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TECHNICAL REPORT No. 53

**Relationships between Polyurethane Elastomer
Structure and Ageing Properties: Part 2:
Effect of Backbone Polyol**

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D Sims
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by

B E Brokenbrow
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SUMMARY

The effects of varying the backbone polyol on the properties of polyurethane elastomers have been investigated.

Unaged polyester urethanes, especially those based on polyethylene and polybutylene adipates (mol wt 2000), were generally tougher but considerably less resistant to hydrolysis than polyurethanes prepared from polyethers of similar molecular weights. Low molecular weight polyols (650 - 1260) led to more highly crosslinked elastomers with improved tensile strength, modulus, hardness, but with reduced flexibility.

Elastomers based on hydroxyl-terminated polybutadiene urethanes, and to a lesser extent polyoxybutylene glycol urethanes (mol wt 1300), showed the best resistance to hydrolysis at 80°C, while those based on polydiethylene adipate (mol wt 1000) and polyoxypropylene glycol (mol wt 1250) showed the best resistance to petrol (STP) at 65°C.

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Reference: WAC/207/034

1 INTRODUCTION

The effects of changes in the chemical structure of polyurethanes are being studied in order that elastomers possessing a satisfactory balance between resistance to ageing and initial mechanical properties may be prepared.

The first report of the present series¹ described the effect of varying the degree of crosslinking on the ageing properties of a typical polyether and a polyester urethane elastomer. It was shown that while unaged polyester urethanes gave the best mechanical properties, polyether urethanes showed superior hydrolytic stability. Optimum ageing properties were obtained with relatively highly crosslinked elastomers of M_c values (molecular weight per branch link) of about 2000.

The present investigation considers the effects of varying the backbone polyol on the ageing properties of polyurethane elastomers, using a variety of polyether and polyester polyols of molecular weights 650 - 2000 in toluene di-isocyanate (TDI) prepolymers crosslinked with 1,1',1''-trimethylol propane (TMP). In addition, a hydroxyl-terminated polybutadiene urethane elastomer, which had previously shown outstanding hydrolytic stability but rather poor resistance to petrol,² together with a hydroxyl-terminated polybutadiene-polyether blend, were assessed for comparison.

2 MATERIALS AND METHODS OF PREPARATION

All the elastomers were prepared via TDI prepolymers using the polyester, polyether and hydroxyl-terminated polybutadiene resins (acid number < 0.5 , H_2O content < 0.02 , average molecular weight 650 - 2000) listed in Table 1.

The polyols, which were either prepared in the laboratory or obtained from commercial sources, 1.0 mole equivalent were reacted with 2.1 moles equivalent TDI (toluene di-isocyanate, Hylene ex-Du Pont UK, an 80/20 mixture of 2,4 and 2,6 isomers) to give prepolymers containing 4.0 - 12.5 per cent free NCO and crosslinked with 0.66 moles equivalent of TMP (pure distilled). The methods of preparation are described in Appendix A.

TABLE 1

Elasto- mer Code No	Type	Backbone Polyol	Average Molecular Weight	Source of Polyol
S 20	Adipate Ester	Ethylene adipate	1000	Fomrez ex-Witco Chemical Co
S 22		Ethylene adipate	2000	" " "
S 23		Diethylene adipate	1000	" " "
S 23A		Diethylene adipate	2000	" " "
S 24		Propylene adipate	2000	" " "
S 25		Butylene adipate	2000	" " "
S 21	Mixed Adipate Ester	(Ethylene adipate (70%) (Propylene adipate (30%)	2000	Laboratory prepared
S 27		(Butylene adipate (70%) (Propylene adipate (30%)	2000	" "
				" "
S 33	Caprolactone Ester	ϵ -caprolactone/ diethylene glycol	2000	" "
S 30	Polyether	Polyoxypropylene glycol	1200	Union Carbide (UK) Ltd
S 26		Polyoxypropylene glycol	2000	" "
S 29		Polyoxybutylene glycol	650	'Polymeg' Quaker Oats Co
S 31		Polyoxybutylene glycol	1300	" " "
S 28		Polyoxybutylene glycol	2000	" " "
S 32A	Hydroxyl- terminated polybutadiene	R 15M		**Sinclair Petrochemicals
*S 32	Polyether- polybutadiene blend	R 15M 50%) Polycybutylene) Glycol 50%)	2250	**Sinclair Petrochemicals Quaker Oats Co

*Chain extended with 2-ethyl hexyl diol not crosslinked with TMP

**now Arco Chemical Co

3 EXPERIMENTAL

British Standard type C dumb-bell test pieces (four per test) were cut from the cast sheets and the width and thickness measured before exposure to the test conditions. Dumb-bells, in sets of four, were suspended in loosely stoppered glass tubes and exposed to some or all of the following environments for 28 days.

Controls	Conditioned in air at 20°C
Hot/dry	Suspended in air at 80°C
Hot/wet	Immersed in boiled out distilled water at 80°C
*Standard Test Fluid	Immersed in dry Standard Test Fluid at 65°C

The charged tubes were placed in circulating air ovens in which the temperatures did not vary by more than $\pm 0.5^\circ\text{C}$ from the test temperature. After 28 days' exposure the tubes and contents were removed from the oven and conditioned at room temperature for 24 hours before testing. After the conditioning period, the groups of four specimens were removed from the tubes, dried from any superficial liquid, and tested for hardness, moduli, extension at break and tensile strength as quickly as possible. Hardness was measured using a micro-indentometer, and the tensile properties were measured by British Standard Methods^{3,4} on a Hounsfield Tensometer. Unaged control specimens cut from the materials were tested by the same methods, and the results used as "unaged" reference points.

4 RESULTS AND DISCUSSION

The visual appearances of the elastomers before and after ageing are recorded in Table 7, Appendix B.

The mechanical properties after ageing are recorded in Table 8, Appendix B and the percentage changes in the original mechanical properties of the elastomers in Tables 4, 5 and 6.

4 1 Visual Appearance

The general condition of the urethane elastomers, both unaged and after ageing in water, STF and dry air, judged by visual and empirical methods of assessment and summarized in Table 7, Appendix B, are described below.

4 1 1 Initial Appearance

All the polyester urethane elastomers, apart from those based on polybutylene adipate and ϵ -caprolactone/glycol polyester which were slightly opalescent, were clear and colourless. Elastomers based on polyethylene and polybutylene

*Standard Test Fluid (STF) consists of a 70/30 v/v mixture of iso-octane and toluene, and is intended to represent a standard "medium to high aromatics" content petrol.⁵

adipates and ϵ -caprolactone were tough and flexible, while those based on poly-diethylene, propylene, ethylene/propylene and butylene/propylene adipate, while appearing to be less tough, were equally flexible.

Elastomers based on polyoxypropylene glycol were slightly opalescent, while those based on polyoxybutylene glycol were transparent but slightly yellow. The polyether elastomers appeared to be equally flexible as the polyester based elastomers but rather less tough; a notable exception was an elastomer based on a low molecular weight (650) polyoxybutylene glycol (S 29) which was tough and rigid. Elastomers based on an hydroxyl-terminated polybutadiene/polyoxybutylene glycol blend (S 32) were yellow, moderately tough and flexible.

4 1 2 Exposure to Dry Air

All the polyester elastomers, apart from slight stiffening, appeared to be little affected by 28 days' exposure to dry air at 80°C, although all, with the exception of those based on polyethylene adipate, showed some yellowing.

Similarly polyether based elastomers, apart from showing rather more yellowing than the polyesters, appeared to be little affected by exposure to dry air. The elastomer based on a hydroxyl-terminated polybutadiene/polyether blend (S 32) showed considerable yellowing.

The yellowing of polyurethanes in the presence of oxygen is apparently governed by the oxidative processes of the products of degradation of the urethane groups. It is believed^{6,7} that the thermal degradation of polyurethanes based on TDI takes place, like photolysis, at the -N-C- bonds with the evolution of CO₂ and the formation of amino groups, the oxidation of which leads to discolouration.

4 1 3 Water Immersion

After 28 days' immersion in water at 30°C all the polyester based urethane elastomers showed catastrophic failures and rapidly disintegrated into brown viscous liquids, their behaviour being identical to elastomers based on polybutylene adipate previously examined.¹ This shows that variations of chemical structure of polyester polyols have little effect on the hydrolytic stability of polyurethane elastomers under these admittedly drastic conditions of test.

On the other hand, polyether and polyether/hydroxyl-terminated polybutadiene based elastomers did not appear to be seriously affected by water immersion, those based on polyoxybutylene glycol being slightly better than those based on polyoxypropylene glycol.

4 1 4 STF (Petrol) Immersion

After 28 days' immersion in petrol at 65°C both polyester and polyether urethane elastomers appeared to be in fairly good condition. During the

immersion period the polyether urethanes were rather more swollen than polyester elastomers but they rapidly recovered to their original dimensions after conditioning for 24 hours at room temperature.

Elastomers based on polydiethylene and polybutylene adipate, ϵ -caprolactone/glycol polyester and polyoxybutylene glycol showed the most discolouration.

4 2 Mechanical Properties

The mechanical properties of the elastomers before and after ageing are recorded in Table 8, Appendix B.

4 2 1 Initial Properties

There were considerable variations in the initial mechanical properties of urethane elastomers of similar crosslink density (Table 2). Tensile strengths varied from 1 - 30 MN/m² and in descending order of strength were those prepared from: polyethylene adipate, polybutylene adipate, ϵ -caprolactone/glycol polyester, mixed polyethylene and polybutylene/polypropylene adipates, hydroxyl-terminated polybutadiene/polyoxybutylene glycol blend, polyoxybutylene glycol, polydiethylene adipate and polyoxypropylene glycol.

Extensions at break varied from 165 per cent for elastomers based on polydiethylene adipate to around 350 per cent for those based on polyethylene adipate, ϵ -caprolactone/glycol polyester and a hydroxyl-terminated polybutadiene/polyether blend; the majority of polyether elastomers gave extension at break values of 180 - 225 per cent while the remainder of the polyester elastomers gave values of 250 - 300 per cent.

In general, polyester based urethane elastomers gave higher hardness values, 70 - 90 BS⁰, and 100 per cent moduli, 1.0 - 2.8 MN/m², than the polyethers which gave values of 45 - 75 BS⁰ and 0.5 - 2.5 MN/m² respectively. The elastomer giving the highest hardness and 100 per cent modulus was S 25 based on polybutylene adipate which gave a value of 88 BS⁰ and 2.8 MN/m², while S 26 based on polyoxypropylene glycol gave the lowest values, 46 BS⁰ and 0.5 MN/m². Elastomers prepared from mixed polyester adipates, in general, provided a compromise between the properties of elastomers based on the individual polyesters.

The high tensile strength of urethanes based on polyethylene adipate is attributable to its ability to undergo reversible oriented crystallisation under stress,⁸ therefore the higher mechanical strength of urethane elastomers based on crystalline or potentially crystallisable polymer intermediates is usually higher than that of elastomers based on amorphous polymers. The inferior tensile strength of elastomers prepared from polyoxypropylene glycol compared to polyoxybutylene glycol and most adipate esters is attributed to their irregular chain structure and lack of reversible crystallinity on extension and may also be due to the fact that about 4 per cent of the end groups of polyoxypropylene glycol of molecular weight 2000 are terminal olefinic groups which are unreactive towards isocyanates.

TABLE 2

EFFECT OF VARIATION OF BACKBONE POLYOLS (MOL WT 2000)
ON PROPERTIES OF UNAGED POLYURETHANE ELASTOMERS

Type	Code No	Backbone Polyol	Tensile Strength (MN/m ²)	Extension at break (%)	Modulus MN/m ² at 100% extension	Hardness BS ^o
Polyester	S 22	Ethylene adipate	24.9	350	1.9	71
	S 23A	Diethylene adipate	2.0	165	1.3	70
	S 24	Propylene adipate	4.8	265	0.9	65
	S 25	Butylene adipate	19.0	300	2.8	88
	S 21	Ethylene/propylene adipate	12.2	300	1.1	72
	S 27	Butylene/propylene adipate	8.4	300	1.3	73
	S 33	ϵ -caprolactone/diethylene glycol	14.1	350	0.8	69
Polyether	S 26	Polyoxypropylene glycol	0.8	210	0.5	46
	S 28	Polyoxybutylene glycol	3.0	225	2.0	71
OH terminated Polybutadiene/ Polyether	S 32	Hydroxyl-terminated polybutadiene/ polyoxybutylene glycol	5.6	365	0.8	61
OH terminated Polybutadiene	S 32A	Hydroxy-terminated polybutadiene	7.1	265	3.5	81

Note 1 MN/m² = 143 lbf/in²

The effects of reducing the molecular weight of the polyol backbone of urethane elastomers are shown in Table 3. The general effects on the mechanical properties of the unaged elastomers were as follows. With the exception of polyethylene adipate based urethanes, where reduction of molecular weight from 2000 to 1000 had little effect on the properties of the elastomer, tensile strength, modulus and hardness increased while extension at break, with exception of urethane based on polydiethylene adipate, decreased.

As mentioned above polyester based urethanes, because of their higher molar cohesive energies are generally stronger than polyether based elastomers of

equivalent average molecular weight. Polyether based urethanes, using low molecular weight polyoxybutylene glycol of average molecular weight could give elastomers of similar ultimate tensile strengths although at the expense of a reduction in elongation at break. It is worth noting however that the form of the stress strain curve for polyethers would be quite different to that normally associated with polyesters.

TABLE 3

EFFECT OF VARYING THE MOLECULAR WEIGHT OF DIFFERENT BACKBONE POLYOLS ON THE PROPERTIES OF UNAGED POLYURETHANE ELASTOMERS

Type	Code No	Backbone Polyol	Average Mol Wt	Tensile Strength (MN/m ²)	Extension at break (%)	Modulus MN/m ² at 100% extension	Hardness BS ⁰
Polyester	S 20	Ethylene adipate	1000	23.8	250	2.8	67
	S 22	Ethylene adipate	2000	24.9	350	1.9	71
	S 23	Diethylene adipate	1000	8.6	190	3.1	74
	S 23A	Diethylene adipate	2000	2.0	165	1.3	70
Polyether	S 30	Polyoxypropylene glycol	1200	3.7	180	1.5	66
	S 26	Polyoxypropylene glycol	2000	0.8	210	0.5	46
	S 29	Polyoxybutylene glycol	650	24.7	150	12.6	81
	S 31	Polyoxybutylene glycol	1300	4.5	190	3.3	75
	S 28	Polyoxybutylene glycol	2000	3.0	225	2.0	71

4 2 2 Ageing in Dry Air

After 28 days' exposure to dry air at 80°C practically all the polyurethane elastomers showed increases in tensile strength and extension at break (Table 4). The elastomers showing the least change were those based on polyethylene adipate. The majority of elastomers of average molecular weight 2000 showed losses of 100 per cent modulus and hardness whereas the lower molecular weight elastomers gave increased values for hardness and 100 per cent modulus.

TABLE 4

EFFECT OF AGEING IN DRY AIR AT 80°C ON PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS BASED ON DIFFERENT BACKBONE POLYOLS OF VARYING MOLECULAR WEIGHT

Type	Code No	Backbone polyol	Average Molecular Weight	Percentage change of original mechanical property			
				Tensile Strength	Extension at break	100% Modulus	Hardness
Polyester	S 20	Ethylene adipate	1000	+ 29	- 4	+95	+13.5
	S 22	Ethylene adipate	2000	+ 30	- 2.5	+ 5	- 3
	S 23	Diethylene adipate	1000	+ 90	+12.1	+20.4	+ 3.0
	S 23A	Diethylene adipate	2000	+ 5	+23	-28	- 4.5
	S 24	Propylene adipate	2000	+ 23	+11	-24	- 2
	S 25	Butylene adipate	2000	+ 4	+13	-66	-24
Polyether	S 21	Ethylene/propylene adipate	2000	+ 73	+11.5	-18	- 3
	S 27	Butylene/propylene adipate	2000	- 24	+ 3	-62	-12
	S 33	ϵ -caprolactone/diethylene glycol	2000	+ 10.5	+11.5	+60.5	-17.5
	S 30	Polyoxypropylene glycol	1200	+113.0	+43.0	+13	- 9
	S 26	Polyoxypropylene glycol	2000	+ 16.5	+16.0	-42	- 8.5
	S 29	Polyoxybutylene glycol	650	+ 16.0	+10.0	+25.5	0
Polybutadiene	S 31	Polyoxybutylene glycol	1300	+ 52.5	+21	-54	-2.7
	S 28	Polyoxybutylene glycol	2000	- 35	+14	-43	-6
	S 32	Hydroxyl-terminated polybutadiene/polyoxybutylene glycol	2000	- 5.5	-12.5	+50	-3

4 2 3 Water Immersion

After 28 days' immersion in water at 80°C (Table 5) it was impossible to determine the physical properties of the polyester urethane elastomers due to their catastrophic failures. The polyether urethanes were in fair condition; S 31 based on polyoxybutylene glycol showed a loss in tensile strength of 42 per cent and S 26 based on polyoxypropylene glycol showed a loss of tensile strength of 25 per cent. These materials were however inferior to S 32A a hydroxyl-terminated polybutadiene urethane which was virtually unaffected by water. S 32, a hydroxyl-terminated polybutadiene/polyether urethane blend, was not so satisfactory as when these polyols were used alone in urethane elastomers.

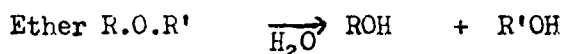
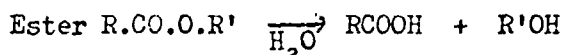
TABLE 5

EFFECT OF IMMERSION IN WATER AT 80°C ON PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS BASED ON DIFFERENT BACKBONE POLYOLS OF VARYING MOLECULAR WEIGHT

Type	Code No	Backbone polyol	Average Molecular Weight	Percentage change of original mechanical property			
				Tensile Strength	Extension at break	100% Modulus	Hardness
Polyester	S 20	Ethylene adipate	1000	All disintegrated into brown viscous liquids			
	S 22	Ethylene adipate	2000				
	S 23	Diethylene adipate	1000				
	S 23A	Diethylene adipate	2000				
	S 24	Propylene adipate	2000				
	S 25	Butylene adipate	2000				
	S 21	Ethylene/propylene adipate	2000				
	S 27	Butylene/propylene adipate	2000				
Polyether	S 33	ϵ -caprolactone/diethylene glycol	2000				
	S 30	Propylene glycol ether	1200	-78	+65	-	-47
	S 26	Propylene glycol ether	2000	-25	+43	-60	-35
	S 29	Polyoxybutylene glycol	650	-68	+31	-84	-9
	S 31	Polyoxybutylene glycol	1300	-42	+11	-70	-12
	S 28	Polyoxybutylene glycol	2000	-92	+97	-55	-10
	S 32A	Hydroxyl-terminated polybutadiene	2400	0.0	-4	+6	-4.0
	S 32	Hydroxyl-terminated polybutadiene/polyoxybutylene glycol	2000	-77	-11	-50	-26

With polyether urethane elastomers a reduction in molecular weight of the backbone polyol led to a corresponding loss of hydrolytic stability which suggests that although crosslink density is increased, a high concentration of urethane groups is detrimental to the hydrolytic stability of polyether urethanes.

In comparing the hydrolytic stability of polypropylene and polybutylene adipate based elastomers with polyoxypropylene and polyoxybutylene glycols (Table 5) it would appear that the inferior hydrolytic stability of the polyesters is due to their acidity.



It is likely that the hydrolysis of ester groups is autocatalysed by the carboxylic group formed on hydrolysis. Adipic acid released on hydrolysis causes autocatalytic decomposition and by using a water immersion test, as in the present investigation, no removal of decomposition products is possible as would be the case when ageing tests are made in conditions of high humidity.

Recent patents⁹ describe polyurethane elastomers which it is claimed possess outstanding hydrolytic stability and were relatively unaffected by 21 days in water at 70°C (however the patent does not make it clear as to whether the elastomers were immersed in water or aged in humid air). The polyurethanes were prepared by ester exchange between diethyl adipate and 1,4-butylene glycol and reacted with diphenyl methane di-isocyanate and had acid numbers approaching zero. The use of polyester urethanes of this kind will be the subject of further investigation.

In spite of claims to the contrary^{10,11} the hydrolytic stability of S33, a polyurethane based on ε-caprolactone/diethylene glycol polyester, was poor.

4 2 4 Petrol STF Immersion

Many of the elastomers were badly affected by immersion in STF. The elastomers least affected by petrol were based on S 23, polydiethylene adipate (mol wt 1000), and S 30, polyoxypropylene glycol (mol wt 1200). With the polyester urethanes a reduction in the molecular weight of the polyol improved petrol resistance, while for polyoxybutylene glycol urethanes the reverse effect was found. This effect has previously been noted¹ with urethanes of varying degree of crosslinking based on polyoxybutylene glycol.

TABLE 6

EFFECT OF IMMERSION IN PETROL (STP) ON PHYSICAL PROPERTIES OF POLYURETHANE ELASTOMERS BASED ON DIFFERENT BACKBONE POLYOLS OF VARYING MOLECULAR WEIGHT

Type	Code No	Backbone polyol	Average Molecular Weight	Percentage change of original mechanical property			
				Tensile Strength	Extension at break	100% Modulus	Hardness
Polyester	S 20	Ethylene adipate	1000	-76	-32	-7	+12
	S 22	Ethylene adipate	2000	-83	-29	-48	-1
	S 23	Diethylene adipate	1000	-33	-16	-6	+1
	S 23A	Diethylene adipate	2000	-45	-35	-21	-3
	S 24	Propylene adipate	2000	-81	-57	-22	-5
	S 25	Butylene adipate	2000	-86	-37	-64	-25
	S 21	Ethylene/propylene adipate	2000	-85	-50	-18	-4
	S 27	Butylene/propylene adipate	2000	-92	-65	-54	-16
	S 33	ϵ -caprolactone/diethylene glycol	2000	-85	-31	-63	-19
Polyether	S 30	Polyoxypropylene glycol	1200	-16	-56	-	-12
	S 26	Polyoxypropylene glycol	2000	+38	-52	-	-26
	S 29	Polyoxybutylene glycol	650	-79	-30	-62	-2
	S 31	Polyoxybutylene glycol	1300	-55	-58	-	-4
	S 28	Polyoxybutylene glycol	2000	-76	-71	-71	-10
Polybutadiene	S 32	Hydroxyl-terminated polybutadiene/polyoxybutylene glycol	2000	-75	-46	-38	-37

5 CONCLUSIONS

The properties of polyurethane elastomers prepared from toluene di-isocyanate/polyol prepolymers crosslinked with TEP varied considerably, being dependent on the particular backbone polyol used in the preparation of the prepolymer. Similarly, the molecular weights of the backbone polyols had considerable influence on the initial mechanical properties of the elastomers. No single backbone polyol was capable of conferring adequate resistance to the elastomers in all the selected environments.

In general, a decrease in the molecular weight of the backbone polyol led to more highly crosslinked elastomers with improved tensile strengths, modulus and hardness but with reduced flexibility. The more highly crosslinked polyether elastomers were usually the most stable to hydrolysis while the more highly crosslinked polyester urethanes were the more resistant to petrol. None of the elastomers based on polyesters were resistant to water at 80°C.

Elastomers based on polyoxybutylene glycol (mol wt 1300) were the most resistant to hydrolysis ether based materials, but these were rather inferior to elastomers based on hydroxyl-terminated polybutadienes. Attempts to improve the physical properties of hydroxyl-terminated polybutadiene based elastomers by blending with polyethers were not very successful.

Polyurethane elastomers based on polydiethylene adipate (mol wt 1000) and polyoxypropylene glycol (mol wt 1250) gave the best resistance to STF at 65°C. There was no marked difference in the resistance of polyether and polyester urethanes to dry air at 80°C.

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TABLE 7
GENERAL CONDITION AND APPEARANCE OF POLYURETHANE ELASTOMERS

Code No.	Elastomer and average molecular weight	Unaged	Water 28 days at 80°C	Dry Air 28 days at 80°C	STF 28 days at 65°C
S 20	Ethylene adipate	(transparent) tough and flexible	catastrophic failure, brown viscous liquid	(transparent) tough	(transparent) tough, slightly rigid
S 22	Ethylene adipate	- ditto -	catastrophic failure, amber viscous liquid	(transparent) tough	(transparent) tough, slightly rigid
S 23	Diethylene adipate	(transparent) fairly tough and flexible	catastrophic failure, dark brown viscous liquid	(slightly yellow) tough	(very slight yellowing) tough, slightly rigid
S 23A	Diethylene adipate	- ditto -	catastrophic failure, brown viscous liquid	(slightly yellow) slightly brittle	(very slight yellowing) tough, slightly rigid
S 24	Propylene adipate	- ditto -	catastrophic failure, dark brown viscous liquid	(slightly yellow) flexible	(transparent) weak, flexible
S 25	Butylene adipate	(opalescent, slightly yellow) tough and flexible	catastrophic failure, rubbery dark brown viscous liquid	(pale yellow) rigid	(slightly yellow) tough and flexible
S 26	Ethylene/propylene adipate 7:3	(transparent) fairly tough and flexible	catastrophic failure, brown viscous liquid	(transparent) flexible	(transparent) flexible
S 27	Butylene/propylene adipate 7:3	(very slightly opalescent) fairly tough and flexible	catastrophic failure, dark brown viscous liquid	(pale yellow) fairly tough	(very slight yellowing) flexible
S 33	ε-caprolactone/diethylene glycol	(slightly opalescent) tough and flexible	catastrophic failure, rubbery dark brown viscous liquid	(opalescent deep yellow) rigid	(slightly yellow) tough, flexible

POLYESTER

16.1

16.2

16.3

METHODS OF PREPARATION

 ϵ -Caprolactone/Glycol Polyester

Pure redistilled anhydrous ethylene glycol, 40.1 g. and dibutyl tin dilaurate, 1.6 g, were heated to 50°C in a three-necked glass flask equipped with thermometer, stirrer, nitrogen-inlet, and equalising pressure dropping funnel to 150°C. ϵ -Caprolactone (pure), 1250 g, and dibutyl tin dilaurate, 3.2 g, were added over 1½ hours and the temperature of the mixture was allowed to rise to 160°C. Heating was continued under nitrogen with continuous stirring at 180 - 185°C for two hours. The acid number of the polymer was 0.73 and the hydroxyl number 49.2 giving an average molecular weight of 2200

Elastomers S 20 - S 33

All the elastomers were prepared via prepolymers as follows.

Toluene di-isocyanate (TDI), 2.1 mole equivalent, was placed into a dried 500 ml glass three-necked flask equipped with thermometer stirrer, nitrogen and vacuum-inlet and heated to 80°C under nitrogen. Melted polyol, 1.0 mole equivalent, previously degassed by heating to 120 - 125°C for 30 minutes and applying a vacuum of 1 mmHg* was added to the TDI over a period of 30 minutes. The mixture was heated under nitrogen with continuous stirring at 80 - 85°C for 3 hours; during the last 30 minutes a vacuum of 1 mmHg was applied.

The TDI prepolymer was transferred to a dried 600 ml beaker and degassed under 1 mmHg vacuum for 10 minutes. 1,1',1''-Trimethylol propane, 0.66 mole equivalent, was stirred into the prepolymer. The mixture was reheated to 80°C and degassed for 10 - 15 minutes at 1 mmHg.

The reaction products were poured into PTFE coated aluminium trays and cured in an oven for 16 h at 90°C to produce sheets 220 x 150 mm approximately 2.5 mm thick.

*1 mmHg = 133.322 N/m²

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TABLE 7

GENERAL CONDITION AND APPEARANCE OF POLYURETHANE ELASTOMERS

	Code No	Elastomer and average molecular weight	Unaged
POLYESTER	S 20	Ethylene adipate 1000	(transparent) to and flexible
	S 22	Ethylene adipate 2000	- ditto -
	S 23	Diethylene adipate 1000	(transparent) fairly tough and flexible
	S 23A	Diethylene adipate 2000	- ditto -
	S 24	Propylene adipate 2000	- ditto -
	S 25	Butylene adipate 2000	(opalescent, slightly yellow) tough and flexible
	S 21	Ethylene/propylene adipate 7:3 2000	(transparent) fairly tough and flexible
	S 27	Butylene/propylene adipate 7:3 2000	(very slightly opalescent) fairly tough and flexible
	S 33	ϵ -caprolactone/diethylene glycol 2000	(slightly opalescent) tough and flexible

16.1

ELASTOMERS

and weight	Unaged	Water 28 days at 30°C	Dry Air 28 days at 80°C	28
1000	(transparent) tough and flexible	catastrophic failure, brown viscous liquid	(transparent) tough	(transpa slightly
2000	- ditto -	catastrophic failure, amber viscous liquid	(transparent) tough	(transpa slightly
1000	(transparent) fairly tough and flexible	catastrophic failure, dark brown viscous liquid	(slightly yellow) tough	(very sl tough, s
2000	- ditto -	catastrophic failure, brown viscous liquid	(slightly yellow) slightly brittle	(very sl tough, s
2000	- ditto -	catastrophic failure, dark brown viscous liquid	(slightly yellow) flexible	(transpa flexible
2000	(opalescent, slightly yellow) tough and flexible	catastrophic failure, rubbery dark brown viscous liquid	(pale yellow) rigid	(slightl and flex
3	2000 (transparent) fairly tough and flexible	catastrophic failure, brown viscous liquid	(transparent) flexible	(transpa
3	2000 (very slightly opalescent) fairly tough and flexible	catastrophic failure, dark brown viscous liquid	(pale yellow) fairly tough	(very sl flexible
col	2000 (slightly opalescent) tough and flexible	catastrophic failure, rubbery dark brown viscous liquid	(opalescent deep yellow) rigid	(slightl flexible

16.3

APPENDIX B

ged	Water 28 days at 80°C	Dry Air 28 days at 80°C	STF 28 days at 65°C
(t) tough le	catastrophic failure, brown viscous liquid	(transparent) tough	(transparent) tough, slightly rigid
to - ly	catastrophic failure, amber viscous liquid	(transparent) tough	(transparent) tough, slightly rigid
(t) fairly flexible	catastrophic failure, dark brown viscous liquid	(slightly yellow) tough	(very slight yellowing) tough, slightly rigid
to - sl	catastrophic failure, brown viscous liquid	(slightly yellow) slightly brittle	(very slight yellowing) tough, slightly rigid
to - sl	catastrophic failure, dark brown viscous liquid	(slightly yellow) flexible	(transparent) weak, flexible
, slightly gh and	catastrophic failure, rubbery dark brown viscous liquid	(pale yellow) rigid	(slightly yellow) tough and flexible
(t) fairly flexible	catastrophic failure, brown viscous liquid	(transparent) flexible	(transparent) flexible
tly fairly flexible	catastrophic failure, dark brown viscous liquid	(pale yellow) fairly tough	(very slight yellowing) flexible
opalescent) flexible	catastrophic failure, rubbery dark brown viscous liquid	(opalescent deep yellow) rigid	(slightly yellow) tough, flexible

16.3

TABLE 7 cont'd

S 3

Code	Elastomer and average molecular weight	Unaged	Water 28 days at 80°C	Dry Air 28 days at 80°C	STF 28 days at 55°C
S 30	Polyoxypropylene glycol	(slightly opalescent) moderately tough and flexible	(deep amber) slightly swollen, very flexible	(slightly yellow) slightly inflexible	(transparent) tough, flexible
S 26	Polyoxypropylene glycol	- ditto -	(amber) slightly swollen, weak and flexible	(pale yellow) flexible	(transparent) weak, flexible
S 29	Polyoxybutylene glycol	transparent (slightly yellow) tough and rigid	(amber) rigid	(pale yellow) rigid	(very slight yellowing) rigid, inflexible
S 31	Polyoxybutylene glycol	transparent (slightly yellow) moderately tough and flexible	(amber) rigid	(pale yellow) fairly rigid	(very slight yellowing) rigid, inflexible
S 28	Polyoxybutylene glycol	- ditto -	(deep amber) brittle	(pale yellow) tough	(very slight yellowing) tough, flexible
S 32	Hydroxyl-terminated polybutadiene/ Polyoxybutylene glycol ether 1:1	(lemon yellow) moderately tough and flexible	(yellow) tough	(amber) tough	(deep amber) slightly swollen, flexible

POLYMER

BUTADIENE

17.1

17.2

17.3

TABLE 8

MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS BEFORE AND AFTER TWENTY-EIGHT DAYS' AGEING

Code No	Polyol Type	Av Mol Wt	Controls (unaged)				80°C Dry				80°C Wet				60°C 52F			
			TS MN/m ²	EB %	H BS ⁰	M (MN/m ²)	TS MN/m ²	EB %	H BS ⁰	M (MN/m ²)	TS MN/m ²	EB %	H BS ⁰	M (MN/m ²)	TS MN/m ²	EB %	H BS ⁰	M (MN/m ²)
						100% 200% 300%				100% 200% 300%				100% 200% 300%				100% 200% 300%
S 20	Ethylene adipate	1000	23.8	250	67	2.8	8.2	-	30.7	240	76	5.5	16.6	-	3.7	170	75	2.6
S 22	Ethylene adipate	2000	24.9	350	71	1.9	3.2	7.4	32.6	340	69	2.0	2.3	4.9	4.1	250	70	1.0
S 23	Diethylene adipate	1000	8.6	190	74	3.1	-	-	16.3	215	76	3.7	12.0	-	5.8	150	75	1.9
S 23A	Diethylene adipate	2000	2.0	155	70	1.3	-	-	2.1	200	67	0.9	2.1	-	1.1	100	68	1.1
S 24	Propylene adipate	2000	4.8	265	75	0.9	2.5	-	5.9	295	64	0.7	2.1	-	0.9	115	62	0.7
S 25	Butylene adipate	2000	19.0	300	88	2.1	3.3	19.0	19.8	340	67	0.3	10.6	19.0	2.7	190	66	1.0
S 21	Ethylene/propylene adipate 7:3	2000	12.2	300	72	1.1	3.1	12.2	21.1	335	70	0.9	2.5	7.65	1.8	150	69	0.3
S 27	Butylene/propylene adipate 7:3	2000	8.4	300	73	1.3	2.7	8.4	6.4	310	64	0.5	1.6	6.4	0.7	105	61	0.6
S 33	ε-caprolactone/diethylene glycol	2000	14.1	350	69	0.8	1.7	4.3	15.6	390	57	1.2	2.0	-	2.0	240	56	0.3

Unable to test
due to severe
swelling and
disintegration

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18.3

TABLE 7 cont'd

ERDE-S3

	Code No	Elastomer and average molecular weight	Unaged	2
POLYETHER	S 30	Polyoxypropylene glycol 1200	(slightly opalescent) moderately tough and flexible	(deep swollen)
	S 26	Polyoxypropylene glycol 2000	- ditto -	(amber weak)
	S 29	Polyoxybutylene glycol 650	transparent (slightly yellow) tough and rigid	(amber)
	S 31	Polyoxybutylene glycol 1300	transparent (slightly yellow) moderately tough and flexible	(amber)
	S 28	Polyoxybutylene glycol 2000	- ditto -	(deep)
BUTADIENE POLYETHER	S 32	Hydroxyl-terminated polybutadiene/ polyoxybutylene glycol ether 1:1 2000	(lemon yellow) moderately tough and flexible	(yellow)

17.1

17.2

ht	Unaged	Water 28 days at 80°C	Dry Air 28 days at 80°C	ST 28 days
1200	(slightly opalescent) moderately tough and flexible	(deep amber) slightly swollen, very flexible	(slightly yellow) slightly inflexible	(transparent) flexible
2000	- ditto -	(amber) slightly swollen, weak and flexible	(pale yellow) flexible	(transparent) flexible
650	transparent (slightly yellow) tough and rigid	(amber) rigid	(pale yellow) rigid	(very slight rigid, inflex
1300	transparent (slightly yellow) moderately tough and flexible	(amber) rigid	(pale yellow) fairly rigid	(very slight rigid, inflex
2000	- ditto -	(deep amber) brittle	(pale yellow) tough	(very slight tough, flexibl
2000	(lemon yellow) moderately tough and flexible	(yellow) tough	(amber) tough	(deep amber) swollen, flexi

APPENDIX B

d	Water 28 days at 80°C	Dry Air 28 days at 80°C	STF 28 days at 65°C
(alescent) ough and	(deep amber) slightly swollen, very flexible	(slightly yellow) slightly inflexible	(transparent) tough, flexible
-	(amber) slightly swollen, weak and flexible	(pale yellow) flexible	(transparent) weak, flexible
(slightly h and	(amber) rigid	(pale yellow) rigid	(very slight yellowing) rigid, inflexible
(slightly rately lexible	(amber) rigid	(pale yellow) fairly rigid	(very slight yellowing) rigid, inflexible
-	(deep amber) brittle	(pale yellow) tough	(very slight yellowing) tough, flexible
(r) ough and	(yellow) tough	(amber) tough	(deep amber) slightly swollen, flexible

17.3

TABLE 8 cont'd
END OF 53

Code No	Polyol Type	Av Mol Wt	Controls (unaged)					80°C Dry					80°C Wet					60°C S.F.				
			TS lb./in. ²	ES %	H BS°	M (lb./in. ²)	M (lb./in. ²)	TS lb./in. ²	ES %	H BS°	M (lb./in. ²)	M (lb./in. ²)	TS lb./in. ²	ES %	H BS°	M (lb./in. ²)	M (lb./in. ²)	TS lb./in. ²	ES %	H BS°	M (lb./in. ²)	M (lb./in. ²)
S 30	Propylene glycol ether	1200	3.7	180	66	1.5	-	11.0	21.0	60	1.7	4.5	-	0.8	300	35	0.2	0.3	0.3	80	-	-
S 26	Propylene glycol ether	2000	0.8	210	45	0.5	0.8	0.9	24.5	42	0.3	0.5	-	0.6	300	30	0.2	0.3	0.5	100	1.1	-
S 29	Polyoxyethylene glycol ether	550	14.7	150	81	2.6	-	21.6	165	81	15.8	-	-	8.0	195	74	2.0	-	-	5.3	105	79
S 31	Polyoxyethylene glycol ether	1300	4.5	190	75	2.3	-	6.8	230	73	1.3	4.0	-	2.6	210	66	1.0	2.4	-	2.6	80	-
S 28	Polyoxyethylene glycol ether	2000	3.0	215	71	2.0	2.5	1.95	256	67	0.7	1.4	-	0.25	440	64	0.15	1.2	2.6	0.7	65	-
S 34A	Oil terminated polybutadiene	2400	7.1	265	81	3.5	5.7	-	-	-	-	-	-	7.1	255	78	3.7	5.8	-	1.1	135	37
S 32	Oil terminated polybutadiene/polyether	2200	5.6	365	61	0.8	1.7	3.0	5.3	320	59	1.2	2.2	1.3	395	45	0.4	0.7	1.3	1.4	100	38

KEY

TS = tensile strength
 ES = extension at break
 M = modulus
 6.9 lb./in.² = 1000 psi

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19.3

Fig

TABLE 8 cont'd

ERDE - 53

Code No	Polyol Type	Polyol	Av Mol Wt	Controls (unaged)						80°C Dry					
				TS MN/m ²	EB %	H BS°	M (MN/m ²)			TS MN/m ²	EB %	H BS°	M (MN/m ²)		
							100%	200%	300%				100%	200%	
S 30	POLYETHER	Propylene glycol ether	1200	3.7	180	66	1.5	-	-	8.0	260	60	1.7	-	
S 26		Propylene glycol ether	2000	0.8	210	46	0.5	0.8	-	0.9	245	42	0.3	-	
S 29		Polyoxybutylene glycol ether	650	24.7	150	81	12.6	-	-	28.6	165	81	15.8	-	
S 31		Polyoxybutylene glycol ether	1300	4.5	190	75	2.3	-	-	6.8	230	73	1.8	-	
S 28		Polyoxybutylene glycol ether	2000	3.0	225	71	2.0	2.5	-	1.95	256	67	0.7	-	
S 32A	BUTADIENE	OH terminated polybutadiene	2400	7.1	265	81	3.5	5.7	-	-	-	-	-	-	
S 32		OH terminated polybutadiene/polyether	2200	5.6	365	61	0.8	1.7	3.0	5.3	320	59	1.2	-	

KEY

TS = tensile strength
 EB = extension at break
 M = modulus
 6.9 MN/m² = 1000 psi

Controls (unaged)						80°C Dry						80°C Wet						60°C STF					
No.	EB %	H BS ^o	M (MN/m ²)			TS MN/m ²	EB %	H BS ^o	M (MN/m ²)			TS MN/m ²	EB %	H BS ^o	M (MN/m ²)			TS MN/m ²	EB %	H BS ^o	M (MN/m ²)		
			100%	200%	300%				100%	200%	300%				100%	200%	300%				100%	200%	300%
7	180	66	1.5	-	-	8.0	260	60	1.7	4.5	-	0.8	300	35	0.2	0.3	0.8	3.1	80	58	-	-	-
8	210	46	0.5	0.8	-	0.9	245	42	0.3	0.5	-	0.6	300	30	0.2	0.3	0.6	1.1	100	34	1.1	-	-
7	150	81	12.6	-	-	28.6	165	81	15.8	-	-	8.0	195	74	2.0	-	-	5.3	105	79	4.8	-	-
5	190	75	2.3	-	-	6.8	230	73	1.8	4.0	-	2.6	210	66	1.0	2.4	-	2.0	80	72	-	-	-
0	225	71	2.0	2.5	-	1.95	256	67	0.7	1.4	-	0.25	440	64	0.45	1.2	2.6	0.7	65	64	-	-	-
1	265	81	3.5	5.7	-	-	-	-	-	-	-	7.1	255	78	3.7	5.8	-	1.1	135	37	0.7	-	-
6	365	61	0.8	1.7	3.0	5.3	320	59	1.2	2.2	4.4	1.3	325	45	0.4	0.7	1.3	1.4	200	38	0.5	-	-

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APPENDIX B

80°C Dry						80°C Wet						60°C STF					
TS MN/m ²	EB %	H BS°	M (MN/m ²)			TS MN/m ²	EB %	H BS°	M (MN/m ²)			TS MN/m ²	EB %	H BS°	M (MN/m ²)		
			100%	200%	300%				100%	200%	300%				100%	200%	300%
8.0	260	60	1.7	4.5	-	0.8	300	35	0.2	0.3	0.8	3.1	80	58	-	-	-
0.9	245	42	0.3	0.5	-	0.6	300	30	0.2	0.3	0.6	1.1	100	34	1.1	-	-
28.6	165	81	15.8	-	-	8.0	195	74	2.0	-	-	5.3	105	79	4.8	-	-
6.8	230	73	1.3	4.0	-	2.6	210	66	1.0	2.4	-	2.0	80	72	-	-	-
1.95	256	67	0.7	1.4	-	0.25	440	64	0.45	1.2	2.6	0.7	65	64	-	-	-
-	-	-	-	-	-	7.1	255	78	3.7	5.8	-	1.1	135	37	0.7	-	-
5.3	320	59	1.2	2.2	4.4	1.3	325	45	0.4	0.7	1.3	1.4	200	38	0.5	-	-

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19.3