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OPTIMIZATION OF HTPB BINDER

Lockheed Propulsion Company
Redlands, California

TECHNICAL REPORT AFRPL-TR-71-123

JANUARY 1972

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RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
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FOREWORD

This is the Final Report issued under Contract No. FO4611-70-C-0050 and covers the period from 1 May 1970 to 30 September 1971. This contract is assigned to Lockheed Propulsion Company, Redlands, California and is monitored by Dr. James Trout, Air Force Rocket Propulsion Laboratory, Edwards, California.

Technical effort under this program has been performed by: W.E. Baumgartner (Chemistry Department Manager), G.E. Myers (Program Manager, G.R. Cann, C. Gustavson, W.E. Heikkila, W.G. Stapleton, all of Lockheed Propulsion Company, and by: D. Grafstein (Esso Program Manager), A.H. Muenker (Esso Project Engineer), and B.E. Hudson, all of Esso Research and Engineering Corporation.

This report contains no classified information.

This report has been reviewed and approved.

Dr. James L. Trout
Air Force Project Engineer

ABSTRACT

The R-45M hydroxyl terminated polybutadiene prepolymer as produced by ARCO is composed of material covering a range of molecular weights, and the different molecular weight fractions were suspected to vary in functionality. This program sought to scale-up the fractionation of the R-45M HTPB prepolymer so that fractions having more narrow molecular weight distribution besides being more strictly di- and trifunctional could be tested in propellants to determine related effects upon cure and mechanical properties.

Scale-up fractionation over silica gel was found to cause non-reproducible structural changes and thus was concluded to be impractical. Fractionation by solvent precipitation produced material having an average molecular weight of 2000 at average functionality of two, and trifunctional material of average molecular weight 6000.

Cure studies suggest that the 2000 molecular weight fraction still contains some low molecular weight trifunctional material that effects cross-linking, and the resulting propellant was found to have poor tensile properties at -65°F. However, tear resistance at 70°F was improved.

Temperature cycling capability of analog motors containing low molecular weight difunctional fractions was compared with those containing the parent R-45M. At approximately the same initial modulus at 70°F, the cycling behavior (-80°F to 160°F) of the two systems was not significantly different.

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GLOSSARY

ARCO-1	Trifunctional R-45M fraction prepared by ARCO (M ~ 5000)
CTPB	Carboxy terminated polybutadiene
DDI	Long chain aliphatic diisocyanate from General Mills
DiA, DiB, DiC, and DiD	Difunctional fractions prepared by fractional precipitation of R-45M (M ~ 1800)
$\bar{f}_n$	Number average functionality = $\Sigma n_i f_i$, where n = mole fraction
$\bar{f}_w$	Weight average (or effective) functionality = $\Sigma n_i f_i^2 / \Sigma n_i f_i$
GPC	Gel Permeation Chromatography
HMDI	Hexamethylene diisocyanate
HTPB	Hydroxy terminated polybutadiene
$\bar{M}_n$	Number average molecular weight
$\bar{M}_w$	Weight average molecular weight
NCO	Isocyanate
R-45M	ARCO free radical initiated HTPB
Telagen-HT-316AM-20	Approximately difunctional Telagen-HT fraction prepared by Aerojet (M ~ 4000)
TDI	Toluene diisocyanate
TPMTI	Triphenyl methane triisocyanate
TriB and TriC	Trifunctional fraction prepared by fractional precipitation of R-45M (M ~ 6000)

SECTION I

INTRODUCTION

The carboxyl and hydroxyl terminated polybutadiene prepolymers (CTPB, HTPB) that have come into use for the manufacture of solid propellants vary in detailed structure, molecular weight distribution and functionality distribution as a result of differences in the prepolymer manufacturing processes. These differences translate into differences in propellant processibility, potlife, cure behavior, mechanical properties and aging characteristics. Moreover, it is not uncommon to experience batch-to-batch variability that, in turn, translates into propellant and motor quality control problems.

The problem reflects the fact that it is as yet difficult to fully characterize prepolymers and to relate changes in prepolymer structure and composition to resulting changes in propellant behavior.

With the increasing emphasis that is being placed upon motor service life, as well as ability to withstand severe temperature cycling, this problem area has received much attention during the past years. This resulted in the development or application of techniques for fractionating prepolymers, at least on a laboratory scale, either by molecular weight (e.g., gel permeation chromatography) or by functionality (e.g., fractionation over silica gel columns) both for the purpose of arriving at more stringent quality control and at a better definition of the relationship between polymer structure and propellant behavior (Ref. 1-5).

As part of this effort, the Air Force in 1969 initiated two programs dealing with the fractionation of HTPB prepolymers for determining the effects of changes in molecular weight and functionality distribution. One program, assigned to Aerojet, was to fractionate HT-Telagen (containing secondary hydroxyls) and emphasize the effect upon propellant behavior of the functionality range ~1.7-2.0 (Ref. 6). A parallel program, assigned to Lockheed Propulsion Company was to fractionate ARCO's R-45M HTPB prepolymer, and emphasize the functionality range 2.0-2.3 in evaluating the individual fractions in propellants.

The R-45M prepolymer is produced via a peroxide initiated free radical polymerization, and it results in material that contains the hydroxyl groups in allylic form. The material, as presently marketed, has an average molecular weight of approximately 3000 and an average hydroxyl functionality of approximately 2.3. Used as a propellant binder ingredient, the R-45M HTPB prepolymer exhibits somewhat unusual behavior in so far as good cure is generally achieved quite rapidly at isocyanate to hydroxyl ratios below one, even in the absence of the usual cure catalysts. According to the manufacturer this behavior is caused by the presence of relatively low molecular weight trifunctional material. This assessment received further support from data obtained upon fractionating R-45M over silica gel columns, which indicated that R-45M was composed of comparatively low molecular weight (MW 2000) trifunctional material plus a significant weight fraction of difunctional material having an average molecular weight of 4000 (Ref. 4).

These early results implied that a change in the polymer's manufacturing process to effect higher average molecular weight might produce a material being more closely difunctional. Alternatively, secondary processing (e.g., solvent precipitation) might be used to upgrade the prepolymer, thus rendering this comparatively inexpensive prepolymer (~50 cents/lb) more ideally suited for use in propellants. This program was therefore initiated as a joint effort between LPC and Esso to perform the following:

(1) Esso to prepare and characterize di and trifunctional fractions of R-45M in sufficient qualtities to allow

(2) LPC to establish whether improved mechanical properties could be achieved using controlled prepolymer functionality compositions, with emphasis upon overall functionalities above 2.0.

SECTION II

SUMMARY

Scale-up of the silica gel fractionation of R-45M HTPB prepolymer gave erratic results indicating structural changes if the material is contacted for any length of time with active SiO_2.

Scale-up fractionation of R-45M (MW 3000, functionality 2.3) by preparative gel permeation chromatography and by solvent precipitation techniques produces fractions wherein the average functionality increases with average molecular weight. The data indicate that R-45M contains 30-50 weight percent polymer that has an average functionality of close to two, and an average molecular weight of 2000. This material is admixed with polymer having a significantly higher molecular weight and higher functionality.

The difunctional material (MW 2000) was shown to cure quite rapidly in the absence of cure catalysts at NCO/OH equivalence ratios below one-to-one, and swelling tests performed with both gumstock and propellant indicate that a crosslinked network is produced at NCO/OH ratios of 0.8. Since both gel permeation chromatography and solvent precipitation techniques separate according to molecular weight rather than functionality differences, it is concluded that the low molecular weight fraction (MW = 2000, f = 2.0) still contains material having higher functionality and acting as an effective crosslinker.

Unexpectedly, cure inhibition at NCO/OH equivalence ratios of 0.8 was experienced when a higher molecular weight fraction (MW 6000, f ~3) was recombined with the MW 2000 material. Raising the NCO/OH equivalence ratio to 1.0 effected cure. Some of these studies were performed without adding antioxidants. To rule out oxidative crosslinking as a possible explanation for the cure behavior of the MW 2000 material, R-45M was heated in the presence of AP at 140°F for periods up to two weeks; there was no indication of a change in the GPC elution curves. This does not as yet rule out lesser degrees of oxidative chain interaction such as might be critical in the cured system.

The effect of the low M difunctional R-45M fractions upon propellant mechanical behavior was compared against R-45M itself and against an HT-Telagen fraction (M = 4000, functionality ~2) obtained from Aerojet. Minithin uniaxial tensile properties were measured, as were tear susceptibilities and analog motor thermal cycling capability, using 84 percent solids with DDI as isocyanate and no bonding agent. Results were as follows:

- At -65°F the low M fractions produced lower strain and higher modulus at -65°F than did R-45M itself. At 70 and 140°F the low M fractions were at least as effective as R-45M itself.

- **Tear resistance** with the low M fractions is probably superior to R-45M at 70°F and differences at -65°F were not clear cut.
- The Telagen fraction (M ~4000) offers no advantages over R-45M in terms of uniaxial tensile behavior. It's tear resistance is inferior to that of the R-45M fractions.
- At equivalent ambient initial modulus, the temperature cycling capability (-80°F to 160°F) with the low M fractions is as good as that with the parent R-45M.

SECTION III

RESULTS AND DISCUSSION

1. PREPARATION OF R-45M FRACTIONS

a. Silica Gel Fractionation

In their functionality program, Esso Research and Engineering had fractionated three different lots of R-45M on an analytical scale (1 gram quantities) over silica gel columns (Ref. 4), and had obtained two distinct peaks consisting essentially of difunctional material (MW 4000) and trifunctional material (MW 2000), the difunctional fraction accounting for 40-50 percent of the initial sample weight. These data supported the manufacturer's contention that the higher functionality material was present in a lower molecular weight fraction.

Against this background this program started with the scale-up of the R-45M HTPB fractionation over silica gel columns using 4-5 inch diameter columns at 50-60 gram prepolymer loading while otherwise maintaining closely similar conditions (SiO_2/polymer ratios, selection of solvents) as were used during the analytical work.

The results, summarized in detail in Appendix A, were unsatisfactory in so far as the scale-up fractionation did not succeed in duplicating the analytical separation of the R-45M into predominantly di and trifunctional fractions. Since repeat silica gel column treatments of the same material additionally provided evidence that the material was being changed chemically upon prolonged contact with silica gel, the attempt of preparing the desired difunctional prepolymer by silica gel fractionation[1] of R-45M was abandoned.

Similarly unsuccessful was an attempt to fractionate R-45M by admixing the material with varying weights of silica gel followed by solvent extraction of the slurry using CCl_4/CH_2Cl_2 solvent mixtures in varying ratios.

b. Fractionation by Gel Permeation Chromatography

Paralleling the early fractionation and polymer characterization efforts at Esso, LPC analyzed the R-45M HTPB prepolymer by gel permeation chromatography, both at an analytical and a preparative scale (Water Associates "Anaprep" GPC). The data that were obtained were in contradiction to the results of the silica gel fractionation in so far as they showed that hydroxyl functionality in the R-45M tends to increase with molecular weight.

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[1] Other workers (Ref. 5) have since reported similarly negative results in attempting to fractionate HTPB prepolymers of active silica gel. Improvements in the silica gel fractionation method can be effected by partially deactivating the SiO_2 with alcohols; this, however, is not expected to alleviate all the scale-up problems.

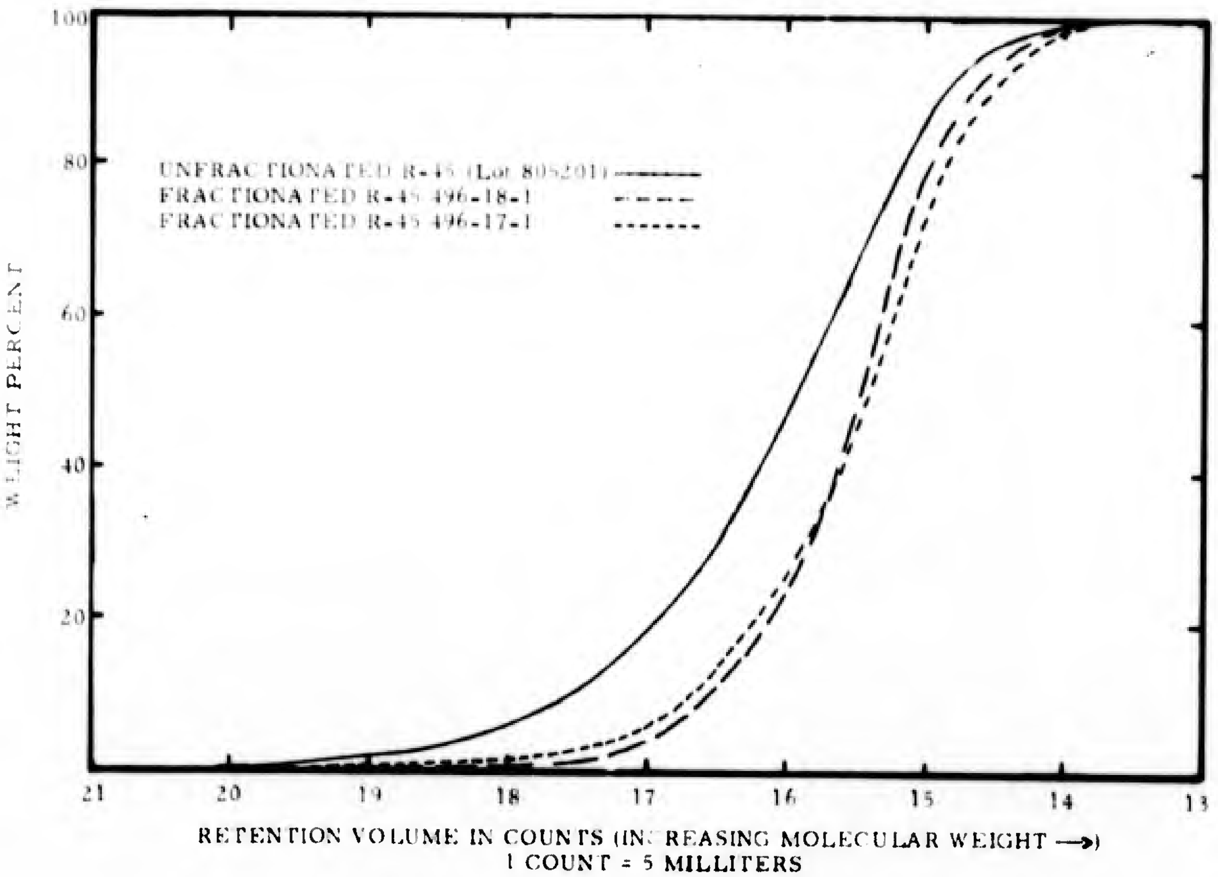

Figure 1 GPC Cumulative Plots (Analytical Mode)

TABLE I

SCALED-UP GPC FRACTIONATION OF R-45M (LOT 805201)(1, 2)

Fraction	Wt %	$\bar{M}_n$	Eq. Wt	f_n	f_v	Relative Reaction Rate
A78-28-3	8.7	10640	2390	4.45		
-4	20.5	4420	1810	2.44		
-5	22.9	2840	1350	2.10		
-6	19.7	2530	1230	2.06		
-7	14.5	2190	1150	1.91		
-8	9.0	2200	1060	2.08		
-9	4.7	2270	1120	2.03		
A78-31-1 (Combined 5, 6, 7 above)	(57.1)	2550	1270	2.01	2.4(3)	1

---

(1) Forty gram total at ten percent R-45 injection concentration in $CHCl_3$.

(2) See Table XIV footnotes for definition of properties listed and Appendix B for description of analytical methods.

(3) Defintion of point of incipient gelation imprecise for this sample.

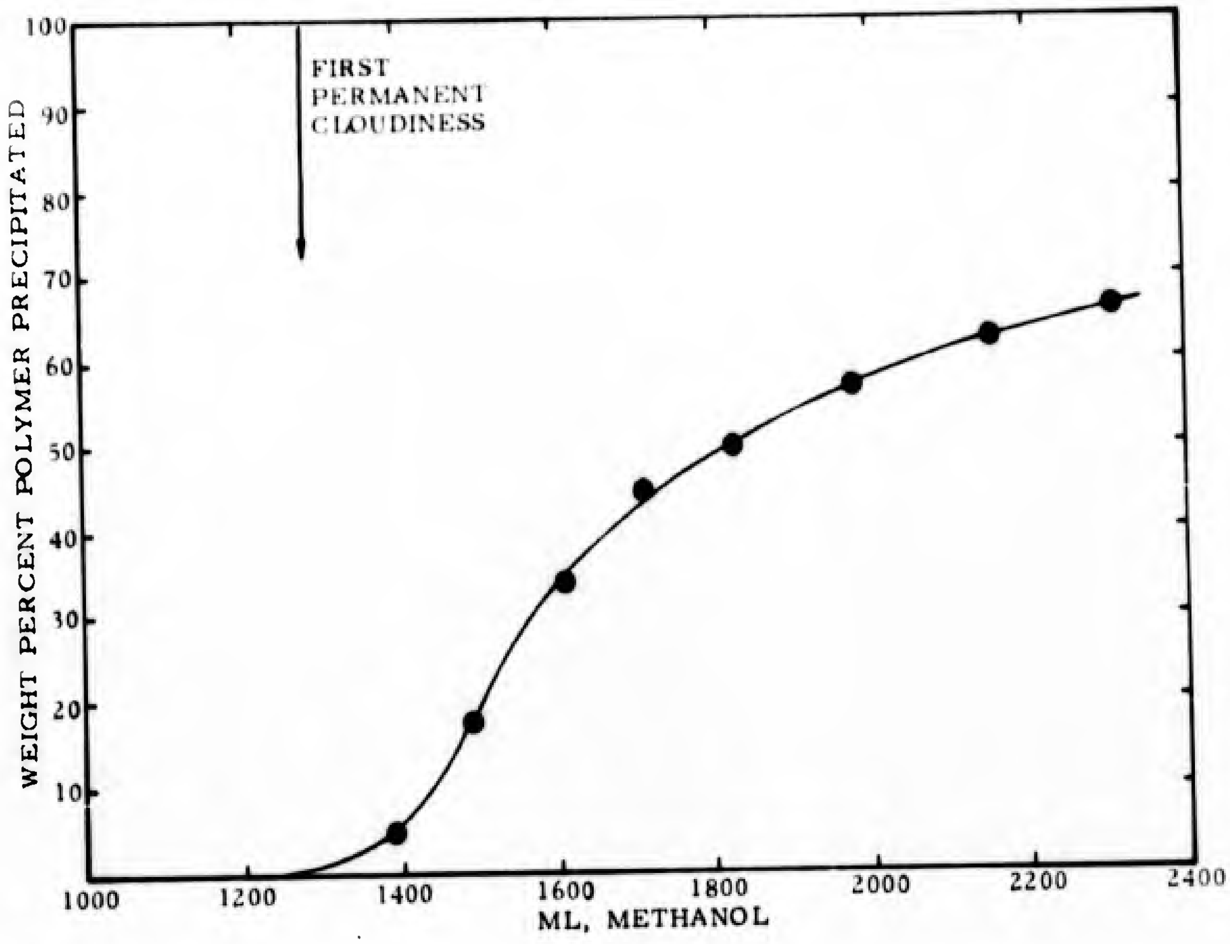

Figure 2 Precipitation of R-45M, Lot 008281, by Addition of Methanol to a 10.0 Wt % Solution of R-45M in Methylene Chloride at Ambient Temperature

TABLE II

FRACTIONATION OF R-45M, LOT 008281 BY PRECIPITATION AT AMBIENT TEMPERATURE

Fraction	Wt % of Fraction	Total Wt %	Eq. Wt	$(\bar{M}n)o$	Functionality
I	8.88	8.88	2219	6700	3.02
II(1)	16.17	25.05	2059	6100	2.96
III(1)	7.32	32.37	1950	5760	2.95
IV	7.35	39.72	1882		
V	9.47	49.19	1845	5400	2.93
VI	13.57	62.76	1643	4170	2.54
VII(2)	33.28	96.04	848	1700	2.0

---

(1) Combined and designated TriA.
(2) Remainder, not precipitated out. Designated DiA.

TABLE III

SCALED-UP PRECIPITATION FRACTIONATION OF R-45M, LOT 008281

Fraction	Wt % of Fraction	Cumulative Wt %	Eq. Wt	$(\bar{M}_n)_o$	Functionality $[(\bar{M}_n)_o/\text{Eq. Wt}]$
I(1)	4.68	4.68	2233	7100	3.18
II(2)	12.58	17.26			
III	16.37	33.63			
IV	9.95	43.58			
V	5.23	48.81			
VI	6.83	55.64			
VII	5.71	61.35			
VIII	3.43	64.78			
IX (diB)(3)	33.11	97.89	785	1600	2.04

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(1) Designated TriB'
(2) Designated TriB
(3) Remainder in solution

(1) Analytical Studies

Several samples were examined using the analytical mode of the GPC, and typical results are shown in Figure 1 as cumulative weight percent plots. This figure includes data for two fractions derived from the silica gel fractionation studies that according to analysis had higher average molecular weight (Fraction 18-1 MW 4650, Fraction 17-1 MW 4250) than the starting material (R-45M, Lot 805201, MW 2900). The GPC data adequately reflected these analytical (vapor phase osmometer) differences, which prompted the evaluation of the GPC's preparative mode for the purpose of obtaining sufficient material for functionality determinations.

(2) Preparative Fractionation

The above experiments indicated that GPC fractionation potentially might produce the discrete functionality fractions desired for the program. However, the conventional one percent injection concentration is definitely marginal for preparation of the 1-2 pound of difunctional material desired. Consequently, the feasibility of obtaining good functionality separation of R-45 at a ten-fold greater concentration was investigated. Forty-four grams of two different lots were fractionated into seven fractions each, using four column injections at ten percent concentration. Table I summarizes the results for Lot 805201, which indicate that removal of the high M, high f species (approximately 30% of the material), and perhaps the lower ten percent, should provide the desired difunctional prepolymer. Refractionation of the first cut would be necessary for preparation of trifunctional prepolymer. Above all the data provided evidence that R-45M increases in functionality as molecular weight increases.

c. Fractional Precipitation of R-45M

In view of the functionality separation achieved with GPC it appeared likely that similar success might result using conventional fractional precipitation methods, and the latter could well provide a better avenue for scale-up.

The initial experiment employed a ten percent solution of Lot 008281 (100 g) in methylene chloride at room temperature. Methanol was added incrementally and after each increment the system was warmed to redissolve the precipitated prepolymer (actually coacervate). After cooling and equilibrating for 24 hours, the precipitated fraction was separated (see Figure 2 for representative precipitation profile).

The precipitation was terminated after six fractions totaling 63 weight percent had been collected. The polymer remaining in solution was designated Fraction VII. Analyses of the seven fractions (Table II) indicate qualitative agreement with GPC fractionation in that functionality increases with molecular weight and essentially difunctional material can be produced.

Subsequently the precipitation fractionation was scaled up by simultaneously processing three one-pound samples of Lot 008281. Corresponding fractions from the three samples were combined prior to characterization analyses. The final results, summarized in Table III, are consistent with the first experiment (Table II); this is also demonstrated by the plot of functionality versus molecular weight shown in Figure 3. Fraction IX in Table III was available in approximately 1-pound quantity and was designated DiB.

Two additional three-pound samples were fractionated to yield two one-pound difunctional fractions. These were each redissolved separately and approximately ten percent of each precipitated by addition of methanol. The resultant fractions were designated DiC and DiD.

From the various scaled-up fractionations, three approximately trifunctional fractions were isolated in one-half pound quantities. These were designated TriB', TriB, and TriC. TriB' and TriB were the first and second cuts from the fractionation producing DiB (Table III) while TriC was the second cut from the fractionation producing DiC.

Detailed characterization of these fractions is described in the following section.

2. CHARACTERIZATION OF PRECIPITATION FRACTIONS

Table IV summarizes the analytical data obtained upon the precipitation fractions and upon two additional fractions, one from Aerojet (HT-Telagen) and one from ARCO. Characterization of these fractions is discussed in the following sections.

a. Infrared Spectra

Figures 4-7 present the 2.5-12 micron region of the infrared spectra for several fractions and their parent lot of R-45M. The higher concentration of hydroxyls in DiB and DiC, due to their low equivalent weight, is evident in the three micron region, as is a small increase in carbonyl (5.9-6 micron).

b. Molecular Size and Functionality

(1) Gel Permeation Chromatography

Figure 8 shows the cumulative size distributions as determined by analytical GPC (1% solution in $CHCl_3$) for DiB, DiC, TriB and their parent R-45M. The difference are qualitatively as expected, although the high molecular weight ends are not strongly differentiated because of the relatively low exclusion limit (6000) of the Styragel columns employed.

(2) Elution from Deactivated Silica Gel

The functionality distribution of two of the fractions (DiB and TriB) was measured by fractional elution from deactivated silica gel. Partial deactivation of the silica was achieved by preparing the silica gel columns with CH_2Cl_2/CH_3OH mixtures.

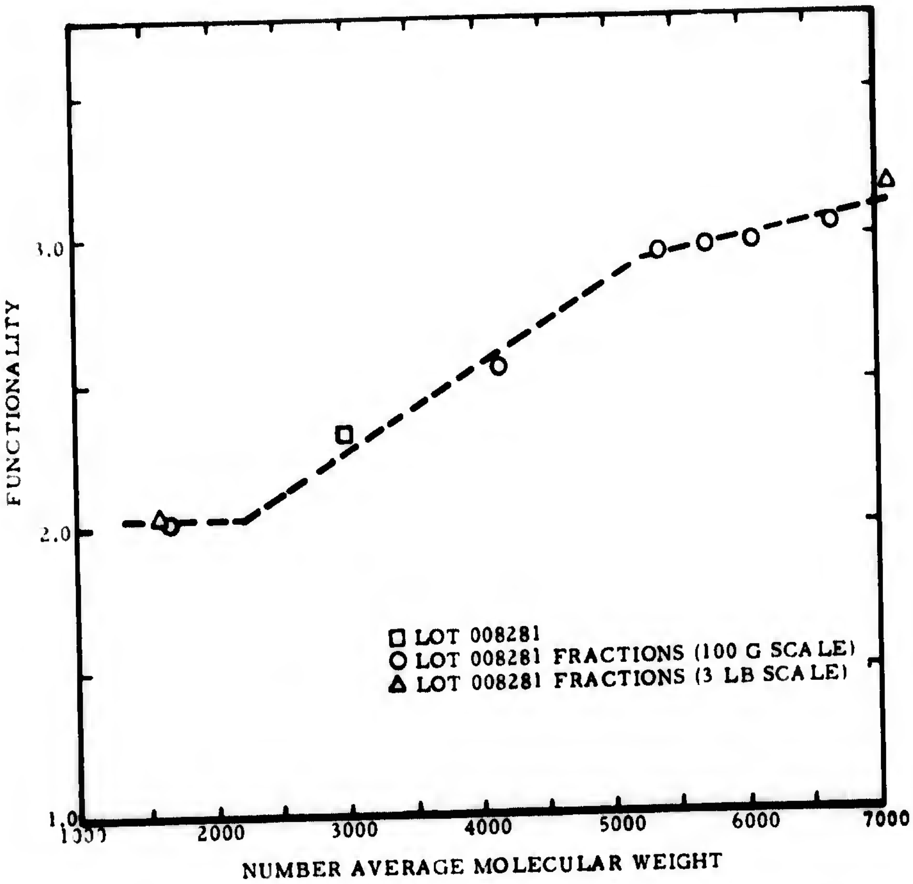

Figure 3 Dependence of Functionality on Molecular Weight for R-45M, Lot 008281, and Precipitation Fractions

TABLE IV

CHARACTERIZATION OF FRACTIONS

Fraction	Laboratory	$\bar{M}_n$ (1)	Eq. Wt.	$\bar{f}_n$ (2)	% NCO Reacted at Gel Point	$\bar{f}_w$ (3)
DiB (4)	Esso	1600	785 (5)	2.04	93-94	2-1
	LPC	1840	940 (5)	1.96		
	ARCO	1800	895 (6)	2.01		
DiC (4)	Esso	1600	821	1.95	99-100	2.00-2.02
	LPC	1800	881	2.04		
	ARCO	1800	840	2.14		
DiD (4)	Esso	1630	823	1.98	98.5-100	2.00-2.03
Telagen-HT-316AM-20 (7)	LPC	4430	1940	2.29		
	Aerojet	3980 (8)	2080 (9)	1.91		
TriB (10)	Esso	6000	2205	2.72	71-74	2.85-2.98
TriC (11)	Esso	6200	2300	2.70	71-72	2.93-2.98
ARCO-1 (12)	Esso	5400	1890	2.86	71.5-73.2	2.84-2.96
	LPC	5320	1690	3.16		
	ARCO	5200	2090	2.48		
R-45, Lot 805201	Esso	2900	1200	2.38		
	LPC	2900				2.6
R-45, Lot 008281	Esso	3025	1297	2.34		2.42
	LPC	2980	1280	2.33		

---

(1) VPO measurements
(2) $\bar{M}_n$/Eq. Wt.
(3) From Stockmayer equation using % NCO reacted at gel point (Ref. 7).
(4) Last cut from fractional precipitation.
(5) Toluene sulfonyl isocyanate procedure.
(6) Infrared
(7) Prepared by General Tire & Rubber using silica gel elution (Ref. 6).
(8) VPO
(9) Infrared
(10) Cut 2 from fractional precipitation.
(11) Cut 2 from fractional precipitation
(12) Prepared by ARCO using a proprietary procedure.

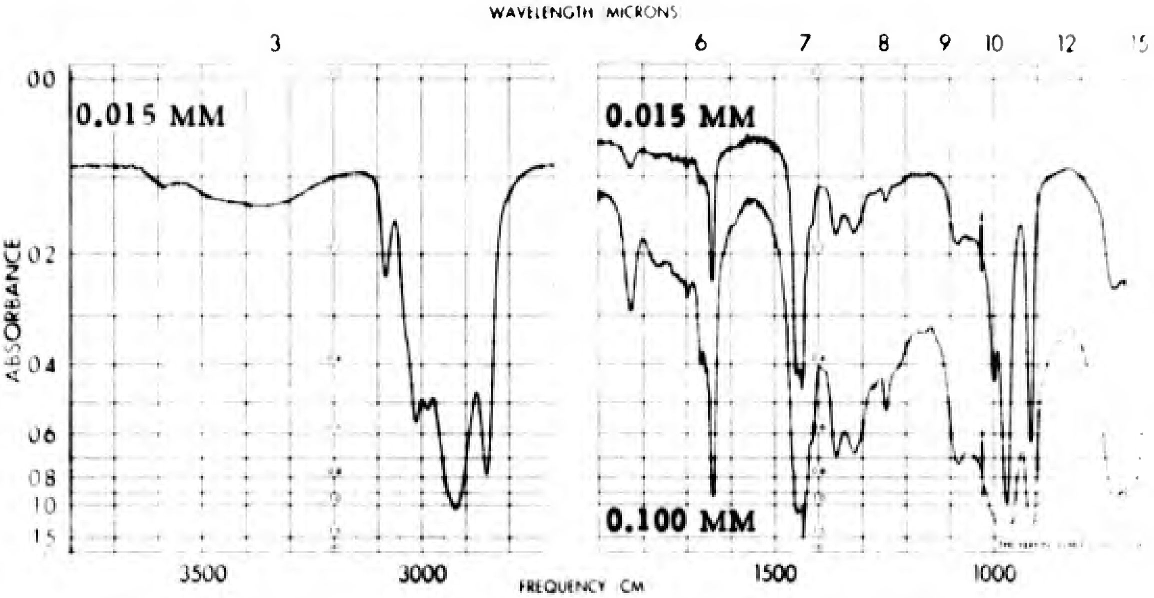

Figure 4 Infrared Spectrum of R-45 HTPB Lot No. 008281 (film thickness: 0.015 and 0.100 MM)

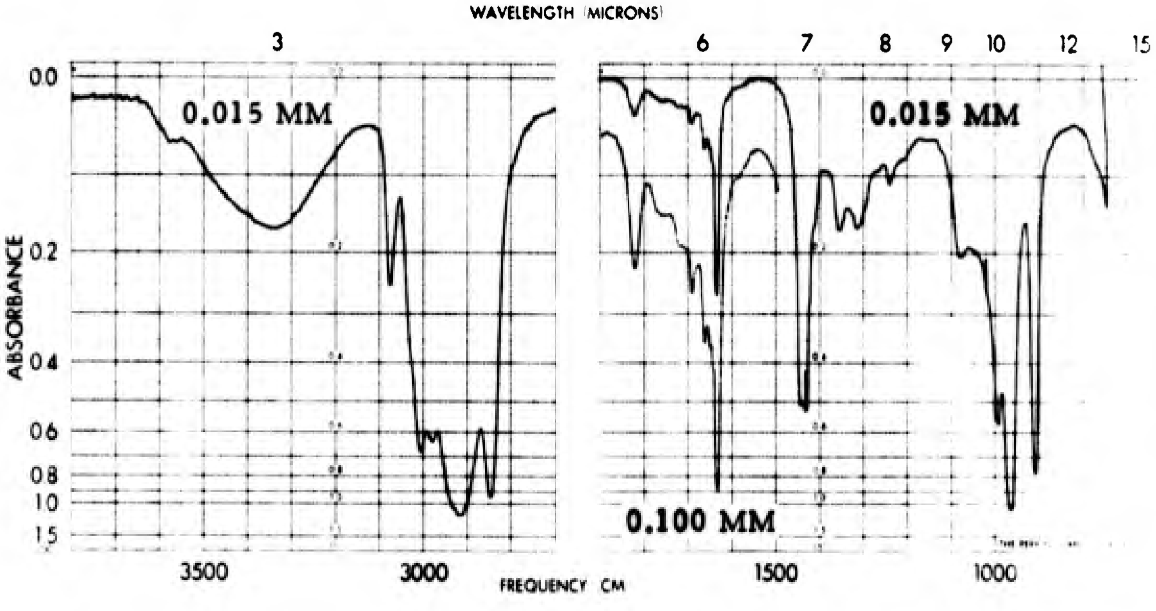

Figure 5 Infrared Spectrum of DiB (film thickness: 0.015 and 0.100 MM)

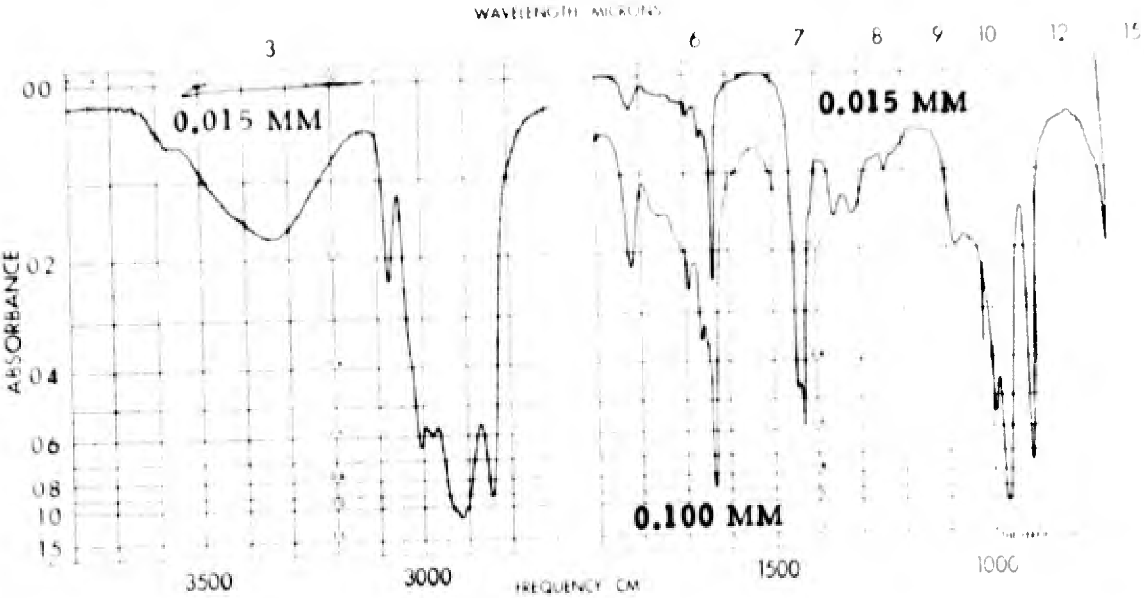

Figure 6 Infrared Spectrum of DiC (film thickness: 0.015 and 0.100 MM)

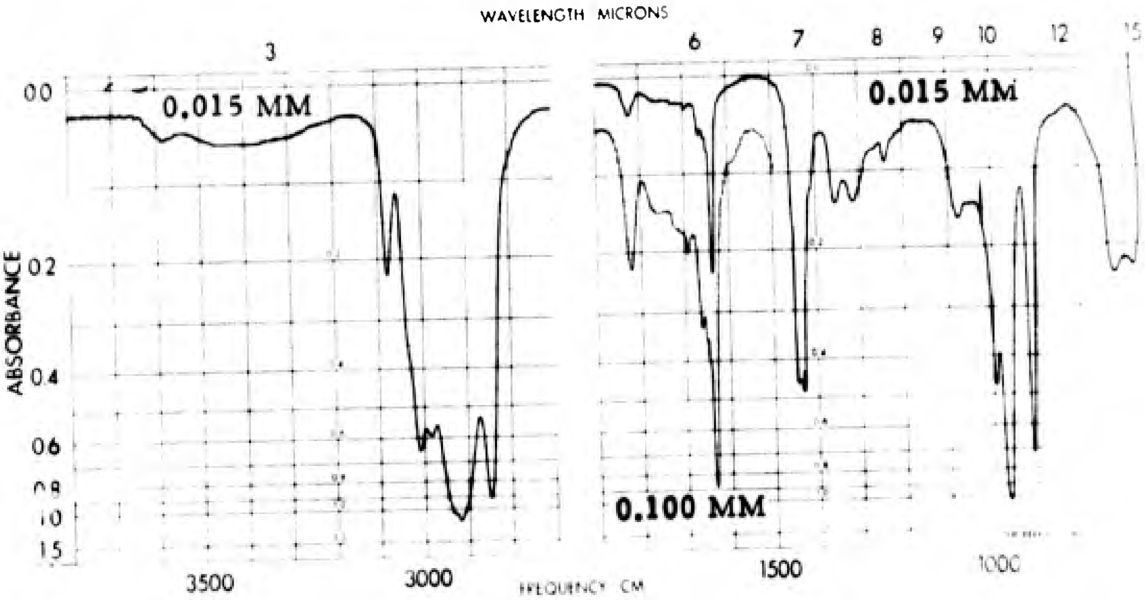

Figure 7 Infrared Spectrum of TriB (film thickness: 0.015 and 0.100 MM)

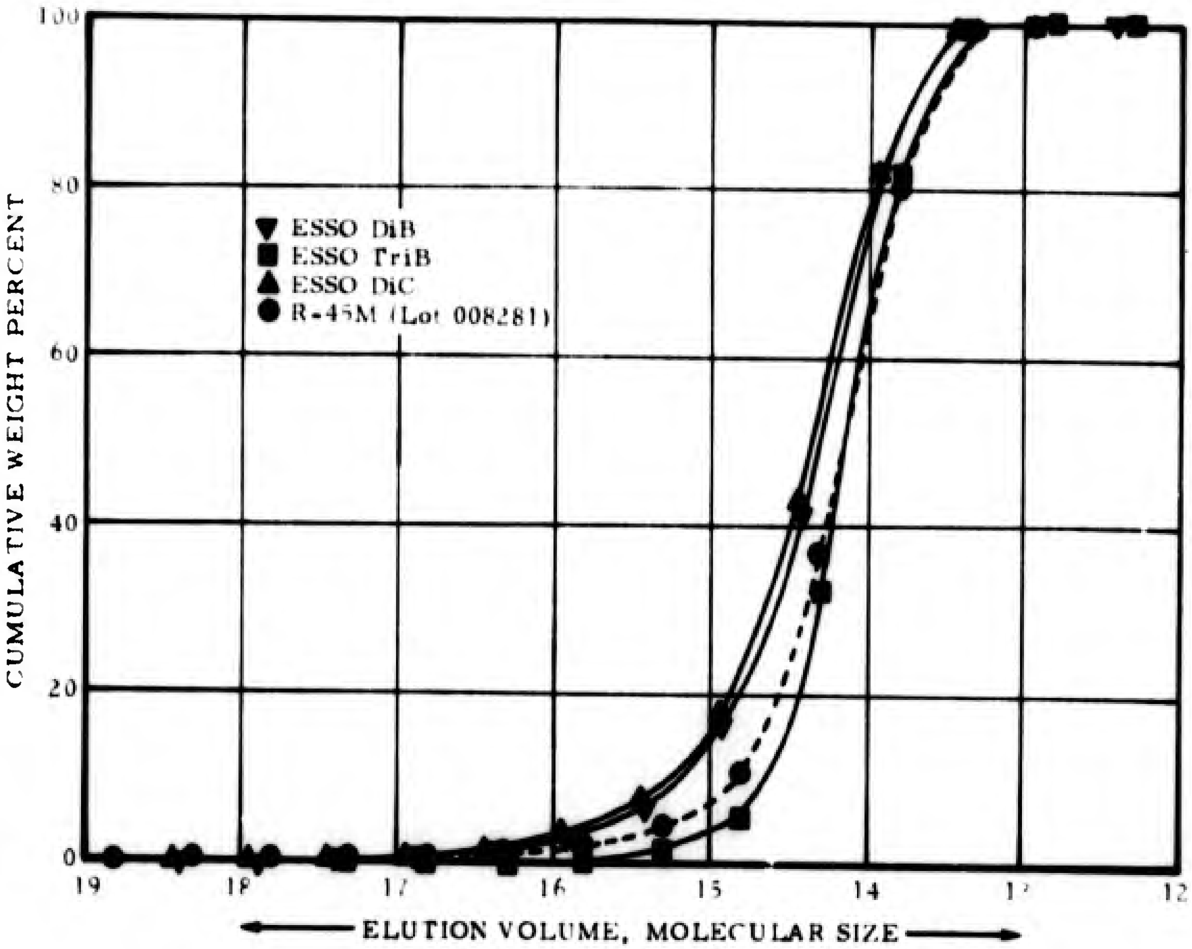

Figure 8 Cumulative Size Distributions

Two runs were conducted upon DiB. The first employed an initial CH_2Cl_2/CH_3OH mixture of 98/2 (by volume) and subsequently eluted with that same composition. The second employed an initial composition of 99/1 and ultimately required a ratio of 97/1 to elute the final fraction. The elution profile for the former run is illustrated in Figure 9 and Tables V and VI summarize analytical data for the fractions.

On the basis of these two fractionations, it appears that DiB contains a very small amount of monofunctional and some trifunctional prepolymer. However, it is difficult to further quantitize the mono- and trifunctional level since analyses of all fractions show only slight, if any, deviation from a nominal difunctional polymer.

From the GPC data the breadth of the molecular weight distribution is characterized by a $\overline{M}_w/\overline{M}_n$ ratio of 1.11; a value of 1.14 results from the combined silica elution data of Tables V and VI. The latter data also yield a calculated $\overline{f}_w/\overline{f}_n$ ratio of 2.00/1.99 = 1.00.

The silica gel for the TriB characterization was initially deactivated with a 99.5/0.5 CH_2Cl_2/CH_3OH mixture. The elution profile is given in Figure 10 and the analytical data are summarized below:

Fraction	Cumulative Wt %	Eq. Wt	$\overline{M}_n$	$\overline{f}_n$
1	8.83	3800	9200	2.42
2	22.89	3080	7600	2.47
3	81.54	2420	7100	2.93
4	95.7	1010	2950	2.92

Since TriB is an early cut (No. 2) in the precipitation fractionation, it is not surprising to see that it contains a wide range of molecular weight and functionality species. Interestingly, however, the data, along with those in Tables I, II, III, V, indicate that R-45M possesses both di- and trifunctional species covering a wide range in molecular weight.

(3) $\overline{M}_n$, $\overline{f}_n$, and $\overline{f}_w$

The following comments summarize the data of Section 2b:

- The precipitation fractions, DiB, DiC, and DiD, are of relatively low molecular weight (1600-1800) and are very nearly difunctional. The fact that they do indeed gel with DDI (and TDI) indicates some effective polyfunctionality in the polymer fraction, the diisocyanate, or both.[2] DiB presumably contains slightly more polyfunctional species than do the other two ($\overline{f}_w$ values plus the added precipitation step in preparing DiC and DiD).

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[2] Figure 32 in Appendix B shows that HMDI and DDI result in the same $\overline{f}_w$ value for a lot of R-45M. This might be taken as evidence that polyfunctionality is in DiB, C, and D rather than in DDI; otherwise both HMDI and DDI must possess the same degree of polyfunctionality (homopolymerization).

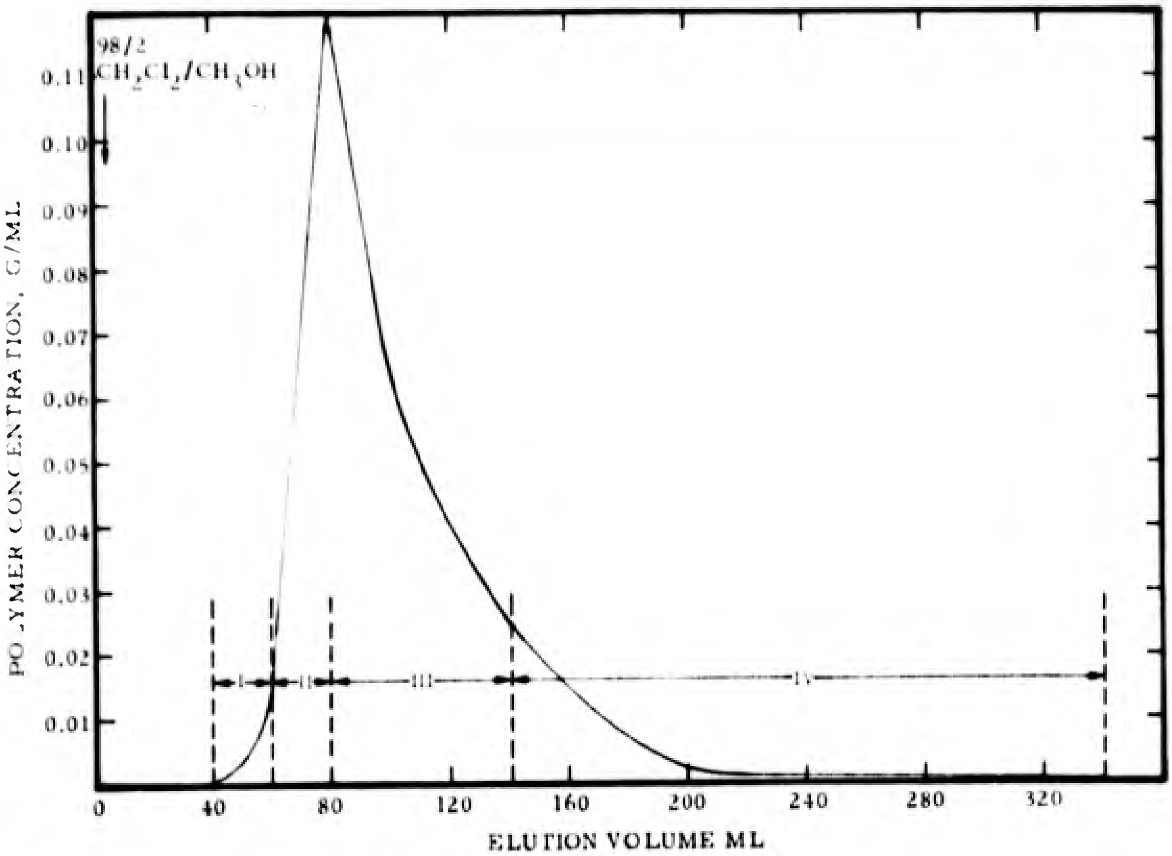

Figure 9 Fractionation of DiB by Column Chromatography using Partially Deactivated Silica Gel (98/2 CH_2Cl_2/CH_3OH). Run 499-68

TABLE V

FRACTIONATION OF DiB ON PARTIALLY DEACTIVATED SILICA GEL*

Run 499-68

Fraction	Wt % of Fraction	Cumulative Wt %	Equivalent Weight		$\overline{M}_n$	Functionality
I	5.32	5.32				
II	39.23	44.55	1103 1094	1098	2140	1.95
III	43.50	88.05	895 860	877	1760	2.0
IV	11.58	99.63	521 517	519	1085	2.09

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* deactivated with 98/2 CH_2Cl_2/CH_3OH

TABLE VI

FRACTIONATION OF DiB ON PARTIALLY DEACTIVATED SILICA GEL*

Run 499-70

Fraction	Wt % of Fraction	Cumulative Wt %	Equivalent Weight	$\overline{M}_n$	Functionality
I	7.43	7.43	2208	4000	1.81
II	57.57	65.00	1160	2370	2.04
III	13.52	78.52	740	1560	2.10
IV	19.35	97.87			

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* deactivated with 99/1 CH_2Cl_2/CH_3OH

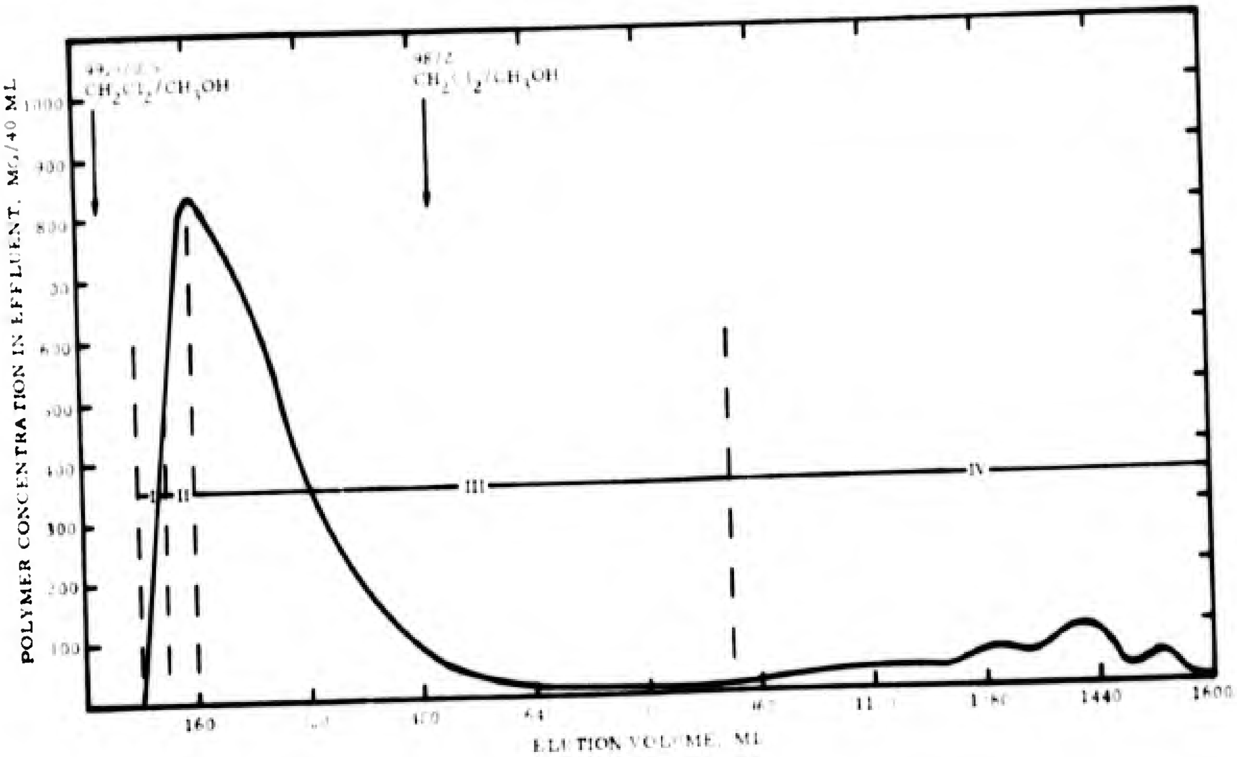

Figure 10 Fractionation of TriB by Column Chromatography using Partially Deactivated Silica Gel (99.5/0.5 to 98/2 CH_2Cl_2/CH_3OH). Run 499-76

- The precipitation fractions, TriB and TriC, are much higher in molecular weight and approach trifunctionality. However, they do contain appreciable quantities of difunctional material.

- All of the data provide a good illustration of the difficulties in establishing $\overline{f}_n$ and of the value in obtaining an independent measure of effective functionality such as given by $\overline{f}_w$. Obviously, there is a great need for continued interlaboratory comparisons and standardization.

c. Reactivity with Isocyanates

Table VII summarizes the results of reaction profiles measured at 80°F, while Figure 11 illustrates the entire profile for several samples. The following points are noteworthy:

- At the five percent level, AP does not influence the reactivity of DiB.

- As expected, TDI initially reacts more rapidly than does DDI but subsequently slows down. Quantitiative treatment of the TDI data is not warranted because the absorptivity of TDI changes due to preferential reaction of the less infrared active para isocyanate group.

- DiD reacts far more rapidly than do DiB and DiC although the differences appear to lessen as the reaction progresses.

- With the exception of DiD, the difference in reactivity between the di and trifunctional precipitation fractions and their parent R-45M (Lot 008281) is qualitatively consistent with differences in reactive group concentration, as indicated by the comparison in Table VIII.

3. EVALUATION OF FRACTIONS IN PROPELLANT

a. General Comments

It is generally accepted within the industry that binder prepolymers must fall in the molecular weight range of approximately 3000-5000 in order to provide an acceptable balance between propellant processibility and mechanical behavior. The precipitation fractions DiB, C, and D obviously fall well below this range and would be expected to impart unacceptable mechanical properties to propellant. On the other hand, the widespread use of uniaxial tensile properties as performance criteria is becoming increasingly suspect. Thus it appeared worthwhile to compare the performance of propellants containing R-45M or its precipitation fractions, using uniaxial tensile properties as well as other properties believed to be potentially more meaningful. The latter included tear susceptibility at -65 and 70°F plus analog motor temperature cycling. In addition, propellant was characterized by sol/gel and degree of swelling.

TABLE VII

REACTIVITY WITH ISOCYANATES

Sample	Isocyanate	Reactivity (80°F) Half Life (Hrs)(1)	Reactivity (80°F) Gel Time (Hrs)(2)	% NCO Reacted at Gel Point(3)
DiB	DDI (with or without 5% AP)	16	105-115	93-94
	TDI	6	50-90	80-87(4)
	TPMTI	----	<1.5	----
DiC	DDI	16	240-250	99-100
DiD	DDI	<1	74-80	99-100
TriB	DDI	28	62-69	71-74
TriC	DDI	28	59-66	71-72
ARCO-I	DDI	75	175-210	72-74
R-45, Lot 805201	DDI	17	61	80.4
	HMDI	12	50	80.6
R-45, Lot 008281	DDI	24	62-71	79
	DDI + 0.75% Ethyl 736	28	120-126	84

---

(1) Time to 50% NCO reaction.
(2) Time to incipient gelation.
(3) Infrared absorbance at 4.42 micron using the 3.4 micron band as internal reference.
(4) Apparent value only. Effective TDI absorptivity changes during reaction.

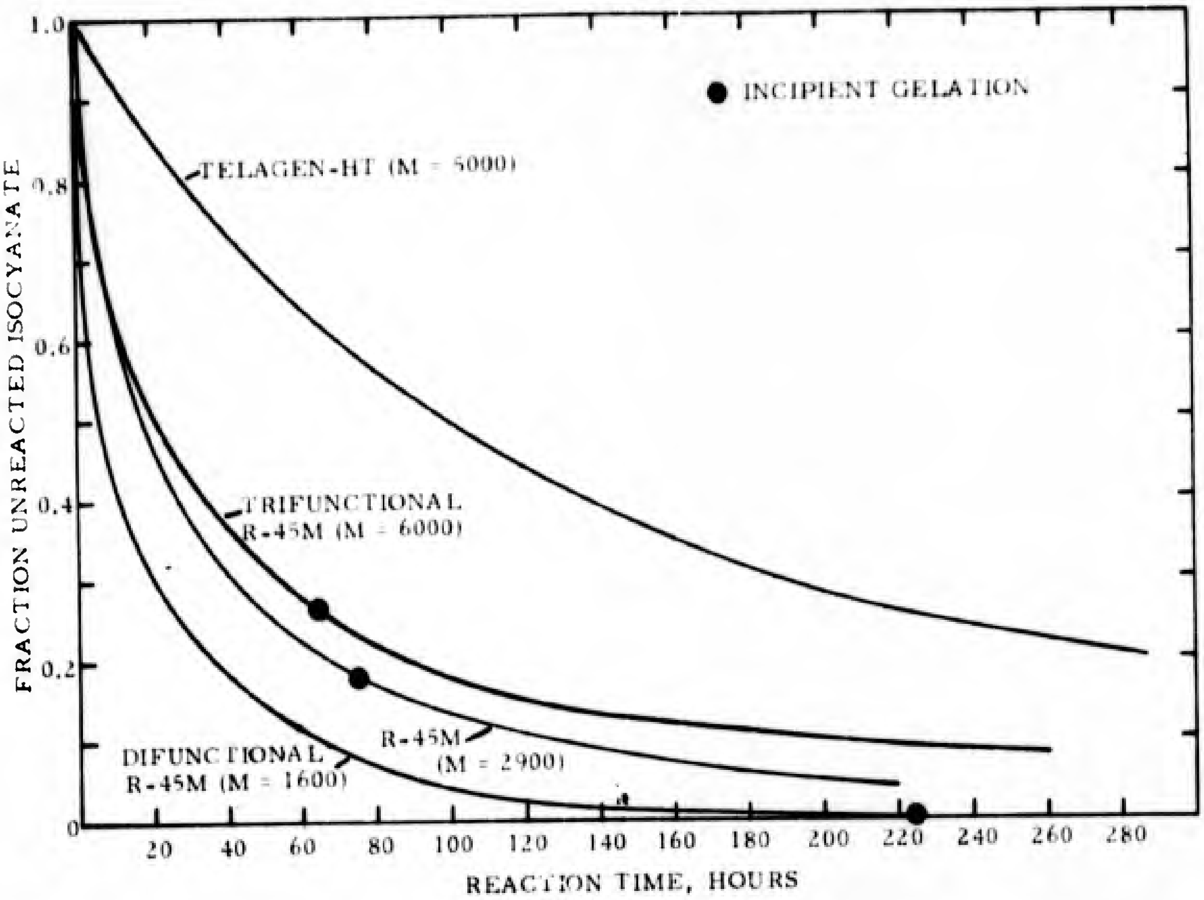

Figure 11 Reaction Profile of Tri and Difunctional R-45M Fractions with DDI at 80°F (Reaction was monitored by infrared measurements of isocyanate band at 4.42 micron.)

TABLE VIII

REACTIVITY AND HYDROXYL CONCENTRATION

	Relative Reactivity*	Relative OH Concentration**
DiB	1.5	1.5
R-45M	1.0	1.0
TriB	0.86	0.60

---

* Relative values of reciprocal half-life (Table VII)
** Relative values of Density/Equivalent Weight

One of the original program goals had been to establish guidelines for an optimum binder composition in terms of prepolymer functionality, i.e., di/tri ratio, and of trifunctional prepolymer versus trifunctional isocyanate as crosslinker. This goal was dropped because of the molecular weight differential introduced with the difunctional fractions and because of the surprising cure of DiB, C, and D in the absence of added trifunctional species.

A limited number of propellant mixes was evaluated using the Telagen-HT-316M-20 fraction supplied by Aerojet. This possessed the more desired molecular weight in the 4000 range but also contained significant amounts of trifunctional species. Preliminary tests at ARCO had also indicated an ability to prepare a difunctional R-45M fraction in that same range. Scale-up to the one-pound scale produced the ARCO-1 fraction, which proved to be more nearly trifunctional, however.

The propellant formulation employed throughout the program is given in Table IX. To emphasize differences arising from the prepolymer samples, bonding agents were deliberately excluded from the formulation. Similarly DDI was emphasized to obviate complications due to unequal reactivities of isocyanate groups. A solids level of 84 percent was selected to preclude any possible processing problems. Except for the preparation of analog motors, all mixes were 200 gram in size and performed in an ARC conical mixer. Propellant was cured at 140°F for ten days, those conditions having been established as yielding approximately steady state Rex hardness.

b. Uniaxial Behavior

Table X summarizes the uniaxial tensile properties (minithin specimens) for R-45M and several fractions at various NCO/OH, using DDI as the sole isocyanate. The values of σ_m, ϵ_m, and E_{sec} (at σ_m) are plotted against the degree of propellant swelling in Figures 12 (70°F) and 13 (-65°F).[3] To clarify the data comparison, lines have been drawn through the R-45M data. The region of primary interest is presumed to be between swell values of 20-30, corresponding to an initial modulus range of approximately 1000-300 psi. Within that region the following conclusions are warranted:

- **In all cases, at least partial cure of propellants containing the fractions was achieved, even at NCO/OH = 0.8. This point will be examined further in Section 3e.**
- **At 70°F DiB propellant possesses significantly greater strain capability than any of the other systems. This is further reflected in a lower modulus for DiB.**
- **At 70°F the Telagen propellant is significantly harder than the others.**

---

[3] The degree of swell should be inversely proportional to binder crosslink density. It therefore provides a rational basis for comparison of properties among systems varying in binder composition.

TABLE IX

PROPELLANT FORMULATION

	Weight Percent
Prepolymer + Curative	15.94
Ethyl 736	0.06
AP, Type II, Size 1	34.00
AP, +48 Mesh	17.00
AP, 8 micron	17.00
Al, Valley H-100	16.00

TABLE X

PROPELLANT UNIAXIAL PROPERTIES WITH DDI[1]

Polymer	Nominal NCO/OH	Sol[2] (%)	Swell[3]	σ_m/σ_b[4] (psi)			ϵ_m/ϵ_b[4] (%)		
				-65°F	70°F	140°F	-65°F	70°F	140°F
R-45M, Lot 008281	0.80	42	28	530/440	65/49	59/57	12/23	44/66	50/54
	0.85[5]	42	38	610/400	71/71	54/51	11/26	39/71	44/53
	0.90	20	19	500/370	106/98	95/95	13/24	18/22	18/18
	1.0	12	13	540/400	130/130	116/116	13/24	9/24	10/10
DiB	0.80	53	28	720/720	69/69	58/54	8/8	116/116	109/130
	0.90	11	17	720/724	130/120	108/108	8/8	18/23	17/17
	1.0	9	14	800/800	140/130	120/120	10/10	16/18	12/12
	----[5]	6	11	630/500	130/130	110/110	10/16	9/9	7/7
DiC	0.80	33	27	890/890	108/94	72/72	6/6	35/48	42/42
	0.90	15	16	690/690	136/136	104/104	6/6	16/16	13/13
	1.0	12	15	810/810	140/140	106/106	7/7	15/18	13/13
DiD	0.80[5]	49	32	670/640	89/93	67/64	9/14	57/69	71/76
Telagen-HT-316AM-20	0.80	18	28	540/500	130/120	97/97	10/17	37/47	31/31
	0.90	11	24	610/330	150/150	114/101	12/19	19/19	22/27
	1.0	6	24	550/330	160/160	125/125	17/27	14/14	10/10

---

(1) Minithins (see Appendix). Duplicate or triplicate samples. Strain rate 0.54 in/in/min.
(2) Weight percent of prepolymer + curative which is soluble in toluene at ambient temperature. Duplicate samples.
(3) Grams of toluene sorbed per gram of binder gel at ambient temperature. Duplicate samples.
(4) Maximum stress/break stress.
(5) Used in analog motors.

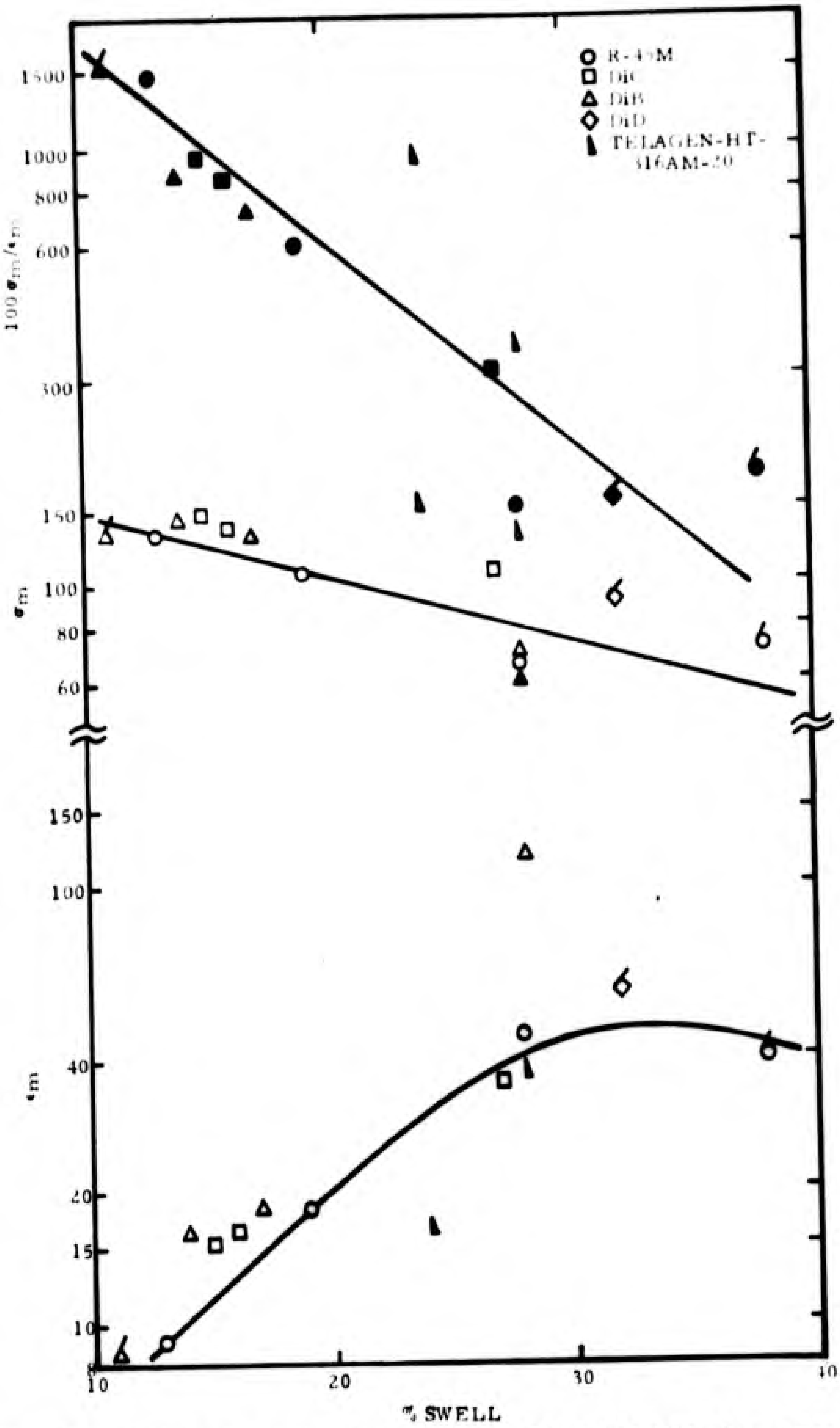

Figure 12 Uniaxial Tensile Properties at 70°F (Minithin Specimens) (Flagged symbols: propellant used in analog motors)

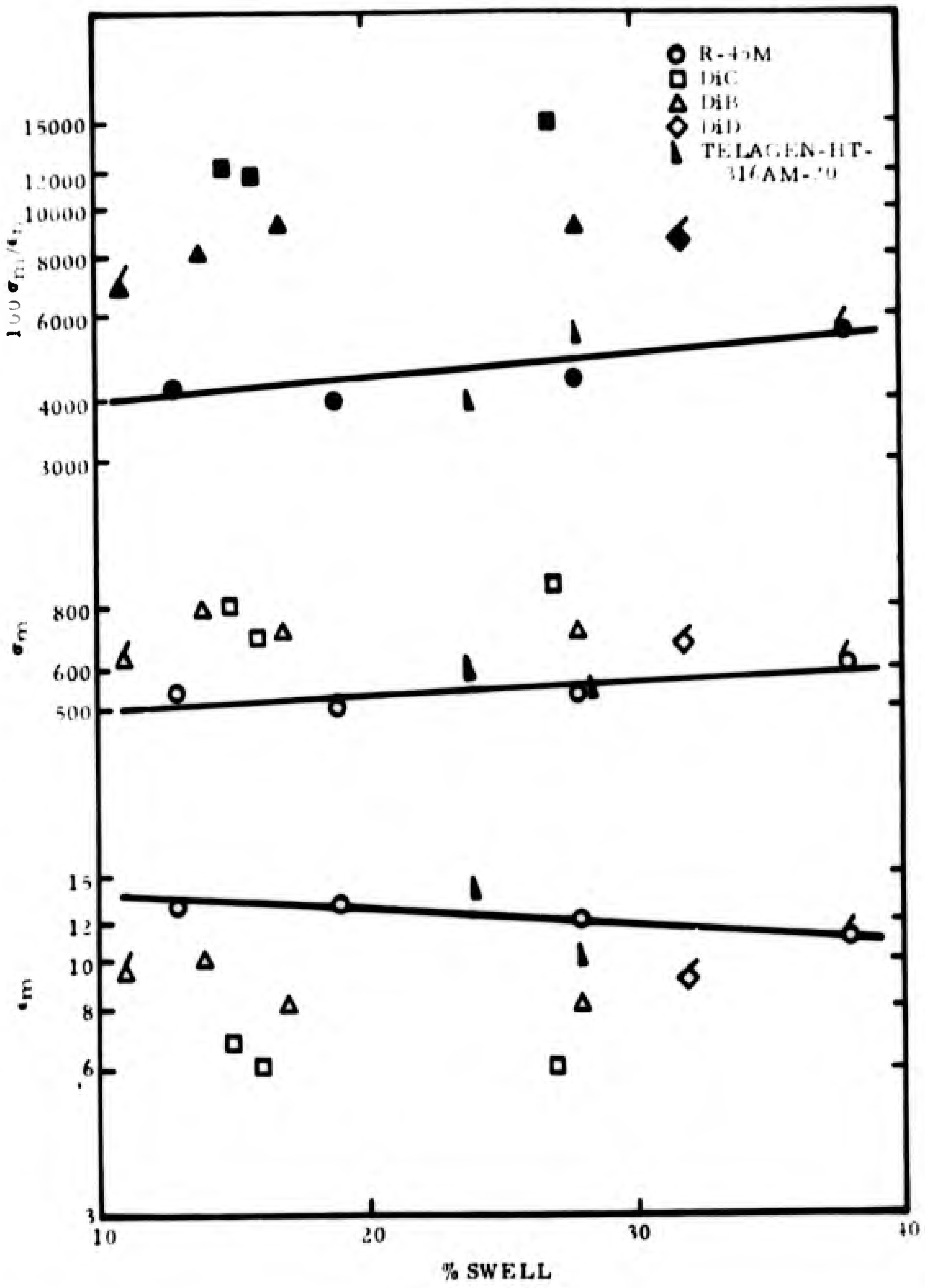

Figure 13 Uniaxial Tensile Properties at -65°F (Minithin Specimens) (Flagged symbols: propellant used in analog motors)

- At -65°F all the R-45M fractions have poorer strain capability (approximately 50%) and greater modulus than the Telagen system or the R-45M itself. This would seem to be the consequence of the greater concentration of curative linkages using the low molecular weight fractions with resultant increases in hydrogen bonding, i.e., effectively greater crosslinking at low temperature. The identity of maximum and rupture values for the R-45M fractions, in contrast to the R-45M and the Telagen fraction, is consistent with this view.

Thus, on the basis of uniaxial behavior one must conclude that the low molecular weight R-45M fractions result in propellant inferior to R-45M itself, particularly at low temperature. Furthermore, the Telagen fraction offers no advantages over R-45M.

c. Tear Behavior

Tear propagation susceptibility is potentially a more meaningful indicator of propellant mechanical capability than is uniaxial tensile behavior. A relatively limited number of studies are available as yet; these have emphasized the determination of "tear energy" (or "surface energy") from measurements of the stress and strain at initiation of cut growth, using constant strain rate tests upon a precut biaxial strip. Interpretation of such a test has been based upon extensions of the Griffith fracture mechanics criterion (Ref. 8).

While similar tests at constant load or constant strain may ultimately prove more informative than a constant strain rate test, the last was selected for this program because of its convenience and cheapness. However, rates of tear growth were measured in addition to the critical stress (σ_0) and strain (ϵ_0) at growth initiation. Tests were performed at two strain rates at -65°F and 70°F upon biaxial strips, 1" x $2\frac{1}{2}$" x 0.1" containing initial cuts (0.16" at 70°F; 0.16" and 0.50" at -65°F).

For comparison purposes relative "tear energies" were calculated simply from the product $\sigma_0 \times \epsilon_0$. Figures 14 and 15 plot such products as a function of degree of swell for a 0.16" initial center cut at -65 and 70°F, while Figure 16 plots the -65°F data using a 0.5" initial center cut. While data scatter is rather large, the conclusion is inescapable that this criterion indicates the R-45M fractions are certainly not inferior to R-45M and may be superior, particularly at 70°F in the 20-30 swell range. The Telagen fraction appears to be inferior at -65°F and equivalent at 70°F to the R-45M fractions.

Turning to the tear rate data, average rates of tear were calculated from the change in crack length between $\Delta c = 0.1$ to 0.4", ignoring the relatively uncertain region between $\Delta c = 0$ to 0.1. (Rate data were not obtained at -65°F with the 0.16 initial cut due to failure at the propellant/wood bond.) Results are given in Figures 17 and 18. Conclusions here are similar to those from the "tear energy" calculations; at 70°F the R-45M fractions again appear superior while the -65°F results are not clear-cut in the 20-30 swell region. Again, the Telagen fraction is inferior to the R-45M fractions.

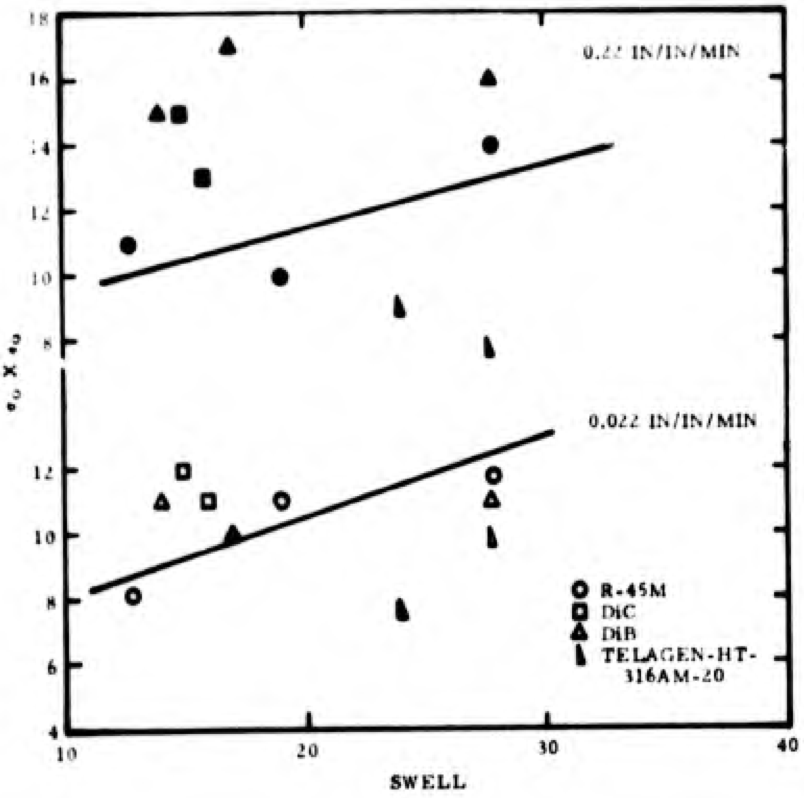

Figure 14 "Tear Energy" at -65°F (0.16 inch initial center cut)

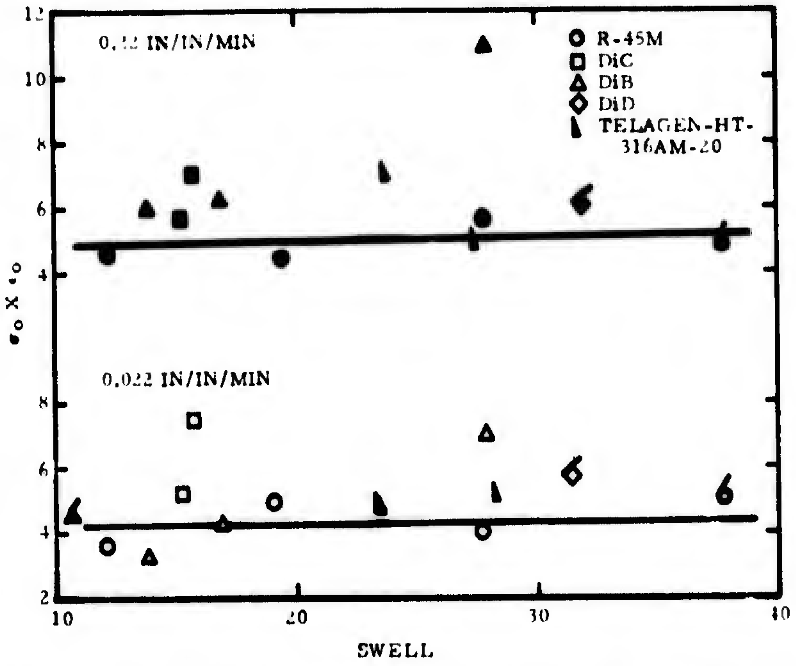

Figure 15 "Tear Energy" at 70°F (0.16 inch initial center cut) (Flagged symbols: propellant used in analog motors)

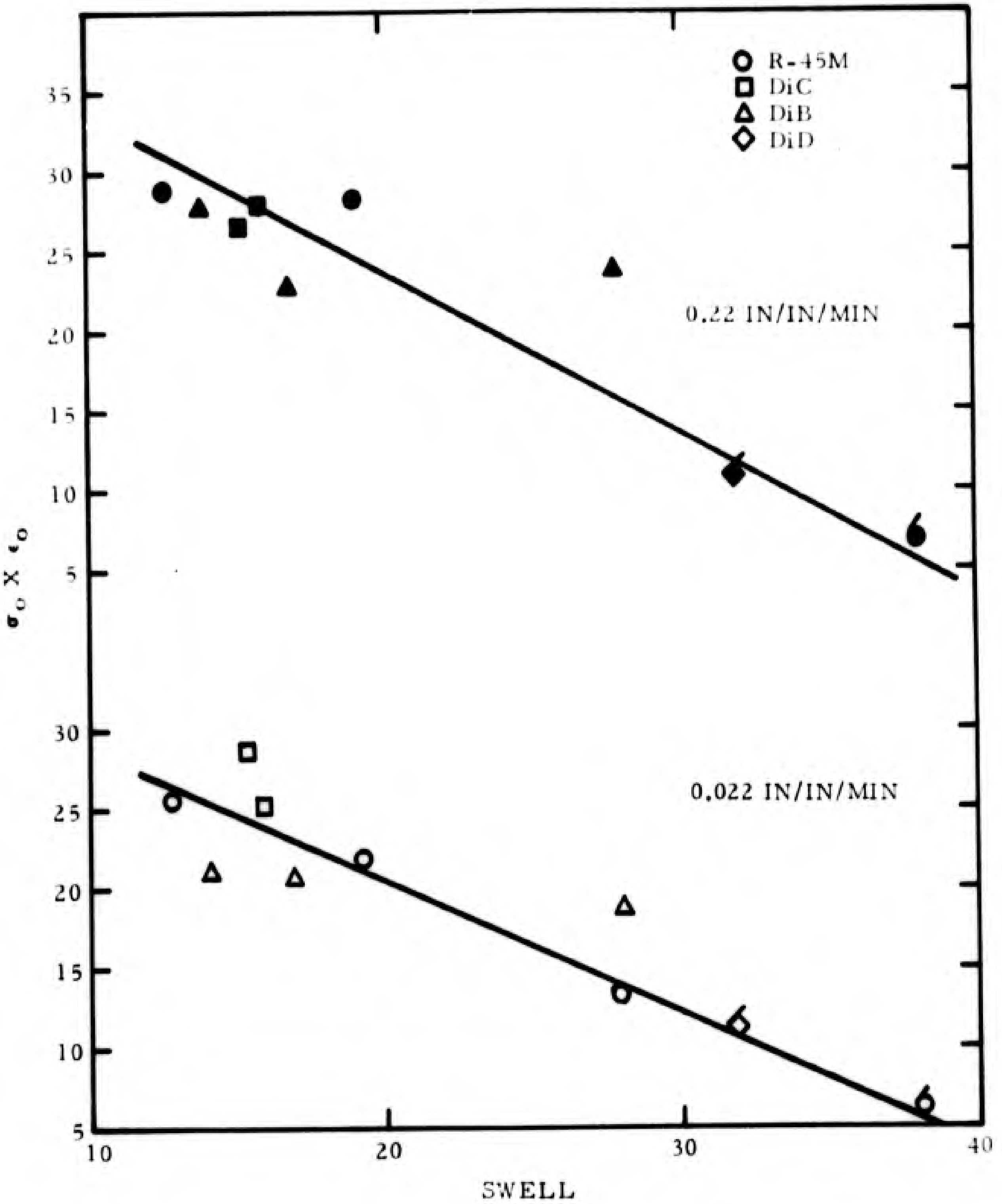

Figure 16 "Tear Energy" at -65°F (0.5 inch initial center cut) (Flagged symbols: propellant used in analog motors)

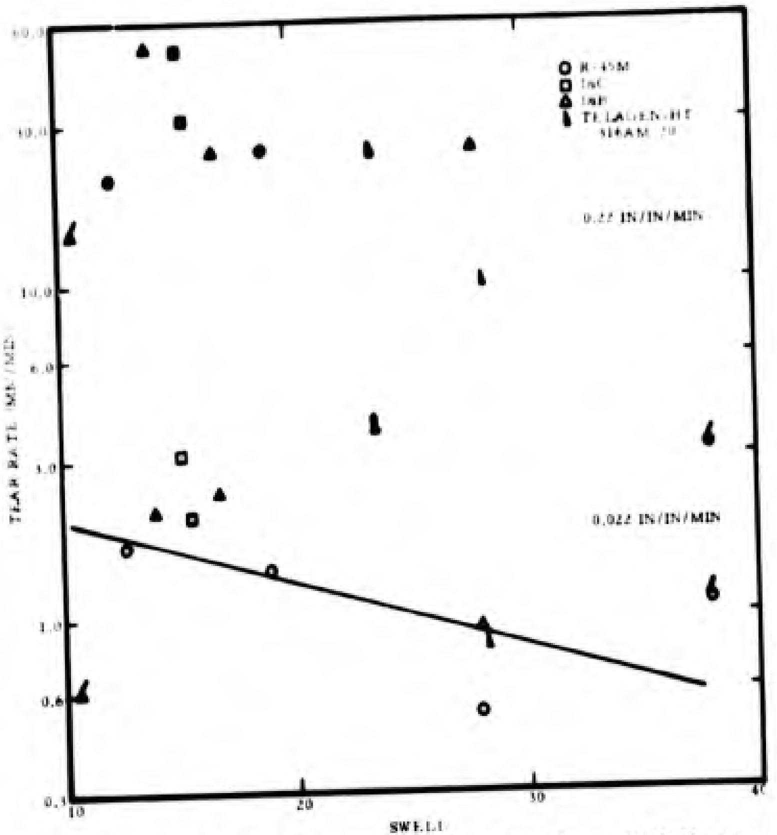

Figure 17 Tear Rate at -65°F (0.5 inch initial cut) (Flagged symbols: propellant used in analog motors)

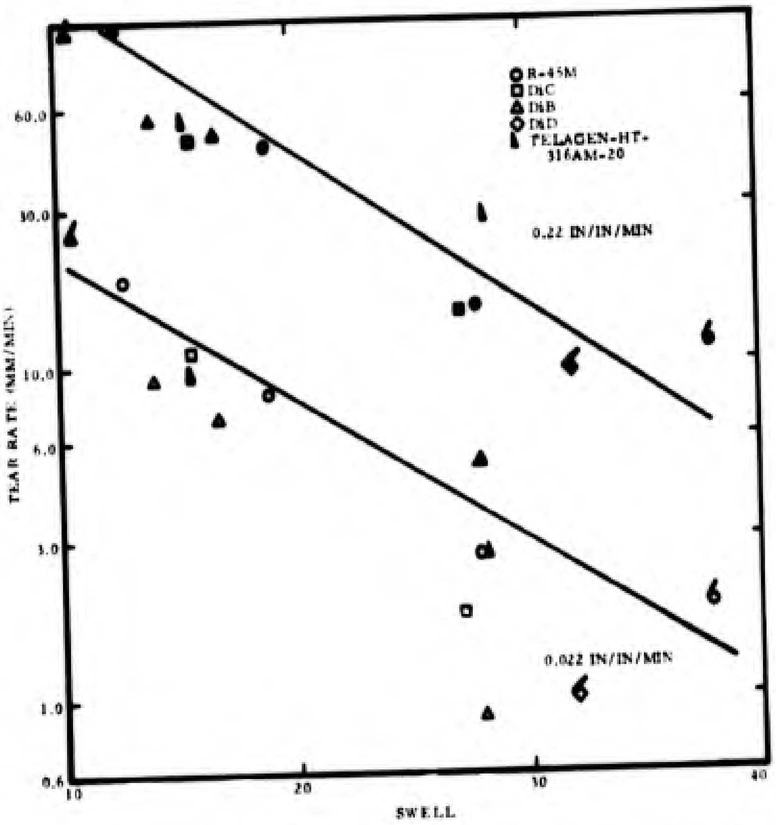

Figure 18 Tear Rate at 70°F (0.16 inch initial cut) (Flagged symbols: propellant used in analog motors)

d. Temperature Cycling of Analog Motors

As a more definitive test of propellant mechanical capability, analog motors were prepared in duplicate from 1500 gram mixes, using R-45M, DiB, and DiD. The standard 84 percent solids formulation (Table IX) was employed with an NCO/OH ratio of approximately 0.8, the aim being a comparison of temperature cycling capability of propellants having approximately equivalent uniaxial properties at 70°F. The DiB propellant proved to be very hard, presumably due to a weigh-out error, and therefore motors were also prepared using the DiD fraction. Uniaxial tensile and biaxial tear properties were also measured upon the same propellant batches (flagged symbols in Figures 12-18).

Propellant was cast into six-inch long by two-inch I. D. steel tubes containing a 0.38-inch O. D. steel cyclindrical mandrel. After a ten day cure at 140°F the mandrel was pulled and X-rays taken. Cycling was conducted in twenty-four hour cycles, eight hours in a 160°F box and sixteen hours in the cold (-21, -40, -60, -80°F) box. At each cold and hot cycle the inner bore diameter was measured with a strain gage; after each three cycles, X-rays were taken.

Table XI summarizes the cycling results for duplicate motors of each formulation. The R-45M and DiD motors all developed bore cracks sometime during the three cycles to -80°F. The DiB motors were both cracked after cooling to ambient from the cure temperature. A "Cumulative Strain" was calculated from the sum of the products of maximum strain at a given low temperature and number of cycles to that temperature; this is equivalent to the total strain employed by Aerojet as a measure of propellant cycling capability (Ref. 6).

As shown in Table XII the available parameters in general are qualitatively consistent with the analog motor cycling behavior. The data are too limited, however, to permit any quantitative conclusions or to select any one propellant parameter as a critical index of cycling capability. One possible exception to these statements is the negative correlation between cycling behavior for DiD and R-45M and their low temperature uniaxial strains (see Figure 13 for -65°F strain comparison).

Thus an overall conclusion of the program is that the low molecular weight difunctional fractions can be formulated to yield propellant which is apparently equivalent in effective mechanical performance to propellant made with R-45M itself. It is possible that this is a reflection of the fact that these low molecular weight species constitute such a major portion of the R-45M.

e. Effect of Prepolymer upon Propellant/Binder Cure

The propellant studies described in the preceding sections demonstrated that at least partial cure was obtained at NCO/OH ratios well below one when using the essentially difunctional R-45M fractions (DiB, DiC, DiD). It was also discovered that addition of small quantities of the trifunctional fractions, TriB or TriC, inhibited propellant cure. Table XIII

TABLE XI

ANALOG MOTOR CYCLING DATA(1)

System	Temperature Range	No. Cycles(2)	Maximum Strain(3)	Failure(4)	Cumulative Strain(5)
R-45M	+140°F—75°F(6)	1	7		
	+140°F—-21°F	3	17.7		
	+156°F—-21°F	3	21.5		
	+156°F—-43°F	3	23.0		
	+158°F—-40°F	3	21.3		
	+160°F—-60°F	3	24.8		
	+160°F—-80°F	3	27.4	✓	352-407
DiD	As above		7		
			22.3		
			21.1		
			24.2		
			22.5		
			21.8		
			29.0	✓	365-423
DiB	+140°F—75°F	1	7	✓	7

---

(1) Duplicate motors

(2) 24-Hour cycle except for first cool-down from cure.

(3) Measured by insertion of strain gage to middle of motor. Strain difference between hot and cold conditions.

(4) Cracking by X-ray, which were obtained initially and every third cycle thereafter.

(5) Sum of product of No. Cycles x Maximum Strains ($\Sigma N \cdot \epsilon$). For R-45M and DiD the indicated range is from the end of the first -80°F cycle to the end of the third -80°F cycle.

(6) Cool down from cure.

TABLE XII

CORRELATION OF PROPELLANT MECHANICAL PROPERTIES WITH TEMPERATURE CYCLING BEHAVIOR

Test Method	Parameter	System R-45M	 DiD	 DiB
1. Analog Motor Temperature Cycling	Maximum strain (%)	27	29	7
	Cumulative strain (%)	352-407	365-423	7
2. Uniaxial Tensile				
a. 70°F	Initial modulus, E_o (psi)	490	410	1900
	ϵ_m (%)	39	57	8.5
b. -65°F	Initial modulus, E_o (psi)	8200	8400	12,000
	ϵ_m (%)	10.5	9	9.5
3. Tear Propagation[1]				
a. 70°F	ϵ_o (%)	15	17	4.8
	σ_o (psi)	33	33	92
	"Tear Energy" $\epsilon_o \times \sigma_o/100$ (psi)	5.0	5.7	4.4
	Rate (mm/min)	2	1	25
b. -65°F	ϵ_o (%)	9.4	11.1	4.9
	σ_o (psi)	67	93	140
	"Tear Energy" $\epsilon_o \times \sigma_o/100$ (psi)	6.4	10.8	7.2
	Rate (mm/min)	1	----	0.6-2(?)

---

(1) At 0.022 in/in/min.

TABLE XIII

EFFECT OF PREPOLYMER UPON PROPELLANT/BINDER CURE

Prepolymer	NCO/OH[1]	Prepolymer Di/Tri[1]	Rex Hardness[2] (Days at 140°F)[3]								
			3	4	5	6	7	8	9	10	15
Gumstock											
DiA/DDI	0.8	----	0	0	3/--	4/--					
	1.0	----	17/13	21/16	25/19	27/21	29/--	28/25	29/29		
DiB/DDI	0.8		3/--	3/3	4/1	3/1					
	0.9		6/--	7/5	9/5	9/5					
	1.0		15/--	17/11	17/13	18/15					
	1.1		21/--	21/17	23/20	22/19					
	0.8					0/0					
DiB/TriB/DDI	0.7	0.8/0.2						0/0			
	0.8	0.8/0.2						0/0			
	1.0	0.8/0.2	22/13				21/20			25/22	
DiB/TriB/TDI	0.8	0.8/0.2								0/0	
DiB/TriC/DDI	0.7	0.8/0.2			0			0			0
	0.7	0.7/0.3			0			0			0
	0.8	0.9/0.1			0			0			0
	0.8	0.8/0.2			0			0			0
	0.8	0.7/0.3			1/0			6/6			6/6
DiB/TriB/TDI/TPMTI (0.8/0.2/0.6/0.2)[1]	0.8	0.8/0.2	0							2/2	
DiB/TDI/TPMTI (1.0/0.6/0.2)	0.8	----	0							0	
DiB/TriB/DDI/HT (0.8/0.2/0.96/0.2)	0.8	0.8/0.2	0							0	
DiB/DDI/HT (1.0/0.96/0.2)	0.8	----	0							0	
TriB/DDI	0.8	----	26/20							32/24	
Telagen[4]/TriC/DDI	0.7	0.8/0.2		5/1				3/3			3/3
	0.8	0.8/0.2		28/18				25/19			46/15
Propellant											
DiB/DDI	0.8	----	Cured in 10 days								
DiC/DDI	0.8	----									
DiD/DDI	0.8	----									
Telagen[4]/DDI	0.8	----									
DiC/TriB/DDI	0.7	0.9/0.1	Too soft to measure after 20 days								
	0.7	0.8/0.2									
	0.7	0.7/0.3									
	0.8	0.9/0.1									

---

(1) Equivalents ratio

(2) Initial over 15 second reading.

(3) Kept under N_2

(4) Telagen-HT-316AM-20

collects the results of rather scattered experiments which bear upon the influence of various prepolymer/curative compositions upon cure.

While the data are by no means fully consistent, it seems clear that the high molecular weight trifunctional species in R-45M do tend to inhibit cure unless the NCO/OH or tri/di ratio is relatively high. This is in distinct contrast to the effect of trifunctional R-45M fractions upon the Telagen-HT fraction. The following speculative explanation of these findings is offered:

(1) The low molecular weight (< 2000) difunctional R-45M fractions contain small quantities of low molecular weight trifunctional species, which function as the crosslinker in diisocyanate/difunctional fraction systems - and may in fact constitute the main crosslinking principle in R-45M itself.

(2) The high molecular weight trifunctional species are relatively ineffective as crosslinkers. This is due partly to rate effects arising from high molecular weight and low hydroxyl concentration (see Figure 11) relative to the low molecular weight species. In addition it is suspected that the trifunctional species may possess one hydroxyl that is non-allylic and/or secondary, thus less reactive.

- NMR measurements by ARCO demonstrate that R-45M hydroxyls are at least 95 percent primary.[4] This does not rule out the possibility that some five percent of the hydroxyls are secondary. Based upon a trifunctional species content of approximately 50 weight percent (~30 equivalent percent), a major fraction of the third hydroxyls present in trifunctional species might therefore be secondary.

(3) At low NCO/OH, substitution of some trifunctional fraction for difunctional both slows the cure process and inhibits final cure due to (a) a lower total OH concentration, (b) a lowering of effective crosslinker concentration, and (c) a consumption of NCO by rapid reaction with primary allylic OH, leaving only a very low NCO concentration for the latter crosslinking process.

(4) This inhibition does not occur with the difunctional Telagen fraction because (a) it contains more trifunctional species than do the R-45M difunctional fractions, (b) its own hydroxyls are secondary and less reactive and thus do not overpower the crosslinker in the R-45M fraction, and (c) no concentration reduction occurs since its equivalent weight (~4000/2) is nearly identical with that of the R-45M trifunctional fractions (~6000/3).

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[4] Private communication, P.W. Ryan, ARCO Chemical Co.

An entirely different mechanism may also contribute to the crosslinking of the difunctional R-45M fractions, namely the free radical processes discussed by UTC (Ref. 9). It is difficult to see, however, how the high molecular weight trifunctional fractions could inhibit such processes.

SECTION IV

SUMMARY OF RESULTS AND CONCLUSIONS

1. RESULTS

The program has produced the following results:

(1) R-45M Fractionation

- Even very short term contact of R-45M with activated silica gel results in irreversible and non-reproducible structural changes in the prepolymer.
- Both GPC and fractional precipitation provide acceptable means of fractionating R-45M on a molecular weight basis, and thus on a functionality basis since functionality increases with greater molecular weight. R-45M appears to contain 30-50 weight percent (~60 mole percent) difunctional species, the remainder being primarily trifunctional but probably with small amounts of mono and tetrafunctional material also present.
- Fractional precipitation yields a prepolymer fraction which is at least 95 mole percent difunctional and may contain small amounts of both mono and trifunctional species. An approximately trifunctional fraction has also been isolated.
- The difunctional fraction has a molecular weight below 2000 while the trifunctional fraction molecular weight is 6000. The difunctional fraction molecular weight is well below the level conventionally regarded as desirable for propellant binders (<2000 versus >4000).

(2) R-45M/Isocyanate Cure

- Difunctional fractions (M < 2000) cure with DDI at NCO/OH <1. The presence of trifunctional R-45M fractions (M = 6000) inhibits that cure but does not interfere with cure when used with a Telagen-HT "difunctional" fraction.
- Cure of the difunctional R-45M fractions and of R-45M itself is believed to be accomplished by a small quantity of low molecular weight trifunctional species.
- Cure inhibition by the high molecular weight trifunctional fractions is due to the effectively lower reaction rate of the latter. This in turn is due to concentration effects plus the possible presence of some secondary hydroxyls on the trifunctional molecules.

(3) Effect of Fractions Upon Propellant Mechanical Behavior

- The Telagen fraction (M~4000) offers no advantages over R-45M in terms of uniaxial tensile behavior. It's tear resistance is inferior to that of the R-45M fractions.
- The low M difunctional fractions result in decreased uniaxial strain capability and higher modulus at -65°F, presumably due to greater secondary intermolecular bonding.
- On the basis of tear energy and tear rate criteria, the low M fractions are at least as good as R-45M itself at 70°F. Conclusions for the -65°F behavior are not clear cut.
- The low M difunctional fractions can be formulated in propellant simultaneously possessing temperature cycling behavior and high temperature tensile properties which are at least as good as those with R-45M itself.

2. CONCLUSIONS AND PRACTICAL IMPLICATIONS

Propellant application experience shows that the R-45M HTPB prepolymer affords desirably low mix viscosity and enables attainment of very high solids loading. The propellants have good ambient and high temperature uniaxial tensile properties, but are deficient in low temperature uniaxial strain capability. Comparatively high cure rates, even in the absence of catalysts, may pose potlife problems.

The disadvantages can be associated with the material's high content of comparatively low molecular weight material. A high content of low molecular weight material, in combination with the reactive nature of the allylic end groups, enhances NCO/OH reaction rates, thus tends to shorten potlife. It also tends to increase the number of secondary (hydrogen) bonds and thus may have an adverse effect upon low temperature mechanical properties.

Changes in the manufacturing process to effect a shift in molecular weight distribution toward higher values without a commensurate increase in the product's functionality can be expected to afford a better binder material, especially if it could be accomplished without excessive increase in the material's viscosity.

Areas that remain clouded are (1) definition of parameters which truly and distinctively describe the temperature cycling capability of propellant and (2) the effect of prepolymer structure upon those properties. It is evident that these areas require further work.

APPENDIX A

SILICA GEL FRACTIONATION OF R-45M

1. ELUTION CHROMATOGRAPHY

In their functionality program Esso fractionated three different lots of R-45M and a single lot of R-15M on a one-gram scale by elution from silica gel with methylene chloride followed by methylene chloride/acetonitrile mixtures (Ref. 4). In general, two discrete peaks were obtained which consisted essentially of difunctional material in the first peak and trifunctional in the second. Characterization of the fractions from all three R-45M lots consistently indicated that difunctional content was approximately 40-45 weight percent with a nominal molecular weight of 4000, the remainder being trifunctional with a nominal molecular weight of 2000. Results for the single R-15M lot were approximately the same.

On this basis the present program began by similarly fractionating one of the same R-45M lots (805201) using 4-5 inch diameter columns with 60-gram polymer loadings. Several composite fractions were prepared in over 100-gram quantity by combining analogous cuts from several such silica gel elution runs. Figure 19 presents typical elution profiles in which the cuts I and III were expected to approximate di and trifunctional fractions, respectively. The first cuts (I) were eluted using the initial solvent, CH_2Cl_2, while the third cuts (III) were eluted using CH_2Cl_2/CH_3CN mixtures. Figure 20 schematically summarizes the preparation of the various composite fractions.

Each of the four composite "difunctional" fractions subsequently was refractionated by one or more procedures either to establish their molecular weight (M) and functionality (f_n) composition or to achieve further purification. Figure 21, for example, is the silica gel elution profile (analytical scale) of fraction 18-1; the data for the subfractions are given in Table XIV (Item (c)).[5] Figures 22-25 illustrate the various post treatments.

The following comments summarize the silica gel elution results:

- None of the composite fractions was regarded as suitable for the program without further purification.
  - Functionality data for 18-1 are not entirely consistent but its effective functionality (f_w) is high and its reaction rate abnormally fast (Items (b) and (c) of Table XIV and Figure 22).
  - Fraction 17-1 contains major amounts of very high functionality species (Items (d) and (e) of Table XIV and Figure 23), consistent with its high viscosity. It has also suffered

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[5] Details of the various characterization methods are given in Appendix B.

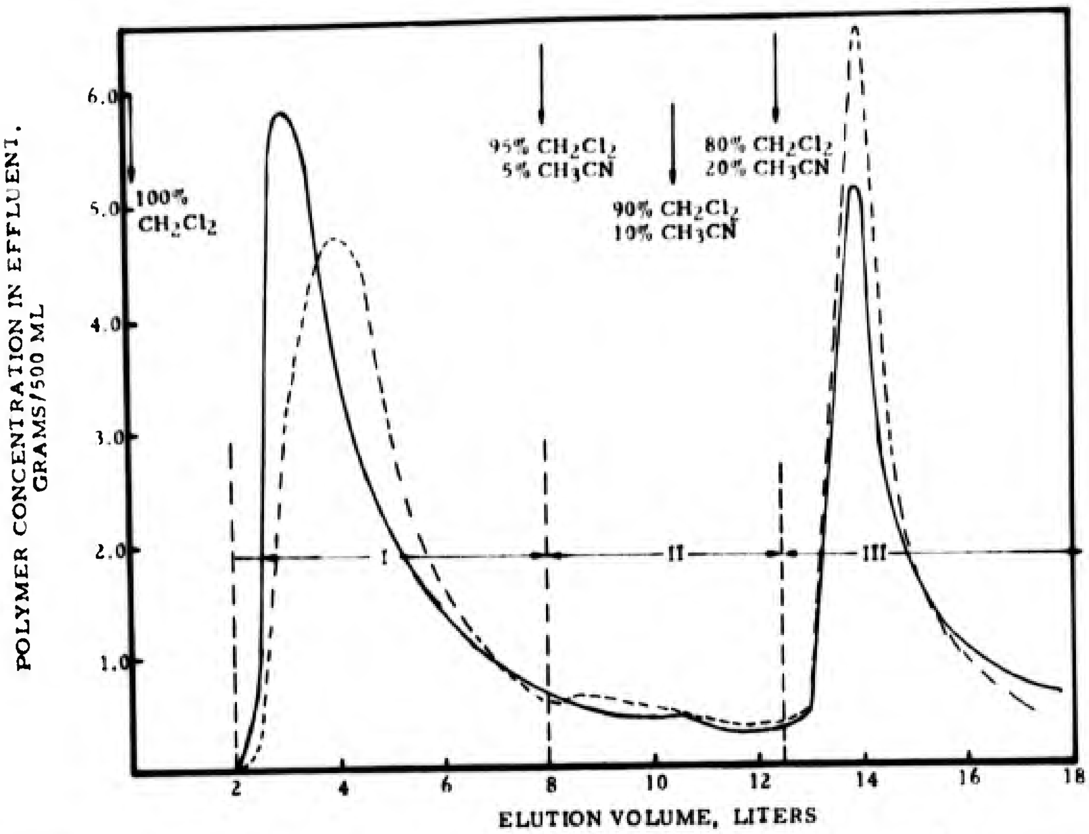


Figure 19 Elution Profile for R-45M, Lot 805201, by Stepwise Elution from Silica Gel (Silica gel/polymer ratio: 38/1. Solid line: Run 496-3, column diameter = 10 cm, Cut I - 47.8 wt %. Dotted line: Run 496-4, column diameter = 12.5 cm, Cut I = 44.5 wt %.)

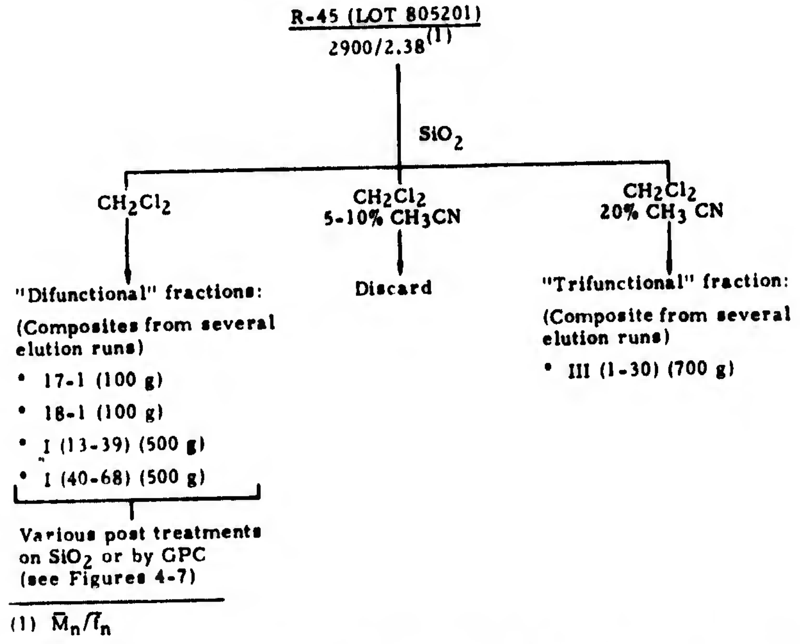


Figure 20 Schematic of Silica Gel Preparation of Composite R-45M Fractions

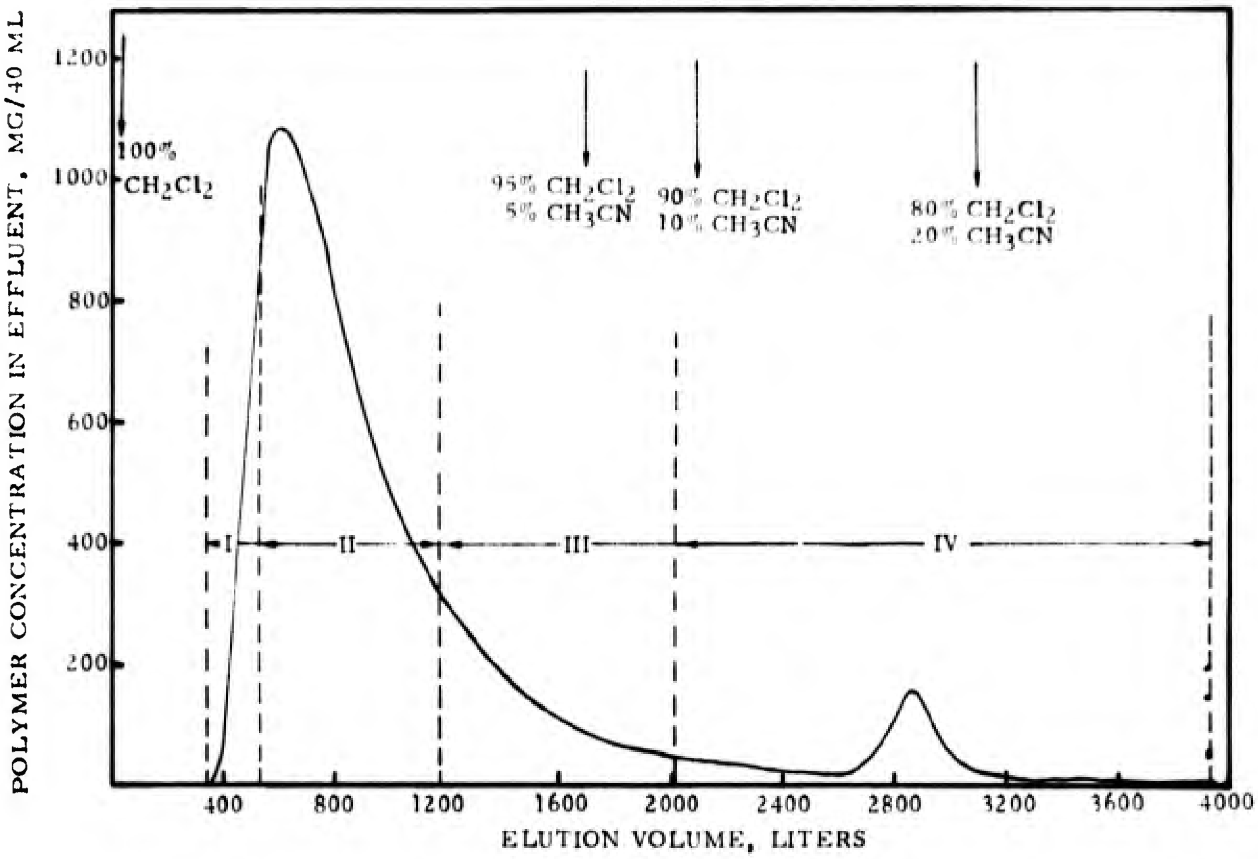


Figure 21 Elution Profile For R-45M Fraction 496-18-I (from 5" column) by Stepwise Elution from Silica Gel (Silica gel/polymer ratio: 56/1, Run 496-31)

TABLE XIV

ANALYTICAL DATA SUMMARY: SILICA GEL FRACTIONATION

Sample	Amount						Relative Reaction Rate$^{(3)}$	Relative Viscosity$^{(4)}$	Infrared$^{(5)}$	
	Wt (g)	%	$\bar{M}_n$	Eq Wt	$f_n^{(1)}$	$f_w^{(2)}$			Relative Association	Relative Carbonyl
(a) R-45M (805201)			2900	1220	2.38	2.6	1	42	4	1
(b) 18-1$^{(6)}$	>100		4650	2455	1.90	2.6	50	76	2	4
(c) Silica gel elution of 18-1$^{(7)}$										
-I		15	6300	2710	2.32					
-II		60	4800	2430	1.98					
-III		12	3600	1680	2.14					
-IV		7	3200	1360	2.35					
(d) 17-1$^{(6)}$	>100		4250	1870	2.34	3.1	4	296	3	5
(e) GPC fractionation of 17-1$^{(8)}$										
-I		28	7670	1570	4.90				3	5
-II		49	4510	1660	2.73				3	5
-III		8	2700	1240	2.17				3	>5
-IV		7	2370	1210	1.97				>3	>5
-V		2								
(f) I (13-39)$^{(6)}$	500		4950	2000	2.48				2	2
(g) Silica gel elution of I (13-39)$^{(7)}$										
-I		22	5900	2670	2.21		1		2	2
-II		47	5400	2325	2.32		1		2	2
-III		9	4100	1905	2.15		1		2	2
-IV		13	3100	1480	2.09		1		3	2
-V		9	2600	1215	2.14		1		3	5
(h) Rechromatograph (silica gel) I (13-39). First peak into two cuts$^{(7)}$										
-Ia		39	6000	2270	2.64					
-Ib		13	4800	1920	2.50					
(i) Rechromatograph (silica gel) I (13-39) using 70/30 CCl_4/CH_2Cl_2 in initial CCl_4. First cut (I) in hot solvent front										
-I		69	8000	1910	4.2					5
-III		22	3540	1600	2.2					
(j) I (40-68)$^{(6)}$	500		5600	2112	2.6	~2.6	1		2	2
(k) Rechromatograph (silica gel) I (40-68)$^{(7)}$										
-I'		78	6250	2390	2.61					
(l) Rechromatograph (silica gel) above fraction I$^{(7)}$										
-I''		91	5400	2208	2.45					
(m) III (1-30)$^{(9)}$	700		1900	705	2.70	~2.7	1		5	3

---

(1) M_n/Eq. Wt

(2) Stockmayer equation

(3) Relative time to 50% NCO conversion. DDI at ambient without catalyst.

(4) Brookfield with B spindle at ambient.

(5) Relative Association: qualitative from IR at ~3.0/2.7μ. Higher numbers reprsent more association. Relative carbonyl: qualitative from IR at 5.9/6.0μ. Higher numbers represent more carbonyl.

(6) Composite fraction from silica gel elution of Lot 805201. First cut using CH_2Cl_2 in initial CH_2Cl_2 column solvent. See Figure 19.

(7) Initial column solvent CH_2Cl_2. First cut CH_2Cl_2 with subsequent enrichment with CH_3CN. See Figure 21.

(8) Styragel packing. $CHCl_3$ solvent. 1% Injection concentration. Ten injections total.

(9) Composite fraction from silica gel elution of Lot 805201. Third cut using 80/20 CH_2Cl_2/CH_3CN. See Figure 19.

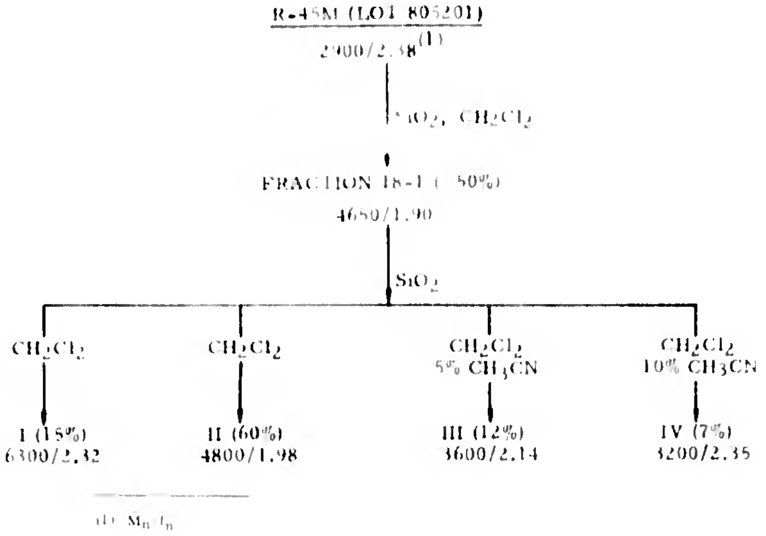


Figure 22 Preparation and Rechromatography of Silica Gel Fraction 18-1

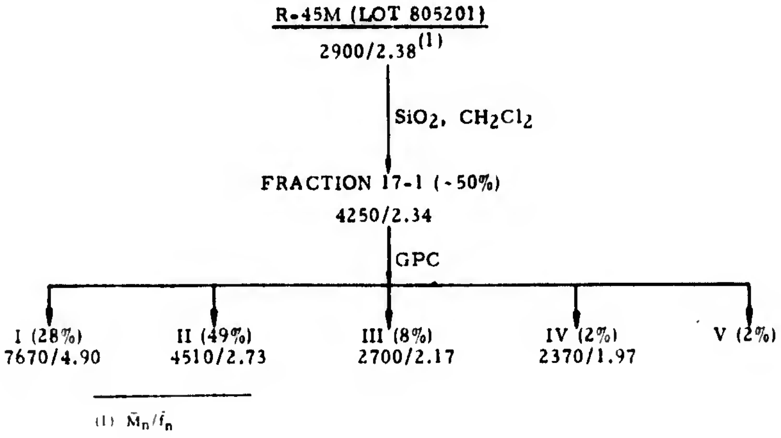
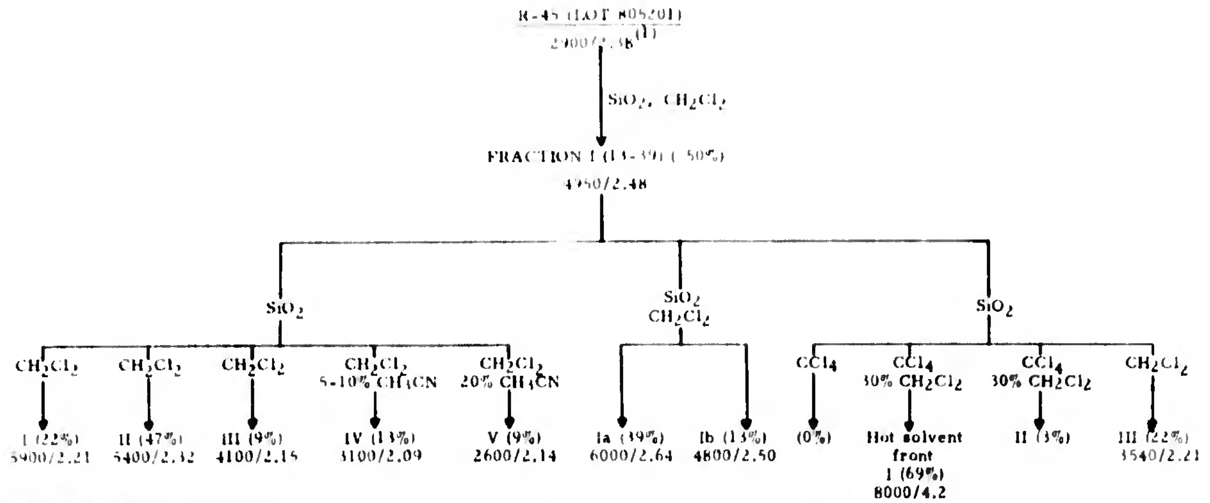
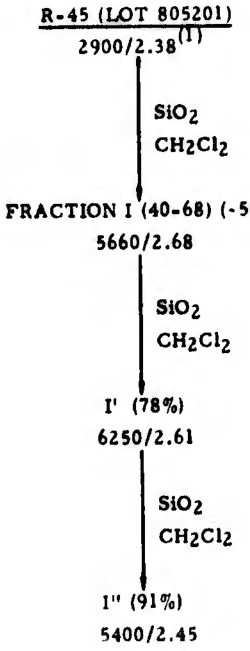


Figure 23 Preparation and Rechromatography of Silica Gel Fraction 17-1



(1) $\bar{M}_n/\bar{f}_n$

Figure 24 Preparation and Rechromatography of Silica Gel Fraction I (13-39)



(1) $\bar{M}_n/\bar{f}_n$

Figure 25 Preparation and Rechromatography of Silica Gel Fraction I (40-68) some degree of oxidation, as evidenced by carbonyl absorption (5.9-6.0 micron) in infrared. (Compare Figures 26, 27, 28)

  - I (13-39) and I (40-68) both have functionalities well above 2 (Items (f) and (j) of Table XIV).
  - III (1-39) must contain significant quantities of difunctional material and hence is not suitable as a trifunctional sample (Item (m) of Table XIV).

- Rechromatographing the cut I fractions using silica gel does not satisfactorily improve their functionality.
  - The first elution peak produced upon rechromatographing I (13-39) was cut into two portions whose f_n values were 2.64 and 2.50 (Item (h) of Table XIV and Figure 24).
  - The first elution peak produced upon rechromatographing I (40-68) possessed an f_n of 2.6 and subsequent rechromatographing of that first peak yielded another first peak whose f_n was 2.45 (Items (k) and (l) of Table XIV and Figure 25).

- Lengthy contact (hours) with silica gel may be causing structural changes in R-45 as indicated by:
  - General increase in carbonyl content.
  - Absence of distinct functionality pattern upon silica gel refractionation.
  - Material having high M, f, and carbonyl content was produced in the hot solvent front present when eluting with 70/30 CCl_4/CH_2Cl_2 from column originally containing only CCl_4 (Item (i) of Table XIV and Figure 24).

2. BATCH EXTRACTION OF R-45M FROM SILICA GEL

In view of the indications above that the lengthy contact times with silica gel may be causing prepolymer structure changes, another method has been briefly explored which employs much shorter exposure times. Specifically, this method involves the following steps.

- Silica gel is stirred with a portion of the solvent before any polymer is added to the gel. This allows for dissipation of any heat of adsorption in the absence of the polymer.

- The polymer is subsequently added in solution to the silica gel slurry. The type of solvent will affect the amount of polymer that is sorbed by the gel.

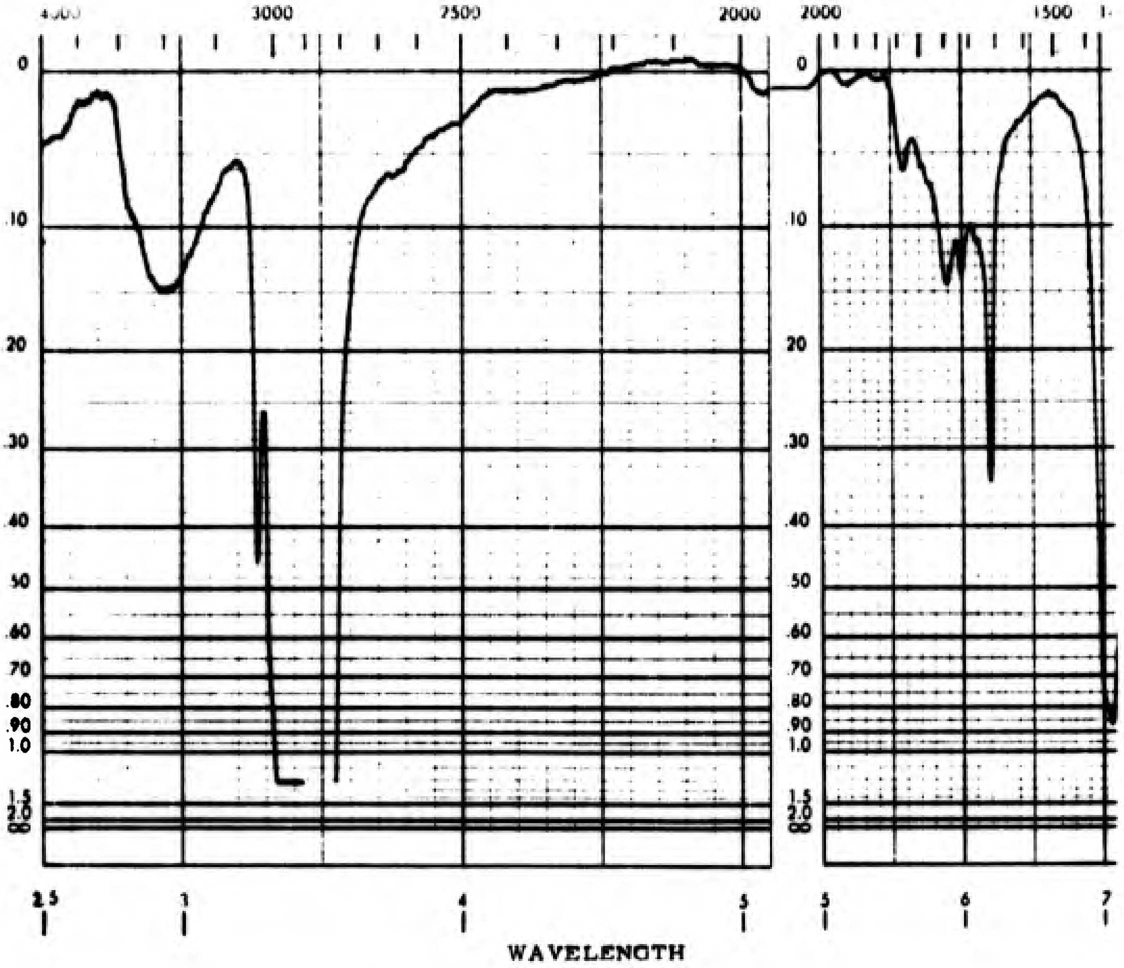


Figure 26 IR Spectrum of 496-17-I

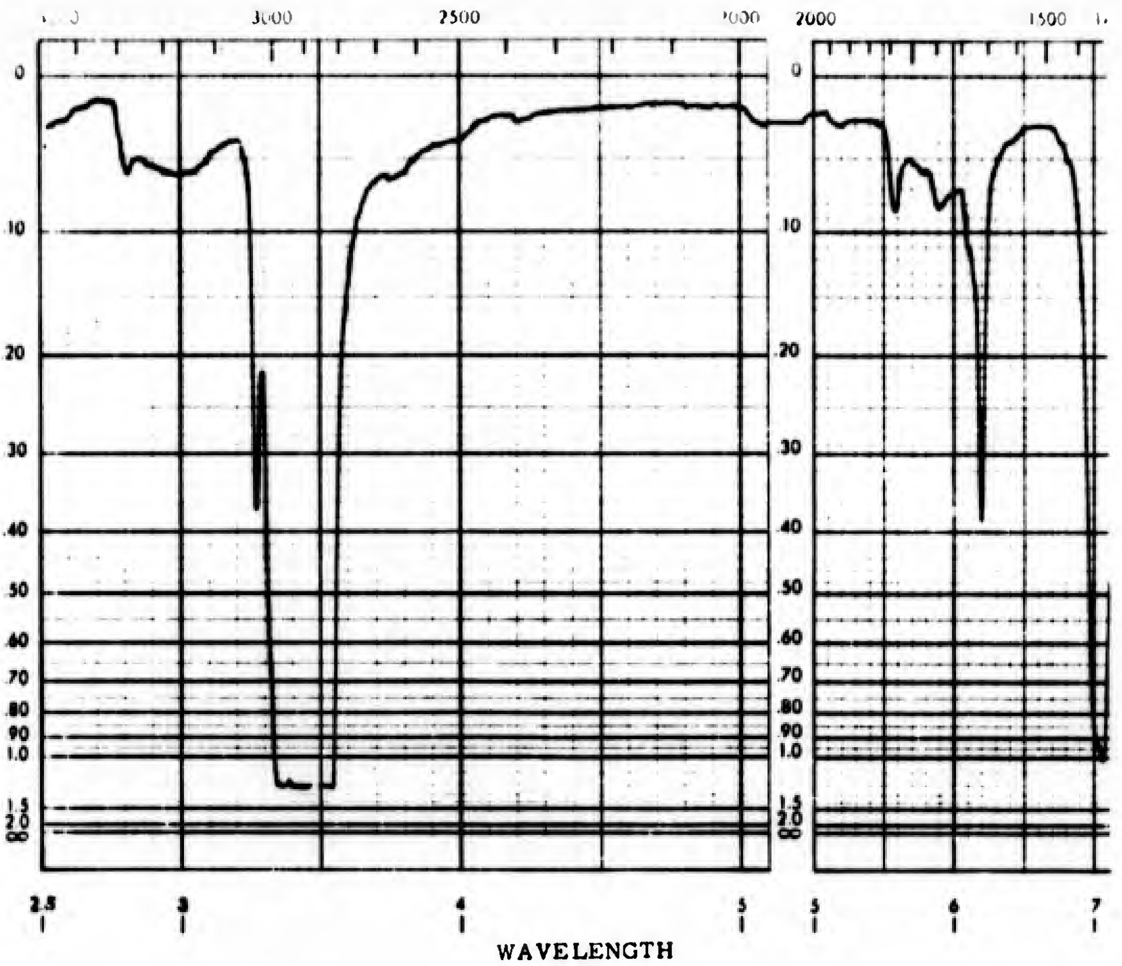


Figure 27 IR Spectrum of 496-18-I

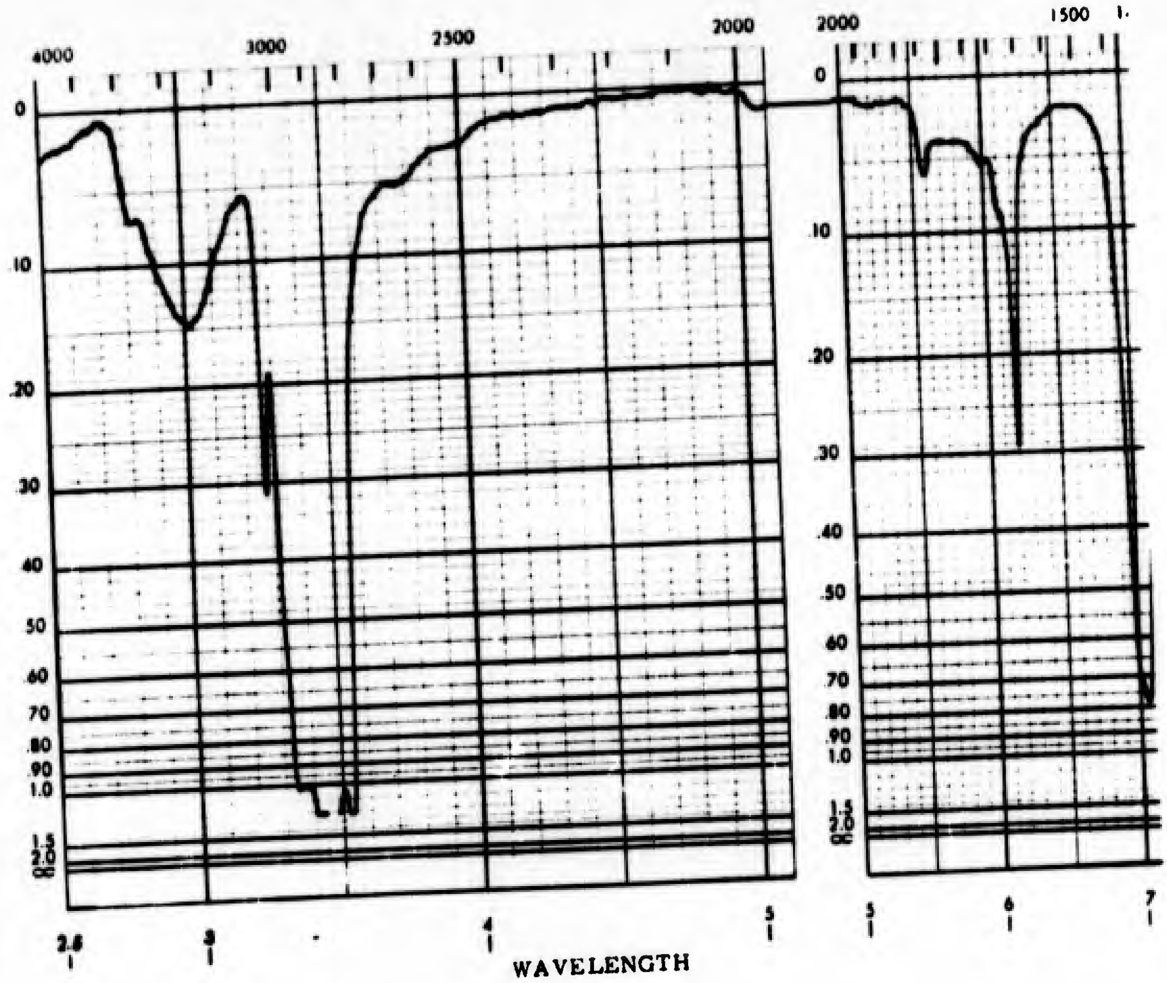


Figure 28 IR Spectrum of R-45M, Lot 805201

- The silica gel-polymer-solvent system is stirred for fifteen minutes and the extract removed by rapid filtration.

- Additional solvent is added to the gel, stirred, and the extract again removed and added to the original filtrate.

Figure 29 shows the amount of polymer unsorbed as a function of the composition of the solvent and at two different silica gel/polymer ratios (Lot 805201). The plot shows an apparent minimum at the 20/80 CH_2Cl_2/ CCl_4 solvent composition. Analysis data for some of the extracted fractions are given below:

Silica Gel/ Polymer Ratio	Solvent	Unsorbed Polymer Wt %	$(M_n)_o$	Eq. Wt	Functionality
10/1	40/60 CCl_4/CH_2Cl_2	31.1	5600	2010	2.79
10/1	100% CH_2Cl_2	31.6	5500	1900	2.89
10/1	100% CCl_4	25.8	7400	----	----
20/1	100% CCl_4	12.2	9800	----	----

The high functionalities (2.79 and 2.89) of the first extracts at the 10/1 silica gel/polymer ratios are unexpected in view of the short contact time (15 minutes).

A second lot (008281) of R-45M was also examined briefly. Twenty cuts were obtained by the procedure illustrated in Figure 30. These were combined into seven fractions with the results shown in Table XV.

Thus it appears that the silica gel sorption fractionation method offers no improvement over the silica gel elution procedure in terms of producing fractions of distinctive functionality.

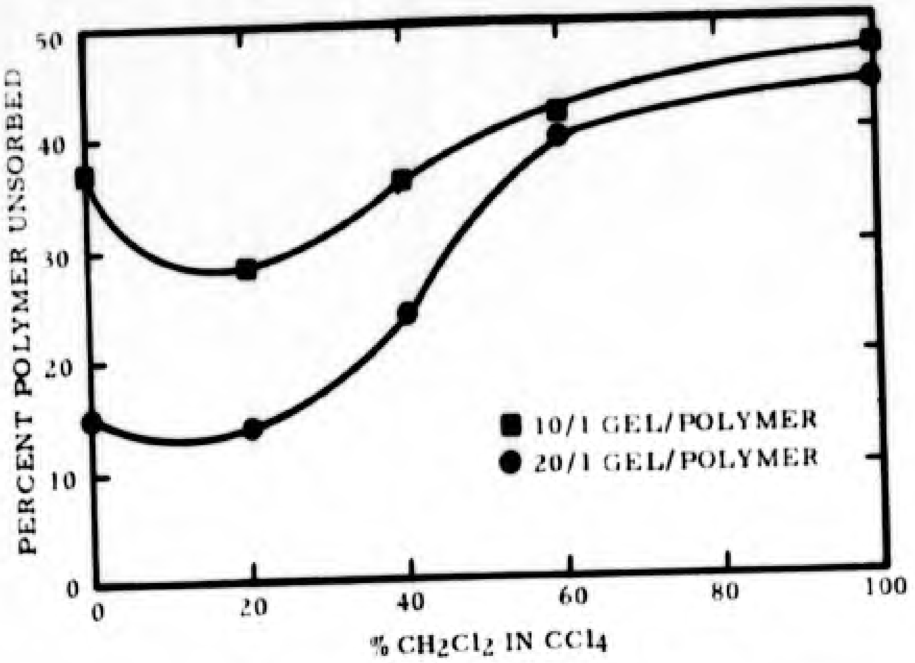


Figure 29 Weight Percent Polymer Extracted as a Function of CH_2Cl_2 Content in the Extracting Solvent

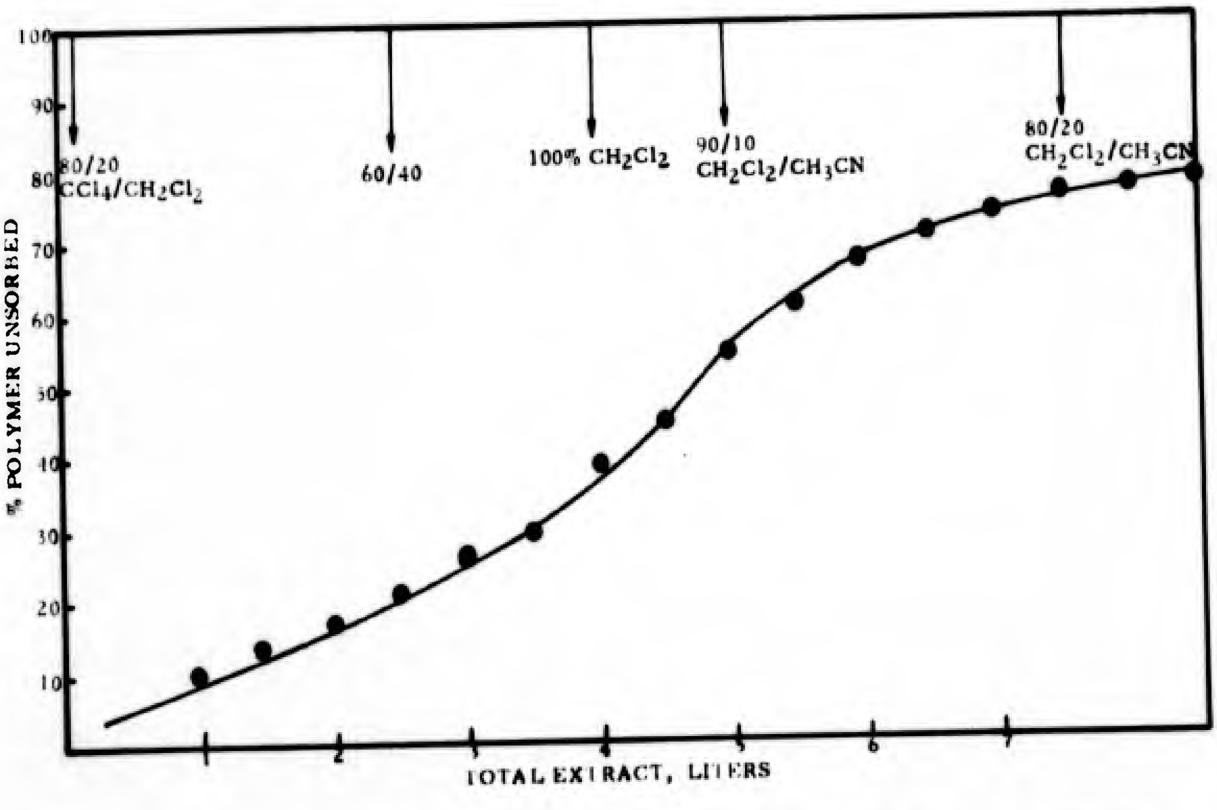


Figure 30 Accumulated Sorption Profile of R-45M Prepolymer from Silica Gel

TABLE XV

CONTINUOUS SORPTION FRACTIONATION (LOT 008281)

Fraction	Wt %	$\bar{M}_n$	Eq. Wt	f_n
1	7.7	8200	3415	2.40
2	11.0	7400	3380	2.17
3	10.1	5600	2212	2.53
4	13.0	4700	2028	2.32
5	11.9	4100	1540	2.66
6	15.5	2600	1053	2.47
7	15.0	2400	658	3.65

APPENDIX B

1. ANALYTICAL METHODS

a. Molecular Weight

At LPC, number average molecular weights ($\bar{M}_n$) were measured using the Hewlett Packard Vapor Phase Osmometer at 37°C in 1,2-dichloroethane. Measurements were performed at three to four concentrations (below 60 g/l) and $\bar{M}_n$ calculated from the zero concentration intercept of 1/M apparent. The solvent calibration constant was determined with benzil for the molecular range below 1000 and with polypropylene glycol, molecular weight 3900, for higher values. Figure 31 gives a representative concentration plot.

Procedures at Esso and ARCO were similar to the above with the following exceptions:

- Esso employed chloroform as solvent and benzil as the sole calibration material.
- ARCO employed ethyl acetate as solvent and pentaerythritol tetralaurate as the sole calibration material.

In general only one determination was performed at each laboratory and the accuracy of the $\bar{M}_n$ value is approximately ±5 percent.

b. Equivalent Weight

Equivalent weights were determined at Esso and LPC by reacting the polymer with excess p-toluenesulfonyl isocyanate in dilute chloroform solution (Ref. 4). Consumption of isocyanate is measured from infrared absorption at 2245 cm^{-1} after standing (sealed from air) overnight. Measurements were performed in duplicate with an average deviation of less than ±5 percent.

At ARCO, equivalent weights were determined by the conventional acetylation method or by IR.

c. Number Average Functionality

Number average functionalities ($\bar{f}_n$) are calculated from the ratio of $\bar{M}_n$ to equivalent weight and are therefore accurate to approximately ±5 percent.

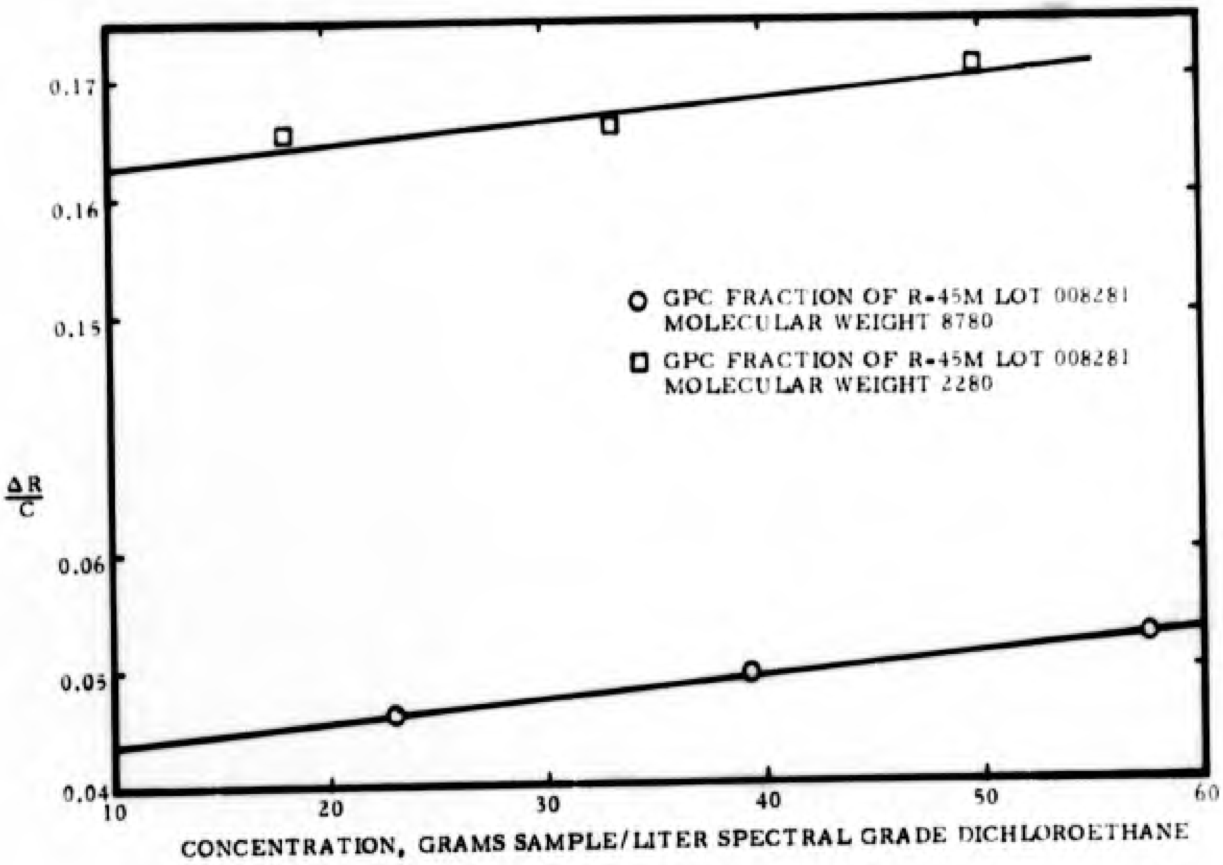


Figure 31 Typical Determinations of Molecular Weight by Vapor Phase Osmometry

d. Weight Average ("Effective") Functionality ($\bar{f}_w$)

These were calculated from Stockmayer's equation (Ref. 7) for the degree of reaction, P_{gel}, at incipient gelation

$$\left(P^2_{NCO}\right)_{gel} \times r = \frac{1}{\left[(\bar{f}_w)_{NCO} - 1\right]\left[(\bar{f}_w)_{OH} - 1\right]}$$

where r is the equivalent ratio of NCO to OH and the $\bar{f}_w$'s are the weight average functionalities. Although this equation assumes equal reactivity of functional groups and negligible side reactions, Strecker and French have demonstrated that it can provide reasonable estimates of CTPB and HTPB weight average, or effective, functionalities (Ref. 10).

Strecker and French established the point of incipient gelation $(P_{NCO})_{gel}$ by monitoring both infrared absorption at 2259 cm^{-1} relative to that of the C-H band at 2840 cm^{-1} and bulk viscosity. We have found it more conventient, particularly with limited quantities, to determine incipient gelation by establishing the point at which insolubility first appears. In either case the flatness of the conversion/time curves in this region minimizes errors in $(P_{NCO})_{gel}$. However, the uncertainty in $(\bar{f}_w)_{OH}$ is probably no better than ± 0.05.

Figure 11 in the body of the report illustrates the procedure and results for the reaction with DDI. Figure 32 shows similar results for the reaction of R-45M (Lot 805201) with DDI and HMDI. Although DDI reacts somewhat more slowly, its degree of reaction, and hence the calculated R-45 functionality, are essentially in agreement with those using HMDI. As expected, the $\bar{f}_w$ is somewhat greater than the $\bar{f}_n$ value of approximately 2.3. Agreement between functionalities with DDI and HMDI indicates that these two diisocyanates are not homopolymerizing to greatly differing extents, if at all.

e. Sol/Gel and Swell

Sol/gel and degree of swell were determined simultaneously upon cured gumstock or propellant by extracting/swelling the material in toluene (solvent to sample ratio of 100:1). A total extraction time of 96 hours was employed, with solvent changed at 24 hour intervals during the initial 48 hours of extraction. Swell is calculated from the ratio of solvent taken up to gel content for material.

$$\text{Swell} = \frac{\text{Weight of Solvent}}{\text{Weight of Gel}}$$

Gel is determined from the ratio of weight for non-extractible binder (prepolymer + curative) to initial binder weight, corrections.

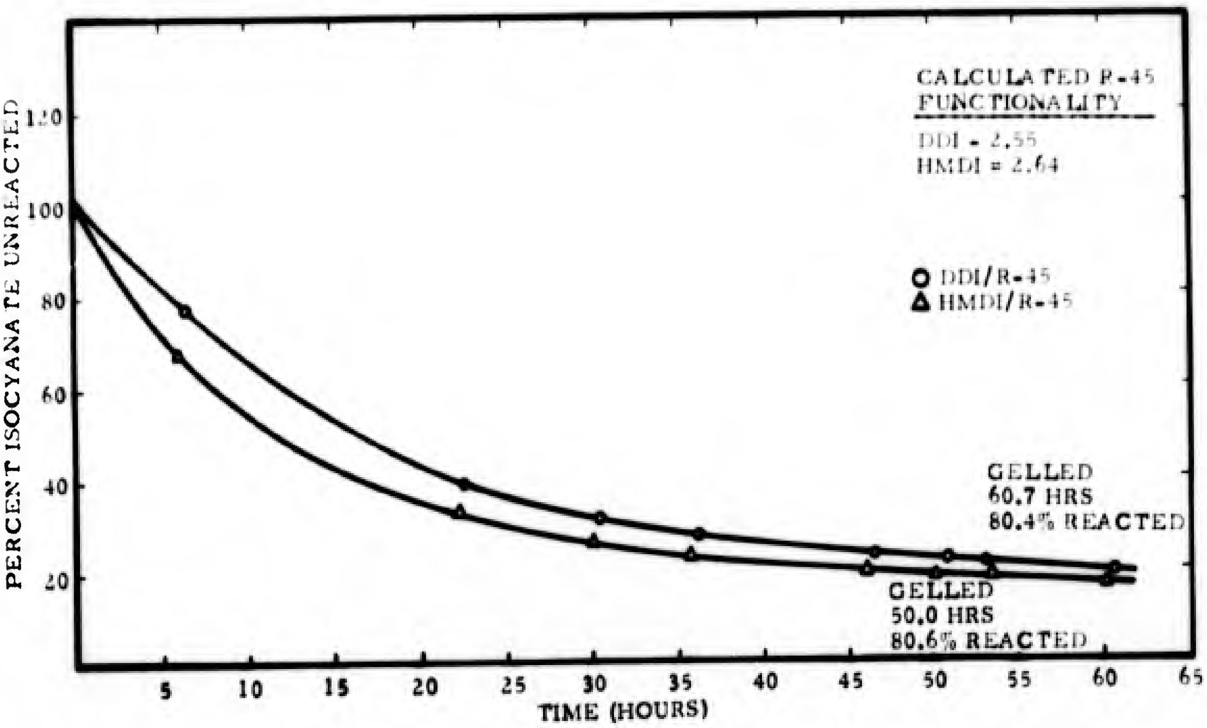


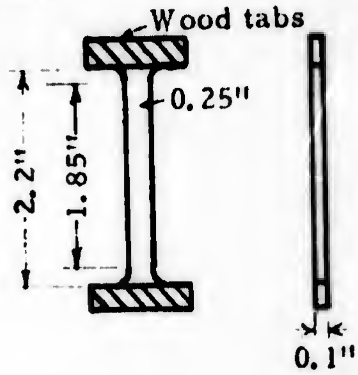
Figure 32 Reaction Profile for R-45M (Lot 805201) with DDI and HMDI

$$\% \text{ Gel} = \frac{\text{Weight of Insoluble Binder Gel}}{\text{Initial Weight of Binder}} \times 100$$

Sample size is approximately 0.5 gram of gumstock or 5 gram of propellant, and in either case the sample is chopped into pieces <1 cm per side before extraction.

2. MINITHIN TENSILE SPECIMENS

These are illustrated in the figure below and are prepared by stamping the propellant from 0.1-inch propellant sections (microtomed) and subsequently bonding to wood tabs.



A comparison of minithin and JANNAF tensile properties for R-45M propellant indicates very similar values, e.g.,

	-80°F		70°F	
	Minithin	JANNAF	Minithin	JANNAF
σ_m	540	620	102	129
ϵ_m	40	42	40	46
E_o	8900	9300	340	270

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11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
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Edwards, California

13. ABSTRACT

The R-45M hydroxyl terminated polybutadiene prepolymer ~~as produced by ARCO~~ is composed of material covering a range of molecular weights, and the different molecular weight fractions were suspected to vary in functionality. This program sought to scale-up the fractionation of the R-45M HTPB prepolymer so that fractions having more narrow molecular weight distribution besides being more strictly di- and trifunctional could be tested in propellants to determine related effects upon cure and mechanical properties.

Scale-up fractionation over silica gel was found to cause nonreproducible structural changes and thus was concluded to be impractical. Fractionation by solvent precipitation produced material having an average molecular weight of 2000 at average functionality of two, and trifunctional material of average molecular weight 6000.

Cure studies suggest that the 2000 molecular weight fraction still contains some low molecular weight trifunctional material that effects crosslinking, and the resulting propellant was found to have poor tensile properties at -65°F. However, tear resistance at 70°F was improved.

Temperature cycling capability of analog motors containing low molecular weight difunctional fractions was compared with those containing the parent R-45M. At approximately the same initial modulus at 70°F, the cycling behavior (-80°F to 160°F) of the two systems was not significantly different.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Functionality						
HTPB Prepolymer						
Molecular weight						
Mechanical properties						
Fractionation						
Cure						
Tear resistance						
Analog motor cycling						