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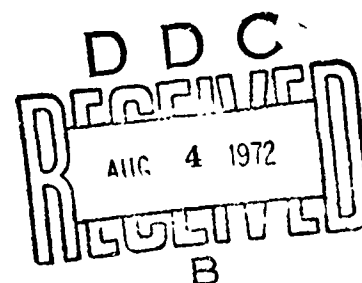
**EXPLOSIVES RESEARCH
AND DEVELOPMENT ESTABLISHMENT**

TECHNICAL REPORT No. 54

**Relationships between Polyurethane Elastomer
Structure and Ageing Properties: Part 3:
Effective Crosslink Structure**

**B E Brokenbrow
D Sims
J Wright**

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Relationships between Polyurethane Elastomer
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Effective Crosslink Structure

by

B E Brokenbrow
D Sims
J Wright

SUMMARY

The effect of varying chemical group structure on the properties of polyurethane elastomers has been investigated.

The introduction of urea and biuret groups into polyester and polyether urethanes by the use of 4,4'-methylene bis-(2-chloroaniline), MOCA, yielded elastomers with superior physical properties to elastomers which contained predominantly urethane groups and were chain extended and/or crosslinked with diols and triols.

MOCA cured polyester urethanes gave higher tensile strengths with better resistance to dry air and STF (petrol) than polyether urethanes cured in the same way; while MOCA cured polyether urethanes were harder and had superior hydrolytic stability compared to polyester urethanes.

The ageing properties of polyurethane elastomers cured with blends of MOCA and 1,1'-trimethylol propane (TMP) were equal to elastomers in which MOCA or TMP were the sole curing agents. A further advantage of the diamine/triol system was the improved processing characteristics of the reaction products, compared with systems which employed MOCA alone which were extremely reactive.

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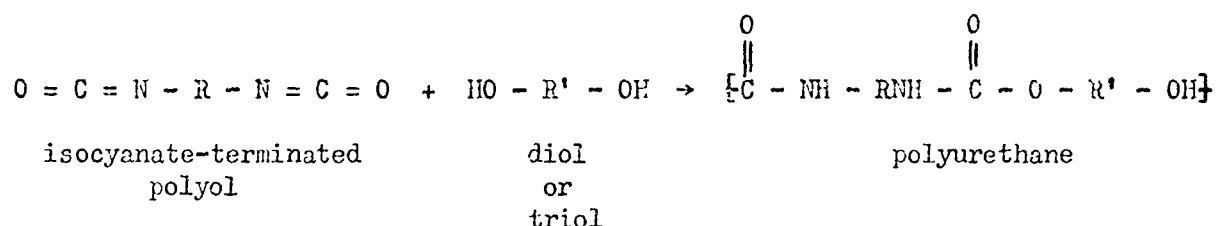
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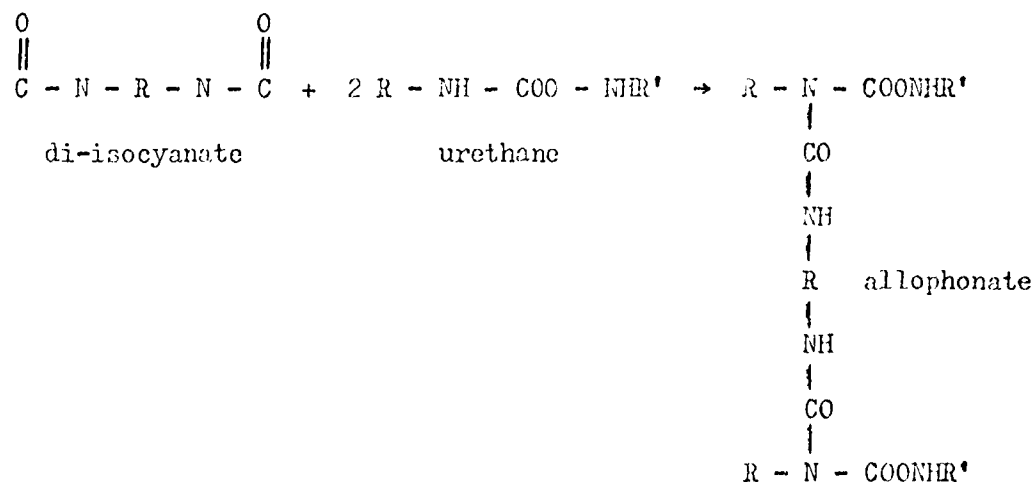
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1 INTRODUCTION

In an attempt to produce polyurethane elastomers with improved ageing properties, the relationships between their chemical structure and their resistance to water, elevated temperatures and STF (petroleum) are being studied. Previous reports^{1,2} have described the effects of varying (i) the degree of crosslinking and (ii) the backbone polyol in elastomers which contained predominantly urethane groups prepared from typical polyester and polyether/toluene di-isocyanate (TDI) prepolymers, chain extended and/or crosslinked with diols and triols as follows:



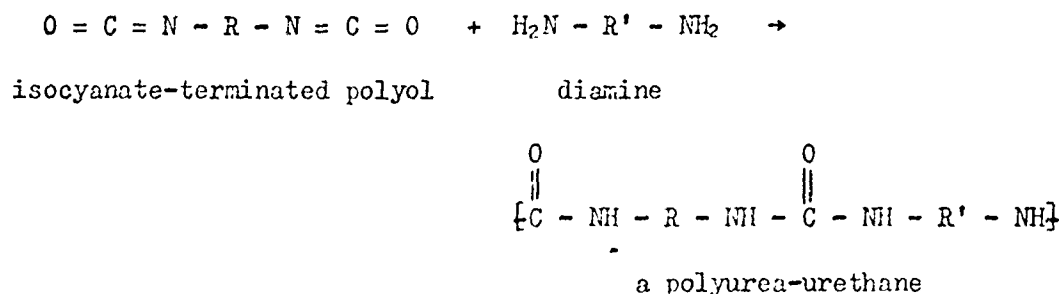
The degree of urethane crosslinking is dependent on the ratio of triol to diol used.¹ In addition, urethane groups formed by the above reaction may slowly and usually at elevated temperatures form further crosslinks either with excess isocyanate in the prepolymer or with added isocyanate, giving allophanate linkages.



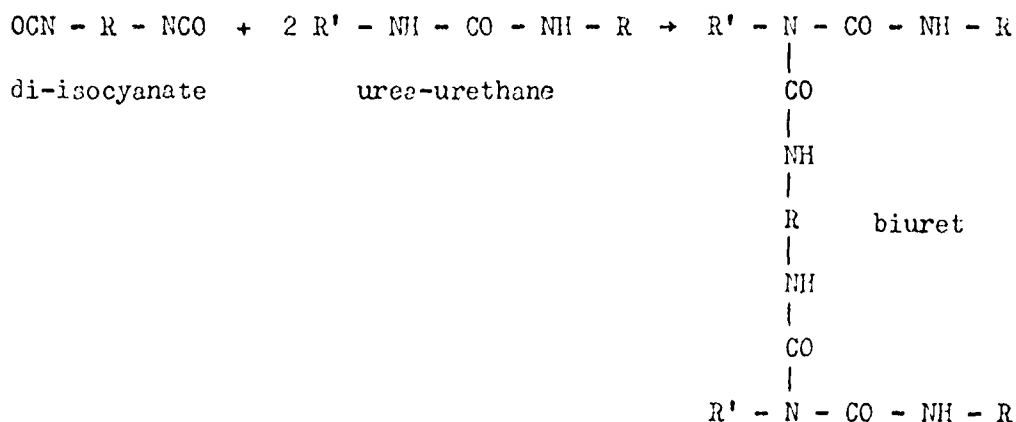
With polyurethane elastomers of this type at similar molecular weights it has been found that polyester urethanes generally show the best initial physical properties, while polyether urethanes show superior hydrolytic stability.^{1,2} Polyester urethanes also generally show both less

discoloration after ageing in air at 80°C and swelling in STF at 65°C than the polyether urethanes. Optimum properties were usually obtained with relatively highly crosslinked elastomers of M_c values (molecular weight per branch link) of 1000 - 2000.

With diamines, for example 4,4'-methylene bis-(2-chloroaniline), MOCA, the following reaction occurs.



The substituted urea groups of the urea-urethane polymer may also react with excess isocyanate, but at considerably faster rates than urethane groups, to form a biuret structure, which is a chain branch point, since it is trifunctional. As the concentration of biuret crosslinks is increased, the inter-chain hydrogen bonding decreases.



The present investigation considers the effects of varying the type of chemical group structure (urethane, urea, biuret etc) present in polyester and polyether urethane elastomers by using a diamine as well as diols and triols to chain extend and/or crosslink (cure) the elastomers.

2 MATERIALS AND METHODS OF PREPARATION

All the elastomers were prepared using (i) a laboratory prepared ethylene/propylene (7:3) adipate polyester (hydroxyl no 59.0, acid no 0.35, % H₂O 0.01, average molecular weight 1900) and (ii) a commercially supplied polyether polyoxybutylene glycol, 'Polymeg' ex-Quaker Oats Co (hydroxyl no 56.7, acid no 0.01, % H₂O 0.01, average molecular weight 2000). 1.0 mole equivalent reacted with toluene di-isocyanate (TDI) [Hylene ex-Du Pont UK, a mixture of 80:20 per cent 2,4 and 2,6 isomers], 2.0 moles equivalent to form isocyanate-terminated prepolymers. The prepolymers were crosslinked or chain extended with either 1,1',1''-trimethylol propane (TMP) or 1,4-butane diol (BD), or 4,4'-methylen bis-(2-chloroaniline) (MOCA) or mixtures thereof as shown in Table 1(a) and (b).

The methods of preparation are described in Appendix A.

TABLE 1(a) $\frac{E}{E_0} = \frac{1}{2}$
POLYURETHANE ELASTOMERS: DIFFERENT CURING AGENTS

Code No	Type	MOCA		TYP		BD		Total % stoichiometric $(\frac{OH + NH_2}{NCO}) \times 100$	Anticipated types of chemical bonding and degree of crosslinking
		(moles)	stoichiometric $NH_2:NCO$	(moles)	stoichiometric	(moles)	stoichiometric $OH:NCO$		
S.61	Polyester prepolymer (1 mole)	0.80	80.0	-	-	-	-	80.0	urea-urethane biuret moderate
S.62		0.415	41.5	0.274	41.5	-	-	83.0	urethane-urea biuret moderate
S.63		0.415	41.5	-	-	0.415	41.5	83.0	urethane-urea biuret slight - moderate
S.75		-	-	-	-	0.83	83.0	83.0	urethane none - slight
S.21		-	-	0.600	91.0	-	-	91.0	urethane/alloyphosphate* moderate
S.65	Polyether prepolymer (1 mole)	0.80	80.0	-	-	-	-	80.0	urea-urethane biuret moderate
S.66		0.415	41.5	0.274	41.5	-	-	83.0	urethane-urea biuret moderate
S.67		0.415	41.5	-	-	0.415	41.5	83.0	urethane-urea biuret slight - moderate
S.73		-	-	-	-	0.83	83.0	83.0	urethane none - slight
S.28		-	-	0.600	91.0	-	-	91.0	urethane/alloyphosphate* moderate

* at elevated temperatures

4.1

4.2

4.3

TABLE 1(a)

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POLYURETHANE ELASTOMERS: DIFFERENT CURING AGENTS

Code No	Type	MOCA		TMP		(mole
		(moles)	X stoichiometric $\text{NH}_2:\text{NCO}$	(moles)	X stoichiometric	
S.61	Polyester prepolymer (1 mole)	0.80	80.0	-	-	-
S.62		0.415	41.5	0.274	41.5	-
S.63		0.415	41.5	-	-	0.41
S.75		-	-	-	-	0.83
S.21		-	-	0.600	91.0	-
S.65	Polyether prepolymer (1 mole)	0.80	80.0	-	-	-
S.66		0.415	41.5	0.274	41.5	-
S.67		0.415	41.5	-	-	0.41
S.73		-	-	-	-	0.83
S.28		-	-	0.600	91.0	-

AGENTS

OCA	TMP		BD		Total stoichiometric $\left(\frac{OH + NH_2}{NCO}\right) \times 100$	Anticipated type chemical bonds degree of cross
stoichiometric $NH_2:NCO$	(moles)	stoichiometric	(moles)	stoichiometric $OH:NCO$		
80.0	-	-	-	-	80.0	urea-urethane biuret
41.5	0.274	41.5	-	-	83.0	urethane-urea biuret
41.5	-	-	0.415	41.5	83.0	urethane-urea biuret
-	-	-	0.83	83.0	83.0	urethane
-	0.600	91.0	-	-	91.0	urethane/allophanate
80.0	-	-	-	-	80.0	urea-urethane biuret
41.5	0.274	41.5	-	-	83.0	urethane-urea biuret
41.5	-	-	0.415	41.5	83.0	urethane-urea biuret
-	-	-	0.83	83.0	83.0	urethane
-	0.600	91.0	-	-	91.0	urethane/allophanate*

* at elevated temperature

4.3

4.2

TMP	BD		Total	Anticipated types of chemical bonding and degree of crosslinking	
stoichiometric	(moles)	stoichiometric OH:NCO	stoichiometric $\left(\frac{OH + NH_2}{NCO}\right) \times 100$		
-	-	-	80.0	urea-urethane biuret	moderate
41.5	-	-	83.0	urethane-urea biuret	moderate
-	0.415	41.5	83.0	urethane-urea biuret	slight - moderate
-	0.83	83.0	83.0	urethane	none - slight
91.0	-	-	91.0	urethane/allophanate*	moderate
-	-	-	80.0	urea-urethane biuret	moderate
41.5	-	-	83.0	urethane-urea biuret	moderate
-	0.415	41.5	83.0	urethane-urea biuret	slight - moderate
-	0.83	83.0	83.0	urethane	none - slight
91.0	-	-	91.0	urethane/allophanate*	moderate

* at elevated temperatures

4.3

4.2

TABLE 1(b)

POLYURETHANE ELASTOMERS: DIFFERENT CONCENTRATIONS OF MOCA

Code No	Type	MOCA		Anticipated types of chemical bonding and degree of crosslinking
		(moles)	% stoichiometric	
S.42	Polyester prepolymer (1 mole)	0.44	44.0	urea - urethane - biuret
S.44		0.52	52.0	" " "
S.61		0.80	80.0	" " "
S.60		0.88	88.0	" " "
				↑ increasing number of biuret crosslinks
S.43	Polyether prepolymer (1 mole)	0.44	44.0	" " "
S.56		0.55	55.0	" " "
S.57		0.60	60.0	" " "
S.64		0.80	80.0	" " "
S.65		0.88	88.0	" " "
				↑ increasing number of biuret crosslinks

3 EXPERIMENTAL

British Standard type E dumb-bell test pieces (4 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 4, 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 (STF)	Immersed in dry Standard Test Fluid at 65°C

*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.³

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 4 specimens were removed from the tubes, dried from a 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^{4,5} 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 2, Appendix B. The mechanical properties of the elastomers are summarised in Table 3, Appendix E and the percentage changes after ageing in the original mechanical properties of the elastomers are recorded in Tables 6 - 15.

4.1 Visual Assessment

The general condition of the polyurethane elastomers, judged by visual and empirical methods of assessment, are described below.

4.1.1 Initially (Unaged)

Unaged polyester urethanes, especially those cured with MOCA, generally showed slightly less discoloration (yellowing) than similarly cured polyether urethane elastomers.

MOCA and mixed MOCA/TMP cured polyurethanes yielded tough elastomers, while those cured with MOCA/BD, BD and TMP were apparently less tough but rather more flexible.

4.1.2 Aged in Dry Air

After 28 days' oven ageing in dry air at 60°C all the elastomers appeared to be stiffer than the unaged controls. The polyether based urethanes showed rather more yellowing than the polyester urethane elastomers.

4.1.3 Water Immersion

After 28 days' immersion in water at 60°C all the polyester urethanes showed severe losses of strength although the breakdown of MOCA, MOCA/TMP and MOCA/BD cured elastomers was not quite so severe as polyester urethanes cured solely by TMP or BD, which completely disintegrated as previously^{1,2} and suggests that the presence of urea and biuret groups may offer some protection to the hydrolytically unstable ester groups.

Apart from severe discoloration all the polyether urethane elastomers appeared to be in fairly good condition.

4 1 4 STF (Petrol) Immersion

Following 28 days' immersion in STF at 65°C all the polyurethane elastomers apart from those cured with BD appeared to be in fairly good condition, except that the polyether urethanes again showed rather more discoloration than the polyester urethanes.

4 2 Mechanical Properties

4 2 1 Initially (Unaged)

The results of mechanical tests summarised in Table 4 show that unaged polyester urethanes gave ultimate tensile properties in the range 10 - 38 MN/m², which with the exception of the butane diol cured material, were much higher than the corresponding values for polyether urethanes (3 - 20 MN/m²). However, the polyether urethanes showed higher modulus and hardness values. This effect is due to the different stress strain curves shown by the two types of urethane. The polyester urethanes show stress crystallisation at high extensions thus increasing greatly the ultimate tensile strength.

Elastomers cured with MOCA or MOCA/BD or MOCA/TMP had superior all round physical properties in both polyester and polyether urethanes than those cured solely with TMP or BD.

TABLE 4

MECHANICAL PROPERTIES OF UNAGED POLYURETHANE ELASTOMERS
EFFECT OF TYPE OF CHEMICAL CURE

Code No	Type	Cure	Tensile Strength (MN/m ²)	Extension at break (per cent)	Modulus (MN/m ²) at extensions of (per cent)			Hardness (BS ⁰)
					100	200	300	
S.61	Polyester	MOCA (80%)	37.7	475	3.8	6.3	10.3	93
S.62		MOCA/TMP	28.8	430	2.5	4.5	8.1	89
S.63		MOCA/BD	33.7	570	1.5	1.7	3.2	85
S.75		BD	9.8	635	0.1	0.4	0.7	43
S.21		TMP	12.2	300	1.1	3.1	12.1	72
S.65	Polyether	MOCA (80%)	14.5	330	5.3	7.0	12.4	94
S.66		MOCA/TMP	15.9	340	2.9	5.2	9.9	89
S.67		MOCA/BD	20.2	535	2.0	3.2	5.1	85
S.73		BD	15.9	470	0.4	1.1	1.3	62
S.28		TMP	3.0	225	2.0	-	-	71

Elastomers cured with blends of MOCA/TMP or MOCA/BD had satisfactory mechanical properties although their moduli and hardness were not as high compared to elastomers cured solely with MOCA. The main advantage of MOCA/polyol mixtures, however, was their reduced reactivity compared with systems in which MOCA was the sole curing agent; this allowed longer mixing and degassing cycles, which in this respect makes diamine/diol or diamine/triol mixtures attractive systems for curing polyurethane elastomers. MOCA/TMP mixtures were preferred to MOCA/BD mixtures, especially in polyester urethanes, the former producing harder elastomers which is attributable to the greater degree of crosslinking introduced by the MOCA/triol system.

In polyester urethanes the main effect of reducing the MOCA concentration (which in effect increases the degree of biuret crosslinking of the elastomer) was a reduction in the hardness and 100 per cent modulus of the elastomers. (Table 5.) In polyethers there appeared to be little effect.

TABLE 5

MECHANICAL PROPERTIES OF UNAGED POLYURETHANE ELASTOMERS
EFFECT OF MOCA CONCENTRATION

Code No	Type	MOCA % stoichiometric	Tensile strength (MN/m ²)	Extension at break (%)	Modulus (MN/m ²) at extensions of (per cent)			Hardness (BS ⁰)
					100	200	300	
S.42	Polyester	44	33.2	380	2.6	5.1	12.8	88
S.44		52	33.0	385	3.5	6.5	14.2	88
S.61		80	37.7	475	3.8	6.3	10.3	93
S.60		88	28.6	455	3.9	6.3	10.3	91
S.43	Polyether	44	14.6	305	5.2	9.0	13.5	93
S.56		55	13.5	290	4.9	8.5		91
S.57		60	14.3	280	5.2	5.2	9.1	92
S.65		80	14.3	330	5.3	7.0	12.4	94
S.64		88	20.0	390	5.3	7.8	12.0	94

The higher strengths of polyurea-urethane elastomers (ie elastomers cured with a diamine such as MOCA) compared with polyurethane elastomers cured with either a diol or triol is attributable to the highly polar nature of the urea group which possesses a strong hydrogen bonding capability. In addition, the urea -NH- group is more reactive to isocyanate than the corresponding urethane -NH- group and formation of biuret crosslinks is likely when excess isocyanate (reducing MOCA concentration) is present, especially at elevated temperatures. However, it has been reported that excessive crosslinking may cause a loss of modulus and softening on repeated deformation, especially with polyester urea-urethanes.^{6,7} Crosslinking is also reported to reduce heat build-up on flexing.

4 2 2 Dry Air

Tables 6 and 7 show the changes in the original mechanical properties of the elastomere after 28 days' exposure to dry air at 80°C. Table 6 shows the effect of different types of chemical cure, while Table 7 shows the effects of different MOCA concentrations.

TABLE 6

CHANGES IN ORIGINAL MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS AFTER
28 DAYS' EXPOSURE TO DRY AIR
EFFECT OF TYPE CHEMICAL CURE

Code No	Type	Cure	Per cent Change of Original Mechanical Property			
			Tensile strength	Extension at break	100% Modulus	Hardness
S.60	Polyester	MOCA (88%)	- 1	+ 2	+20	+ 4
S.61		MOCA (80%)	- 2	- 2	+24	+ 2
S.62		MOCA/TMP	+ 11	+ 3	+20	+ 1
S.63		MOCA/BD	+ 49	- 4	- 7	+ 4
S.75		BD	+ 9	+13	0	- 2
S.21		TMP	+ 73	+12	-18	- 3
S.64	Polyether	MOCA (88%)	- 85	+31	+ 6	+ 1
S.65		MOCA (80%)	+160	+51	0	0
S.66		MOCA/TMP	+ 2	+31	-28	-18
S.67		MOCA/BD	+ 28	+10	+20	+ 4
S.73		BD	- 17	+26	-25	- 6
S.10		TMP	- 55	+14	-43	- 6

TABLE 7

CHANGES IN ORIGINAL MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS AFTER 28 DAYS' EXPOSURE TO DRY AIR AT 80°C
EFFECT OF MOCA CONCENTRATION

Code No	Type	% MOCA Stoichio-metric	Per cent Change of Original Mechanical Property			
			Tensile Strength	Extension at break	100% Modulus	Hardness
S.42	Polyester	44	+ 31	+24	- 8	+2
S.44		52	- 1	+12	0	+2
S.61		80	- 2	- 2	+24	+2
S.60		88	- 1	+ 2	+20	+4
S.43	Polyether	44	+ 99	+61	-31	-1
S.56		55	+112	+57	-31	+1
S.57		60	+161	+73	-10	+2
S.65		80	+160	+51	0	0
S.64		88	+ 85	+31	+ 6	+1

MOCA cured polyester urethanes were the least affected by exposure to dry air judged by the relatively small changes in their original ultimate mechanical properties. MOCA/TMP and BD cured polyester urethanes also showed relatively small changes in tensile strength while MOCA/BD and TMP cured polyester urethanes showed increases in tensile strength. MOCA cured polyether urethanes showed considerable increases in their original tensile strengths, but, blends of MOCA with BD or TMP, BD and TMP cured polyethers, showed smaller changes in tensile strength.

4 2 3 Water Immersion

After 28 days' immersion in water at 80°C (Table 8) the polyether urethanes were in much better condition than the polyester urethane elastomers. Polyester urethane elastomers cured with MOCA, MOCA/TMP and MOCA/BD were still intact but too weak to test, whilst those cured with BD and TMP completely disintegrated, as in previous assessments.^{1,2}

TABLE 8

CHANGES IN ORIGINAL MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS AFTER
28 DAYS' IMMERSION IN WATER AT 80°C
EFFECT OF TYPE OF CHEMICAL CURE

Code No	Type	Cure	Per cent Change of Original Mechanical Property			
			Tensile strength	Extension at break	100% Modulus	Hardness
S.60	Polyester	MOCA 88%	Too weak to test			
S.61		MOCA 80%	"	"	"	"
S.62		MOCA/TMP	"	"	"	"
S.63		MOCA/BD	"	"	"	"
S.75		BD	Disintegrated			
S.21		TMP	"			
S.64	Polyether	MOCA 88%	-86	-10	-62	- 7
S.65		MOCA 80%	-80	+27	-73	- 9
S.66		MOCA/TMP	-21	+79	-48	-16
S.67		MOCA/BD	-78	-19	-85	-26
S.73		BD	-65	+80	Too weak	Too weak
S.28		TMP	-92	+97	-55	-10

Of the polyether urethanes assessed for hydrolytic stability MOCA or TMP cured urethanes showed the greatest losses of tensile strength, while S.66, a MOCA/TMP cured elastomer, showed the least change.

Table 9 shows that in MOCA cured polyether urethanes a reduction in the concentration of the curing agent (ie increased biuret crosslinking) tended to give elastomers with better retention of tensile strength although the extension at break shows considerable increase on ageing.

TABLE 9

CHANGES IN ORIGINAL MECHANICAL PROPERTIES OF POLYETHER URETHANE ELASTOMERS
AFTER 28 DAYS' IMMERSION IN WATER AT 80°C
EFFECT OF MOCA CONCENTRATION

Polyether Urethane Code No.	MOCA % Stoichio- metric	Per cent Change of Original Mechanical Property			
		Tensile strength	Extension at break	Modulus at 100% extension	Hardness
S.43	44	-64	+126	-69	- 5
S.56	55	-50	+210	-88	-18
S.57	60	-45	+220	-65	- 4
S.65	80	-80	+ 27	-73	- 9
S.64	88	-86	- 10	-62	- 7

The water immersion results for the best material in Table 9 containing increased biuret crosslinking, however, are not as good as those for S.66 which was based on a MOCA/TMP mixed curing system. Therefore a series of polyether urethanes was made using various ratios of TMP/MOCA.

The original mechanical properties of the mixed cured polyethers were not as high as those for MOCA but the hydrolytic stability of TMP/MOCA cured elastomers S.53, S.66 and S.66A, as judged by changes in their 100 per cent modulus, were the most satisfactory of the elastomers cured in this way. (Table 10.)

TABLE 10

MOCA/TMP CURED POLYETHER URETHANE ELASTOMERS
ORIGINAL PROPERTIES AND EFFECTS OF 28 DAYS' IMMERSION IN WATER AT 80°C

Polyether Urethane Code No	% Stoichiometric		Original Mechanical Properties						% Change in Original Mechanical Properties			
	MOCA	TMP	Total	Tensile strength (MN/m ²)	Extension at break (%)	Modulus at 100% extension	Hardness BS ⁰	Tensile strength	Extension at break	100% Modulus	Hardness	
S.37	38.5	28.5	67.0	6.4	190	3.7	89	+ 62	+185	-78	-12	
S.54	44.0	33.0	77.0	5.7	170	4.1	88	+ 25	+195	-76	-10	
S.53	33.0	50.0	83.0	5.1	180	3.1	87	+117	+170	+39	- 1	
S.66	41.5	41.5	83.0	15.9	340	2.9	89	- 21	+ 79	-48	-16	
S.66A	47.5	47.5	95.0	11.6	355	4.3	91	+ 40	+ 69	-49	- 9	

4 2 4 STF (Petrol) Immersion

After 28 days' immersion in STF at 65°C, the most effective curing system for polyester urethanes was either MOCA or MOCA/TMP, whilst MOCA was the most effective in polyether urethanes. Although polyester urethanes showed the best retention of extension at break and hardness properties, polyether urethanes generally showed the best retention of 100 per cent modulus. Polyurethane elastomers cured with BD or MOCA/BD were generally unsatisfactory, especially when judged by their losses of 100 per cent modulus and hardness.

TABLE 11

CHANGES IN ORIGINAL MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS AFTER 28 DAYS' IMMERSION IN STF AT 65°C
EFFECT OF TYPE OF CHEMICAL CURE

Code No	Type	Cure	Per cent Change of Original Mechanical Property			
			Tensile strength	Extension at break	100% Modulus	Hardness
S.60	Polyester	MOCA 88%	-50	-4	-21	0
S.61		MOCA 30%	-44	-11	+5	0
S.62		MOCA/TMP	+1	+6	-48	0
S.63		MOCA/BD	-65	-18	-53	0
S.75		BD	-40	-9	Too weak to test	Too weak to test
S.21		TMP	-85	-50	-18	-4
S.64	Polyether	MOCA 88%	-63	-45	-11	-7
S.65		MOCA 80%	-42	-32	-11	-6
S.66		MOCA/TMP	-75	-50	-14	-18
S.67		MOCA/BD	-71	-40	-5	-12
S.73		BD	-63	-16	-25	-16
S.28		TMP	-76	-71	(no result, failed at 80% extension)	-10

Table 12 shows that the effect of increased biuret crosslinking, obtained by using considerably less than stoichiometric quantities of MOCA curing agent, produced polyester urethane elastomers with improved resistance to STF although retention of 100 per cent modulus tended to fall with increasing crosslinking. In general, the polyester urethanes showed rather better all round retention of physical properties compared to the polyether urethanes after immersion in STF.

TABLE 12

CHANGES IN ORIGINAL MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS
AFTER 28 DAYS' IMMERSION IN STF AT 65°C
EFFECT OF MOCA CONCENTRATION

Code No	Type	MOCA % Stoichiometric	Per cent Change of Original Mechanical Property			
			Tensile strength	Extension at break	Modulus at 100% extension	Hardness
S.42	Polyester	↑ increased biuret crosslinking 44	-20	+ 1	-23	-2
S.44			-52	-12	-17	0
S.61			-44	-11	+ 5	0
S.60			-50	- 4	-21	0
S.43	Polyether	↑ increased biuret crosslinking 44	-54	-54	-42	-6
S.56			-61	-50	-31	-9
S.57			-57	-46	-11	-7
S.65			-42	-32	-11	-6
S.64			-63	-45	-11	-7

Table 13 shows the effects of immersion in STF on the physical properties of polyurethane elastomers cured with MOCA/TMP blends. The best polyether urethanes cured in this way S.37 and S.54, apart from rather greater losses of hardness, were superior to polyether urethanes cured solely by MOCA (Table 12), but were not quite as good as S.42, a MOCA cured polyester urethane, and S.62, a MOCA/TMP cured polyester urethane, examined previously (Tables 11 and 12).

TABLE 13

CHANGES IN ORIGINAL MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS
AFTER 28 DAYS' IMMERSION IN STF AT 65°C
EFFECT OF MOCA/TMP CONCENTRATION

Code No	Type	% Stoichiometric			Per cent Change of Original Mechanical Property			
		MOCA	TMP	Total	Tensile strength	Extension at break	100% Modulus	Hardness
S.37	Polyether	38.5	28.5	67.0	-28	-34	-5	-12
S.53		33.0	50.0	83.0	-43	-50	-	-14
S.54		44.0	33.0	77.0	-35	-53	-	-13
S.66		41.5	41.5	83.0	-75	-50	-14	-18
S.66A		47.5	47.5	95.0	-31	-49	+23	-11
S.62	Polyester	41.5	41.5	83.0	+1	+6	-48	0

5 CONCLUSIONS

The introduction of urea and biuret groups into the structure of polyurethane elastomers by the use of a diamine curing agent 4,4'-methylene bis-(2-chloro-aniline), MOCA, produced elastomers with superior physical properties initially compared with polyurethanes cured with a polyol 1,1',1"-trimethylol propane (TMP). The TMP cured elastomers which contained urethane crosslinks showed superior hardness and moduli to BD cured elastomers, which also contained a large number of urethane groups, but were predominantly linear.

MOCA cured polyester urethane elastomers possessed higher initial tensile strengths and in general showed better resistance to dry air at 80°C and STF at 65°C than polyether urethanes cured in the same way. On the other hand, MOCA cured polyether elastomers were harder initially and considerably more resistant to water at 80°C than MOCA cured polyester urethanes.

Polyester urethane elastomers with a relatively high degree of biuret crosslinking, which was achieved by using less than stoichiometric quantities of MOCA, showed lower hardnesses and moduli initially compared to less highly crosslinked MOCA cured polyester urethanes. The hydrolytic stability of MOCA cured polyether urethanes and the STF resistance of polyester urethanes improved with biuret crosslinking.

A reasonable compromise between initial mechanical properties and resistance to dry air at 80°C, coupled with resistance to water or STF, was achieved with polyether urethane elastomers cured with blends of MOCA and TMP. For

example, satisfactory resistance to STF, coupled with fair hydrolytic stability was obtained with S.37 cured with 38.5% MOCA and 28.5% TMP (stoichiometric). Satisfactory hydrolytic stability coupled with fair resistance to STF was obtained with S.53 cured with 53% MOCA and 50% TMP and S.66 and 66A cured with 41.5% MOCA/41.5% TMP and 47.5% MOCA/47.5% TMP respectively.

A further advantage of MOCA/TMP blends was the reduced reactivity of the curing system compared to systems in which MOCA was the sole curing agent.

6 REFERENCES

- | | | |
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APPENDIX A

METHODS OF PREPARATION

Prepolymers

All the elastomers were prepared via prepolymers as follows.

Toluene di-isocyanate (TDI), 2.0 moles 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. Crosslinking or chain extending agents: TMP or MOCA or BD or mixtures thereof (Tables 1(a) and (c)), were stirred into the prepolymer. The mixture was reheated to 80°C and degassed for 3 - 15 minutes at 1 mmHg.

The reaction products were poured into PTFE coated aluminium trays and cured in an oven for 16 hours 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 2

GENERAL CONDITION AND APPEARANCE OF POLYURETHANE ELASTOMERS

Code No	Type	% Stoichiometric				Unaged Controls	Dry Air 28 Days at 80°C	Water 28 Days at 80°C	STF 28 Days at 65°C
		MOCA	TMP	BD	Total				
S.42	Polyester	44.0	-	-	44.0	clear, tough	little change	dark brown, very weak	little change
S.44		52.0	-	-	52.0	clear, tough	little change	dark brown, very weak	little change
S.60		88.0	-	-	88.0	very slightly yellow, tough	slightly more yellow	dark brown, very weak	little change
S.61		80.0	-	-	80.0	very slightly yellow, tough	slightly more yellow	dark brown, weak	slightly more yellow
S.62		41.5	41.5	-	83.0	clear, moderately tough	slightly more yellow	dark brown, weak, tacky	little change
S.63		41.5	-	41.5	83.0	clear, flexible	very slightly more yellow and weaker	dark brown, soft and weak	slightly more yellow
S.75	Polyether	-	-	83.0	83.0	slightly opalescent, flexible	little change	catastrophic failure, brown liquid	slightly opaque, weaker
S.21		-	91.0	-	91.0	clear, moderately tough	little change	catastrophic failure, brown liquid	little change
S.37		28.5	38.5	-	67.0	very slightly yellow, tough, rigid	NT	amber, fairly tough	slightly more yellow
S.43		44.0	-	-	44.0	very slightly yellow, tough rigid	slightly more yellow	amber, fairly tough	slightly more yellow
S.53		33.0	50.0	-	83.0	very slightly yellow, tough, rigid	NT	amber, fairly tough	slightly more yellow
S.54		44.0	33.0	-	77.0	very slightly yellow, tough	NT	amber, fairly tough	slightly more yellow
S.56	Polyether	55.0	-	-	55.0	very slightly yellow, tough	NT	amber, fairly tough	slightly more yellow
S.57		60.0	-	-	60.0	very slightly yellow, tough, rigid	slightly more yellow	amber, fairly tough	little change
S.54		88.0	-	-	88.0	very slightly yellow, tough	slightly more yellow	pale amber, fairly tough	slightly more yellow
S.65		80.0	-	-	80.0	very slightly yellow, tough	slightly more yellow	pale amber, fairly tough	slightly more yellow
S.66		41.5	41.5	-	83.0	clear, flexible	slightly more yellow	amber, fairly tough	little change
S.67		41.5	-	41.5	83.0	very slightly yellow, flexible	slightly more yellow	amber, fairly tough	slightly more yellow
S.73		-	-	83.0	83.0	clear, flexible	slightly more yellow	amber, weak and flexible	deep amber, swollen
S.28		-	91.0	-	91.0	clear, moderately tough	slightly more yellow	deep amber, fairly tough	slightly more yellow

Key: MOCA = 4,4'-methylene bis-(2-chloroaniline)

TMP = 1,1,1-trimethylol propane

BD = 1,4-butane diol

NT = not examined

20.1

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TABLE 2

GENERAL CONDITION AND APPEARANCE OF POLYURETHANE ELASTOMERS

Code No	Type	% Stoichiometric				Unaged Controls	
		MOCA	TMP	BD	Total		
S.42	Polyester	44.0	-	-	44.0	clear, tough	1
S.44		52.0	-	-	52.0	clear, tough	1
S.60		88.0	-	-	88.0	very slightly yellow, tough	s
S.61		80.0	-	-	80.0	very slightly yellow, tough	s
S.62		41.5	41.5	-	83.0	clear, moderately tough	s
S.63		41.5	-	41.5	83.0	clear, flexible	v
S.75		-	-	83.0	83.0	slightly opalescent, flexible	1
S.21		-	91.0	-	91.0	clear, moderately tough	1
S.37	Polyether	28.5	38.5	-	67.0	very slightly yellow, tough, rigid	NT
S.43		44.0	-	-	44.0	very slightly yellow, tough rigid	sl
S.53		33.0	50.0	-	83.0	very slightly yellow, tough, rigid	NT
S.54		44.0	33.0	-	77.0	very slightly yellow, tough	NT
S.56		55.0	-	-	55.0	very slightly yellow, tough	NT
S.57		60.0	-	-	60.0	very slightly yellow, tough, rigid	sl
S.64		88.0	-	-	88.0	very slightly yellow, tough	sl
S.65		80.0	-	-	80.0	very slightly yellow, tough	sl
S.66		41.5	41.5	-	83.0	clear, flexible	sl
S.67		41.5	-	41.5	83.0	very slightly yellow, flexible	sl
S.73		-	-	83.0	83.0	clear, flexible	sl
S.28		-	91.0	-	91.0	clear, moderately tough	sl

Key: MOCA = 4,4'-methylene bi
 TMP = 1,1,1-trimethylol
 BD = 1,4-butane diol
 NT = not examined

POLYURETHANE ELASTOMERS

Metric		Unaged Controls	Dry Air 28 Days at 80°C	Water 28 Days at 80°C	28 Days
ID	Total				
5	44.0	clear, tough	little change	dark brown, very weak	little change
	52.0	clear, tough	little change	dark brown, very weak	little change
	88.0	very slightly yellow, tough	slightly more yellow	dark brown, very weak	little change
	80.0	very slightly yellow, tough	slightly more yellow	dark brown, weak	slightly change
	83.0	clear, moderately tough	slightly more yellow	dark brown, weak, tacky	little change
	83.0	clear, flexible	very slightly more yellow and weaker	dark brown, soft and weak	slightly change
	83.0	slightly opalescent, flexible	little change	catastrophic failure, brown liquid	slightly change
	91.0	clear, moderately tough	little change	catastrophic failure, brown liquid	little change
5	67.0	very slightly yellow, tough, rigid	NT	amber, fairly tough	slightly change
	44.0	very slightly yellow, tough rigid	slightly more yellow	amber, fairly tough	slightly change
	83.0	very slightly yellow, tough, rigid	NT	amber, fairly tough	slightly change
	77.0	very slightly yellow, tough	NT	amber, fairly tough	slightly change
	55.0	very slightly yellow, tough	NT	amber, fairly tough	slightly change
	60.0	very slightly yellow, tough, rigid	slightly more yellow	amber, fairly tough	little change
	88.0	very slightly yellow, tough	slightly more yellow	pale amber, fairly tough	slightly change
	80.0	very slightly yellow, tough	slightly more yellow	pale amber, fairly tough	slightly change
	83.0	clear, flexible	slightly more yellow	amber, fairly tough	little change
	83.0	very slightly yellow, flexible	slightly more yellow	amber, fairly tough	slightly change
	83.0	clear, flexible	slightly more yellow	amber, weak and flexible	deep amber
	91.0	clear, moderately tough	slightly more yellow	deep amber, fairly tough	slightly change

Key: MOCA = 4,4'-methylene bis-(2-chloroaniline)
 TMP = 1,1,1-trimethylol propane
 BD = 1,4-butane diol
 NT = not examined

APPENDIX B

Controls	Dry Air 28 Days at 80°C	Water 28 Days at 80°C	STF 28 Days at 65°C
ow, tough	little change	dark brown, very weak	little change
ow, tough	little change	dark brown, very weak	little change
tough	slightly more yellow	dark brown, very weak	little change
	slightly more yellow	dark brown, weak	slightly more yellow
	slightly more yellow	dark brown, weak, tacky	little change
	very slightly more yellow and weaker	dark brown, soft and weak	slightly more yellow
, flexible	little change	catastrophic failure, brown liquid	slightly opaque, weaker
ough	little change	catastrophic failure, brown liquid	little change
w, tough, rigid	NT	amber, fairly tough	slightly more yellow
w, tough rigid	slightly more yellow	amber, fairly tough	slightly more yellow
w, tough, rigid	NT	amber, fairly tough	slightly more yellow
w, tough	NT	amber, fairly tough	slightly more yellow
w, tough	NT	amber, fairly tough	slightly more yellow
w, tough, rigid	slightly more yellow	amber, fairly tough	little change
w, tough	slightly more yellow	pale amber, fairly tough	slightly more yellow
w, tough	slightly more yellow	pale amber, fairly tough	slightly more yellow
	slightly more yellow	amber, fairly tough	little change
, flexible	slightly more yellow	amber, fairly tough	slightly more yellow
	slightly more yellow	amber, weak and flexible	deep amber, swollen
ugh	slightly more yellow	deep amber, fairly tough	slightly more yellow

= 4,4'-methylene bis-(2-chloroaniline)

= 1,1,1-trimethylol propane

= 1,4-butane diol

= not examined

TABLE 3

MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS BEFORE AND AFTER 28 DAYS' AGEING

Ex 154

Code No	Type	% Stoichiometric				Controls (Unaged)				80°C Dry				80°C Wet				65°C STF			
		MOCA	TMP	BD	Total	TS MN/m ²	EB %	H BS ⁰	H (MN/m ²) at per cent	TS MN/m ²	EB %	H BS ⁰	H (MN/m ²) at per cent	TS MN/m ²	EB %	H BS ⁰	H (MN/m ²) at per cent	TS MN/m ²	EB %	H BS ⁰	H (MN/m ²) at per cent
									100 200 300				100 200 300				100 200 300				100 200 300
S.42		44.0	-	-	44.0	33.2	380	88	2.6 5.1 12.8	43.6	470	90	2.4 4.0 7.5	-	-	-	-	26.6	385	86	2.0 4.4 10.8
S.44	A	52.0	-	-	52.0	32.8	385	88	3.6 5.2 14.2	32.5	430	90	3.6 5.2 9.8	-	-	-	-	15.6	340	88	3.0 5.1 10.4
S.60	A	88.0	-	-	88.0	28.6	455	91	3.9 6.3 10.3	28.2	465	95	4.7 6.9 11.1	-	-	-	-	14.2	435	91	3.1 4.7 7.1
S.61	A	80.0	-	-	80.0	37.7	475	93	3.8 6.3 10.3	36.9	465	95	4.7 6.9 11.0	-	-	-	-	21.2	425	93	4.0 6.3 10.0
S.62	A	41.5	-	-	83.0	28.8	430	89	2.5 4.5 8.1	32.0	445	90	3.0 5.1 8.8	-	-	-	-	29.2	455	89	1.3 2.8 6.2
S.63	A	41.5	-	41.5	83.0	33.7	570	85	1.5 1.7 3.2	50.1	550	88	1.4 2.3 4.1	-	-	-	-	11.8	465	85	0.7 1.5 2.8
S.75	A	-	-	83.0	83.0	9.8	635	43	0.1 0.4 0.7	10.7	720	42	0.1 0.3 0.5	-	-	-	-	5.9	575	-	<0.1 0.2 0.4
S.21	A	-	91.0	-	91.0	12.2	300	72	1.1 3.1 12.1	21.1	335	70	0.9 2.5 7.5	-	-	-	-	1.8	150	69	0.9 - -
S.37		38.5	28.5	-	67.0	6.4	190	89	3.7 - -	10.3	320	88	3.1 5.0 7.7	10.4	540	78	0.8	4.6	125	78	3.5 - -
S.43		44	-	-	44.0	14.6	305	93	5.2 9.0 13.5	29.1	490	92	3.6 6.3 9.3	5.3	690	88	1.6 2.2 2.8	6.7	140	87	3.0 - -
S.53		33	50.0	-	83.0	5.1	180	87	3.1 - -	6.3	250	86	2.4 4.4 -	11.1	490	76	0.6 1.3 2.5	2.9	90	75	- - -
S.54		44	33.0	-	77.0	5.7	170	88	4.1 - -	8.2	270	90	3.5 5.8 -	7.1	500	79	1.0 1.8 2.9	3.7	80	76	- - -
S.56	A	55	-	-	55.0	13.5	290	91	4.9 8.5 -	28.6	455	92	3.4 5.6 9.0	6.7	900	75	0.6 1.0 1.5	5.3	145	83	3.4 - -
S.57	A	60	-	-	60.0	14.3	280	92	5.2 9.1 -	37.4	485	94	4.7 6.7 10.5	7.9	890	88	1.8 2.3 3.0	6.1	150	85	4.4 - -
S.64	A	88	-	-	88.0	19.9	330	94	5.3 7.8 12.0	36.9	510	95	5.6 8.3 11.6	2.8	350	87	2.0 2.5 2.7	7.4	215	87	4.7 7.8 -
S.65	A	80	-	-	80.0	14.3	330	94	5.3 7.0 12.4	37.3	500	94	5.3 7.7 10.7	2.8	420	86	1.4 2.0 2.5	8.3	225	88	4.7 6.3 -
S.66	A	41.5	41.5	-	83.0	15.9	340	89	2.9 5.2 9.9	17.8	445	73	2.1 3.1 6.5	12.6	610	75	1.5 2.3 3.8	4.0	170	73	2.5 - -
S.66A	A	47.5	47.5	-	95.0	11.6	355	91	4.3 6.1 8.9	17.6	330	88	5.2 7.6 13.4	16.2	600	83	2.2 3.0 4.4	8.0	180	81	5.3 - -
S.67	A	41.5	-	41.5	83.0	20.2	535	85	2.0 3.2 5.1	25.8	590	89	2.4 3.4 4.9	4.5	435	63	0.3 0.4 0.4	5.9	370	75	1.9 3.3 4.8
S.73		-	-	83.0	83.0	15.9	470	62	0.4 1.1 1.3	13.2	595	58	0.3 - 0.4	5.5	845	-	-	5.9	395	52	0.3 1.1 2.3
S.28		-	91.0	-	91.0	3.0	225	71	2.0 - -	1.95	255	67	0.7 1.4 -	0.25	440	64	0.45 1.2 2.6	0.7	65	64	- - -

MOCA = tensile strength

EB = extension at break

H = hardness

M = modulus

MOCA = 4,4'-methylene bis-(2-chloroaniline)

TMP = 1,1'-trimethylol propane

BD = 1,4-butane diol

- = too weak to test or failed before this mechanical property was obtained.

Note: 6.9 MN/m² = 1000 psi

S No 17/71/GJ/BS

21.3

21.2

21.1

TABLE 3

MECHANICAL PROPERTIES OF POLYURETHANE ELASTOMERS BEFORE AND AFTER 28 DAYS' AGEING

EKDESY

Code No	Type	% Stoichiometric				Controls (Unaged)						80°C Dry			
		MOCA	TMP	BD	Total	TS MN/m ²	EB %	H BS ⁰	M (MN/m ²) at per cent			TS MN/m ²	EB %	H BS ⁰	a 10
									100	200	300				
S.42	POLYESTER	44.0	-	-	44.0	33.2	380	88	2.6	5.1	12.8	43.6	470	90	2.
S.44		52.0	-	-	52.0	32.8	385	88	3.6	5.2	14.2	32.5	430	90	3.
S.60		88.0	-	-	88.0	28.6	455	91	3.9	6.3	10.3	28.2	465	95	4.
S.61		80.0	-	-	80.0	37.7	475	93	3.8	6.3	10.3	36.9	465	95	4.
S.62		41.5	41.5	-	83.0	28.8	430	89	2.5	4.5	8.1	32.0	445	90	3.
S.63		41.5	-	41.5	83.0	33.7	570	85	1.5	1.7	3.2	50.1	550	88	1.
S.75		-	-	83.0	83.0	9.8	635	43	0.1	0.4	0.7	10.7	720	42	0.
S.21		-	91.0	-	91.0	12.2	300	72	1.1	3.1	12.1	21.1	335	70	0.
S.37	POLYETHER	38.5	28.5	-	67.0	6.4	190	89	3.7	-	-	10.3	320	88	3.
S.43		44	-	-	44.0	14.6	305	93	5.2	9.0	13.5	29.1	490	92	3.
S.53		33	50.0	-	83.0	5.1	180	87	3.1	-	-	6.3	250	86	2.
S.54		44	33.0	-	77.0	5.7	170	88	4.1	-	-	8.2	270	90	3.
S.56		55	-	-	55.0	13.5	290	91	4.9	8.5	-	28.6	455	92	3.
S.57		60	-	-	60.0	14.3	280	92	5.2	9.1	-	37.4	485	94	4.
S.64		88	-	-	88.0	19.9	390	94	5.3	7.8	12.0	36.9	510	95	5.
S.65		80	-	-	80.0	14.3	330	94	5.3	7.0	12.4	37.3	500	94	5.
S.66		41.5	41.5	-	83.0	15.9	340	89	2.9	5.2	9.9	17.8	445	73	2.
S.66A		47.5	47.5	-	95.0	11.6	355	91	4.3	6.1	8.9	17.6	330	88	5.
S.67		41.5	-	41.5	83.0	20.2	535	85	2.0	3.2	5.1	25.8	590	89	2.
S.73		-	-	83.0	83.0	15.9	470	62	0.4	1.1	1.3	13.2	595	58	0.
S.28		-	91.0	-	91.0	3.0	225	71	2.0	-	-	1.95	256	67	0.

KEY: TS = tensile strength
 EB = extension at break
 H = hardness
 M = modulus

MOCA = 4,4'-methylene bis(4-chlorophenyl isocyanate)
 TMP = 1,1,1'-trimethylolpropane triisocyanate
 BD = 1,4-butanediol
 - = too weak to test mechanical properties

MONOMERS BEFORE AND AFTER 28 DAYS' AGEING

Controls (Unaged)						80°C Dry						80°C Wet							
2	EB %	H BS ⁰	M (MN/m ²) at per cent			TS MN/m ²	EB %	H BS ⁰	M (MN/m ²) at per cent			TS MN/m ²	EB %	H BS ⁰	M (MN/m ²) at per cent			TS MN/m ²	EB %
			100	200	300				100	200	300				100	200	300		
2	380	88	2.6	5.1	12.8	43.6	470	90	2.4	4.0	7.5	-	-	-	-	-	-	26.6	385
3	385	88	3.6	5.2	14.2	32.5	430	90	3.6	5.2	9.8	-	-	-	-	-	-	15.6	340
6	455	91	3.9	6.3	10.3	28.2	465	95	4.7	6.9	11.1	-	-	-	-	-	-	14.2	435
7	475	93	3.8	6.3	10.3	36.9	465	95	4.7	6.9	11.0	-	-	-	-	-	-	21.2	425
8	430	89	2.5	4.5	8.1	32.0	445	90	3.0	5.1	8.8	-	-	-	-	-	-	29.2	455
7	570	85	1.5	1.7	3.2	50.1	550	88	1.4	2.3	4.1	-	-	-	-	-	-	11.8	465
8	635	43	0.1	0.4	0.7	10.7	720	42	0.1	0.3	0.5	-	-	-	-	-	-	5.9	575
2	300	72	1.1	3.1	12.1	21.1	335	70	0.9	2.5	7.5	-	-	-	-	-	-	1.8	150
9	190	89	3.7	-	-	10.3	320	88	3.1	5.0	7.7	10.4	540	78	0.8	1.4	2.4	4.6	125
9	305	93	5.2	9.0	13.5	29.1	490	92	3.6	6.3	9.3	5.3	690	88	1.6	2.2	2.8	6.7	140
9	180	87	3.1	-	-	6.3	250	86	2.4	4.4	-	11.1	490	76	0.6	1.3	2.5	2.9	90
9	170	88	4.1	-	-	8.2	270	90	3.5	5.8	-	7.1	500	79	1.0	1.8	2.9	3.7	80
9	290	91	4.9	8.5	-	28.6	455	92	3.4	5.6	9.0	6.7	900	75	0.6	1.0	1.5	5.3	145
9	280	92	5.2	9.1	-	37.4	485	94	4.7	6.7	10.5	7.9	890	88	1.8	2.3	3.0	6.1	150
9	390	94	5.3	7.8	12.0	36.9	510	95	5.6	8.3	11.6	2.8	350	87	2.0	2.5	2.7	7.4	215
9	330	94	5.3	7.0	12.4	37.3	500	94	5.3	7.7	10.7	2.8	420	86	1.4	2.0	2.5	8.3	225
9	340	89	2.9	5.2	9.9	17.8	445	73	2.1	3.1	6.5	12.6	610	75	1.5	2.3	3.8	4.0	170
9	355	91	4.3	6.1	8.9	17.6	330	88	5.2	7.6	13.4	16.2	600	83	2.2	3.0	4.4	8.0	180
9	535	85	2.0	3.2	5.1	25.8	590	89	2.4	3.4	4.9	4.5	435	63	0.3	0.4	0.4	5.9	320
9	470	62	0.4	1.1	1.3	13.2	595	58	0.3	-	0.4	5.5	845	-	-	-	-	5.9	395
9	225	71	2.0	-	-	1.95	256	67	0.7	1.4	-	0.25	440	64	0.45	1.2	2.6	0.7	65

MOCA = 4,4'-methylene bis-(2-chloroaniline)

TMP = 1,1'1"-trimethylol propane

BD = 1,4-butane diol

- = too weak to test or failed before this mechanical property was obtained.

Note: 6.9 MN/m² =

APPENDIX B

AYS' AGEING

80°C Dry						80°C Wet						65°C STF					
TS MN/m ²	EB %	H BS ⁰	H (MN/m ²) at per cent			TS MN/m ²	EB %	H BS ⁰	H (MN/m ²) at per cent			TS MN/m ²	EB %	H BS ⁰	H (MN/m ²) at per cent		
			100	200	300				100	200	300				100	200	300
43.6	470	90	2.4	4.0	7.5	-	-	-	-	-	-	26.6	385	86	2.0	4.4	10.8
32.5	430	90	3.6	5.2	9.8	-	-	-	-	-	-	15.6	340	88	3.0	5.1	10.4
28.2	465	95	4.7	6.9	11.1	-	-	-	-	-	-	14.2	435	91	3.1	4.7	7.1
36.9	465	95	4.7	6.9	11.0	-	-	-	-	-	-	21.2	425	93	4.0	6.3	10.0
32.0	445	90	3.0	5.1	8.8	-	-	-	-	-	-	29.2	455	89	1.3	2.8	6.2
50.1	550	88	1.4	2.3	4.1	-	-	-	-	-	-	11.8	465	85	0.7	1.5	2.8
10.7	720	42	0.1	0.3	0.5	-	-	-	-	-	-	5.9	575	-	<0.1	0.2	0.4
21.1	335	70	0.9	2.5	7.5	-	-	-	-	-	-	1.8	150	69	0.9	-	-
10.3	320	88	3.1	5.0	7.7	10.4	540	78	0.8	1.4	2.4	4.6	125	78	3.5	-	-
29.1	490	92	3.6	6.3	9.3	5.3	690	88	1.6	2.2	2.8	6.7	100	87	3.0	-	-
6.3	250	86	2.4	4.4	-	11.1	490	76	0.6	1.3	2.5	2.9	90	75	-	-	-
8.2	270	90	3.5	5.8	-	7.1	500	79	1.0	1.8	2.9	3.7	80	76	-	-	-
28.6	455	92	3.4	5.6	9.0	6.7	900	75	0.6	1.0	1.5	5.3	145	83	3.4	-	-
37.4	485	94	4.7	6.7	10.5	7.9	890	88	1.8	2.3	3.0	6.1	150	85	4.6	-	-
36.9	510	95	5.6	8.3	11.6	2.8	350	87	2.0	2.5	2.7	7.4	215	87	4.7	6.8	-
37.3	500	94	5.3	7.7	10.7	2.8	420	86	1.4	2.0	2.5	8.3	225	88	4.7	6.3	-
37.8	445	73	2.1	3.1	6.5	12.6	610	75	1.5	2.3	3.8	4.0	170	73	2.5	-	-
37.6	330	88	5.2	7.6	13.4	16.2	600	83	2.2	3.0	4.4	8.0	180	81	5.3	-	-
5.8	590	89	2.4	3.4	4.9	4.5	435	63	0.3	0.4	0.4	5.9	320	75	1.9	3.3	4.8
3.2	595	58	0.3	-	0.4	5.5	845	-	-	-	-	5.9	395	52	0.3	1.1	2.3
1.95	256	67	0.7	1.4	-	0.25	440	64	0.45	1.2	2.6	0.7	65	64	-	-	-

4,4'-methylene bis-(2-chloroaniline)

Note: 6.9 MN/m² = 1000 psi

1,1'1"-trimethylol propane

1,4-butane diol

Too weak to test or failed before this mechanical property was obtained.

S No 17/71/CJ/BS