

## Polyurethanes as Cryogenic Adhesives

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### Synopsis

Polyurethanes containing the polyether backbone were found to give superior adhesives at cryogenic temperatures as compared to epoxy resins. However, the adhesives showed poor performance at 250 and 400°F. The adhesives were prepared from 2,4-toluene diisocyanate (TDI)-terminated polyether polyols and cured with 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA, du Pont). The addition of free TDI causes an increase in elevated temperature strength when an equivalent amount of MOCA was used.

### INTRODUCTION

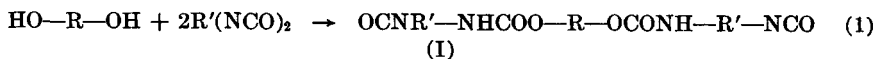
The object of this program was to develop a practical polyurethane adhesive showing good tensile shear strength over the temperature range of  $-423^{\circ}\text{F.}$  to  $400^{\circ}\text{F.}$

In the past there has appeared very little literature describing the chemical constitution of polyurethanes used for cryogenic applications.<sup>1-3</sup> However, Bodnar and Kelly<sup>4</sup> described an Adiprene L (Du Pont) resin as an adhesive formulation showing good strength at  $-65^{\circ}\text{F.}$  (7470 psi). In this latter composition the chemical structure was disclosed to probably be a poly-1,4-butylene oxide polyglycol reacted with 2,4-toluene diisocyanate in the ratio of 2:3. More recently, a paper was presented<sup>5</sup> which described polyurethanes with tensile shear strengths of 5463 psi at  $-423^{\circ}\text{F.}$  and 201 psi at  $250^{\circ}\text{F.}$  after room temperature curing.

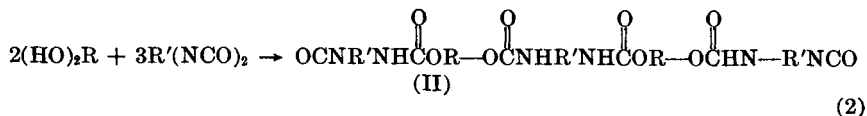
### EXPERIMENTAL AND RESULTS

In this program prepolymers were first prepared from aliphatic saturated diols or triols with 2,4-toluene diisocyanate; later studies showed polyether polyols to have superior cryogenic adhesive properties when used in the prepolymer synthesis. In addition, curing agents based on aromatic amines were superior to aliphatic amines or polyesters terminated with hydroxy groups. MOCA (Du Pont) (3,3'-dichloro-4,4'-diaminodiphenylmethane) was found to be the most useful curing agent.

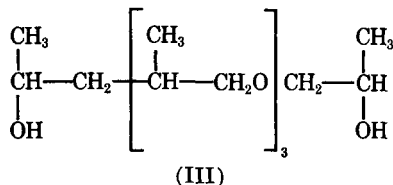
The reactions between diisocyanates and polyols were controlled to produce adducts containing NCO endgroups and a varied number of carbamate linkages within the molecule. Di-adducts were prepared by the addition of a polyol to the diisocyanate according to eq. (1).



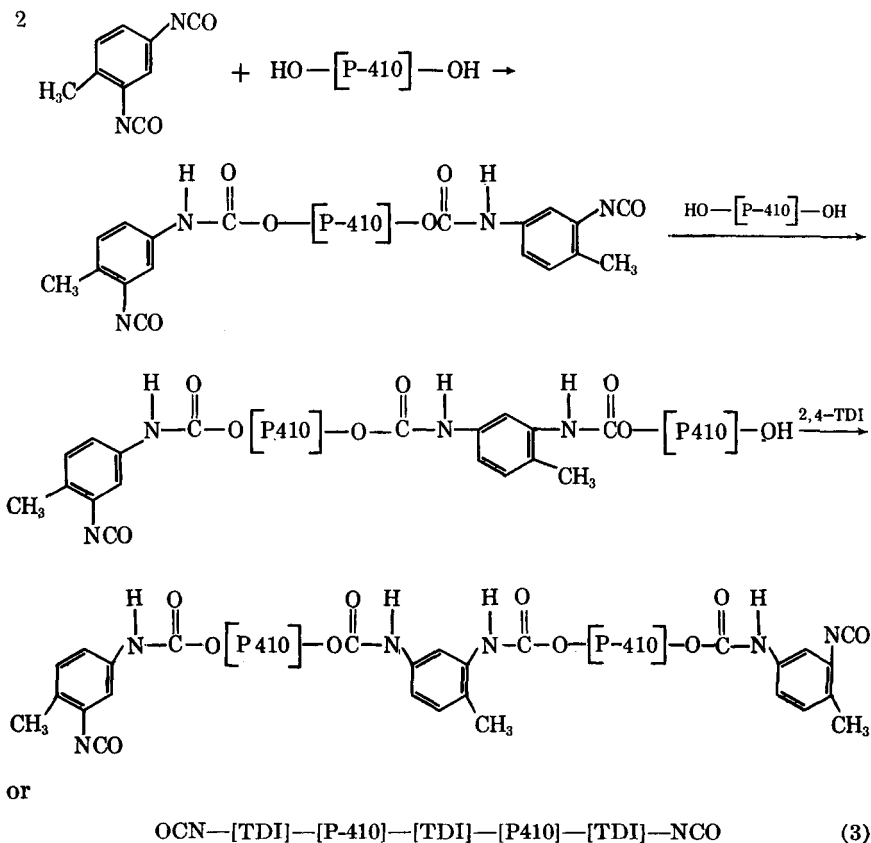
More complex adducts were prepared by the reaction of di- and trihydroxy polyethers with diisocyanates. As the di-adducts, these were made with or without solvent (ethyl acetate), according to eq. (2).



With Pluracol P-410 (Wyandotte Chemical Co.), III,



abbreviated HO-[P-410]-OH, the reactions are as shown in eqs. (3):



### Preparations

Some examples of typical preparations are given below.

#### *Preparation of a Polyurethane Prepolymer (409-39)*

**Reactants.** Reactants were 2,4-toluene diisocyanate (TDI), M.W. 174.2 (0.1875 mole, 32.7 g.); polyoxypropylene glycol (Pluracol P-410), M.W. 400 (0.1250 mole, 50.0 g.).

**Apparatus.** The apparatus consisted of a one-liter resin kettle, stirrer, thermometer, condenser with drying tube, dropping funnel, and heating mantle.

**Procedure.** The apparatus was carefully dried and flushed with nitrogen. The TDI was placed in the kettle and heated to 50°C. The Pluracol P-410 was placed in the dropping funnel and added dropwise during 2 hr. while the pot temperature was maintained at  $65 \pm 3^\circ\text{C}$ . Stirring at that temperature was continued for 2 hr. after final addition. The product was a very viscous, sticky syrup; NCO calculated, 6.35%; found, 6.63%.

#### *Preparation of a Polyurethane Prepolymer (409-40)*

**Reactants.** Reactants were 2,4-toluene diisocyanate (TDI), M.W. 174.2 (0.1875 mole, 32.7 g.); polyoxypropylene glycol (Pluracol P-710), M.W. 700 (0.1250 mole, 87.5 g.).

**Apparatus.** The apparatus used consisted of a one-liter resin kettle, stirrer, thermometer, condenser with drying tube, dropping funnel, and heating mantle.

**Procedure.** The apparatus was carefully dried and flushed with nitrogen. The TDI was placed in the kettle and heated to 50°C. with stirring. The Pluracol P-710 was placed in the funnel and added dropwise during 2 hr. while the pot temperature was maintained at  $65 \pm 3^\circ\text{C}$ . Stirring at that temperature was continued for an additional 2 hr. after all the Pluracol P-710 was added. The product was a clear syrup; NCO calculated, 4.37%; found, 5.56%.

#### *Preparation of a Polyurethane Prepolymer (428-104-2)*

**Reactants.** Reactants were 2,4-toluene diisocyanate (TDI), M.W. 174.2 (0.2 mole, 34.8 g.); polyoxypropylene glycol (Dow P1000) M.W. 1000 (0.1 mole, 100.0 g.); *o*-chlorobenzoyl chloride (CBC) (0.12 g.).

**Apparatus.** The apparatus consisted of a 500-ml. resin kettle, stirrer, thermometer, condenser with drying tube, dropping funnel, and heating mantle.

**Procedure.** The apparatus was carefully dried and flushed with nitrogen. The TDI and CBC were placed in the kettle and heated to 50°C. The Dow P1000 was placed in the funnel and added dropwise during 2 hr., a pot temperature of  $65 \pm 3^\circ\text{C}$ . being maintained. Stirring at that temperature was continued for 2 hr. after final addition. The product was a clear syrup (428-104-1); NCO calculated, 6.23%; found, 6.27%.

TABLE I. Polyurethane Cryogenic Adhesives

Sample no.	Composition <sup>a</sup>	Tensile shear strength on aluminum, psi			T-peel at 73°F., psi <sup>b</sup>
		-320°F.	73°F.	250°F.	
352-54-2	Polyglycol P1000 (M.W. 1000)/2,4-TDI, 2/1 adduct (428-104-2), % NCO = 8.6, cured with MOCA (5:1.4)	5930	2560	740	
432-61-6	PTMEG 1103 (M.W. 1103)/2,4-TDI, 2/1 adduct (428-117-3), % NCO = 8, cured with MOCA (5:1.6)	6650	2120	844	
432-61-2	PTMEG 2005 (M.W. 2005)/2,4-TDI, 2/1 adduct (439-42-2), % NCO = 6, cured with MOCA (5:1.0)	5580	1750	958	
432-49-4	Witco ED-2000 (M.W. 2000)/2,4-TDI, 2/1 adduct, (428-87-3), % NCO = 12.3, cured with MOCA (2:0.6)	2570	2370	964	
432-63-2	Voranol 2700 (M.W. 2700)/2,4-TDI, 2/1 adduct (428-85-3), % NCO = 12.2, cured with MOCA (2:0.8)	5830	1620	558	
405-133-1	Pluracol P-710 (M.W. 775)/2,4-TDI, 2/1 adduct (399-44), % NCO = 8.43, cured with MOCA (5:1.3)	1595	1563	56	
405-121-3	Pluracol P-410 (M.W. 400)/4,4'-diphenylmethane diisocyanate, 2/1 adduct, (409-97), % NCO = 9.33, cured with MOCA (5:0.6)	4200	1940	301	
405-137-5	Pluracol P-710 (M.W. 775)/2,4-TDI, 3/2 adduct, % NCO = 4.42, cured with MOCA (5:0.4)	6090	837	76	

*(continued)*

To 37.1 g. of 428-104-1 was added 2.9 g. TDI and the mixture was thoroughly stirred (428-104-2); NCO calculated, 9.0%; found, 8.60%.

### Physical Testing

The physical testing data are presented in Tables I and II. In most cases the adhesives were tested at 400, 250, 73, and -320°F. using 0.064 in. thick Alclad aluminum 2014-T6, Federal Specification QQ-A-255. Some adhesives were tested on #321 stainless steel 0.064 in. thick, Federal Specification QQ-S-766. The stainless was etched with sulfuric acid-dichromate according to procedure B described in the data sheet for Borden's Epiphen 825A. The samples were cured at 100°C. for 2 hr., unless otherwise specified, and equilibrated before testing for 7 days at room temperature (73°F.) in a constant temperature-humidity room. The tensile shear strength was determined by using a Tinius Olsen Electromatic universal

TABLE I (continued)

Sample no.	Composition <sup>a</sup>	Tensile shear strength on aluminum, psi			T-peel at 73°F., psi <sup>b</sup>
		-320°F.	73°F.	250°F.	
432-94-5	439-108-3 <sup>c</sup> + MOCA (5/1.4)	5390	2280	862	
450-28-4	450-28-4 <sup>d</sup> + MOCA (5/1.4)	4180	2090	640	
432-103-6	452-3-2 (an adduct from 0.15 mole PTMEG-1103 + 0.06 mole Dover 1000 + 0.04 mole TDI, % NCO = 9%) + MOCA (5/1.0)	>6950	3140	1104	16
432-103-8	452-5-2 (an adduct from 0.07 mole PTMEG 1103, 0.03 mole Dover 1000 and 0.20 mole DPMDI, % NCO = 9.0) + MOCA (5/1.4)	4025	2890	1255	
432-76-1	439-79-4 <sup>e</sup> + MOCA (5/1.9)	2660	2850	1240	
432-67-1	428-120-3 <sup>f</sup> + MOCA (5/1.4)	5920	2870	1070	

<sup>a</sup> Sources: polyglycol, poly(oxypropylene glycol), Dow Chemical Co.; PTMEG, poly(oxybutylene glycol), Quaker Chemical Co.; Witco ED 2000, poly(oxypropylene glycol), Witco Chemical Co.; Pluracols P-410 and P-710, poly(oxypropylene glycol), Wyandotte; Voranol, poly(oxypropylene glycol), Dow.

<sup>b</sup> ASTM Standard T-peel test, No. D1876-61T, using a 10 mil thick nickel-chrome wire spacer for glue line thickness.

<sup>c</sup> Prepolymer prepared from 0.14 mole Pluronic L 61 (Wyandotte) and 0.2 mole TDI (2,4 isomer) using 0.6 ml. *o*-chlorobenzoyl chloride. The % NCO was increased to 9% for the particular fraction for adhesive uses.

<sup>d</sup> Prepolymer prepared from 0.2 mole of 4,4'-diphenylmethane diisocyanate (DPMDI) and 0.1 mole PTMEG 2005 using 0.9 ml. *o*-chlorobenzoyl chloride. The % NCO was increased to 12% before using as an adhesive.

<sup>e</sup> Prepolymer prepared from 0.40 mole TDI (65/35 2,4/2,6 isomer) and 0.25 mole Dow P1000 using 0.6 ml. *o*-chlorobenzoyl chloride. The % NCO content was increased at the end to 12% for this particular adhesive.

<sup>f</sup> 428-120-3—Prepolymer prepared from 0.1 mole TDI (2,4 isomer) and 0.05 mole PTMEG G 3196 using 0.15 ml. *o*-chlorobenzoyl chloride. The % NCO was increased to 9% before using as an adhesive.

testing machine. The cryostat was obtained from Hofman Laboratories, Inc., Newark, New Jersey. It is a stainless steel Dewar flask having the dimensions 20<sup>3</sup>/<sub>4</sub> in. height, 7<sup>1</sup>/<sub>4</sub> in. outside diameter, 18 in. inside depth, and 6 in. inside diameter. It is constructed with a copper heat radiation shield between the inner and outer walls. The Dewar is evacuated to about 2 × 10<sup>-6</sup> mm. Hg by connecting it to the high vacuum system of a Kinney Evaporator, Model KSE-2. All internal surfaces facing the vacuum are gold plated. The liquid nitrogen is added to the cryostat which is used in conjunction with the Tinius Olsen Electomatic universal testing machine.

### Polyurethane Adhesives: Diisocyanate Prepolymers

Prepolymers were prepared from 2,4-toluene diisocyanate (TDI) or from a mixture of 65% of the 2,4-isomer and 35% of the 2,6-isomer (TDI-65, 35) or from diphenylmethane diisocyanate (DPMDI). Polypropylene glycols and polytetramethylene ether glycols were used. The NCO:OH ratio was

TABLE II  
Commercial Polyurethane Prepolymers Used as Cryogenic Adhesives

Sample no.	Composition	Tensile shear strength on aluminum, psi <sup>a</sup>				T-peel at 73°F., psi
		-320° F.	73° F.	250° F.	400° F.	
405-41-2	Adiprene L-100 + MOCA (10/1.1)	2950				
432-2	Adiprene L-213 + MOCA (5/2.5)	2450				
405-97-1	Adiprene L-315 + MOCA (5/2)	6500	4085	1315	40 <sup>b</sup>	
405-97-2	Adiprene L-315 + MOCA (5/1)	6430	4580	1365	25 <sup>c</sup>	
432-60-4	Adiprene L-315 (5/1.5)	6520	2160	473		
405-97-3	Adiprene L-167 + MOCA (8/1)	7870 <sup>d</sup>	1890	781		
432-54-4	Adiprene L-167 + MOCA (5/1)	7800 <sup>e</sup>	1264	848		15
432-61-7	Polycin U56 + MOCA (5/1.6)	1950	1580	489		
405-109-A	Polycin U56 + Polycin 12 (7.4/2.7)	4380	1183	241		
432-44-2	Vibrathane 6005 + MOCA (10/0.95)	6850	990	166		
432-51-3	Vibrathane 6006 + MOCA (5/1)		1300	294		
432-44-3	Vibrathane 6006 + MOCA (5/1.0)	7070	1300	294		
432-51-4	Vibrathane 6008 + MOCA (10/1)	2760 <sup>f</sup>	390			

<sup>a</sup> Average of 3 determinations.

<sup>b</sup> Sample 432-66-1.

<sup>c</sup> Sample 432-66-2.

<sup>d</sup> Metal failure at 8000 psi for two samples.

<sup>e</sup> Metal failure.

<sup>f</sup> Sample 432-44-4.

either 2:1 or 1.6:1, and TDI was then added to these materials to increase the NCO content to the desired amount.\* All the preparations were made at 50–60°C.

All the diisocyanate prepolymers contained *o*-chlorobenzoyl chloride equivalent to the per cent H<sub>2</sub>O in the polyol plus 0.1% of the total weight of reactants.

## DISCUSSION

The purpose of this program was to develop polyurethane adhesives with good low temperature properties and having a tensile shear strength at 400°F. of 800 psi on aluminum. Using the polyurethane adhesives and

\* In order to increase the aromaticity of the adhesive more TDI and MOCA were added. It was felt that such an increase in aromaticity of the adhesive would favor better high temperature strength.

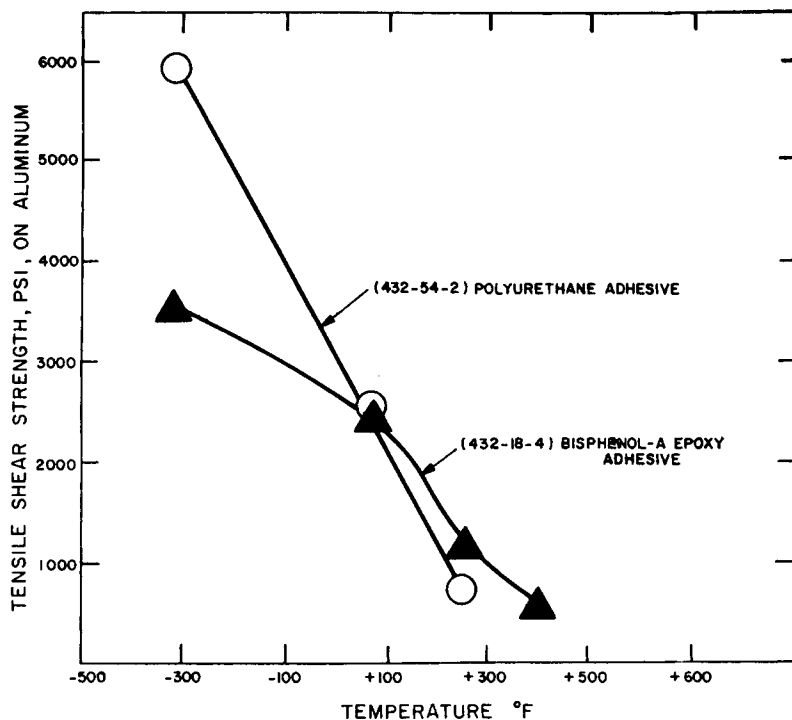


Figure 1.

curing with MOCA gave adhesives which were useful for the range  $-453$  to  $250^{\circ}\text{F}$ . At  $400^{\circ}\text{F}$ . the strengths dropped to values of the order of 20–100 psi. In a further study,\* special catalysts were used to improve the  $400^{\circ}\text{F}$ . strength so that values in excess of 1000 psi were obtained. The only disadvantage with this latter modified system is that the cure temperature required was  $165^{\circ}\text{C}$ ., whereas temperatures close to room temperature were desired.

Polyethers derived from poly(oxypropylene glycol) or poly(tetramethylene glycol) gave results similar to those shown in Table I. The samples prepared from higher molecular weight polyols were more stable to sudden gelation. In addition, *o*-chlorobenzoyl chloride of 0.1% concentration was added above that necessary to react with the water content of the polyol. This material acted as an effective gelation inhibitor.

The isocyanate content appears to be critical, since higher NCO content requires more MOCA to be effectively cured. This increases the aromaticity of the system and improves the tensile shear strength at  $250^{\circ}\text{F}$ . However, prepolymers with added TDI are more moisture-sensitive and have short pot-lives. The use of 4,4'-diphenylmethane diisocyanate (DPDMI) as in sample 405-121-3 did not give the expected increase in high temperature properties, as seen in Table I. However, the use of Dover

\* This investigation involved the cyclization of polyisocyanates to polyisocyanurates, and the results will form the subject of another paper.<sup>6</sup>

1000,  $\text{HOCH}_2\text{CH}_2\text{O}-\text{C}_6\text{H}_4\text{C}-(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2\text{OH}$  (ethylene oxide adduct of bisphenol A) did cause some improvement in the tensile shear values at 250°F. as seen in samples 432-103-6 and 432-103-8.

Several commercial polyurethane prepolymers were also evaluated, and results are shown in Table II. Among the latter samples the Adiprene systems gave the best results and compare favorably with our samples in Table I. It should be noted that the strength at 400°F. is 25 or 40 psi.

In conclusion, polyurethanes that were cured at 100°C. (or at room temperature) could not be modified to increase their high temperature (400°F.) strength. It is considered that the urethane linkage is not stable at 400°F., as a consequence of which the adhesives fail. In addition, the polyether backbone is too flexible at 400°F. Work in progress has shown that although more aromatic polyethers were substituted, failure at 400°F. still occurred.

Figure 1 shows a comparison of one of our polyurethanes with an epoxy adhesive. It is noted that the epoxy resins are stronger at 400°F. but weaker than the polyurethanes at cryogenic temperatures. The latter results are attributed to the increased flexibility of the polyurethanes due to their polyether structural backbone.

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### References

1. Hertz, J., *Advan. Cryogenic Eng.*, **7**, 336 (1962).
2. Smith, M. B., and S. E. Susman, *Advan. Cryogenic Eng.*, **8**, 300 (1963).
3. Kausen, R. C., *Materials Design Eng.*, **60**, 108 (Sept. 1965).
4. Bodnar, M. J., and E. R. Kelly, *Adhesives Age*, **2**, 29 (April 1959).
5. Roseland, L. M., paper presented at 7th National Society of Aerospace Materials and Process Engineers Symposium on Adhesives and Elastomers for Environmental Extremes, Los Angeles, California, May 20-22, 1964, Section 7.
6. Sandler, S. R., and F. R. Berg, in preparation.

### Résumé

Les polyuréthanes contenant une chaîne principale polyéther sont supérieurs du point de vue adhésion aux températures cryogéniques aux résines époxy habituelles. Toutefois ces adhésifs montraient de faibles performances à 250 et 400°F. Les adhésifs ont été préparés au départ de polyols polyéthers terminés par des unités 2,4-toluènes diisocyanées et traités avec du MOCA (Du Pont) (3,3'-dichloro-4,4'-diaminodiphénylméthane). L'addition de TDI libre cause une augmentation de la force à température élevée lorsque la quantité équivalente de MOCA est utilisée.

### Zusammenfassung

Polyurethane mit einer Polyätherhauptkette liefern den Epoxyharzen bei sehr tiefen Temperaturen überlegene Klebstoffe. Die Klebstoffe zeigten jedoch bei 250 und 400°F ein unbefriedigendes Verhalten. Die Klebstoffe wurden aus Polyätherpolyolen mit 2,4-Toluoldiisocyanat-(TDI)-endgruppen dargestellt und mit MOCA (Dupont) (3,3'-Dichlor-4,4'-diamino-diphenylmethan) gehärtet. Der Zusatz von freiem TDI verursacht bei Verwendung einer äquivalenten Menge von MOCA eine Zunahme der Festigkeit bei erhöhten Temperaturen.

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