

## The Analysis of Polyurethane Foams.

### I. Identification of Components\*

B. DAWSON, S. HOPKINS, and P. R. SEWELL,  
*Dunlop Research Centre, Erdington, Birmingham 24, England*

#### Synopsis

A scheme of qualitative analysis is presented for the identification of the constituents of polyurethane foam products, or indeed polyurethane-type materials in general. Elastomeric and cellular polyurethanes are analyzed by hydrolysis to simpler compounds which are then separated and identified. The methods of identification employed include infrared and nuclear magnetic resonance spectroscopy, gas chromatography, and thin-layer chromatography.

#### INTRODUCTION

Flexible polyurethane foams may be divided into two types—conventional water-blown foams and microporous elastomers. Conventional foams are usually produced by a one-shot technique and in some cases may also incorporate a physical agent such as a fluorocarbon to assist the blowing. Microporous elastomers may be made from prepolymers with diamine-type chain extenders or by one-shot formulations relying entirely on physical blowing by materials such as a fluorocarbon being volatilized by the exotherm. Although polyethers have been used almost exclusively for the latter type, both polyesters and polyethers have been used extensively in the production of conventional water-blown foams. The microporous elastomers may be made in a shaped mold to give an integral noncellular skin on which the texture of the mold surface is reproduced.

This paper deals with the analysis of polyurethane foams in terms of the identification of the components. The advent of gas-blown elastomers has led to the inclusion in this scheme of materials not normally found in water-blown foams, and the methods described are applicable in principle if not in scope to any polyurethane product.

The most direct method of examining polyurethane foams is by infrared spectroscopy, using the ATR technique, but the scope of this is limited. Its main uses are: (1) as a classification test for polyurethanes; (2) to distinguish between polyester and polyether types; (3) to indicate aromatic components by the presence of an absorption at about  $6.25\ \mu$ ; (4) to indicate

\* Presented at the 2nd S.P.I. International Cellular Plastics Conference, New York, November 1968.

the use of water or diamine as a chain extender by an absorption at about  $6.1 \mu$  due to urea groups, but this is not sufficient to identify such an agent; generally the absence of a  $6.0$ – $6.1 \mu$  absorption may indicate that a hydroxy-type chain extender has been used instead of water or diamine.

Points 2 and 3 above are useful in pursuing the initial separation stages described below.

Infrared spectroscopy is not useful in (5) the identification of the polyester component and chain extenders of either diol or diamine type; (6) the identification of the diisocyanate. While the presence of an aliphatic or aromatic diisocyanate may be deduced from an examination of the  $6.25 \mu$  region, it is very difficult to identify the diisocyanate (except perhaps in the case of naphthalene diisocyanate). It is impossible to tell the isomer ratio of toluene diisocyanate.

Although polyurethane foams are normally insoluble, they may often be solubilized by refluxing in formic acid for a few hours. This affords a method of obtaining an NMR spectrum from the formic acid solution which is usually sufficient to identify the polyol material, although the solvent resonances tend to obscure the polyurethane aromatic signals.

As direct methods of examination are usually incapable of identifying all the constituents, it is necessary to resort to a method involving total hydrolysis and identification of the separated hydrolysis fragments. The method of hydrolysis is by aqueous alkali in a pressure vessel at  $150^\circ\text{C}$  for 16 hr. Initial separation into amine fraction, acid fraction, and glycol/polyol fraction is carried out by ether extraction, and these fractions are subsequently characterized in greater detail.

A scheme for the characterization of linear polyurethanes has been described.<sup>1</sup> This work is an extension of that reported previously.<sup>2</sup>

### HYDROLYSIS AND INITIAL SEPARATION

About 1 g of foam and a solution of 2.5 g potassium hydroxide in 15 ml water are placed in a stainless steel screw-capped pressure vessel and heated at  $150^\circ\text{C}$  overnight. After cooling and opening, the contents are emptied into a separating funnel having a Teflon tap and extracted four times with 20-ml portions of ether.

In the case of polyester foam, evaporation of the ether gives the amine derived from the diisocyanate and also from amine chain extenders. The remaining aqueous solution is made just acid by the addition of concentrated hydrochloric acid and again extracted with ether. Evaporation of this ether extract gives the acid of the polyester backbone. The aqueous solution is then made alkaline by the addition of potassium hydroxide pellets and saturated by adding potassium carbonate. This solution is extracted with ether in a liquid-liquid extraction apparatus for at least 6 hr. Suitable apparatus has been described.<sup>3</sup> Evaporation of the ether yields the glycol parts of the polyester together with any hydroxy chain extender.

For polyether foams, the polyether and amines come out together in the first ether extraction. After removal of the ether, hydrochloric acid is

added to convert the amines to their hydrochlorides and the polyether is removed by ether extraction. Sometimes a better separation may be achieved by evaporating to dryness the amine hydrochloride/polyol mixture prior to extracting the polyol. The hydrochloric acid fraction is made alkaline with potassium hydroxide and the free amine is then extracted with ether.

Each hydrolyzate fraction is examined by infrared spectroscopy. This is sufficient to identify the acid, as in our experience adipic acid is the only dibasic acid likely to be encountered. Waxy and liquid hydroxy acids are formed from castor oil products and polycaprolactones, respectively. The identification of the polyol may be carried out by infrared spectroscopy, but

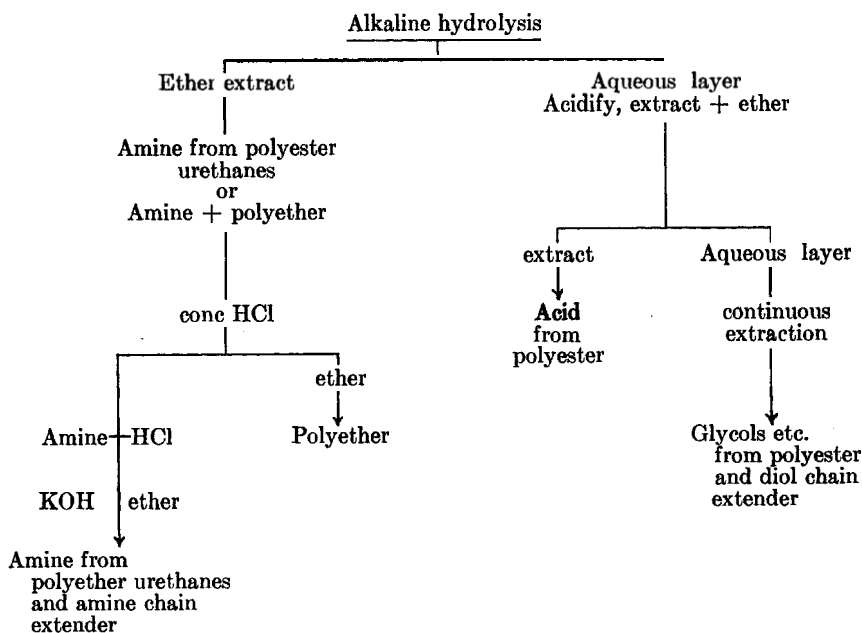


Fig. 1. Diagram showing the course of separation of hydrolysis fractions.

it is possible that more information may be forthcoming from the use of NMR spectroscopy. The infrared spectrum of the amine fraction generally identifies the major component, but thin-layer chromatography is required for the complete identification of the mixture. It is often impossible to resolve mixtures of diols by infrared spectroscopy and a combination of this with the other methods described below is necessary.

Aliphatic diamines are more soluble than aromatic diamines in aqueous media and hence are more difficult to extract with ether. Additional water should not be added and the hydrolysate should be extracted at least six times with 10-ml portions of ether.

The scheme of the extraction is shown in Figure 1.

### EXAMINATION OF AMINES BY THIN-LAYER CHROMATOGRAPHY

Adsorbents for thin-layer chromatography were obtained from E. Merck A. G., Darmstadt, Germany.

MOCA, Hylene W, and LD 813 are products of E. I. du Pont de Nemours & Co., Wilmington, Delaware.

LK 1443 and Desmodur M are products of Farbenfabriken Bayer A. G., Leverkusen, Germany.

#### Aromatic Diamines

With silica gel adsorbent, four eluant systems have been used, which together with the four different development processes enable the aromatic diamines to be distinguished from one another. The details are shown in Tables I and II. Aliphatic diamines are not detected by these systems. Some aromatic diamines may exhibit more than one spot on the chromatogram, presumably because of the presence of isomers or impurities. This is the case for methylene-bis(aniline), MOCA, and LK 1443; and when only one *R<sub>f</sub>* value is given this refers to the major component. The isomer ratio of

TABLE I  
Thin-Layer Chromatography of Aromatic Diamines

No.	Diamine	<i>R<sub>f</sub></i> in eluant <sup>d</sup>			
		EI	EII	EIII	EIV
1	2,4-Toluenediamine	0.36	0.43	0.30	0.18
2	2,6-Toluenediamine	0.43	0.63	0.47	0.24
3	Methylene-bis(aniline)	0.40	0.55	0.39	0.20
4	1,5-Naphthalenediamine	0.47	0.60	0.52	0.39
5	<i>p</i> -Phenylenediamine	0.22	0.51	0.31	0.08
6	<i>m</i> -Phenylenediamine	0.36	0.41	0.30	0.07
7	<i>o</i> -Phenylenediamine	0.40	0.44	0.35	0.19
8	MOCA <sup>a</sup>	0.58	0.66	0.61	0.52
9	Dichlorobenzidine	0.58	0.64	0.57	
10	<i>o</i> -Tolidine	0.53	0.70	0.59	0.35
11	LK 1443 <sup>b</sup>	0.53	0.54	0.40	0.30
		0.58	0.72	0.58	0.37
		0.64	0.81	0.68	0.46
			0.93	0.82	0.48
12	LD 813 <sup>c</sup>	0.44	0.56	0.37	0.33
		0.51	0.61	0.43	0.54
		0.55	0.70	0.50	
		0.62	0.78	0.56	
				0.70	

<sup>a</sup> Methylene bis(*o*-chloroaniline).

<sup>b</sup> Diethyl tolylenediamine, commercial sample; only major spots recorded.

<sup>c</sup> Modification of MOCA, commercial sample.

<sup>d</sup> EI, Toluene-pyridine 40:10; EII, methylene dichloride-cyclohexane-diethylamine 30:15:5; EIII, cyclohexane-ethyl acetate-diethylamine 25:20:5; EIV, toluene-acetone-0.880 ammonia 40:10:2.

TABLE II  
Color Reactions for Aromatic Diamines<sup>a</sup>

Diamine no. <sup>b</sup>	Eluant and developer combination <sup>c</sup>						
	EI	EIII	EII	EIII	EIV	EIV	EIV
	+ RI	+ RI	+ RII	+ RII	+ RIII A	+ RIII B	+ RIII C
1	bl	—	r	r	br y	bl	bl
2	bl	—	y	y	y	bl	bl
3	br	—	or	or	v	v	or
4	v	—	v	v	ygr	g	v
5	or	—	v	v	v	m	m
6	bl	—	or	or	y	bl	m
7	ybr	—	bl gr	r	br	y	y
8	br (sd)	—	—	—	none	br (p)	or
9	br (sd)	—	—	—	—	—	—
10	br (sd)	—	—	—	gr (p)	gr (p)	or
11	bl	bl	br (p)	br (p)	y	vgr	y
	y	bl	br (p)	br (p)	y	ygr	y
	y	bl	y	br (p)	y	ygr	y
	—	bl	y	br (p)	y	ygr	y
12	g	—	r	r	none	br	br
	v	—	r	r	none	br	br
	g	—	r	r	—	—	—
	br	—	r	r	—	—	—
	—	—	—	r	—	—	—

<sup>a</sup> Key to colors: bl, blue; br, brown; v, violet; y, yellow; r, red; or, orange; gr, green; m, mauve; g, grey; (p), pale color; (sd), slowly develops. This list of colors is intended only as a guide; variation in shade will occur in practice.

<sup>b</sup> Amines numbered as in Table I.

<sup>c</sup> Color developing reagents: RI, 2,6-dibromo-*p*-benzoquinone-4-chlorimine (called chlorimine below), 1% solution in toluene; RII, 1,2-naphthoquinone-4-sulfonic acid, sodium salt, 1% solution in 50% aqueous isopropanol (chromatograms eluted in EI are sprayed with a solution of 10% diethylamine in toluene after RII); RIII, consists of reagents A, B, and C used successively: A, 5 ml collidine, 5 ml glacial acetic acid, 95 ml isopropanol, 0.3 g ninhydrin (triketo hydrindene hydrate) (spray and heat after drying in air for 15 min); B, 0.1% chlorimine in toluene; C, 4% 1,2-naphthoquinone-4-sulfonic acid in 50% aqueous isopropanol. In addition, all the aromatic amines may be detected as spots of inhibited fluorescence when the eluted chromatogram prepared from silica gel PF 254/366 is viewed under ultraviolet radiation in a darkroom after removal of residual solvent.

toluene diisocyanate used in polyurethane manufacture may be determined in this way. The amine fraction from the hydrolysis is chromatographed on silica gel PF254/366, using eluant EII (see Table I). After elution, the positions of the 2,4- and 2,6-isomers are located by viewing the plate under an ultraviolet lamp and the appropriate zones of adsorbent are separately removed from the plate and extracted with isopropyl alcohol. The solutions obtained are diluted to a known volume and examined by ultraviolet spectroscopy. From the absorption and the extinction coefficients, the relative concentrations and hence the isomer ratio may be calculated.

The extinction coefficients  $E_{1\text{ cm}}^{1\%}$  at 290  $m\mu$  are 256 and 135 for 2,4-toluenediamine and 2,6-toluenediamine, respectively.

### Aliphatic Diamines

Aliphatic diamines are examined as the hydrochlorides on silica gel, using a freshly prepared mixture of 20 parts acetone-30 parts ether-2 parts ammonia (0.880) as the eluting solvent. After elution the plate is dried in air for 5 min and in a 100°C oven for a further 5 min and then sprayed with Draggendorff reagent<sup>4</sup> (Munier modification<sup>5</sup>). Methylene-bis(cyclohexylamine) (from Hylene W or Desmodur M) gives two orange/brown

TABLE III  
Thin-Layer Chromatography of Aliphatic Diamines\*

Amine	<i>R<sub>f</sub></i>	Color
HMDA	0.30	pale purple
MBCHA	0.45	orange/brown
	0.55	

\* Adsorbent, silica gel G; eluant, acetone/ether/0.880 ammonia 20:30:2; reagent, basic bismuth nitrate/tartaric acid (see Kirchner<sup>4</sup> and Munier<sup>5</sup>); HMDA, hexamethylenediamine; MBCHA, methylene-bis(cyclohexylamine).

spots at 0.45 and 0.55 whereas hexamethylene diamine (from hexamethylene diisocyanate) gives a rather pale purple spot of *R<sub>f</sub>* about 0.30. (Hylene W and Desmodur M are both dicyclohexyl methane diisocyanate.) These *R<sub>f</sub>* values are not very reproducible owing to the variable nature of the eluant. Aromatic diamines appear to travel with the solvent front in this treatment (Table III).

### Examination of Diols by Thin-Layer Chromatography

The application of TLC to diol examination is limited by the lack of selective spray reagents, although 1,2-diols may be picked out by use of periodate/rosaniline reagent.<sup>6</sup> Alumina and silica adsorbents have been found effective, although the separations are not always adequate and for this reason more than one system of separation is preferred. Chromic acid spray reagent is ineffective when eluting solvents such as acetic acid become bound to the adsorbent. The periodate/rosaniline reagent gives purple spots on a pink background, irrespective of the identity of the 1,2-diol, and appears to be more effective on silica than on alumina. Details are given in Table IV.

### Examination of Diols by NMR Spectroscopy

Often the characterization of a mixture of diols may be very difficult by infrared spectroscopy, but NMR spectroscopy can be much more useful in their identification. The most suitable system is to dissolve the diols in

pyridine containing a trace of tetramethyl silane (TMS) as an internal reference standard. The chemical shifts are given in Table V, together with indications of the types of signals.

TABLE IV  
Thin-Layer Chromatography of Diols and Triols\*

Diol or Triol	<i>R<sub>f</sub></i>				
	I	II	III	IV	V
Ethylene glycol	0.36	0.36	0.24	0.25	0.25
1,2-Propanediol	0.51	—	0.33	—	0.44
1,4-Butanediol	0.45	0.53	0.48	—	—
Diethylene glycol	0.27	0.29	0.1T <sup>b</sup>	—	—
Triethylene glycol	0.20	0.20	0.15T	—	—
1,6-Hexanediol	0.60	0.64	—	0.30	—
1,2,6-Hexanetriol	0.27	0.23	—	—	0.15
1,1,1-Trimethylol propane	0.48	0.56	0.15	—	—
Neopentyl glycol	0.68	0.77	—	0.43	—
Dipropylene glycol	0.49	0.57	—	0.20	—
2,2,4,4-Tetramethyl-1,3-cyclobutanediol	0.89	—	—	0.71	—
Glycerol	—	—	—	—	0.07

\* I, Silica gel PF, ethyl acetate-acetone 50:50; II, silica gel PF, diethyl ether-methanol 90:10 (Mulder<sup>1</sup>); III, alumina G, ethyl acetate, three runs; IV, silica gel PF, ethyl acetate; V, alumina G, chloroform-toluene-acetic acid 77:17:6; periodate rosaniline spray (Conacher and Rees<sup>6</sup>). The adsorbents were used as 0.3-mm thick layers activated for 1 hr at 110°C. With the exception of V, the spots were revealed by a chromic acid spray followed by heating at 110°C.

<sup>b</sup> T indicates "tailing."

TABLE V  
NMR Data for Diols and Triols (Chemical Shift in  $\tau$  Values)\*

Diol or Triol	CH—O	CH <sub>2</sub> —O	CH <sub>2</sub>	CH <sub>3</sub>
Ethylene glycol		6.05 (s)		
1,2-Propanediol	5.88	6.22 (d)		8.68 (d)
1,3-Propanediol		6.02 (t)	7.97	
1,4-Butanediol		6.18	8.16	
2,3-Butanediol	6.04			8.59
1,3-Butanediol	5.8	5.99 (t)	8.06	8.68 (d)
Neopentyl glycol		6.27 (s)		8.92 (s)
2,2,4,4-tetramethyl-1,3-cyclobutanediol	6.2			8.7
1,1,1-Trimethylol propane		6.03 (s)	8.25	8.97 (t)
1,6-Hexanediol		6.24	8.47	
1,2,6-Hexanetriol	6.1	6.2	8.23	
2-Methyl-2,4-Pentanediol	5.65			8.2-8.8

\* s = singlet; d = doublet; t = triplet. Multiple absorptions in other cases.

Diethylene glycol and triethylene glycol not really distinguishable from ethylene glycol. Spectra were obtained on a Perkin-Elmer R 10 instrument operating at 60 Mc/s.

### Examination of Diols by Gas Chromatography

Gas chromatographic examination of diol mixtures may be carried out directly, using a special type of column packing—Porapak Q. Diols and triols obtained from the hydrolysis of polyurethanes may be applied in acetone solution. Details and results are shown in Table VI.

TABLE VI  
Gas Chromatographic Data for Diols and Triols<sup>a</sup>

Diol or Triol	Retention time, min
Ethylene glycol	5.6
1,2-Propanediol	8.0
1,3-Propanediol	11.2
2,3-Butanediol	11.5
1,3-Butanediol	14.3
1,4-Butanediol	17.5
2,2-Dimethyl-1,3-propanediol	18.9
Glycerol	19.1
Diethylene glycol	19.8
2-Methyl-2,4-pentanediol	20.7
Dipropylene glycol	25.8
2,2,4,4-Tetramethyl-1,3-cyclobutanediol	29.0
1,6-Hexanediol	29.6
Triethylene glycol	33.5
1,1,1-Trimethylol propane	34.4
1,2,6-Hexanetriol	35.9

<sup>a</sup> Chromatograph, Perkin-Elmer 800; column, 1 m × 2 mm i.d. (stainless steel); packing, Porapak Q (Waters Associates Inc.) 50–80 mesh; column temperature program, 140°–250°C at 3.3°/min then isothermally at 250°C; carrier gas and flow, nitrogen at 30 ml/min (outlet); detector: flame ionization.

### CONCLUSIONS

The use of the methods described here have given satisfactory analyses of many types of foams and other samples of polyurethanes carried out over the past few years.

Our thanks are due to our colleagues J. Blenkin, B. W. Mapperley, R. K. Smith, and D. W. Skidmore for their assistance in this work.

### References

1. J. L. Mulder, *Anal. Chim. Acta*, **38**, 563 (1967).
2. P. J. Corish, *Anal. Chem.*, **31**, 1298 (1959).
3. J. Haslam and H. A. Willis, *Identification and Analysis of Plastics*, Illife Books, London, 1965, p. 112.
4. J. J. Kirchner, *Thin-Layer Chromatography*, in *Techniques of Organic Chemistry*, Vol. XII, Interscience, New York, 1967, p. 160.
5. R. Munier, *Bull. Soc. Chim. Biol.*, **35**, 1225 (1953).



6. H. B. S. Conacher and D. I. Rees, *Analyst*, **91**, 55 (1966).

For additional information see also:

7. O. L. Hollis, *Anal. Chem.*, **38**, 309 (1966).
8. J. D. Burger, *J. Gas Chromatog.*, **6**, 177 (1968).
9. A. Mathias and N. Meller, *Anal. Chem.*, **38**, 472 (1966).
10. A. Bassl, H.-J. Heckemann, and E. Baumann, *J. Chromatog.*, **36**, 4, D79 (1968).
11. D. Braun and E. Mai, *Kunststoffe*, **58**, 637 (1968).

Received March 27, 1969

Revised July 18, 1969