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DEVELOPMENT OF HALTHANE ADHESIVES FOR PHASE-3 WEAPONS:
STATUS REPORT NO. 2

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ABSTRACT

Five new adhesives of the polyurethane type have been developed to meet requirements for the current Phase-3 nuclear weapons. They are designated Halthanes to avoid confusion with Adiprenes. Four of these adhesives are made from LLL-developed MDI-terminated prepolymers cured with a blend of polyols. The fifth is made from an LLL-developed prepolymer terminated with Hylene W and cured with aromatic diamines. All of the adhesives have low moduli over a wide temperature range, bond rapidly and well to most substrates, and are compatible with weapons components. This report updates information reported in Chemistry Department Technical Notes Nos. 75-23, 75-24, and UCID-16990. Characterization and compatibility studies are continuing.

INTRODUCTION

Restrictions imposed by the Occupational Safety and Health Administration (OSHA) on the use of methylene bis(2-chloro-aniline) (MOCA) forced the development of alternatives to the widely used Adiprene L-100/MOCA. We were able to meet the requirements of earlier weapons systems with Adiprene L-315/polyol and Adiprene LW-520/methylenedianiline (MDA).¹ For current Phase-3 systems, however, L-315/polyol is too sensitive to the wide temperature extremes likely to be encountered, 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 one or more adhesives to meet weapons requirements.

DISCUSSION

Requirements for Adhesives

We reviewed the requirements for adhesives for Phase-3 weapons in UCID-16990.² These remain the same except for the following modifications. There has been some relaxation of the high temperature requirement; most systems will now require satisfactory behavior up to 55 to 70°C. In addition, there has been more emphasis on short fixturing times for some systems; handling times of about four hours are now desired. To satisfy the latter, we developed the adhesives 73-15 and 73-19, which are accelerated with ferric acetylacetonate (FAA). These adhesives have essentially the same properties as their counterparts, 73-14 and 73-18, but set up much faster. Halthane 73-14 does not cure well in a low-humidity atmosphere. The others, including 73-15, will cure in a low-humidity atmosphere.

Composition of Halthane Adhesives

The composition of Halthane adhesives was discussed in detail in UCID-16990, along with suggestions for synthesis of the prepolymers. Table 1 summarizes the composition of the prepolymers, and Table 2 shows the composition of the curing agents, including the two accelerated curing agents, 15 and 19.

Table 1. Prepolymer component ratios and analyses.

	Prepolymer	
	73	87
Component, %		
PolyMeg 1000	47.6	—
PolyMeg 2000	7.4	77.6
MDI	45.0	—
Hylene W	—	22.4
Analysis, %		
Free Diisocyanate	21-23	6-8
Total NCO	10.2-10.6	3.6-3.8

Table 2. Curing-agent formulations.

Component	Curing agent			
	14	15	18	19
PolyMeg 1000	90	90	85	85
1,4-Butanediol	10	10	10	10
Quadrol	—	—	5	5
FAA	—	0.0156	—	0.0107

Curing-Agent Formulation

The polyol curing agents are primarily the same polyether that is used in the prepolymer, with 1,4-butanediol added to speed the cure. The polyols are warmed to melt them, if necessary, and blended. They must be dried thoroughly, since they are hygroscopic and may contain some water as received. Water will compete with the isocyanate-hydroxyl reaction, diminishing strength and causing bubbles in the adhesive. The ratios of the polyols are given in Table 2. The ferric acetylacetonate (FAA) must be dissolved in the butanediol prior to adding the other components.

Mixing Ratios and Procedures

The equivalent weights of the curing agents HGH-14 and HGH-18 were determined in a round-robin test³ to be 256 and 224, respectively, which are in good agreement with calculated values. The recommended mixing ratios shown in Table 3 are based on 1:1 equivalents of the prepolymers and the appropriate curing agent.

The curing agents will partially solidify on standing at room temperature or below. They must be warmed sufficiently (to about 50°C) to melt all components and must be well mixed to ensure uniformity, since some portions will crystallize preferentially. The curing agents should be cooled to room temperature before mixing with the prepolymer to ensure long working time.

Table 3. Formulation of Halthane adhesives.

Component	Halthane				
	73-14	73-15	73-18	73-19	87-1
Prepolymer 73	62.0	62.0	65.0	65.0	—
Curing agent 14	38.0	—	—	—	—
Curing agent 15	—	38.0	—	—	—
Curing agent 18	—	—	35.0	—	—
Curing agent 19	—	—	—	35.0	—
Prepolymer 87	—	—	—	—	93.0
TOLUX 60/40	—	—	—	—	7.0

If hand mixing is used, it should be thorough and continued for three minutes. Hangup in the corners of the mixing container should be avoided. If bubble-free specimens are desired, the mix should be centrifuged or vacuum degassed before use.

CHARACTERIZATION OF HALTHANE ADHESIVES

Although most of the work characterizing the Halthane adhesives has been done at Lawrence Livermore Laboratory, considerable work was done at the Bendix Corporation's Kansas City Division at the request of LLL.³⁻⁶ This was done to supplement the effort at LLL, and also because some equipment, including the Rheometrics Mechanical Spectrometer, was lacking at LLL. The mechanical spectrometer was used extensively in the developmental stage of this work, and in the final characterization, to study the effects of temperature on the cured adhesives.

Characterization of Halthane Prepolymers

Table 4 shows some data determined by Bendix on one lot each of the 73 and 87 prepolymers.⁶ Gel permeation chromatography (GPC) was used to determine number average ($\bar{M}_n$) and weight average ($\bar{M}_w$) molecular weights, and to determine the free diisocyanate. Molecular weight dispersity (MWD) is obtained by

dividing the weight average molecular weight by the number average molecular weight, i.e., $MWD = \bar{M}_w/\bar{M}_n$.

Table 4. Characterization of Halthane 73 and 87 prepolymers.

	Prepolymer	
	73	87
Elemental analysis, %		
C	68.27	66.46
H	7.55	10.31
N	5.00	2.15
Equivalent wt	397	1127
Total NCO, %	10.58	3.73
NCO nitrogen, %	3.53	1.24
Free MDI, %	21.5	—
MDI-NCO, %	7.22	—
Free Hylene W, %	—	5.86
Hylene W-NCO, %	—	1.91
Terminal NCO, %	3.36	1.82
GPC analysis		
$\bar{A}_n$	114 Å	219 Å
$\bar{A}_w$	160 Å	321 Å
Q factor	22	21
$\bar{M}_n$	2508	4615
$\bar{M}_w$	3520	6741
MWD	1.40	1.46

Efforts were made to determine the oligomer distribution using reverse phase liquid chromatography after capping the prepolymers with monofunctional alcohols (to prevent interference and further reaction with traces of moisture). The 73 prepolymer was separated into more than 50 components, and the 87 prepolymers into more than 25 components. The identification of the oligomers must await further work, including separation and identification of the oligomers in the starting polyethers.

The haziness in the 73 prepolymer was found to be due to a reaction product of traces of water with MDI; it is a disubstituted urea with the following structure:

Characterization of Curing Agents

Due to some uncertainty in the equivalent weights of the curing agents, as indicated in UCID-16990, a round-robin test program³ was conducted to determine appropriate values and acceptable analytical techniques. Nominal values for the curing agents HGH-14 and -18 are shown in Table 5. It was recommended that the procedure described in ASTM E-222-73 (acetylation reflux) be adopted for the hydroxyl number (used in the calculation of the equivalent weight) determination. For acid number, the Quaker Oats procedure is preferred to the ASTM D-2849-69 procedure. The Quaker Oats method essentially uses a 30 g sample dissolved in 100 ml chloroform, and titration 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.

Table 5. Nominal values for Halthane polyol curing agents.

Curing agent	OH No.	Equivalent wt	Acid No.	Water, %
HGH 14	218-220	255-257	0.02	0.02
HGH 18	250	224	0.02	0.04

Chemical Analysis of Cured Halthane Adhesives

The Halthane adhesives are composed of carbon, hydrogen, nitrogen, and oxygen, as shown in Table 6. Spectrochemical analysis showed no significant amounts of other elements; silicon was found up to 10 ppm, and iron and tin were found at 15 ppm in one specimen which had been mixed in a tinned can. Chlorine analysis showed only 0.009% (90 ppm). The ferric acetylacetonate catalyst used in 73-15 and 73-19 adds less than 10 ppm iron.

Table 6. Analysis of Halthane adhesives.

Adhesive	Element, wt%			
	C	H	N	O
73-14	68.04	9.40	3.20	19.36
73-18	66.84	9.07	3.32	20.77
87-1	66.45	10.11	3.50	19.14

Chemical Structures of Halthane Adhesives

Idealized structures of Halthanes 73-14 and 73-15 are:

The structures of Halthanes 73-18 and 73-19 are similar but contain some cross-linking: same as the foregoing, plus

The structure of Halthane 87-1 is somewhat complicated due to both urethane and urea linkages, and some cross-linking from the polymeric MDA in the Tonox 60/40:

Properties of Halthane Adhesives

The properties of polyurethanes will depend on mixing ratios (stoichiometry) and on thermal history. They are also, of course, dependent on the test temperature and the strain rate. The Halthanes are not yet fully characterized as to how they are affected by strain rate and test temperature. Properties may also be affected by compounds added to the formulation to improve such properties as bonding and wetting. For example, we have found that adding a small amount of an epoxy-silane (Silane A-187, Union Carbide) improves the bonding to some substrates; however, it also appears to improve the bulk tensile strength. The properties listed in Table 7 should be considered tentative.

Bulk Properties

Typical bulk properties of room temperature cured Halthanes are given in Table 7.

Table 7. Some properties of Halthane adhesives.

Property	Halthane				
	73-14	73-15	73-18	73-19	87-1
Initial viscosity, Pa·s	4	4	3	3	25
Viscosity after 1 hr, Pa·s	46	21 ^a	94	26 ^a	300
Pot life (100-g mass), min	154	24 ^b	72	25 ^b	98
Shore A hardness (instant/10 s):					
16 hr	50/27		54/41		74/68
7 da	77/77		73/71		85/80
Handling time, hr	24	4	16	4	8
Ring tensile properties (10 cm/min, 23°C)					
Tensile modulus, MPa	15		5	5	30
Rupture strength, MPa	34		25	44	60
Rupture strain	6		5	4	4.4
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 to 2.0		1.9 to 2.0		1.9 to 2.0
Glass transition temperature (T _g), °C	-50°		-40°		-70°

^aViscosity after 0.5 hr, Pa·s.

^bFifty g mass.

Dynamic Shear Modulus

The behavior of these types of materials depends upon temperature and strain rate (or frequency). One way of evaluating changes in properties according to temperature is to measure the shear storage modulus at a low frequency over a range of temperatures, including the range the material is expected to be exposed to. Figure 1 shows the shear storage modulus of Halthanes 73-14, 73-18, and 87-1 at 0.1 Hz from -120 to 120°C. The behavior of 73-15 and 73-19 would be expected to be similar to 73-14 and 73-18, respectively. These tests were made by Bendix, Kansas City Division, under purchase orders from LLL.⁴⁻⁶

By this technique the glass transition temperature (T_g) of 73-14 is about -50°C. The T_g of 73-18 is about -40°C, reflecting the influence of the cross-linking induced by the tetrafunctional Quadrol. Both 73-14 and 73-18 show a broad plateau of relatively constant, rubbery behavior from below zero to 70° or more. The plateau for 73-18 is extended, also due to its cross-linking.

The T_g of 87-1 is even lower, about -70°, and the modulus shows a fairly constant drop with increasing temperature from about -60 to 80°. Its behavior over this temperature range is similar to Adiprene LW-520/Tonox.

The behavior of the Halthanes as functions of both temperature and frequency (or strain rate at low strains) can be described by master curves obtained by plotting the reduced shear storage modulus ($G'_r = G \cdot 298/T$) against $\log A_T f$ according to the method of Ferry.⁷ The Williams-Landel-Ferry equations for the Halthanes were calculated to be:

$$\begin{aligned} \text{Halthane 73-18: } \log A_T &= -12.5(T-T_0)/(158 + T-T_0) \\ &T_0 = 298 \text{ K} \\ \text{Halthane 87-1: } \log A_T &= -16.8(T-T_0)/(224 + T-T_0) \end{aligned}$$

The master curves for 73-18 and 87-1 are shown in Fig. 2, and were obtained by measuring the shear storage modulus at nine frequencies from 0.01 to 3.0 Hz and at temperatures from about -90 to 25°C. The specimens of 73-18 used in this work by Bendix

Fig. 1. Shear storage modulus at 0.1 Hz of Halthane adhesives as a function of temperature.

Fig. 2. Shear storage modulus master curves for Halthane 73-18 and 87-1.

are somewhat lower modulus than those reported in their other studies; reduced shear storage moduli in the range from $\log A_T f$ from -2 to about 4 should be approximately 1 to 2 MPa higher.

Although the dynamic shear modulus is determined as a function of frequency, the data may be used to estimate the shear modulus as a function of strain rate at small strains. Under these conditions, the frequency in radians per second is equivalent to the strain rate in reciprocal units of seconds.

Adhesion Properties

Most of our testing of the Halthanes in adhesion has been done with butt-tensile tests. These tests are usually made with aluminum right cylinders with a diameter of 28.68 mm (1.129 in.). The contact surfaces of the aluminum are degreased and etched with acid dichromate before bonding. Butt-tensile adhesive strength on aluminum of the Halthanes 73-14, 73-18, and 87-1 is shown as a function of room temperature cure time in Fig. 3. The bond strength appears to drop off somewhat in the 30-to-60 day period, but at the most recent 240-day test the bond strength was back to the earlier maximum.

Some butt-tensile adhesion tests have been made on other substrates of interest, as shown in Table 8. Most of these bond

Table 8. Butt-tensile adhesion strength of Halthane adhesives.

Substrates	Halthane adhesives, bond strength, MPa			
	73-18	73-19	73-14	73-15
Al/Al	7.6	5.8	10.7	10.9
Be/Be	4.6	—	—	—
Fe/Fe	5.4	—	—	—
Ni/Ni	3.2	6.7	—	—
SS/SS	5.7	7.4	5.5	7.4
D-38/SS	5.6	—	—	—
D-38/D-38	5.7	—	—	—
D-38/TPX	3.1	—	—	—
W/W	6.3	5.1	—	—

Fig. 3. Butt-tensile adhesive strength of Halthane vs room temperature curing time.

strengths are lower than the Al/Al bond strength. The addition of ferric acetylacetonate may improve the bond strength in some cases, although it appears to lower it slightly in the bonding of 73-19 to aluminum. Additional adhesion testing is in progress.

Permeability to Gases

The permeability of Halthane adhesives to a number of gases is shown in Table 9. Tests were run on room temperature cured sheets, 110 mm diam and about 0.5 to 1 mm thick (Halthane 73-18 was 1.07 mm, 73-14 was 0.52 mm, and 87-1 was 0.79 mm). They were tested in a Dow Cell, according to ASTM D-1434-66, Method M, using gases as supplied by Matheson Gas Products. Data determined previously on Adiprene L-100/MOCA¹ are included for comparison. The Halthane adhesives are quite permeable to these gases and their permeabilities are quite similar to those of Adiprene L-100/MOCA.

Table 9. Gas permeability coefficients of Halthane adhesives.

Gas	Permeability coefficient, $\text{nm}^2/\text{Pa}\cdot\text{s}(\text{cm}^3_{\text{STP}}\cdot\text{cm}/\text{s}\cdot\text{cm}^2\cdot\text{cm Hg})$			
	73-14	73-18	87-1	Adiprene L-100/MOCA
Argon	23(3×10^{-10})	38(5.1×10^{-10})	56(7.4×10^{-10})	35(4.6×10^{-10})
Helium	71(9.5×10^{-10})	98(1.3×10^{-9})	120(1.6×10^{-9})	69(9.2×10^{-10})
Hydrogen	98(1.3×10^{-9})	105(1.4×10^{-9})	180(2.4×10^{-9})	90(1.2×10^{-9})
Carbon monoxide	15(2×10^{-10})	8.3(1.1×10^{-10})	44(5.9×10^{-10})	13(1.7×10^{-10})
Carbon dioxide	180(2.4×10^{-9})	65(8.7×10^{-10})	143(1.9×10^{-9})	233(3.1×10^{-9})
Nitrous oxide	270(3.6×10^{-9})	46(6.1×10^{-10})	113(1.5×10^{-9})	263(3.5×10^{-9})
Nitric oxide	40(5.3×10^{-10})	35(4.7×10^{-10})	98(1.3×10^{-9})	44(5.9×10^{-10})

Equilibrium Moisture Content and Moisture Takeup Rate

Equilibrium moisture content data were obtained on samples 5 mm x 10 mm x 1 to 2 mm thick using the Du Pont (CEC) Solids Moisture Analyzer.⁶ Specimens of the three Halthane adhesives 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 content. The values are reported as weight percent water.

Equilibrium moisture contents at 43% relative humidity for the Halthanes are all about 0.5%. Complete details are shown in Table 10.

Table 10. Equilibrium moisture content of Halthanes.

Material	Thickness, cm	Days							
		0% R.H. ^a		11% R.H.		43% R.H.		64% R.H.	
		15	30	15	30	15	30	15	30
Halthane 73-14	0.267	0.0133	0.0286	0.1224	0.1324	—	0.4921	0.7716	0.8026
Halthane 73-18	0.233	0.0131	0.0310	0.1217	0.1326	0.5622	0.5077	0.8726	0.8444
Halthane 87-1	0.203	0.0261	0.0822	0.1420	0.1633	0.5414	0.5105	0.8525	0.8263

^aMoisture content.

Moisture rate gain, i.e., the rate of moisture takeup of the adhesive in going from a low humidity environment to a higher humidity, and moisture rate loss was about the same for all three Halthanes. The procedure was to place several specimens of each material in desiccators at 0% and 43% relative humidity until well equilibrated. Then the samples were transferred to either the higher or lower R.H. desiccator, samples were removed at various periods of time, and the moisture content determined. Moisture loss and gain rates are shown in Fig. 4 for Halthane 87-1; the rates for 73-14 and 73-18 are very similar.

Compatibility

Preliminary results show all the Halthanes to have about the same compatibility with weapons components as Adiprene L-100/MOCA. In contact with LiH, the polyol-cured adhesives appear to generate somewhat more hydrogen than do the amine-cured adhesives. Studies at Pantex show the Halthanes to have satisfactory compatibility with LX10 and RX-03-BB. Don Seaton (memo of February 27, 1976) has given approval for use of Halthane 73-14, 73-18, and 87-1 for *device assembly* with RX-03-BB, LX10, LX04-1, LX07, and PBX 9404.

Fig. 4. Moisture gain and loss for Halthane 87-1.

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