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**Wyandotte**

**SYNTHESIS OF LOW TEMPERATURE  
OIL RESISTANT URETHANE  
ELASTOMERS**

QUARTERLY PROGRESS REPORT No. 3

1 April 1963

FOR

ROCK ISLAND ARSENAL  
ROCK ISLAND, ILLINOIS

CONTRACT No. DA-20-018-ORD-24883



**WYANDOTTE CHEMICALS CORPORATION  
WYANDOTTE, MICHIGAN**

# Wyandotte Chemicals Corporation

wyandotte • michigan

April 30, 1963

Subject: Quarterly Progress Report No. 3  
Contract No. DA 20-018-ORD-24883

Gentlemen:

This enclosed report is sent to you at the request of Non-Metallic Materials Section, Rock Island Arsenal Laboratories.

Any comment or correspondence concerning the material contained in this report should be directed to:

Commander  
Non-Metallic Materials Section  
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Rock Island, Illinois

Yours very truly,

WYANDOTTE CHEMICALS CORPORATION



S. L. Axelrood  
Polymer Research Department

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ARMY ORDNANCE CONTRACT NO. DA 20-018-ORD-24883

NON-METALLIC MATERIALS SECTION

ROCK ISLAND ARSENAL LABORATORIES

QUARTERLY PROGRESS REPORT NO. 3

COVERING PERIOD 1 JANUARY 1963 TO 31 MARCH 1963

SYNTHESIS OF LOW TEMPERATURE

OIL RESISTANT URETHANE ELASTOMERS

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WYANDOTTE CHEMICALS CORPORATION

WYANDOTTE, MICHIGAN

## FOREWORD

This report was prepared by the Polymer Research Department, Industrial Chemicals Division of Wyandotte Chemicals Corporation, Wyandotte, Michigan under Army Ordnance Contract No. DA-20-018-ORD-24863. This work is being technically administered under the direction of the Non-Metallic Materials Section of the Rock Island Arsenal Laboratories, Rock Island, Illinois with Messrs. R. Shaw and Z. Ossefort acting as Project Engineers.

The personnel of Wyandotte Chemicals Corporation assigned to this project are Messrs. S. Axelrod, Project Leader, and W. Lajiness under the general direction of Drs. E. J. Fujiwara and K. C. Frisch.

This report covers the period 1 January 1963 to 31 March 1963.

### ABSTRACT

Urethane and urethane-urea elastomers were prepared and their properties evaluated this third quarter. The low temperature flexibility specification was met for the first time by an elastomer prepared and tested this quarter (PR 1622-K, Table III). This elastomer was prepared by using diol triol blends which serve as mutual plasticizers reducing the crystallinity of the individual polyols at low temperatures. This approach has produced elastomers with the best low temperature properties of any yet prepared. The diol components had a major effect on lowering torsional modulus at  $-55^{\circ}\text{C}$ .

The type of diisocyanate was varied on a 4500 molecular weight polyether triol (Pluracol TPE 4542)-o-dichlorobenzidine (DCB), 1/1  $\text{NH}_2/\text{OH}$  ratio elastomers. Quasi prepolymers were prepared for this diisocyanate study in order to obtain liquid diisocyanate components. Properties varied considerably with variation of the diisocyanate.

Urethane elastomers containing no urea linkages were evaluated and compared to similar elastomers containing urea linkages in attempt to evaluate more closely the effect of the various components, urethane, urea, and polyether backbone on properties of the resultant elastomers.

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## INTRODUCTION

There are military needs for materials that are chemical and oil resistant and possess elastomeric properties over a broad range of climatic conditions ranging from that encountered in the tropics to the arctic regions. Many commercial urethane elastomers possess properties which make them serviceable under normal or more prevalent conditions. However, they do not possess the combined properties of low temperature flexibility and oil resistance.

The objective of this program is the development of a urethane elastomer(s) with the following target properties:

- a. Tensile Strength - 1200 psi. Min. (ASTM D412).
- b. Ultimate Elongation - 200% Min. (ASTM D412).
- c. Compression Set, ASTM D395, Method B, after 70 Hrs. at 212°F. - Max. 50%.
- d. Compression Set, ASTM D1229, or Hrs. at -67°C. - Max. 50%.
- e. Oil Swelling, ASTM No. 3 Oil 70 Hrs. at 212°F. - Limits 0 to 10% (ASTM D471).
- f. No cracks, breaks, fissures after testing in accordance with ASTM D746 at -67°F.
- g. Young's Modulus of Elasticity at -67°F. Max. 10,000 psi. (ASTM D1053).
- h. Uncured and cured elastomers shall be stable for extended periods of storage at ambient temperatures. Little or no change in properties shall be observed after storage for periods up to 2 years. - Max. 10%.
- i. Vulcanizates of the elastomer shall show retention of a minimum of 75% of original tensile and elongation after 70 hours in a circulating air oven at 212°F. (ASTM D573-53).

Although the final elastomer(s) are not limited to the above target properties, the key targets for achievement are (e) and (g).

A review of the properties of urethane elastomers which had previously been developed at Wyandotte, revealed a trend towards improved low temperature flexibility when higher molecular weight polyether polyols were used. Theoretical considerations indicated that if higher molecular weight polyether polyols were to be used, the low temperature flexibility performance could be improved. Oil resistance requirements were met by certain Wyandotte developed polyether elastomers based on lower molecular weight polyether polyols. However, as the polyether molecular weight increased, the oil resistance dropped. A survey of the open urethane literature and data from Wyandotte urethane research revealed that solvent (oil) resistance may be improved by a number of factors, including types of diamine, diisocyanate and polyol used and variations of same. The problem, in view of the above considerations, has been resolved to gaining low temperature flexibility by the use of high molecular weight polyether polyols and investigating which of the factors that improve the solvent (oil) resistance does not appreciably affect the low temperature flexibility. In addition to high molecular weight polyether polyols, it is anticipated that other types of high molecular weight polyols may be used, e.g. polyesters. By using blends of polyols, it is expected that they may be mutually plasticizing at low temperatures.

During the first quarter a statistically designed set of experiments investigating 5 variables at two levels were completed. This investigation was based on the above considerations. Two aromatic diamines (MOCA and DCB) were compared at two levels of amine to hydroxyl ratio. Two aromatic diisocyanates (TDI and MDI) at two levels of concentration were also compared. Two polyols of 1500 equivalent weight were utilized to round

out the five variables. These polyols are Pluracol TP-4542 and Teracol 30. The use of ortho dichlorobenzidine (DCB) at a 1.5  $\text{NH}_2/\text{OH}$  ratio in combination with tolylene diisocyanate and the polypropylene-ethylene ether triol came the closest to meeting the Army specification for an oil resistant rubber with good low temperature flexibility.

Preparation and evaluation of urethane-urea elastomers were continued in the second quarter. Based on work performed in the first quarter, dichlorobenzidine (DCB) and toluene diisocyanate were the diamine and diisocyanate chosen for the bulk of this work. The amine to hydroxyl ratio was varied on urethane-urea elastomer formulations based on two polyether triols, a 5200 molecular weight polypropylene ether triol and a 7000 molecular weight polyether triol containing a large percentage of ethylene oxide. The amine to hydroxyl ratio was varied from 1.5 to 2.5 in the series based on the former triol, from 1.5 to 10 on the latter triol. There was surprisingly little variation in torsional modulus at  $-55^\circ\text{C}$ . with variations in amine to hydroxyl ratio, even over the range from 1.5 to 10.0/1. However, as the amine to hydroxyl ratio increased from 1.5/1 to 10/1, the room temperature torsional modulus increased from 260 to 3200. Introduction of ethylene oxide into the polyether chain decreases the oil absorption at the expense of increased water absorption.

In the past third quarter the above studies were continued. Other isocyanates were investigated and mutual plasticizing effects of blends of polyols were investigated.

EXPERIMENTAL PROCEDURE

The experimental procedure was essentially the same as described in Quarterly Progress Report 2, 1 January 1963. Efforts to remove unsaturation in the polyethers have been initiated. This will be reported next quarter together with properties of elastomers prepared from these improved polyols. A new Clash-Berg torsional modulus apparatus has been purchased that permits measurement of 12 samples successively. This apparatus will permit efficient evaluation of low temperature torsional modulus of elastomers over a temperature range.

## RESULTS AND DISCUSSION

Table I lists properties of elastomers prepared from 70-30 blends of 5200 molecular weight polypropylene ether triol or tetrol-polytetramethylene glycol (Teracol 30, 3000 molecular weight). The triol based o-dichlorobenzidine (DCB)-toluene diisocyanate (TDI) elastomers had better low temperature torsional moduli. Table I also lists the effect of plasticizing these formulations, using either a liquid medium nitrile rubber (Hycar 1312X4) or a polyether triol (molecular weight = 22,000). It was found that the liquid nitrile rubber did not appreciably affect the oil resistance of the elastomers but adversely affected their low temperature flexibility. The elastomers prepared with the high molecular weight polyether had an improvement in low temperature torsional moduli but were weak at room temperature.

Table II lists a comparison of urethane-urea elastomers prepared from a 4500 molecular weight triol (Pluracol TPE-4542) and the 5200 molecular weight polypropylene ether triol with blends of these triols with crystallizing diols. In these elastomers, the diamine was DCB, the diisocyanate TDI. At  $-55^{\circ}\text{C}$ ., the blends of triol and 3000 molecular weight polytetramethylene ether glycol (Teracol 30) have better torsional moduli than the elastomers based solely on the triols. The elastomer containing 30% Pluracol E-6000 (6000 molecular weight polyethylene oxide) had poor torsional modulus at  $-55^{\circ}\text{C}$ . Apparently the 30% of Pluracol E-6000 in this elastomer is too much, leading to crystallization at  $-55^{\circ}\text{C}$ .

In Table III, Pagination No. PR1622-K, an elastomer containing only 20% Pluracol E6000 and 30% Teracol 30 had excellent torsional modulus at  $-55^{\circ}\text{C}$ ., meeting the specification. The remaining polyol was Pluracol TPE-4542, the diamine DCB and the diisocyanate TDI. Comparison could be made between elastomers PR1622-F, Table I, and PR1622-H, Table III, in which each elastomer was plasticized with the 22,000 molecular weight triol. The effects on properties were similar to those on the unplasticized elastomers, PR1622-B and PR1622-I, Table II.

Table IV lists the effect of various diisocyanates on the properties of Pluracol TPE-4542-DCB based elastomers. Quasi-prepolymers were prepared at a 4/1 NCO/OH ratio from Pluracol TPE-4542 and each of the diisocyanates and these prepolymers were reacted with a Pluracol TPE-4542-DCB blend. By using this technique, developed last quarter, it was possible to process these diisocyanates more easily into the final elastomer. Table V lists stress-strain properties of these elastomers at elevated temperatures run at Rock Island Arsenal (R. I. Lab Report 63-ES-31). p-Phenylene diisocyanate, 1,5-naphthalene diisocyanate and bitolylene diisocyanate each are interesting when compared to tolylene diisocyanate due to their superior stress-strain properties, both at ambient and elevated temperatures, improved oil resistance, and lower water absorption, at the expense of slightly higher low temperature torsional modulus and somewhat increased processing difficulties.

Table VI lists properties of additional samples which were prepared from Pluracol TPE-4542 and the various diisocyanates, omitting all diamines. These samples had very low mechanical strength due to the fact that they had no reinforcing urea linkages. Low temperature torsional moduli were similar.

Table VII lists properties of urethane polymers prepared from various polyols and TDI. Again, these polymers had low mechanical strength due to the lack of urea linkages. The one exception was the Teracol 30 polymer in which the crystallinity of the polymer on stretching provided the reinforcement. However, this same polymer also crystallized at low temperature, providing poor low temperature flexibility. As the urethane content of the polypropylene ether triols decreased, and the triol cross-linking decreased, the flexibility at  $-55^{\circ}\text{C}$ . improved.

TABLE I

Effect of Plasticizers on Properties of Two Polyether-DCB-TDI Elastomers

Pageination No.	FR1622-B	FR1622-D	FR1622-F	FR1622-C	FR1622-E	FR1622-G
Polyol	30% Teracol 30 + 70% Exp. (1750 eq. wt.)	30% Exp. Triol 5200	30% Teracol 30 + 70% Exp. (1400 eq. wt.)			
Diisocyanate	TDI	TDI	TDI	TDI	TDI	TDI
Diamine	DCB	DCB	DCB	DCB	DCB	DCB
ME <sub>2</sub> /OH Ratio	1.0	1.5	1.5	1.0	1.5	1.5
Plasticizer,	None	Nitrile	Triol 22000	None	Nitrile	Triol 22000
30 pts/100 polyol blend						
Ultimate strength, psi	1280	560	790	1250	555	400
Ultimate elongation, %	540	400	320	410	520	540
100% Modulus, psi	465	230	435	480	215	190
Hardness, Shore A	78	63	74	78	61	56
ASTM No. 3 Oil						
70 hrs. at 212°F.,						
Wt. change, %	45.1	46.5	46.1	40.5	40.2	51.2
Vol. change, %	51.3	51.1	51.7	45.7	45.6	58.5
Water absorption, 24 hrs. at 75°F.,						
Wt. change, %	2.16	2.26	4.11	2.30	2.33	5.46
Torsional modulus, G, psi (E = 3G)	-60°C 47,000	-60°C 63,500	-62.5°C 25,400	-60°C 103,000	156,000	-62.5°C 87,800
	-52°C 5,000	-52°C 8,140	-51 °C 2,510	-52°C 13,100	29,600	-51 °C 7,290
	-47°C 3,080	-46°C 5,330	-42.5°C 1,640	-46°C 8,200	19,300	-42 °C 1,965
Temperature where E = 10,000, °C.	-50	-42	-52	-40	-35	-44

TABLE II

Effect of Blending Polyether Diols on Triols on Properties of Resultant Polyether TDI-DCB Elastomers

Page	FR- 1601-P	1601-Q	1606-D	1606-L	1622-B	1622-I	1602-M
Polyol	Pluracol TPE-4542	Triol 5200	70% Triol 5200 30% Pluracol E-6000	70% Triol 5200 30% Pluracol	70% Triol 5200 30% Teracol 30	70% Pluracol TPE-4542 30% Teracol 30	Pluracol Teracol 30
Calculated Cross-Link Density, eqivs./10,000 gm. Elastomer	1.29	1.22	0.89	0.63	0.50	0.76	0
from triol	2.5	2.0	1.43	1.43	1.43	1.43	2.5
from excess TDI	3.79	3.22	2.32	2.03	1.93	2.19	2.5
Total	1/1	1.5/1	1.5/1	1.5/1	1/1	1/1	1/1
NE <sub>2</sub> /OH Ratio	1023	1388	1300	720	1280	1600	3122
Original Properties	217	216	1010	160	540	490	1450
Stress-Strain	655	834	420	485	465	540	696
Ultimate strength, psi	80	86	78	69	67	81	83
Ultimate elongation, %	45	50	69	69	51.4	51.4	72
Modulus, 100% 300%	28.2	23.3	35.9	-----	45.1	35.9	46.3
Hardness, Shore A	32.2	26.8	41.7	-----	51.3	40.7	51.2
Environmental Properties							
Compression set							
70 hrs at 212°F.							
ASTM No. 3 Oil							
70 hrs. at 212°F.							
Wt. change, %							
Vol. change, %							
Water absorption, 24 hrs. at 75°F.							
Wt. change, %							
Torsional Modulus, °C.							
Temp. where E = 10,000 psi, °C.							

TABLE III

Various Blended Polyether-DCB-TDI Urethane-Urea Elastomers

Page	FR1622-H	FR1622-I	FR1622-J	FR1622-K	FR1626-B
Polyol	30 pts. Teraccol 30 70 pts. Pluracol TFE-4542	30% Teraccol 30 70% Pluracol TFE-4542	30% Teraccol 30 40% Pluracol TFE-4542 30% Exp. Triol 7000	30% Teraccol 30 20% Pluracol E-6000 50% Pluracol TFE-4542	Pluracol TP-6040
Diisocyanate	DCB 1.5 TDI	DCB 1.0 TDI	DCB 1.38 TDI	DCB 1.1 TDI	DCB 1.5 TDI
Calculated Cross-link Density, equiv./10,000 gm. Elastomer	0.74 1.43 2.17	0.76 1.43 2.19	0.78 1.43 2.21	0.54 1.43 1.97	0.50 1.43 1.93
from triol	1270 350 600 1130 80	1600 490 540 960 81	460 160 325 ---	760 250 420 ---	1365 370 660 1175 80
Total	52.2	51.4	81.6	70.5	56.3
Tensile strength, psi	29.1	35.9	44.0	46.6	35.5
Elongation, %	33.9	40.7	47.0	54.0	40.7
100% Modulus, psi	5.9	2.3	33.3	16.3	2.0
300% Modulus, psi	127,000	40,500	12,900	21,800	Incomplete
Hardness, Shore A	19,300	11,150	9,100	3,380	"
Compression set, 70 hrs at 212°F.	7,500	5,280	4,170	2,500	"
ASTM No. 3 Oil, 70 hrs. at 212°F.					
Wt. change, %					
Vol. change, %					
Water absorption, 24 hrs. at 75°F.					
Wt. change, %					
Torsional modulus, psi					
-65°C.					
-55°C.					
-47°C.					
-41°C.					
Temp. where E = 10,000 psi, °C.	-43	-43	-45	-55	16.

TABLE IV

Effect of Various Diisocyanates on Properties of the Resultant Plurecol TPB-4542-DCB Urethane-Urea Elastomer

(NH<sub>2</sub>/OH = 1.0)

Diisocyanate	FR1611-J	FR1613-D	FR1614-K	FR1615-C	FR1616-C	FR1617-C	FR1618-C
	p-Phenylene diisocyanate	1,5-Naphthalene diisocyanate	p-Xylylene diisocyanate	Toluene diisocyanate	Methylene bis(4-Phenyl-diisocyanate)	Bitolylene diisocyanate	Diisocyanate
	PPDI	NDI	XDI	TDI	MDI	TODI	DADI
			*NH <sub>2</sub> /OH = 1.5				
	895	1140	1425	750	790	1200	775
	205	150	210	185	220	185	215
	390	785	985	480	415	875	420
	75	75	87	68	70	82	74
	29.5	34.5	36.6	41.9	30.9	34.6	38.6
	33.9	39.5				35.0	
	3.1	2.7	2.2	3.2	2.9	2.5	2.5
		490,000		198,000	202,000	252,000	
	236,000		31,600				228,000
	27,000	12,170	13,600	9,970	62,800	18,500	48,000
	6,530	3,300	4,610	5,420	16,250	7,300	
	2,450		2,080				7,570
	-44	-44	-43	-43	-37	-43	-41

Original Properties

Ultimate strength, psi

Ultimate elongation, %

100% Modulus, psi

Hardness, Shore A

70 hrs. at 212°F.

ASTM No. 3 OLI

Wt. Change, %

Vol. Change, %

Water absorption,

24 hrs. at 25°C.

Torsional Modulus, °C.

-65

-64

-63

-62

-61

-60

-59

-58

-57

-56

-55

-54

-53

-52

-51

-50

-49

-48

-47

Temperature where

E = 10,000, °C.

ROCK ISLAND ARSENAL LABORATORY  
 REPORT NO. 63-ES-31  
 Wyandotte Chemical Corporation

7 March 1963

TABLE V  
 PHYSICAL PROPERTIES OF URETHANE VULCANIZATES TESTED AT  
 AMBIENT AND ELEVATED TEMPERATURES

Properties Measured	Control	TEMPERATURES																		
		PR1606-12	PR1606-11	PR1611-J	PR1612-H3	PR1613-D	PR1615-C3	PR1616-C2	PR1617-C2	PR1617-C4	PR1618-C2	PR1618-C3								
Tested at Room Temperature:																				
Tensile Strength, psi.	4000	460	500	810	270	1020	600	710	1200	1120	620	950								
Modulus @ 100% E, psi.	250			520		630	400	620	870	840	520	470								
Modulus @ 200% E, psi.	520					980						820								
Elongation, %	650	105	105	205	110	215	220	145	200	180	210	230								
Hardness, Shore A	62	68	77	75	58	74	68	77	82	80	69	69								
Tested at 300°F:*																				
Tensile Strength, psi.	1160	250		510	190	580	290	410	650	550	370	340								
Elongation, %	340	40		75	70	105	50	80	80	50	80	50								
Tested at 400°F:*																				
Tensile Strength, psi.	450	90	140	420	Specimen	330	130	300	410	360	260	220								
Elongation, %	420	20	200	100	melted	90	100	50	100	105	150	100								

\* Specimens conditioned 6 minutes at temperature indicated prior to testing.

This information is furnished with the understanding that it will not be used in such a manner as to indicate or imply endorsement or approval by the U. S. Government.

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TABLE VI

Properties of Urethanes Prepared from Pluracol TPE-4542 and Various Diisocyanates

Pagination No.	PR1611-K	PR1615-D	PR1616-D	PR1617-D	PR1618-D	PR1613-E
Diisocyanate	p-Phenylene	TDI	MDI	TODI	DADI	1,5-Naphthalene Diisocyanate
Tensile Str. psi	155	137	154	133	153	172
Elongation, %	135	110	110	133	200	110
100% Modulus, psi	123	128	150	116	97	154
Hardness, Shore "A"	39	39	41	35	34	40
<u>ASTM No. 3 Oil 70 Hrs. at 212°F.</u>						
Wt. Change, %	65.8	64.0	54.1	67.9	68.1	61.6
Wt. Change, %	68.4	70.2	60.1	72.0	75.2	68.9
<u>Water Absorption 24 Hrs. at 75°F.</u>						
Wt. Change, %	3.36	3.65	2.6	3.4	2.9	3.5
<u>Torsional Modulus</u>						
-64°C.	194,000		156,000			154,000
-58	63,000					
-55			31,200			9,550
-52			3,220	5,300		
-50	6,120	4,070	2,310			
-48						
-45	<2,000	<2,000		<2,000	<2,000	<2,000
Temp. where E = 10,000, °C.	-48	-49	-50	-52	-48	-52

TABLE VII

Properties of Various Polyol-TDI Urethanes

Polyol	PRI615-D	PRI627-C	PRI627-D	PRI626-A	PRI605-N	PRI627-A	PRI627-B
Type	Pluracol TFE-4542 Triol	Pluracol TP-4040 Triol	Pluracol TP-5240 Triol	Pluracol TP-6040 Triol	Tetracol 30 Diol	Pluracol P-1010 Diol	P-1310 Diol
Eq. Wt.	1500	1382	1753	1933	1460	525	641
NCO/OH Ratio	1.225	1.222	1.310	1.07	1.225	1.09	1.11
% TDI	6.67	7.1	6.1	4.59	9.95	15.25	13.1
Original Properties							
Tensile Str. psi	137	133	131	109	2570	164+	Liquid
Elongation, %	110	120	140	230	560	1300+	
100% Modulus	128	114	108	60	1159	64	
Hardness, Shore A	39	30	31	22	94		
ASTM No. 3 Oil, 70 hrs. at 212°F.							
Wt. Change, %	64.0	73.9	86.6	110.7	127.2	37.0	
Vol. Change, %	70.2	79.9	96.1	117.2	138.5	42.9	
Water absorption, 24 hrs. at 75°F.							
Wt. Change, %	3.65	2.5	2.4	2.2	0.9	3.0	
Torsional Modulus, °C.							
-62		135,000	103,000	62,500	96,300	189,000	
-60							
-55		22,000	6,950	3,250	73,000		
-50		2,320	<2,000	<2,000	53,500	131,000	
-45	4,070 <2,000						
Temperature where E = 10,000 psi °C.	-49	-51	-54	-55	>>-50	>>-50	
Calculated Cross-Link Density From Branching, Equiv./10,000 g	1.40	1.42	1.02	0.56			
From Excess TDI, Equiv./10,000 g	1.43	1.43	1.43	0.35	1.43	1.43	1.43
Total	2.83	2.85	2.45	0.91	1.43	1.43	1.43

### CONCLUSIONS

- I. Blends of diols and polypropylene ether triols combined with ortho-dichlorobenzidine and toluene diisocyanate at a 1/1  $\text{NH}_2/\text{OH}$  ratio may be utilized to prepare elastomers that meet the low temperature flexibility requirements.
- II. Although certain of these diols may be crystallizing at  $-55^\circ\text{C}$ . when used as the sole polyol in the urethane-urea elastomers, when blended with other polyols, they are plasticized, reducing this tendency to crystallize. However they still tend to crystallize on stretching, thereby improving the tensile strength.
- III. Urethane polymers containing no urea linkages offer a convenient method of measuring the potential of polymers based on a polyol system to meet low temperature torsional modulus requirements.
- IV. The effect of various diisocyanates on properties of the urethane-urea elastomers has been characterized. Several of the elastomers prepared from these diisocyanates have improved oil resistance and mechanical strength both at ambient and elevated temperatures. These diisocyanates were p-phenylene diisocyanate, 1,5-naphthalene diisocyanate, and bitolylene diisocyanate. However, they had slightly higher low temperature modulus and were more difficult to process.

### FUTURE PROGRAM

A program for next quarter is outlined below. This quarter, it has been proven that the low temperature flexibility may be attained by blends of high molecular weight polypropylene ether triols and crystalline diols. However, the oil absorption remains a problem. Also, the mechanical strength tends to be somewhat low when the high molecular weight polypropylene ether triols are used. The primary approaches to be used next quarter to improve these deficits are:

1. The high molecular weight triols will be "cleaned up" by removing most of the impurities that cause chain termination.
2. Other crystalline high molecular weight diols will be tried, including polyester diols. By varying the diol content, the effect of triol cross-link density will be characterized.
3. Other candidate diamines will be tried, including:
  - A. p,p'-Diamino sulfone
  - B. p,p'-Diamino diphenyl oxide
  - C. m, p-Phenylene diamines containing negative substitution on the benzene ring.
  - D. Other candidate diamines
4. More work with diisocyanates:
  - A. Diphenyl oxide diisocyanate
  - B. Durene diisocyanate
  - C. p-Phenylene diisocyanate
  - D. 1,5-Naphthalene diisocyanate
  - E. Bitolylene diisocyanate
  - F. Other candidate diisocyanates

5. Blends of high molecular weight polyether polyols and assorted low molecular weight polyols.
6. Elastomers based on assorted alkalene oxide block and heterogeneous high molecular weight polyols.
7. On request, any of the more interesting elastomers will be machine cast, providing the raw materials are available in sufficient quantities.
8. Preparation of urethane-urea elastomers containing no urethane or urea hydrogens.