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HIGH PERFORMANCE POLYURETHANE ELASTOMERS.
PART 1. LABORATORY AGEING TRIALS

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Explosives Research and Development Establishment
Waltham Abbey, England

January 1972

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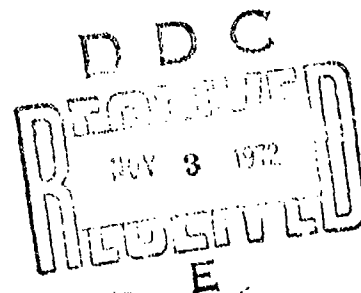
**EXPLOSIVES RESEARCH
AND DEVELOPMENT ESTABLISHMENT**

TECHNICAL REPORT No.77

**High Performance Polyurethane Elastomers:
Part 1: Laboratory Ageing Trials**

**B E Brokenbrow
D Sims
J Wright**

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High Performance Polyurethane Elastomers:
Part 1: Laboratory Ageing Trials

by

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SUMMARY

A range of polyurethane elastomers based on di-isocyanate prepolymers of polyether, hydroxyl-terminated polybutadiene, polyester adipate and caprolactone polyols have been prepared and their ageing properties assessed under a wide variety of laboratory simulated environmental conditions, including exposure to dry air (80 - 100°C), ultraviolet radiation; immersion in oil at 100°C, STF (65°C) and water (50 - 100°C).

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SUMMARY

A range of polyurethane elastomers based on di-isocyanate prepolymers of polyether, hydroxyl-terminated polybutadiene, polyester adipate and caprolactone polyols have been prepared and their ageing properties assessed under a wide variety of laboratory simulated environmental conditions, including exposure to dry air (80 - 100°C), ultraviolet radiation; immersion in oil at 100°C, STF (65°C) and water (50 - 100°C).

Individual elastomers were capable of resisting many, but usually not all of these conditions, although certain urethane elastomers prepared from polyethers, average molecular weight 1000 - 2000, provided a reasonably acceptable compromise of properties under most conditions.

Elastomers based on hydroxyl-terminated polybutadiene/modified 4,4'-diphenyl methane di-isocyanate prepolymers possessed initial mechanical properties which were superior to those prepared hitherto, whilst still retaining outstanding resistance to hydrolysis.

Polyester based urethane elastomers showed good resistance to dry air and fuels but their resistance to water at temperatures above 50°C was poor. The addition of polycarbodiimides slightly improved the water resistance of polyester urethanes, whilst ultraviolet absorbers in conjunction with an antioxidant pair, based on a mixture of butylated hydroxy propylene and dilauryl thiodipropionate, appeared to enhance the photo-oxidative stability of polyester urethanes.

Reference: WAC/213/018

1 INTRODUCTION

Previous investigations^{1-5,12} by the present authors have shown that the ageing properties of polyurethane elastomers are strongly dependent on the chemical structure of the elastomer. For example, the type of backbone polyol, its molecular weight, the degree of crosslinking and the effective chemical group structure in the polymer chain had a marked influence on the initial physical properties of the unaged elastomers and their resistances to ageing when exposed to dry air, water and STF. Hydroxyl-terminated polybutadienes, for example, produced urethane elastomers with superior hydrolytic stability to elastomers prepared with conventional polyether and polyester backbone polyols.²

The main objective of the present investigation was to make practical use of the information obtained earlier and to prepare a series of polyurethane elastomers based on adipate and caprolactone esters, polyethers and hydroxyl-terminated polybutadiene polyols and assess their ageing characteristics under a wider range of laboratory simulated environmental conditions than hitherto examined. The effects of additives, including ultraviolet absorbers and antioxidants, would also be examined in those elastomers showing any marked shortcomings when exposed to a specific environment.

2 MATERIALS AND METHODS OF PREPARATION

Six laboratory prepared elastomers and one elastomer prepared from a commercially supplied polyether/toluene di-isocyanate prepolymer were evaluated.

Details of the formulations of elastomers are summarised in Table 1. The elastomers were prepared in 1000 g batches by the methods previously described in References 1 - 5.

TABLE 1

DETAILS OF ELASTOMERS SELECTED FOR AGING TRIALS

Elastomer No	Polym	CR functionality	Acid No mg KOH/g	Hydroxyl No mg KOH/g	Water (per cent)	Average molecular weight	Moles equivalent	Di-isocyanate	Moles equivalent	Crosslinker/chain extender	Moles equivalent
S 140	Hydroxyl-terminated butadiene (a)	2.5	0.0	43.0	0.1	3000	1.0	4,4'-diphenyl methane modified (b) (mol wt 288)	2.51	N,N'-bis-(2-hydroxypropyl aniline, (c))	1.25
S 147	ϵ -caprolactone ester (d)	2.0	0.3	56.1	0.03	2000	1.0	toluene (e)	2.20	1,1',1''-tri-methylol propane, methylene-bis-(2-chloroaniline)	0.33 0.50
S 155	ϵ -caprolactone ester (f)	2.0	0.3	212.0	0.03	530	1.0	toluene (e)	2.10	1,4-butane diol, 1,1',1''-trimethylol propane	0.50
S 160	oxy 1,4-butylene glycol (h)	2.0	0.01	56.7	0.02	1980	1.0	toluene (e)	2.20	1,1',1''-trimethylol propane, methylene-bis-(2-chloroaniline)	0.33 0.50
S 173	oxy 1,4-butylene glycol (g)	2.0	0.01	109.4	0.01	1050	1.0	4,4'-diphenyl methane modified (b) (mol wt 288)	2.20	1,1',1''-trimethylol propane	1.0
S 176	Ethylene adipate 90% (i) Propylene adipate 10% (j)	2.0 2.0	0.42 0.55	59.0 59.0	0.02 0.01	1900	0.9 0.1	toluene (k)	2.20	1,1',1''-trimethylol propane, methylene-bis-(2-chloroaniline)	0.33 0.50
S 200	oxy 1,4-butylene glycol (l)	2.0	-	-	-	2000 (estimated)	-	toluene (e)	not known	4,4'-methylene bis-(2-chloroaniline)	1.32

(a) Esso ex-Arco Chemical Co

(b) Isomate 143; ex-Upjohn Co

(c) Isomol C100 ex-Upjohn Co

(d) Niaz D560 ex-Union Carbide Co

(e) Nylene T M 808; 2,4:2,6 isomers ex-DuPont UK

(f) Niaz D510 Union Carbide

(g) Polymag 1000 ex-Quaker Oats Co

(h) Polymag 2000 ex-Quaker Oats Co

(i) Formvar P7-37 ex-Witco Chemical Co

(j) Formvar P7-67 ex-Witco Chemical Co

(k) Nylene T 100% 2,4 isomer ex-DuPont UK

(l) Adiprene 123 ex-DuPont UK

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3 EXPERIMENTAL

British Standard type C dumb-bell test specimens 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 dry air at 20°C, 65 per cent rh for 28 days
Hot/dry	Suspended in dry air at 80°C for 28 days
Hot/dry	Suspended in dry air at 100°C for 28 days
Hot/wet	Suspended over water at 100°C for 14 days
Hot/wet	Immersed in water at 50°C for 28 days
Hot/wet	Immersed in water at 80°C for 14 days
Hot/wet	Immersed in water at 80°C for 28 days
*Standard Test Fluid (Petrol)	Immersed in STF at 65°C for 28 days
**ASTM Oil No 1	Immersed in oil at 100°C for 9 days

The charged tubes were placed in circulating air ovens in which the temperature 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 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^{4,7} on a Hounsfield Type E Tensometer at a constant rate of extension of 500 mm/min. Unaged control specimens cut from the elastomers were tested by the same methods, and the results used as 'unaged' reference points.

3.1 Ultraviolet Radiation

Dumb-bell specimens as described above were exposed in sets of 5 for 10 days to radiation from 2 kW high pressure xenon discharge lamp previously described.⁹ The specimens were attached to cardboard frames moulded to and attached to the circumference of the inner wall surface of the drum. The temperature of the specimens was 29 - 31°C and the relative humidity of the air surrounding the specimens 34 - 36 per cent. The specimens were tested after exposure as in Section 3.

Note: *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.⁸

**ASTM Oil No 1 (ex-Esco Petroleum) is a petroleum based oil to ASTM Specification D471/57T, 1957.

3 2 Low Temperature Flexibility

The low temperature flexibility of the elastomers was determined by a method described recently¹⁰ in which the torsional modulus of the material is determined as a function of temperature.

4 RESULTS AND DISCUSSION

4 1 Properties of Unmodified Polyurethane Elastomers

The results of mechanical tests and the percentage changes in original mechanical properties of the unmodified polyurethane elastomers after ageing are summarized in Table 2. Stress strain curves of the elastomers are reproduced in Figures 1 - 7. A histogram showing changes in the tensile strength of elastomers is reproduced in Figure 8.

4 1 1 S 140 Hydroxyl-Terminated Polybutadiene Urethane

This hydroxyl-terminated polybutadiene urethane elastomer was initially hard and rather inflexible giving a high 100 per cent modulus of 12.4 MN/m^2 . The tensile strength of the elastomer, 16.7 MN/m^2 , was almost double that previously reported¹ for hydroxyl-terminated polybutadiene/toluene di-isocyanate pre-polymers crosslinked with diols such as 2-ethyl hexane 1,3-diol and 1,4-butane diol. This increase in strength is attributed to the introduction into the elastomer structure of the more bulky aromatic modified 4,4'-diphenyl methane di-isocyanate and N,N'-bis-[2-hydroxy propyl aniline] crosslinking agent.

The stress strain curve for the elastomer (Figure 1) is untypical of unfilled rubbery materials and indicates the elastomer to be relatively non-crystalline due to the absence of a region of strain hardening.

The elastomer showed outstanding hydrolytic stability being relatively unaffected by water at $50 - 100^\circ\text{C}$ for periods up to 28 days. The effects of exposure to ultraviolet radiation and immersion in oil at 100°C were slight. During exposure to dry air at 80 and 100°C however, the elastomer stiffened as shown by losses of original extension at break of 55 - 65 per cent, whilst its tensile strength was practically unchanged.

The resistance of the elastomer, to STF (petrol) at 65°C for 28 days was poor as shown by the losses of tensile strength, elongation at break and hardness.

4 1 2 S 147 ϵ -Caprolactone Polyester Urethane (Ester MW 2000)

This elastomer was based on the higher molecular weight caprolactone polyester. This elastomer was a toluene di-isocyanate-terminated prepolymer crosslinked with NOCA/TMP. The elastomer gave satisfactory initial mechanical properties with a tensile strength of 26.1 MN/m^2 and an extension at break of 535 per cent. The stress strain curve for the elastomer (Figure 1) is typical of

soft tough rubbery materials shows the elastomer to be relatively highly crystalline at stress levels above 10.0 MN/m^2 . The elastomer had fairly good resistance to dry air at 80 and 100°C , although some stiffening was apparent, as shown by increases in tensile strength and losses of extension at break. However, the character of the stress strain curve (Figure 3) for the elastomer after heat ageing is basically similar to that of the unaged control.

Apart from elastomer S 200 based on a commercial polyether prepolymer, elastomer S 147 showed the greatest losses of original mechanical properties of all the unmodified elastomers examined after exposure to ultraviolet radiation. The elastomer stiffened after immersion in oil at 100°C and showed considerable losses of extension at break and tensile strength after 28 days' immersion in STF at 65°C .

The hydrolytic stability of the elastomer S 147 was reasonable after 28 days' immersion in water at 50°C and after 14 days at 80°C . However, after 28 days at 80°C and 14 days at 100°C the elastomer was severely degraded by water, thus confirming our previous observations³ of the limited hydrolytic stability at elevated temperatures of urethane elastomers prepared from caprolactone polyesters.

4 1 3 S 155 ϵ -Caprolactone Polyester Urethane (Ester MW 500)

Elastomer S 155 was prepared from a relatively low molecular weight caprolactone polyester/toluene di-isocyanate prepolymer cured with a diol/triol blend. Nevertheless, the unaged elastomer gave good mechanical properties with a tensile strength of 40.0 MN/m^2 and an extension at break of 300 per cent.

The stress strain curve for the elastomer (Figure 1) is typical of hard strong crystalline rubbery materials.

After exposures to dry air at 80 - 100°C (Figure 4), ultraviolet radiation and oil at 100°C the elastomer stiffened appreciably as shown by increases in its 100 per cent modulus, suggesting that further crosslinking occurred during ageing.

The elastomer gave poor resistance to STF at 65°C and its hydrolytic stability was inferior to that of elastomer S 160 which was based on the higher molecular weight caprolactone ester.

4 1 4 S 160 Polyether Urethane (Ether MW 2000)

This polyurethane elastomer was based on a polyoxybutylene glycol/toluene di-isocyanate prepolymer, cured with a blend of TMP and MOCA. The unaged elastomer gave moderate mechanical properties although its initial tensile strength 11.6 MN/m^2 was comparatively low. The stress strain curve for the material (Figure 1) is almost linear and indicates that the elastomer is less crystalline than the elastomers based on the polycaprolactone esters.

After 28 days' ageing in dry air at 80°C the elastomer showed increased in both tensile strength and 100 per cent modulus, whilst after the same period at 100°C losses of tensile strength, extension at break and hardness occurred, which appears to confirm the opinion⁵ that the upper operational temperature limit for polyether urethanes is in the region of 80°C.

Although the tensile strength of the elastomer was relatively unaffected by exposure to ultraviolet radiation, an increase in 100 per cent modulus occurred with considerable losses of extension at break. The elastomer also stiffened considerably after immersion in oil at 100°C. The elastomer showed fair resistance to STF after 28 days' immersion at 65°C and to water, after ageing for periods of 14 to 28 days at 50 - 100°C.

4 1 5 S 173 Polyether Urethane (Ether MW 1000)

This elastomer was based on the lower molecular weight polyoxybutylene glycol/modified 4,4'-diphenyl methane di-isocyanate prepolymer crosslinked entirely with TMP.

The stress strain curve for the elastomer (Figure 1) shows the elastomer to be less flexible, but rather more crystalline, than the higher molecular weight polyether urethane S 160 described previously in Section 4 1 4.

The resistance of the elastomer to dry air at 80 and 100°C and to STF at 65°C was inferior to S 160 based on the higher molecular weight polyether, as shown by greater losses of original mechanical properties. Elastomer S 173 stiffened after exposure to ultraviolet radiation and immersion in oil at 100°C as shown by considerable increases in 100 per cent modulus and also by increases in tensile strength, especially after immersion in hot oil.

4 1 6 S 200 Commercial Polyether Urethane

This elastomer was based on a commercial polyoxybutylene glycol toluene di-isocyanate prepolymer, cured entirely with MOCA. Although the mechanical properties of the unaged elastomer were rather better than polyether urethanes S 160 and S 173, the resistance of the elastomer to water and STF was inferior to that of the experimental polyether urethane S 160. The elastomer showed relatively good resistance to dry air at 80°C and also to immersion in oil at 100°C.

4 1 7 S 176 Polyester Adipate Urethane (Ester MW 2000)

This elastomer was based on an ethylene/propylene 90:10 adipate ester/100 per cent 2,4 toluene di-isocyanate isomer prepolymer, cured with a blend of MOCA and TMP. The unaged elastomer showed good mechanical properties with a tensile strength of 32 MN/m² and an extension at break of 550 per cent. The stress strain curve of the elastomer (Figure 1) shows it to be a typical soft tough crystalline rubber similar to the other polyester urethanes examined, ie S 147 and S 155. The elastomer, apart from stiffening to some extent (Figure 7) showed satisfactory resistance to dry air at 80 and 100°C, ultraviolet radiation, oil at 100°C and STF at 65°C. Although the elastomer showed reasonably good resistance after 28 days' immersion in water at 50°C it was severely degraded after immersion at 80 and 100°C.

TABLE 2

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

Code No	Elastomer Type	Initial properties (unaged)				Percentage change of original mechanical property after ageing for																			
		TS (MN/m ²)	M 100 (MN/m ²)	EB (%)	H (ES ⁰)	28 days dry air (80°)				28 days dry air (100°)				10 days ultraviolet				9 days oil (100°)				28 days STF (50°)			
						TS	M	EB	H	TS	M	EB	H	TS	M	EB	H	TS	M	EB	H	TS	M	EB	H
S 140	Hydroxyl-terminated polybutadiene	16.7	12.4	175	97	-3.6	-	-54.0	0	-3.0	-	-63.0	0	-6.5	+11.2	-29.0	0	-30.0	-32.0	-17.0	-13.0	-74.0	-	-66.0	-35.0
S 147	ϵ -Caprolactone ester (M _n 2000)	26.1	3.1	535	87	+36.0	+19.0	-35.0	-1.0	+8.0	-10.0	-21.0	-10.0	-26.0	+19.0	-43.0	-2.0	+28.0	+58.0	+93.0	+7.0	-66.0	+6.0	-42.0	-3.0
S 155	ϵ -Caprolactone polyester (M _n 500)	40.7	7.1	310	82	+3.0	+135.0	-32.0	+21.0	+29.0	+94.0	-18.0	+21.0	+7.0	+82.0	-21.0	0	+40.0	+96.0	+6.0	+18.0	-65.0	-54.0	-18.0	-9.0
S 150	Polyether (M _n 2000)	11.6	4.3	355	89	+52.0	+21.0	-7.0	-3.0	-24.0	+3.0	-24.0	-9.0	-3.0	+16.0	-47.0	-1.0	+133.0	-9.0	+79.0	-3.0	-31.0	+23.0	-49.0	-11.0
S 173	Polyether (M _n 1000)	14.1	4.6	180	82	-7.0	-	-47.0	+9.0	-26.0	-	-47.0	+4.0	+11.0	+91.0	-28.0	-1.0	+134.0	+176.0	-3.0	+6.0	-66.0	-	-53.0	-2.0
S 200	Polyether (commercial)	17.6	4.0	420	88	+19.0	+4.0	+25.0	-7.0	-	-	-	-	-34.1	0	-33.3	0	+5.0	-95.0	+120.0	-7.0	-62.0	+4.0	-32.0	0
S 176	Polyester adipate (M _n 2000)	32.2	3.6	555	88	+32.0	+28.0	-24.0	-2.0	-7.0	-25.0	-8.0	-7.0	+2.0	+31.0	-32.0	+1.0	+37.0	-6.0	+62.0	-5.0	-20.0	+6.0	-30.0	-1.0

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TABLE 2 (Contd)

Code No	Elastomer Type	Initial properties (unaged)				Percentage change of original mechanical property after ageing for											
		TS (ksi/ft ²)	M 100 (KV/m ²)	EB (%)	H (BS°)	28 days water (50°C)				14 days water (80°C)				28 days water (80°C)			
						TS	M	EB	H	TS	M	EB	H	TS	M	EB	H
S 140	Hydroxyl-terminated polybutadiene	16.7	12.4	175	97	+12.0	+25.0	-23.0	0	-0.6	+23.0	-26.0	0	+12.0	+6.6	-23.0	0
S 147	ε-caprolactone polyester (M _n 2070)	26.1	3.1	535	87	-30.0	+6.0	-34.0	-1.0	-18.0	+71.0	+52.0	+1.0	Disintegrated			
S 155	ε-caprolactone polyester (M _n 500)	40.7	7.1	310	82	-55.0	-55.0	-29.0	-7.0	-84.0	-72.0	-8.0	-22.0	-97.0	-94.0	+3.0	-66.0
S 160	Polyether (M _n 2000)	11.6	4.3	355	89	+27.0	+7.0	-10.0	0	+41.0	-16.0	+93.0	-7.0	+40.0	-49.0	+69.0	-9.0
S 173	Polyether (M _n 1000)	14.1	4.6	180	82	-38.0	+57.0	-39.0	0	-21.0	0	-11.0	0	-29.0	-4.0	-17.0	-4.0
S 200	Polyether (commercial)	17.6	4.0	420	88	-	-	-	-	-61.0	-79.0	+44.0	-21.0	-61.0	-79.0	+44.0	-21.0
S 176	Polyester (M _n 2000)	32.2	3.6	555	88	-11.0	+34.0	-23.0	-17.0	Too soft to test				Disintegrated			
										Too soft to test				Too soft to test			

Key: TS = tensile strength at break

M100 = modulus at 100 per cent extension

EB = percentage extension at break

H = hardness

- = not tested or no value obtained

M_n = average molecular weight (nominal)

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4 2 Properties of Polyurethane Elastomers Prepared with Alternative Chain Extenders and Crosslinking Agents (Methods of Cure)

In an attempt to improve certain of the properties of the unmodified polyurethane elastomers described in Section 4 1, the use of alternative crosslinking and chain extending agents to those used in these elastomers was investigated. Apart from these changes, the formulations of the elastomers and the methods of test were the same as those described in Sections 2 and 3.

Details of the alternative curing systems, the mechanical properties of the unaged elastomers and the percentage changes in original mechanical properties of the elastomers after ageing are summarised in Table 3. The results are compared with those of Table 2 in the discussion below.

4 2 1 Hydroxyl-Terminated Polybutadiene Urethanes

Elastomer S 143 was identical to S 140 based on a hydroxyl-terminated polybutadiene, except that the N,N'-bis-(2-hydroxy propyl aniline) was replaced with 2-ethyl hexane 1,3-diol.

This replacement gave an elastomer with greater extension at break with little sacrifice in other properties. However the resistance to STF was not improved and remained unsatisfactory.

4 2 2 ϵ -Caprolactone Polyester Urethanes (Ester MW 2000)

The MOCA/TMP cure of elastomer S 147 was replaced with 100 per cent MOCA in S 148, and with 100 per cent TMP in S 152.

In elastomer S 148 the effect of a 100% MOCA cure was to produce further improvements in the already satisfactory initial mechanical properties. Although a slight improvement in resistance to dry air at 80°C was achieved the resistance of the elastomer to STF at 65°C and water at 80°C remained poor.

The effect of introducing 100 per cent TMP cure into elastomer S 151 was to produce a much softer elastomer than the MOCA/TMP cured material, with inferior ageing properties compared to elastomer S 147. These results confirm those already obtained from TMP cured polyesters.¹²

4 2 3 ϵ -Caprolactone Polyester Urethanes (Ester MW 500)

S 154 elastomer was prepared using a MOCA/TMP cure. Although this alternative method of cure produced an elastomer with slightly improved initial mechanical properties, the hydrolytic stability of the elastomer after immersion in water at 80°C remained poor.

4 2 4 Polyether Urethanes (Ether MW 2000)

In an attempt to improve the initial tensile strength of the elastomer S 160 and to reduce its tendency to stiffen during immersion in oil at 100°C, elastomers S 161 cured with 100 per cent MOCA and S 165 cured with 100 per cent N,N'-bis-(2-hydroxy propyl aniline) were prepared to compare with S 160 cured with a blend of MOCA and TMP. Elastomer S 161 gave improved initial mechanical properties with enhanced resistance to oil at 100°C; but its resistance to STF at 65°C and water at 80°C was inferior to that of the TMP/MOCA cured elastomer S 160. Elastomer S 165 cured with N,N'-bis-(2-hydroxy propyl aniline) was very soft and flexible initially and showed very poor resistance to STF at 65°C.

4 2 5 Polyether Urethane (Ether MW 1000)

Elastomer S 175 was prepared in which the TMP of S 173 was replaced with BD. This change should produce an elastomer with a more linear structure than that from a triol cure. The 1,4-butane diol cured elastomer was both more flexible and stronger than the triol cured elastomer S 173. In addition, the diol cured elastomer showed improved resistance to dry air and water at 80°C together with marginally improved resistance to STF at 65°C.

TABLE 3

EFFECT OF ALTERNATIVE CHAIN EXTENDERS/CROSSLINKING AGENTS ON AGING PROPERTIES OF POLYURETHANE ELASTOMERS

Code No	Elastomer type	Crosslinking/ chain extending material	Initial properties (unaged)				Percentage change of original mechanical property after ageing for											
			TS (N/cm ²)	M 100 (N/cm ²)	EB (%)	H (65°C)	28 days dry air (20°C)						9 days oil (100°C)					
							TS	M	EB	H	TS	M	EB	H	TS	M	EB	H
S 140	hydroxy-terminated polybutadiene	hydroxy propyl aniline	16.7	12.4	175	97	-3.6	-	-54.0	0	-30.0	-32.0	-17.0	-13.0	-0.6	+23.0	-26.0	0
S 145		2-ethyl hexyl 1,3-diol	15.8	10.2	255	97	+11.0	+64.0	-59.0	+3.0	-27.0	-15.0	-33.0	+23.0	0	+34.0	-53.0	0
S 147	ε-caprolactone polyester (Mn 1000)	MCCA/TMP	26.1	3.1	535	87	+36.0	+79.0	-35.0	-1.0	+28.0	+58.0	+93.0	+7.0				
S 148		MCCA	37.3	4.1	605	93	+8.0	+41.0	-31.0	0	-	-	-	-				
S 151		TMP	9.3	1.7	420	73	+42.0	+41.0	-33.0	-4.0	-	-	-	-				
S 155	ε-caprolactone polyester (Mn 100)	B2/TMP	40.7	7.1	310	82	+3.0	+135.0	-32.0	+21.0	+40.0	+96.0	+6.0	+18.0	-97.0	-94.0	+3.0	-65.0
S 154		MCCA/TMP	42.2	6.3	335	85	-	-	-	-	-	-	-	-	-98.0	-95.0	+1.0	-65.0
S 160		MCCA/TMP	11.6	4.3	355	89	+52.0	+21.0	-	-3.0	+133.0	-	+79.0	-3.0	+40.0	-49.0	+69.0	-9.0
S 161	polyether polyester (Mn 1000)	MCCA	29.4	6.2	505	95	-7.0	+1.0	-18.0	-1.0	-3.0	-10.0	+50.0	-1.0	-87.0	-47.0	-37.0	-9.0
S 165		hydroxy propyl aniline	6.1	1.0	875	30	-48.0	-22.0	+11.0	0	-	-	-	-	-	-	-	-
S 173	polyether (Mn 1000)	TMP	14.1	4.6	120	82	-7.0	-	-47.0	+9.0	+134.0	+176.0	-3.0	+6.0	-29.0	-4.0	-17.0	-4.0
S 175		BD	16.1	3.9	345	86	+83.0	+67.0	-29.0	-5.0	-	-	-	-	-17.0	+13.0	-12.0	-3.0

Key: Mn = average molecular weight (nominal)

TS = tensile strength at break

M100 = modulus at 100 per cent extension

EB = percentage extension at break

H = hardness

MCCA = methylene bis-(2-chloroaniline)

TDP = 1,1',1''-triethylol propane

BD = 1,4-butane diol

- = not tested or value not recorded

(10)

11.2

11.3

4 3 Effect of Additives on the Properties of Polyurethane Elastomers

In an attempt to improve certain of the known shortcomings of some of the elastomer types described in Sections 4 1 and 4 2, for example resistance to photo-oxidation, the effects that various additives and/or stabilisers had on the ageing properties of the elastomers were assessed. The methods of preparation, basic formulations and testing procedures were identical with those described in Sections 2 and 3.

Details of the additives used, the initial mechanical properties of the elastomers and percentage changes in their original mechanical properties after ageing are summarized in Table 4. The properties of the modified elastomers and their comparison to the unmodified controls are summarised below.

HTPB Elastomer S 141 contained 2½ per cent by weight of an oil soluble nigrosine dyestuff. The initial mechanical properties of the elastomer containing dyestuff were similar to those of the unmodified elastomer S 140. The elastomer containing nigrosine showed slightly better resistance to dry air at 80°C compared with the unmodified elastomer but stiffened rather more during exposure to ultraviolet radiation and was inferior to S 140 as regards resistance to STF at 65°C.

HTBB Elastomer S 142 contained 2½ per cent by weight of carbon black. The initial mechanical properties of the elastomer and its resistance to dry air at 80°C and ultraviolet radiation were inferior to the unmodified elastomer S 140.

HTPB Elastomer S 144 was a syntactic* foam prepared by introducing 10 per cent by weight of hollow glass spheres to unmodified elastomer S 140. The material was buoyant, showing fair initial mechanical properties with fairly good ageing characteristics as shown by changes in original mechanical properties after ageing in water and dry air at 80°C, and ultraviolet light. The resistance of the material to STF at 65°C however was poor.

HTPB Elastomer S 146 contained 15% carbon black. However, no evidence of any reinforcing action was observed. The carbon black filled elastomer possessed reasonable resistance to dry air and water at 80°C like the unfilled elastomer.

ε-Caprolactone polyester urethane S 149 contained 2½ per cent by weight of an oil soluble nigrosine dyestuff. The introduction of the dyestuff gave a reduction in strength of the unaged elastomer compared to the unmodified material and no marked improvement in the resistance of the elastomer to dry air and water at 80°C was achieved, although there appeared to be a slight improvement in the resistance of the elastomer to ultraviolet light and STF at 65°C.

*Syntactic foam is a buoyant composite consisting of a hollow spherical filler in a polymer matrix. These materials have generally good compression behaviour.

ϵ -Caprolactone polyester urethane S 150 contained both an ultraviolet absorber and an antioxidant based on a mixture of butylated hydroxy toluene and dilauryl thiodipropionate, as recommended in Reference 11. The unaged elastomer showed good initial mechanical properties with rather better ageing properties of exposure to dry air at 80°C and ultraviolet light than was obtained with the unmodified elastomer S 147.

ϵ -Caprolactone polyester urethane S 156 containing 24% carbon black showed a reduction in initial mechanical properties compared with the unmodified material S 155. However S 156, stiffened rather less in both dry air at 80°C and ultraviolet radiation compared with the unmodified elastomer. No improvement in resistance of the elastomer to water or STF was achieved.

ϵ -Caprolactone polyester urethane S 158 contained the ultraviolet absorber and antioxidant pair used in elastomer S 150 and gave an elastomer with improved initial mechanical properties compared with the unmodified elastomer S 155. The additives appeared to have little effect on the already reasonably satisfactory ageing properties of the elastomer towards dry air and ultraviolet radiation.

Polyether urethane S 163 contained 2.5 per cent by weight carbon black and 0.6 per cent by weight of the antioxidant mixture described above but gave no improvement, either in initial mechanical properties or resistance to ageing, compared to the unmodified polyether elastomer S 160.

Polyether urethane S 164 contained 0.6% antioxidant together with 10 per cent by weight of zinc oxide which was added with the object of improving the photo-oxidative stability of unmodified polyether elastomer S 160. The presence of zinc oxide however led to a deterioration in the initial mechanical properties of the elastomer and to considerable stiffening of the elastomer during exposure to dry air at 80°C. The elastomer was relatively unaffected by exposure to ultraviolet radiation.

Polyether urethane S 167 was a chemical modification of S 160 where 50% of the backbone polyether polyol was replaced with a hydroxyl-terminated polysiloxane. This had the effect of softening the elastomer and considerably increasing its extension at break. The elastomer gave fair resistance to dry air at 80°C and STF at 65°C but was affected by contact with water.

Polyester urethane S 177 contained 2.5 per cent by weight of polycarbodiimide added with the object of improving the hydrolytic stability. The elastomer showed some deterioration in initial mechanical properties but its resistance to hydrolysis was improved slightly.

Polyester urethane S 178 contained 2.5 per cent polycarbodiimide and an ultraviolet stabilizer and an antioxidant mixture. This elastomer again showed some deterioration in its initial mechanical properties but showed good ageing properties in dry air at 80°C and ultraviolet radiation, and gave slightly better resistance to water at 80°C compared with the unmodified elastomer S 176.

TABLE 4

EFFECT OF ADDITIVES ON AGEING PROPERTIES OF POLYURETHANE ELASTOMERS

Code No	Elastomer type	Additive	Initial properties (unaged)		Percentage change of original mechanical property after ageing for																	
					28 days dry air (80°C)						10 days ultraviolet						28 days water (80°C)					
			TS KN/m ²	M 100	EB (%)	H BS ⁰	TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H	TS	M 100	EB	H
S 140		Nil	16.7	12.4	175 97	-	3.6	-	-54.0	0	-6.5	+11.2	-28.0	0	+12.0	+6.6	-23.0	0	-74.0	-	-66.0	-35.0
S 141		2% oil soluble nigrosine (a)	16.0	12.4	215 98	-	3.1	+27.0	-47.0	0	+6.0	+17.0	-65.0	0	-	-	-	-	-86.0	-	-67.0	-45.0
S 142		2% carbon black (b)	11.8	-	37 98	-	66.0	-	-57.0	-3.0	-46.0	-	-73.0	+1.0	-	-	-	-	-	-	-	-
S 144	hydroxyl-terminated polybutadiene	10% hollow glass spheres (c)	9.2	8.9	115 97	-	13.0	-	-35.0	-1.0	+9.0	-	-26.0	+1.0	+17.0	-	-48.0	+1.0	-88.0	-	-26.0	-70.0
S 146		15% carbon black (b)	16.2	-	95 89	-	16.0	-	-49.0	0	-	-	-	-	+6.9	-	-52.0	-3.0	-	-	-	-
S 147		Nil	26.1	3.1	535 87	-	36.0	+19.0	-35.0	-1.0	-26.0	+19.0	-43.0	-2.0	-	-	Disintegrated	-	-66.0	+6.0	-42.0	-5.0
S 149	ε-caprolactone polyester (Mw 2000)	2.5% oil soluble nigrosine (a)	15.4	2.7	510 85	-	23.0	+19.0	-30.0	-5.0	+36.0	+11.0	-22.0	-2.0	-	-	Disintegrated	-	-55.0	+20.0	-36.0	-1.0
S 150		0.3% UV absorber (d), 0.6% antioxidant (f)	31.4	2.8	560 85	-	2.0	+32.0	-36.0	-1.0	-15.0	+25.0	-32.0	-1.0	-	-	Disintegrated	-	-	-	-	-
S 155		Nil	40.7	7.1	310 82	-	3.0	+135.0	-32.0	+21.0	+7.0	+82.0	-21.0	0	-97.0	-94.0	+3.0	-66.0	-65.0	-54.0	-18.0	-9.0
S 156	ε-caprolactone polyester (Mw 500)	2.5% carbon black (b)	24.6	8.1	285 78	-	6.0	+98.0	-39.0	+21.0	-6.0	+22.0	-33.0	+1.0	-97.0	-98.0	+33.0	-62.0	-76.0	-81.0	-32.0	-4.0
S 158		0.3% UV absorber (g), 0.6% antioxidant (f)	37.8	6.7	325 80	-	22.0	+163.0	-34.0	+24.0	+8.0	+72.0	-26.0	+1.0	-	-	-	-	-	-	-	-
S 160		Nil	11.6	4.3	355 89	-	52.0	+21.0	-7.0	-3.0	-3.0	+16.0	-47.0	-2.0	+40.0	-49.0	+69.0	-9.0	-31.0	+23.0	-49.0	-11.0
S 163		2.5% carbon black (b), 0.6% antioxidant (f)	12.1	2.5	490 76	-	68.0	-40.0	-45.0	+4.0	-60.0	+36.0	-67.0	+4.0	-61.0	-48.0	-15.0	-41.0	-74.0	-29.0	-80.0	-26.0
S 164	polyether (Mw 2000)	10.0% zinc oxide, 0.6% antioxidant (f)	4.6	2.2	345 78	-	89.0	+27.0	+3.0	-3.0	-9.0	+14.0	-38.0	-5.0	-	-	-	-	-	-	-	-
S 167		50% polyether replaced with silicone polyol (h)	8.8	1.5	840 67	-	23.0	+73.0	-38.0	0	-	-	-	-	0	-	-61.0	-33.0	-13.0	+27.0	-47.0	-3.0
S 176		Nil	32.2	3.6	555 88	-	32.0	+28.0	-24.0	-2.0	+2.0	+31.0	-32.0	+1.0	-	-	Disintegrated	-	-20.0	+6.0	-30.0	-1.0
S 177	polyester (Mw 2000)	2.5% polycarbodiimide (i)	26.7	2.5	570 88	-	9.0	-4.0	-17.0	-16.0	-	-	-	-	-70.0	-16.0	-5.0	-6.0	-29.0	0	-25.0	-17.0
S 178		2.5% polycarbodiimide (i), 0.12% UV absorber (j), 0.6% antioxidant (f)	23.5	2.7	545 87	-	2.0	+11.0	-25.0	0	-1.0	+33.0	-35.0	-1.0	-85.0	+19.0	-81.0	+10.0	-	-	-	-

Mw = average molecular weight (nominal)

(a) Oil Soluble Nigrosine ex-ICI Dyestuffs Div

(b) Carbon black Vulcan 3F ex-Cabot Chemical Co

(c) Aerospheres ex-JBC Plastics

(d) Tinurin 320 ex-Geigy

(f) Irganox 1076 0.1% butylated hydroxy toluene ex-Geigy

Advastab 0.5% diallyl thiodipropionate ex-Geigy

(g) Tinopol RFP ex-Geigy

(h) Silicone XR 6188 intermediate ex-Dow Corning

(i) Stabamul ICD ex-Bayer

(j) Tinurin P ex-Geigy

4 4 Low Temperature Flexibility

Table 5 compares the low temperature flexibility of five polyurethane elastomers described in the present work together with those of typical rubbers and two polyurethane elastomers examined previously.¹⁰

TABLE 5

Elastomer No	Type	T ₇₀ [*] , °C
S 140	hydroxyl-terminated polybutadiene/MDI/EHD	-40
S 147	ε-caprolactone polyester (MW 2000)/TDI/MOCA/TMP	-63
S 155	ε-caprolactone polyester (MW 500)/TDI/TMP/BD	+18
	polyether (MW 2000)/TDI/MOCA	-59
S 175	polyether (MW 1000)/MDI/BD	-85
S 176	ethylene/propylene adipate polyester/TDI/MOCA/TMP	+16
	propylene adipate polyester/TDI/hexane triol	-25
	natural rubber	-52
	nitrile	-25
	chloroprene	-37
	polysulphide	-46
	epichlorhydrin	-20
	acrylate	-10

*Temperature at which torsional modulus is 70 MN/m²

Apart from polyester urethane elastomer S 176 which is highly crystalline and the low molecular weight caprolactone ester S 155, it will be seen that polyurethane elastomers are available possessing low temperature flexibility properties equal to or better than most conventional synthetic rubber elastomers.

4 5 Effect of Elastomer Thickness on Hydrolytic Stability

A limited investigation was made as to the effects of different film thicknesses on the original mechanical properties and hydrolytic stability of a polyurethane elastomer S 140 based on a hydroxyl-terminated polybutadiene which gave outstanding resistance to water previously.

The results are summarised in Table 6 below and in Figures 9 and 10.

TABLE 6

Range of values		Original properties (unaged)				Percentage changes in original mechanical properties after 28 days in water at 80°C		
Thickness (mm)	Cross sectional area (mm ²)	Tensile strength (MN/m ²)	100% modulus (MN/m ²)	Extension at break (%)	Tensile strength	100% modulus (MN/m ²)	Extension at break	
0.86-0.91	3.50- 3.70	17.4	12.4	203	-6.3	+15.0	-39.0	
1.12-1.17	3.70- 4.70	18.2	12.7	200	-1.5	+22.0	-35.0	
2.15-2.23	8.70- 9.00	15.7	12.3	157	-4.5	+22.0	-41.0	
2.71-2.82	11.10-11.30	16.0	11.7	182	-1.9	+25.0	-38.0	
2.90-3.00	11.70-12.10	14.3	11.2	163	-0.7	+27.0	-40.0	

Table 6 and Figures 9 - 10 suggest that there is a trend for tensile strength, 100 per cent modulus and extension at break to increase with decreasing film thickness, which is attributable to the fact that the number of macroscopic flaws, occluded air bubbles etc present in a thin film will be less than those present in a thicker film.

After immersion in water for 28 days at 30°C, the thinner films appear to change rather more in strength than the thicker films. Losses of extension at break were similar but the thicker elastomers showed greater increases in 100 per cent modulus. Nevertheless over the range of thicknesses 0.26 - 3.00 mm the hydroxyl-terminated polybutadiene polyurethane elastomer showed very good resistance to hydrolysis.

7. CONCLUSIONS

A range of polyurethane elastomers have been prepared with satisfactory ageing properties when exposed to a wide variety of laboratory simulated environmental conditions. None of the elastomers gave satisfactory initial mechanical properties coupled with satisfactory resistance to all the selected conditions (Table 7) although certain polyether urethane elastomers prepared from polyoxybutylene glycols (average molecular weight 1000 - 2000) provided a reasonably acceptable compromise of properties under most conditions. These conditions included periods up to 28 days in dry air at 80 and 100°C, ultraviolet radiation, ASTM oil at 100°C, STP (petrol) at 65°C, water at 50, 80 and 100°C and retention of flexibility at low temperatures.

Hydroxyl-terminated polybutadiene/modified 4,4'-diphenyl methane diisocyanate prepolymers crosslinked with 2-ethyl hexane 1,3-diol gave tough flexible elastomers with outstanding resistance to water at temperatures up to 100°C. The addition of hollow glass spheres to this elastomer produced a useful buoyant syntactic foam with satisfactory mechanical properties, coupled with good resistance to water.

The hydrolytic stability of the polyester urethanes, based either on caprolactone or adipate polyesters, was unsatisfactory, especially at temperatures above 50°C, although the caprolactone polyesters were rather better than the adipate polyesters in this respect. The addition of 2½ per cent polycarbodiimide to the polyester adipate urethane elastomer slightly improved its resistance to water. Adipate polyester urethanes showed rather better resistance to fuels compared to the caprolactone polyester urethanes.

The addition of ultraviolet absorbers and an antioxidant pair based on a mixture of butylated hydroxyl toluene and dialkyl thiodipropionate (see Table 7) appeared to give some improvement to the photo-oxidative/oxidative stabilities of the polyester urethane elastomers but this is difficult to substantiate by accelerated ageing trials. In this respect, most of the elastomers examined in the present investigation are also being exposed to natural weathering in temperate, hot/wet and hot/dry tropical environments; the results of these trials will be reported at a later date.

TABLE 7

PROPERTIES OF POLYURETHANE ELASTOMERS

Type of elastomer	Initial mechanical properties	Ageing properties after					Low temperature flexibility
		28 days dry air (30 - 100°C)	14 days ultraviolet radiation	9 days ASTM oil (100°C)	28 days STF (65°C)	10 - 28 days water (50 - 100°C)	
Hydroxyl-terminated polybutadiene	SATISFACTORY-GOOD Flexibility improves with 2-ethyl hexane 1,3-diol cure or use of TDI (see (2))	FAIR	SATISFACTORY	SATISFACTORY	POOR	GOOD	GOOD
ϵ -caprolactone polyester Mw 2000	GOOD Strength improves by increasing EHT/DLTP antioxidant % MOCA in cure	SATISFACTORY especially with EHT/DLTP antioxidant	SATISFACTORY especially with UV absorber and EHT/DLTP antioxidant	SATISFACTORY	POOR	SATISFACTORY <50°C POOR >50°C	GOOD
ϵ -caprolactone polyester Mw 500	GOOD either with diol/triol or diamine/triol cure	SATISFACTORY	SATISFACTORY	SATISFACTORY	POOR	SATISFACTORY <50°C POOR >50°C	POOR
polyether Mw 2000	FAIR-SATISFACTORY Strength improves by increasing % MOCA in cure	SATISFACTORY (up to 80°C)	SATISFACTORY	FAIR Improves with 100% MOCA cure	FAIR	SATISFACTORY with MOCA/TMP cure	GOOD
polyether Mw 1000	SATISFACTORY Diol cure Probably best - diamine too reactive	SATISFACTORY (up to 80°C)	SATISFACTORY	FAIR	POOR	SATISFACTORY	GOOD
ethylene/propylene adipate polyester Mw 1000	GOOD	SATISFACTORY especially with EHT/DLTP antioxidant	SATISFACTORY especially with UV absorber	GOOD	GOOD	SATISFACTORY <50°C POOR >50°C Slight improvement with 2.5% polycarbodiimide	POOR

The addition of oil soluble nigrosine dyestuff appeared to be of some advantage in hydroxyl-terminated polybutadiene and caprolactone esters and was preferred to carbon black, since carbon black tended to reduce the initial tensile strength and provide less protection on ageing.

6 REFERENCES

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GLOSSARY

BD	1,4-butane diol
BHT	butylated hydroxy toluene
DLTP	dilauryl thiodipropionate
MDI	modified 4,4'-diphenyl methane di-isocyanate
MOCA	methylene bis-(2-chloroaniline)
TDI	toluene di-isocyanate
TMP	1,1',1''-trimethylol propane
MW	average molecular weight, nominal

S No 48/72/GC

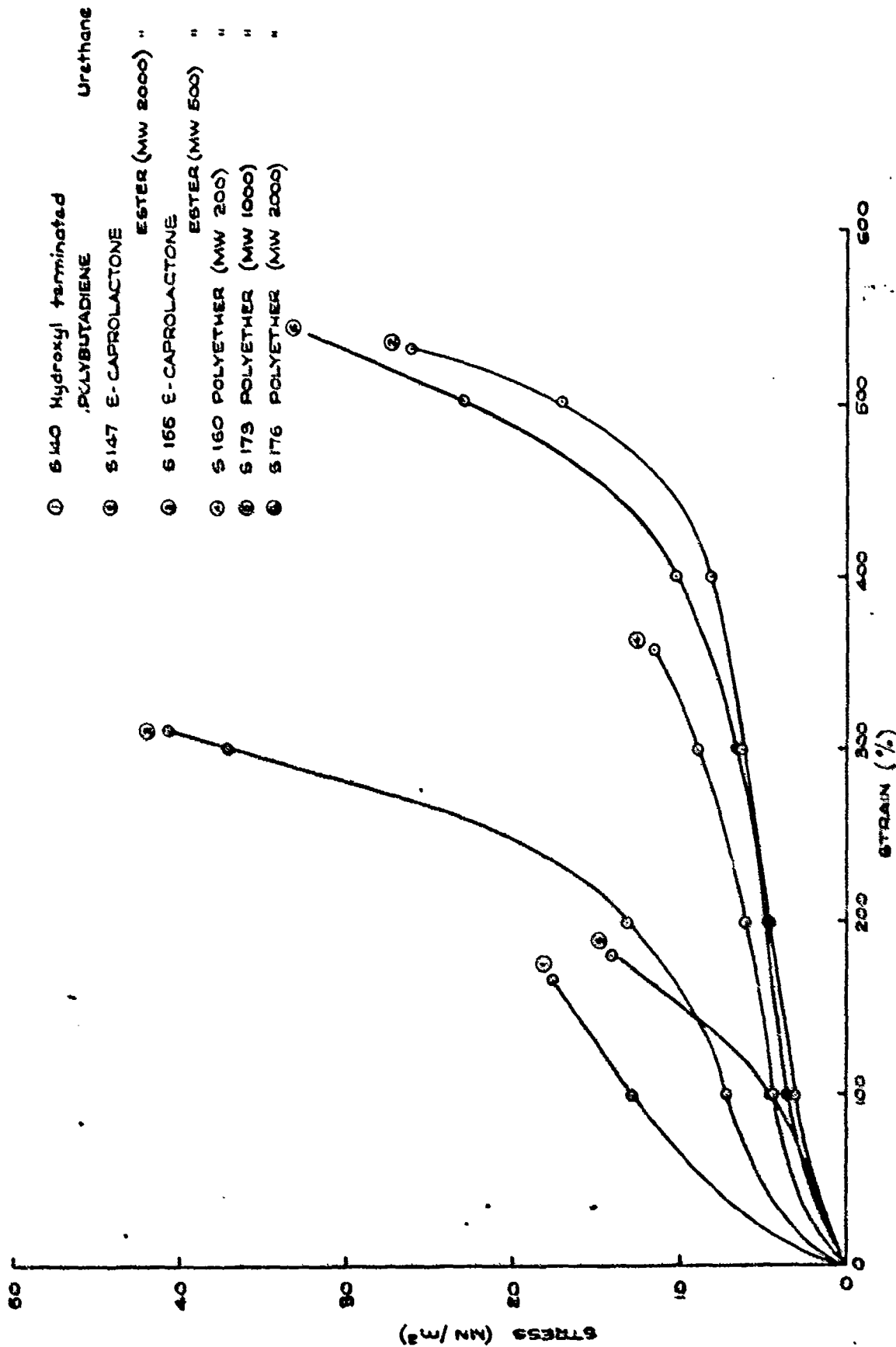


FIG. 1.1 STRESS/STRAIN CURVES OF SELECTED POLYURETHANE ELASTOMERS

21.1

21.2

21.3

- ① UNAGED
- ② DRY AIR AT 80°C (28 days)
- ③ WATER AT 80°C (28 days)
- ④ STF AT 65°C (28 days)

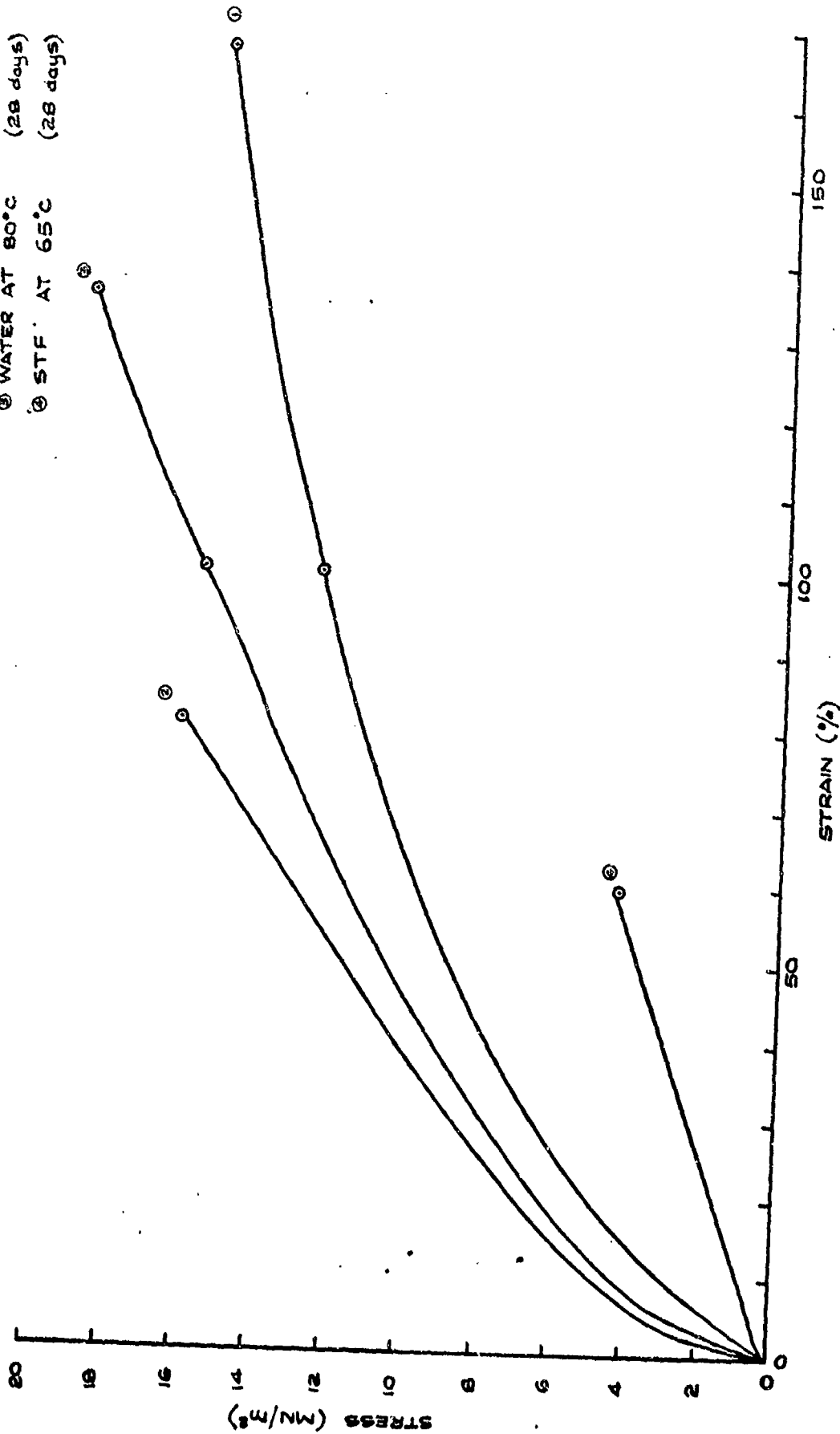


FIG. 2 EFFECT OF AGEING ON MECHANICAL PROPERTIES OF HYDROXYL TERMINATED POLYBUTADIENE
URETHANE ELASTOMER (S 140)

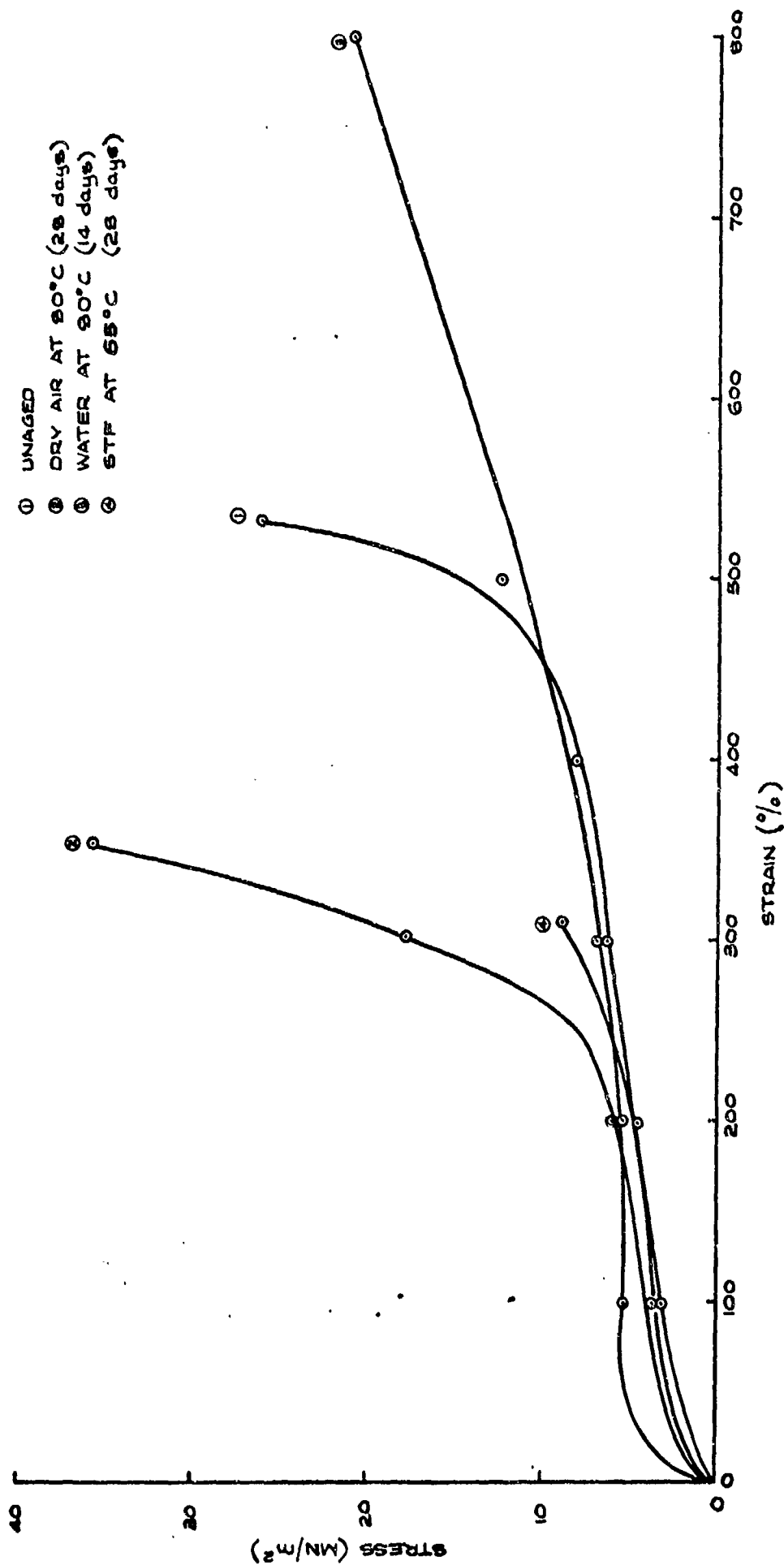


FIG. 3 EFFECT OF AGEING ON MECHANICAL PROPERTIES OF ϵ -CAPROLACTONE POLYESTER URETHANE
 (ESTER MW 2000) (S147)
 23.1

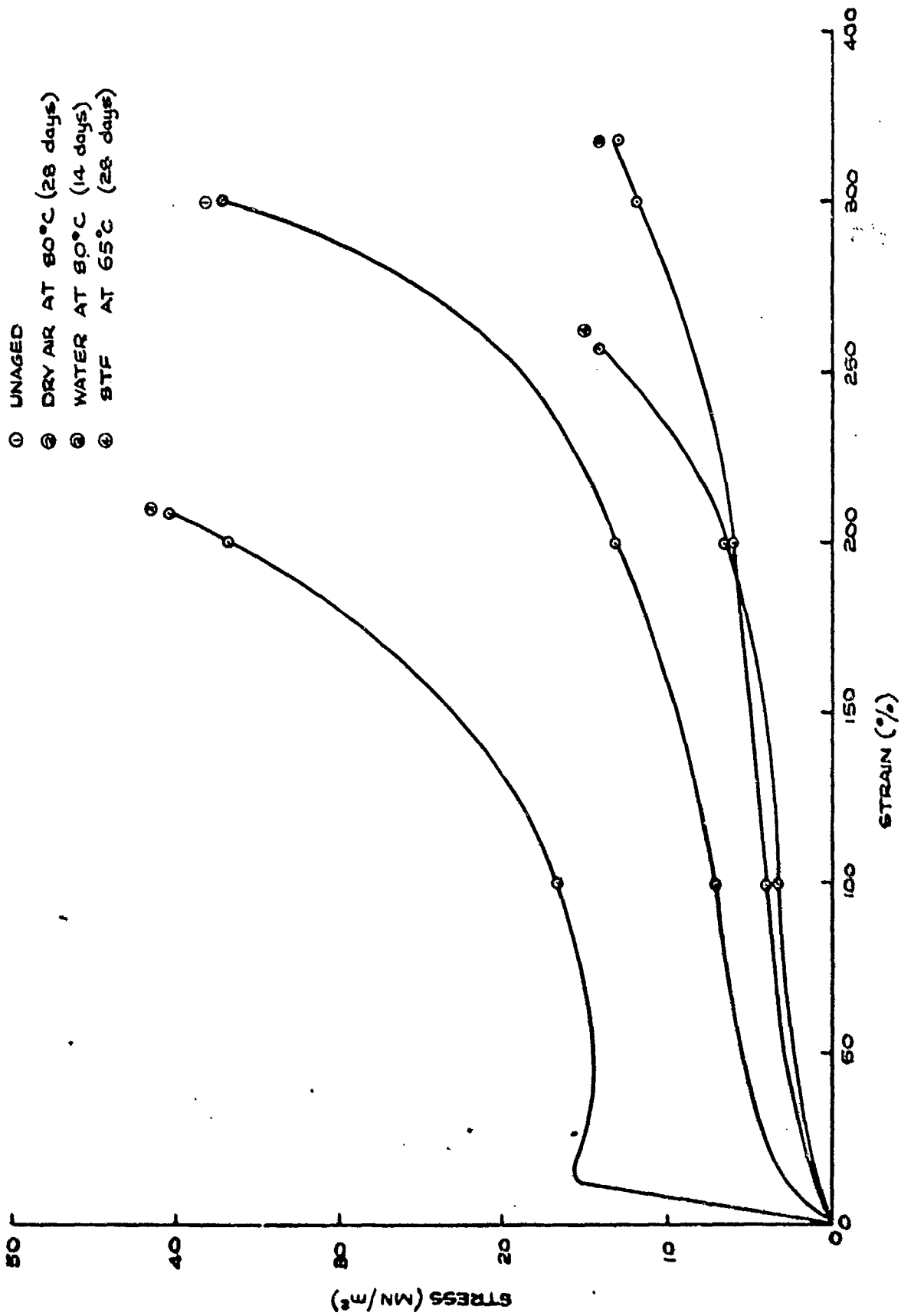


FIG. 4 EFFECT OF AGEING ON MECHANICAL PROPERTIES OF ϵ -CAPROLACTONE POLYESTER URETHANE

24.3 (ESTER MW 500) (S 155)

24.1

24.2

- ① UNAGED
- ② DRY AIR AT 80°C (28 days)
- ③ WATER AT 80°C (28 days)
- ④ STF AT 65°C (28 days)

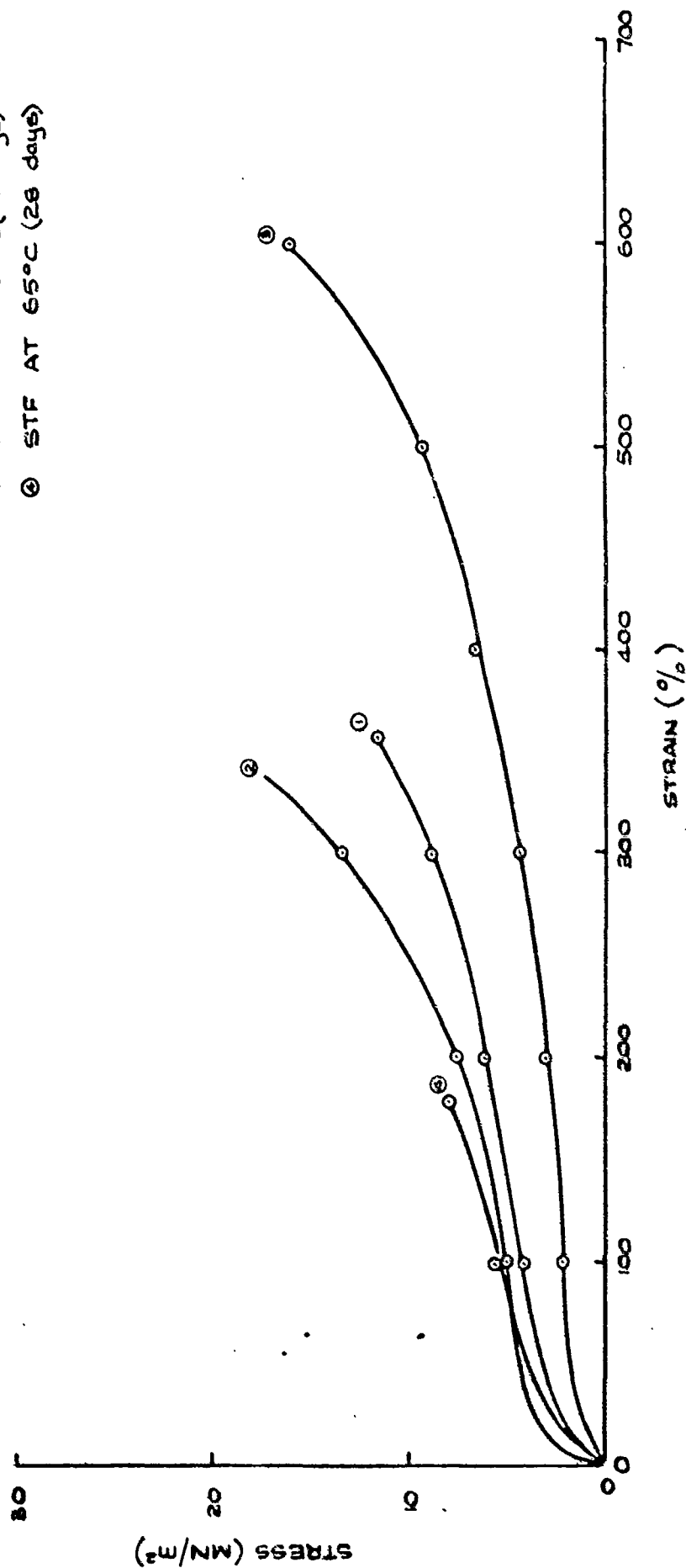


FIG. 5 EFFECT OF AGEING ON MECHANICAL PROPERTIES OF POLYETHER URETHANE

(ETHER MW 2000) (S160)

- ① UNAGED
- ② DRY AIR AT 80°C (28 days)
- ③ WATER AT 80°C (28 days)
- ④ STF AT 65°C (28 days)

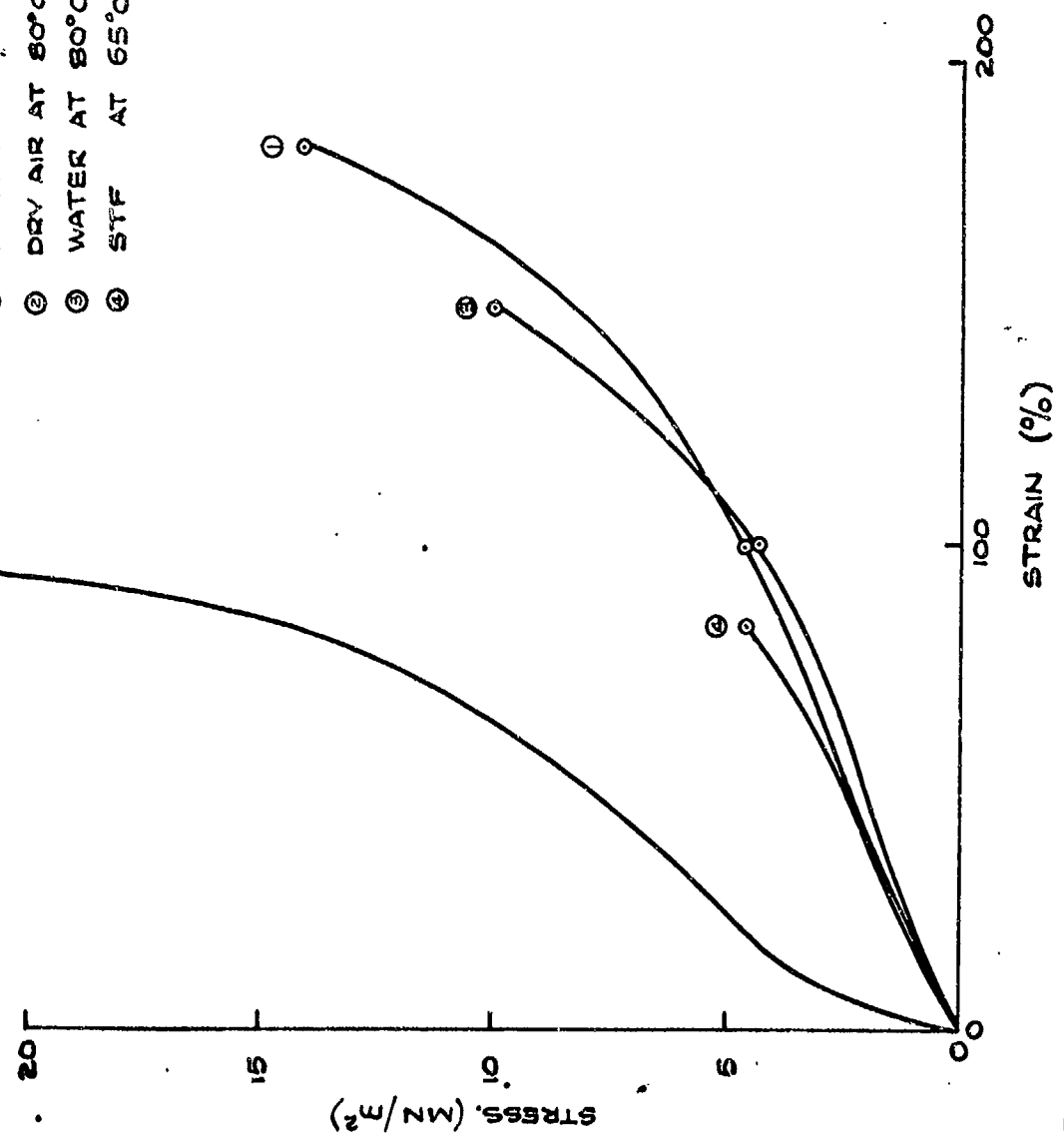


FIG 6. EFFECT OF AGEING ON MECHANICAL PROPERTIES OF POLYETHER URETHANE
 26.1 26.2 26.3 (ETHER MW 1000) (5173)

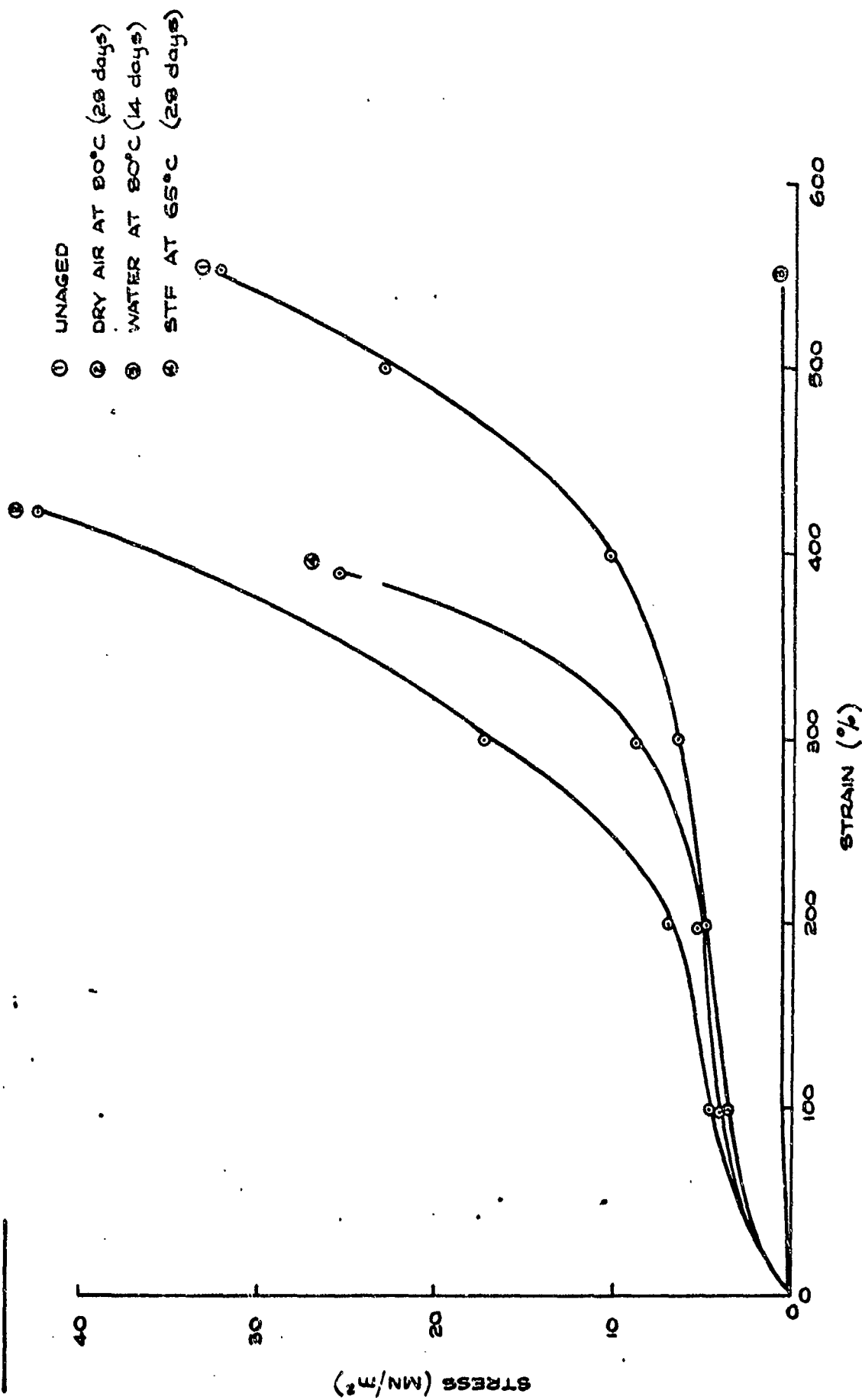
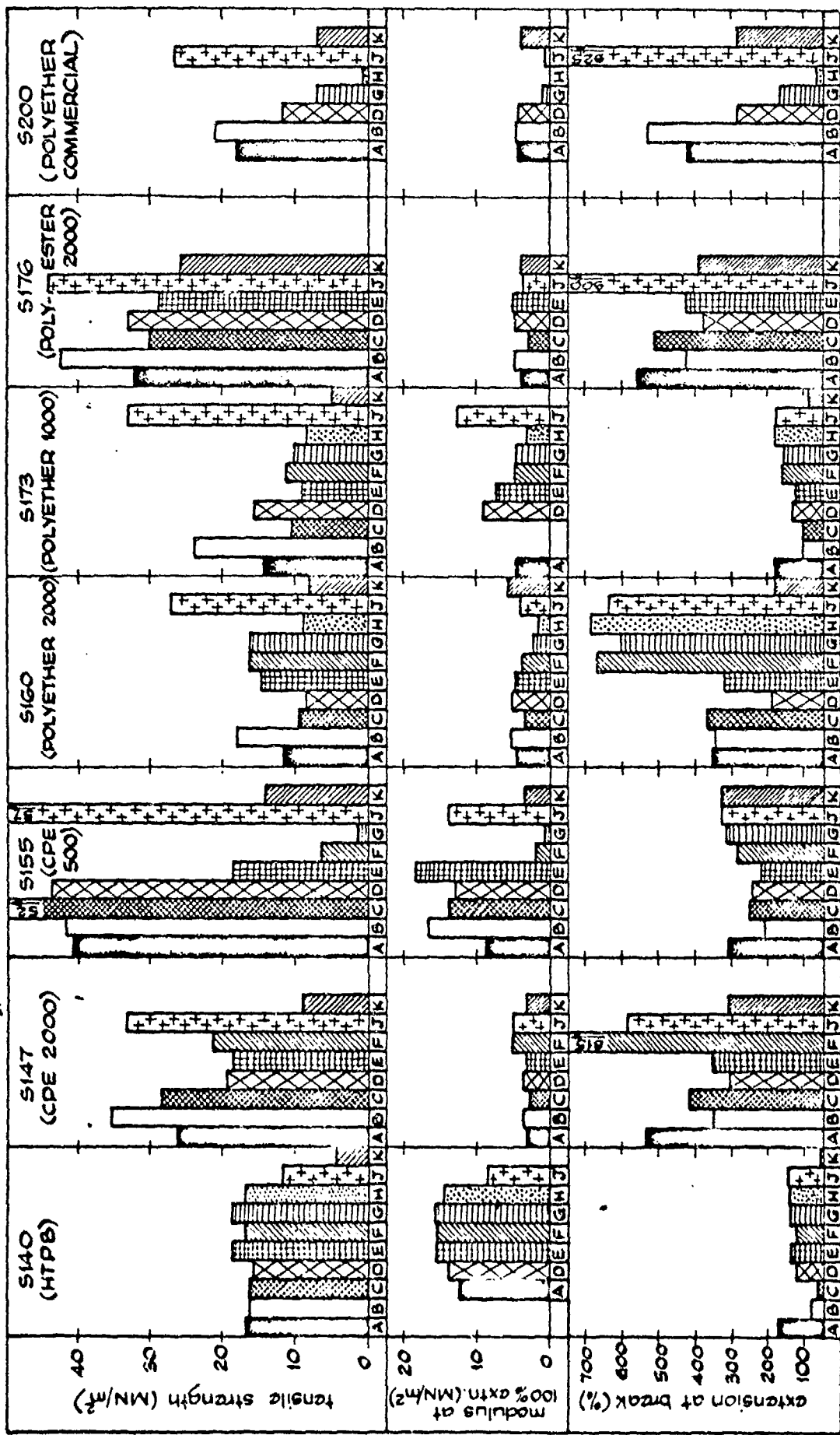


FIG. 7 EFFECT OF AGEING ON MECHANICAL PROPERTIES OF POLYESTER URETHANE

27.1 27.2 27.3 (ESTER MW 2000) (S 176)



A = Original property
 B = After 28 days in dry air at 80°C
 C = After 28 days in dry air at 100°C
 D = After 10 days in UV (2kW xenon arc)
 E = After 28 days in water at 50°C
 F = After 14 days in water at 80°C
 G = After 28 days in water at 80°C
 H = After 14 days over water at 100°C
 I = After 9 days in ASTM oil N°1 at 100°C
 J = After 28 days in STF* at 65°C
 K = After 28 days in STF* at 65°C
 * (STF = 70:30 v/v iso-octane:toluene)

FIG. 8 THE EFFECT OF AGEING IN ENVIRONMENTS ON TENSILE PROPERTIES OF POLYURETHANE RUBBERS

28.3

28.2

28.1

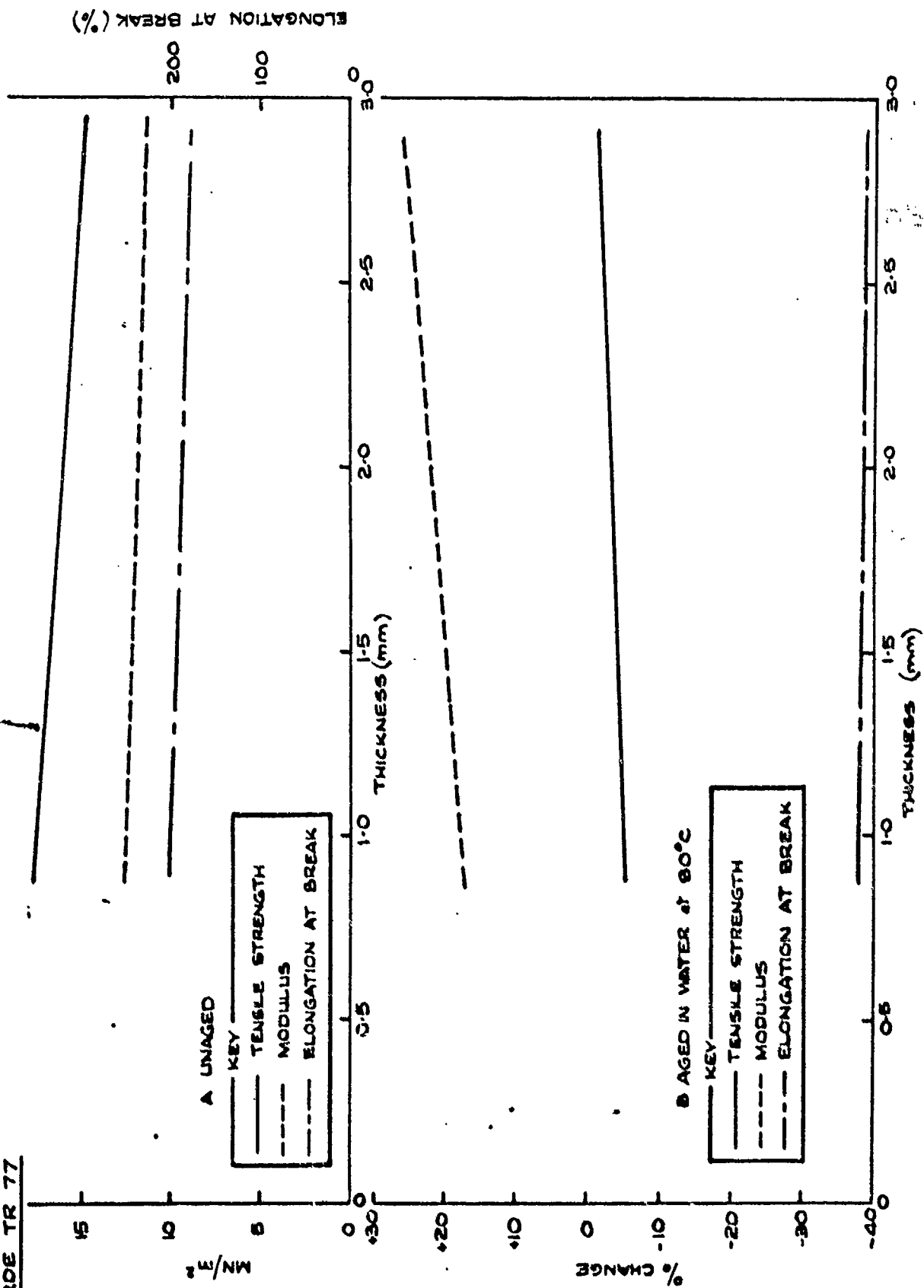


FIG. 9 EFFECT OF THICKNESS ON PHYSICAL PROPERTIES OF A POLYURETHANE