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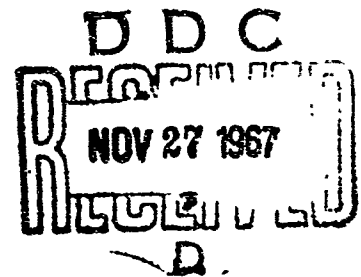
MINISTRY OF TECHNOLOGY

**EXPLOSIVES RESEARCH
AND DEVELOPMENT ESTABLISHMENT**

TECHNICAL MEMORANDUM No. 21/M/66

**The Accelerated Ageing of
some Commercial Polyurethane Rubbers**

**B.L. Hollingsworth
K.J. Ledbury
- A.L. Stokoe**



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The Accelerated Ageing of
some Commercial Polyurethane Rubbers

by

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Reference: WAC/174/020

1. SUMMARY

Nineteen commercial polyester urethane rubbers, and one commercial polyether urethane rubber have been subjected to accelerated laboratory ageing for periods of up to two years under hot/dry, hot/wet, and hot/humid conditions, and for up to two years immersed in Standard Test Fluid.

The results obtained on the polyether urethane were similar to those obtained in previous trials. The best polyester urethane (a development material) had a life under hydrolytic conditions of five to eight times that normally expected from commercially available polyester urethanes. ()

2. INTRODUCTION

During the past five years, polyurethane rubbers have been increasingly proposed for use in Service equipment, such as solid tyres, tank track pads, seals, bellows and flexible fuel tanks. These rubbers are attractive because of their relative ease of fabrication, high strength and elongation, excellent fuel and oxidation resistance, and good abrasion properties. To date, there has been little Service use due to the poor hydrolytic stability of the polyester urethanes. While the polyether urethanes have superior hydrolytic stability, their mechanical properties and resistance to petrol are normally inferior to those of the polyester urethanes.

The commercial manufacturers recognise this limitation on the wider application of polyester/polyurethane rubbers, and in the past two to three years have devoted considerable efforts to the production of materials of increased hydrolytic stability. It was, therefore, decided to examine the ageing behaviour of a range of commercially-produced polyurethane rubbers under hot/dry and hot/wet conditions, and the effect of immersion in petrol for protracted periods. One polyether urethane and nineteen polyester urethanes were included in the trial. Most of the polyester urethanes contained an anti-hydrolysis agent to increase their hydrolytic stability. In a similar trial, both polyester and polyether urethanes were examined some years ago at E.R.D.E. (1), but the present trial was mounted due to the claim that significant improvements in the hydrolytic stability of the polyester urethane rubbers have been made.

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3. MATERIALS

The polyurethane rubbers are referred to throughout the Memo by code numbers. All were supplied by the manufacturers as sheets of cured rubber. The rubbers P.U.17 to P.U.20 are later modifications of P.U.7.

4. EXPERIMENTAL

British Standard type C-dumb-bell test pieces (2) were cut from the sheets supplied, and the width and thickness measured before exposure to the test conditions. Dumb-bells, in sets of four, were suspended in loosely stoppered glass tubes and exposed to some or all of the following environments:

Hot/dry Suspended in air at 40°, 70° or 100°C.
Hot/wet Immersed in boiled out distilled water at 40°, 70° or 90°C.
Hot/humid Suspended above boiled out distilled water at 40°, 60°, 70° or 90°C.

Standard
Test Fluid Immersed in Standard Test Fluid at 40° or 65°C.

Standard Test Fluid (S.T.F.) 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. At the end of each exposure period, the required number of tubes were removed from the ovens, and the tubes and contents conditioned at room temperature (approximately 15°C) for 24 hours before testing. After the conditioning period, the groups of four specimens were removed from the tubes, dried from superficial liquid, and tested for hardness, elongation at break, and tensile strength as quickly as possible. Hardness was measured using a micro-indentometer, and the tensile properties were measured by British Standards methods (2,4) on a Hounsfield Tensometer. Specimens cut from the materials as received were tested by the same methods, and the results used as "unaged" reference points.

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5. RESULTS AND DISCUSSION

The results are given in Tables 1 to 5 (pp 7 - 11), and are discussed below.

5.1 Ageing Under Hot/Dry Conditions

Samples P.U.3 to P.U.10 and P.U.12 to P.U.20 were not aged under hot/dry conditions, due to the limited amount of each available. The polyester urethane P.U.1 had high initial strength of 6190 p.s.i., but in 24 weeks at 70°C, its strength fell to 30 p.s.i. At 40°C, the deterioration was much less rapid, and after 2 years its strength was still 1360 p.s.i. The elongation at break and the hardness showed only insignificant changes until the tensile strength reached a very low value. This feature is common to all the polyurethanes examined. After ageing for 52 weeks at 70°C and 40°C, P.U.2 had lost 62 and 40 per cent respectively of its initial tensile strength of 2930 p.s.i. Again, only small changes in elongation at break and hardness occurred during 52 weeks ageing.

The polyether urethane P.U.11 deteriorated more slowly than the polyester urethanes, retaining approximately one-third of its initial tensile strength after 52 weeks at 100°C. After 52 weeks at 70° and 40°C, the tensile strength was reduced by 52 and 46 per cent respectively. The elongation at break and hardness were, again, practically unchanged.

5.2 Ageing Under Hot/Wet Conditions

After immersion in water at 70°C, sample P.U.1 became too weak to test after 2 weeks, and sample P.U.6 became too weak to test after 3 weeks. These results are typical of the results normally obtained with polyester urethanes. Sample P.U.2 was completely degraded after 4 weeks immersion, while samples P.U.8 and P.U.9 only became too weak to test after 8 weeks. P.U.7, of which only a small sample was received, had only lost twenty per cent of its initial tensile strength after immersion for 4 weeks. The polyether polyurethane P.U.11 dropped from an initial tensile strength of 4090 p.s.i. to a strength of 480 p.s.i. after 52 weeks immersion, a result typical of the polyether urethanes. Sample P.U.10 dropped in tensile strength from 2530 p.s.i. to 840 p.s.i. after 12 weeks immersion. This result is unusual for a polyester urethane, and other evidence indicates that this sample may be a mixed polyester polyether urethane.

In general, the samples showed increased elongation at break in the period before very drastic reductions in tensile strength had taken place. This is attributed to absorption of water, which then acts as a plasticiser.

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5.3 Ageing Under Hot/Humid Conditions

Most tests have been carried out at 70°C, in air saturated with water vapour above boiled out distilled water. For convenience, this has been considered to be 100 per cent relative humidity. The results are generally similar to those obtained on immersion in water at 70°C. P.U.1 and P.U.6 were too weak to test after 2 weeks exposure, and P.U.2, 3, 4, 5 and 8 after 4 weeks. P.U.9 and P.U.16 were too weak after 8 weeks, and P.U.12, 13 and 15 after 12 weeks. The samples P.U.17 to 19, which are similar to P.U.7, only failed after 20 weeks, while the best of the variants on P.U.7, sample P.U.20, still retained some strength after 24 weeks exposure. The polyether urethane P.U.11 showed a similar reduction in tensile strength after 52 weeks exposure, to that obtained by immersion in water for the same period.

The samples again showed increases in elongation at break in the early stages of exposure, but the increases were not so great as those obtained by immersion in water. The loss in tensile strength with time is comparable, whether the sample is immersed in water or held in an atmosphere of 100 per cent relative humidity, with the latter condition causing slightly more severe degradation. Sample P.U.7 was reduced from a tensile strength of 4450 p.s.i. to 3850 p.s.i. by immersion in water at 70°C for 4 weeks while at 100 per cent relative humidity at 70°C; in four weeks the strength dropped to 3660 p.s.i. Similarly, P.U.10 dropped from 2530 to 840 p.s.i. after immersion for 12 weeks at 70°C, and dropped from 2530 to 780 p.s.i. after 12 weeks at 70°C and 100 per cent relative humidity. The slightly greater rate of degradation under humid conditions is thought to be due to the presence of a higher concentration of oxygen in the humid atmosphere than in the boiled out distilled water used for the hot/wet conditions. Whilst the polyurethanes are generally fairly resistant to oxidation, a small amount of oxidation may occur in the rubber in the water-swollen state, leading to the difference in severity between hot/wet and hot/humid ageing.

The results on P.U.11 show that deterioration, as measured by tensile strength, is very temperature dependent. Approximately the same degree of degradation is reached after exposure for 2 weeks at 90°C, for 12 weeks at 70°C or more than one year at 40°C.

5.4 Immersion in Standard Test Fluid

In S.T.F. at 40° and 65°C, the tensile strength of P.U.1 showed a sharp fall during the first week's immersion, and then a slow steady drop. After 2 years' immersion, the sample still retained some useful strength. The elongation at break and the hardness both showed marked changes after one week's immersion, and then little change until the tensile strength had fallen to a low value. The volume swelling did not change significantly

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during the test period, indicating that equilibrium swelling has been obtained during the first week of immersion. The initial change in physical properties is similar to that expected for swelling and plasticisation of a rubber by a fluid. When approximately 5 per cent by volume of water was added to the S.T.F. and the tube shaken occasionally during the test period, the deterioration of P.U.4 was more rapid than in S.T.F. alone. This pattern of change in physical properties is common to all the polyester urethanes examined, indicating that during the first 12 weeks of immersion in S.T.F., swelling and plasticisation are the predominating causes of change, and not degradation. After longer periods, traces of moisture in the S.T.F. appear to have caused some hydrolytic degradation.

No tests were carried out on P.U.11 due to its limited availability. It is known that the polyether urethanes swell considerably in S.T.F., and suffer a greater loss in physical properties than do the polyester urethanes in the same time under the same conditions. This is shown by P.U.10 which is thought to be a mixed polyester polyether urethane.

6. CONCLUSIONS

The commercial polyester and polyether urethanes examined slowly deteriorate when subjected to hot/dry conditions for long periods. When immersed in water or in contact with moisture at elevated temperatures, the deterioration of the polyester urethanes is rapid, and the rate is markedly temperature dependent. Under similar conditions, the polyether urethanes deteriorate more slowly. Immersion of the polyester urethanes in S.T.F. at elevated temperatures leads first to swelling and plasticisation, and then to slow deterioration, unless water is present, when rapid degradation takes place.

Elongation at break and hardness do not appear to be satisfactory physical properties from which to measure the degradation taking place in the polyurethanes.

While the rate of degradation of the polyester urethanes examined in this trial is still greater than could be accepted in a rubber for Service use, the best samples submitted (P.U.17 to 20) have shown a life of 5 to 8 times that which has hitherto been anticipated from polyester urethanes. Continuing developments with the P.U.17 to 20 series hold out the hope that a polyester urethane rubber which will meet Service requirements with respect to hydrolytic stability will be produced in the fairly near future.

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7. REFERENCES

1. Harding, G.W., E.R.D.E. Technical Memorandum No. 10/11/60.
2. B.S. 903: Part A 2: 1955.
3. B.S. 2751: 1956.
4. B.S. 903: Part A 7: 1957.

TABLE 1

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TABLE 1

Effect of Hot/Dry Conditions on Polyester Urethanes P.U.1 and P.U.2

Rubber		P.U.1			P.U.2		
Conditions of Test	Period of Exposure, weeks	T.S.	E _b	H	T.S.	E _b	H
Material as received	0	6190	675	87	2930	540	92
Dry 40° ± 0.5°C	1	6020	670	76	2820	520	92
	2	5620	740	73			
	4	6340	685	74			
	12	5840	700	73	2960	520	92
	24	4930	590	73			
	52	3870	630	69	1750	510	92
Dry 70° ± 0.5°C	104	1360	720	71			
	1	6200	675	75			
	2	5820	715	77	2780	440	90
	4	4550	635	75	2840	540	90
	12	2700	750	65	2540	550	91
	24	30	340	<30			
	52	Too weak to test			1100	330	86

The following abbreviations are used throughout Tables 1 to 5

- T.S. = Tensile Strength, pounds/inch²
- E_b = Elongation at break, per cent.
- H = Hardness, British Standard degrees.

/TABLE 2

TABLE 2

Effect of Hot/Wet and Hot/Humid Conditions on Polyst

Rubber		P.U.1			P.U.2			P.U.3			P.U.4			P.U.5	
Conditions of Test	Period of Exposure, weeks	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b
Material as received		6190	675	87	2930	540	92	3130	560	94	3120	550	93	3990	510
60°C, 100% r.h.	0.5							2000	550	90	2040	600	89	3260	510
	1.0							1660	490	91	1750	510	90	2590	510
	2							1200	480	91	1230	530	90	2710	510
	4							600	480	88	490	150	88	620	150
70°C, 100% r.h.	1	500	790	42				960	530	89	1030	530	89	860	370
	2	Too weak to test			680	330	83	660	150	89	680	110	92	500	85
	4				Too weak to test			Too weak to test			Too weak to test			Too weak to test	
	8														
	12														
70°C, immersed in water.	1	1200	790	42	660	350	81								
	2	Too weak to test			Too weak to test										
	4														
	8														
	12														

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TABLE 2

Test Conditions on Polyester Urethanes P.U.1 to P.U.10

P.U.4			P.U.5			P.U.6			P.U.7			P.U.8			P.U.9			P.U.10		
T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H
20	550	93	3990	510	95	5570	722	86	4450	380	98	3540	530	67	2440	615	66	2530	425	69
40	600	89	3260	510	95															
50	510	90	2590	510	96															
30	530	90	2710	510	95															
90	150	88	620	150	93															
30	530	89	860	370	93	Too weak to test			3910	370	98	2340	645	63	1690	580	64	1200	490	76
80	110	92	500	85	94				3650	385	97	1460	655	68	1430	640	69	1600	510	69
Too weak to test			Too weak to test						3660	365	97	100	560	67	710	670	71	1120		76
												Too weak to test			Too weak to test			830	530	76
																		780	660	76
						1020	795	30				2130	660	65	2000	690	63	1300	530	76
						Too weak to test			3850	370	97	450	680	69	1140		68	1000		80
												Too weak to test			Too weak to test			1010	690	75
																		840	760	

B

TABLE 3

TABLE 3

Effect of Wet and Dry Standard Test Fluid on Polyester U

Rubber		P.U.1				P.U.2				P.U.3			P.U.4			P.1
Conditions of Test	Period of Exposure, weeks	T.S.	E _b	H	S	T.S.	E _b	H	S	T.S.	E _b	H	T.S.	E _b	H	T.S.
Material as received		6190	675	87	-	2930	540	92	-	3130	560	94	3120	550	93	3990
Immersion in S.T.F. at 65° ± 0.5°C	1	4490	740	67	13.8											
	2	3710	710	64	13.5	2290	720	82	17.3							
	4	3700	690	66	13.9	2190	730	82	17.4							
	12	3050	690	63	13.4	2030	700	82	19.4							
	24	2130	675	64	14.0											
	52	530	610	43		1480		82								
	104	230	10	<30	15.6											
Immersion in S.T.F. at 40° ± 0.5°C	1	4820	740	67	13.3					2210	650	90	2340	680	91	2520
	2	4340	725	68	13.5	2190	680	86	15.1							
	4	4380	715	68	13.4	2250	690	86	15.5	1980	680	90	2040	700	90	2810
	12	4290	710	67	13.3	2260	670	86	15.4							
	24	3340	740	66	13.9											
	52	1690	655	54		1900		88	15.8							
	104	570	680	<30	13.1											
Immersion in S.T.F. and 5% v/v water at 40°C	3	3270	745	69												
	5	2590	630													
	12	990	740													

*S = Volume Swell, per cent

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TABLE 3

and Dry Standard Test Fluid on Polyester Urethanes P.U.1 to P.U.10

P.U.3			P.U.4			P.U.5			P.U.6			P.U.7			P.U.8			P.U.9			P.U.10			
T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	
3130	560	94	3120	550	93	3990	510	95	5570	722	86	4450	380	98	3540	530	67	2440	615	66	2530	425	69	
							4700	900	<30						1830	610	66	1900	630	68	1090	370	79	
							3620	740	<30						2450	560	67	1830	630	67	1170	380	79	
							4320	860	<30	3590	340	92	2620	615	68	1890	670	68	1790	480	83			
													2250	670		2065	600		1360	450				
2210	650	90	2340	680	91	2520	620	93																
1980	680	90	2040	700	90	2810	600	92																

*S = Volume Swell, per cent

B

TABLE 4

TABLE 4

The Effect of Hot/Humid Conditions and Immersion in Standard Test Fluid on Pol

Conditions of Test	Period of Exposure, weeks	P.U.12			P.U.13			P.U.14			P.U.15			P.U.16		
		T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	
Material as received		2370	675	80	3370	460	76	5460	670	95	3430	780	79	3750	420	
60° ± 0.5°C, 100% r.h.	1	1730	810	64				4090	680	92	2100	800	73	3280	475	
	2	1660	715	67				4650	625	92	2460	810	77	2870	430	
	3	1520	770	64				4860	640	91	1880	840	78	2560	450	
	4	1790	700	63	420	420	73	4410	680	89	2080	840	79	2320	435	
	8	1190	790	61	3450	480	70				1210	770	74	640	10	
	12				2760	475	68									Too weak to
	16	540	545		2546	475	58	3010	740	98	1190	800	87			
	24	Too weak to test			1640	545	41									
	40							2530	690	93						
52							2180	805	88							
70° ± 0.5°C 100% r.h.	1	1470	690	57	2970	440	72	4210	700	90	1940	900	66	3410	500	
	2	1400	680	61				4010	670	90	1628	870	66	2380	500	
	3	1220	660	57				4170	685	90	1120	850	71	1190	335	
	4	1290	700	59	2960	485	68	4150	690	85	1150	800	69	1300	350	
	8	510	470	55	1610	556	38				780	660	70			Too weak to
	12	Too weak to test			Too weak to test			Insufficient sample for further tests			Too weak to test					
	16															
	20															
24																
Immersion in S.T.F. at 40°C	2															
	4															
	8															
	12															
Swelling in S.T.F. at 40°C	6 days															

Two samples of P.U.20 were received. The test data on the second sample ar

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TABLE 4

Strength and Immersion in Standard Test Fluid on Polyester Urethanes P.U.12 to P.U.20

P.U.14			P.U.15			P.U.16			P.U.17			P.U.18			P.U.19			P.U.20					
T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H	T.S.	E _b	H			
60	670	95	3430	780	79	3750	480	92	3490	370	93	4960	500	84	5600	550	84	3510	300	96	4540	435	90
90	680	92	2100	800	73	3280	475	97															
650	625	92	2460	810	77	2870	430	89															
660	640	91	1880	840	78	2560	450	87															
410	680	89	2080	840	79	2320	435	88															
			1210	770	74	640	10	95															
						Too weak to test																	
010	740	95	1190	800	87																		
530	690	93																					
180	805	88																					
210	700	90	1940	900	66	3410	580	86	3270	435	95	3920	570	87	4340	660	79	4290	485	94			
010	670	90	1628	870	86	2380	500	86	3070	410	76	3270	595	76	3700	730	76	4310	510	79			
170	685	90	1120	830	71	1190	335	90															
150	690	85	1150	800	69	1300	350	97	2740	430	94	3000	595	87	2680	730	87	3830	470	92	4030	505	92
			780	660	70	Too weak to test			1560	410	92	1370	600	90	1510	860	94	2640	550	93	2040	530	90
insufficient sample for further tests			Too weak to test						810	370	99	820	500	99	740	670	97	1990	545	94	1320	495	90
									420	200	95	460	250	96	325	220	94	724	435	82			
									Too weak to test			Too weak to test			Too weak to test			500	260	92			
																		270	180	75			
									3010	365	85	4190	540	76	4015	620	71	4120	420	86			
									3350	390	92	3970	510	88	4105	595	82	3590	395	95			
									3150	360	92	4250	530	89	4210	600	83	4050	415	95			
									3310	390	92	4310	540	86	4170	610	81	4090	420	94			
									21.8%			24.8%			28.7%			21.8%			17.4%		

received. The test data on the second sample are marked with an asterisk.

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TABLE 5

3

TABLE 5

Effect of Hot/Dry, Hot/Wet, and Hot/Humid Conditions on Polyether Ur

Conditions of Test	Period of Exposure, weeks	T.S.	E _b	H	Conditions of Test	Period of Exposure, weeks	T.S.	E _b	H
Material as received		4090	640	93	Material as received		4090	640	93
Dry, 40° ± 0.5°C	4	2960	585	93	Immersed in water, 40° ± 0.5°C	4	2680	550	95
	12	2780	615	93		12	1920	520	
	24	2350	540	94		24	2850	550	
	52	2200	615	99		52	1410	510	
Dry, 70° ± 0.5°C	2	3580	640		Immersed in water, 70° ± 0.5°C	2	1920		
	4	3190	630			4	1050		
	12	2740	665			12	660		
	24	2440	630	95		24	600		
	52	1970	660			52	400		
	64	2045	670	99					
Dry, 100° ± 0.5°C	2	3480	745		Immersed in water, 90° ± 0.5°C	2	560	225	85
	4	2540	785			4	340	90	87
	12	1120	835			12	Too weak to test		
	24	890	620	94					
	52	940	440						

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TABLE 5

Effect of Hot/Dry, Hot/Wet, and Hot/Humid Conditions on Polyether Urethane P.U.11

H	Conditions of Test	Period of Exposure, weeks	T.S.	E _b	H	Conditions of Test	Period of Exposure, weeks	T.S.	E _b	H
93	Material as received		4090	640	93	Material as received		4090	640	93
93	Immersed in water, 40° ± 0.5°C	4	2680	550	95	40°C, 100% r.h.	4	1990	530	
93		12	1920	520			12	1960	520	95
94		24	2850	550			24	2860	530	
99		52	1410	510			52	1730	545	93
							96	2100	545	99
	Immersed in water, 70° ± 0.5°C	2	1920			70°C, 100% r.h.	2	1320	715	
		4	1050				4	1100	725	
		12	660				12	690	330	
95		24	600				24	790	315	92
99		52	480				52	530	155	
	Immersed in water, 90° ± 0.5°C	2	560	225	85	90°C, 100% r.h.	2	520	170	89
		4	340	90	87		4	550	150	91
94		12	Too weak to test				12	Too weak to test		

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