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James D. LeMay
Benjamin Mendoza

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Compatibility of Halthane 88-3 Urethane Adhesive with the Replacement Cleaning Solvent D-Limonene

James D. LeMay & Ben Mendoza[1]

Lawrence Livermore National Laboratory

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Introduction

D-Limonene, (R)1-methyl-4-isopropenyl-1-cyclohexene, has been identified as a leading replacement for chlorinated solvents traditionally used to clean electrical assemblies and critical components in some phases of weapons production. Unfortunately, d-limonene has a much lower vapor pressure than the chlorinated solvents it replaces (<2 torr at ambient). This makes its complete elimination from cleaned subassemblies potentially difficult, and gives rise to concerns about the compatibility of d-limonene with materials in the warhead.

During the past year many WR polymers and adhesives have been surveyed for their compatibility with d-limonene. Preliminary test results obtained at Sandia (Albuquerque) and Allied-Signal (KCD) showed that Aluminum/Halthane 88-3/Aluminum joints were destroyed during exposure to saturated d-limonene vapor. The cause of bond failure appeared to be d-limonene induced swelling of the Halthane polymer. This report describes recent work performed at LLNL to study the swelling behavior and bond strength degradation of Halthane 88-3 resulting from exposure to d-limonene vapor.

Experimental

Halthane 88-3 is a two-part, elastomeric polyurethane adhesive. Part A is Halthane 88 prepolymer (polytetramethylene, MW ~2000, terminated with hydrogenated MDI). The curative, Part B, is Asilamine 170, a hybrid aromatic amine mixture (a non-mutagenic replacement for the XU-205 diamine curative used in Halthane 88-2). The adhesive is formulated by mixing 21 parts Asilamine 170 to 100 parts Halthane 88.

Bulk slabs, aluminum lap-shear specimens, and aluminum foil bonded "witness" specimens were exposed to d-limonene vapor at ambient temperature in sealed Pyrex desiccators (volume ~9L). A total of three experiments were performed. In the first and second, specimens were exposed for short times to saturated d-limonene vapor (over liquid). In the third, specimens were exposed for long times to low concentration d-limonene vapors (less than saturated). Combined, the experiments provided information on the d-limonene absorption behavior of Halthane 88-3 in both bulk and bonded films, and the effect of d-limonene absorption on Halthane 88-3 lap-shear bonds.

Aluminum bonded lap-shear specimens were prepared per ASTM D-1002 with a 1" x 0.5" bond area and a bond thickness of 0.007". The aluminum adherends were not subjected to any preparatory surface treatments (e.g., sand blasting, FPL etch, etc.) other than cleaning with Solvent 140.

Because accurate weight gain measurements of the lap-shear specimens were expected to be difficult to obtain (due to the relatively large mass of the aluminum adherends), light weight "witness" specimens (1" X 0.5") were prepared. These specimens were sandwiches of 1" x 0.5" x 0.001" aluminum foil pieces bonded with a 0.010-.020" thick layer of Halthane 88-3.

[1]Work performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under contract Number W-7405-ENG-48.

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Two Halthane 88-3 cure states were examined: (1) cure at room temperature (R.T.) for 20-30 days, and (2) cure at R.T. for several days + 60 hours at 75°C + at least two days at R.T. The 75°C postcure yields a state of cure that is roughly equivalent (in hardness) to several months at R.T.

Results & Discussion

Experiment #1 - Swelling In Saturated Vapor.

The purpose of this experiment was to determine the general swelling response of Halthane 88-3 in *saturated* d-limonene vapor. Specimens exposed in the experiment included "bulk" polymer disks (1" dia. x 1/8" thick) and foil bonded witness specimens.

Fig. 1 shows the absorption of d-limonene by R.T. cured Halthane 88-3 during 1000+ hours of exposure to saturated vapor. The upper graph shows the weight gain and the lower the thickness change for bulk and witness specimens as a function of exposure time. (Although not shown, similar results were exhibited by the 75°C postcured Halthane 88-3. Therefore, the state of cure appears to have little effect on the observed swelling behavior.) The upper graph in Fig. 1 shows that Halthane bonds pick up less d-limonene than bulk Halthane (about 1/3 less after ~600 hours). The Halthane bond does eventually swell more through the thickness (see lower graph in Fig. 1), which is expected because that is the only direction in which the constrained film can swell. The discontinuity in the %wt gain curve of the witness sample (at about 600 hrs) is currently unexplained. It will be shown in a moment that this phenomenon is unimportant with regards to the bond strength, because bond failure occurs well before the Halthane has absorbed the 12 wt% d-limonene associated with this event.

Elastomers in bonded films are expected to swell less than in bulk because of the swelling stresses generated in the constrained film. The swelling behavior is controlled by the hydrostatic component of the applied stress field. If the field generates a hydrostatic pressure, then swelling is reduced with increasing pressure. Likewise, swelling is enhanced if a tensile hydrostatic component is generated. Because the bonded Halthane film is two-dimensionally constrained, swelling results in a biaxial compressive stress in the film plane which generates a hydrostatic pressure component that slows further swelling of the Halthane.

Note that the witness specimens fail to show a detectable change in thickness during the first 100-150 hours of exposure even though the specimens have gained 4-5 wt% d-limonene. This suggests that large swelling stresses are not generated in the bonded film until the %wt gain exceeds ~5 wt%. This observation is in agreement with the loss in bond strength observed in the Experiments #2 and #3.

Experiment #2 - Bond Strength In Saturated Vapor.

The purpose of this experiment was to determine the rate at which *saturated* d-limonene vapor degrades the shear strength of Al/Halthane 88-3/Al lap-shear bonds. Only R.T. cured Halthane lap-shear bonds were tested. The specimens were exposed for 6, 12, 24, 30, 48, and 100 hours. Baseline, or "zero-time exposure", strength data were obtained by testing unexposed lap-shear specimens.

Fig. 2 shows lap shear strength as a function of exposure time. The leftmost point (filled circle) is the baseline strength of the bond. Also plotted (on the second Y-axis) is the %wt gain in the lap-shear specimens, which proved to be easier to measure than expected. (Data is also included for witness samples exposed with the lap-shear specimens). Each point is the average of 5 specimens. The results show that the Halthane 88-3 bond suffers a significant drop in strength after only ~24 hours of exposure. The weight gain by the Halthane at this point is 4-7 wt%.

Experiment #3 - Bond Strength In Low Concentration Vapors

The purpose of this experiment was to determine the effect of long-term exposure to low concentration d-limonene vapors on Halthane 88-3 bond strength. Six vapor concentrations were used spanning the possible concentration range expected in the weapon: 0.05, 0.1, 0.2, 0.5, 1, and 2 g d-limonene per 7.5 L of free volume.

In each test were exposed 10 lap-shear specimens and 10 witness specimens (5 for each state of cure), and a bulk slab of Halthane 88-3 polymer (approximately 5" x 1.5" x 0.125"). The slab was added to scale the total amount of Halthane in the test to that in the weapon (~16 g/7.5 L). The total amounts of Halthane contributed by each specimen type breaks down as follows:

10 lap shear specimens	0.8 g
10 witness specimens	1.4 g
1 slab	17.0 g
Total	19.2 g

Fig. 3 shows the %wt gain for each specimen type in each of the six vapor concentrations. The values are the average of 5 specimens. Also shown is the "theoretical" %wt gain based on the assumption that all the d-limonene is absorbed by the Halthane. This value is intended for comparative purposes only; it does not reflect the apparent loss of traces of d-limonene, or previously noted differences in absorption for bonded films and unconstrained, bulk Halthane. Fig. 3 demonstrates, that given sufficient time, thin bonds of Halthane 88-3 will absorb significant quantities of d-limonene vapor even in the presence of a large mass of bulk polymer. This suggests that the presence of other d-limonene-liking polymers in the weapon will not prevent the Halthane 88-3 bond from eventually seeing the vapor.

Fig. 4 shows lap-shear bond strength vs %wt gain for specimens exposed to the six vapor concentrations. Data are shown for both the R.T. and 75°C cured Halthane 88-3. The postcured Halthane exhibits about 15% higher bond strength, but both cures show similar strength degradation trends with d-limonene absorption. Note that a detectable change in shear strength is not observed until 2-3 wt% d-limonene is absorbed. A more noticeable loss in strength is observed when the bond picks up >6 wt% d-limonene. This result is in excellent agreement with Experiment #2 (shown by the dashed line curve in Fig. 6). It should be noted that the reduction in strength is exaggerated by the use of a semilog scale for the plot. It may be more useful to note that the bond loses ~50% of its baseline strength when the d-limonene weight gain approaches 8 wt%.

Conclusions

The shear strength of an Al/Halthane 88-3/Al bond becomes significantly degraded when the polymer film absorbs >6 wt% d-limonene. This apparently occurs because of the stresses generated by swelling in the constrained bond line.

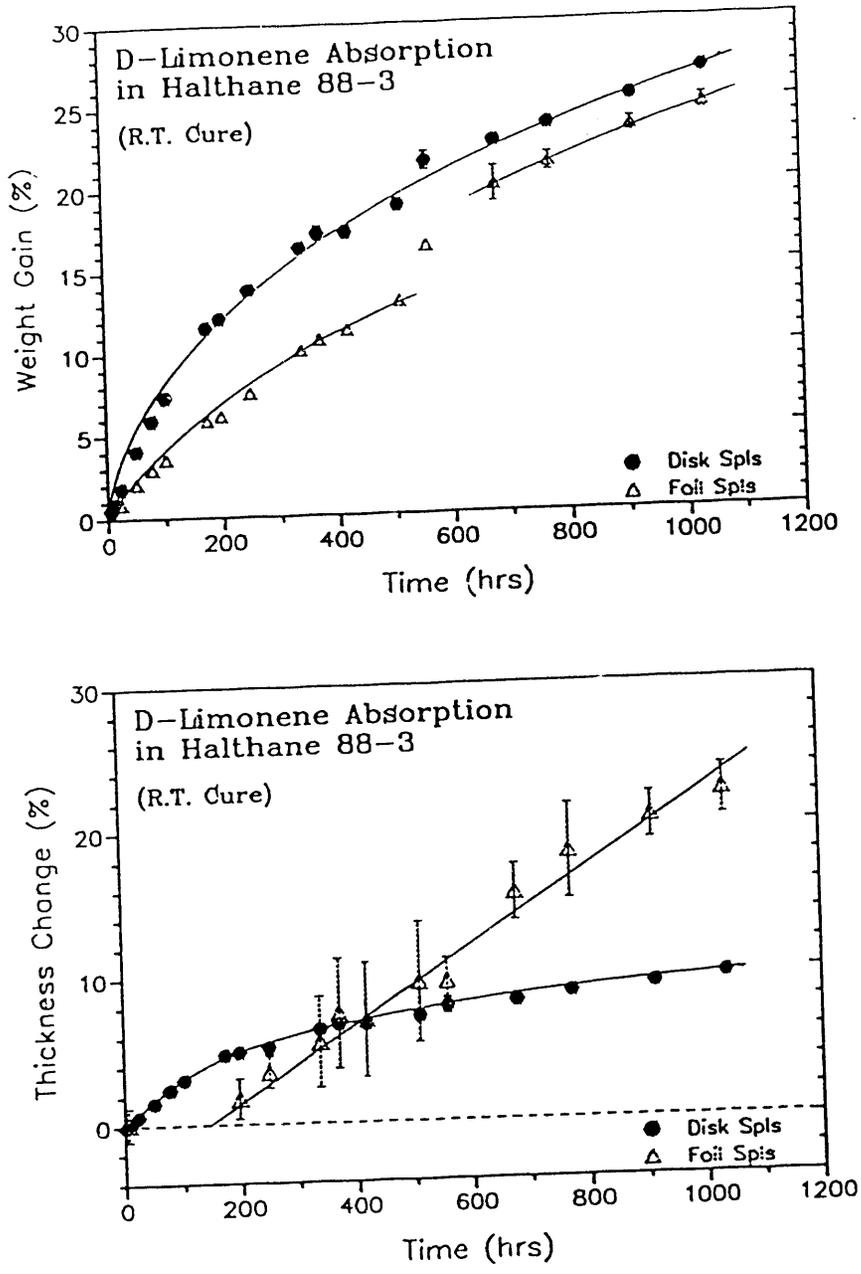

Figure 1. Absorption of saturated d-limonene vapor in R.T. cured Halthane 88-3. Upper: Percent weight gain vs exposure time. Lower: Percent thickness change vs exposure time. Data shown for both bulk disk and foil bonded specimens

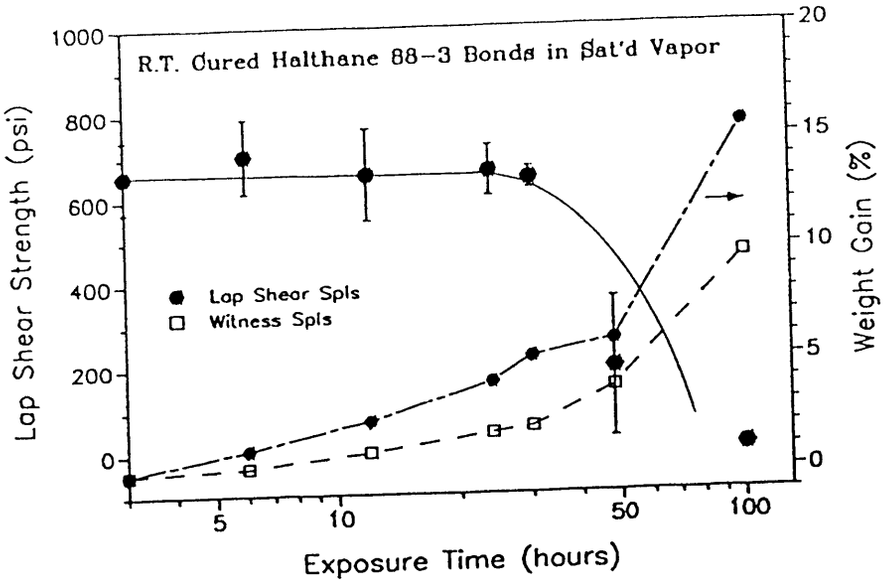

Figure 2. Lap-shear strength and specimen weight gain vs exposure time in saturated d-limonene vapor.

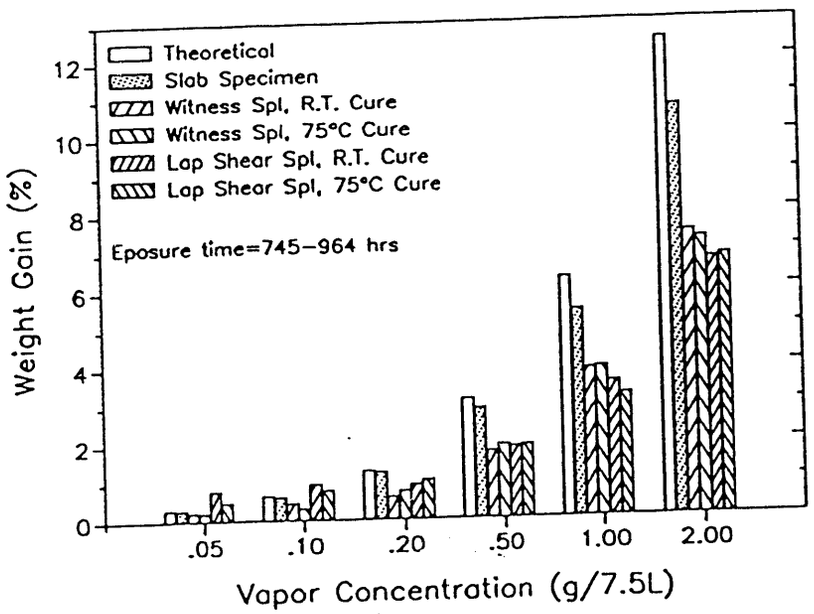

Figure 3. Weight gain of all specimen types in Experiment #3 after exposure to various d-limonene vapor concentrations for times indicated. "Theoretical" %wt gains calculated for each desiccator as 100%*(wt. d-limonene/wt. Halthane).

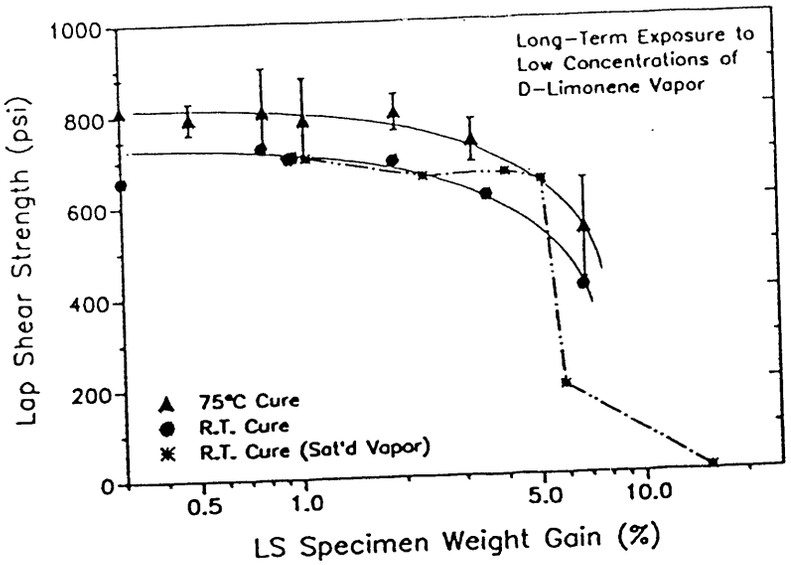

Figure 4. Lap-shear strength vs specimen weight gain for specimens exposed to six different low-concentration d-limonene vapors. Dashed curve shows data plotted from Figure 2.

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