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SHORT-TERM AGING STUDY AT 90°C IN AIR: HALTHANE 73-18 AND 73-18A

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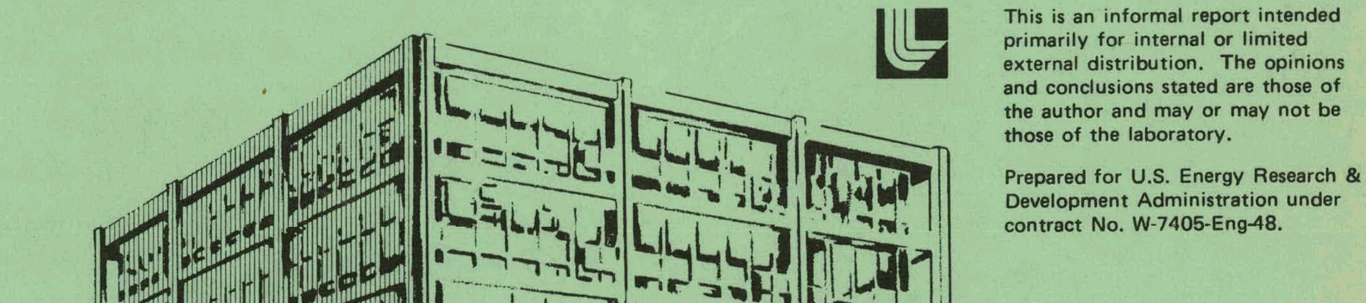

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SHORT-TERM AGING STUDY AT 90° C IN AIR: HALTHANE 73-18 AND 73-18A

ABSTRACT

A ninety-day aging study was performed on Halthane 73-18A to determine the thermal aging effects due to the presence of DABCO, a catalyst. Samples were taken after 14 days, 30 days, 60 days, and 90 days of exposure to air at 90° C. Tests used to evaluate aging effects were: ring tensile, differential scanning calorimetry, dynamic dielectric spectroscopy, and solvent swell.

Results of tensile tests indicated an increase in tensile properties that peaked at 30 days and decayed to 70% loss of peak strength in 90 days. DSC, DDS, and solvent swell data all followed the same trend. Comparative analysis of all data support the hypothesis that the presence of DABCO increases the oxidative cleavage of the polyether chain segment.

INTRODUCTION

Halthane 73-18 designates an MDI-terminated* polyether prepolymer that has been cured with a mixture of 1,4-butanediol, tetramethylene ether glycol (1000 $\overline{M}_n$), and Quadrol, a crosslinker.† During the early development of application techniques for this base adhesive system, engineers requested an acceleration of the reaction rate so the polymer could be used in areas requiring shorter fixturing items. Halthane 73-18A is the same base system containing 0.02 phr DABCO,‡ which acts as a catalyst for the MDI-diol portion of the reaction.

While DABCO satisfactorily accelerates the system, there is concern over its effect on the molecular chain at elevated temperatures. To study this behavior, we performed a short-term aging study. Samples were taken after

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*MDI is 4,4'-Diphenylmethane diisocyanate.

†Quadrol — N,N,N',N'-tetrakis (2-hydroxy propyl) ethylene diamine (Wyandotte Chemical Corporation).

‡DABCO — triethylene diamine (Houdry Process Corporation).

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14 days, 30 days, 60 days, and 90 days of exposure to air at 90°C. One master batch of Halthane 73-18A was prepared and cast into sheet forms to serve for all aging tests. At the end of each sampling period, a sample sheet was removed from the oven and allowed to equilibrate to ambient conditions for at least 16 hours before testing. To differentiate between normal oxidative cleavage and any increase due to the effects of DABCO, Halthane 73-18 was used as a control.

TEST RESULTS

Since the loss of mechanical properties was of prime concern, ring tensile tests were the logical first means of evaluation. The ring-tensile-test results (Table 1) clearly show an initial improvement followed by loss of mechanical properties (see Figs. 1 and 2).

The maxima in breaking stress and stress moduli at 30 days show the effect of heat and the accelerator DABCO on the state of cure. From the work of A. Singh,* we already knew that oxidative degradation in polyether urethane is by scission of the polyether-chain segment. While some oxidative scission does appear to take place in the Halthane 73-18, the rate of degradation is significantly lower than in Halthane 73-18A.

Another indication of the activity of DABCO is observed by comparing the 30-day samples of 73-18 and 73-18A (Table 1). After 30 days at 90°C, Halthane 73-18A showed an 18% higher breaking stress than Halthane 73-18. It is apparent that two opposing processes are at work at the same time: an increase in the state of cure and crosslink density, and a scission process. The increase in crosslink density was the dominant process until sometime after 30 days at 90°C, the scission process becoming dominant thereafter.

Either loss of hard-section aggregates or damage to soft sections could account for the loss of mechanical properties after 30 days. We used differential scanning calorimetry (DSC) to examine the state of the hard-section crystallinity (see Fig. 3). The DSC results on Halthane 73-18A indicate two crystalline transitions: a minor endotherm shows a low-order transition that peaked in the 50-70°C range, and a more pronounced endotherm shows a transition

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*A. Singh, "Chemical Stress Relaxation in Crosslinked Polyurethane Elastomers," in *Advances in Urethane Science and Technology, Vol. 1* (Technomic, Stanford, Co., 1971), Kurt C. Frisch, ed.

Table 1. Tensile properties — Halthane 73-18 and 73-18A after aging at 90°C in air.

	14 days		30 days		60 days		90 days	
Property	73-18	73-18A	73-18	73-18A	73-18	73-18A	73-18	73-18A
Initial modulus, MPa	5.08	6.24	4.61	7.13	4.16	4.99	3.65	3.33
Mid-range modulus, MPa	3.89	4.49	3.10	5.02	2.55	3.25	2.12	2.03
Breaking stress, MPa	46.23	35.37	41.29	50.45	39.95	32.54	31.14	15.16
Strain at rupture	4.83	4.38	5.40	4.73	6.19	6.05	6.82	6.33

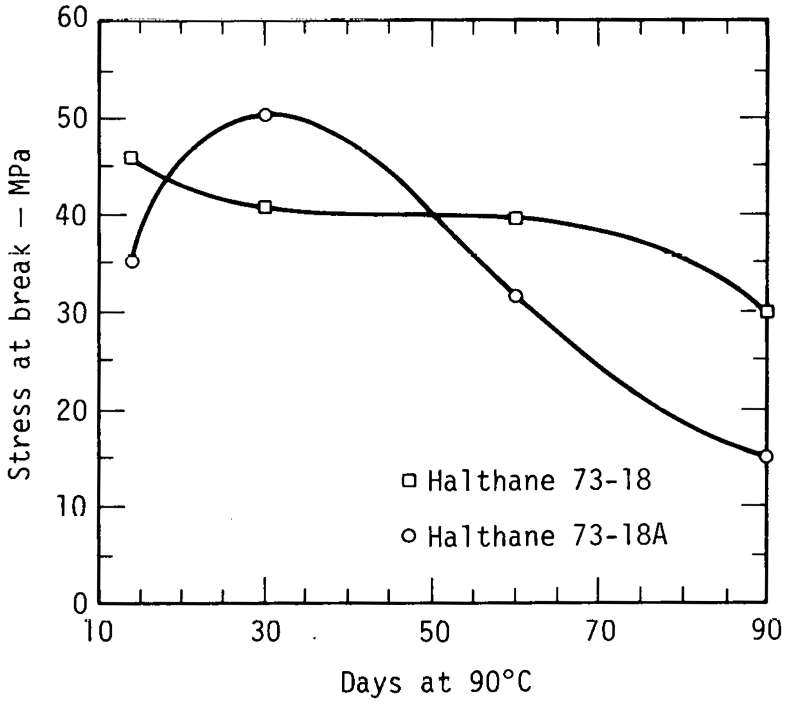

Fig. 1. Effect of aging on breaking stress of sample and control.

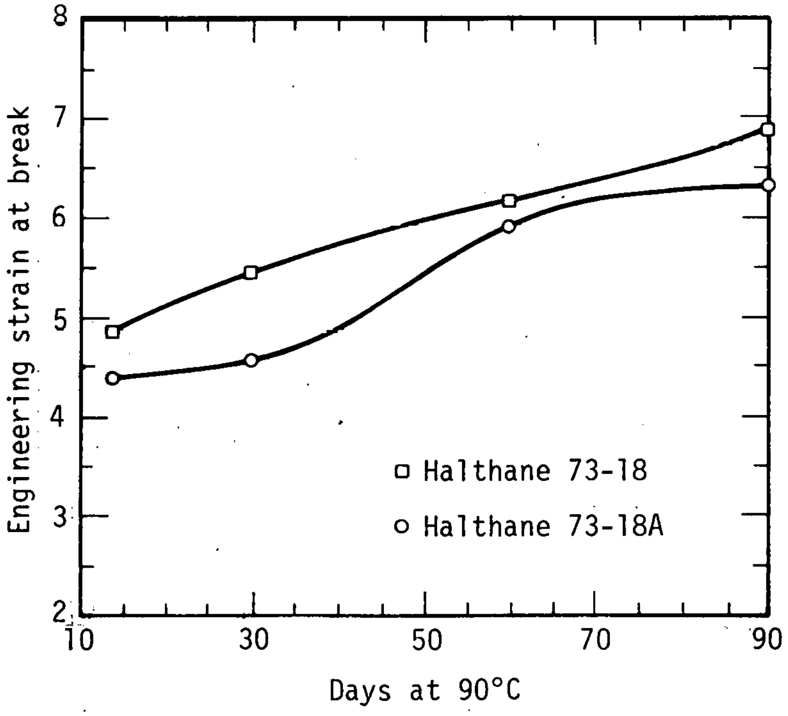

Fig. 2. Effect of aging on engineering strain of sample and control.

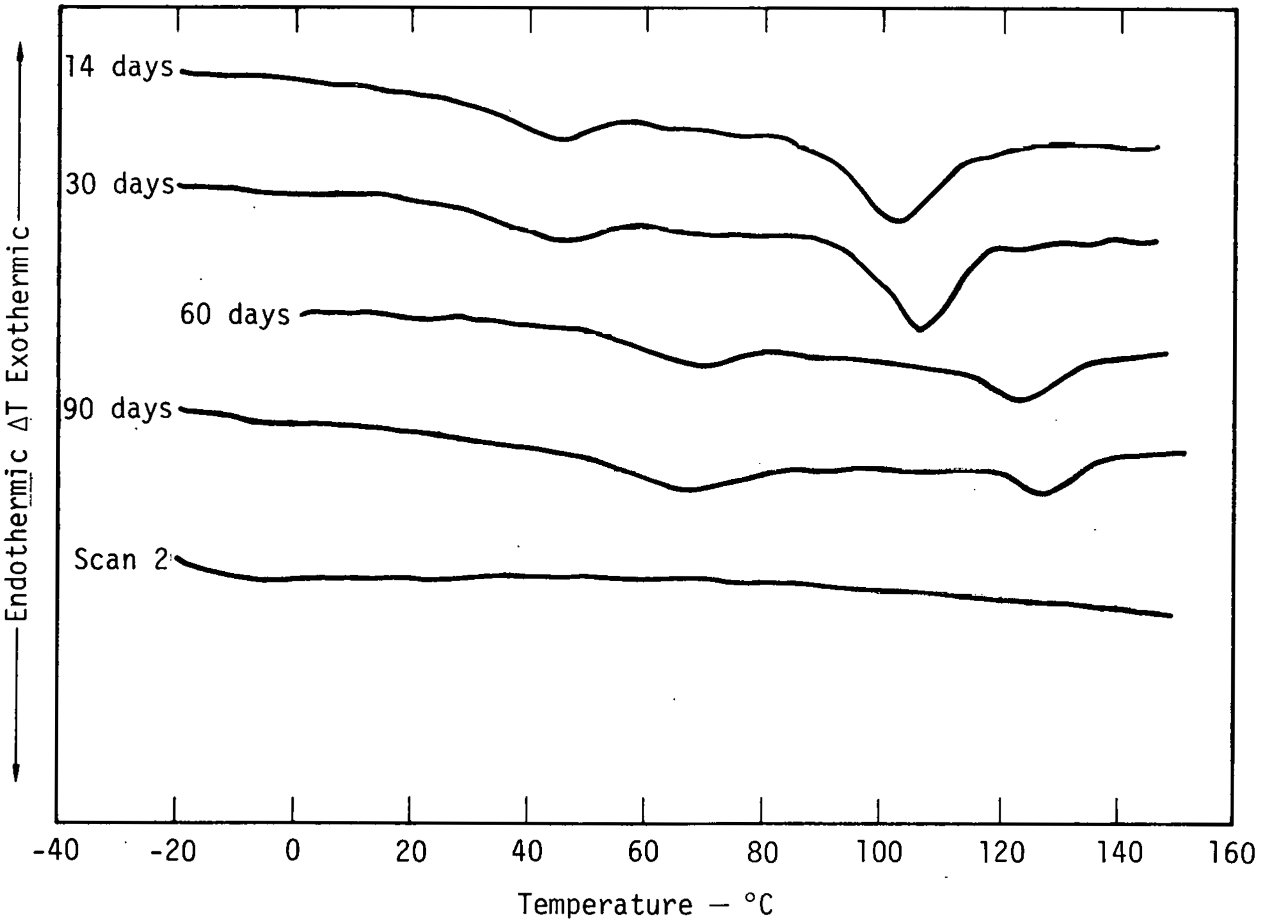

Fig. 3. DSC of Halthane 73-18A after various times at 90° C in air. All DSC tests consisted of two scans. Scan 2 is typical of an immediate repeat for all tests.

that peaked in the 110-125° C range. The minor endotherm is thought to be due to crystallinity in the polyether chain, while the major endotherm is due to the hard-section crystallinity. Several pertinent statements can be based on these results.

- The volume of hard-section crystallinity reaches a maximum after 30 days at 90° C and decreases thereafter, shown by the high-temperature endotherm reaching its maximum value at 30 days.
- The "perfection" of remaining crystallites improves with time at temperature, as indicated by the shift of the endotherm to higher temperatures.

The DSC on Halthane 73-18 is somewhat different (Fig. 4). It shows no significant crystallinity in the polyether chain before 90 days at 90° C. There is no dramatic loss of hard-section crystalline volume and the "perfection" of hard-section crystallites appears to stabilize sometime after 14 days at 90° C.

It is apparent that DABCO drives the urethane reaction to a higher degree of completion. The loss of crystalline volume in the aged Halthane 73-18A is not enough to account for the breaking-stress loss, since about the same level of crystallinity in the aged Halthane 73-18 (as shown by high-temperature endotherms in Figs. 3 and 4 for 60 or 90 days) yields much higher strength. We therefore turned our attention to the condition of the soft section. It has already been demonstrated that scission in the soft section produces an increase in chain ends, which in turn lowers the soft-section glass transition temperature (T_g).* If T_g is affected, the activation energy for the soft-section rotation should also be affected. To evaluate this, we used dynamic dielectric spectroscopy (DDS). Two frequencies (100 Hz and 1 kHz) were used to observe the dispersion of soft-section regions. The heating rate was held constant at 0.5° C/min from -40° C to 150° C. The results of this DDS are shown in Table 2, where it should be noted that the quoted activation energies are approximate and are only used to demonstrate a trend. Activation energies are more properly measured at five frequencies.

The trend toward lower activation energies and lower temperatures for the 100-Hz dispersion peak is consistent with a loss of molecular weight and an associated increase in chain ends. In addition to the above subtle trend, a transition was noted at higher temperatures that more clearly established scission in the soft section (see Table 3).

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*J. J. Aklonis, W. J. MacKnight, and M. Schen, *Introduction to Polymer Viscoelasticity* (John Wiley & Sons, New York, 1972), p. 42.

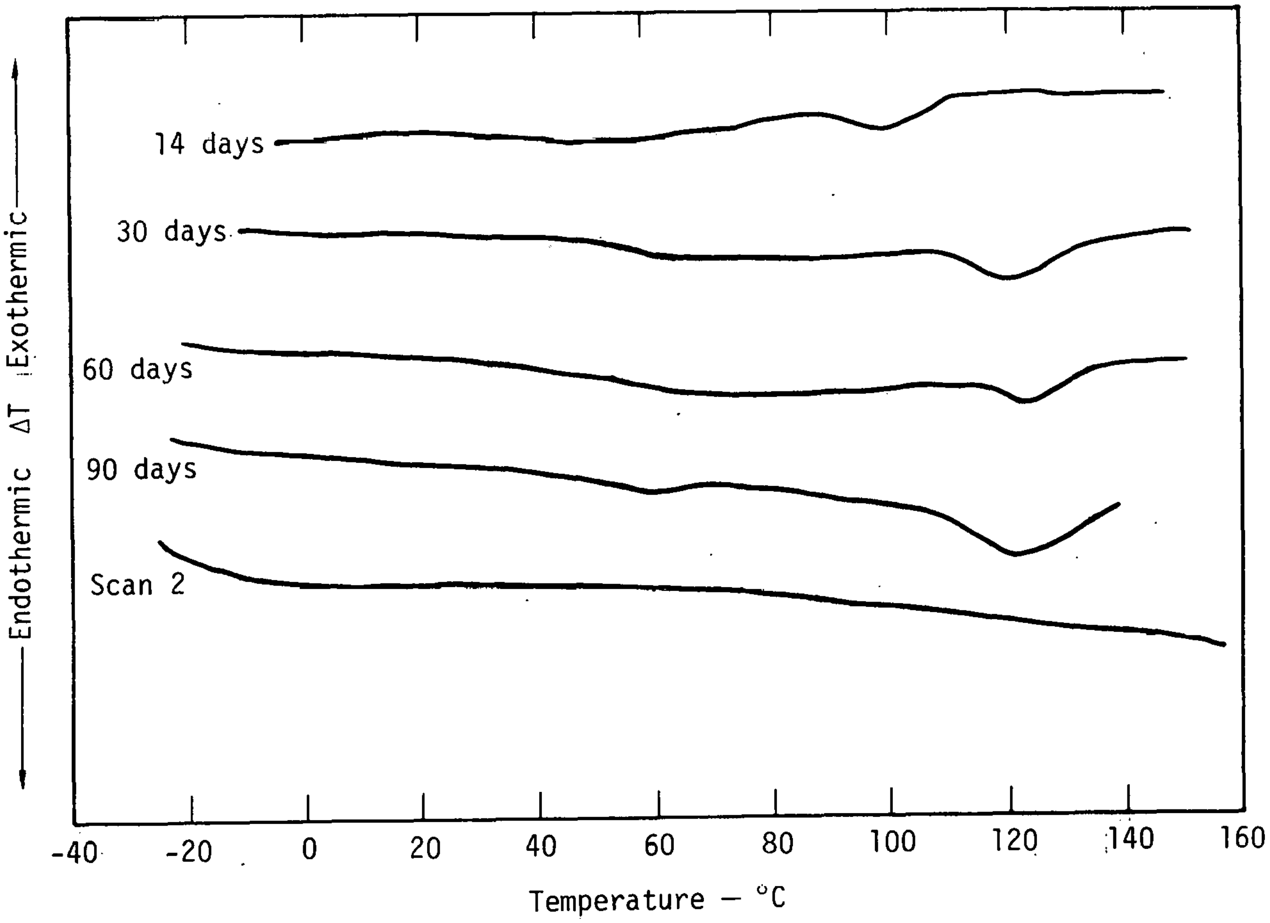

Fig. 4. DSC of Halthane 73-18 after various times at 90°C in air. All DSC tests consisted of two scans. Scan 2 is typical of an immediate repeat for all tests.

Table 2. Temperatures of DDS dispersion peaks.

	14 days	30 days	60 days	90 days
Halthane 73-18A				
Dispersion peak at 100 Hz, °C	-16	-18	-19	-20
Activation energy, kcal/mole	44	38	36	30
Halthane 73-18				
Dispersion peak at 100 Hz, °C	-17	-15	-16	--
Activation energy, kcal/mole	44	45	40	--

Table 3. Temperatures (° C) of the high-temperature dispersion peak in DDS at 100 Hz.

	14 days	30 days	60 days	90 days
Halthane 73-18A	112	114	105	98
Halthane 73-18	154	117	126	127

The transition observed at higher temperatures is reversible with temperature. The shift of this event to lower temperatures with aging time parallels the same trend noted in tensile properties. Crystallinity of the hard section does not appear to be involved, since the high-temperature dispersion appears at temperatures below the dissociation temperature of the hard-section aggregates in aged Halthane 73-18A. The element responding during this dispersion is probably the increasingly larger volume of soft-section chain ends and is the first sign of approaching the melt transition temperature (T_m). It is interesting to note that soft-section damage was observed dielectrically after 14 days into the aging study by the shift of the high-temperature dispersion peak, which is in the region of T_m, as compared to unaged controls.

We confirmed change in crosslink density by using solvent swell measurements (Table 4).

Table 4. Solvent swell (in toluene) of aged samples. Solvent swell is expressed as percent increase over a control cured 90 days at room temperature.

Polymer	14 days	30 days	60 days	90 days
Halthane 73-18A	20%	29%	42%	44%
Halthane 73-18	12%	21%	28%	39%

Conclusion

We have demonstrated that the presence of DABCO contributes to an increase in oxidative cleavage in polyether urethanes at 90° C in air. While there is evidence to indicate some decrease in hard-section volume, the major damage due to this cleavage appears to be centered in the soft sections. An increase in chain ends negates the high strength potential of remaining hard sections because of the decreased constraint of the hard sections in tension.

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