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Development of Halthane Adhesives for Phase 3 Weapons: Summary Report

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December 5, 1980



Lawrence
Livermore
National
Laboratory

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Development of Halthane Adhesives for Phase 3 Weapons: Summary Report

ABSTRACT

Seven new polyurethane adhesives have been developed to meet the requirements for current Phase 3 nuclear weapons. These adhesives, designated Halthanes, avoid the use of the curing agent methylene bis(2-chloroaniline), which has been restricted by OSHA. All of the Halthanes use LLNL-developed prepolymers: four are made from MDI-terminated prepolymers cured with a blend of polyols and three are made from Hylene-W-terminated prepolymers cured with aromatic diamines. All of the adhesives have low to intermediate moduli over a wide temperature range, bond rapidly and well to most substrates, and are compatible with weapons components.

INTRODUCTION

Restrictions imposed by the Occupational Safety and Health Administration (OSHA) on the use of methylene bis(2-chloroaniline) (MOCA) forced the development of alternative adhesives to the widely used Adiprene L-100/MOCA. The requirements of earlier weapons systems were met with Adiprene L-315/polyol and Adiprene LW-520/methylenedianiline (MDA).¹ However, L-315/polyol is too sensitive to the wide temperature extremes likely to be encountered in the current Phase 3 systems, and the LW-520/MDA

system is too viscous and has too short a working time. We reviewed commercially available adhesives and concluded that none of them met all the requirements set by weapons engineers and designers. We then embarked on a synthesis program to develop adhesives to meet weapons requirements.

This report updates and replaces Chemistry Department Technical Notes Nos. 75-23 and 75-24 and LLNL Reports UCID-16990² and UCID-17348.³

SUMMARY

A family of new urethane adhesives called Halthanes has been developed at Lawrence Livermore National Laboratory (LLNL) to meet the requirements of current Phase 3 nuclear weapons. All of the Halthanes are based on LLNL-developed prepolymers. The 73-series Halthanes are made from prepolymers terminated with 4,4-methylene bis(phenyl isocyanate) (MDI) and cured with a blend of polyols. The 87- and 88-series Halthanes are made from a prepolymer terminated with Hylene W (hydrogenated MDI) and cured with aromatic diamines. The chemicals used in Halthane

synthesis are not currently subject to OSHA restrictions.

The Halthanes have been characterized to determine how well each would meet design requirements. The polyol-cured systems (the 73 series) react more slowly and have lower viscosities than the amine-cured 87 and 88 series systems. The 87 and 88 series have higher bond strengths than the 73 series in aluminum-to-aluminum butt-tensile tests at room temperature (9 to 15 MPa, compared to 5 to 7 MPa). Bond strengths on aluminum are higher than on most of the other materials tested, and decrease

TABLE 1. Some typical properties of Halthanes.

Property	73-14	73-15	73-18	73-19	87-1	87-2	88-2
Initial viscosity, Pa·s	4	4	3	3	25	28	25
Viscosity after 1 hr, Pa·s	46	21 ^a	94	26 ^a	300	54 ^a	72 ^a
Pot life (100-g mass), min	154	24 ^b	72	25 ^b	98	66	46
Shore A hardness (instant/10 μs):							
16 hr	50/27		54/41		74/68	72/65	88/87
4 hr				24/3			
8 hr		59/50		45/22			
7 da	77/77		73/71		85/80	89/80	97/92
Handling time, hr	24	4	16	4	8	6	4
Ring tensile properties (10 cm/min, 23°C):							
Tensile modulus, MPa	15	20	5(6.4) ^c	5(7.3) ^c	30	37	67
Rupture strength, MPa	34	42	25	44	60	27	32
Rupture strain	6	6	5	4	4.4	3.3	3.3
Compressive modulus, MPa	25		14		30		
Thermal conductivity, W/(m·k)(-50 to +100°C)							
				0.22-0.21			
Linear coefficient of thermal expansion, 10 ⁻⁴ °C ⁻¹ (+30 to 75°C)							
	1.9		1.9		1.9		
	to		to		to		
	2.0		2.0		2.0		
Glass transition temperature (T _g), °C	-56	-54	-50	-50	-80	-77	-76

^aViscosity after 0.5 hr, Pa·s.

^bFifty g mass.

^cDetermined on "dog-bone" specimen (ASTM D 638), with extensometer.

with increasing temperature. The 73-series Halthanes have a lower modulus and higher elasticity than the 87 and 88 series over the military temperature range (-54 to 74°C), because less reinforcement is provided by the MDI-1,4-butanediol (BDO) hard segments than is provided by the Hylene-W-diamine hard segments. The compatibility of Halthanes with other weapons components should be comparable to that of the Adiprene

L-100/MOCA adhesive used previously. The permeabilities of the adhesives to a number of common gases and water vapor are very similar to those we reported previously for Adiprene adhesives.

Table 1 compares typical bulk properties of the Halthanes cured at room temperature. Properties will depend on mixing ratios (stoichiometry) and on thermal history.

REQUIREMENTS FOR ADHESIVES

Because the design of the Phase 3 weapons was incomplete when we started our development program, we were able to get only qualitative requirements from the design engineers and physicists. These were as follows:

1. Viscosity no higher than that of L-100/MOCA, or 40 Pa·s initially. A lower viscosity is desirable.

2. A working time of at least one hour.

3. Cure time such that the adhesive has sufficient bond strength to permit removal of tools and clamping fixtures after 16 hours or, for some applications, 4 to 8 hours.

4. Adhesive tensile strength on metals and high explosives (specifically LX-10) of approximately 7 MPa over the temperature range of -50 to

70°C. For some other applications a breaking stress of at least 10 MPa is desirable.

5. A low tensile modulus over a wide temperature range; some elasticity even at -50°C. The adhesive should retain a reasonable portion of this modulus to at least 75°C. For one application, it must not "flow" at 150°C.

6. Compatibility with high explosives and other weapon components.

7. Service life of 20 to 25 years under military conditions.

In our development of new adhesives, we addressed each design requirement by controlling the structure of different adhesive components. We

grouped the design requirements into four structure/property relationships:

1. The chemical structure of the prepolymer and the curing agent determines the viscosity, working time, and cure rate.

2. The structure of the polymer/substrate interface determines the adhesive strength.

3. The molecular architecture of the hard and soft segments controls the modulus of elasticity of each polyurethane adhesive.

4. The segmental structure of the polymer and the environment in which it is used directly affect its use-life and compatibility with other weapon components.

COMPOSITION OF HALTHANES

Our adhesive formulations were adjusted so that the structure of the prepolymer, curing agent, and accelerator produced viscosities, working times, and cure rates close to those specified in the design requirements. We developed three types of adhesives; all three contain polyether soft segments of the type used in Adiprene L-100, polytetramethylene ether glycols (PolyMegs). The 73-series Halthanes contain MDI-BDO hard segments; the 87- and 88-series contain aromatic diamine hard segments.

The 73-series Halthane prepolymers are composed of a blend of PolyMegs with molecular weights of 1000 and 2000 and MDI in a ratio of 1.0 mole blend PolyMeg to 3.5 moles MDI. The 87- and 88-series Halthane prepolymers are composed of 2000-MW PolyMeg and Hylene W in ratios of 1.0 mole PolyMeg to 2.3 and 2.8 moles Hylene W, respectively. Reactant ratios and analyses are given in Table 2.

We chose MDI rather than TDI (2,4 toluene diisocyanate or mixtures of the 2,4- and 2,6-isomers) for our prepolymer 73 synthesis because MDI has a considerably lower vapor pressure and is thus safer to handle. OSHA has proposed tight restrictions on the concentration of TDI in the atmosphere of working areas. The Hylene W used in the Halthane 87 and 88 prepolymers is a blend of isomers made by hydrogenation of MDI. It also has a low volatility, but may be a contact irritant.

The polyol blends used to cure the prepolymer 73 contain the polyether used in the prepolymer plus some BDO which forms the hard segments and interconnects the soft segments; BDO has the same structure as the polyether repeat unit. Curing agents HGH-18 and 19 contain some Quadrol (N, N, N', N'-tetrakis(2-hydroxypropyl)ethylene-diamine), which crosslinks the adhesive, providing better high-temperature properties and a faster cure. Ferric acetylacetonate (FAA) catalyzes the

TABLE 2. Prepolymer component ratios and analyses.

Prepolymer	Component, wt%				Analysis, wt%	
	PolyMeg 1000	PolyMeg 2000	MDI	Hylene W	Free diisocyanate	Total NCO
73	47.6	7.4	45	—	23.2	10.5
87	—	77.6	—	22.4	6.8	3.7
88	—	74.0	—	26.0	10-11	5.2

E, 08
400
1135.1
807.7

urethane reaction; i.e., it accelerates the cure of 73-15 and 73-19 Halthanes.

Prepolymer 87 is cured with Tonox 60/40, a blend of aromatic amines containing 60% Tonox and 40% m-phenylenediamine. Tonox is a polymeric MDA with a functionality greater than 2; thus the cured material has some crosslinks. Tonox 60/40 is similar to the eutectic of MDA and m-phenylene-diamine used at Union Carbide (Y-12) for many years and has been used extensively in curing epoxies. Because it is a blend of aromatic amines and contains MDA, it should be used with caution, since MDA has been found to be carcinogenic in rat feeding tests. Prepolymer 88 can be cured with Tonox 60/40 (Halthane 88-1) or with Ciba-Geigy's curing agent XU-205 (Halthane 88-2). Curing agent XU-205 is a liquid mixture of aromatic diamines,

TABLE 3. Curing-agent formulations for 73-series Halthanes.

Curing agent	Component, wt%			
	PolyMeg 1000	BDO	Quadrol	FAA
HGH-14	90	10	—	—
HGH-15	90	10	—	0.0156
HGH-18	85	10	5	—
HGH-19	85	10	5	0.0107

containing MDA, 4,4'-methylene-bis(2-ethyl-aniline), and a similar monosubstituted diamine, 4-amino-3-ethylphenyl-4'-aminophenyl-methane.

The ratios of the components of the curing agents for the 73 series are given in Table 3.

PREPARATION OF HALTHANES

PREPOLYMER SYNTHESIS

The polyethers and the diisocyanates must be dried before reaction, and the MDI must be filtered to remove dimer and polyureas. The reaction is carried out at $60 \pm 5^\circ\text{C}$ under a dry nitrogen or other dry atmosphere, with moderate stirring and provision for temperature control.⁴ (Higher temperatures promote allophanate reactions.) The polyethers are added slowly to the diisocyanate.

CURING-AGENT PREPARATION

The polyol curing agents are warmed sufficiently to melt all components (to about 50°C) and blended. They must be well mixed to assure uniformity, as some portion will crystallize preferentially on cooling. They must also be dried thoroughly, since they are hygroscopic and may contain some water as received. Water will compete with the

isocyanate-hydroxyl reaction, diminishing the adhesive's strength and causing bubbles to form. The ferric acetylacetonate should be dissolved in the 1,4-butanediol before the other components are added.

MIXING RATIOS AND PROCEDURES

The recommended mixing ratios shown in Table 4 are based on 1:1 equivalents of the prepolymers and the appropriate curing agent.

The curing agents should be cooled to room temperature before they are mixed with the prepolymer to ensure long working time. If the mixing is done by hand, it should be thorough and continue for three minutes. Hang-up in the corners of the mixing container should be avoided. Paper cups and wooden tongue depressors should not be used for mixing because they usually contain some water.

CHARACTERIZATION OF HALTHANES

Although most of the work characterizing the Halthane adhesives was done at Lawrence Livermore National Laboratory (LLNL), considerable work was done at the Bendix Corporation's Kansas City Division.⁵⁻⁹ Work was done at Bendix partly to

supplement the LLNL effort and partly because some equipment, including the Rheometrics mechanical spectrometer, had not yet been received at LLNL. The mechanical spectrometer was used extensively, both in the development stage of this

TABLE 4. Recommended ratios of prepolymers and curing agents for Halthane adhesives.

Component	Halthane						
	73-14	73-15	73-18	73-19	87-1	87-2	88-2
Prepolymer 73	62	62	65	65			
HGH-14	38						
HGH-15		38					
HGH-18			35				
HGH-19				35			
Prepolymer 87					93	90	
Prepolymer 88							88
Tonox 60/40					7		
XU-205						10	12

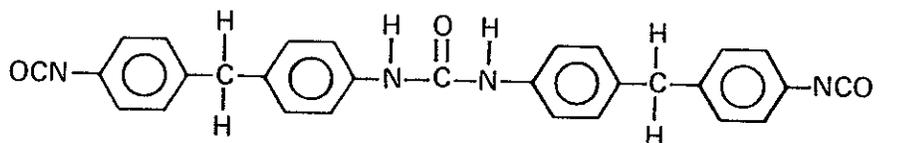
work and in the final characterization, to study the effect of temperature on the cured adhesives.

CHARACTERIZATION OF PREPOLYMERS

Table 5 shows the results of some analyses by Bendix of the 88 prepolymer and of one lot each of the 73 and 87 prepolymers.^{8,9} Gel permeation chromatography (GPC) was used to determine

number average (M_n) and weight average (M_w) molecular weights, and to determine the free diisocyanate. Molecular weight dispersity (MWD) is the weight average molecular weight divided by the number average molecular weight, i.e., $MWD = M_w/M_n$.

The haziness sometimes observed in the 73 prepolymer is believed to be caused by the reaction product of water with MDI to produce a disubstituted urea with the following structure:



CHARACTERIZATION OF CURING AGENTS

We conducted a round-robin test program⁵ to determine appropriate values for the equivalent weights of the curing agents and acceptable analytical techniques. Nominal values for the curing agents HGH-14, -15, -18, and -19 are shown in Table 6. The acetylation reflux procedure described in ASTM E-222-73 is recommended to determine the hydroxyl number (which is used in the calculation of the equivalent weight). For acid number, the Quaker Oats procedure is preferred to the ASTM D-2849-69 procedure. The Quaker Oats method uses a 30-g sample dissolved in 100 ml of chloroform and titrated with dilute methanolic KOH using phenolphthalein indicator. For water,

any of the standard Karl Fischer techniques are acceptable, although it is recommended that the Aquatest II instrumentation be used.

CHEMICAL ANALYSES OF CURED HALTHANES

The Halthanes are composed of carbon, hydrogen, nitrogen, and oxygen, as shown in Table 7. Spectrochemical analysis showed no significant amounts of other elements: up to 10 ppm silicon; 15 ppm iron and tin in one specimen that had been mixed in a tinned can; and only 0.009% (90 ppm) chlorine. The FAA catalyst used in 73-15 and 73-19 adds less than 10 ppm iron. Trace metals were determined spectrochemically; the results are shown in Table 8.

TABLE 5. Chemical analysis of Halthane prepolymers.

	73	87	88
Element, %:			
Carbon	68.27	66.46	67.27
Hydrogen	7.55	10.31	10.95
Nitrogen	5.00	2.15	2.66
Equivalent wt	397	1127	830
Total NCO, %	10.58	3.73	5.07
NCO nitrogen, %	3.53	1.24	
Free MDI, %	21.5		
MDI-NCO, %	7.22		
Free Hylene W, %		5.86	10-11
Hylene W-NCO, %		1.91	
Terminal NCO, %	3.36	1.82	
GPC analysis ^a :			
A _n	114 A	219 A	
A _w	160 A	321 A	
Q factor	22	21	
M _n	2508	4615	
M _w	3502	6741	
MWD	1.40	1.46	

^aA = Styrene-equivalent length.

n = number average.

w = weight average.

M = molecular weight.

MWD = molecular weight disparity.

TABLE 6. Chemical analysis of Halthane polyol curing agents.

	HGH-14 and HGH-15	HGH-18 and HGH-19
OH number	218-220	250
Equivalent weight	255-257	224
Acid number	0.02	0.02
Water, %	0.02	0.04

TABLE 7. Elemental composition of Halthanes, wt%.

Element	73-14	73-18	87-1	88-2
Carbon	68.04	66.84	66.45	68.48
Hydrogen	9.40	9.07	10.11	10.24
Nitrogen	3.20	3.32	3.50	3.66
Oxygen ^a	19.36	10.24 20.77	19.94	17.62

^aOxygen by difference.

TABLE 8. Trace-metal impurities in Halthanes, ppm.

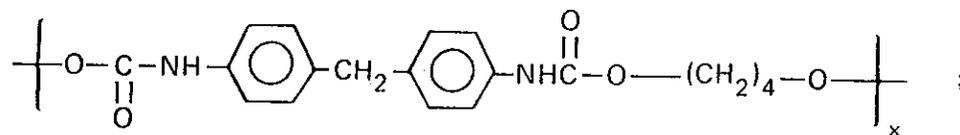
Impurity	73-14	73-18	87-1	87-2	88-2
Ca	7	7	10	3	3
Si	7	9	10	2	2
Na	nd (4)	nd (4)	10	nd (3)	3
Fe	4	15	2	1	0.5
Al	1	0.9	1	0.2	0.3
Mg	0.4	1	1	1	0.6
Ni	nd (0.4)	0.9	1	nd (0.3)	nd (0.3)
Pb	4	1	nd (0.5)	nd (0.3)	nd (0.3)
Sn	7	15	0.3	nd (0.1)	nd (0.1)
B	0.4	0.4	0.1	0.1	0.05
Ti	0.1	0.1	0.1	0.2	3
Ag	0.04	0.04	0.05	0.03	0.03
Be	0.04	0.09	0.04	0.03	nd (0.03)
Cu	0.04	0.1	0.04	0.03	0.03
Cr	nd (0.04)	0.4	nd (0.04)	nd (0.03)	nd (0.03)
Mn	nd (0.04)	0.07	nd (0.04)	nd (0.03)	nd (0.03)

nd = not detected. (The number in parenthesis is the limit of resolution for the element.)

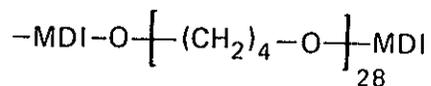
CHEMICAL STRUCTURE OF HALTHANES

The idealized structures of Halthanes 73-14 and 73-15 are:

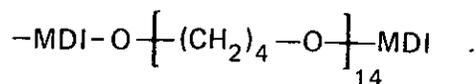
hard segments



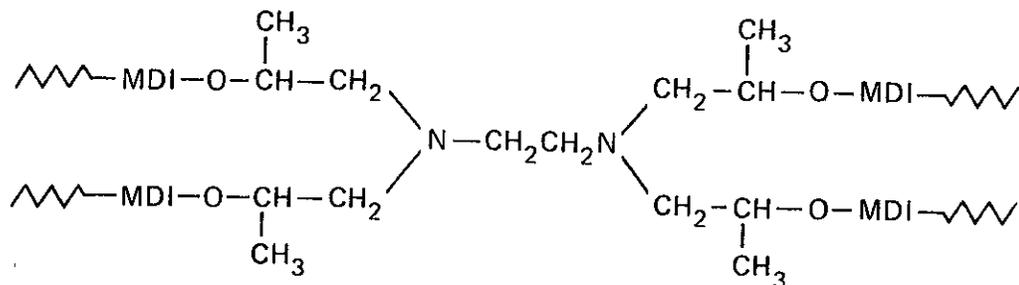
soft segments



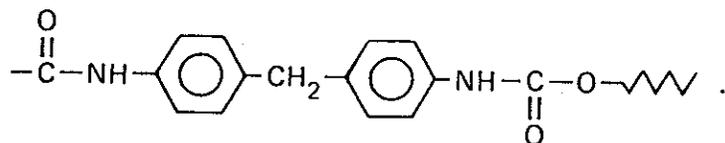
and



The structures of Halthanes 73-18 and 73-19 are similar but three dimensional because of the tetra-functional crosslinking agent Quadrol. The chemical structure of a crosslink site is shown below.

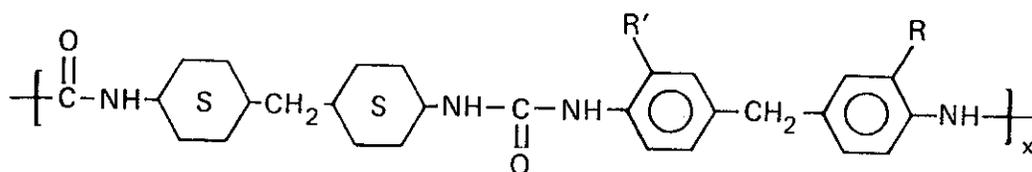


where MDI is

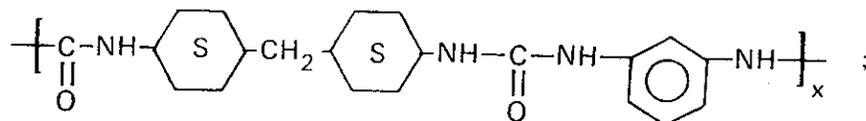


The structure of Halthane 87-1 is more complicated because it has both urethane and urea linkages and some crosslinking from the polymeric MDA in the Tonox 60/40. The structure of Halthanes 87-2 and 88-2 are very similar to that of 87-1, but some of the diamines contain ortho ethyl groups:

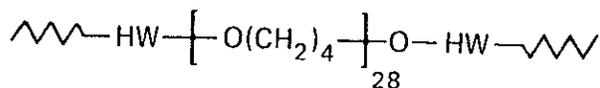
hard segments



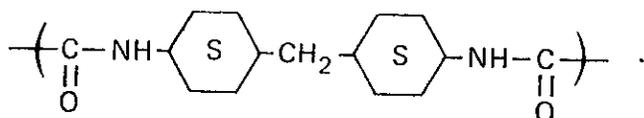
and



soft segments



where HW is



R and R' are hydrogens for 87-1 and either hydrogens or ethyl groups for 87-2 and 88-2.

PHYSICAL PROPERTIES OF HALTHANES

ADHESION PROPERTIES

The adhesive strengths of the Halthanes on various substrates were measured with butt-tensile tests. Most of the bonds tested were on aluminum right cylinders, 28.68 mm (1.129 in.) in diameter. The contact surfaces of the aluminum were degreased and etched with acid dichromate before bonding. The effects of room-temperature cure time on the butt-tensile adhesive strengths of several Halthanes on aluminum are shown in Figs. 1 and 2. The bond strength appears to drop somewhat in the 30 to 60 day period, but with longer aging the bond strength returns to near original values. Complete data on the effect of age on aluminum-to-aluminum butt-tensile strengths of all Halthanes are shown in Table 9.

The bond strengths of the Halthanes on other materials are usually lower than on aluminum, as the data in Table 10 show. The addition of ferric acetylacetonate (FAA) improves the bond strength in some cases, although it appears to lower it slightly in the bonding of 73-19 to aluminum.

As might be expected, the butt-tensile strength of Halthane adhesives decreases with increasing temperature, as is shown in Table 11 and Fig. 3. The polyol-cured adhesives are more sensitive to temperature between -20 and -50°C than the diamine-

cured adhesives because of their higher soft-segment glass transition temperature, $T_g(\text{SS})$.

PERMEABILITY TO GASES

The permeability of Halthane adhesives to a number of gases is shown in Table 12. Room-temperature-cured sheets, 110 mm in diameter and about 0.5 to 1 mm thick were tested in a Dow Cell, according to ASTM D-1434-66, Method M, using gases supplied by Matheson Gas Products. Data determined previously on Adiprene L-100/MOCA¹ are included for comparison. The Halthanes were permeable to all gases tested and their permeabilities were similar to those of Adiprene L-100/MOCA.

EQUILIBRIUM MOISTURE CONTENT AND MOISTURE TAKEUP RATE

Equilibrium moisture content data were obtained on 5-by-10-mm samples, 1 to 2 mm thick, using the Du Pont (CEC) Solids Moisture Analyzer.⁸ Specimens of Halthanes 73-14, 73-18, and 87-1 were conditioned at 0, 11, 43, and 64% relative humidity for 15 and 30 days, and then tested for moisture

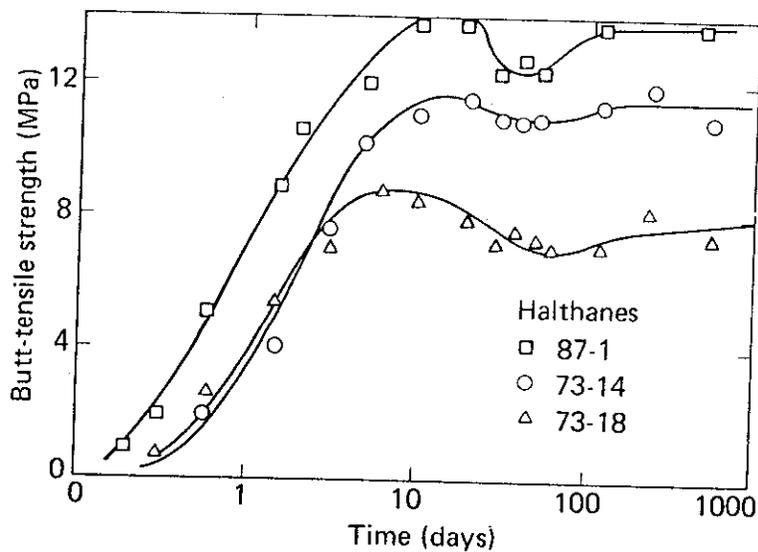


FIG. 1. Butt-tensile adhesive strength of Halthanes 73-14, 73-18, and 87-1 on aluminum substrates, cured and tested at room temperature.

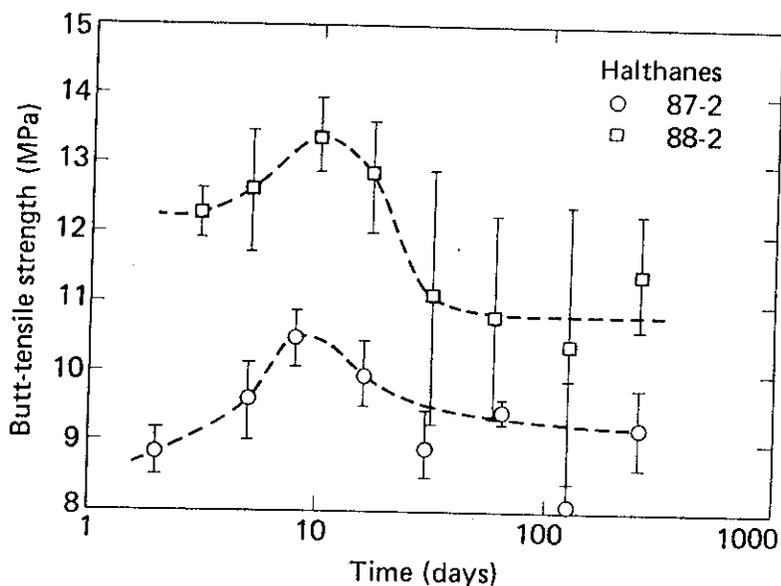


FIG. 2. Butt-tensile adhesive strength of Halthanes 87-2 and 88-2 on aluminum substrates, cured and tested at room temperature.

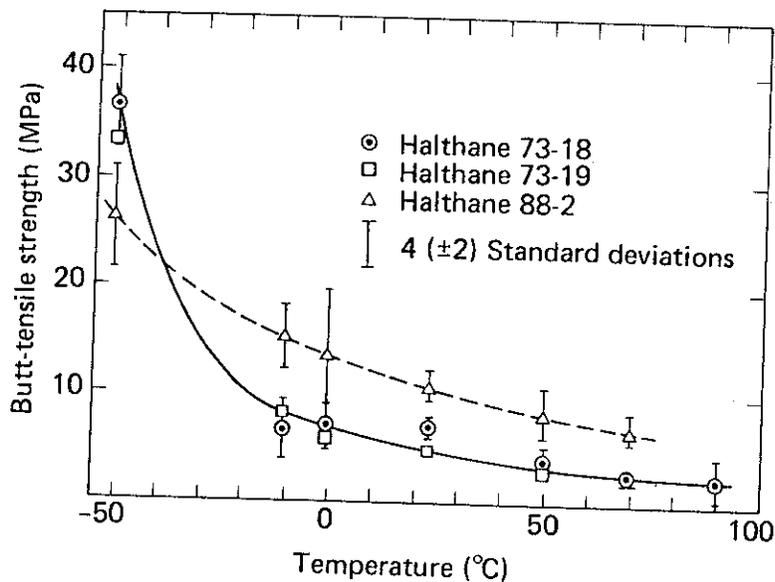


FIG. 3. The effect of temperature of the butt-tensile strength of Halthanes 73-18, 73-19, and 88-2 on aluminum substrates.

TABLE 9. Effect of cure time at 23°C on the butt-tensile strength of Halthanes joining aluminum to aluminum, MPa. The numbers in parentheses are $(\sigma/\bar{x}) \cdot 100$.

Age, Days	73-14	73-15	73-18	73-19	87-1	87-2	88-2
2	10.7 (3)	9.0 (8)	7.2 (7)	6.0 (6)	12.2 (6)	8.8 (2)	12.3 (2)
4-5	10.7 (7)	11.2 (3)	7.4 (9)	6.1 (5)	12.4 (7)	9.6 (3)	12.5 (3)
8-10	10.7 (6)	10.4 (5)	7.6 (5)	6.2 (4)	12.1 (4)	10.5 (2)	13.4 (2)
16-17	10.4 (8)	8.7 (11)	7.4 (6)	5.2 (7)	12.6 (5)	10.0 (3)	12.8 (4)
30-32	10.4 (3)	8.3 (8)	6.8 (5)	5.6 (11)	12.2 (5)	8.9 (3)	11.1 (8)
60-61	10.1 (4)	9.4 (3)	7.1 (5)	5.3 (2) ^a	11.9 (7)	9.4 (1)	10.8 (7)
119-122	11.4 (5)	9.3 (7)	7.3 (8)	5.9 (3)	13.8 (2)	8.0 (11)	10.4 (10)
238-241	11.9 (6)	10.6 (10)	8.2 (4)	5.9 (3)	14.3 (5)	9.2 (3)	11.5 (3)
465-469	9.7 (5)	8.3 (31)	7.3 (6)	9.4 (6)	13.8 (7)		

^a72 days.

73-18
~ 1090 PSI

87-2 = 11.9 ± 1
~ 1720 PSI

TABLE 10. Butt-tensile strengths of Halthanes.

Substrates	73-18	73-19	73-14	73-15
Al/Al	7.6	5.8	10.7	10.9
Be/Be	4.6	5.2	—	2.2
Fe/Fe	5.4	2.2	—	5.0
Ni/Ni	3.2	6.7	—	4.4
SS/SS	5.7	7.4	5.5	10.6
D-38 ^a /SS	5.6	5.0	—	6.8
D-38/D-38	5.7	5.8	—	7.8
D-38/TPX ^b	3.1	3.6	—	1.9
W/W	6.3	5.1	—	7.7

^aDepleted uranium.

^bPoly (4-methyl pentene-1).

TABLE 11. Effect of temperature on the butt-tensile strength of some Halthanes on aluminum, MPa. The numbers in parentheses are $(\sigma/\bar{x}) \cdot 100$.

Test temperature, °C	Halthanes				
	73-18	73-19	87-1	87-2	88-2
-50	36.8 (8)	32.9 (27)	23.3 (7)	24.7 (4)	26.2 (10)
-10	6.9 (19)	8.1 (13)	17.4 (4)	15.7 (5)	15.5 (9)
0	7.3 (15)	6.6 (3)	12.4 (9)	11.6 (4)	13.8 (22)
23	7.1 (5)	5.3 (2)	16.1 (9)	9.4 (1)	10.8 (7)
50	4.0 (13)	3.5 (7)	7.7 (7)	7.4 (10)	8.3 (20)
70	2.5 (5)	2.3 (7)	5.4 (6)	5.6 (23)	6.9 (11)
90	2.5 (19)	2.3 (18)	2.9 (10)	—	—

TABLE 12. Gas permeability coefficients of Halthanes

Gas	Halthane 73-14 ^a		Halthane 73-18 ^b		Halthane 87-1 ^c		Adiprene L-100/MOCA	
	SI units ^d	ASTM units ^e × 10 ⁹	SI units ^d	ASTM units ^e × 10 ⁹	SI units ^d	ASTM units ^e × 10 ⁹	SI units ^d	ASTM units ^e × 10 ⁹
Argon	23	0.3	38	0.51	56	0.71	35	0.46
Helium	71	0.95	98	1.3	120	1.6	69	0.92
Hydrogen	98	1.3	105	1.4	180	2.4	90	1.2
Carbon monoxide	15	0.2	8.3	0.11	44	0.59	13	0.17
Carbon dioxide	180	2.4	65	0.87	143	1.9	233	3.1
Nitrous oxide	270	3.6	46	0.61	113	1.5	263	0.35
Nitric oxide	40	5.3	35	4.7	98	1.3	44	0.59

^a0.52-mm-thick sample.

^b1.07-mm-thick sample.

^c0.79-mm-thick sample.

^dnm²/Pa·s.

^ecm³_{stp} cm² cm Hg.

content. The results are reported in Table 13. Equilibrium moisture contents of the Halthanes at 43% relative humidity are all about 0.5 wt% water.

Moisture gain and loss rates were determined by equilibrating several specimens of each material in desiccators at 0 and 43% relative humidity, transferring the samples to the desiccator with either the higher or lower relative humidity, removing the samples after various periods of time, and determining their moisture content. Moisture gain and loss rates for Halthane 87-1 are shown in Fig. 4; the rates for 73-14 and 73-18 are very similar.

COMPATIBILITY

Preliminary results¹⁰⁻¹¹ show that the compatibility of the Halthanes with weapons components is comparable to that of Adiprene L-100/MOCA. In contact with LiH, the polyol-cured adhesives appear to generate somewhat more hydrogen than the amine-cured adhesives. Studies at Pantex show that the Halthanes have satisfactory compatibility with LX-04-1, LX-10, and RX-03-BB.¹⁰ Halthanes 73-14, 73-18, and 87-1 have been approved for device assembly with RX-03-BB, LX-10, LX-04-1, LX-07, and PBX 9404.¹²

TABLE 13. Equilibrium moisture content of Halthanes, as wt% water.

Relative humidity, %	Days	Halthanes		
		73-14 ^a	73-18 ^b	87-1 ^c
0	15	0.0133	0.0131	0.0261
	30	0.0286	0.0310	0.0822
11	15	0.1224	0.1217	0.1420
	30	0.1324	0.1326	0.1633
43	15	—	0.5622	0.5414
	30	0.4921	0.5077	0.5105
64	15	0.7716	0.8726	0.8525
	30	0.8026	0.8444	0.8263

^a0.267-cm-thick sample.

^b0.233-cm-thick sample.

^c0.203-cm-thick sample.

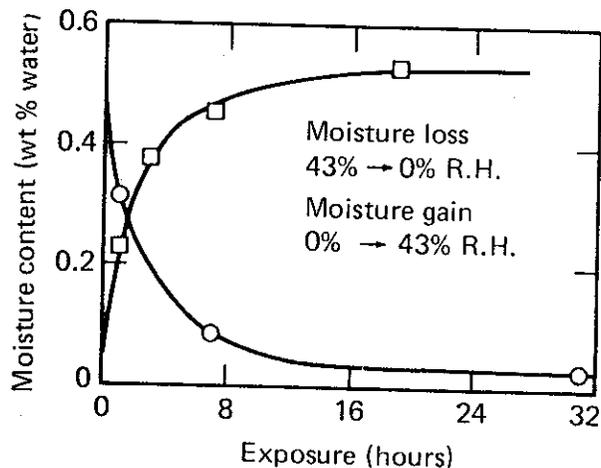


FIG. 4. Moisture gain and loss rates for Halthane 87-1.

ACCELERATED AGING

Althouse and Hetherington¹³ studied aging processes in Halthanes 73-18, 73-18A (accelerated with DABCO, triethylene diamine), and 73-19. Halthanes 73-18 and 73-19 show only minor effects of thermal aging, mainly ordering of the polyether soft domains. Halthane 73-18A degraded by polyether chain scission and has been discontinued.

SPECIFIC HEATS OF CURED HALTHANES

Table 14 shows the specific heats for cured Halthanes 73-18, 87-1, and 88-2 from -50 to 100°C. Their specific heats at 25°C are about 1800 to 1900 J/(kg·K).

ANELASTIC PROPERTIES OF HALTHANES

Time-dependent processes such as molecular motion of pendant groups or of the polymer chain itself can result in a lag of the strain behind stress. The dependence of elastic strain on time (or in this case frequency) as well as on stress is known as an anelastic effect. One way of studying the anelastic behavior of polymers is by following the complex dynamic shear modulus, G^* , as a function of oscillation frequency:

$$G^* = G' + iG'' \quad (1)$$

where G' is the shear storage modulus and G'' is the shear loss modulus.

Time-temperature superposition allows data obtained at experimentally attainable frequencies at one temperature to be shifted along the time or frequency axis to extend the frequency range of data taken at some nearby temperature.¹⁴

We measured the dynamic shear storage and loss moduli at 0.1, 0.315, 1.0, 3.15, and 10 Hz from -150 to 250°C. A typical low-temperature modulus curve for 73-series Halthanes is shown in Fig. 5. At high temperature, uncrosslinked 73-series Halthanes begin to flow at about 100°C, whereas crosslinked 73-series Halthanes cannot flow (see Fig. 6). Above about 180°C, crosslinked adhesives degrade and the modulus drops. The 87- and 88-series Halthanes have much stiffer hard segments

TABLE 14. Specific heats of some cured Halthanes J/(kg·K).

Temperature	73-18	87-1	88-2
-50	1210 ^a	1530	1430
-25	1590	1610	1540
0	1770	1720	1670
25	1880	1830	1790
50	1940	1920	1880
75	2000	1990	1940
100	2040	2050	1990

^aA discontinuity occurs in the specific heat near the glass transition temperature T_g .

and the shear modulus at room temperature (between the hard- and soft-segment glass transitions) is an order of magnitude higher than for the corresponding 73-series adhesives (compare Figs. 5 and 7). The 87- and 88-series Halthanes also tend to post-cure at about 100°C. A more complete discussion of the modulus-temperature behavior of these adhesives is given elsewhere.¹⁵

Shifting the modulus-frequency measurements at different temperatures with respect to some constant reference temperature T_r produces a so-called master curve for the modulus at T_r as a function of

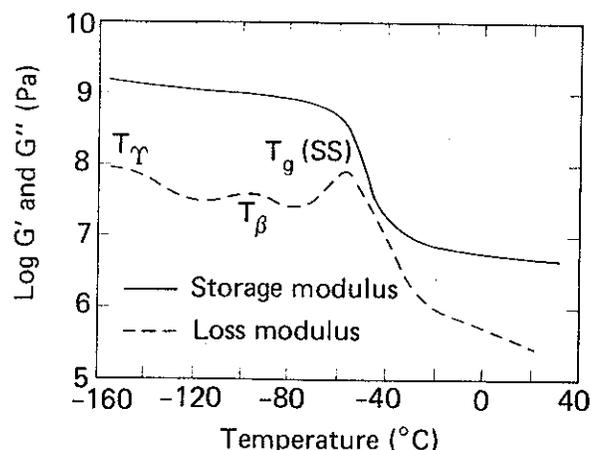


FIG. 5. The low-temperature dynamic mechanical spectrum of Halthane 73-14. Two secondary relaxations, T_β and T_γ , are shown as peaks in the loss modulus at -100 and -150°C. The soft-segment glass transition, $T_g(SS)$, occurs at about -50°C. The frequency of oscillation was held at 0.1 Hz during the measurement.

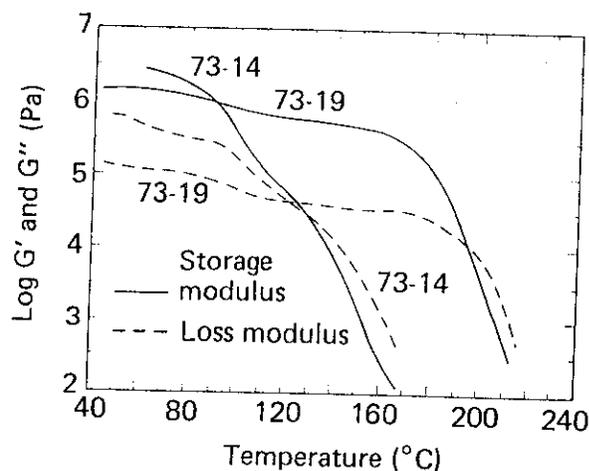


FIG. 6. The high-temperature dynamic mechanical spectrum of Halthanes 73-14 and 73-19. The storage and loss moduli are controlled by the presence or absence of the crosslinking agent Quadrol in the hard segments. In the linear urethane (73-14), viscous flow follows the melting of the hard segments, whereas in the crosslinked urethane (73-19) the modulus drops only when the polymer begins to degrade. The frequency of oscillation during these measurements was 0.1 Hz.

frequency. This behavior has been studied extensively in linear homopolymers^{16,17} and the required shift factor obeys the Williams-Landel-Ferry (WLF) equation:

$$\log a_t = -C_1(T - T_r)/(C_2 + T - T_r) \quad (2)$$

When the glass transition temperature T_g is chosen as T_r , the "universal" values for coefficients C_1 and C_2 are often obtained ($C_1 = 17.44$, $C_2 = 51.6$).¹⁸ We chose to shift from a reference temperature near the soft segment glass transition temperature so we could compare our coefficients to "universal" values. Over the temperature range in which the WLF equation applies, the amount of frequency shift in the modulus-frequency master curve at T_g required to generate the master curve at another temperature T is given by substituting that temperature into the WLF equation.

Figure 8 shows the 73-Series Halthane master curves generated by time-temperature superposition about the reference temperature -42°C . Halthanes 73-14 and 73-15 are not chemically crosslinked and flow at very low frequency (10^{-14} Hz) or high temperature (100°C). Halthanes 73-18 and 73-19, which

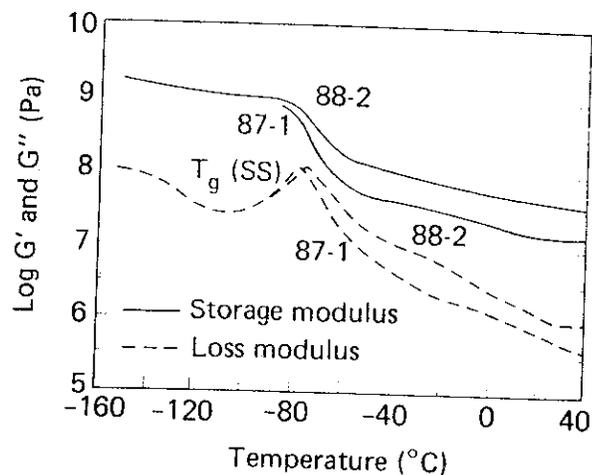


FIG. 7. The low-temperature dynamic mechanical spectrum of Halthanes 87-1 and 88-2. The relaxation strength of these Halthanes is smaller than those of the 73-series because of the aromatic hard segments' stiffness. The higher concentration of hard segments is also responsible for the higher storage modulus of Halthane 88-2 above the soft-segment glass transition, $T_g(\text{SS})$, at -80°C . The loss moduli show the glass transition of the soft segments and a secondary relaxation at about -150°C . The frequency of oscillation was held at 0.1 Hz during the measurement.

contain crosslinks, do not flow at low frequencies as is shown by the absence of a second dip in the modulus. Slight differences in the soft-segment glass transition between crosslinked and uncrosslinked 73-series urethanes cause the two-order-of-magnitude frequency shift in the master curves.

Figure 9 shows the 87- and 88-series Halthane master curves for the reference temperature -62°C . The relaxation strength (difference between the modulus above and below the soft-segment glass transition temperature) for these polymers is an order of magnitude less than that of the 73-series adhesives. The difference between low-frequency moduli of Halthane 87-1 and 87-2 is caused by the differences in chemical structure of the hard segments. Halthane 87-1 contains TONOX 60/40 (a mixture of 60% 4,4' methylene dianiline and 40% m-phenylene diamine) and Halthane 87-2 contains XU-205 (a mixture of 3,3' substituted 4,4' methylene dianiline). If the concentration of hard segments is increased, the modulus of the adhesive increases in the rubbery plateau region (above the T_g of the soft segments). This explains the higher modulus of Halthane 88-2 than 87-2 at room temperature.

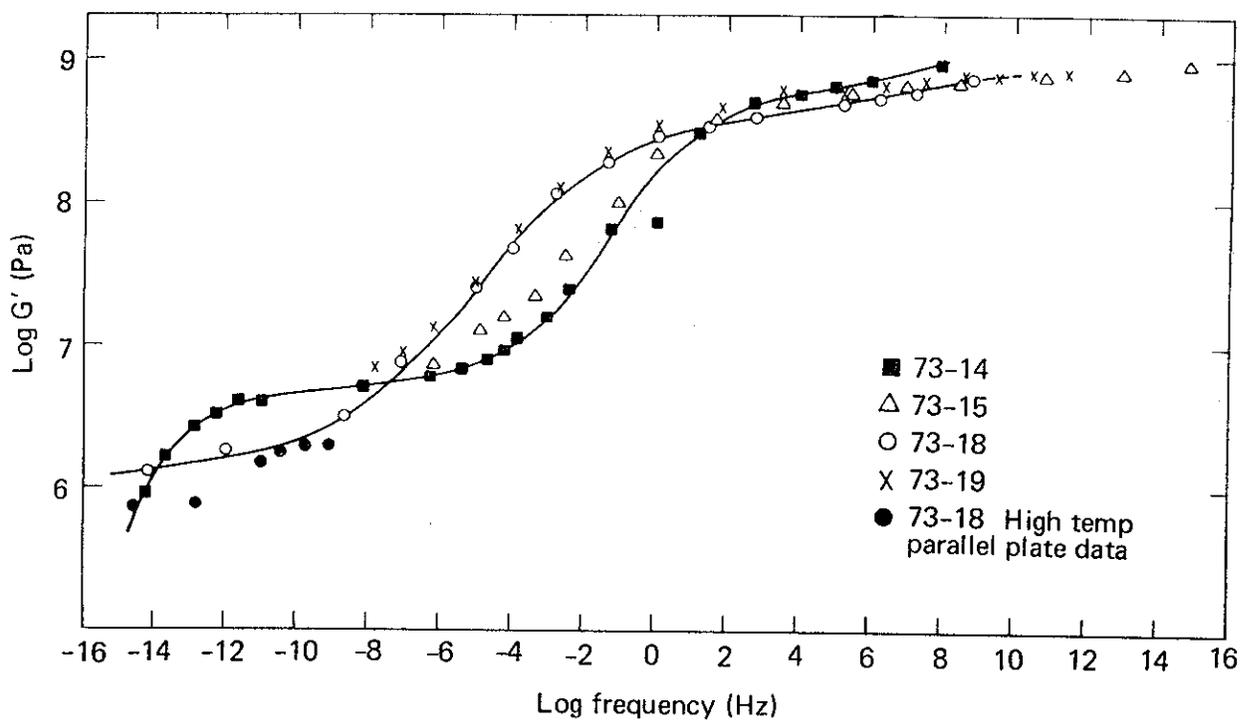


FIG. 8. Halothane 73-series modulus-frequency master curves for a reference temperature of -49°C .

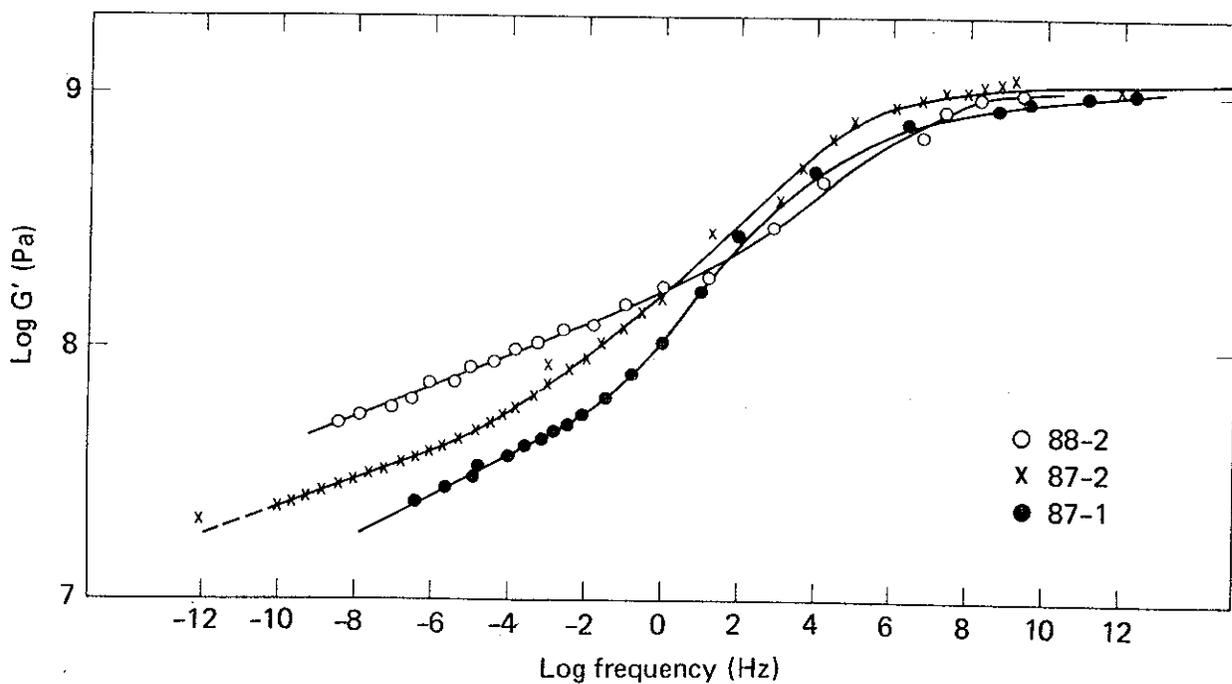


FIG. 9. Halothane 87- and 88-series modulus-frequency master curves for a reference temperature of -62°C .

Table 15 lists the WLF coefficients and the glass transition temperatures of 73-, 87-, and 88-series Halthanes based on shifting these polymers about the soft-segment glass transition. The glass transition temperature was determined from the position of the maximum in the loss modulus at 0.1 Hz. Some caution should be used in shifting the data to very high temperatures (low frequencies) with the WLF equation since this equation is only applicable over a temperature range of about 100°C.

The WLF coefficients obtained for Halthanes 73-14, 73-15, 87-1, and 88-2 are quite close to the universal values proposed by Williams, et al.¹⁸ However, the crosslinked 73-series Halthanes have WLF coefficients that are larger than the universal values by about a factor of 2. This can be explained by applying the free volume theory to the WLF equation.¹⁶

$$C_1 = B/2.303f_0 \quad (3)$$

$$C_2 = f_0/\alpha_f \quad (4)$$

The C_1 coefficient should increase with a decrease in fractional free volume (f_0) and the C_2 coefficient could increase or decrease depending on the relationship between the fractional free volume and

TABLE 15. Glass transition temperatures and WLF coefficients of cured Halthanes.

Sample	$T_g(\text{SS})^\circ\text{C}$	$T_g(\text{HS})^\circ\text{C}^a$	C_1	C_2^b
73-14	-56.7	92	13.0	64.8
73-15	-53.8	81	12.6	51.4
73-18	-49.2	85	30.4	111.1
73-19	-49.4	85	32.9	123.5
87-1	-79	185	7.93	47.9
87-2	-77	196	23.1	116.2
88-2	-76	188	11.8	63.2

^aThis transition shifts from sample to sample as a result of reorganization of urethane hard segments for different thermal histories.

^bAt $T_f = -42^\circ\text{C}$.

the coefficient of volume expansion (α_f). Since crosslinking reduces the free volume of the polymer, C_1 should increase, as is found. If the theory is correct, α_f must decrease twice as much as f_0 to account for the observed increase in C_2 . It is well known that the thermal expansion coefficient decreases with increased crosslinking. Thus, the changes observed in the WLF coefficients on going from linear to crosslinked adhesives are not unreasonable.

ACKNOWLEDGMENTS

We wish to thank all those who have contributed to this program, especially Barbara McKinley for the preparation and testing of ring-tensile specimens, for adhesive strength measure-

ments, and for computer processing of these and other data, Leonard E. Caley for dynamic property measurements and Norriss W. Hetherington for statistical analysis and advice.

MATERIALS AND SUPPLIERS

Adiprenes (urethane polymers)
 BDO (1,4-butanediol)
 FAA (ferric acetylacetonate)
 Halthanes (urethane polymers)
 Hylene W (hydrogenated MDI)
 MDA (methylene dianiline)
 MDI (methylene diphenyl isocyanate;
 methylene bis(4-phenyl isocyanate))
 PolyMegs (polytetramethylene ether glycols)
 Quadrol (N,N,N',N'-tetrakis(2-hydroxypropyl)
 ethylenediamine)
 Tonox, Tonox 60/40
 XU-205

Du Pont
 GAF Corporation
 McKenzie Chemical Works
 Bendix Corporation, Kansas City Division
 Du Pont, Mobay
 Du Pont, E. V. Roberts
 Mobay
 Quaker Oats
 Wyandotte
 Naugatuck Chemical, Division U. S. Rubber
 Ciba-Geigy

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Material Preparation Information for Explosives Reference Guide

JWK Recommendations

1. Material preparation-related information should be included but it should be based on AEC-DOE star materials.
2. HMX high-energy plastic bonded explosives (PBX 9404 and LX-10).
3. TATB 'wooden' explosive (LX-17).
4. PETN for EBW detonators.
5. Extrudable explosive for firing sets.

Topics

1. Synthesis
2. Formulation
3. Specifications and analysis
4. Fabrication
5. Quality control

Approach

1. Define representative operations for each of the star materials.

2. Obtain pictures for representative operations from Holston, Pantex, Mound, LANL, LLNL and Sandia

3. Prepare storyboards for each material with pictures and brief text outline.
*Kury, Green, Humphrey, Varosh, Pagoria, Swansiger
others?*

4. Review for sensitive information.
who?

5. Integrate into appropriate levels in Reference Guide.
*Kury, Sauers
others?*