

AD-750 563

HIGH PERFORMANCE POLYURETHANE ELASTOMERS.
PART 2. MILLABLE ELASTOMERS AND SYNTACTIC
FOAMS

B. E. Brokenbrow, et al

Explosives Research and Development Establishment
Waltham Abbey, England

January 1972

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

AD 750563

ERDE TR 83

BR29104

ERDE TR 83



UNLIMITED

MINISTRY OF DEFENCE

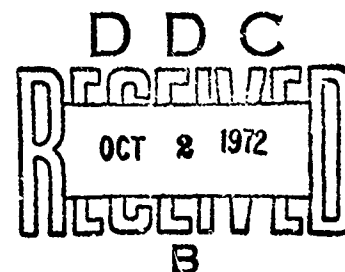
**EXPLOSIVES RESEARCH
AND DEVELOPMENT ESTABLISHMENT**

TECHNICAL REPORT No. 83

**High Performance Polyurethane Elastomers:
Part 2: Millable Elastomers and Syntactic Foams**

**B E Brokenbrow
D Sims
J Wright**

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. Department of Commerce
Springfield, VA 22151



**WALTHAM ABBEY
ESSEX**

**January
1972**

MINISTRY OF DEFENCE
EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

Technical Report No 83

January 1972

High Performance Polyurethane Elastomers:
Part 2: Millable Elastomers and Syntactic Foams

by

B E Brokenbrow
D Sims
J Wright

SUMMARY

Polyurethane elastomers based on millable sulphur cured polycaprolactone, polyoxy 1,4-butyleneglycol and hydroxyl terminated polybutadiene/di-isocyanate precursors, chain extended with unsaturated diols, together with liquid cast polyoxy 1,4-butyleneglycol di-isocyanate prepolymers filled with small hollow spheres (syntactic foams) were assessed to determine their resistance to water (80°C) and Standard Test Fluid (65°C). Two commercially supplied urethane elastomers, one based on a low molecular weight polyether/toluene di-isocyanate prepolymer cured with methylene-bis-(2-chloroaniline), the other on a higher molecular weight polyether/4,4'-methylene bis-cyclohexyl di-isocyanate prepolymer, cured with methylene bis-aniline were also assessed for comparison.

A millable caprolactone urethane elastomer gave fair resistance to STF at 65°C coupled with a very low permeability to STF at 30°C, whilst a millable polyether urethane elastomer gave good resistance to water at 80°C. A low density buoyant polyether based syntactic foam, filled either with hollow glass or 'fly-ash' spheres, gave good resistance to water at 80°C.

Further copies of this technical report can be obtained from Defence Research Information Centre, Station Square House, St Mary Cray, Orpington, Kent. BR5 3RE

CONTENTS

	Page No
1 Introduction	1
1 1 Millable Elastomers	1
1 2 Syntactic Foams	2
2 Materials and Methods of Preparation	2
2 1 Millable Elastomers	3
2 2 Syntactic Foams	3
3 Experimental	4
3 1 Mechanical Properties	4
3 2 Permeability	4
4 Results and Discussion	4
4 1 Millable Urethanes	5
4 2 Syntactic Foams	8
5 Conclusions	8
6 References	9
Appendix: Formulations and Methods of Preparation	11

1 INTRODUCTION

1.1 Millable Elastomers

Previous reports by the present authors¹⁻⁶ have described the ageing properties of polyurethane elastomers prepared from liquid castings, during exposure to various laboratory simulated environments. These elastomers were prepared with hydroxyl terminated polyol/di-isocyanate prepolymers, cured with diols/triols and/or diamines. However, other polyurethane elastomers^{7,8} which are claimed to possess good resistance to oils and solvents and known as millable urethanes are cured either with sulphur or peroxides. Possible advantages of millable urethane elastomers are that they are prepared with conventional rubber processing equipment and the curing systems used are likely to be less toxic than MOCA [methylene bis-(2-chloroaniline)], which is widely used in high performance liquid casting urethane elastomers. In addition, pigments and fillers such as carbon black may be more readily incorporated into the millable elastomers, thus possibly producing elastomers with superior physical properties and resistance to photo-oxidation compared with liquid cast polyurethane elastomers.

Uncured millable polyurethane elastomers are essentially thermoplastic materials capable of undergoing flow when processed on a rubber mill and contain reactive groups which may be crosslinked with suitable sulphur or peroxide curing agents. The polymer chain is usually linear or slightly branched, and unlike polyol/di-isocyanate prepolymers used for liquid castings which contain excess di-isocyanate; difunctional polyols and di-isocyanates are reacted in nearly stoichiometric proportions. Curing potential is introduced into millable urethane systems by the introduction of olefinic $-C=C-$ groups, contained either in the relatively high molecular weight hydroxyl terminated polyol or in a relatively low molecular weight di- or tri-functional chain extender or crosslinking agent such as 2-butene 1,4-diol or trimethylol propane monoallyl ether.

With ϵ -caprolactone based millable urethanes for example,⁹ unsaturation was achieved, either by the use of an unsaturated diol initiator and/or an unsaturated diol or triol chain extender.

Millable polyether based copolymers and terpolymers have been prepared using mixtures of cyclic oxides, such as tetrahydrofuran ethylene or propylene oxide and allyl glycidyl ether¹⁰ which yield $-CH_2O - CH_2 - CH = CH$ as the R group pendant to the main chain.

Similarly, a millable polyurethane based on a commercially available polyether/toluene di-isocyanate prepolymer was used for comparative purposes in the present investigation, the polyol is polyoxy 1,4-butylen glycol in which unsaturation is introduced probably by the inclusion of 5 - 10 per cent glycerol alpha-allyl ether."

The millable elastomers assessed in the present work were cured with sulphur, which involves the use of mixtures containing sulphur, catalysts and accelerators of the thiazole class, which are likely to form sulphur bridges

in the vicinity of unsaturated portions of the molecule, including mono-sulphide, polysulphide, vicinal polysulphide crosslinks and cyclic monosulphides. For comparative purposes a commercial low molecular weight polyoxy 1,4-butylene glycol/toluene di-isocyanate prepolymer cured with MOCA was also assessed.

1.2 Syntactic Foams

Polyurethane elastomers, which appear to bridge the gap between liquid castings and blown foams, may be prepared by dispersing hollow spherical fillers into liquid casting elastomers. A previous preliminary assessment of hydroxyl terminated polybutadiene urethane elastomers filled with hollow glass spheres³ suggested that such materials may be of potential Service interest for applications where a hydrolytically stable buoyant low density elastomeric foam is required. Composites of this type prepared from polyester, epoxide, phenolic and polyvinyl chloride resins filled with small hollow glass and phenolic spheres 5 - 150 μm in diameter have been described previously.¹² These materials are commonly known as 'syntactic' foams (Greek 'syntaxis' meaning orderly arrangement). Suggested applications for such materials include deep submergence buoyancy, structural composites and load bearing insulation, rocket nose cones and fins, and sonar windows (some acoustic properties of syntactic foams are similar to seawater).^{13,14} Similarly, hollow spheres of carbon filled with an inert gas have been used in nylon and epoxide resins and are of interest for application as low density heat shield for re-entry vehicles.¹⁵ More recently it has been found that ash recovered from electricity generating stations which use pulverized coal as a fuel, contains a small proportion of low density thin-walled hollow spheres ('Cenospheres')¹⁶ of silicate glass 20 - 200 μm diameter. The use of 'Cenospheres' as a light-weight filler for electrical insulation,¹⁷ in composite with cement, clay and resin binders¹⁸ and as a buoyancy material¹⁹ have been reported. 'Cenospheres' are said to be competitive in price with manufactured hollow-glass spheres.¹⁸

In the present investigation the ageing properties of liquid cast elastomers based on a recently developed commercial polyether, believed to be polyoxy 1,4-butylene glycol (average mol wt 1900)/di-isocyanate prepolymer cross-linked with methylene bis-aniline, both unfilled and containing hollow spheres, were assessed. This particular polyether di-isocyanate prepolymer is of interest as the aliphatic di-isocyanate 4,4'-methylene bis-cyclohexyl di-isocyanate which is used is a material which we have not examined previously; also the curing agent methylene bis-aniline may be less toxic than methylene bis-(2-chloroaniline).

The main objectives of the present work were to prepare polyurethane millable elastomers and syntactic foams and to assess their ageing resistance in water at 80°C, STF, and diester lubricant, STF/water mixtures at 65°C.

2 MATERIALS AND METHODS OF PREPARATION

Brief details of the compositions of the elastomers are given below. Formulations and methods of preparation are described in the Appendix.

2 1 Millable Elastomers

	S194 (g)	S195 (g)	S192 (g)
poly ε-caprolactone/toluene di-isocyanate/ trimethylol propane monoallyl ether	100	-	-
*polyoxy 1,4-butylene glycol/toluene di-isocyanate/glycerine alpha-monoallyl ether	-	100	-
hydroxyl terminated polybutadiene/ 4,4'-diphenyl methane di-isocyanate	-	-	100
2-butene 1,4-diol	-	-	13.6
carbon black HAF	30	30	30
2-benzothiazyl disulphide	4	4	4
mercaptobenzothiazole	1	1	1
sulphur	0.75	0.75	0.75
zinc chloride/2-benzothiazyl disulphide	0.35	0.35	0.35
cadmium stearate	0.50	0.50	0.50
Polyether Control	S196 (g)		
polyoxy 1,4-butylene glycol/toluene di-isocyanate prepolymer	100		
methylene bis-(2-chloroaniline)	25		
*probable composition			

2 2 Syntactic Foams

	S210 (g)	S211 (g)	S212 (g)	S217 (g)	S216 (g)	S218 (g)	S219 (g)
Polyoxy 1,4-butylene glycol/ 4,4'-methylene bis-cyclohexyl di-isocyanate/methylene bis-aniline elastomer	100	100	100	100	100	100	100
Hollow glass spheres	-	12.5	18.0	20.0	-	-	-
Hollow carbon spheres	-	-	-	-	12.5	-	-
Hollow 'fly-ash' spheres	-	-	-	-	-	12.5	20.0

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

3 EXPERIMENTAL

3.1 Mechanical Properties

British Standard type C dumb-bell test pieces (five 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 five, were suspended in loosely stoppered glass tubes and exposed to some or all of the following environments:

Controls	Conditioned in air at 20°C
Hot/wet	Immersed in boiled out distilled water at 80°C for 28 days
Phosphate Diester Lubricant	Immersed in 'Skydrol' at 65°C for 9 days
*Standard Test Fluid	Immersed in STF at 65°C for 28 days
STF/Water 90/10	Immersed in STF/water mixture at 65°C for 10 days

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 the required period of 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 five specimens were removed from the tubes, dried from 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^{21,22} on a Hounsfield Type E Tensometer at a constant rate of extension of 500 mm/min. Unaged control specimens cut from the materials were tested by the same methods, and the results used as "unaged" reference points.

3.2 Permeability

The permeability of selected elastomers to STF (petrol) at 30°C was determined by the method described.²³

4 RESULTS AND DISCUSSION

The results of mechanical tests and the percentage changes in original properties of the urethane elastomers are summarised in Tables 1 and 3. The permeabilities of the elastomers to STF (petrol) at 30°C are compared with

*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.²⁰

other typical synthetic elastomers in Table 2.

4.1 Millable Urethanes

Table 1 shows that both sulphur cured polyoxy 1,4-butylene glycol and polycaprolactone millable urethane elastomers gave satisfactory all round initial mechanical properties. In fact, sulphur cured polyether elastomers showed equally satisfactory initial properties to MOCA [methylene bis-(2-chloroaniline)] cured polyether urethanes previously examined.⁴⁻⁶ Although the sulphur cured hydroxyl terminated polybutadiene elastomer showed less satisfactory initial mechanical properties, the elastomer showed good resistance to water at 80°C, although its resistance to STF at 65°C was poor. The ageing properties of the elastomers were similar to those of diol and diamine cured hydroxyl terminated polybutadiene elastomers examined previously.^{2,6} The sulphur cured polycaprolactone urethane elastomer gave fairly good resistance to STF and STF/water mixtures at 65°C but poor resistance to water at 80°C. Table 2 below shows that the permeability of the millable polycaprolactone elastomer to STF at 30°C was low, and at least as good as the best of the synthetic elastomers which were evaluated for comparison.²³

On the other hand, the sulphur cured polyether elastomer whilst giving good resistance to water at 80°C was not resistant to STF and STF/water mixtures at 65°C. The MOCA cured low molecular weight polyether assessed for comparison, whilst giving good resistance to STF and STF/water mixture at 65°C showed poor resistance to water at 80°C.

None of the elastomers were capable of resisting phosphate based diester lubricant at 65°C.

TABLE 1

CHANGES IN MECHANICAL PROPERTIES OF MILLABLE POLYURETHANE ELASTOMERS AFTER AGEING IN VARIOUS ENVI

Code No	Elastomer type	Initial properties (unaged)				Percentage				
						28 days in water 80°C				
		TS (MN/m ²)	M 100 (MN/m ²)	EB (%)	H (BS°)	TS	M 100	EB	H	
S192	hydroxyl terminated polybutadiene/sulphur cure	7.5	-	75	93	-15.0	-	- 7.0	- 1.0	-
S194	polycaprolactone/sulphur cure	29.2	5.3	345	84	Too weak to test				-
S195	polyether/sulphur cure	26.1	4.2	380	78	-11.0	-48.0	+ 36.0	-18.0	-
S196	polyether/MOCA cure (control)	35.1	33.0	115	99	-47.0	-61.0	+150.0	-10.0	-

Key: TS = tensile strength at break
M 100 = modulus at 100 per cent extension
EB = percentage extension at break

H = hardn
MOCA = methy

TABLE 2

Code No	Elastomer
S192	sulphur cured hydroxyl terminated polybutadiene urethane
S194	sulphur cured polycaprolactone ureth
S195	sulphur cured polyether urethane
S196	MOCA cured polyether urethane
	Nitrile
	PVC/nitrile
	Neoprene WRT

PROPERTIES OF MILLABLE POLYURETHANE ELASTOMERS AFTER AGEING IN VARIOUS ENVIRONMENTS

Initial properties (unaged)				Percentage change of original mechanical properties								
				28 days in water 80°C				28 days STF 65°C				
TS (MN/m ²)	M 100 (MN/m ²)	EB (%)	H (BS°)	TS	M 100	EB	H	TS	M 100	EB	H	TS
7.5	-	75	93	-15.0	-	- 7.0	- 1.0	-60.0	-	-20.0	-35.0	-71.0
29.2	5.3	345	84	Too weak to test				-40.0	-25.0	-20.0	-19.0	-56.0
26.1	4.2	380	78	-11.0	-48.0	+ 36.0	-18.0	-59.0	-55.0	-20.0	-36.0	-57.0
35.1	33.0	115	99	-47.0	-61.0	+150.0	-10.0	-21.0	0.0	-19.0	0.0	-42.0

length at break
100 per cent extension
extension at break

H = hardness
MOCA = methylene bis-(2-chloroaniline)

TABLE 2

Code No	Elastomer	Thickness (mm)	Permeability (ml/m ² /day)
S192	sulphur cured hydroxyl terminated polybutadiene urethane	2.15	3640
S194	sulphur cured polycaprolactone urethane	1.68	57
S195	sulphur cured polyether urethane	1.83	530
S196	MOCA cured polyether urethane	1.34	1570
	Nitrile	2.0	220
	PVC/nitrile	2.0	145
	Neoprene WRT	2.0	1160

ING IN ARIOUS ENVIRONMENTS

Percentage change of original mechanical property after ageing for													
in water		28 days STF 65°C				9 days STF/Water 90/10 65°C				10 days Skydrol 60°C			
EB	H	TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H
- 7.0	- 1.0	-50.0	-	-20.0	-35.0	-71.0	-	-33.0	-42.0	Too weak to test			
Weak test		-40.0	-25.0	-20.0	-19.0	-56.0	-47.0	- 6.0	-37.0	Too weak to test			
+ 36.0	-18.0	-59.0	-55.0	-20.0	-36.0	-57.0	+ 1.0	+ 1.0	-51.0	Too weak to test			
+150.0	-10.0	-21.0	0.0	-19.0	0.0	-42.0	-47.0	+39.0	0.0	Too weak to test			

H = hardness

MOCA = methylene bis-(2-chloroaniline)

Customer	Thickness (mm)	Permeability (ml/m ² /day)
oxyl terminated thane	2.15	3640
ycaprolactone thane	1.68	57
ether urethane	1.83	530
er urethane	1.34	1570
	2.0	220
	2.0	145
	2.0	1160

TABLE 1

CHANGES IN MECHANICAL PROPERTIES OF MILLABLE POLYURETHANE ELASTOMERS AFTER AGEING IN VARIOUS ENVIRONMENTS

Code No	Elastomer type	Initial properties (unaged)					Percentage change of original mechanical property after ageing for																			
							28 days in water 80°C					28 days STF 65°C					9 days STF/Water 90/10 65°C					10 days Skydrol 66°C				
		TS (MN/m ²)	M 100 (MN/m ²)	EB (%)	H (BS°)		TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H				
S192	hydroxyl terminated polybutadiene/sulphur cure	7.5	-	75	93	-15.0	-	- 7.0	- 1.0	-60.0	-	-20.0	-35.0	-71.0	-	-33.0	-42.0	Too weak to test								
S194	polycaprolactone/sulphur cure	29.2	5.3	345	84	Too weak to test					-40.0	-25.0	-20.0	-19.0	-56.0	-47.0	- 6.0	-37.0	Too weak to test							
S195	polyether/sulphur cure	26.1	4.2	380	78	-11.0	-48.0	+ 36.0	-18.0	-59.0	-55.0	-20.0	-36.0	-57.0	+ 1.0	+ 1.0	-51.0	Too weak to test								
S196	polyether/MOCA cure (control)	35.1	33.0	115	99	-47.0	-61.0	+150.0	-10.0	-21.0	0.0	-19.0	0.0	-42.0	-47.0	+39.0	0.0	Too weak to test								

Key: TS = tensile strength at break
M₁₀₀ = modulus at 100 per cent extension
EB = percentage extension at break

H = hardness
MOCA = methylene bis-(2-chloroaniline)

TABLE 2

Code No	Elastomer	Thickness (mm)	Permeability (ml/cm ² /day)
S192	sulphur cured hydroxyl terminated polybutadiene urethane	2.15	3640
S194	sulphur cured polycaprolactone urethane	1.68	57
S195	sulphur cured polyether urethane	1.83	530
S196	MOCA cured polyether urethane	1.34	1570
	Nitrile	2.0	220
	PVC/nitrile	2.0	145
	Nec. rene WRT	2.0	1160

TABLE 3

CHANGES IN MECHANICAL PROPERTIES OF SYNTACTIC POLYURETHANE FOAMS AFTER AGEING IN VARIOUS ENVIRONMENTS

Code No	Elastomer type	Additive (% by wt)	Initial properties (unaged)					Percentage change of original mechanical property after ageing for									
								28 days water 80°C					28 days STF 65°C				
			TS (MN/m ²)	M 100 (MN/m ²)	EB (%)	H (BS°)		TS	M 100	EB	H		TS	M 100	EB	H	
S210		nil	24.8	8.9	270	93		- 2.5	-45.0	+35.0	-20.0		-58.0	-54.0	-15.0	-17.0	
S211		Glass spheres (12.5)	12.1	7.8	200	97		0	-43.5	+35.0	- 9.5		-61.0	-95.0	-50.0	-17.0	
S212		Glass spheres (18.0)	5.4	4.0	215	90		+15.0	-35.0	+18.5	- 1.0		-55.0	-85.0	-12.0	-58.0	
S217	Polyether/ 4,4'-methylene bis-cyclohexyl di-isocyanate/ methylene bis-aniline	Glass spheres (20)	7.6	5.9	270	90		+38.0	-59.5	+29.5	-16.5		-72.0	-78.0	-33.0	-39.0	
S216		carbon spheres (12.5)	6.3	4.8	195	98		-53.0	-90.0	+30.0	+29.0		-54.0	-	-23.0	-18.0	
S218		'fly-ash' spheres (12.5)	11.9	5.8	325	94		- 5.1	-24.1	+17.0	-		-60.0	-33.0	-48.0	-	
S219		'fly-ash' spheres (20.0)	7.3	5.4	240	95		+55.0	-29.6	+50.0	-		-44.0	-31.5	-48.0	-	

Key: TS = tensile strength at break
M 100 = modulus at 100 per cent extensionEB = percentage extension at break
H = hardness

7.1

7.2

TABLE 3

CHANGES IN MECHANICAL PROPERTIES OF SYNTACTIC POLYURETHANE FOAMS AFTER AGEING IN VARIOUS ENV

Code No	Elastomer type	Additive (% by wt)	Initial properties (unaged)				Per 28 days wat	
			TS (MN/m ²)	M ₁₀₀ (MN/m ²)	EB (%)	H (BS ⁰)	TS	M ₁₀₀
S210	Polyether/ 4,4'-methylene bis-cyclohexyl di-isocyanate/ methylene bis-aniline	nil	24.8	8.9	270	93	- 2.5	-45.0
S211		glass spheres (12.5)	12.1	7.8	200	97	0	-43.5
S212		glass spheres (18.0)	5.4	4.0	215	90	+15.0	-35.0
S217		glass spheres (20)	7.6	5.9	270	90	+38.0	-59.5
S216		carbon spheres (12.5)	6.8	4.8	195	98	-53.0	-90.0
S218		'fly-ash' spheres (12.5)	11.9	5.8	325	94	- 5.1	-24.1
S219		'fly-ash' spheres (20.0)	7.3	5.4	240	95	+55.0	-29.6

Key: TS = tensile strength at break
M 100 = modulus at 100 per cent extension

EB = perce
H = hardn

7.1

7.2-

OF SYNTACTIC POLYURETHANE FOAMS AFTER AGEING IN VARIOUS ENVIRONMENTS

ative y wt)	Initial properties (unaged)				Percentage change of original mechanical property							
					28 days water 80°C				28 days STF 65°C			
	TS (MN/m ²)	M 100 (MN/m ²)	EB (%)	H (BS°)	TS	M 100	EB	H	TS	M 100	EB	H
	24.8	8.9	270	93	- 2.5	-45.0	+35.0	-20.0	-58.0	-54.0	-15.0	-17.0
(12.5)	12.1	7.8	200	97	0	-43.5	+35.0	- 9.5	-61.0	-95.0	-50.0	-17.0
(18.0)	5.4	4.0	215	90	+15.0	-35.0	+18.5	- 1.0	-55.0	-85.0	-12.0	-58.0
(20)	7.6	5.9	270	90	+38.0	-59.5	+29.5	-16.5	-72.0	-78.0	-33.0	-39.0
(12.5)	6.8	4.8	195	98	-53.0	-90.0	+36.0	+29.0	-54.0	-	-23.0	-18.0
(12.5)	11.9	5.8	325	94	- 5.1	-24.1	+17.0	-	-60.0	-33.0	-48.0	-
(20.0)	7.3	5.4	240	95	+55.0	-29.6	+50.0	-	-44.0	-31.5	-48.0	-

at break
er cent extension

EB = percentage extension at break
H = hardness

7.1

7.2

7.3

ING IN VARIOUS ENVIRONMENTS

Percentage change of original mechanical property after ageing for											
28 days water 80°C				28 days STF 65°C				9 days STF/Water 90/10 65°C			
TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H
- 2.5	-45.0	+35.0	-20.0	-58.0	-54.0	-15.0	-17.0	-62.0	-56.0	-19.0	-27.0
0	-43.5	+35.0	- 9.5	-61.0	-95.0	-50.0	-17.0	-65.0	-76.0	0.0	-35.0
+15.0	-35.0	+18.5	- 1.0	-55.0	-85.0	-12.0	-58.0	-67.0	-75.0	-16.0	-36.0
+38.0	-59.5	+29.5	-16.5	-72.0	-78.0	-33.0	-39.0	-37.0	+ 5.0	+26.0	-37.0
-53.0	-90.0	+36.0	+29.0	-54.0	-	-23.0	-18.0	-53.0	-89.0	+18.0	-37.0
- 5.1	-24.1	+17.0	-	-60.0	-33.0	-48.0	-	-62.0	-62.0	+14.0	-
+55.0	-29.6	+50.0	-	-44.0	-31.5	-48.0	-	-60.0	-61.0	-21.0	-

EB = percentage extension at break

H = hardness

73

4 2 Syntactic Foams

The addition of hollow spheres to a liquid cast polyether urethane elastomer based on a polyoxy 1,4-butylen glycol/4,4'-methylene bis-cyclohexyl di-isocyanate prepolymer cured with methylene bis-aniline produced buoyant composites of lower density, tensile strength and 100 per cent modulus compared with the unfilled elastomer. Optimum processing characteristics were obtained with 12½ to 20 per cent 'fly-ash' and glass spheres, whilst additions of more than 12½ per cent carbon spheres produced elastomers with poor flow and casting characteristics. Similarly, optimum mechanical properties both initially and after ageing were obtained with additions of hollow spheres at loadings of 12½ per cent rather than 20 per cent. Although the initial mechanical properties of the glass and 'fly-ash' filled elastomers were somewhat inferior to the unfilled elastomers they showed satisfactory resistance to water at 80°C. Elastomers filled with carbon spheres gave inferior resistance to water compared with glass and 'fly-ash' filled materials, but their resistance to STF/water mixture at 65°C was rather better than either unfilled 'fly-ash' or glass filled elastomers. The unfilled MOCA free polyether urethane elastomer showed good resistance to water although its resistance to STF and STF/water mixtures at 65°C was poor.

5 CONCLUSIONS

A range of methylene bis-(2-chloroaniline) (MOCA) free urethane elastomers based on sulphur cured millable elastomers and liquid cast elastomers filled with hollow spheres (syntactic foam) were prepared and evaluated.

Sulphur cured, carbon black filled polycaprolactone and polyether urethane elastomers gave good mechanical properties initially. The polycaprolactone elastomer was very impermeable to STF at 30°C and showed fairly good retention of physical properties after 28 days' immersion in STF and STF/water at 65°C; the resistance of the elastomer to water at 80°C however, was poor. The polyether elastomer on the other hand, showed good resistance to water at 80°C but poor resistance to STF and STF/water at 65°C and was inferior in this respect to a MOCA cured liquid cast polyether urethane evaluated for comparison. None of the elastomers was found to be capable of resisting phosphate diester lubricant at 65°C.

Buoyant, low density syntactic foams prepared from a polyether urethane filled with hollow spheres showed fairly good mechanical properties coupled with good resistance to water at 80°C, although the resistance of these materials to STF, as well as the unfilled polyether evaluated for comparison, was poor. The unfilled polyether based on a polyoxy 1,4-methylene glycol/4,4'-methylene bis-cyclohexyl di-isocyanate cured with methylene bis-aniline, which is probably less toxic than MOCA, gave good mechanical properties initially, coupled with very good resistance to water at 80°C.

6 REFERENCES

- 1 Brokenbrow B E, Sims D, Wright J ERDE Technical Report No 20, July 1970
- 2 idem ERDE Technical Report No 39, August 1970
- 3 idem ERDE Technical Report No 77, (in publication)
- 4 idem Rubb J, 1971, 153 (6), 48
- 5 idem Rubb J, 1971, 153 (7), 44
- 6 idem Rubb J, 1971, 153 (8), 45
- 7 Hirsty S M Adiprene C M Urethane Rubber, Du Pont Technical Report
- 8 Trappe G Advances in Polyurethane Technology, Eds Buist, J M, Gudgeon, H, MacLaren, London, 1968, p 41
- 9 Kincaid H, et al Rubb Plast Age, Dec 1967, p 1367
- 10 Ossefurt Z T, Veroeven W M I E C Prod Res Dev, 1967, 6, 2
- 11 Ludbrook B D The Stability of Rubber Networks Report No 1, RAPRA, May 1970
- 12 Alford H E, Veatch F Am Chem Soc Div Organic Coatings and Plastics Chemistry, 1961, 21, 192
- 13 Davis J W, Johnson R W 22nd Annual Meeting Reinforced Plastics Div, Society Plastics Industry, 1967, Section 17C, p 1
- 14 Bepristo A J, Johnson B R 23rd Annual Technical Conf Reinforced Plastics/Composites Div, Society Plastics Industry, 1968, Section 7C p 1
- 15 Shaver R G, Powers W M Materials and Processes for the 70's 15th National SAMPE Symposium (1969), 1970, 15, 254
- 16 Raask E J Inst Fuel, Sept 1968
- 17 Raask E, Stannett A W Electl Times, 12 March 1971
- 18 Raask E Br Chem Engng, 1970, 15(9), 1165
- 19 Johnson A A et al Ocean Engng, 1970, 2, 45

- | | |
|----|---|
| 20 | BS 2751 : 1956 |
| 21 | BS 903 : Part A2 : 1956 |
| 22 | BS 903 : Part A7 : 1957 |
| 23 | Richards R W, Sims D,
Stokoe A L |
| | ERDE Technical Report (to be published) |

APPENDIX

FORMULATIONS AND METHODS OF PREPARATION

MILLABLE ELASTOMERS

Formulations of gum stocks

S194

	mole equivalent
a NIAX 520 polycaprolactone polyol (av mol wt 830, hydroxyl no 135, acid no 0.3)	0.5
NIAX 540 polycaprolactone polyol (av mol wt 1250, hydroxyl no 90, acid no 0.3)	0.5
b Hylene TM, a mixture of 80 : 20 2,4 and 2,6 isomers toluene di-isocyanate	2.0
c trimethylol propane monoallyl ether	1.0

Method

The mixed caprolactone polyols and the trimethylol propane were heated to 65°C under nitrogen in a three-necked Quickfit 500 ml flask equipped with stirrer, thermometer and nitrogen inlet and stirred until homogeneous. The toluene di-isocyanate was added and the mixture stirred for 30 minutes at 80 - 85°C. The reaction product was poured into PTFE coated aluminium trays and cured for 12 h at 100°C.

S195 was a commercially supplied polyether urethane known as

d Adiprene CM and is probably based on the following formulation

	mole equivalent
polyoxy 1,4-butylene glycol	1.0
toluene di-isocyanate	2.0
c glycerine alpha-monoallyl ether	1.0

S192

	mole equivalent
e Hydroxyl terminated polybutadiene R.15M (OH functionality 2.3)	1.0
f Isonate 143L (modified 4,4'-diphenyl methane di-isocyanate)	2.5

APPENDIX

Method

The hydroxyl-terminated polybutadiene was heated to 105°C in a three-necked 'Quickfit' flask equipped with stirrer, thermometer, nitrogen and vacuum inlet, the resin was degassed for 30 minutes under 5 mmHg, vacuum cooled to 40°C and Isonate 143L added. Stirring was continued to 1 h at 40 - 50°C and the prepolymer degassed for 5 minutes under 1 mmHg vacuum. The reaction product was poured into PTFE coated aluminium trays and cured for 16 h at 95 - 100°C.

Formulations of Elastomers

	Compounded stock		
	S195	S195	S192
	parts by weight		
Gum stock S194 caprolactone/TDI prepolymer	100	-	-
" " S195 polyoxy 1,4-butylene glycol/TDI prepolymer	-	100	-
" " S192 hydroxyl terminated polybutadiene/MDI prepolymer	-	-	100
2-butene 1,4-diol	-	-	13.6
g carbon black HAF	30	30	30
2-benzthiazyl disulphide	4	4	4
mercaptobenzothiazole	1	1	1
sulphur	0.75	0.75	0.75
h zinc chloride/2-benzthiazyl disulphide	0.35	0.35	0.35
cadmium stearate	0.50	0.50	0.50

The above mixes were dispersed on a 'Bridge' Rubber mill and press cured for 1/2 h at 120°C.

S196 Liquid Cast Polyether Urethane

	8
i Polyoxy 1,4-butylene glycol (av mol wt 500)/toluene di-isocyanate prepolymer (9.5% free NCO)	250
Methylene-bis-(2-chloroaniline) 86% theoretical	62.5

Key to Suppliers

- a Niox 520 and Niox 540, Caprolactone polyols ex-Union Carbide.
- b Hylene TM, toluene di-isocyanate ex Du-Pont (UK).
- c Trimethylol propane monoallyl ether and glycerine alpha-allyl ether ex-Kodak.
- d Adiprene CM, millable polyether urethane ex-Du Pont (UK).
- e R.15M, hydroxyl terminated polybutadiene ex-Arco Chemicals.
- f Isonate 143L, modified 4,4'-diphenyl methane di-isocyanate ex-Upjohn.
- g Carbon black HAF ex-Cabot Chemicals.
- h Caytur 4 ex-Du Pont.
- i Polyether prepolymer ex-Du Pont.

Syntactic foams

	S210 (Unfilled elastomer for comparison)	S211	S212	S217	S216	S218	S219
		(parts by weight)					
j	Polyoxy 1,4-butylene glycol (av mol wt 1900) 4,4'-methylene bis-cyclohexyl di-isocyanate prepolymer (4.75% free NCO) 100 parts cured with methylene bis- aniline (95% theory) 10.6 parts)	100	100	100	100	100	100
k	Hollow glass spheres	12.5	18.0	20.0	-	-	-
l	Hollow carbon spheres	-	-	-	12.5	-	-
m	Hollow 'fly-ash' spheres	-	-	-	-	12.5	20.0
	Method of preparation (unfilled elastomer S210)						

The polyether prepolymer was heated to 105°C and degassed under 1 mmHg vacuum for 5 minutes, methylene bis-aniline preheated to 110°C was added to the prepolymer with stirring, the mixture was degassed for 3 minutes at 105°C and the reaction product poured into PTFE coated aluminium trays and cured for 16 h at 100°C.

Method of preparation (syntactic foams)

The method of preparation was the same as described above, except that the spheres were added to the polyether prepolymer, dispersed by stirring and the mixture degassed for 10 minutes at 90 - 100°C, prior to the addition of MDA curing agent.

APPENDIX

Key to Suppliers

- j Polyether prepolymer Adiprene LD 2699 ex-Du Pont (UK).
- k Atmospheres ex-JBC Plastics (Dewsbury).
- l Carbo-Spheres ex-General Technologies Corp US.
- m Cenospheres ex-Central Electricity Research Laboratories, Leatherhead.

S No 46/72/BS

Technical Report No 83 Explosives Research and Development Establishment HIGH PERFORMANCE POLYURETHANE ELASTOMERS: PART 2: MILLABLE ELASTOMERS AND SYNTHETIC FOAMS Brokenbrow B E, Sims D, Wright J January 1972 15 pp, 3 tabs, no figs Polyurethane elastomers based on millable sulphur cured polycaprolactone, polyoxy 1,4-butylene glycol and hydroxyl terminated polybutadiene/di-isocyanate precursors, chain extended with unsaturated diols, together with liquid cast polyoxy 1,4-butylene glycol di-isocyanate prepolymers filled with small hollow spheres (syntactic foams) were assessed to determine their resistance to water (80°C) and Standard Test Fluid (65°C). Two commercially supplied urethane elastomers, one based on a low molecular weight polyether/toluene di-isocyanate prepolymer cured with methylene-bis-(2-chloroaniline), the other on a higher molecular weight polyether/4,4'-methylene bis-cyclohexyl di-isocyanate prepolymer, cured with methylene bis-aniline were also assessed for comparison. /(over)	Technical Report No 83 Explosives Research and Development Establishment HIGH PERFORMANCE POLYURETHANE ELASTOMERS: PART 2: MILLABLE ELASTOMERS AND SYNTHETIC FOAMS Brokenbrow B E, Sims D, Wright J January 1972 15 pp, 3 tabs, no figs Polyurethane elastomers based on millable sulphur cured polycaprolactone, polyoxy 1,4-butylene glycol and hydroxyl terminated polybutadiene/di-isocyanate precursors, chain extended with unsaturated diols, together with liquid cast polyoxy 1,4-butylene glycol di-isocyanate prepolymers filled with small hollow spheres (syntactic foams) were assessed to determine their resistance to water (80°C) and Standard Test Fluid (65°C). Two commercially supplied urethane elastomers, one based on a low molecular weight polyether/toluene di-isocyanate prepolymer cured with methylene-bis-(2-chloroaniline), the other on a higher molecular weight polyether/4,4'-methylene bis-cyclohexyl di-isocyanate prepolymer, cured with methylene bis-aniline were also assessed for comparison. /(over)
Technical Report No 83 Explosives Research and Development Establishment HIGH PERFORMANCE POLYURETHANE ELASTOMERS: PART 2: MILLABLE ELASTOMERS AND SYNTHETIC FOAMS Brokenbrow B E, Sims D, Wright J January 1972 15 pp, 3 tabs, no figs Polyurethane elastomers based on millable sulphur cured polycaprolactone, polyoxy 1,4-butylene glycol and hydroxyl terminated polybutadiene/di-isocyanate precursors, chain extended with unsaturated diols, together with liquid cast polyoxy 1,4-butylene glycol di-isocyanate prepolymers filled with small hollow spheres (syntactic foams) were assessed to determine their resistance to water (80°C) and Standard Test Fluid (65°C). Two commercially supplied urethane elastomers, one based on a low molecular weight polyether/toluene di-isocyanate prepolymer cured with methylene-bis-(2-chloroaniline), the other on a higher molecular weight polyether/4,4'-methylene bis-cyclohexyl di-isocyanate prepolymer, cured with methylene bis-aniline were also assessed for comparison. /(over)	Technical Report No 83 Explosives Research and Development Establishment HIGH PERFORMANCE POLYURETHANE ELASTOMERS: PART 2: MILLABLE ELASTOMERS AND SYNTHETIC FOAMS Brokenbrow B E, Sims D, Wright J January 1972 15 pp, 3 tabs, no figs Polyurethane elastomers based on millable sulphur cured polycaprolactone, polyoxy 1,4-butylene glycol and hydroxyl terminated polybutadiene/di-isocyanate precursors, chain extended with unsaturated diols, together with liquid cast polyoxy 1,4-butylene glycol di-isocyanate prepolymers filled with small hollow spheres (syntactic foams) were assessed to determine their resistance to water (80°C) and Standard Test Fluid (65°C). Two commercially supplied urethane elastomers, one based on a low molecular weight polyether/toluene di-isocyanate prepolymer cured with methylene-bis-(2-chloroaniline), the other on a higher molecular weight polyether/4,4'-methylene bis-cyclohexyl di-isocyanate prepolymer, cured with methylene bis-aniline were also assessed for comparison. /(over)

A millable caprolactone urethane elastomer gave fair resistance to STF at 65°C coupled with a very low permeability to STF at 30°C, whilst a millable polyether urethane elastomer gave good resistance to water at 80°C. A low density buoyant polyether based syntactic foam, filled either with hollow glass or 'fly-ash' spheres, gave good resistance to water at 80°C.

A millable caprolactone urethane elastomer gave fair resistance to STF at 65°C coupled with a very low permeability to STF at 30°C, whilst a millable polyether urethane elastomer gave good resistance to water at 80°C. A low density buoyant polyether based syntactic foam, filled either with hollow glass or 'fly-ash' spheres, gave good resistance to water at 80°C.

A millable caprolactone urethane elastomer gave fair resistance to STF at 65°C coupled with a very low permeability to STF at 30°C, whilst a millable polyether urethane elastomer gave good resistance to water at 80°C. A low density buoyant polyether based syntactic foam, filled either with hollow glass or 'fly-ash' spheres, gave good resistance to water at 80°C.

A millable caprolactone urethane elastomer gave fair resistance to STF at 65°C coupled with a very low permeability to STF at 30°C, whilst a millable polyether urethane elastomer gave good resistance to water at 80°C. A low density buoyant polyether based syntactic foam, filled either with hollow glass or 'fly-ash' spheres, gave good resistance to water at 80°C.