

AD-750 551

HTPB POLYMER IMPROVEMENT

W. D. Allan, et al

Lockheed Propulsion Company

Prepared for:

Air Force Rocket Propulsion Laboratory

September 1972

DISTRIBUTED BY:

**NTIS**

National Technical Information Service  
U. S. DEPARTMENT OF COMMERCE  
5285 Port Royal Road, Springfield Va. 22151

# AD 750551

## HTPB POLYMER IMPROVEMENT

LOCKHEED PROPULSION COMPANY  
REDLANDS, CALIFORNIA

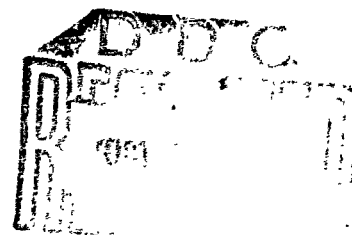
APPROVED FOR  
PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED

TECHNICAL REPORT AFRPL-TR-72-89

SEPTEMBER 1972

NATIONAL TECHNICAL  
INFORMATION SERVICE

AIR FORCE ROCKET PROPULSION LABORATORY  
RESEARCH AND TECHNOLOGY DIVISION  
AIR FORCE SYSTEMS COMMAND  
UNITED STATES AIR FORCE  
EDWARDS, CALIFORNIA



|                                 |                                                   |
|---------------------------------|---------------------------------------------------|
| ACCESSION for                   |                                                   |
| NTIS                            | White Section <input checked="" type="checkbox"/> |
| DDC                             | Brit. Section <input type="checkbox"/>            |
| UNANNOUNCED                     | <input type="checkbox"/>                          |
| JUSTIFICATION                   |                                                   |
| BY                              |                                                   |
| DISTRIBUTION/AVAILABILITY CODES |                                                   |
| Dist.                           | AVAIL. and/or SPECIAL                             |
| A                               |                                                   |

When U.S. Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise, or in any manner licensing the holder or any person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

UNCLASSIFIED

Security Classification

## DOCUMENT CONTROL DATA - R &amp; D

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

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  |                                                                                                                  |                      |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|------------------------------------------------------------------------------------------------------------------|----------------------|
| 1. ORIGINATING ACTIVITY (Corporate author)<br>Lockheed Propulsion Company<br>P.O. Box 111<br>Redlands, California 92373                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |  | 2a. REPORT SECURITY CLASSIFICATION<br>Unclassified                                                               |                      |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  | 2b. GROUP                                                                                                        |                      |
| 3. REPORT TITLE<br><br>HTPB POLYMER IMPROVEMENT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  |                                                                                                                  |                      |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates)<br>Technical Report,                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |  |                                                                                                                  |                      |
| 5. AUTHOR(S) (First name, middle initial, last name)<br><br>W. D. Allan, W. E. Baumgartner and G. E. Myers, 1 May , '72 through 31 August 1972                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |  |                                                                                                                  |                      |
| 6. REPORT DATE<br>September 1972                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |  | 7a. TOTAL NO. OF PAGES<br>36                                                                                     | 7b. NO. OF REFS<br>1 |
| 8a. CONTRACT OR GRANT NO.<br>F04611-72-C-0038                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |  | 8b. ORIGINATOR'S REPORT NUMBER(S)<br>625-I-2                                                                     |                      |
| b. PROJECT NO.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |  | 9b. OTHER REPO. NO(S) (Any other numbers that may be assigned this report)<br>AFRPL TR-72-89                     |                      |
| c.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |  |                                                                                                                  |                      |
| d.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |  |                                                                                                                  |                      |
| 10. DISTRIBUTION STATEMENT<br><br>Approved for Public Release; Distribution Unlimited                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |  |                                                                                                                  |                      |
| 11. SUPPLEMENTARY NOTES                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |  | 12. SPONSORING MILITARY ACTIVITY<br>Air Force Rocket Propulsion Laboratory<br>Edwards Air Force Base, California |                      |
| 13. ABSTRACT<br><br>From among the laboratory preparations of modified R-45M HTPB prepolymer that were previously examined, four were produced in a pilot plant for evaluation in 90-percent solids propellant. The pilot plant samples covered a molecular weight range from 2700 to 4100 and possessed weight average functionalities between 2.0 and 2.1. Propellant processability in each case was inferior to that of standard R-45M. On the basis of tensile properties and crack propagation tests, no distinctive differences in propellant mechanical behavior were apparent. Detailed comparison of thermal cycling behavior will be made in the final program phase. |  |                                                                                                                  |                      |

1a

IL

# HTPB POLYMER IMPROVEMENT

SEPTEMBER 1972

IC

## FOREWORD

This is the second Technical Summary Report issued under Contract F04611-72-C-0038, "HTPB Polymer Improvement", a program being conducted by Lockheed Propulsion Company, Redlands, California, and monitored by the Air Force Rocket Propulsion Laboratory (Robert L. Limoges, Second Lieutenant, MKPA, Program Monitor). The program is being conducted in cooperation with the manufacturer of the R-45 HTPB prepolymer: the Atlantic Richfield Corporation (ARCO), Philadelphia, Pennsylvania; and with the Government Research Laboratory, Esso Research and Engineering, Linden, New Jersey. Participating technical personnel are Dr. W. E. Baumgartner (Program Manager), Dr. G. E. Myers (Project Engineer), W. D. Allan and W. E. Heikkila at Lockheed Propulsion Company; Dr. P. W. Ryan and K. C. Ramey at ARCO; and A. E. Muenker at Esso.

Publication of this report does not constitute Air Force approval of the report's findings and conclusions. It is published only for the exchange and stimulation of ideas.

Robert L. Limoges  
Second Lieutenant  
MKPA

## ABSTRACT

From among the laboratory preparations of modified R-45M HTPB prepolymer that were previously examined, four were produced in a pilot plant for evaluation in 90-percent solids propellant. The pilot plant samples covered a molecular weight range from 2700 to 4100 and possessed weight average functionalities between 2.0 and 2.1. Propellant processability in each case was inferior to that of standard R-45M. On the basis of tensile properties and crack propagation tests, no distinctive differences in propellant mechanical behavior were apparent. Detailed comparison of thermal cycling behavior will be made in the final program phase.



## TABLE OF CONTENTS

| <u>Section</u>                                    | <u>Page</u> |
|---------------------------------------------------|-------------|
| I INTRODUCTION                                    | 1           |
| II SUMMARY                                        | 3           |
| III RESULTS                                       | 5           |
| 1. PREPOLYMER PREPARATION AND CHARACTERIZATION    | 5           |
| a. Analytical Results                             | 5           |
| b. Parameter Correlation                          | 9           |
| 2. EVALUATION IN PROPELLANT                       | 9           |
| a. Propellant Processability                      | 9           |
| b. Propellant Tensile Behavior                    | 16          |
| c. Propellant Fracture Mechanics                  | 16          |
| d. Strain/Temperature Cycling of JANNAF Specimens | 30          |
| 3. CONCLUSIONS                                    | 30          |
| IV FUTURE WORK                                    | 33          |
| <br><u>Appendix</u>                               |             |
| A LABORATORY SAMPLE CHARACTERIZATION SUMMARY      | 35          |

## LIST OF ILLUSTRATIONS

| <u>Figure</u> |                                                                                                  | <u>Page</u> |
|---------------|--------------------------------------------------------------------------------------------------|-------------|
| 1             | Prepolymer Viscosity versus $\bar{M}_n$                                                          | 11          |
| 2             | Prepolymer $\bar{f}_w$ versus $\bar{M}_n$                                                        | 12          |
| 3             | Relative End-of-Mix Viscosity versus $\bar{M}_n$                                                 | 14          |
| 4             | Tensile Behavior of Control Sample (90-percent Solids); NCO/OH = 0.80; 0.54 in./in./min          | 19          |
| 5             | Tensile Behavior of Control Sample (90-percent Solids); NCO/OH = 0.80; No MT-4; 0.54 in./in./min | 20          |
| 6             | Tensile Behavior of Sample F-2 (90-percent Solids); NCO/OH = 0.95; 0.54 in./in./min              | 21          |
| 7             | Tensile Behavior of Sample F-2 (90-percent Solids); NCO/OH = 1.0; No MT-4; 0.54 in./in./min      | 22          |
| 8             | Tensile Behavior of Sample G-2 (90-percent Solids); NCO/OH = 0.85; 0.54 in./in./min              | 23          |
| 9             | Tensile Behavior of Sample G-2 (90-percent Solids); NCO/OH = 0.85; No MT-4; 0.54 in./in./min     | 24          |
| 10            | Tensile Behavior of Sample R-2 (90-percent Solids); NCO/OH = 0.95; 0.54 in./in./min              | 25          |
| 11            | Tensile Behavior of Sample R-2 (90-percent Solids); NCO/OH = 0.95; No MT-4; 0.54 in./in./min     | 26          |
| 12            | Tensile Behavior of Sample S-2 (90-percent Solids); NCO/OH = 1.05; 0.54 in./in./min              | 27          |

## LIST OF TABLES

| <u>Table</u> |                                                                                         | <u>Page</u> |
|--------------|-----------------------------------------------------------------------------------------|-------------|
| I            | ANALYTICAL CHARACTERIZATION OF PILOT PLANT SAMPLES                                      | 6           |
| II           | COMPARISON OF ANALYTICAL PARAMETERS: LABORATORY VERSUS PILOT PLANT SAMPLES              | 7           |
| III          | SOLVENT PRECIPITATION FRACTIONATION OF PILOT PLANT SAMPLES                              | 8           |
| IV           | COMPARISON OF MEASURED AND CALCULATED PARAMETERS FOR SOLVENT PRECIPITATED FRACTIONATION | 10          |
| V            | PROPELLANT PROCESSABILITY (90% SOLIDS); VISCOSITY (KP AFTER HOURS)                      | 13          |
| VI           | RELATIVE PROPELLANT VISCOSITY AFTER 3 HOURS AT 40°C                                     | 15          |
| VII          | PROPELLANT MECHANICAL PROPERTIES AT 90 PERCENT SOLIDS (From Instron Load/Time Trace)    | 17          |
| VIII         | COMPARATIVE TENSILE PROPERTIES                                                          | 18          |
| IX           | TENSILE PARAMETERS FROM TRUE STRESS/STRAIN CURVES FOR 90 PERCENT SOLIDS PROPELLANT      | 28          |
| X            | PROPELLANT CRACK PROPAGATION                                                            | 29          |
| XI           | TEMPERATURE/STRAIN CYCLING RESULTS                                                      | 31          |

## GLOSSARY

|                                                 |                                                               |
|-------------------------------------------------|---------------------------------------------------------------|
| ARCO                                            | Atlantic Richfield Corporation                                |
| B, C, E, F,<br>G, K, L, M,<br>N, N', O,<br>P, Q | Laboratory preparations of prepolymer                         |
| EOM                                             | End of mix                                                    |
| Esso                                            | Government Research Laboratory, Esso Research and Engineering |
| $\bar{f}_n$                                     | Number average functionality                                  |
| $\bar{f}_w$                                     | Weight average functionality                                  |
| GPC                                             | Gel permeation chromatography                                 |
| HTPB                                            | Hydroxy-terminated polybutadiene                              |
| IPDI                                            | Isophorane diisocyanate                                       |
| KP                                              | Kilopoise                                                     |
| LPC                                             | Lockheed Propulsion Company                                   |
| $\bar{M}_n$                                     | Number average molecular weight                               |
| $\bar{M}_w$                                     | Weight average molecular weight                               |
| MT-4                                            | Bonding agent                                                 |
| NCO/OH                                          | Isocyanate to hydroxyl equivalents ratio                      |
| p                                               | poise                                                         |
| RR                                              | Round Robin R-45M. Lot 110225                                 |
| R-45M                                           | ARCO HTPB. Free radical polymerized                           |
| TSI                                             | Toluene sulfonyl isocyanate                                   |
| VPO                                             | Vapor phase osmometer                                         |
| $\eta$                                          | Prepolymer viscosity in poise                                 |
| $\sigma_{in}/\epsilon_m$                        | Stress and strain at maximum load (stress)                    |
| $\sigma_b/\epsilon_b$                           | Stress and strain at rupture                                  |

(The reverse is blank)

## SECTION I

## INTRODUCTION

The commercially available ARCO R-45M HTPB prepolymer is being extensively studied for applications in highly loaded solid propellants and possesses some advantage over CTPB prepolymers in those systems. It does have some deficiencies, however, in potlife control and in balancing mechanical properties at low and high temperatures, which presumably are caused by the material's low molecular weight ( $\bar{M}_n \sim 3000$ ), high functionality ( $f_w \sim 2.3$ ), and high reactivity of its functional groups.

This program was established to determine whether the available variations in ARCO's free radical polymerization process could produce a modified R-45M possessing superior characteristics for use in solid propellants. In the program ARCO was to prepare 11 prepolymer samples under laboratory conditions/scale, each sample representing specific variations in their polymerization process. Those samples were to be characterized by both ARCO and Esso and evaluated in propellant on a small scale by LPC. Subsequently, three of those prepolymer lots were to be scaled up to the pilot plant level, characterized, and evaluated for propellant performance.

The first report under the program described the results of the characterization and evaluation of the laboratory samples (Ref 1). Those samples possessed a wide range of average molecular weight and average functionality. Their propellants also exhibited a wide range of processability, controlled primarily by molecular weight. However, propellant tensile properties generally showed relatively minor variations among the samples, i.e., molecular weight and functionality had little effect upon tensile behavior.

From the available data three prepolymers were selected for scaleup, covering the molecular weight range from about 2500 to 4000 and possessing functionalities very close to 2.0. This report describes the characterization and evaluation of the pilot plant samples.

---

(Ref 1). Baumgartner, W.E. and Myers, G.E., HTPB Polymer Improvement, AFRPL-TR-72-50, LPC Report No. 625-I-1, June 1972

(The reverse is blank)

## SECTION II

## SUMMARY

From the polymerization process conditions previously employed in producing 14 laboratory samples of R-45M type prepolymers, ARCO has used four conditions on the pilot plant scale to produce four prepolymers at the 25- to 50-pound level. These were characterized analytically by ARCO and Esso, and evaluated by LPC in 90-percent solids propellant (Oronite-6 plasticizer, IPDI curative, with and without MT-4).

The analytical results are summarized as follows:

- Reproducibility between pilot plant and laboratory preparations is excellent.
- $\bar{M}_n$  varied from 2700 to 4100 with  $\bar{f}_w$  values between 2.0 to 2.1.
- Solvent precipitation fractionation took place on the basis of molecular weight and/or equivalent weight, with some indication that  $\bar{f}_w$  increases with  $\bar{M}_n$ .

Evaluation in propellant showed the following:

- Processability of the pilot plant samples was inferior to that of standard R-45M. However, this may be at least partially the consequence of higher impurity levels occasioned by incomplete pilot plant cleanup.
- No clear superiority over standard R-45M was observed from tensile properties or from crack propagation tests. (Some indication of improved thermal cycling capability was obtained from feasibility tests of a simultaneous strain/temperature cycling procedure, but these results must still be regarded with caution.)

However, this somewhat unexpected failure of material having higher molecular weight and functionalities close to two, to produce improved propellant mechanical behavior could be the consequence of relying largely upon uniaxial tensile tests for the mechanical properties evaluation. The last phase of the program will evaluate in greater detail the thermal cycling capability of propellants prepared from three of the pilot plant prepolymers.

(The reverse is blank)

## SECTION III

## RESULTS

## 1. PREPOLYMER PREPARATION AND CHARACTERIZATION

Four prepolymers were prepared in the ARCO pilot plant at approximately the 50-pound level; three of them were prepared under conditions duplicating those used for the laboratory samples F, G, and R\*, while the fourth (S-2) involved a further process modification. Initial preparations contained unacceptably high iron levels due to reactor startup problems. The repeat preparations tended toward higher iron levels than possessed by the laboratory samples but were regarded as satisfactory for the program. After preparation, all samples were stored under nitrogen in air-tight containers. Pilot plant samples have been designated F-2, G-2, R-2, and S-2 to distinguish them from the laboratory samples F, G, etc.

## a. Analytical Results

The samples were characterized by number average molecular weight, analytical GPC, equivalent weight, number average and weight average functionality, viscosity, and impurities using methods described in the previous report (Ref 1). In addition, preparative scale fractionations were conducted by solvent precipitation at ARCO and the fractions also were characterized.

Table I summarizes the analysis results for the pilot plant samples, and Table II compares several parameters for pilot plant versus laboratory preparations. The following points are noted:

- $\bar{M}_n$  varies from about 2700 to 4100 and polydispersities are nearly equal.
- $\bar{f}_n$  values are all 2.0 within experimental error whereas values of  $\bar{f}_w$  are between 2.0 and 2.1.
- S-2 appears to be equivalent to R-2.
- Reproducibility between laboratory and pilot plant is excellent.

ARCO separated each of the pilot plant samples into three fractions by addition of methanol to a 10-percent cyclohexane/acetone solution at 25°C. Table III summarizes the analytical values for the fractions and Table IV compares the corresponding parameters for each of the original prepolymers with those calculated from the fractionation data. The fractionation obviously took place on the basis of both  $\bar{M}_n$  and equivalent weight. Table III indicates that  $\bar{f}_w$  increases with molecular weight, but some doubt is cast upon that conclusion by the comparison of measured and observed  $\bar{f}_w$

---

\* A tabulation of analytical results obtained for the laboratory samples is included as Appendix A for reference purposes.

TABLE I  
ANALYTICAL CHARACTERIZATION OF PILOT PLANT SAMPLES

| Sample | Lab  | $\bar{M}_n$ |      | $M_w/M_n$ | $\bar{M}_n$ | $\bar{f}_n$ | $\bar{f}_w$ (b) | $\eta$<br>(p. 30°C) | H <sub>2</sub> O<br>(ppm) | Fe<br>(ppm) | Peroxide<br>(mg/1000.g) | Volatiles<br>(%) |
|--------|------|-------------|------|-----------|-------------|-------------|-----------------|---------------------|---------------------------|-------------|-------------------------|------------------|
|        |      | VPO         | GPC  | (GPC)     | Eq Wt (a)   |             |                 |                     |                           |             |                         |                  |
| F-2    | ARCO | 4050        | 3910 | 1.65      | 2000        | 2.02        | 2.02            | 104                 | 500                       | 1           | 15                      | 0.1              |
|        | Esso | 4110        |      |           | 2110        | 1.95        | 2.03            |                     |                           |             |                         |                  |
|        | Avg  | 4080        |      |           | 2060        | 1.99        | 2.03            |                     |                           |             |                         |                  |
| G-2    | ARCO | 2960        | 2840 | 1.57      | 1450 (c)    | 2.04        | 2.04            | 50                  | 300                       | 8           | 15                      | 0.1              |
|        | Esso | 3060        |      |           | 1520        | 2.01        | 2.11            |                     |                           |             |                         |                  |
|        | Avg  | 3010        |      |           | 1490        | 2.03        | 2.08            |                     |                           |             |                         |                  |
| R-2    | ARCO | 2760        | 2630 | 1.52      | 1430        | 1.93        | 2.03            | 42                  | 300                       | 1           | 20                      | 0.1              |
|        | Esso | 2750        |      |           | 1400        | 1.96        | 2.09            |                     |                           |             |                         |                  |
|        | Avg  | 2760        |      |           | 1420        | 1.94        | 2.06            |                     |                           |             |                         |                  |
| S-2    | ARCO | 2730        | 2600 | 1.5       | 1430        | 1.90        | 2.03            | 38                  | 500                       | 2           | 15                      | 0.1              |
|        | Esso | 2670        |      |           | 1390        | 1.92        | 2.06            |                     |                           |             |                         |                  |
|        | Avg  | 2700        |      |           | 1410        | 1.91        | 2.05            |                     |                           |             |                         |                  |

(a) TSI

(b) Procedure modified by addition of catalyst to permit completion in 8 hours rather than several hundred hours.

(c) Acetic anhydride



TABLE II  
COMPARISON OF ANALYTICAL PARAMETERS:  
LABORATORY VERSUS PILOT PLANT SAMPLES

| Sample | Parameter <sup>(a)</sup> |                      |                     |                    |
|--------|--------------------------|----------------------|---------------------|--------------------|
|        | $\bar{M}_n^{(b)}$        | Eq Wt <sup>(c)</sup> | $\bar{f}_n$         | $\bar{f}_w^{(d)}$  |
| F      | 4100/4080<br>(-1%)(e)    | 2270/2060<br>(-9%)   | 1.81/1.99<br>(+10%) | 2.03/2.03<br>(0)   |
| G      | 3100/3010<br>(-3%)       | 1770/1490<br>(-15%)  | 1.75/2.03<br>(+16%) | 2.04/2.08<br>(+2%) |
| R      | 2530/2760<br>(+9%)       | 1220/1420<br>(+16%)  | 2.08/1.94<br>(-7%)  | 2.10/2.03<br>(-3%) |

(a) Laboratory/pilot plant

(b) VPO

(c) TSI

(d) Laboratory samples without catalyst. Pilot plant samples with catalyst.

(e) Percent change from laboratory to pilot plant.

TABLE III  
SOLVENT PRECIPITATION FRACTIONATION OF PILOT PLANT SAMPLES

| Fraction | Weight<br>Percent | $\bar{M}_n$ |      | Equivalent<br>Weight<br>(TSI) | $f_n$      | $f_w$      |
|----------|-------------------|-------------|------|-------------------------------|------------|------------|
|          |                   | VPO         | GPC  |                               |            |            |
| F-2      | 1                 | 2160        | 2100 | 1090                          | 1.99       | 2.02       |
|          | 2                 | 5300(4650)  | 4280 | 2380(2930)                    | 2.20(1.95) | 2.16(2.16) |
|          | 3                 | 5800        | 4720 | 2440                          | 2.38       | 2.24       |
| G-2      | 1                 | 1890        | 1950 | 940                           | 2.02       | 2.02       |
|          | 2                 | 4180(3555)  | 3660 | 1890(1860)                    | 2.22(1.91) | 2.15(2.22) |
|          | 3                 | 4720        | 4300 | 1960                          | 2.41       | 2.35       |
| R-2      | 1                 | 1570        | 1530 | 670                           | 2.36       | 2.05       |
|          | 2                 | 3320(3230)  | 3000 | 1750(1640)                    | 1.90(1.97) | 2.02(2.17) |
|          | 3                 | 4350        | 3730 | 1920                          | 2.26       | 2.20       |
| S-2      | 1                 | 1620        | 1770 | 760                           | 2.12       | 2.08       |
|          | 2                 | 3430(3660)  | 3060 | 1750(1710)                    | 1.76(2.14) | 2.06(2.12) |
|          | 3                 | 3900        | 3540 | 1960                          | 1.99       | 2.15       |

( ) = Esso values

in Table IV, which indicates that some modification of the fractions may have occurred during their preparation. Such modification, however, did not significantly affect molecular and equivalent weights.

#### b. Parameter Correlation

The first interim report presented crossplots for a number of the measured prepolymer parameters to determine what correlations might exist. Figures 1 and 2 illustrate two such plots when data points for the pilot plant samples are included. Figure 1 demonstrates that both laboratory and pilot plant samples follow the same  $\eta/\bar{M}_n$  relationship, and Figure 2 confirms that the ARCO polymerization process can vary molecular weight and functionality independently.

### 2. EVALUATION IN PROPELLANT

The four pilot plant prepolymer samples and a control (standard R-45M, Lot 008281) were evaluated at the 1-gallon mix scale in propellant containing 90-percent solids, 3-percent Oronite-6 plasticizer, and cured with IPDI. The evaluation was made at a minimum of two NCO/OH ratios with MT-4 bonding agent, and at one NCO/OH ratio without MT-4. Cure was at 160°F for 7 days.

#### a. Propellant Processability

The propellants were processed in a 1-gallon vertical Baker-Perkins mixer modified with a bottom discharge valve for casting directly from the mixer. A 170-minute mix cycle was employed, including 90 minutes after completing the addition of solids and 30 minutes final mix after curative addition. The end-of-mix (EOM) and potlife viscosities were determined by means of a Brookfield viscometer and a T-F bar. Table V summarizes the viscosity data.

As expected, much higher propellant viscosities were observed in the propellants containing MT-4 than in those that had no bonding agent. Where MT-4 was present, all of the pilot plant samples had EOM viscosities higher than those of the control (except sample S-2 at an NCO/OH ratio of 1.05). The relationship between prepolymer  $\bar{M}_n$  and the relative EOM viscosity of the pilot plant samples is presented in Figure 3, along with the previous data for the laboratory samples. Within the data scatter, EOM viscosity is controlled generally by prepolymer  $\bar{M}_n$ , with deviations probably occasioned by reactivity differences.

Table VI lists the relative mix viscosities 3 hours after EOM for the formulations containing MT-4. These values were obtained by smoothing the data from Table VI and are judged to be accurate to  $\pm 0.05-0.1$ . Processability therefore is in the order of Control > F, R > G, S. It is possible, however, that the poorer processability of the pilot plant samples to some extent may be due to their relatively high iron content. As noted earlier this is a temporary deficiency that should be obviated in further production. In the present study, no casting difficulties were encountered with any of the test formulations.

TABLE IV  
COMPARISON OF MEASURED AND CALCULATED PARAMETERS  
FOR SOLVENT PRECIPITATED FRACTIONATION

| Sample | $\bar{M}_n$ |               | Equivalent Weight |               | $\bar{i}_w$ |               |
|--------|-------------|---------------|-------------------|---------------|-------------|---------------|
|        | Measured(a) | Calculated(b) | Measured          | Calculated(c) | Measured    | Calculated(d) |
| F-2    | 4080        | 4161(3904)(e) | 2060              | 1932(2127)    | 2.03        | 2.15(2.15)    |
| G-2    | 3010        | 3191(2960)    | 1490              | 1491(1480)    | 2.08        | 2.14(2.19)    |
| R-2    | 2760        | 2824(2784)    | 1420              | 1341(1301)    | 2.06        | 2.06(2.15)    |
| S-2    | 2700        | 2752(2835)    | 1410              | 1353(1339)    | 2.05        | 2.08(2.12)    |

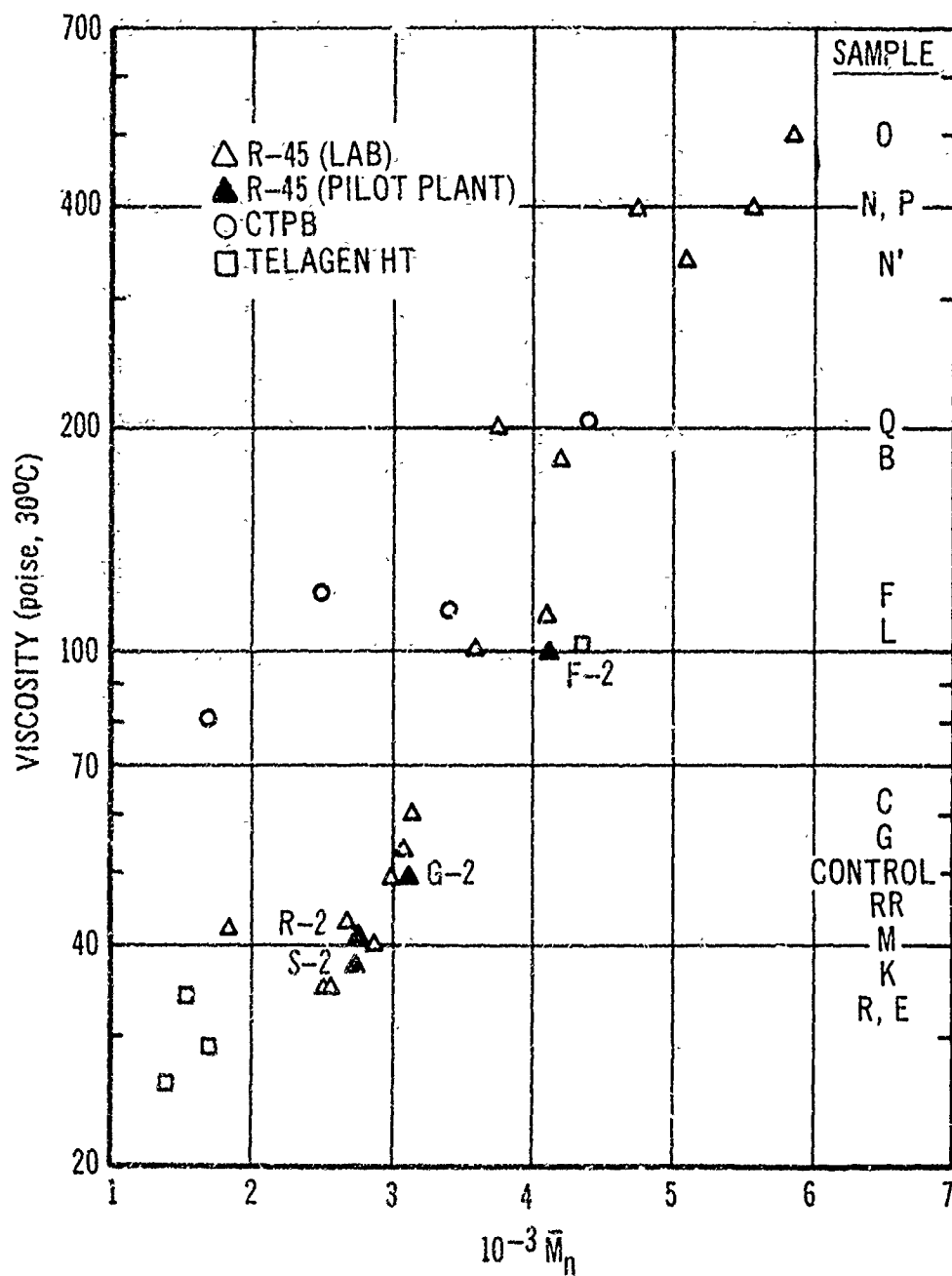
(a) VPO

$$(b) \quad \bar{M}_n = \frac{1}{\sum \frac{w_i}{M_{n_i}}}$$

$$(c) \quad \text{Eq Wt} = \frac{1}{\sum \frac{w_i}{E_i}}$$

$$(d) \quad f_w = \sum w_i^f w_i$$

(e) ( ) indicates values calculated using Esso's values for mid-fraction

Figure 1 Prepolymer Viscosity versus  $\bar{M}_n$

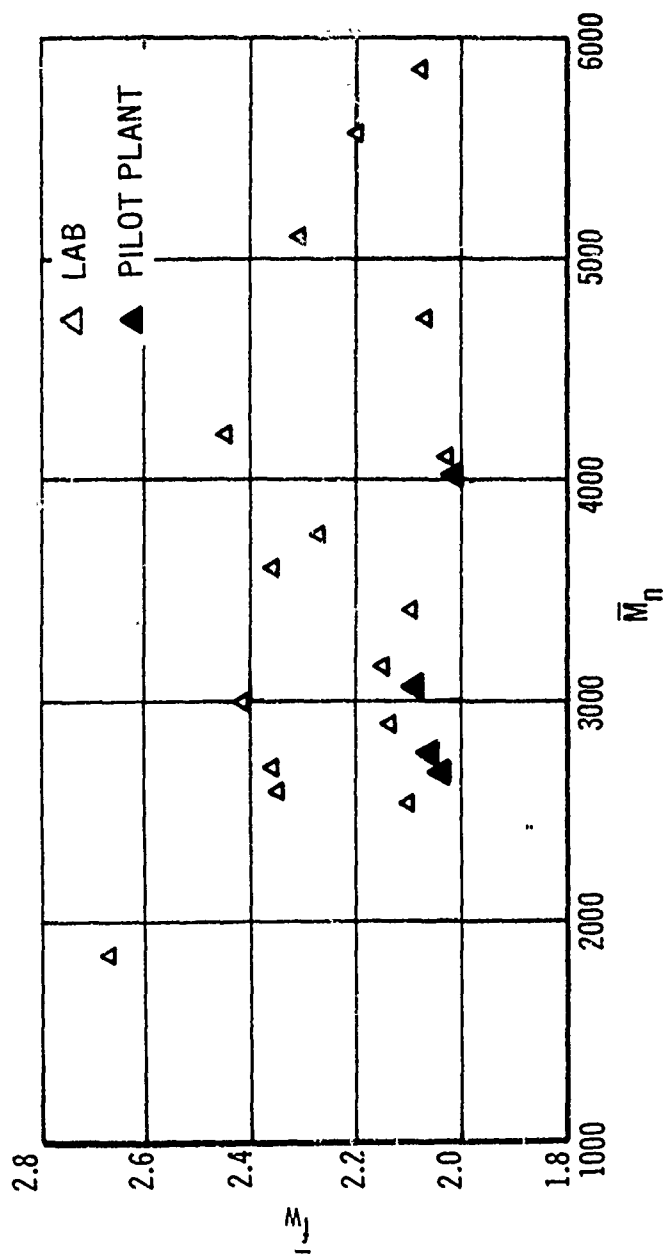


Figure 2 Prepolymer  $\bar{f}_w$  versus  $\bar{M}_n$

TABLE V  
PROPELLANT PROCESSABILITY (90% SOLIDS);  
VISCOSITY (KP AFTER HOURS)<sup>(a)</sup>

| Sample                  | NCO/OH         | EOM | Hours      |          |              |          |          |          |          |
|-------------------------|----------------|-----|------------|----------|--------------|----------|----------|----------|----------|
|                         |                |     | <u>1/2</u> | <u>1</u> | <u>1 1/2</u> | <u>2</u> | <u>3</u> | <u>4</u> | <u>5</u> |
| Control<br>(Lot 008281) | 0.80           | 28  |            |          |              |          |          |          |          |
|                         | 0.80 - No MT-4 | 14  |            |          |              |          |          |          |          |
|                         | 0.75           | 32  | 34         |          |              | 43       | 43       | 44       |          |
| F-2                     | 0.95           | 42  | 55         |          | 58           | 56       | 56       |          |          |
|                         | 0.95 - No MT-4 | 12  | 54         | 60       | 60           | 64       |          |          |          |
|                         | 1.00           | 46  |            |          |              |          |          |          |          |
| G-2                     | 0.85           | 48  |            |          | 69           | 74       |          | 65       |          |
|                         | 0.85 - No MT-4 | 19  |            |          |              |          |          |          |          |
|                         | 0.90           | 40  |            |          |              |          |          |          |          |
| R-2                     | 0.90           | 42  |            |          |              | 63       | 59       | 52       | 62       |
|                         | 0.95           | 38  |            |          |              |          |          |          |          |
|                         | 0.95 - No MT-4 | 11  | 20         |          |              | 28       |          |          |          |
| S-2                     | 1.00           | 44  | 65         |          |              | 67       |          |          | 74       |
|                         | 1.05           | 32  |            |          |              |          |          |          |          |
|                         | 1.05 - No MT-4 | 23  | 35         |          | 35           |          |          |          |          |

<sup>(a)</sup> Kilopoise. EOM = end of mix. Brookfield at 102°F. Total mix time = 170 minutes, including 90 minutes after solids addition complete and 30 minutes after curative addition. EOM viscosity measured 15 ± 5 minutes after termination of mixing.

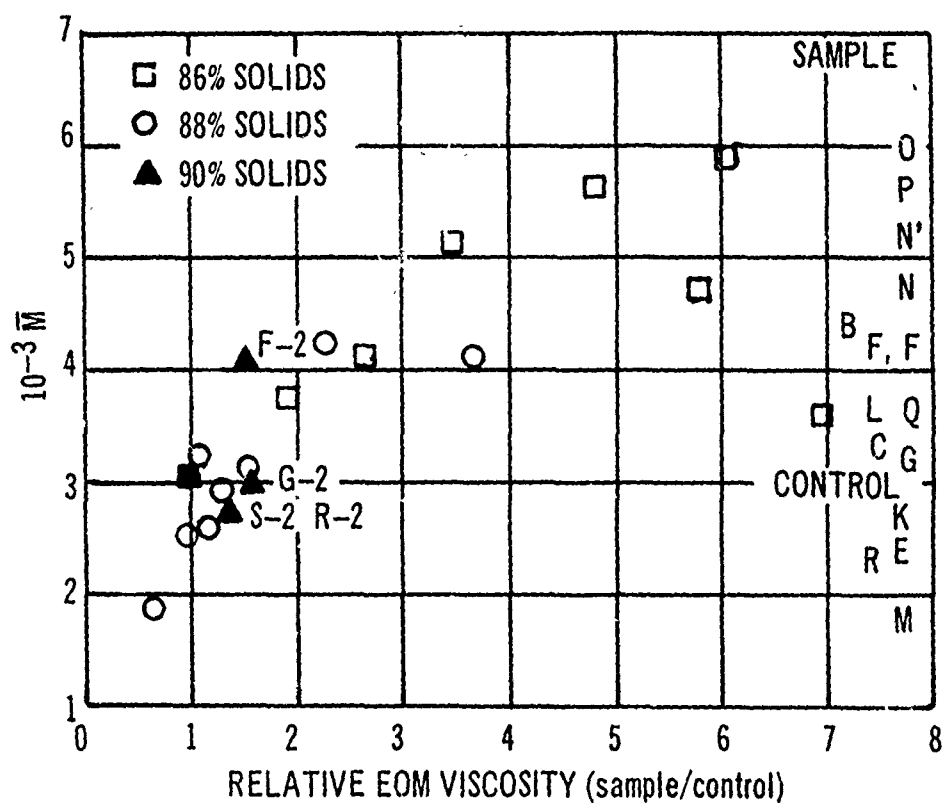
Figure 3 Relative End-of-Mix Viscosity versus  $\bar{M}_n$



TABLE VI  
RELATIVE PROPELLANT VISCOSITY AFTER 3 HOURS AT 40°C<sup>(a)</sup>

| <u>Sample</u> | <u>Relative Viscosity</u> |
|---------------|---------------------------|
| Control       | 1.0                       |
| F-2           | 1.3                       |
| G-2           | 1.6                       |
| R-2           | 1.4                       |
| S-2           | 1.7                       |

---

(a) MT-4 formulations

## b. Propellant Tensile Behavior

Uniaxial tensile properties at -65, 70, and 140°F were measured at a strain rate of 0.54 in./in./min using the minithin tensile specimens previously described (Ref 1).

### (1) Summary of Conventional Tensile Parameters

Table VII summarizes, for all formulations tested, the values of tensile parameters as conventionally reported. These include initial modulus  $E_0$ , stress and strain at maximum load  $(\sigma/\epsilon)_m$ , and stress and strain at rupture  $(\sigma/\epsilon)_b$ . Additionally, swell and gel measurements, which are indicative of binder crosslink density, are included for each of the formulations tested. The effect of MT-4 is to "harden" the propellant at higher temperatures and to increase strain at -65°F.

### (2) Comparison at Constant 75°F $\sigma_m$

To permit comparison of tensile properties under similar conditions, NCO/OH ratios were selected that produced values for  $\sigma_m$  at 75°F between 140 and 160 psi. Resultant conventional tensile parameters are given in Table VIII. On this basis none of the prepolymer samples is clearly superior to the control lot.

### (3) True Stress/Strain Curves and Parameters

Figures 4 through 12 present true stress/strain curves at a single NCO/OH ratio for formulations both with and without MT-4; the ratio chosen was that closest to the value employed above. The tensile parameters from these curves are presented in Table IX. As with the laboratory samples, no clear superiority above the control lot over the full temperature range can be observed.

## c. Propellant Fracture Mechanics

Crack propagation measurements were conducted at -65 and 70°F in an attempt to distinguish more clearly among the pilot plant samples. Propellant strips measuring 3 by 1 by 0.1 inch were bonded to wooden tabs along the 3- by 0.1-inch edges and, after a 0.5-inch edge cut was made, were pulled at a rate of 0.2 in./min. Stress and strain at initiation of cut growth were measured, as well as the subsequent rate of growth from 0.5- to 0.7-inch cut length.

Data scatter was such that the only significant difference observed (see Table X) was a larger critical stress and strain, and hence fracture energy, for F-2 propellant at 70°F. How meaningful a superiority this may be--for motor thermal cycling, for example--is not clear, although

TABLE VII  
PROPELLANT MECHANICAL PROPERTIES AT 90 PERCENT SOLIDS<sup>(a)</sup>  
(From Instron Load/Time Trace)

| Sample                  | NCO/OH  | Shore A<br>EOC(b) | -65°F          |                                    |                                    | +75°F          |                                    |                                    | +140°F         |                                    |                                    | Percent<br>Gel(c) | Percent<br>Swell(d) |
|-------------------------|---------|-------------------|----------------|------------------------------------|------------------------------------|----------------|------------------------------------|------------------------------------|----------------|------------------------------------|------------------------------------|-------------------|---------------------|
|                         |         |                   | E <sub>o</sub> | ( $\sigma/\epsilon$ ) <sub>m</sub> | ( $\sigma/\epsilon$ ) <sub>b</sub> | E <sub>o</sub> | ( $\sigma/\epsilon$ ) <sub>m</sub> | ( $\sigma/\epsilon$ ) <sub>b</sub> | E <sub>o</sub> | ( $\sigma/\epsilon$ ) <sub>m</sub> | ( $\sigma/\epsilon$ ) <sub>b</sub> |                   |                     |
| Control<br>(Lot 008281) | 0.75    | 74/57             | 9,700          | 580/15                             | 580/20                             | 470            | 85/29                              | 70/37                              | 385            | 70/28                              | 70/29                              | 56.5              | 18.8                |
|                         | 0.80    | 80/67             | 17,000         | 600/14                             | 600/16                             | 740            | 140/26                             | 140/28                             | 530            | 120/28                             | 120/30                             | 65.2              | 17.6                |
|                         | 0.80(e) | 69/60             | 12,000         | 520/10                             | 470/15                             | 420            | 70/22                              | 70/28                              | 300            | 60/24                              | 60/28                              | 63.5              | 32.0                |
| F-2                     | 0.95    | 83/76             | 12,000         | 590/11                             | 590/13                             | 640            | 170/26                             | 170/29                             | 630            | 130/26                             | 130/28                             | 71.1              | 15.4                |
|                         | 1.0     | 86/70             | 10,000         | 600/12                             | 600/13                             | 880            | 210/28                             | 200/29                             | 720            | 160/28                             | 160/31                             | 82.5              | 13.8                |
|                         | 1.0(e)  | 70/42             | 12,700         | 564/10                             | 540/12                             | 340            | 60/24                              | 56/33                              | 180            | 40/27                              | 39/32                              | 53.5              | 21.1                |
| G-2                     | 0.85    | 83/73             | 14,000         | 600/10                             | 600/11                             | 760            | 150/28                             | 140/30                             | 590            | 120/30                             | 120/31                             | 68.4              | 15.2                |
|                         | 0.85(c) | 74/51             | 11,000         | 550/9                              | 540/13                             | 270            | 60/28                              | 60/33                              | 160            | 50/34                              | 50/38                              | 43.2              | 31.2                |
|                         | 0.90    | 85/76             | 10,000         | 610/12                             | 610/12                             | 980            | 190/25                             | 190/26                             | 760            | 160/26                             | 160/26                             | 74.8              | 15.3                |
| R-2                     | 0.90    | 78/53             | 12,000         | 640/12                             | 640/13                             | 390            | 90/32                              | 90/39                              | 230            | 60/35                              | 60/38                              | 55.1              | 17.5                |
|                         | 0.95    | 80/65             | 10,000         | 630/10                             | 620/11                             | 550            | 150/25                             | 140/27                             | 500            | 110/29                             | 110/30                             | 68.5              | 15.7                |
|                         | 0.95(c) | 80/53             | 15,000         | 600/9                              | 590/11                             | 370            | 70/23                              | 60/36                              | 190            | 50/31                              | 50/38                              | 40.7              | 28.4                |
| S-2                     | 1.00    | 83/66             | 11,000         | 640/11                             | 630/12                             | 520            | 130/27                             | 126/32                             | 370            | 90/30                              | 90/32                              | 60.9              | 15.5                |
|                         | 1.05    | 88/74             | 15,000         | 660/9                              | 650/10                             | 830            | 160/25                             | 152/29                             | 515            | 110/27                             | 110/28                             | 63.2              | 12.1                |

- (a) Minithins. Triplicate specimen. ( $\sigma/\epsilon$ )<sub>m</sub> at maximum load. ( $\sigma/\epsilon$ )<sub>b</sub> at failure.  
 (b) EOC = end of cure. Initial/15 seconds  
 (c) Percent Gel = percent of original prepolymer plus curative which is insoluble in toluene.  
 (d) Percent Swell = weight of toluene swollen gel x 100/weight of dry gel.  
 (e) No MT-4

TABLE VIII  
COMPARATIVE TENSILE PROPERTIES<sup>(a)</sup>

| Sample                  | NCO/OH               | $E_o/\sigma_m/\epsilon_m$ <sup>(b)</sup> |            |            |
|-------------------------|----------------------|------------------------------------------|------------|------------|
|                         |                      | -65°F                                    | 75°F       | 140°F      |
| Control<br>(Lot 008281) | 0.80                 | 17,000/600/14                            | 740/140/26 | 530/120/28 |
| F-2                     | 0.925 <sup>(c)</sup> | 13,000/580/10                            | 540/150/25 | 590/120/25 |
| G-2                     | 0.85                 | 14,000/600/10                            | 760/150/28 | 590/120/30 |
| R-2                     | 0.95                 | 10,000/630/10                            | 550/150/25 | 500/110/29 |
| S-2                     | 1.05                 | 15,000/660/9                             | 830/160/25 | 515/110/27 |

(a) Comparison at NCO/OH ratio which has  $\sigma_m$  at 75°F between 140-160 psi. MT-4 formulations

(b)  $\sigma_m$  and  $\epsilon_m$  at maximum stress from Instron curves

(c) Extrapolated from 0.90 and 0.95 NCO/OH

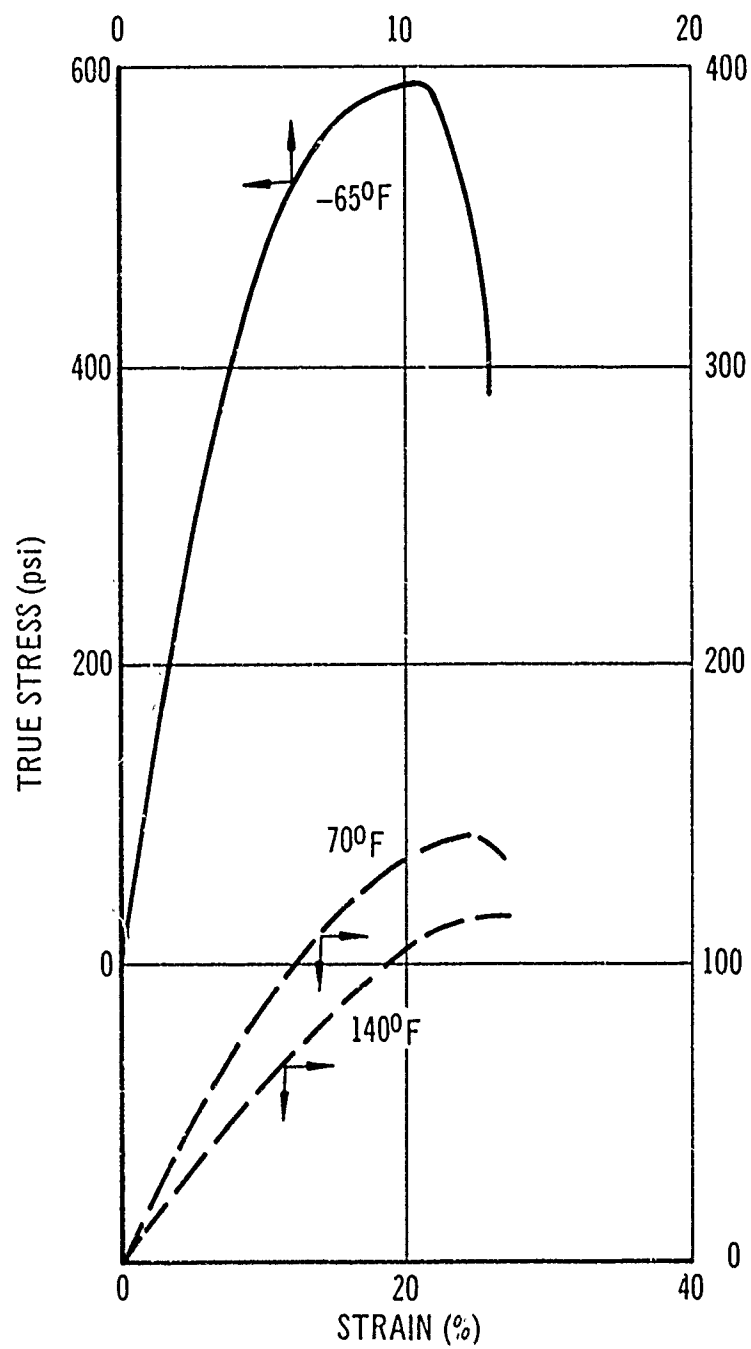


Figure 4 Tensile Behavior of Control Sample (90-percent Solids); NCO/OH = 0.80; 0.54 in./in./min

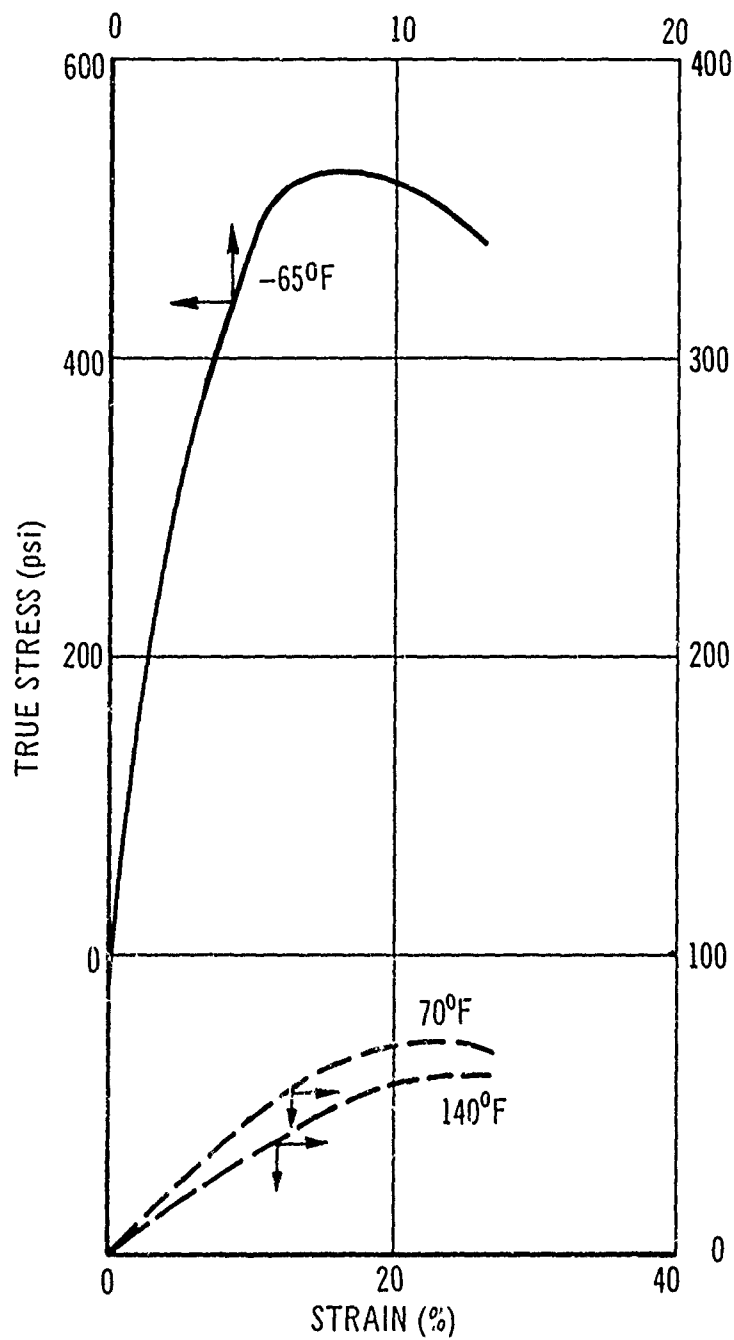


Figure 5 Tensile Behavior of Control Sample (90-percent Solids);  
NCO/OH = 0.80; No MT-4; 0.54 in./in./min

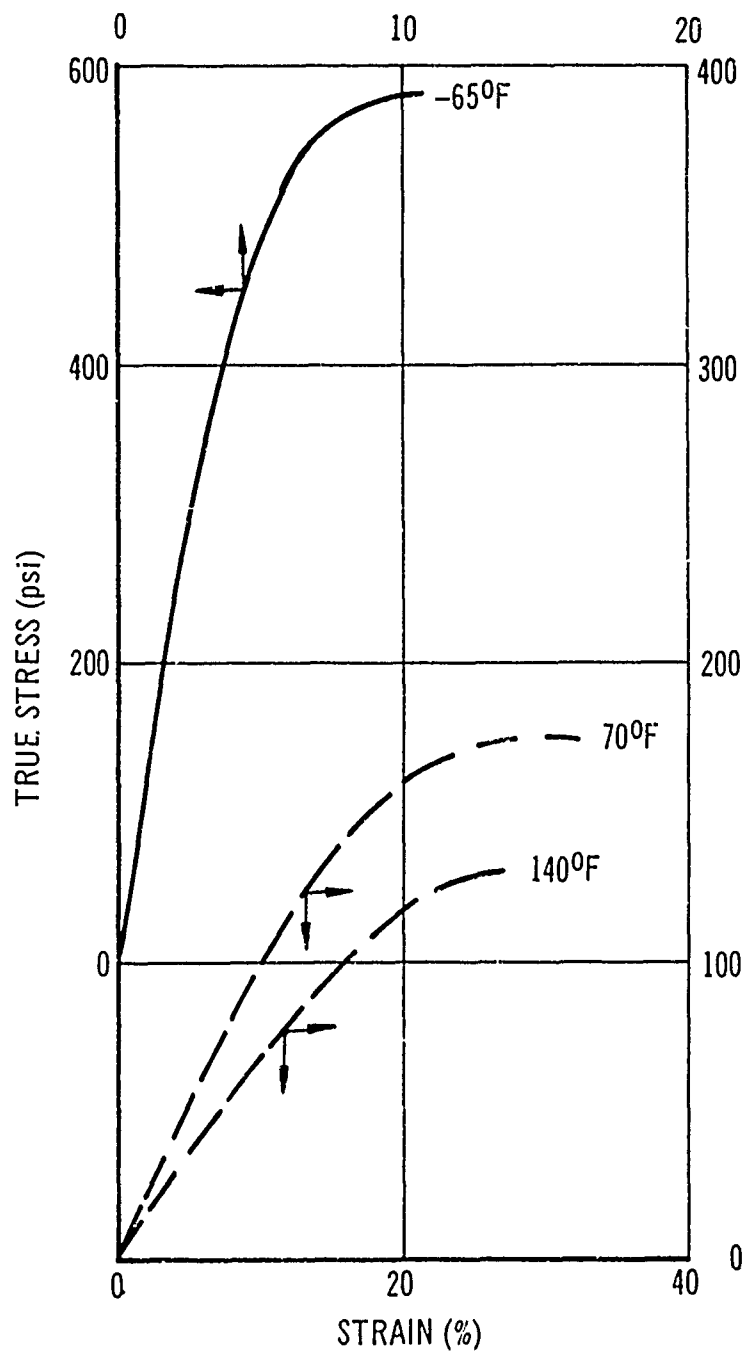


Figure 6 Tensile Behavior of Sample F-2 (90-percent Solids);  
NCO/OH = 0.95; 0.54 in./in./min

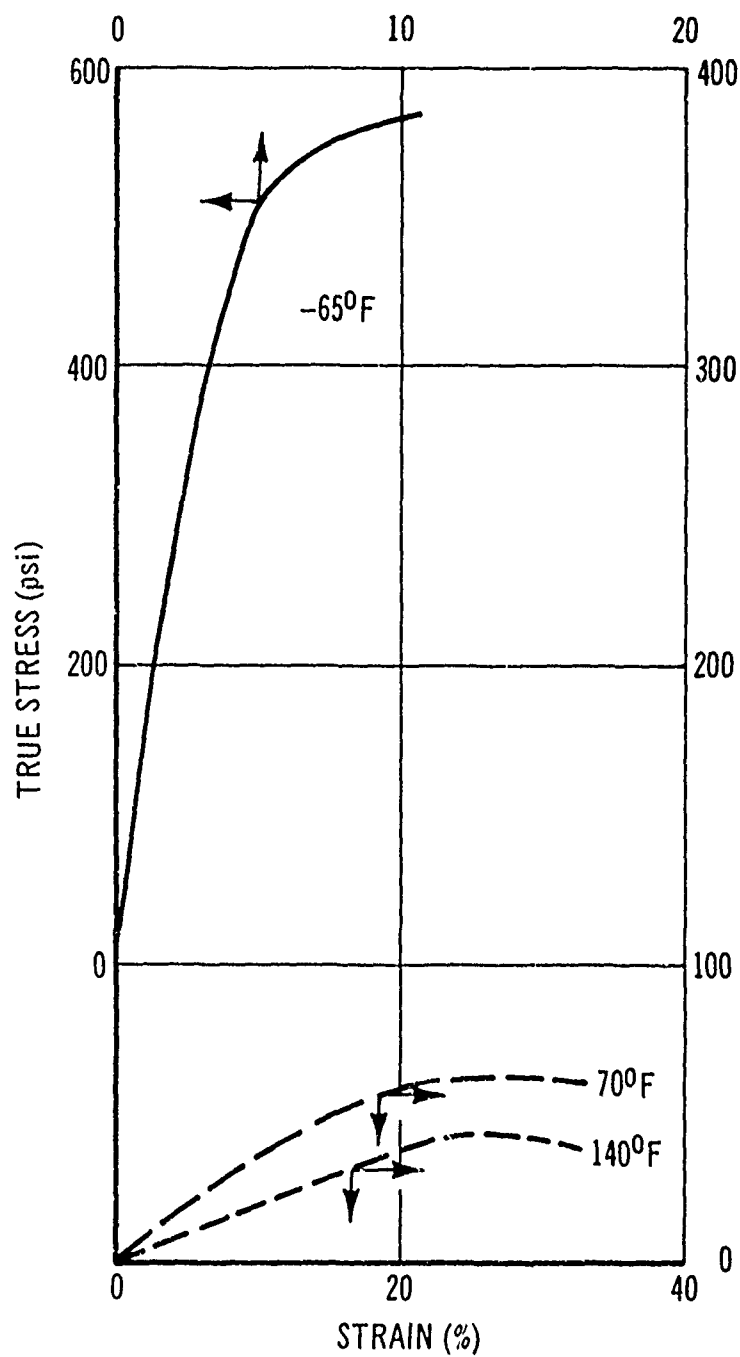


Figure 7 Tensile Behavior of Sample F-2 (90-percent Solids);  
NCO/OH = 1.0; No MT-4; 0.54 in./in./min



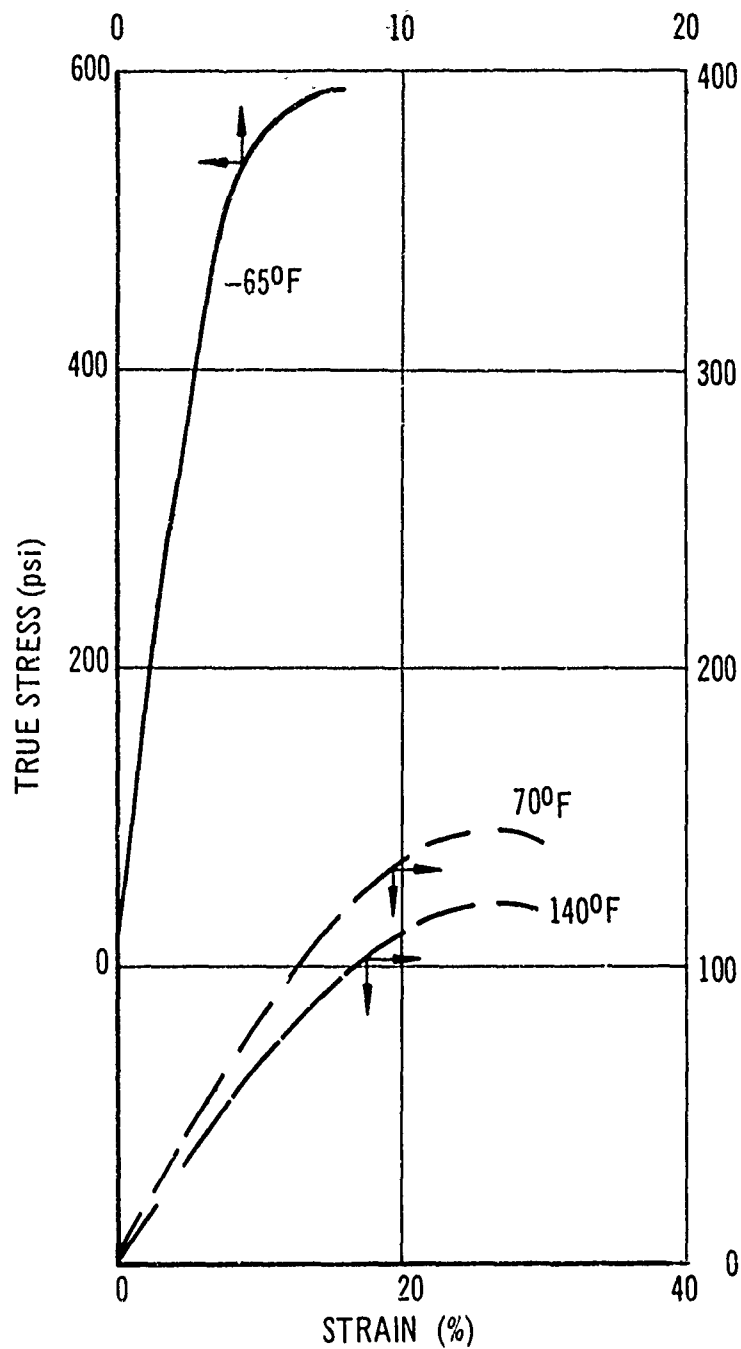


Figure 8 Tensile Behavior of Sample G-2 (90-percent Solids); NCO/OH = 0.85; 0.54 in./in./min

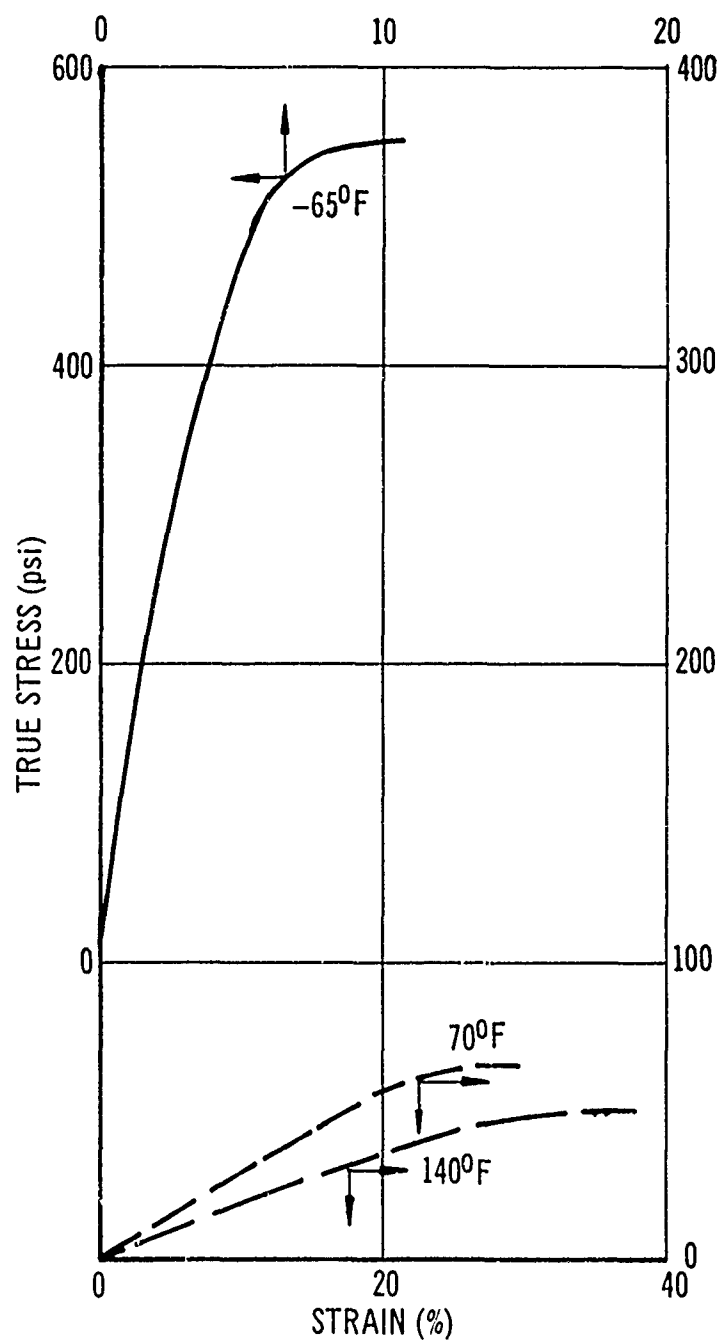


Figure 9 Tensile Behavior of Sample G-2 (90-percent Solids);  
NCO/OH = 0.85; No MT-4; 0.54 in./in./min

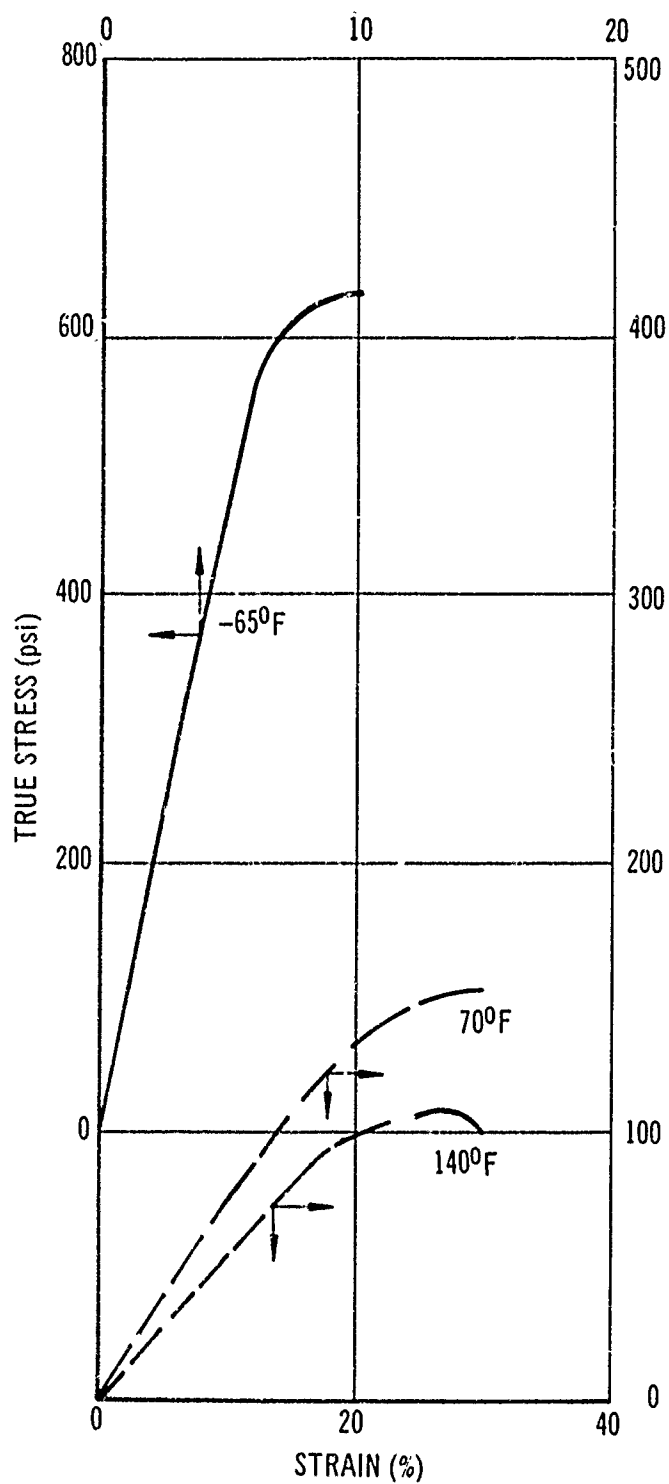


Figure 10 Tensile Behavior of Sample R-2 (90-percent Solids); NCO/OH = 0.95; 0.54 in./in./min

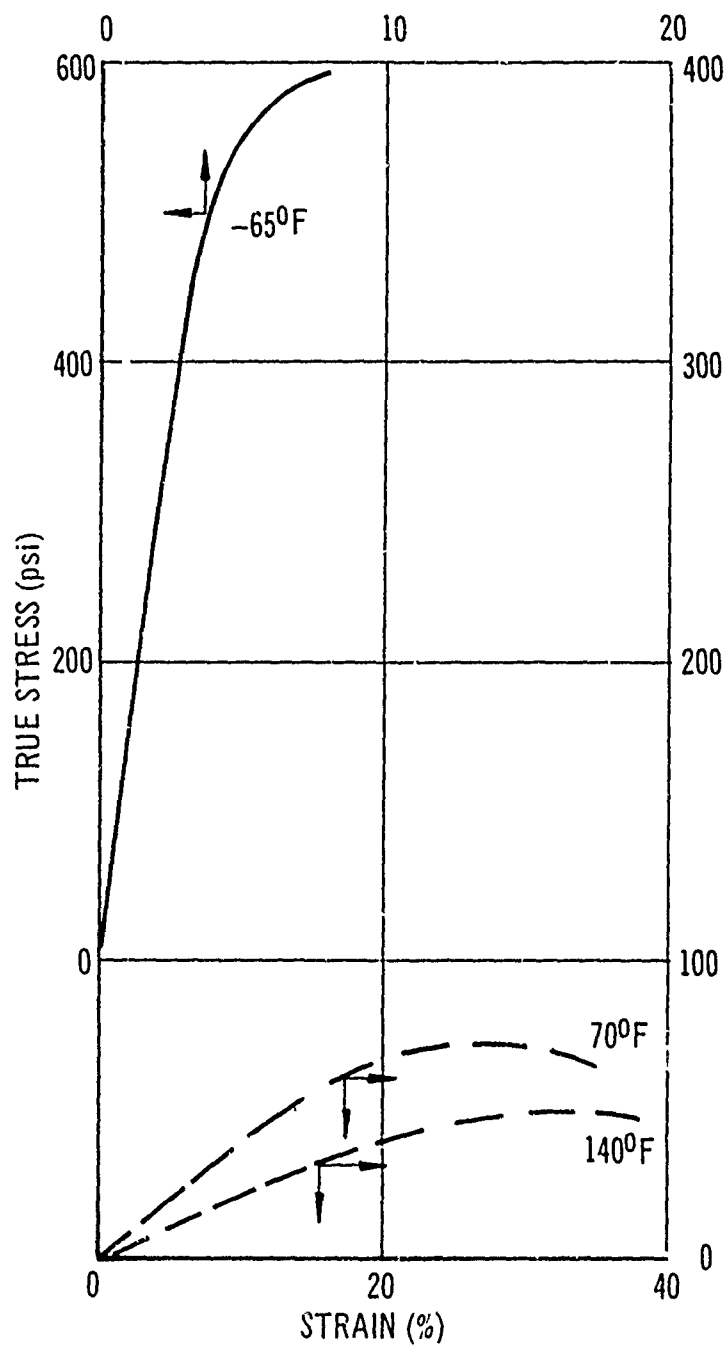


Figure 11 Tensile Behavior of Sample R-2 (90-percent Solids);  
NCO/OH = 0.95; No MT-4; 0.54 in./in./min

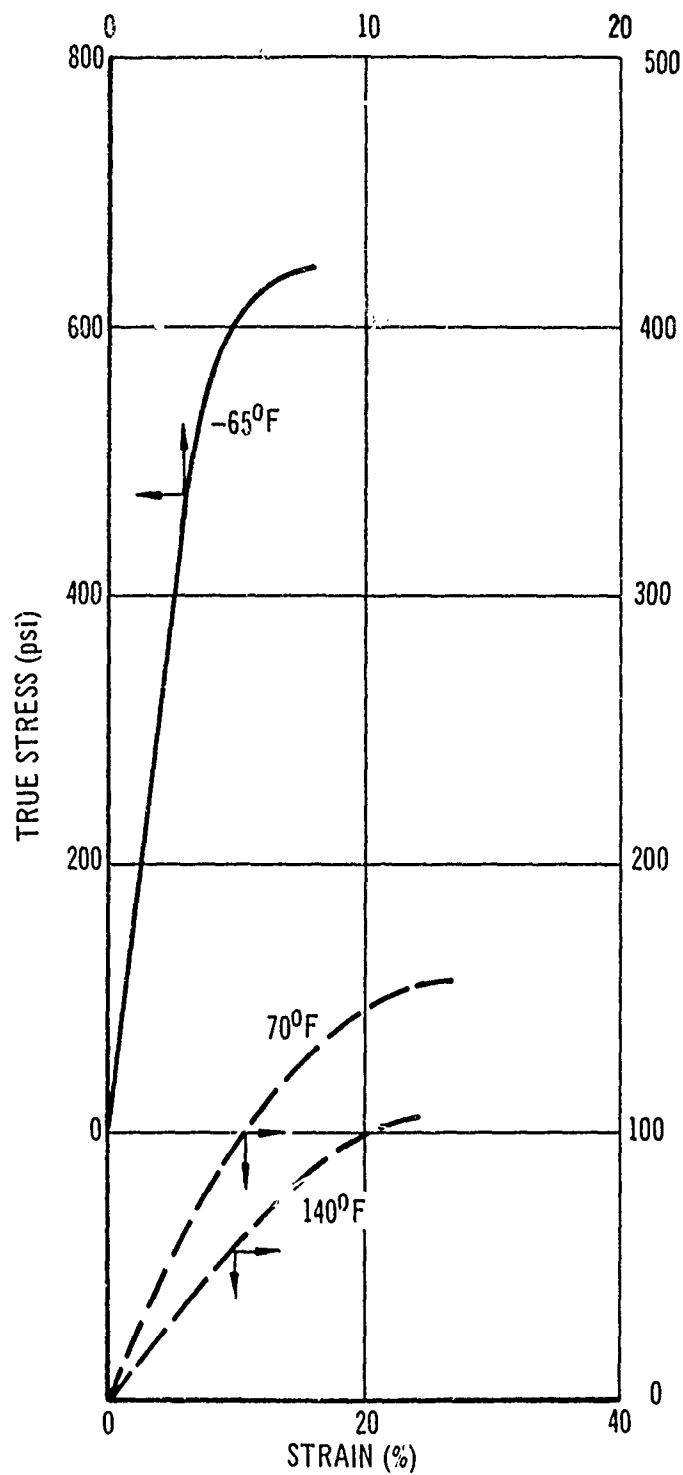


Figure 12 Tensile Behavior of Sample S-2 (90-percent Solids); NCO/OH = 1.05; 0.54 in./in./min

TABLE IX  
TENSILE PARAMETERS FROM TRUE STRESS/STRAIN CURVES FOR  
90 PERCENT SOLIDS PROPELLANT

| Sample                  | NCO/OH  | -65°F  |          |            |            | +75°F |          |            |            | -140°F |          |            |            |
|-------------------------|---------|--------|----------|------------|------------|-------|----------|------------|------------|--------|----------|------------|------------|
|                         |         | $E_o$  | Yield(a) | Maximum(a) | Rupture(a) | $E_o$ | Yield(a) | Maximum(a) | Rupture(a) | $E_o$  | Yield(a) | Maximum(a) | Rupture(a) |
| Control<br>(Lot 008281) | 0.75    | 9,700  | 325/2    | 560/16     | 560/19     | 470   | 65/12    | 80/27      | 80/29      | 390    | 50/12    | 65/21      | 65/27      |
|                         | 0.80(b) | 12,000 | 320/2    | 575/8      | 475/13     | 420   | 50/11    | 70/23      | 70/23      | 300    | 50/18    | 60/24      | 60/27      |
|                         | 0.80    | 17,000 | 410/3    | 590/11     | 380/14     | 740   | 100/11   | 140/24     | 40/27      | 530    | 85/12    | 120/25     | 110/27     |
| F-2                     | 0.95    | 12,000 | 450/4    | 580/11     | ---        | 640   | 130/12   | 170/27     | 170/33     | 630    | 100/15   | 130/27     | ---        |
|                         | 1.00    | 10,000 | 475/5    | 590/11     | ---        | 880   | 180/17   | 210/27     | 200/30     | 720    | 120/15   | 160/27     | 160/30     |
|                         | 1.00(b) | 12,700 | 450/4    | 570/11     | ---        | 340   | 45/12    | 60/27      | 55/32      | 180    | 40/21    | 45/27      | 35/32      |
| G-2                     | 0.85(b) | 11,000 | 410/3    | 550/11     | ---        | 270   | 60/21    | 65/30      | ---        | 160    | 45/25    | 50/38      | ---        |
|                         | 0.85    | 14,000 | 500/4    | 590/8      | ---        | 760   | 110/13   | 150/27     | 140/30     | 590    | 95/15    | 120/27     | 120/30     |
|                         | 0.90    | 9,800  | 540/5    | 600/11     | ---        | 980   | 160/14   | 190/24     | ---        | 760    | 140/17   | 160/25     | ---        |
| R-2                     | 0.90    | 12,000 | 500/4    | 640/11     | ---        | 390   | 70/16    | 90/30      | 90/35      | 230    | 50/18    | 60/32      | 60/35      |
|                         | 0.95    | 9,800  | 560/6    | 630/11     | ---        | 550   | 120/16   | 150/30     | ---        | 500    | 95/18    | 110/27     | 100/30     |
|                         | 0.95(b) | 15,000 | 500/4    | 590/8      | ---        | 370   | 60/15    | 70/33      | 65/35      | 190    | 35/18    | 50/32      | 50/38      |
| S-2                     | 1.00    | 11,000 | 530/5    | 620/8      | ---        | 520   | 100/16   | 130/32     | ---        | 370    | 65/15    | 90/30      | ---        |
|                         | 1.05    | 15,000 | 550/3    | 640/8      | ---        | 830   | 100/10   | 160/27     | ---        | 520    | 80/14    | 110/24     | ---        |

(a) Values of  $\sigma/\epsilon$ 

(b) No MT-4

TABLE X  
PROPELLANT CRACK PROPAGATION (a)

| Sample  | NCO/OH | -65°F             |                     |              |             | +70°F             |                     |              |             |
|---------|--------|-------------------|---------------------|--------------|-------------|-------------------|---------------------|--------------|-------------|
|         |        | (b)<br>$\sigma_c$ | (c)<br>$\epsilon_c$ | (d)<br>$f_c$ | (e)<br>Rate | (b)<br>$\sigma_c$ | (c)<br>$\epsilon_c$ | (d)<br>$f_c$ | (e)<br>Rate |
| Control | 0.00   | 290               | 5.4                 | 2.8          | 0.05        | 75                | 6.0                 | 0.8          | 0.6         |
| F-2     | 0.95   | 380               | 4.0                 | 2.7          | 0.1         | 110               | 9.0                 | 1.8          | 0.6         |
| G-2     | 0.85   | 430               | 4.6                 | 3.5          | 0.1         | 68                | 7.4                 | 0.9          | 0.5         |
| R-2     | 0.95   | 325               | 4.0                 | 2.3          | 0.1         | 64                | 7.3                 | 0.8          | 0.5         |

(a) Constant elongation rate (0.2 in./min). Specimen 1 x 3 x 0.1 in. Initial edge cut of 0.5 in. Triplicate specimens at 70°F and at least duplicate at -65°F.

(b) Critical stress, psi.

(c) Critical strain, %.

(d) Fracture energy, lb/in.

(e) Rate of crack growth from 0.5 to 0.7 in.

it seems possible that F-2 at a lower NCO/OH ratio might possess improved crack resistance while maintaining high-temperature capability.

d. Strain/Temperature Cycling of JANNAF Specimens

Since neither the tensile nor the crack propagation data gave evidence of major differences among the propellants, the feasibility of a laboratory test for evaluating relative capability to withstand motor thermal cycling was examined. Standard JANNAF specimens (four of each propellant in parallel) were slowly strained on an Instron tester from 0 to 15.5 percent, while the temperature was simultaneously decreased from 140 to -65°F over a 90-minute period. The cycle was then reversed to permit return within 90 minutes to the original crosshead displacement and to 140°F. Total load for the four specimens was recorded continuously.

Available data are summarized in Table XI in terms of the rate of load reduction (-65°F) and qualitative observations of sample damage. Although these results must be considered highly preliminary, they indicate definite potential for laboratory characterization of thermal cycling capability and the possibility of improved behavior for R-2 and S-2.

3. CONCLUSIONS

- (1) Good duplication is shown between ARCO's laboratory and pilot plant processing.
- (2) Propellant processability with the pilot plant samples is poorer than with standard R-45M. This may be partially a reflection of higher contents of residual catalytic impurity (iron compounds) resulting from limited use of the pilot plant reactor.
- (3) On the basis of the tests employed in evaluating mechanical behavior, no clear superiority is apparent for pilot plant samples relative to standard R-45M.



TABLE XI  
TEMPERATURE/STRAIN CYCLING RESULTS

| <u>Sample</u> | <u>NCO/OH</u> | <u>Load<br/>Reduction<br/>Rate<sup>(a)</sup></u> | <u>Number Cycles and Specimen Condition<sup>(b)</sup></u>                                                                 |
|---------------|---------------|--------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------|
| Control       | 0.80          | 9                                                | 23 full cycles; 3 specimens broken and 1 with no cracks                                                                   |
| F-2           | 0.95          | 7                                                | 36 full cycles plus 7 cycles without cooling (between 13th and 14th full cycles); 3 specimens with cracks and 1 uncracked |
| R-2           | 0.95          | 4                                                | 38 full cycles; 2 specimens cracked, 1 failed after 30 cycles                                                             |
| S-2           | 1.05          | 2                                                | 35 cycles; 1 specimen failed, 3 with cracks                                                                               |

(a) Pounds per cycle. Slope of straight line through maximum load (-65 degrees)/cycle plot.

(b) Three-hour cycle. Visual observation of condition.

(The reverse is blank)

## SECTION IV

## FUTURE WORK

The original program plan called for final evaluation of one pilot plant prepolymer at the 10-gallon mix level with emphasis upon analog motor thermal cycling tests. In view of the results obtained to date and with the realization that different temperature cycling behavior may not be apparent from uniaxial tensile data, the program has been redirected to permit a more detailed evaluation of three pilot plant samples (F-2, R-2, S-2) at the 1- or 2½-gallon mix level. For each of these prepolymers and control, thermal cycling capability will be compared using analog motors as well as the laboratory strain/temperature cycling test.

(The reverse is blank)

# Appendix A

## LABORATORY SAMPLE CHARACTERIZATION SUMMARY

| Parameter                                           | RR(1)                                                                                                                                      | B     | C    | E    | F    | G     | K     | L    | M    | N      | N'     | O     | P     | Q     | R    | Control(2) |
|-----------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|-------|------|------|------|-------|-------|------|------|--------|--------|-------|-------|-------|------|------------|
| $\bar{M}_n$ (VPO)                                   |                                                                                                                                            |       |      |      |      |       |       |      |      |        |        |       |       |       |      |            |
| Mean                                                | 2700                                                                                                                                       | 4200  | 3150 | 2590 | 4100 | 3100  | 2890  | 3600 | 1850 | (4720) | (5100) | 5840  | 5560  | 3750  | 2530 | 3000       |
| RSD(3)                                              | 1.7%                                                                                                                                       | 7.3%  | 3.8% | 3.0% | 5.7% | 7.4%  | 7.2%  | 4.5% | 2.4% |        |        | 4.5%  | 15.8% | 12.3% |      |            |
| $\bar{M}_n$ (GPC)                                   | 2930                                                                                                                                       | 3840  | 3050 | 2520 | 3830 | 2960  | 2800  | 3620 | 2260 | 5510   | 4330   | 5680  | 4800  | 3930  |      |            |
| $\bar{M}_w/\bar{M}_n$ (GPC)                         | 1.66                                                                                                                                       | 1.94  | 1.72 | 1.63 | 1.68 | 1.56  | 1.52  | 1.93 | 2.29 | 2.20   | 1.79   | 1.88  | 1.83  | 1.53  |      |            |
| $\bar{M}_w$ (GPC)                                   | 4900                                                                                                                                       | 7450  | 5250 | 4100 | 6450 | 4600  | 4250  | 7000 | 5200 | 10400  | 7750   | 10200 | 9050  | 7200  | 3420 |            |
| Eq. Wt. (TSI)                                       |                                                                                                                                            |       |      |      |      |       |       |      |      |        |        |       |       |       |      |            |
| Mean                                                | 1220                                                                                                                                       | 2180  | 1630 | 1360 | 2270 | 1770  | 1500  | 1930 | 900  | 3300   | 3030   | 3180  | 3070  | 2180  | 1220 | 1290       |
| RSD(3)                                              | 2.1%                                                                                                                                       | 3.3%  | 4.2% | 3.0% | 3.5% | 2.6%  | 2.8%  | 3.5% | 3.3% | 4.7%   | 2.1%   | 2.6%  | 6.2%  | 2.2%  |      |            |
| Eq. Wt. (AA)                                        |                                                                                                                                            |       |      |      |      |       |       |      |      |        |        |       |       |       |      |            |
| Mean                                                | 1320                                                                                                                                       | 2380  | 2690 | 1470 | 2380 | 1730  | 1640  | 2080 | 1050 | 3330   | 3230   | 3330  | 2170  | 1280  |      |            |
| $\bar{f}_n$ (4)                                     |                                                                                                                                            |       |      |      |      |       |       |      |      |        |        |       |       |       |      |            |
| Mean                                                | 2.21                                                                                                                                       | 1.93  | 1.93 | 1.91 | 1.81 | 1.75  | 1.93  | 1.87 | 2.05 | (1.43) | (1.68) | 1.84  | 1.8'  | 1.72  | 2.08 |            |
| RSD(3)                                              | 3.8%                                                                                                                                       | 10.6% | 8.0% | 6.0% | 9.2% | 10.0% | 10.0% | 8.0% | 5.7% |        |        | 7.1%  | 22.5% | 14.5% |      |            |
| $\bar{f}_w$ (5)                                     |                                                                                                                                            |       |      |      |      |       |       |      |      |        |        |       |       |       |      |            |
| Mean                                                | 2.36                                                                                                                                       | 2.45  | 2.15 | 2.33 | 2.03 | 2.04  | 2.14  | 2.36 | 2.67 | 2.07   | 2.31   | 2.08  | 2.18  | 2.27  | 2.10 | 2.42       |
| RSD(3)                                              | 1.9%                                                                                                                                       | 2.2%  | 1.0% | 7.3% | 0.4% | 1.4%  | 3.1%  | 6.3% | 1.3% | 1.5%   | 1.6%   | 1.9%  | 6.4%  | 5.1%  |      |            |
| $\eta$ (6)                                          | 43                                                                                                                                         | 182   | 60   | 35   | 112  | 54    | 40    | 100  | 42   | 400    | 340    | 500   | 400   | 200   | 35   | 49         |
| Reactivity(7)                                       |                                                                                                                                            | 0.29  | 0.28 | 0.33 | 0.42 | 0.15  | 0.29  | 0.85 | 0.55 | 0.13   | 0.26   | 0.15  | 0.17  | 0.18  | 0.32 | 0.37       |
| (1) Round Robin R-45M Lot 110225                    | (5) From degree of DDI conversion at incipient gelation (ambient temperature.                                                              |       |      |      |      |       |       |      |      |        |        |       |       |       |      |            |
| (2) R-45M Lot 008281                                | (6) Brookfield at 30°C. Poise                                                                                                              |       |      |      |      |       |       |      |      |        |        |       |       |       |      |            |
| (3) Relative Standard Deviation for all data points | (7) Relative reactivity. Fraction of NCO (DDI) reacted after 10 hours at ambient. From reaction profile for determination of $\bar{f}_w$ . |       |      |      |      |       |       |      |      |        |        |       |       |       |      |            |
| (4) $\bar{M}_n$ /TSI equivalent weight              |                                                                                                                                            |       |      |      |      |       |       |      |      |        |        |       |       |       |      |            |

(The reverse is blank)