; System 2: 84% NH_4ClO_4, 8% Al

2) Importance of Particle Packing

The importance of packing of solid particles is well known as exemplified by the extensive use of bi- and trimodal particle

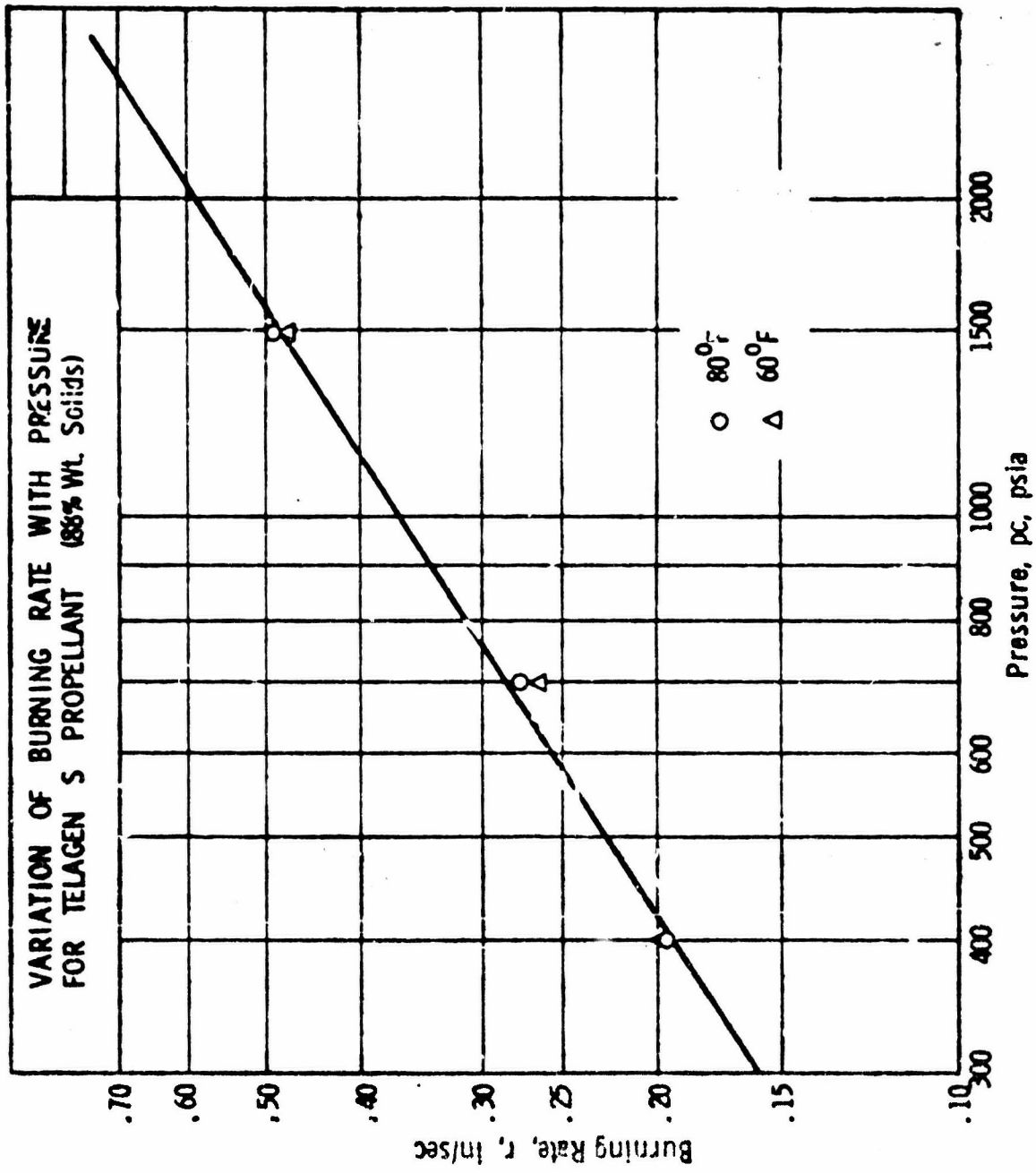
VARIATION OF BURNING RATE WITH PRESSURE
FOR TELAGEN S PROPELLANT (86% Wt. Solids)
80°F
60°F
Burning Rate, r, in/sec
.70
.60
.50
.40
.30
.25
.20
.15
.10
300
400
500
600
800
1000
1500
2000
Pressure, pc, psia

Figure 9

blends in solid propellants to obtain improved mechanical behavior. The ballistic requirements will normally establish an average particle size for the fillers of a solid propellant, but there are limitless numbers of particle size distributions which will have the same average particle size. As a result, the task of determining which blend of particle size distributions will achieve the highest solids loading in a propellant with reasonable mechanical properties is a tedious one.

b. Effect of Packing on Viscosity of Filled Liquids

A convenient method for determining the effectiveness of particle packing is by measuring the effect of particle packing on the viscosity of a liquid. The Eilers equation[1] shown below relates the relative viscosity (η_r) of a suspension to particle packing and loading.

$$\eta_r = \frac{\eta}{\eta_0} = \left[1 + \frac{1.25\,\phi}{1-(\phi/\phi_f)}\right]^2$$

where η and η_0 are the viscosities of the filled and unfilled liquids, ϕ is the volume fraction of solids, and ϕ_f is the maximum volume fraction solids (at which $\eta_r = \infty$). The parameter ϕ_f is a function of the particle packing, and for uniform sized spheres is 0.74 by theory.

Measurements of the viscosities of monodispersed suspensions fit an equation of the form proposed by Eilers with $\phi_f = 0.605$ which is approximately the theoretical for orthorhombic packing.

c. Similarity of Viscosity and Modulus of Filled Systems

The use of Eilers relation with the viscosity (η) replaced by Young's modulus (E)[2] has been proposed for the analogous elastic problem of rubbers containing fillers. Some success was achieved by T. Smith[3] in application of an equation of the Eilers type to solid propellants.

Therefore, the best packing of particles of different sizes will give a slurry with the lowest viscosity and for a given solids content will give a propellant with the lowest modulus. The maximum loading that such a packing would allow must, of course, be determined by its effect in a propellant system.

d. Effect of Particle Size Distribution on Viscosity

The use of particles of different size allows much more efficient packing of particles. Horsfield[4] calculated that a suspension with a solids concentration of 85.1% by volume is possible by use of particles of five different sizes.

---

[1] H. Eilers, Kolloid, Zeit. 102, 165 (1954).
[2] J. Rehner, J. Appl. Phys., 11, 638 (1943).
[3] T. L. Smith, Trans. Soc. of Rheology, 3, (1959).
[4] H. Horsfield, J. Soc. Chem. Ind., 5, 107 (1934).

A number of investigators have experimentally studied suspension of bimodal distributions of solids up to 74% by volume. These studies show that the viscosity of concentrated suspensions could decrease markedly if the particle size ratio and relative amounts of small to large spheres were chosen properly.

e. Approach

The approach to more highly loaded solid propellants consists of two distinct steps. The first involves the determination of the blends of available oxidizer particle sizes which give a slurry with a minimum viscosity (best packing of particles). The second step is the determination of the maximum solids loading which may be achieved with the blend determined in the first step. The work reported here is the first step of this approach.

f. Particle Sizes

Some available particle sizes of NH_4ClO_4 with the exception of 3-9μ particles which were used as received, were screened to a narrower range of particle sizes for a study of the effect of particle size on the relative viscosity of a slurry. The oxidizers used were 3-9μ, 43-104μ, 104-250μ, and 250-495μ. These will be referred to as monomodal systems.

The particle size distribution by sieve analysis and the average particle size for each monomodal system is given in Table XI. The particle size distribution of the fine grind is 3-9μ with an average of 6μ.

g. Viscosity Measurements with the Haake Rotovisko Viscometer

The viscosity measurements made with a Haake Rotovisko (Type RV) viscometer equipped with a multiple measuring head (50-500) and the Haake Circulator (Type RBD) at 30°C were consistent up to a volume fraction of solids loading of approximately 0.45 depending on the oxidizer system. At higher solids loadings the measured viscosities were lower than the values which would be expected from the extrapolated curve of relative viscosity (η_r) vs volume fraction of solids loading (ϕ).

h. Viscosity Measurements with the Brookfield Synchro-Lectric Viscometer

Viscosities were determined with a Brookfield Synchro-Lectric Viscometer (Type HBF) in an effort to obtain accurate measurements at the higher solids loading and as a check on the values obtained using the Haake Rotovisko viscometer. The Brookfield measurements were consistently higher than those obtained using the Haake Rotovisko viscometer (Figure 10). With the standard Brookfield spindles the viscosities fell below the extrapolated values at about 0.55 volume fraction solids due to the thixotropic nature of the slurry (Figures 11-14). More accurate measurements were made in the higher ranges using the Brookfield Heliopath Stand and the T-shaped spindle. With the higher viscosity measurements the determination of the maximum solids loading at

infinite viscosity for each blend by extrapolation of the plot $1/(\eta_r - 1)$ vs $1/\phi$ became more accurate. The Haake circulation bath (Type NBD) was used to maintain a standard temperature of 30°C.

Table XI

PARTICLE SIZE DISTRIBUTION AND AVERAGE PARTICLE SIZE OF NH_4ClO_4 USED FOR SLURRY VISCOSITY STUDIES

Tyler Sieve No.	Sieve Opening Size, μ	Distribution %	Average Particle Size, μ
32	495	34	
35	420	32	419
42	350	29	
48	297	5	
65	210	29	
100	149	31	
150	105	15	148
200	75	11	
325	44	9	
765	-	5	
150	105	27	
200	75	36	71.2
325	44	36	

i. Viscosity of Oxidizer Blends

The monomodal NH_4ClO_4 systems were blended and the relative viscosities of slurries in Cronite-6 were determined. The blend compositions are summarized in Table XII, and the viscosity data are shown in Table XIII and Figures 11-23.

Blends 1-6, compositions of which are given in Table XII, were a series of bimodal and trimodal blends selected at random, the viscosities of which were measured to determine the viscosity differences between blends and the accuracy with which the viscosity could be measured. The data were consistent, and the viscosity of the blends were easily distinguishable with the exception of Blends 1 and 2, the viscosities of which were very close.

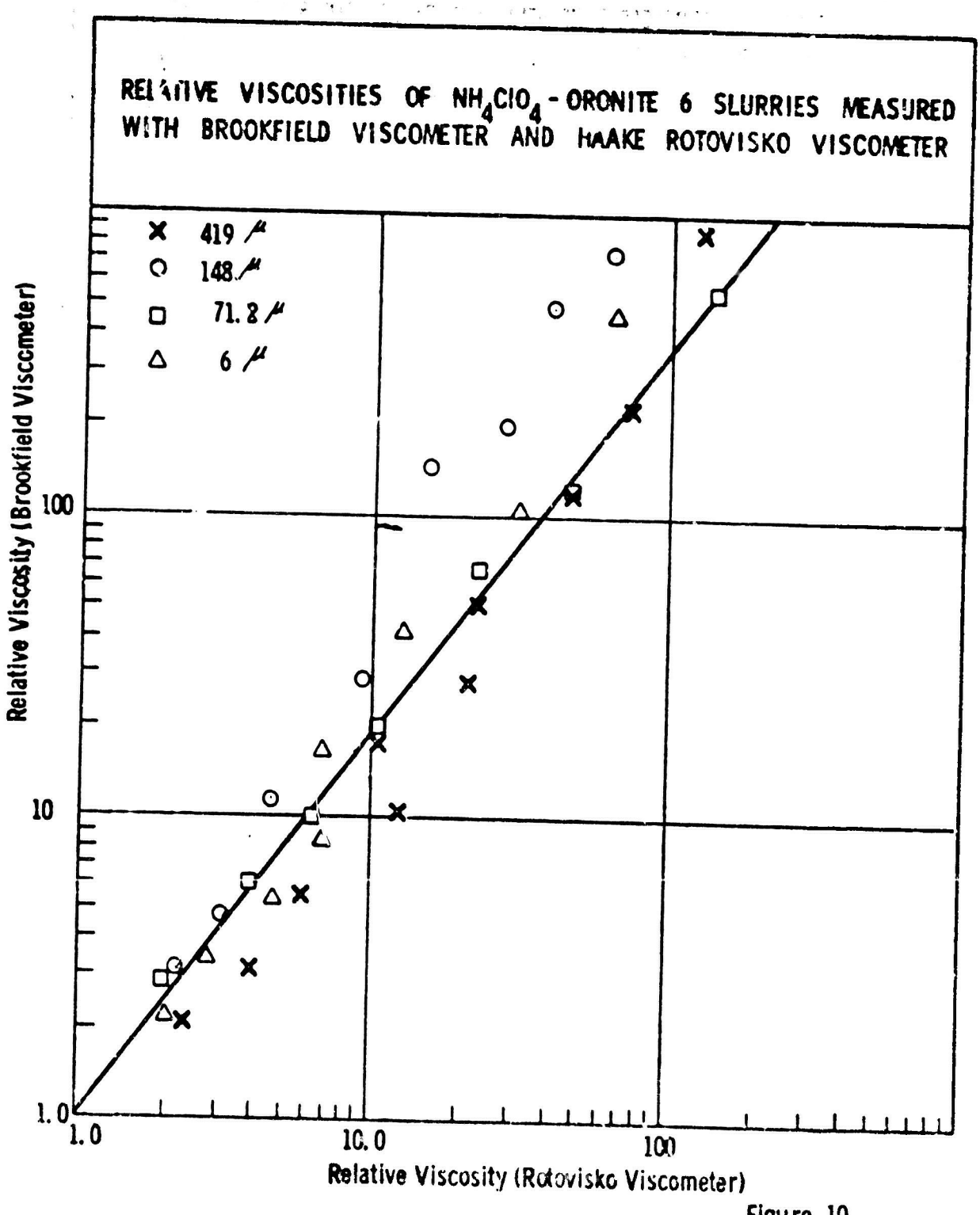
RELATIVE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES MEASURED WITH BROOKFIELD VISCOMETER AND HAAKE ROTOVISKO VISCOMETER
419 μ
148 μ
71.8 μ
6 μ
Relative Viscosity (Brookfield Viscometer)
100
10
1.0
1.0
10.0
100
Relative Viscosity (Rotovisko Viscometer)

Figure 10

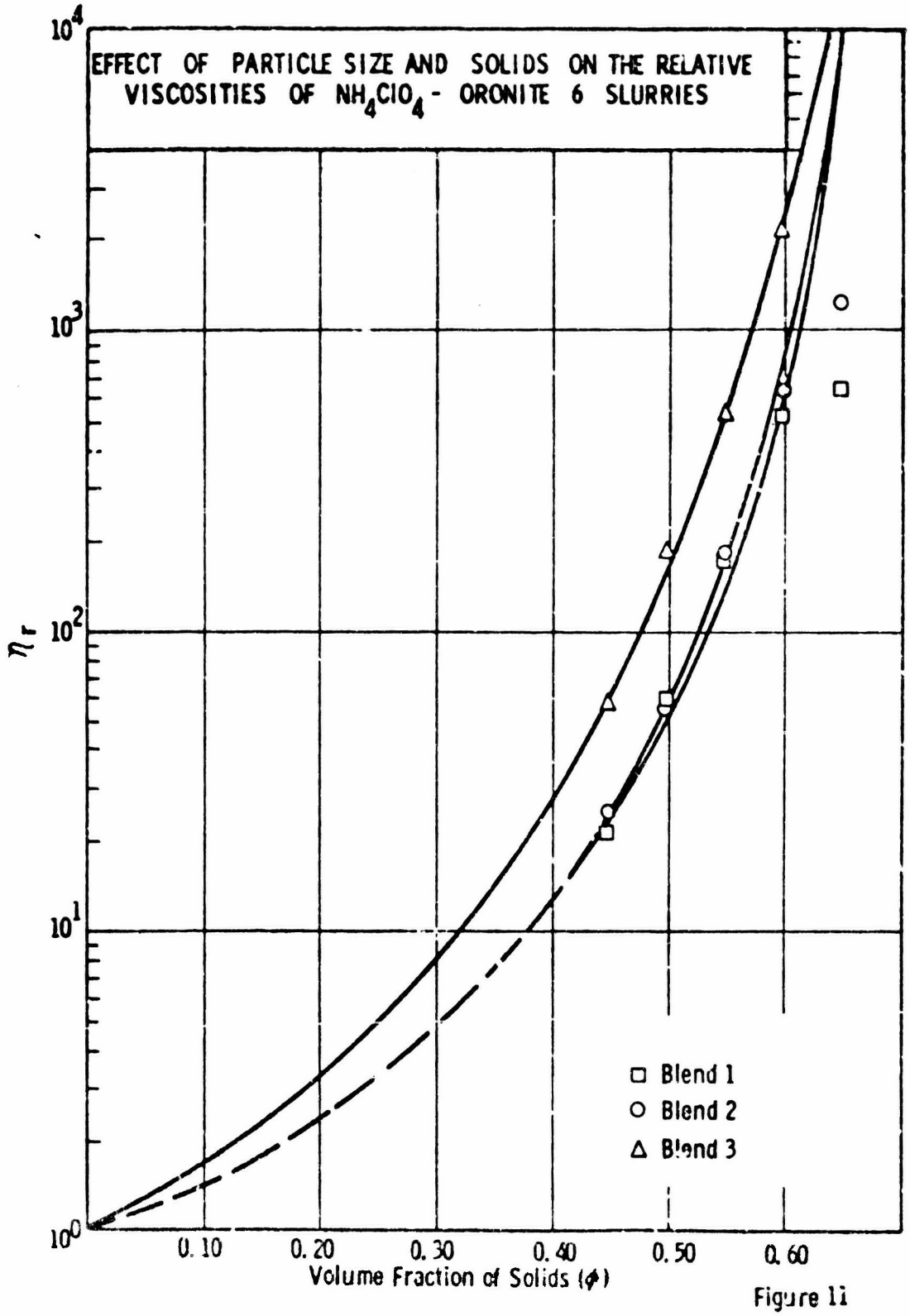
EFFECT OF PARTICLE SIZE AND SOLIDS ON THE RELATIVE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
10^4
10^3
10^2
10^1
10^0
η_r
0.10
0.20
0.30
0.40
0.50
0.60
Volume Fraction of Solids (ϕ)
Blend 1
Blend 2
Blend 3

Figure 11

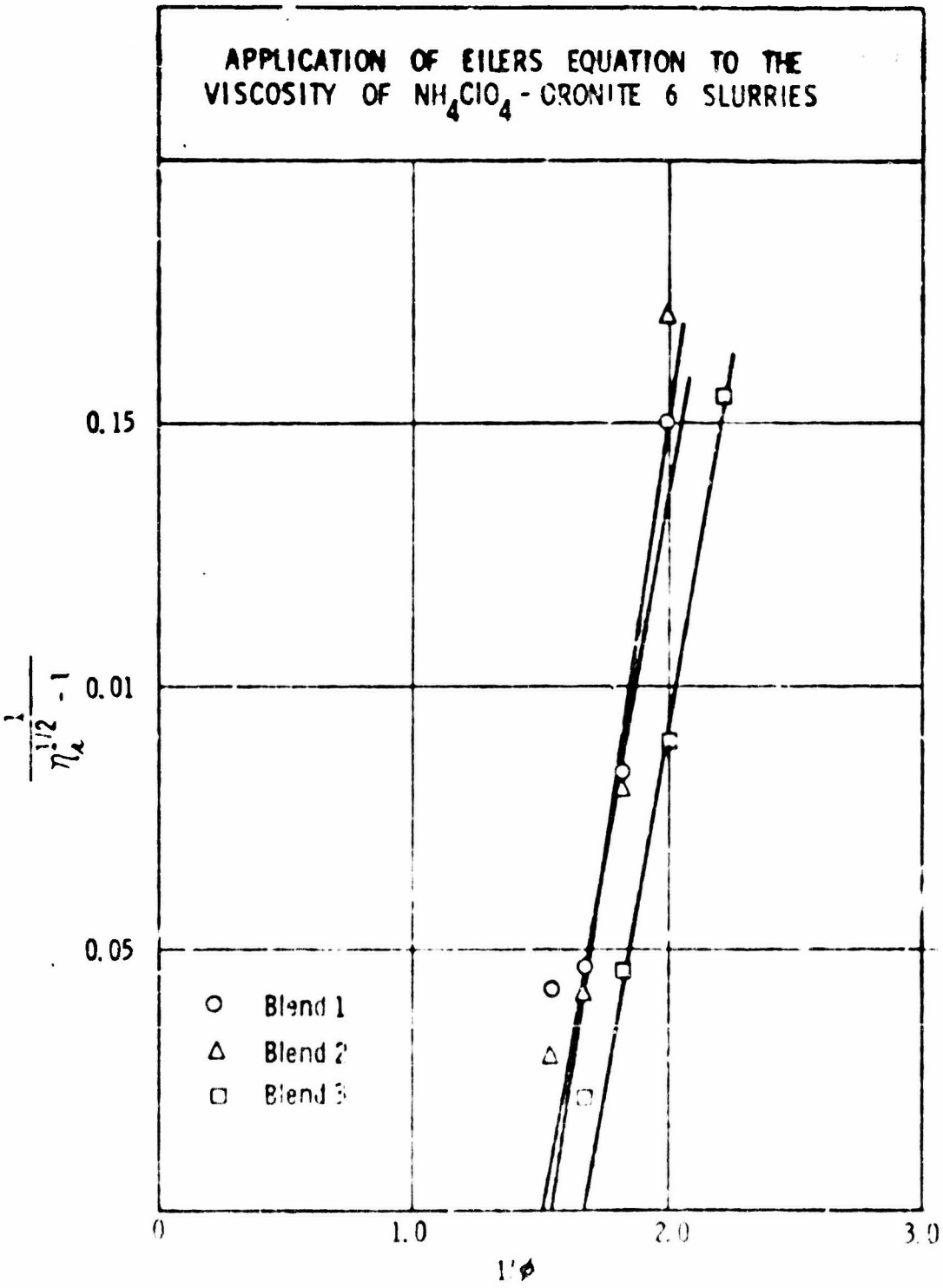
APPLICATION OF EILERS EQUATION TO THE VISCOSITY OF NH_4ClO_4 - CRONITE 6 SLURRIES
$\frac{1}{\eta_r^{1/2}} - 1$
0.15
0.01
0.05
Blend 1
Blend 2
Blend 3
0
1.0
2.0
3.0
$1'\phi$

Figure 12

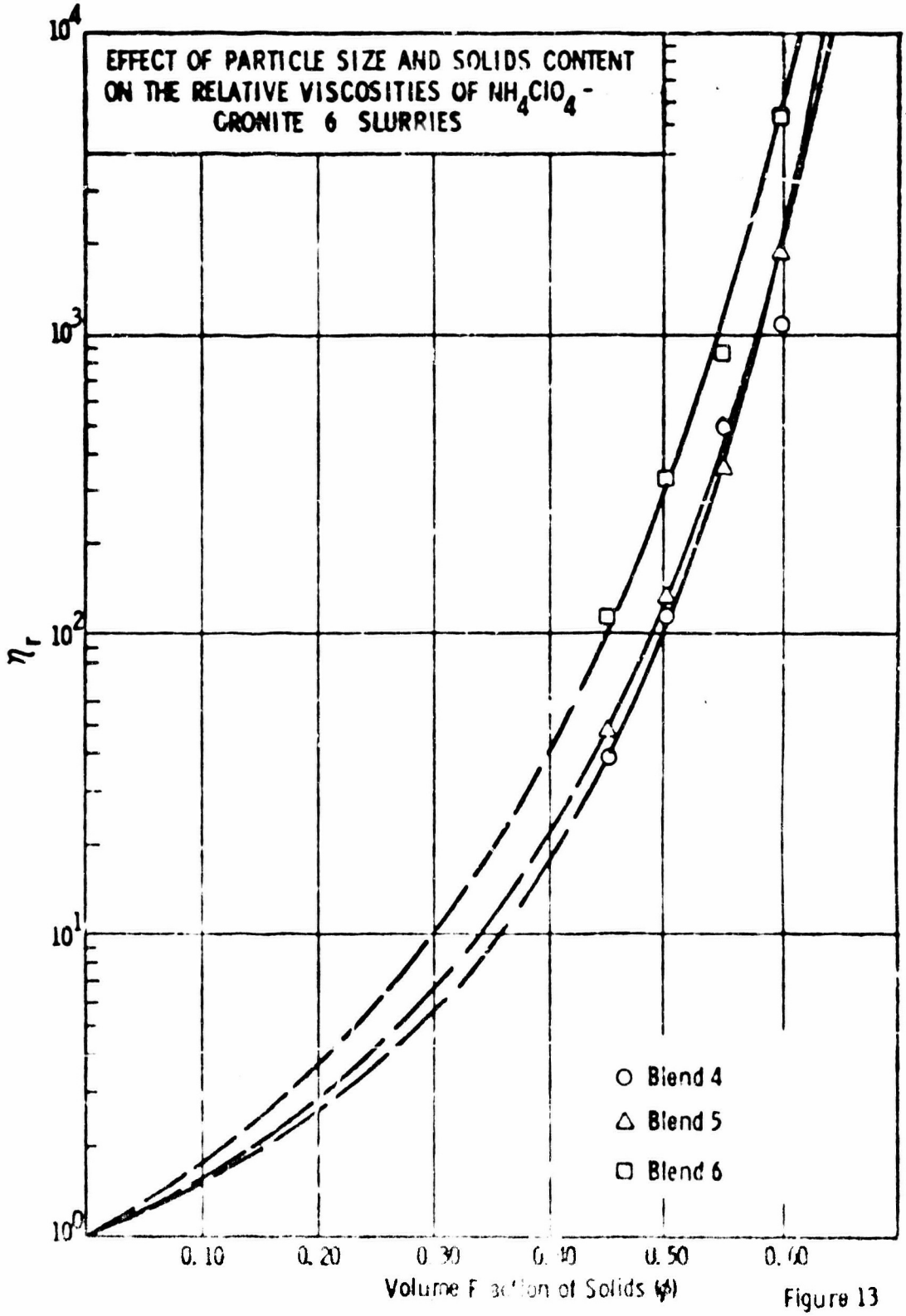
EFFECT OF PARTICLE SIZE AND SOLIDS CONTENT ON THE RELATIVE VISCOSITIES OF NH_4ClO_4 - GRONITE 6 SLURRIES
10^4
10^3
10^2
10^1
10^0
η_r
0.10
0.20
0.30
0.40
0.50
0.60
Volume Fraction of Solids (ϕ)
○ Blend 4
△ Blend 5
□ Blend 6

Figure 13

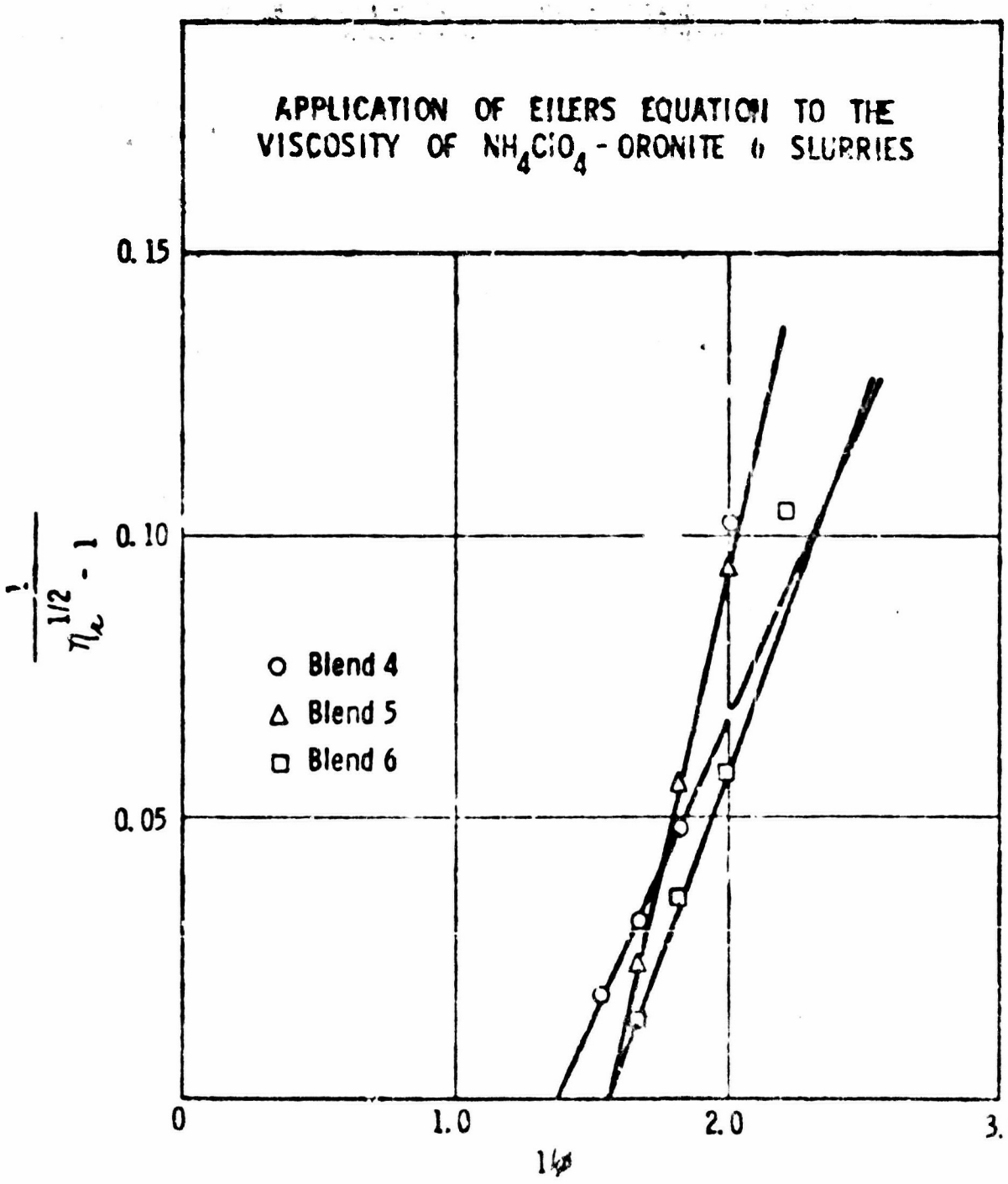
APPLICATION OF EILERS EQUATION TO THE VISCOSITY OF NH_4ClO_4 - ORONITE 6 SLURRIES
0.15
0.10
0.05
$\frac{1}{\eta_r^{1/2}} - 1$
Blend 4
Blend 5
Blend 6
0
1.0
2.0
3.0
1/ϕ

Figure 14

Table XII

COMPOSITION AND AVERAGE PARTICLE SIZE OF NH_4ClO_4 BLENDS USED FOR SLURRY VISCOSITY STUDIES

Blend No.	Composition, Wt% of Average Particle Size, μ				Average Particle Size, μ	Mean Deviation[a]
	6	71.2	148	419		
1	-	-	50.00	50.00	283	136
2	-	50.00	-	50.00	245	173
3	50.00	-	-	50.00	211	220
4	-	33.33	33.33	33.33	213	139
5	33.33	-	33.33	33.33	190	159
6	33.33	33.33	-	33.33	165	168
7	-	-	84.16	15.48	180	86.7
8	-	68.72	-	31.28	180	148
9	57.87	-	-	42.13	180	201
10	-	56.94	14.35	28.71	180	139
11	45.37	-	18.21	36.42	180	176
12	41.43	19.52	-	39.05	190	186
13	35.80	-	32.10	32.10	180	157
14	49.12	-	12.72	38.16	180	184
15	22.21	-	51.86	25.93	180	130
16	13.00	-	65.25	21.75	180	112

[a] This indicates the spread of the blend, but has little meaning for these non-Gaussian distributions

Table XIII

VISCOSITIES OF NH_4ClO_4-CROMITE 6 SLURRIES AT 30°C

Blend No.	Vol. Fract. (ϕ)	$1/\phi$	ζ_r	$\eta_{sp} \times 10^3$	η_r	$\eta_r^{1/3}$	$\eta_r^{1/3}-1$	$\frac{1}{\eta_r^{1/3}-1}$
1	0.45	2.22	0.657	0.864	22.6	4.65	3.65	0.274
	0.50	2.00		2.36	59.0	7.68	6.68	0.150
	0.55	1.82		6.80	170.0	13.03	12.03	0.0831
	0.60	1.67		20.2	504.0	22.46	21.46	0.0466
	0.65	1.54		24.3	608.0	24.62	23.62	0.0423
2	0.45	2.22	0.649	0.992	24.8	4.98	3.98	0.251
	0.50	2.00		2.18	54.4	7.35	6.35	0.157
	0.55	1.82		7.26	181.5	13.47	12.47	0.0803
	0.60	1.67		25.0	624.0	25.00	24.00	0.0416
	0.65	1.54		48.3	1208.0	34.78	33.78	0.0296
3.	0.45	2.22	0.602	2.28	57.0	7.46	6.46	0.155
	0.50	2.00		5.94	148.4	12.19	11.19	0.0894
	0.55	1.82		21.1	528.0	22.96	21.96	0.0456
	0.60	1.67		86.7	2168.0	46.60	45.60	0.0219
4	0.45	2.22	0.725	1.54	38.4	6.19	5.19	0.193
	0.50	2.00		4.68	117.0	10.81	9.81	0.102
	0.55	1.82		19.4	484.8	22.00	21.00	0.0477
	0.60	1.67		43.2	1080.0	32.85	31.85	0.0314
	0.65	1.54		128	3200.0	56.52	55.52	0.018
5	0.45	2.22	0.641	1.96	49.0	7.0	6.0	0.167
	0.50	2.00		5.38	134.4	11.60	10.60	0.094
	0.55	1.82		14.5	361.6	19.02	18.02	0.0555
	0.60	1.67		75.2	1880.0	43.40	42.40	0.0236
6	0.45	2.22	0.641	4.54	113.6	10.63	9.63	0.104
	0.50	2.00		13.5	357.6	18.38	17.38	0.0576
	0.55	1.82		35.2	880.0	29.62	28.62	0.0349
	0.60	1.67		212	5300.0	72.70	71.70	0.0140
7	0.45	2.22	0.658	2.800	70	8.38	7.38	0.136
	0.50	2.00		19.8	496	22.30	21.30	0.0470
	0.55	1.82		37.4	936	30.60	29.60	0.0337
	0.60	1.67		240	6000	77.60	76.60	0.0131
	0.63	1.54		320	8000	89.50	88.50	0.0113
8	0.45	2.22	0.637	9.20	230	15.2	14.2	0.0704
	0.50	2.00		29.4	736	27.2	26.2	0.0382
	0.55	1.82		86.4	2160	46.6	45.6	0.0219
	0.60	1.67		435	10900	104.4	103.4	0.00967

Table XIVI (Cont)

Blend No.	Vol. Fract. (ϕ)	λ/ϕ	ϕ_f	$\eta_{sp} \times 10^3$	η_r	$\eta_r^{\frac{1}{2}}$	$\eta_r^{\frac{1}{2}}-1$	$\frac{1}{\eta_r^{\frac{1}{2}}-1}$
9	0.45	2.22	0.667	5.20	130	11.4	10.4	0.0962
	0.50	2.00		11.5	288	17.0	16.0	0.0625
	0.55	1.82		27.2	680	26.1	25.1	0.0398
	0.60	1.67		83.2	2080	45.6	44.6	0.0224
	0.65	1.54		204	51000	225.8	224.8	0.00445
10	0.45	2.22	0.662	5.40	126	11.23	10.23	0.098
	0.50	2.00		25.9	648	25.50	24.50	0.048
	0.55	1.82		65.6	1640	40.50	39.50	0.0253
	0.60	1.67		147	3675.5	60.61	59.61	0.0168
	0.62	1.61		352	8800.0	93.80	92.80	0.0108
11	0.45	2.22	0.671	9.76	244	15.61	14.61	0.0683
	0.50	2.00		23.7	592	24.40	23.40	0.0428
	0.55	1.82		57.6	1440	37.90	36.90	0.0272
	0.60	1.67		176	4400	66.40	65.40	0.0153
12	0.45	2.22	0.645	7.20	180	13.42	12.42	0.0805
	0.50	2.00		18.2	456	21.40	20.40	0.0492
	0.55	1.82		49.6	1240	35.20	34.20	0.0293
	0.60	1.67		230	5760	75.90	74.90	0.0134
13	0.45	2.22	0.686	8.16	204	14.28	13.28	0.0754
	0.50	2.00		21.1	528	22.96	21.96	0.0456
	0.55	1.82		32.0	800	28.30	27.30	0.0366
	0.60	1.67		96.0	2400	49.00	48.00	0.0208
	0.63	1.59		205	5120	71.60	70.60	0.0142
14	0.45	2.22	0.642	9.92	248	15.75	14.75	0.0678
	0.50	2.00		23.4	584	24.04	23.04	0.0433
	0.55	1.82		60.8	1520	39.00	38.00	0.0263
	0.60	1.67		346	8640	93.10	92.10	0.0109
15	0.45	2.22	0.676	2.80	70	8.38	7.38	0.0136
	0.50	2.00		11.8	296	17.24	16.24	0.0613
	0.55	1.82		27.2	680	26.15	25.15	0.0392
	0.60	1.67		67.2	1680	41.00	40.00	0.0250
	0.63	1.59		99.2	2480	49.80	48.80	0.0205
16	0.45	2.22	0.662	2.64	66	8.13	7.13	0.140
	0.50	2.00		11.0	276	16.62	15.62	0.0640
	0.55	1.82		25.6	640	25.40	24.40	0.0410
	0.60	1.67		86.4	2160	46.50	45.50	0.0220
	0.63	1.59		131	3280	57.27	56.27	0.0177

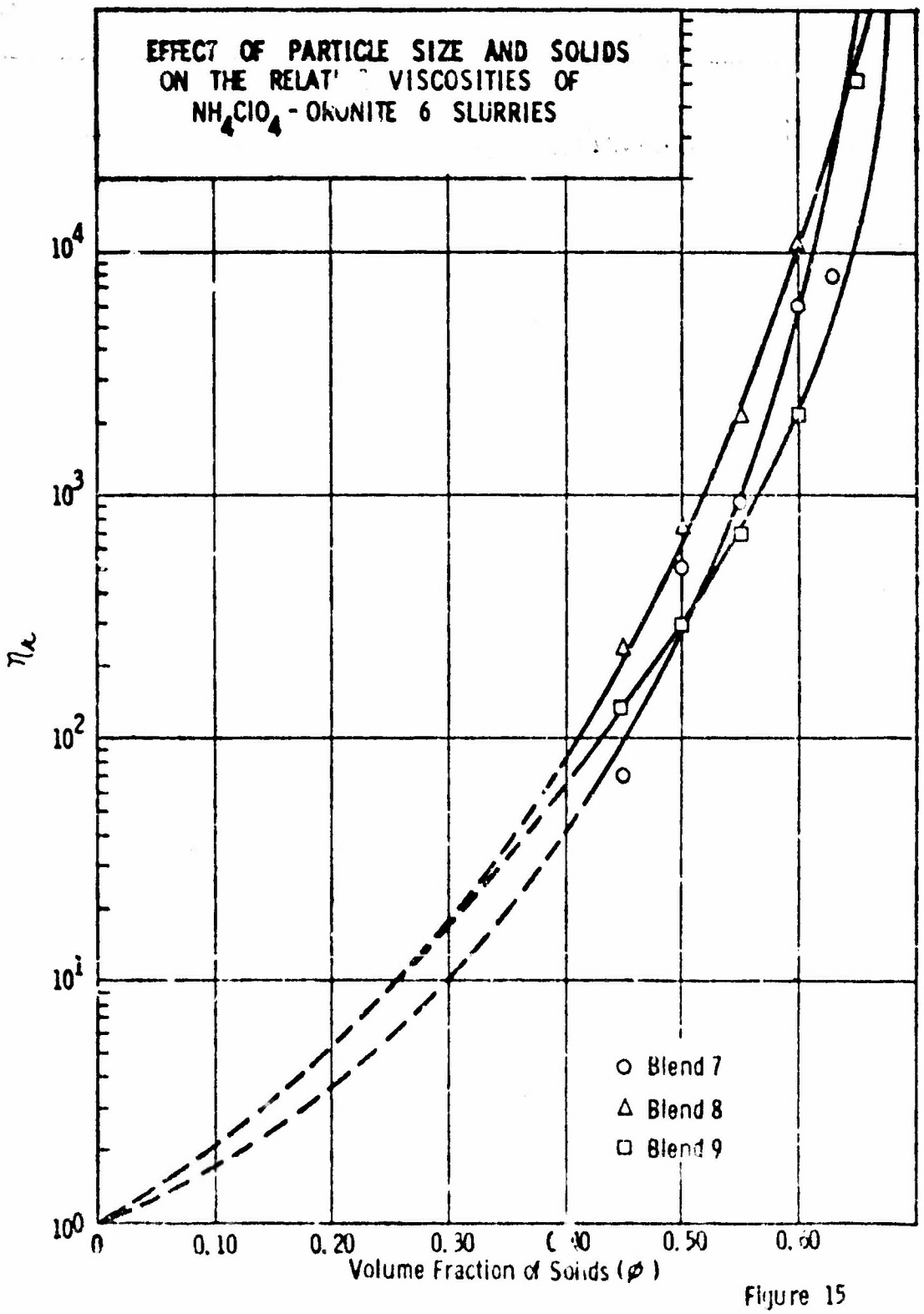
EFFECT OF PARTICLE SIZE AND SOLIDS ON THE RELAT' VISCOSITIES OF NH4ClO4 - OKONITE 6 SLURRIES
10^4
10^3
10^2
10^1
10^0
η_r
0
0.10
0.20
0.30
0.50
0.60
Volume Fraction of Solids (ø)
Blend 7
Blend 8
Blend 9

Figure 15

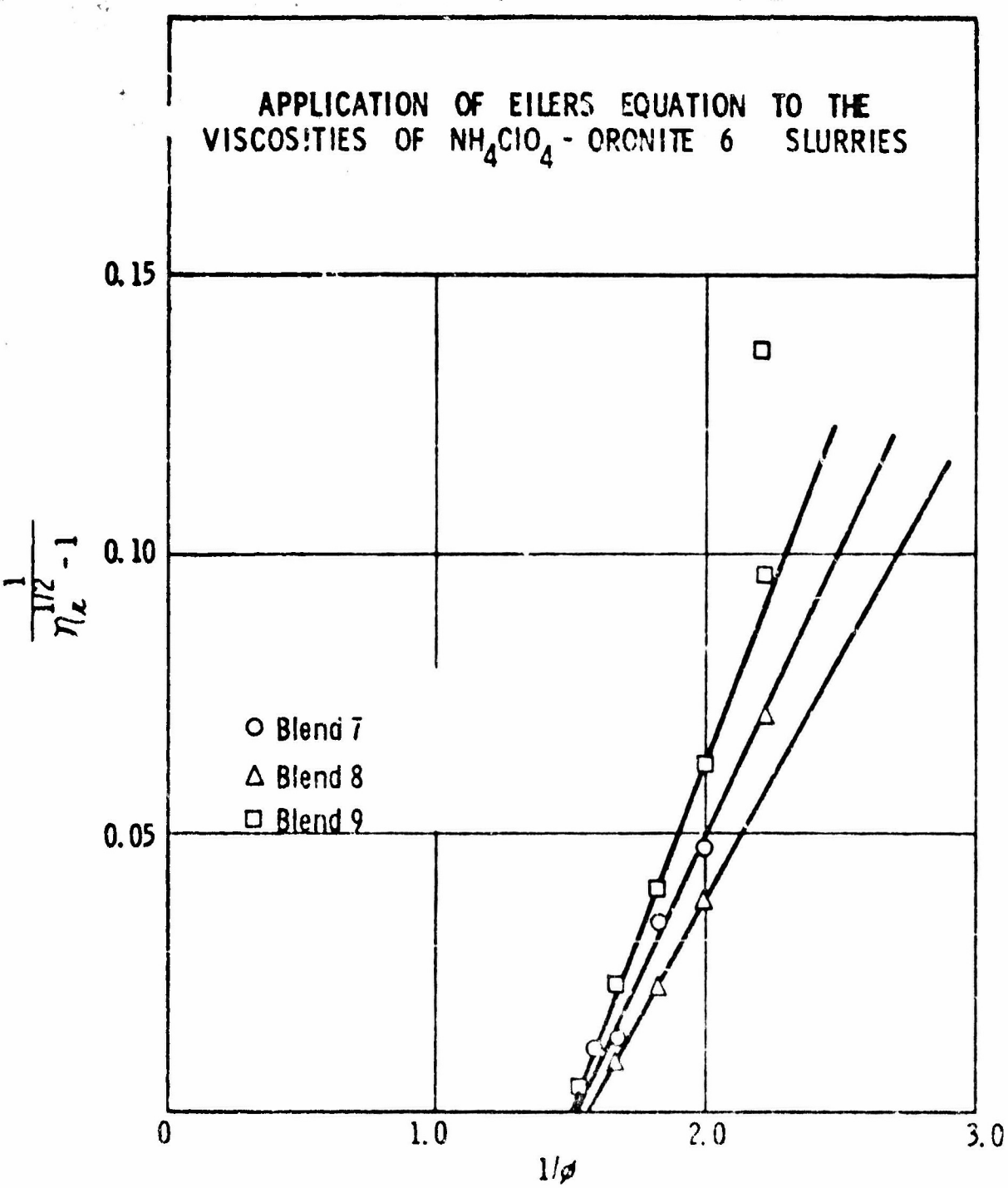
APPLICATION OF EILERS EQUATION TO THE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
0.15
0.10
0.05
$\frac{1}{\eta_r^{1/2}} - 1$
Blend 7
Blend 8
Blend 9
0
1.0
2.0
3.0
$1/\phi$

Figure 16

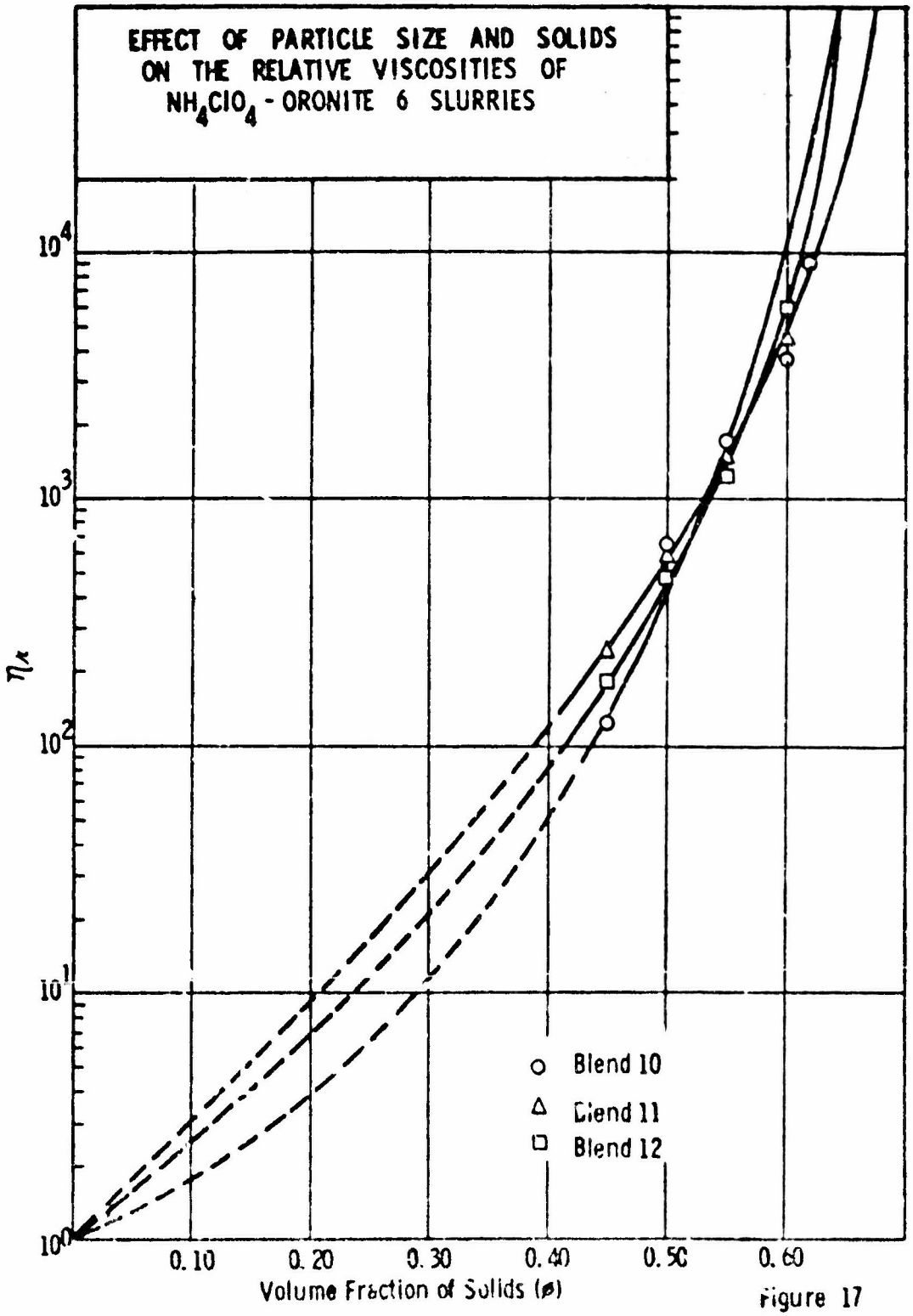
EFFECT OF PARTICLE SIZE AND SOLIDS ON THE RELATIVE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
10^4
10^3
10^2
10^1
10^0
η_r
0.10
0.20
0.30
0.40
0.50
0.60
Volume Fraction of Solids (ø)
Blend 10
Blend 11
Blend 12

Figure 17

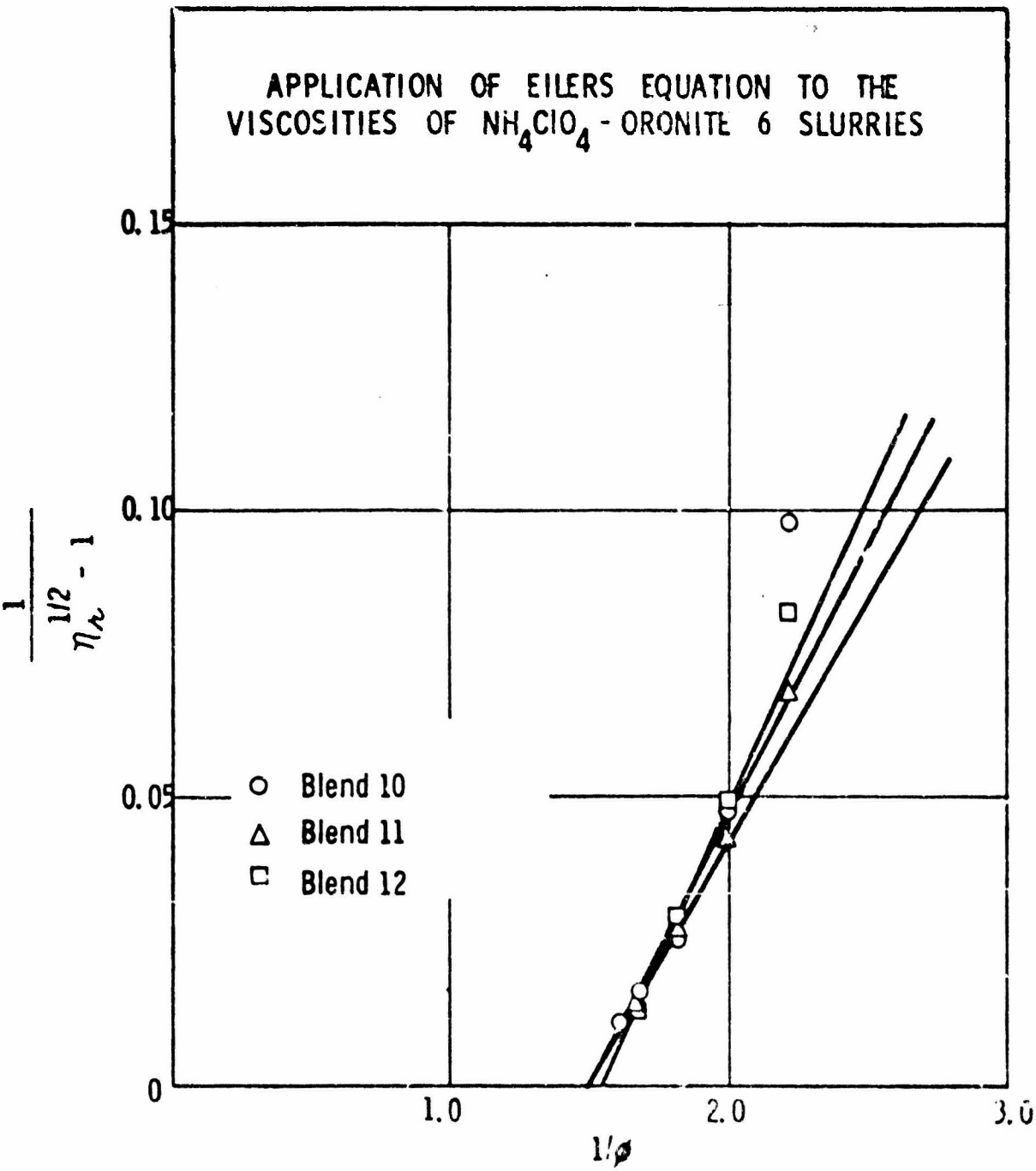
APPLICATION OF EILERS EQUATION TO THE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
0.15
0.10
0.05
0
$\frac{1}{\eta_r^{1/2}} - 1$
Blend 10
Blend 11
Blend 12
1.0
2.0
3.0
$1/\phi$

Figure 18

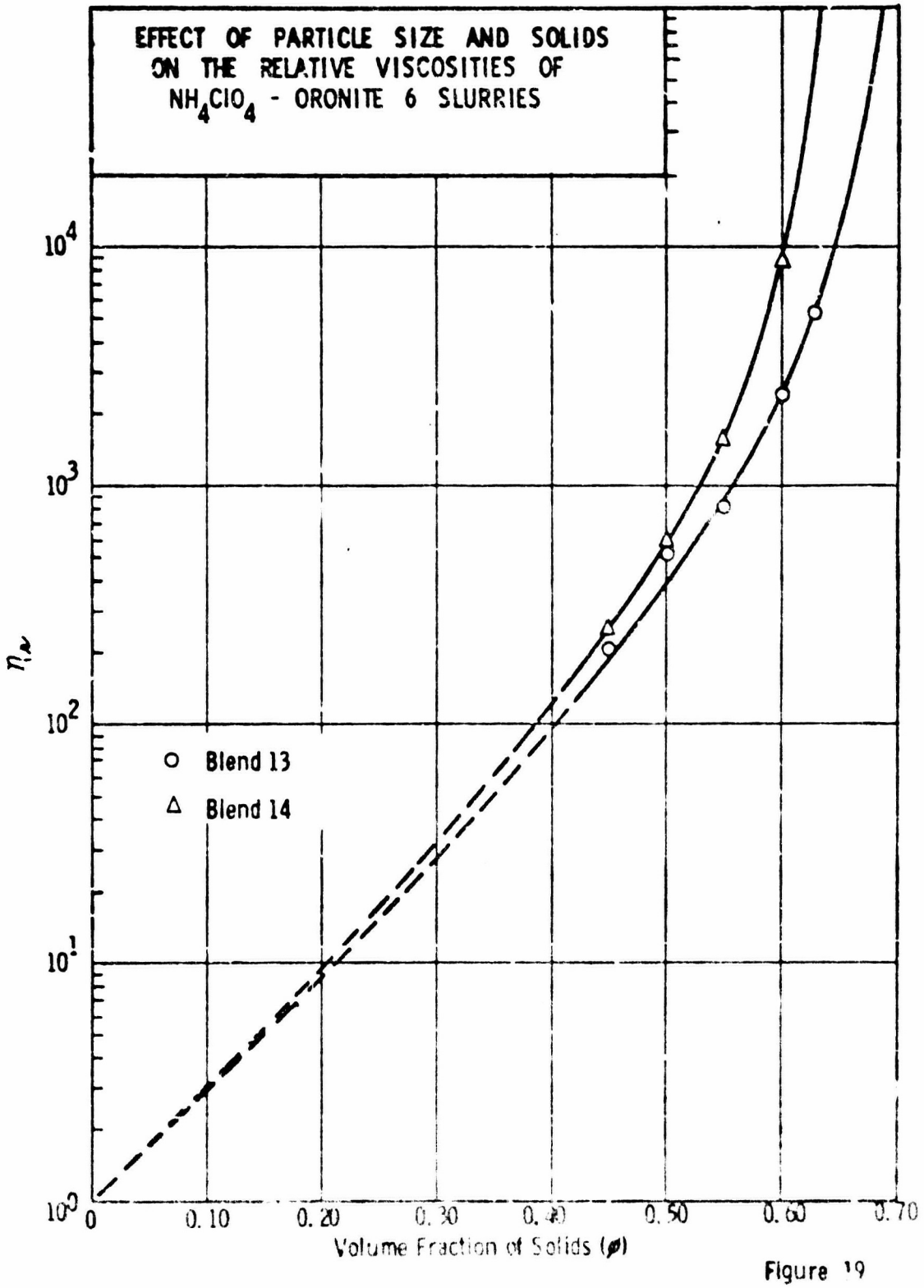
EFFECT OF PARTICLE SIZE AND SOLIDS ON THE RELATIVE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
10^4
10^3
10^2
10^1
10^0
η_r
Blend 13
Blend 14
0
0.10
0.20
0.30
0.40
0.50
0.60
0.70
Volume Fraction of Solids (ϕ)

Figure 19

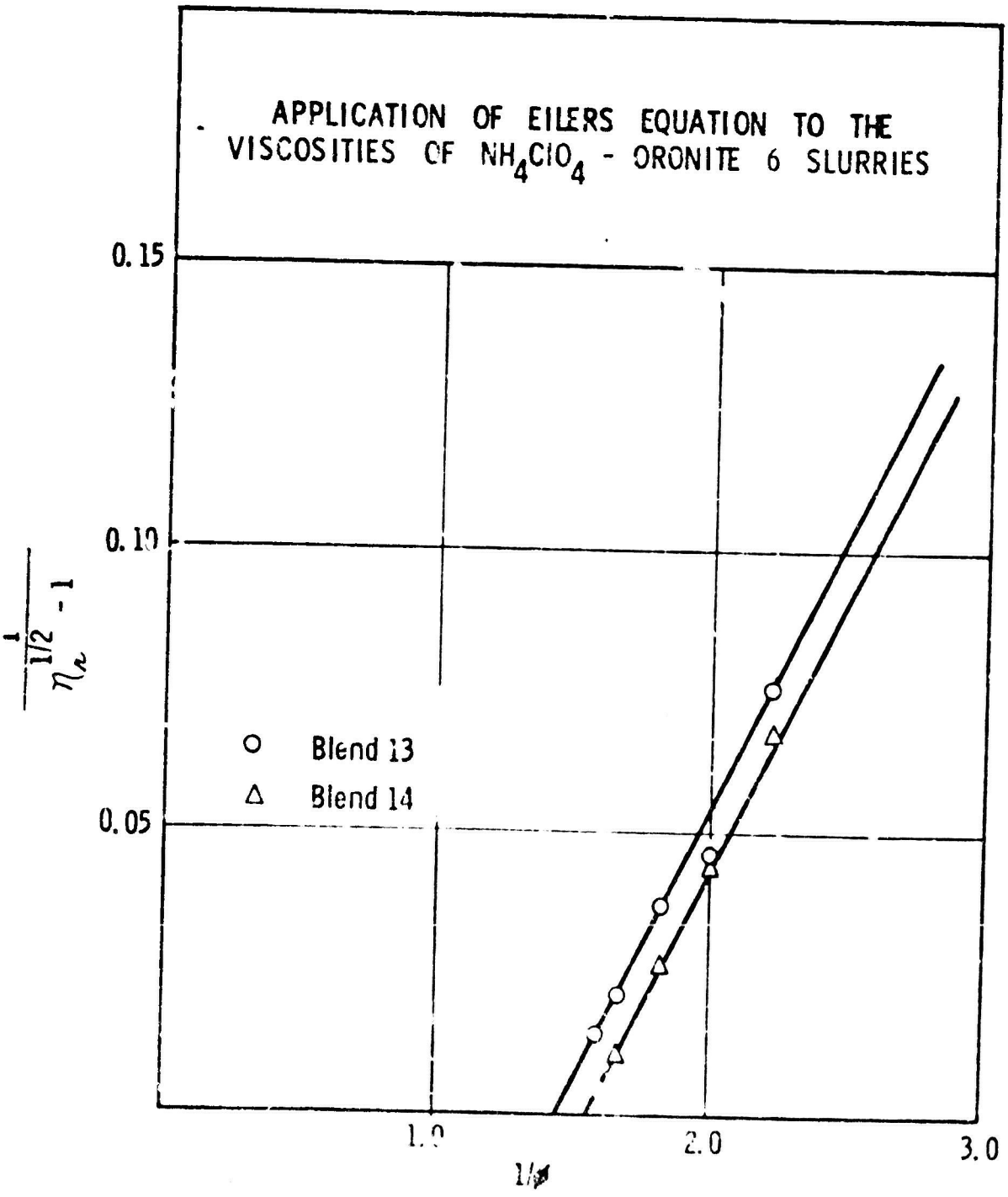
APPLICATION OF EILERS EQUATION TO THE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
0.15
0.10
0.05
$\frac{1}{\eta_r^{1/2}} - 1$
Blend 13
Blend 14
1.0
2.0
3.0
$1/\phi$

Figure 20

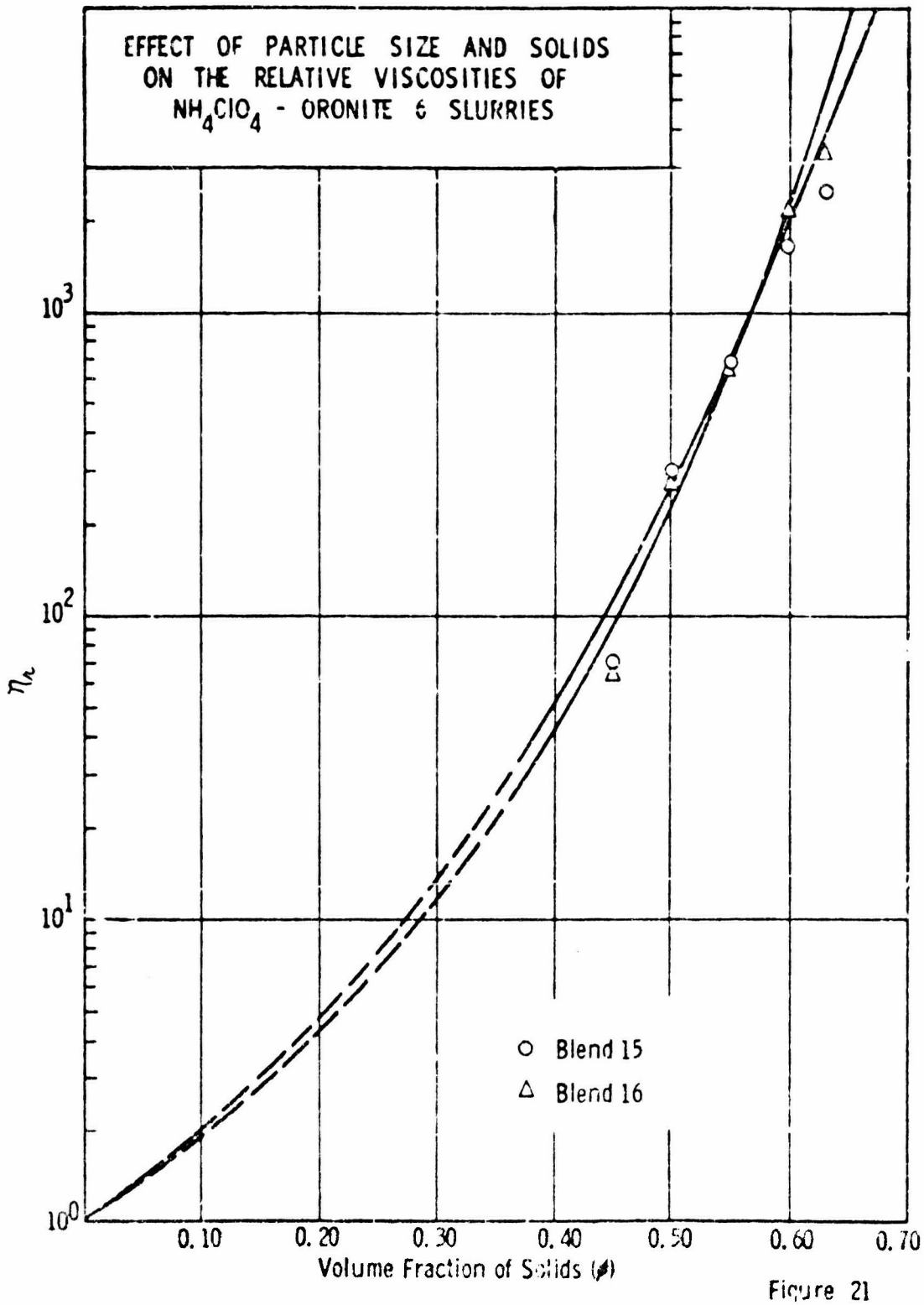
EFFECT OF PARTICLE SIZE AND SOLIDS ON THE RELATIVE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
10^3
10^2
10^1
10^0
η_r
0.10
0.20
0.30
0.40
0.50
0.60
0.70
Volume Fraction of Solids (ϕ)
Blend 15
Blend 16

Figure 21

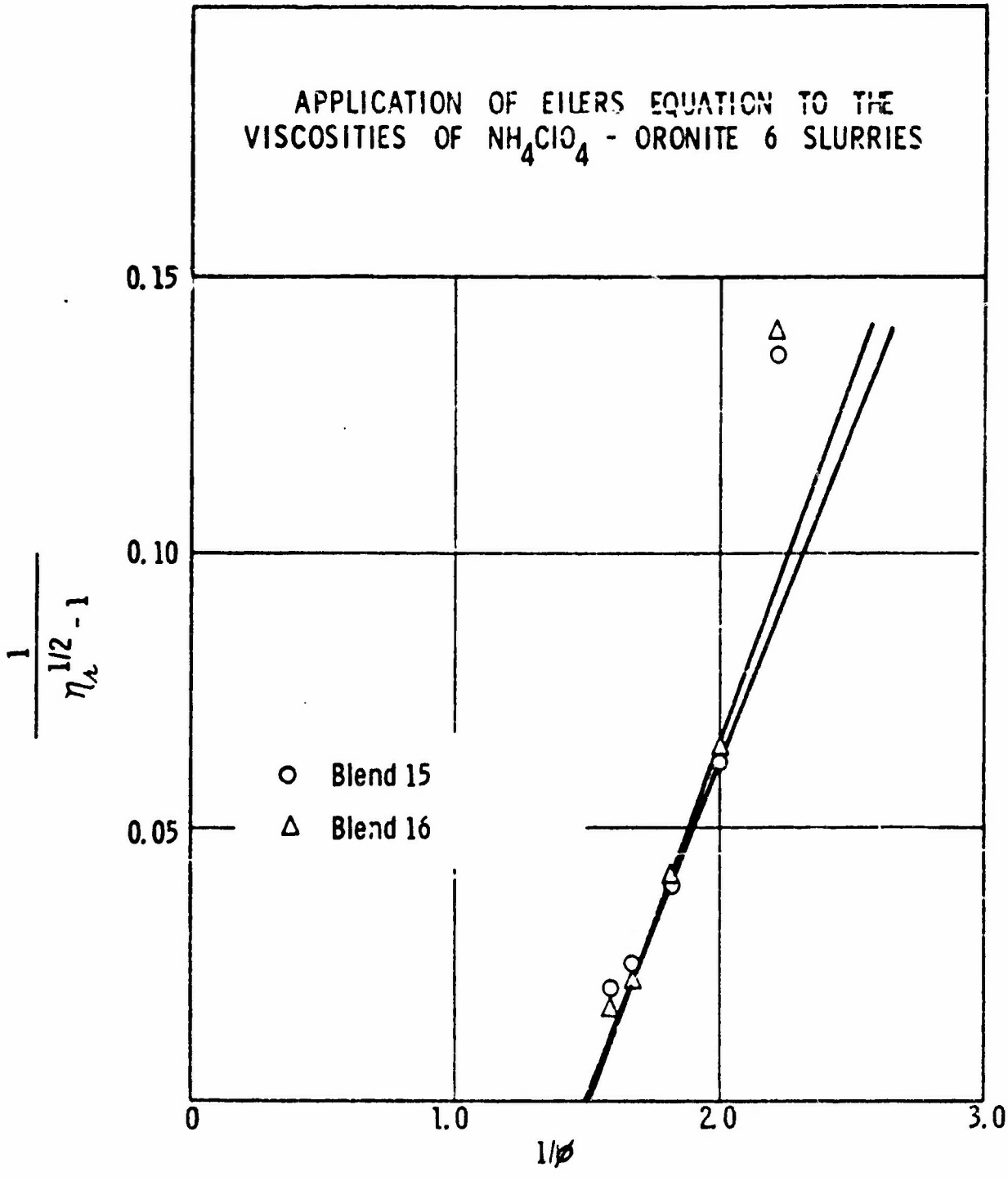
APPLICATION OF EILERS EQUATION TO THE VISCOSITIES OF NH_4ClO_4 - ORONITE 6 SLURRIES
0.15
0.10
0.05
$\frac{1}{\eta_r^{1/2} - 1}$
Blend 15
Blend 16
0
1.0
2.0
3.0
$1/\phi$

Figure 22

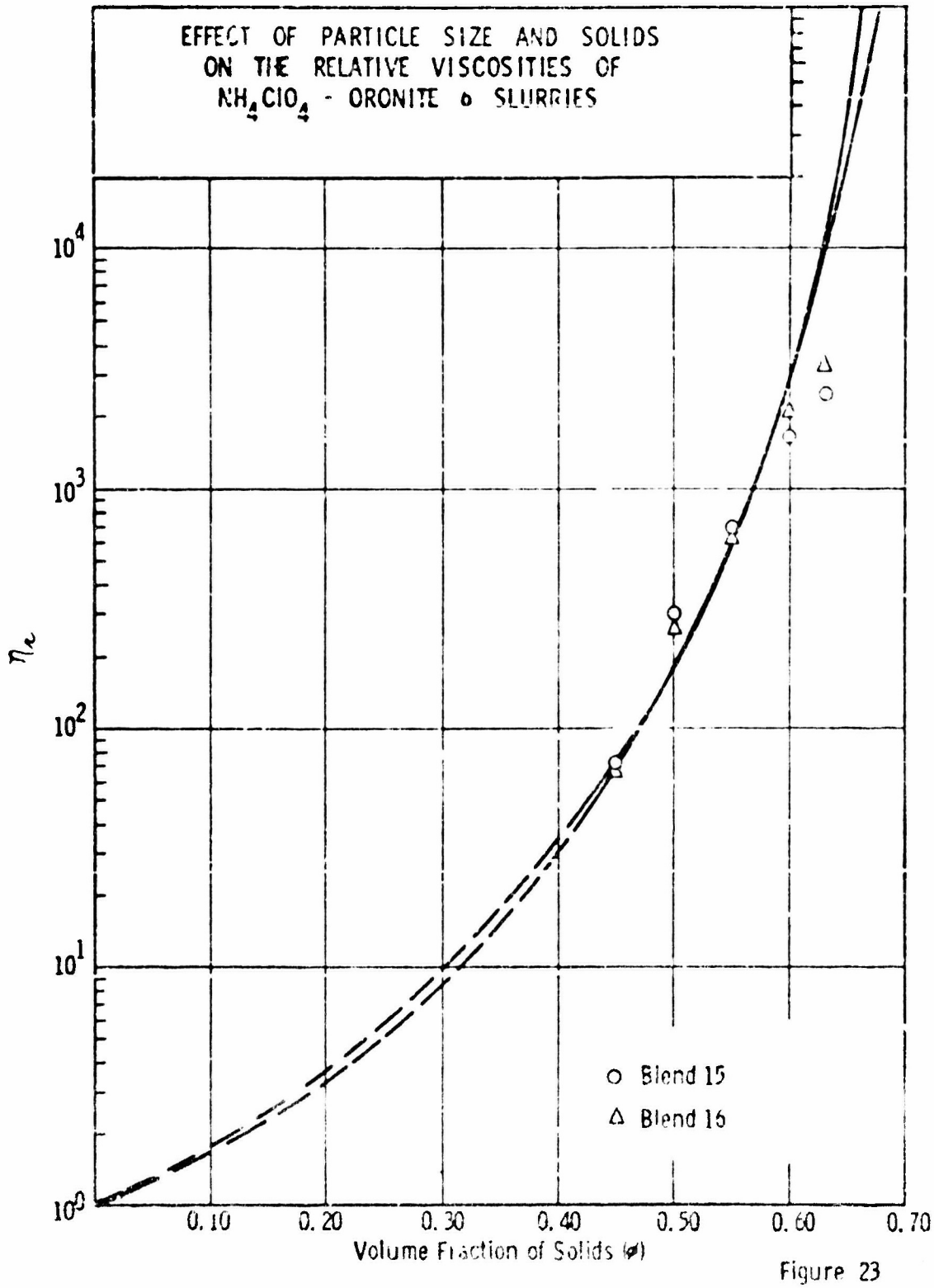
EFFECT OF PARTICLE SIZE AND SOLIDS
ON THE RELATIVE VISCOSITIES OF
NH_4ClO_4 - ORONITE 6 SLURRIES
10^4
10^3
10^2
10^1
10^0
η_r
0.10
0.20
0.30
0.40
0.50
0.60
0.70
Volume Fraction of Solids (ϕ)
○ Blend 15
△ Blend 16

Figure 23

An average particle size of 180μ was maintained in formulating Blends 7-16 in order to maintain a useful burning rate range. Blends 7-12 were made up using various particle sizes to give the 180μ average. Blend 11, with a 2 to 1 ratio of the 419μ to 148μ particle size NH_4ClO_4, gave Cronite 6 slurries with the lowest relative viscosity.

Blends 13-16 were then prepared to produce variants of Blend 11 with different ratios of the 419μ to 148μ particle size NH_4ClO_4, maintaining the 180μ particle size average.

A plot of ϕ_f vs ratio of 419μ to 148μ particle sizes in the blend is given in Figure 24 including that for Blend 11. Blend 13 (1 to 1 ratio) had the highest ϕ_f and will be used for propellant studies. It is expected that some additional minor modifications in the blends will have to be made in the course of the propellant studies.

C. PHASE II

1. Introduction

Phase II will involve preliminary study of the compatibility of the candidate prepolymer, curing agents, or suitable models with advanced oxidizers and fuels. Materials which are compatible will be tested in propellants.

2. Use of Modal Systems

The use of model compounds to study the chemical interaction between binder components and oxidizers or fuels has proven to be a powerful tool. The model compound allows the chemist to carry out analyses which are difficult or impossible to achieve with the prepolymers and curing agents used to prepare propellants. The result is that not only are incompatibilities uncovered, but information concerning the nature of the incompatibility is also obtained.

The model compound or compounds should be a low molecular weight replica of some structural or chemical characteristic of the prepolymer or curing agent. It is not always necessary that a single model show all the characteristics of its counterpart. In some cases it is expedient and convenient to use several models each showing only one characteristic of the material of interest. This approach has been used in this program where 3 model compounds are used to describe the chemical behavior of Telagen S.

A useful characteristic of the model compound is its volatility so that analysis by gas-liquid chromatography (GLC) is possible. GLC is a very useful method for discovering and studying unexpected chemical interactions. All the models used in this program have this property.

3. Model Compounds

Three compounds were used as models for the hydroxy terminated Telagen S. These were 2-octanol (J. T. Baker Chemical Co., 99% pure by GLC),

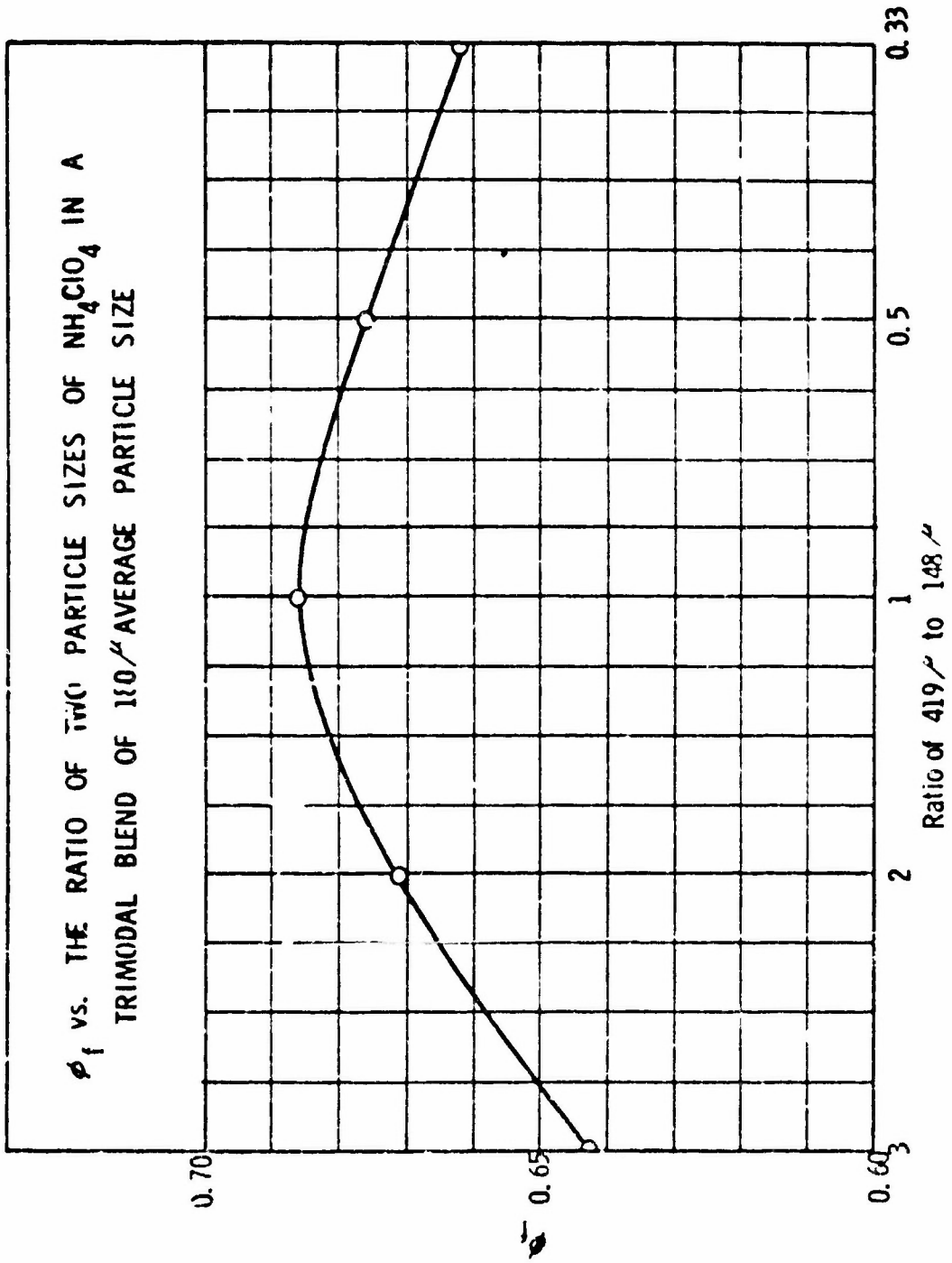
ϕ_f vs. THE RATIO OF TWO PARTICLE SIZES OF NH_4ClO_4 IN A TRIMODAL BLEND OF 110 μ AVERAGE PARTICLE SIZE
0.70
0.65
0.60
ϕ_f
0.33
0.5
1
2
3
Ratio of 419 μ to 148 μ

Figure 24

1-decanol (Eastman Kodak Co., white label, pure by GLC) and 1,7-octadiene (Columbian Carbon Company, used as received). The first two compounds represent the primary and secondary hydroxy groups of the potential prepolymer while the olefin is characteristic of the residual unsaturation. In a similar fashion the carboxy terminated Telagen S was represented by 1-nonanoic acid (Emery Industries Inc., redistilled, b.p. 129°C/5 mm; pure by GLC), 2-ethylhexanoic acid (Union Carbide Corp., pure by GLC and used as received) and 1,7-octadiene.

Phenyl isocyanate (Eastman Kodak Co., white label; redistilled b.p. 166°C; pure by GLC) was used as a model isocyanate and the solvents, n-hexane (Fisher Scientific Co., spectroanalyzed grade) and toluene (J. T. Baker, Reagent grade; distilled from sodium) were used to represent the hydrocarbon portions of Telagen S, Bibenzyl, toluene and phenylcyclohexane were used as internal markers for the GLC studies.

In addition to these models which were previously reported[1] 1-butyl isocyanate (Eastman Kodak Co., practical grade, redistilled, b.p. 111-112°C) a model isocyanate, 1-benzoyl-2-ethylaziridine, a model aziridine, 1,2-epoxycyclohexane (Research Organic Chemicals Co., C.P.) a model epoxide and propionic (J. T. Baker Chemical Co., reagent grade) and hexanoic (Matheson, Coleman, and Bell, practical grade) acids, model carboxylic acids, were used in the continued studies of the effects of advanced fuels and oxidizers on binder ingredients. The aziridine was prepared by the reaction of benzoyl chloride with 2-ethylaziridine and distilled, b.p. 82-85°C at 0.2 mm.

4. Method for Studying Compatibility of Fuels with Model Compounds

The samples were prepared in a tared 1 dram shell vial within a weighing bottle. The tared bottle and vial were put into a dry nitrogen atmospheric box where the fuel sample was put into the shell vial. The weighing bottle was sealed, removed from the dry box in order to weigh the fuel and then returned to the dry box. The shell vial was fitted with a rubber serum cap after introduction of 0.5 ml of a solution containing a model compound, and removed from the box for gas chromatographic analysis. Chromatograms for some of the model compounds are shown in the previous quarterly report (AFRPL-TR-66-159).

Stored or heated, samples were sealed into 2-ml ampules prepared essentially by the method described above.

The gas chromatographic analyses were performed on an F & M Model 500 Gas Chromatograph equipped with a katharometer detector. A sample size of 10μ l was used for each analysis. Table XIV shows the column conditions used for the separations. Typical chromatograms are shown in Figures 25-27.

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[1] D. E. Johnson and A. J. Di Milo, First Quarterly Report No. AFRPL-TR-66-159, Contract AF 04(611)-11419, July 1966

GAS-LIQUID CHROMATOGRAM OF THE REACTION MIXTURE OF n-BUTYL ISOCYANATE AND 2-OCTANOL IN BENZENE

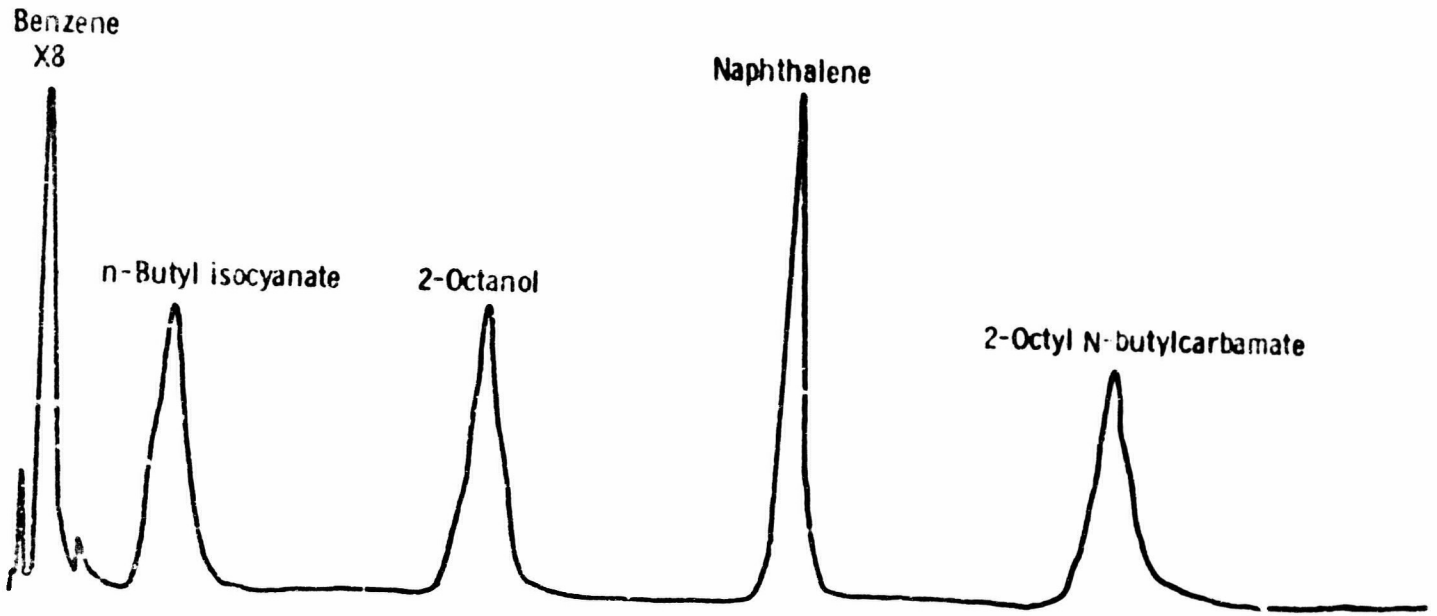

Figure 25

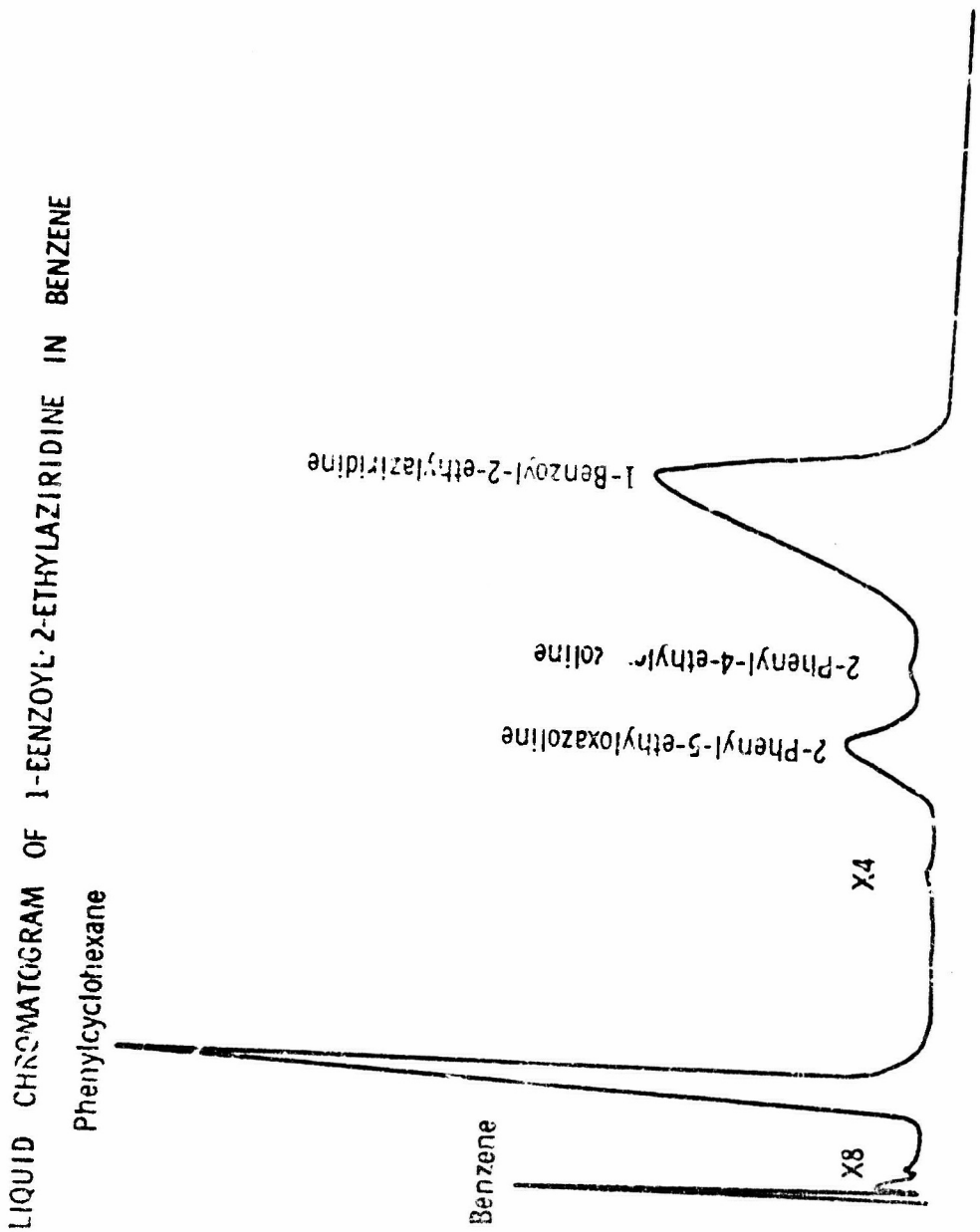
GAS-LIQUID CHROMATOGRAM OF 1-BENZOYL-2-ETHYLAZIRIDINE IN BENZENE
Phenylcyclohexane
Benzene
X8
X4
2-Phenyl-5-ethyloxazoline
2-Phenyl-4-ethyl
oline
1-Benzoyl-2-ethylaziridine

Figure 26

GAS-LIQUID CHROMATOGRAM OF A MIXTURE OF 1, 2-EPOXYCYCLOHEXANE AND HEXANOIC ACID IN BENZENE

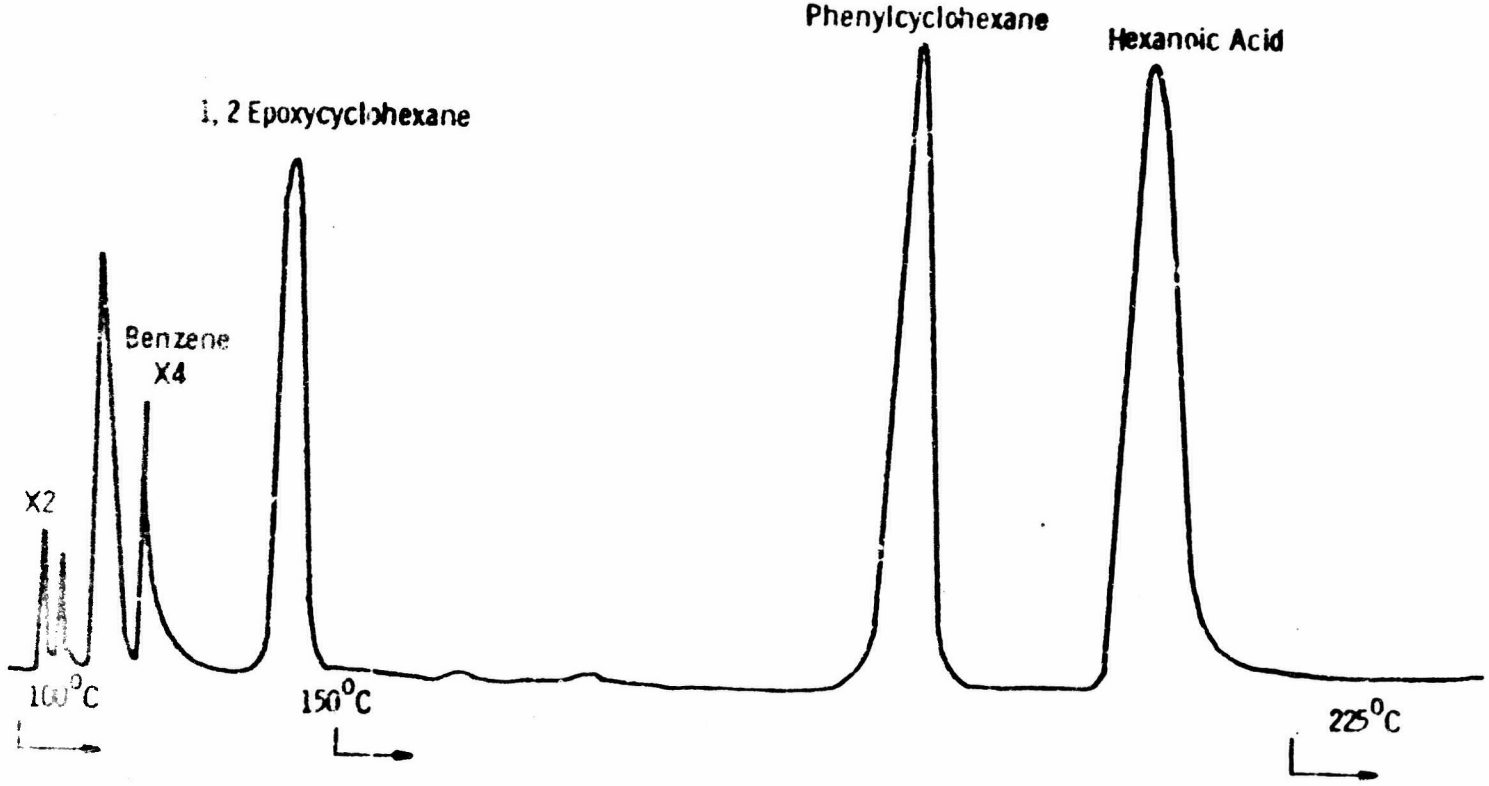

Figure 27

Table XIV

CHROMATOGRAPHIC CONDITIONS FOR ANALYSIS OF MODEL SYSTEMS BY GLC

	Materials Analyzed		
	Alconol-Isocyanate	Aziridine-Acid	Epoxide-Acid
Column Material	4[a]	2[b]	1[c]
Temperature, °C	75 - 225	115	100 - 225[d]
Heating Rate, °C/min	21	-	-
Gas Flow, ml/min	100	100	60
Injection Port Temp., °C	200	175	200
Block Temp., °C	300	300	300
Bridge Current, m.a.	150	150	150

[a] 2' x 1/4" stainless steel; 20% DC 705 on 80-100 mesh Diatoport S.
[b] 1½ x 1/4" stainless steel; 5% Carbowax 6000 on 80-100 mesh Diatoport S.
[c] 4' x 1/4" stainless steel; 10% carbowax 20M on 60-80 mesh Diatoport S.
[d] Stepwise heating: 100°/3 min; 150°C/10 min; 225°C to end.

5. Long Term Compatibility Studies of Model Acid, Hydroxy, Unsaturated and Isocyanate Compounds with Advanced Fuels

Long term compatibility studies indicated that over a period of 34 days at 50°C alcohols and unsaturated compounds were stable in the presence of LMH-1 (untreated), chrome passivated beryllium and LMH-2 (untreated), but carboxylic acids were quite unstable (Table XV). A sample of phenyl isocyanate in LMH-1 evolved sufficient gas pressure to rupture the sample vial when it was opened.

6. Compatibility of Model Isocyanate Compounds with Advanced Fuels and Oxidizers

n-Butyl isocyanate was unstable in the presence of the three fuels (as received) when held at 50°C for 18 hours (Table XVI). The order of loss of isocyanate was LMH-2 > Be > LMH-1. The type of isocyanate, aromatic or alkyl, made little difference in stability with the fuels (Table XVII).

Table XV

LOSS (%) OF BINDER COMPONENTS IN CONTACT WITH ADVANCED FUELS (UNTREATED)

(34 days at 50°C)

Component	Fuel/Component Weight Ratio	LMH-1	Be	LMH-2
n-Nonanoic Acid	2	55.5	48.5	100
2-Ethylhexanoic Acid	2	42.5	34.0	100
1-Decanol	2	0	7.5	1.0
2-Octanol	2	0	5.5	1.0
1,7-Octadiene	8	5.0	2.0	-

Table XVI

LOSS (%) OF n-BUTYL ISOCYANATE IN CONTACT WITH ADVANCED FUELS (UNTREATED)

(18 hours)

Fuel	Fuel/Component Weight Ratio	Temp. °C 23	50
LMH-1	12	5	12
Be	13	23	31
LMH-2	9	-	40

Table XVII

LOSS (%) OF ISOCYANATE IN CONTACT WITH ADVANCED FUELS AND OXIDIZERS

(18 hours at 50°C)

Fuel or Oxidizer	C_6H_5NCO	$n\text{-}C_4H_9NCO$
LMH-1	8.4	12
Be	26.0	31
LMH-2	-	40
HAP	-	18

7. Compatibility of Model Binder Components with HAP

The study of model binder components with the oxidizer HAP indicated that alcohols, carboxylic acids and unsaturated compounds were stable in the presence of HAP but n-butyl isocyanate showed some instability (see Table XVIII). It should be noted that these results would not necessarily be true for combinations of these functional groups. It has been reported that allyllic alcohols are incompatible with HAP.

Table XVIII

LOSS (%) OF BINDER COMPONENTS ON HAP

(after 18 hours)

Component	HAP/Component, Weight Ratio	23°C	50°C
n-Nonanoic Acid	11	0	0
2-Ethylhexanoic Acid	11	0	0
1-Decanol	8	0	0
2-Octanol	8	0	0
1,7-Octadiene	28	3	4
n-Butyl Isocyanate	28	15	18

8. Compatibility of a Model Isocyanate Curing System with Advanced Fuels, Oxidizer, and Mixtures of Fuels and Oxidizer

A model isocyanate curing system was studied in the presence of beryllium, LMH-2, HAP, and mixtures of HAP and advanced fuels. A comparison with a control experiment of the reaction between 1-butyl isocyanate and 2-octanol indicated that the presence of beryllium or LMH-2 had no effect on the rate of formation or the amount of the urethane product (Table XIX). It was also noted that there was an initial loss of 6% and 12%, respectively, of isocyanate when beryllium or LMH-2 was present. Possibly the isocyanate was reacting with a small amount of water present on the surface of the untreated advanced fuels. As indicated previously the isocyanates were not completely unreactive in the presence of advanced fuels (Tables XVI and XVII). Losses of isocyanate up to 40% were observed in the presence of the untreated advanced fuel when no alcohol was present. The greater loss of isocyanate could be ascribed to homopolymerization of the isocyanate and the reaction of isocyanate with water to form carbamic acid. The subsequent thermal decomposition of the carbamic acid could produce an amine, which would react further with the isocyanate to form a urea derivative, and carbon dioxide. The latter possibility was substantiated by the fact that in all previous compatibility studies of isocyanates with advanced fuels gas formation was observed.

The oxidizer, HAP, was an excellent catalyst for the formation of urethanes. The reaction of 1-butyl isocyanate and 2-octanol at 50°C in the presence of HAP was essentially complete after 4 hours (Table XX), whereas the same reaction without HAP was only 15% complete (Table XIX). The isocyanate reaction in the presence of HAP was complete after 150 minutes at a temperature of 23°C indicating that the reaction at 50°C was considerably faster (Table XXI).

Table XIX

RATE OF REACTION OF n-BUTYL ISOCYANATE AND 2-OCTANOL IN CONTACT WITH ADVANCED FUELS AT 50°C[a]

Control (no additives)

Time, hr	R-NCO %	R-OH %	Prod %	Σ(R-OH+Prod) %
0	100	100	0	100
4	84	86	10	96
8	74	74	21	95
18	51	55	37	92
24	42	44	48	93
48	19	21	72	93
		Be[b]		
4	80	86	15	101
8	65	70	21	91
18	48	57	36	93
24	36	37	47	84
48	16	23	67	90
		LMH-2[b]		
8	70	81	21	102
18	38	51	43	94
24	27	37	50	87
44	10	23	69	92

[a] NCO to OH = 1:1 equivalent ratio.
[b] Fuel to component weight ratio is 2.2:1.

Table XX

RATE OF REACTION OF n-BUTYL ISOCYANATE AND 2-OCTANOL IN CONTACT WITH HAP AND WITH A MIXTURE (1:1) OF HAP AND Be AT 50°C[a]

HAP[b]

Time, hr	R-NCO %	R-OH %	Urethane %	Σ(R-OH+Urethane) %
4	7	9	64	73
8	6	9	60	69
18	5	8	63	71
24	4	12	61	73
48	4	10	60	70

HAP-Be Mixture[c]

4	4	15	56	71
8	5	20	44	64
18	4	28	47	69
24	-	18	37	55
48	-	18	34	52

[a] NCO to OH = 1:1 equivalent ratio; for control see Table XIX.
[b] Solids to component ratio is 2.2:1.
[c] Solids to component ratio is 1:1.

Table XXI

RATE OF REACTION OF n-BUTYL ISOCYANATE AND 2-OCTANOL WITH HAP AND WITH A MIXTURE (1:1) OF HAP AND Be OR LMH-2 AT 23°C[a]

HAP[b]

Time, (min)	R-NCO %	R-OH %	Urethane %	Σ(ROH+Urethane) %
0	100	100	0	100
30	52	52	33	85
60	27	32	52	84
90	19	23	52	86
150	12	14	58	72
210	14	14	59	73
1610	13	12	50	62

HAP-Be Mixture[c]

30	77	80	16	96
60	60	72	35	107
90	32	32	46	78
150	14	21	47	68
210	26	27	44	71
1610	21	32	40	72

HAP-LMH-2 Mixture[c]

30	72	79	8	87
60	52	70	15	85
90	50	65	17	82
150	27	43	20	53
210	15	37	20	57
1610	13	31	17	48

[a] NCO to OH = 1:1 equivalent ratio.
[b] Solid to component weight ratio is 2.2:1.
[c] Solid to component weight ratio is 1:1.

The main difference, besides catalysis, in the reaction of isocyanate with alcohol in the presence and absence of HAP was the amount of urethane that was found in solution. In both cases, with and without HAP, the respective consumption of isocyanate and alcohol were approximately equal indicating a stoichiometric reaction. The observation of less urethane than expected for the extent of reaction when HAP was present (Tables XX and XXI might be caused by adsorption of the urethane on the surface of HAP.

The combination of an advanced fuel and HAP decreased the rate of the isocyanate-alcohol reaction. As a result there was an increased loss of isocyanate to side reactions and a considerable decrease in the detectable amount of urethane product (Tables XX and XXI).

9. The Effect of Drying Be and LMH-2 on Compatibility with a Model Isocyanate Curing System

Initial loss of n-butyl isocyanate in the isocyanate-alcohol reaction in the presence of chrome passivated Be and LMH-2 was ascribed to the side reaction of isocyanate with water. The amount of isocyanate lost to this side reaction was small but comparison with dried samples of chrome passivated Be and LMH-2 showed a complete reduction of this loss of isocyanate on Be and a 50% reduction of the loss on LMH-2 (Table XXII).

10. Compatibility of Model Aziridine and Epoxy Compounds with Advanced Fuels and Oxidizers

Solutions of the various model compounds were added to the solid fuel, oxidizer or mixture of the two and periodically analyzed by gas chromatography for concentration changes.

1-Benzoyl-2-ethylaziridine and 1,2 epoxyhexane were compatible with LMH-1, chrome passivated Be and LMH-2 at 50°C for 18 hours (Table XXIII). Both compounds were incompatible with HAP at 23° for 18 hours. The reaction of the aziridine and epoxide with an appropriate carboxylic acid was very slow at 23°; thus, the loss of both compounds was probably due to a HAP catalyzed homopolymerization (Table XXIV).

Binder systems utilizing aziridines and epoxides of the model types used in this study would not be practical when used with the oxidizer HAP.

11. Compatibility of Telagen S and Curing Agents with Advanced Fuels

A mixture of hydroxyl terminated Telagen S and untreated LMH-1 showed gas bubbles when kept at 135°F for four days. No bubbles or other reactions were observed in mixtures of the prepolymer with chrome coated Be or of the prepolymer and untreated LMH-2 after 20 days at 135°F. Similar results were obtained in mixtures of the isocyanates and advanced fuels. A mixture of MDI, CTI and LMH-1 showed gas bubbles when stored at 135°F for 14 days. Similar mixtures using chrome coated Be and LMH-2 gave no evidence of gas evolution under the same conditions.

Table XXII

THE EFFECT OF DRYING[a] Be AND LMH-2 ON COMPATIBILITY WITH n-BUTYL ISOCYANATE AND 2-OCTANOL AT 50°C

Run No.	Time, hr		Chromatographic Areas RNCO	ROH	Total	RNCO %	Deviation from Control
1	8	Control	869	1240	2109	41.2	-
		Be	687	1060	1747	39.3	1.9
		LMH-2	629	1072	1701	37.0	4.2
2	4	Control	787	820	1607	49.0	-
		Be	735	784	1519	48.4	0.6
		LMH-2	654	791	1445	45.3	3.7
		Be (dried)	729	747	1476	49.3	-0.3
		LMH-2 (dried)	697	775	1472	47.4	1.6

[a]Be and LMH-2 dried over P_2O_5 at 80°C and 1 mm vacuum for 72 hours.

Table XXIII

COMPATIBILITY OF 1,2-EPOXYHEXANE AND 1-BENZOYL-2-ETHYLAZIRIDINE WITH ADVANCED FUELS AND OXIDIZER[a]

(18 hours at 50°C)

	Epoxide %	Aziridine %
Control	49.3	67.5
Be	49.8	68
LMH-1	50.6	69
LMH-2	49.3	68
Be + HAP	0	-
LMH-2 + HAP	0	-
HAP	-	22.7[b,c]

[a]Percents based on sum of marker and compound listed.
[b]63% of this was oxazolines.
[c]At 23°C, 41% aziridine of which 48% was oxazolines.

Table XXIV

COMPATIBILITY OF 1,2-EPOXYHEXANE + HEXANOIC ACID AND 1-BENZOYL-2-ETHYLAZIRIDINE + PROPIONIC ACID WITH HAP[a]

	Temp, °C	Aziridine %	Acid %	Epoxide %	Acid %
Control	23	58.4	39.8	35.6	59.8
	50	-	-	33.0	59.5
HAP	23	13.6[b]	36.2	27.5	59.8
	50	-	-	3.6	56.5

[a] Percents based on sum of marker and compound listed.
[b] 2-Phenyl-4-ethyloxazoline.

While energetic plasticizers TMETN ($CH_3C[CH_2ONO_2]_3$) and NEMMC ($O_2NOCH_2CH_2OCON[NO_2]CH_3$) inhibit the cure of binders, they did not prevent the cure of propellants formulated with them.

Binder samples containing LMH-1 gave evidence of foaming during a 135°F cure. Samples with chrome coated Be and LMH-2 did not foam and cured within 5 days at 135°F. Impact sensitivities of the above samples were greater than 100 cm/2 kg weight, the limit of the apparatus used.

Propellant mixtures were prepared using the candidate binder and the advanced fuels. TMETN, NEMMC or IDP were used as the plasticizers, along with NH_4ClO_4 as the oxidizer. All propellants cured after three days at 135°F. No foaming was observed in the small (0.5 gm) samples.

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5 AUTHOR(S) (Last name, first name, initial)

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11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
	Air Force Rocket Propulsion Laboratory Research and Technology Division Edwards, California Air Force Systems Command, United States Air Force

13 ABSTRACT

(U) The investigation and characterization of the saturated hydrocarbon binder developed under Contract AF 04(611)-10386 for use in solid rocket propellants were continued. Forty-five pounds of a secondary hydroxy terminated Telagen S were delivered to Aerojet and characterized. Functionality determined from the crosslink density of a binder (1.9) is higher than that determined from the molecular weight to equivalent weight ratio (1.65). The difference may be due to nonfunctional units in the prepolymer. Aluminum metal does not interfere with cure stoichiometry of "workhorse" propellants, but the interference of certain plasticizers was further demonstrated. Binders were made from the Telagen S prepolymers and characterized by uniaxial tensile behavior at 77°F, stress relaxation at 77° and 150°F, compression after swelling in toluene, gel and sol fractions, and Mooney-Rivlin constants. Linear relations were demonstrated between the gel fraction, the Mooney-Rivlin C_1 constant, the crosslink density, and the logarithm of the initial uniaxial tensile modulus. Swelling studies in a large number of solvents indicate a CED value of about 80 for the binder. Propellants were made on a 400-gm scale and were characterized. The pressure exponent for burning rate was 0.7 for these propellants (88 wt% solids). The relative viscosity of NH_4ClO_4-Cronite 6 slurries was at a minimum for an oxidizer blend of 35.80%, 32.10% and 32.10% by weight of particles averaging 6, 148, and 419 μ, respectively. This blend was selected to prepare a high solids loaded propella...

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Saturated Hydroxy Terminated Polybutadienes						
Saturated Carboxy Terminated Polybutadienes						
Effect of Plasticizers on Isocyanate Curing Agents						
Effect of Pretreated Plasticizers on Isocyanate Curing Agents						
Effect of Plasticizer-Isocyanate Interaction on Mechanical Behavior of Urethane Binders						
Effect of Plasticiser-Isocyanate Interaction on Mechanical Behavior of Urethane Propellants						
Effect of Fillers on Viscosity of Liquids						
Viscosity of NH_4ClO_4-Cronite 6 Slurries						
Compatibility of Advanced Oxidizers with Saturated Polybutadienes						
Be						
LMH-1, LMH-2						
HAP						

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