ARMY RESEARCH LABORATORY

Hydrolytic Stability of Polyurethane-Coated Fabrics Used for Collapsible Fuel Storage Containers

by James M. Sloan

ARL-TR-6949 **June 2014**

NOTICES

Disclaimers

Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

ARL-TR-6949 **June 2014**

Hydrolytic Stability of Polyurethane-Coated Fabrics Used for Collapsible Fuel Storage Containers

James M. Sloan
Weapons and Materials Research Directorate, ARL

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
June 2014

2. REPORT TYPE
Final

3. DATES COVERED (From - To)
October 2012–February 2014

4. TITLE AND SUBTITLE
Hydrolytic Stability of Polyurethane-Coated Fabrics Used for Collapsible Fuel Storage Containers

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
James M. Sloan

5d. PROJECT NUMBER
AH80

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: RDRL-WMM-G
Aberdeen Proving Ground, MD 21005-5069

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-6949

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Collapsible fuel tanks fabricated from urethane-coated nylon fabric were first introduced by the military during the Vietnam conflict. Their performance then and until recently, particularly in any humid tropic environment, has been less than satisfactory. These urethane-based coatings were extremely susceptible to ultraviolet and hydrolytic degradation. Hydrolysis is a chemical reaction with water that chemically and structurally breaks down the urethane coating, resulting in cracking or extreme softening of the urethane polymer. Hydrolysis can be quite rapid in certain urethane systems. In this report, the hydrolytic stability of several currently manufactured urethane-coated fabrics used in collapsible fuel storage containers is investigated. We immerse these fabrics in water held at an elevated temperature of 180 °F (81 °C). The mechanical strengths were evaluated over several immersion times to assess the degree of hydrolysis occurring for each urethane-coated fabric. We also used Fourier transform infrared spectroscopy to follow the chemical changes occurring at the coated fabric surface. The results show that the coated fabrics available from Reliance and the Cooley TR 3186 and TR 3219 products performed very poorly in our testing. The Reliance fabric fell apart after only 42 days of water immersion, while the two Cooley fabrics fell apart after 70 days. The three materials available from Seaman performed very well, exhibiting minimal hydrolysis.

15. SUBJECT TERMS
collapsible fuel tanks, polyurethane, hydrolysis, mechanical strength, peel adhesion

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			James M Sloan
Unclassified	Unclassified	Unclassified	UU	22	**19b. TELEPHONE NUMBER** (*Include area code*) 410-306-0685

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Contents

List of Figures

List of Tables

1. Introduction

Collapsible fabric fuel tanks have provided critical tactical bulk petroleum storage for military operations for over 50 years. Beginning in the 1940s with the 900 to 3000-gal pillow tanks, collapsible fabric tanks have evolved into the primary tactical fuel storage vessels now used by all of the military services (*1*). Initially, fabric tanks were used to supplement large, bolted-steel fuel storage tanks and to store small quantities of fuel in remote locations. Early collapsible tanks were made from thick Nitrile thermoset rubber-coated fabric materials that were heavy and required several Soldiers and a significant amount of materials-handling equipment to deploy.

Technological advances in materials and fabrication techniques led to the manufacture of larger and lighter coated fabric tanks made from thinner thermoplastic urethane-coated fabrics. The new technologies permitted the development, manufacture, and fielding of collapsible tanks with capacities greater than 200,000 gal. These tanks can be deployed rapidly and recovered using fewer personnel and less equipment. The success of the large-capacity collapsible tank rendered the labor-intensive bolted tanks obsolete, and they were removed from the U.S. Army inventory.

The Army currently has a large number of fabric-reinforced elastomer tanks ranging in size from 100 to 210,000 gal used for storing fuels and water in the field. Examples of 50,000-gal fuel tanks are shown in figure 1. Collapsible fuel tanks, fabricated from urethane-coated nylon fabric, were first introduced by the military during the Vietnam conflict. Their performance then and until recently, particularly in any humid tropic environment, has been less than satisfactory. Unless formulated and produced according to stringent limitations, urethane-based fabric coatings were extremely susceptible to ultraviolet and hydrolytic degradation. At that time, tanks had to hold high-aromatic gasoline as well as diesel and jet propulsion fuels (*2*). The only urethane that could handle the high-aromatic gasoline fuels was polyester urethane, which was more vulnerable to hydrolysis than polyether urethane. Advancements were made in better understanding the mechanism of the degradation process in the 1980s. Suppliers then added hydraulic stabilizers to the polyester urethanes to prolong their service life. The problem continued to linger resulting in the deterioration and ultimate failure of external tank surfaces and seams even when protective agents had been incorporated into the tank coatings.

Figure 1. Examples of 50,000-gal fabric-reinforced elastomer tanks.

In 1990, the U.S. Army directed that these tanks would no longer be used for long-term storage of gasoline fuels. This change in policy allowed a shift in emphasis from high-aromatic (gasoline) fuel-resistant coatings to more hydrolytically stable materials; thus, polyether urethanes could now be given more consideration as candidate fabric coatings. Concurrently, the Army focused on determining the causes of coating and seam failures (*3*, *4*). Those studies demonstrated unequivocally that those failures were attributable to the leaching out of protective stabilizers from tank materials by contact with fuel puddles on the outer tank surface. The leaching action occurred regardless of the fuel type but was particularly severe in the case of diesel fuel. Because of this fuel's low volatility and slower evaporation rate, any puddles on the tank surface prolong the extraction process, resulting in more extensive damage. Examples of tank materials that have been leached by puddles of fuel followed by hydrolysis are shown in figures 2–5. Military specifications for fuel tanks prior to that work merely based requirements for hydrolytic stability on the urethane's ability to resist deterioration after immersion in water at 160 °F (*5*). After that, work materials were aged in water after extraction in fuel. This requirement was added to subsequent fuel tank specifications.

Figure 2. Fabric blistering due to hydrolysis.

Figure 3. Fabric seams coming apart due to hydrolysis.

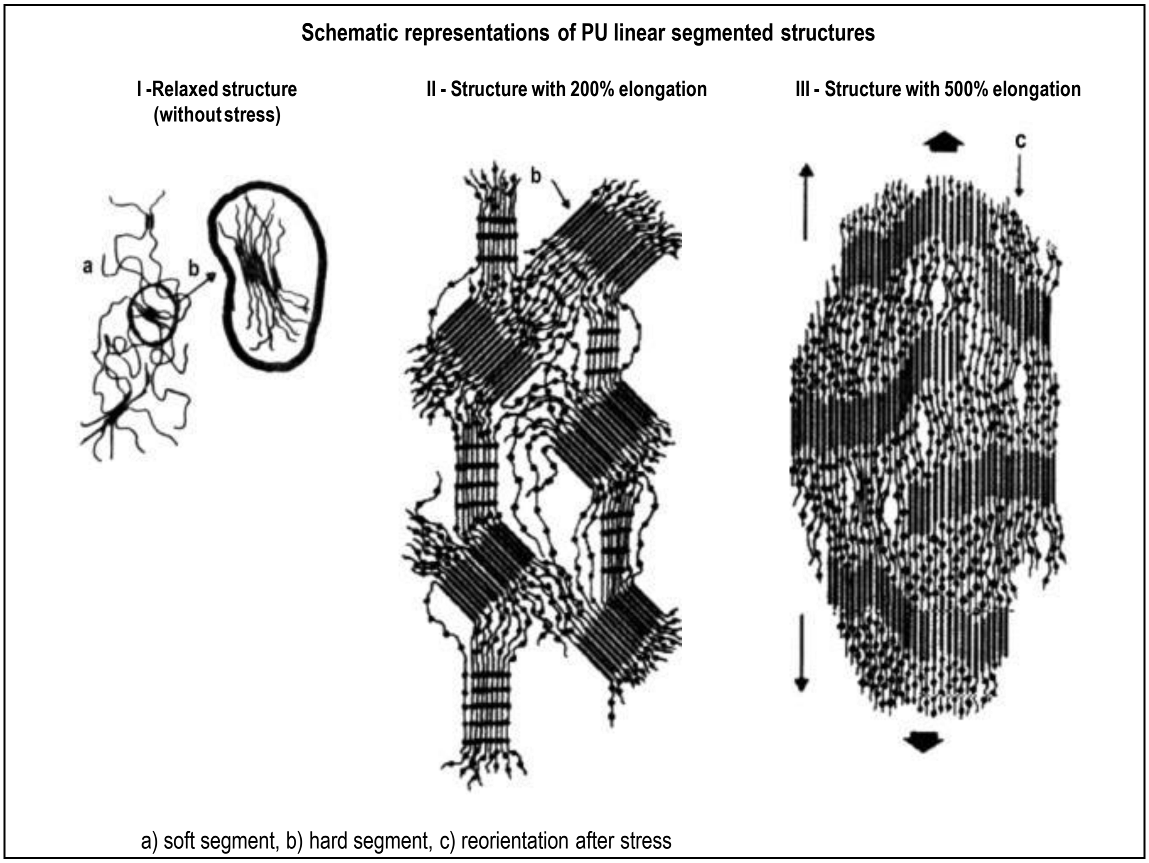

Figure 4. Schematic of urethane morphology.

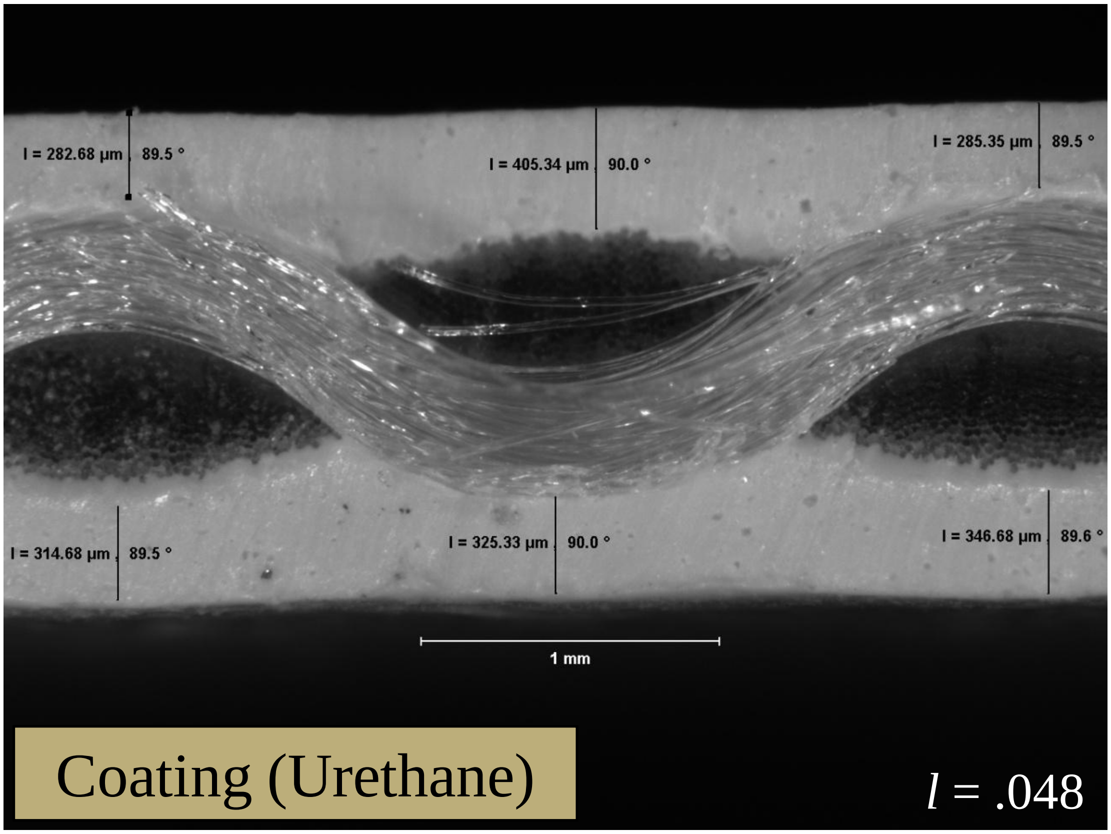

Figure 5. Side view micrograph of urethane-coated fabric.

To evaluate this effect, various methods have been used to study hydrolytic stability of urethane elastomers. Several researchers immersed the elastomers in water temperatures varying between 50 °C and 100 °C (*6–10*). Other researchers used a high-humidity chamber that was varied between 70% and 100% humidity (*11–13*). Generally, it was found that the polyester-based urethanes hydrolyzed more rapidly than that of their polyester-based counterparts.

2. Experimental

2.1 Characterization

2.1.1 Seam Breaking Strength at Room Temperature

Three seam-breaking-strength specimens 1 in. wide (parallel to the seam) and extending (perpendicular to the seam) 3 in. beyond both edges of the seam were punched out and tested at room temperature in accordance with ASTM D751 (*14*). Reported values are expressed in pounds per inch, and failure within the seam on any specimen constitutes failure of this test.

2.1.2 Seam Peel Adhesion at Room Temperature

Three peel-adhesion specimens 1 in. wide (perpendicular to the seam) and of sufficient seam length to determine both the initial and after conditioning tests on the same specimen were used and tested at room temperature in accordance with ASTM D413 (*15*). Reported values are expressed in pounds per inch of width.

Infrared spectra for all the polymer samples were collected using a Fourier transform infrared spectroscopy (FTIR) spectrometer (Nicolet Magna 560 Series) equipped with a Gateway (Specac) accessory and a seven-reflection attenuated total reflectance crystal (ZnSe, refractive index = 2.4). The accessory contains a pressure mechanism that assures good sample-to-crystal contact. All IR spectra were collected using 128 scans and 4-cm^{-1} resolution.

2.2 Materials

Polyurethane elastomers are phase-segregated linear block copolymers that contain an ordered hard segment phase and a soft rubbery phase. The hard segment phase is responsible for the cross-linking in the elastomer. Figure 3 shows a schematic of this structure. These microstructures of polyurethanes are well known for controlling the physical properties of these phase-separated materials, such as tensile strength, tear strength, and puncture resistance. For this study, we obtained currently manufactured polyurethane-coated fabrics as well as several candidate coated fabrics. Samples were obtained from commercial coating sources familiar with fuel storage tank construction and fabrication. Seven polyurethane-coated fabrics were procured: three from Cooley Inc. (Cranston, RI), one from Reliance Coated Fabrics (Mansfield, TX), and three from Seaman Corporation (Wooster, OH). The polyurethane-coated fabric consists of nylon- or polyester-woven fabric that is coated on both sides with polyurethane rubber to create a rubber composite. Figure 4 shows a micrograph of the side view of this assembly for the Cooley Inc. polyurethane-coated fabric. Details about the coating method were not available. Coating thicknesses were all very consistent between manufacturers, ranging between 1.4 and 1.6 mm (approx .05 in.). Table 1 gives the relevant physical properties of these materials. Fabric densities ranged from 41.6 oz/yd^2 to 45.2 oz/yd^2; this is an important characteristic physical property because the increase in fabric densities results in heavier fuel storage containers, which are more difficult to deploy.

Table 1. Physical properties of urethane fabrics.

		Fabric Density oz/yd^2	Coating Thickness (interior) mils	Coating Thickness (exterior) mils
Cooley 3186	**Nylon**	**45.2**	**21.2**	**22.3**
Cooley 3219	**Polyester**	**40.3**	**20.6**	**20.1**
Seaman 80889	**Nylon**	**40.9**	**20.9**	**20.1**
Reliance OB 193	**Nylon**	**44.4**	**21.4**	**23**
Seaman 80502	**Nylon**	**41.6**	**23.5**	**20.5**
Seaman 337	**Nylon**	**42**	**25.1**	**25.2**

3. Results

Urethane coatings are particularly susceptible to undergo hydrolysis, which is a chemical reaction with water, resulting in chemical breakdown of the urethane coating, resulting in cracking or extreme softening of the urethane polymer. Hydrolysis can be quite rapid in certain urethane systems so we evaluated the resistance to hydrolysis of these urethane-coated fabrics. Since hydrolysis of the urethane coating would not affect the strength of the base fabrics due to the nylon/polyester woven fabric, accounting for all of the composite tensile strength, it is preferable to evaluate the hydrolytic stability in the bond line where the urethane coating is fully responsible for the mechanical strength. Figures 6 and 7 compare the seam-breaking strengths measured at room temperature after water immersion at 180 °F at time increments of 28, 42, and 70 days. All materials provided adequate mechanical integrity after 28 days of immersion; however, all of the materials' seam-breaking strengths decreased with water immersion. The inside coating of this tank material became hard and brittle after the samples that had been exposed to water for 42 days and beyond, which is indicative of a failure due to hydrolysis (see figure 8). The seams made from the Cooley TR 3186 and TR 3219 materials also failed after immersion in water for 70 days at 180 °F and exhibited cracks in the interior white coating from hydrolysis caused by water immersion. This type of deterioration normally happens with ester-type urethanes. The Cooley TR 3186 material was used by Avon Engineered Fabrics in recent years to manufacture and supply fuel tanks to the military.

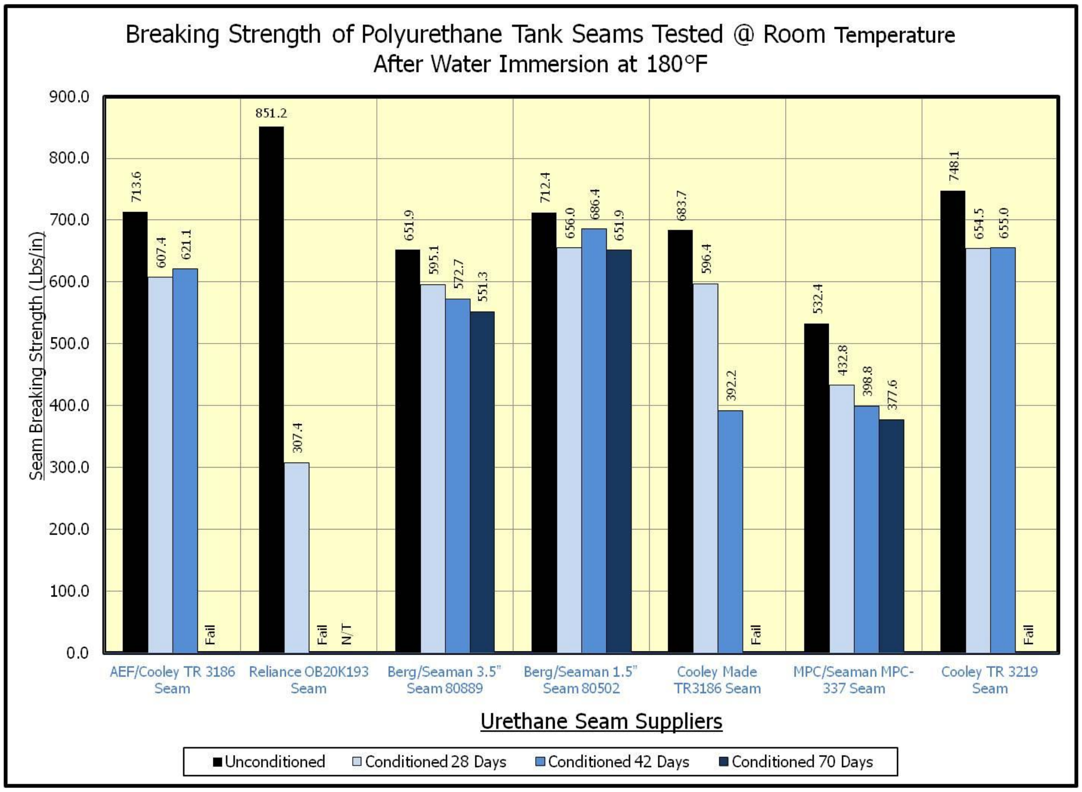

Figure 6. Breaking tensile strength of fabric seams after immersion in water at 180 °F.

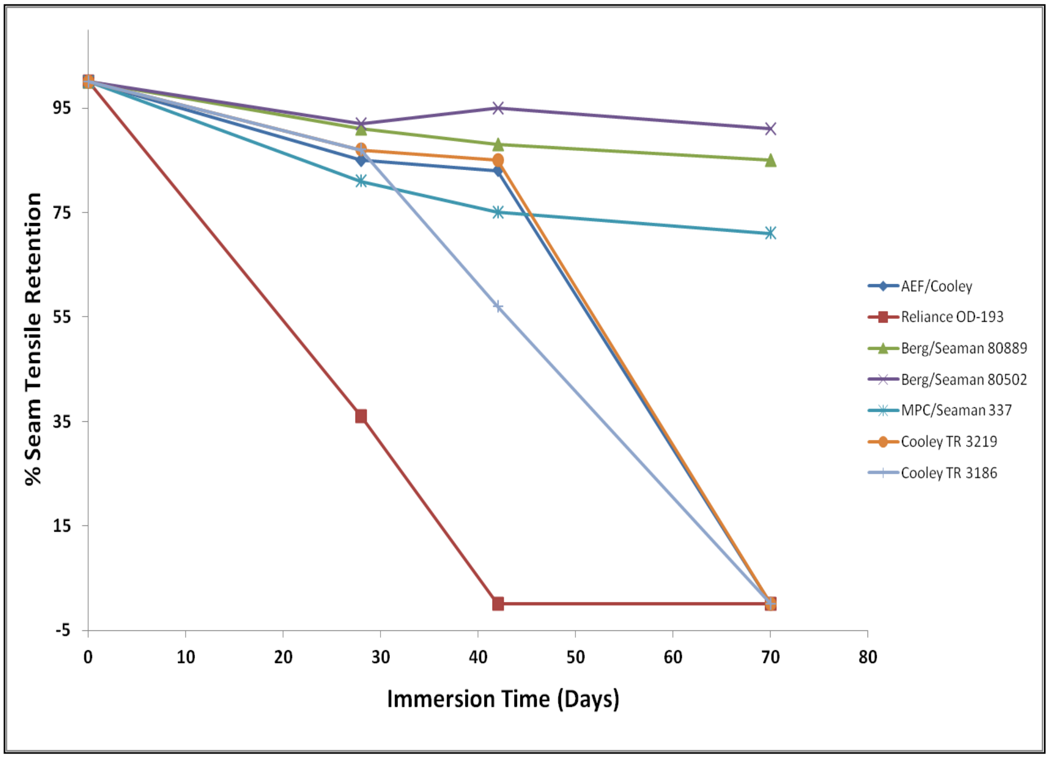

Figure 7. Seam tensile strength retention of fabric seams after immersion in water at 180 °F.

Figure 8. Reliance coated fabric after 42-day immersion showing advanced hydrolysis.

The retention rates for all seven materials studied are presented in figure 9. This graph points out the poor performance of the materials manufactured by Cooley, in that all fabrics exhibited 0% retention after being immersed for 70 days. The Reliance material, used to manufacture 20,000 fuel tanks for the military in 2002, exhibited a significant amount of deterioration after only 28 days of immersion at 180 °F. As seen in figure 9, this seam retained only 36% of its original breaking strength after 36 h. The three coated fabrics from Seaman Corporation, the Berg/Seaman 80889 (3.5-in. seam width), Berg/Seaman 80505 (1.5-in. seam width), and MPC/Seaman 337, all performed well in our testing. The Berg/Seaman 80889 and 80505 retained approximately 95% of its original seam strength while the MPC/Seaman 337 retained 75%.

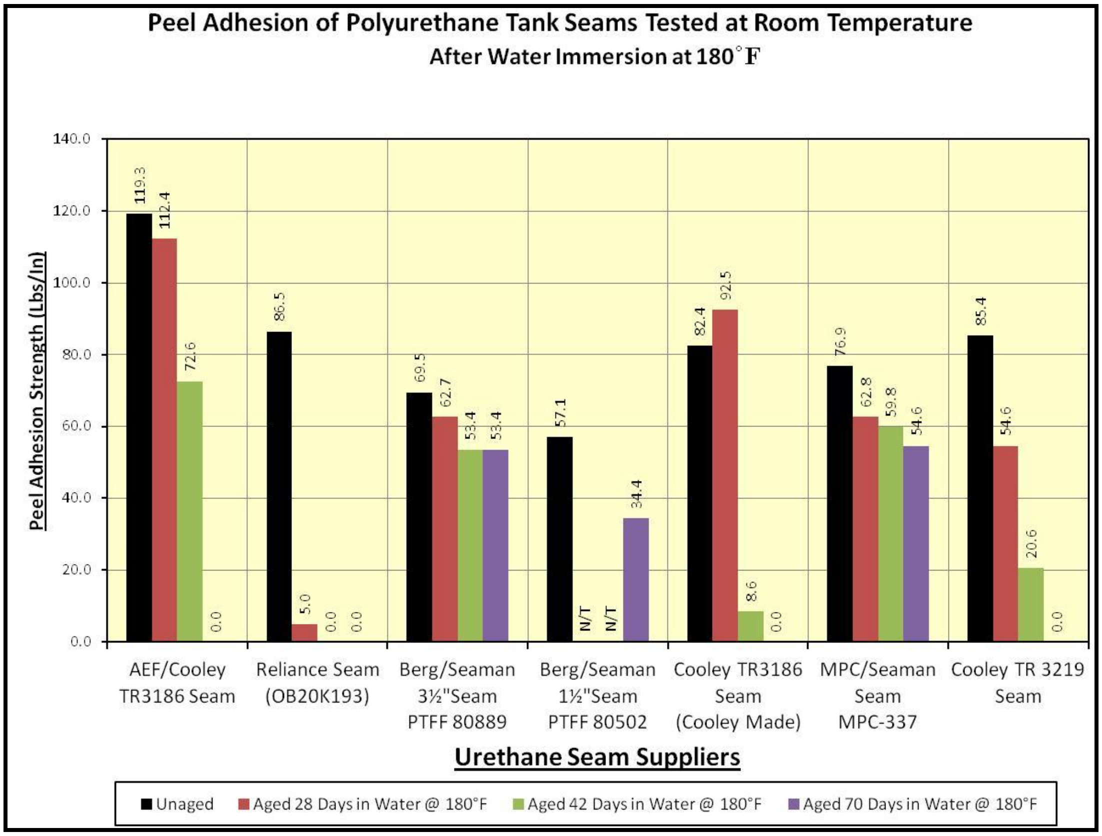

Figure 9. Peel adhesion of fabric seams after immersion in water at 180 °F.

Figure 10 compares the seam peel adhesion measured at room temperature after water immersion at 180 °F for time increments of 28, 42, and 70 days. The seam peel adhesion is an excellent test method to determine the resiliency of the bond line to hydrolysis. As seen in the seam breaking strength results (figures 7 and 8), the Reliance seam performed very poorly in the peel adhesion testing. This seam failed to provide any peel adhesion strength after a 42-day water immersion cycle exhibiting significant surface cracking on the interior coating (fuel side). The seam provided a 5-lb/in. peel adhesion value after the 28-day immersion—a critical failure. All the other Cooley materials performed slightly better, though the seam structures failed the 70-day water immersion test. All the seams constructed with the Seaman fabrics performed well and provided excellent peel adhesion values even after immersion in water for 70 days at 180 °F. As with the seam tensile strengths, the Cooley and Reliance fabrics performed poorly. The Reliance fabric failed almost immediately while the Cooley fabric showed no strength retention after the 72-h immersion time. The Berg/Seaman 80889 and 80505 retained approximately 80% of its original seam strength while the MPC/Seaman 337 retained 60%.

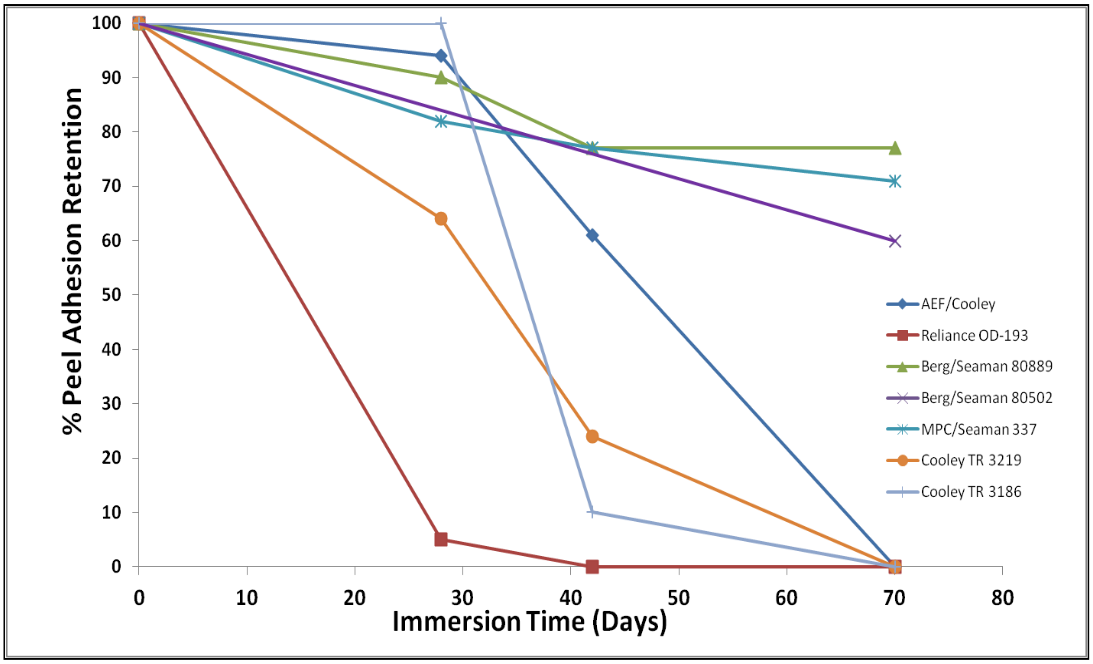

Figure 10. Seam peel adhesion strength retention of fabric seams after immersion in water at 180 °F.

FTIR was conducted on these polymers to identify molecular changes occurring within the polymer domains. FTIR looks only at the chemical events occurring at the surface and does not yield information on the bulk polymer composite. Figure 11 shows the progression of the infrared spectra with immersion time of the Seaman coated fabric. The FTIR spectrum at 0 h show two carbonyl peaks at 1700 cm^{-1} and 1720 cm^{-1}, which can confidently be assigned to a hydrogen-bonded carbonyl and a nonhydrogen-bonded carbonyl (*16*), respectively. The 1700-cm^{-1} band appears to shift to lower frequencies ending at 1660 cm^{-1}. The FTIR spectra show growth of two new carbonyl peak formations at 1778 cm^{-1} and 1750 cm^{-1} with increasing water immersion time. The 1778 cm^{-1} is due to an acidic carbonyl that results from the reaction of a urethane carbonyl and water molecule. In addition, a decrease in 1525 cm^{-1} is associated with the amide II band (**ν**(C-N)), and a decrease in 1628 cm^{-1} is associated with the amide I band [**ν**(C=O)], indicating urethane bond cleavage (*17–19*). These molecular groups are responsible for cross-linking the urethane chains to provide mechanical and structural integrity. While the urethane inherently contains ether groups as part of the molecular backbone, new ether groups form as evident from the widening of IR bands in the 1300- to 1000-cm^{-1} region. This is a result of direct insertion of OH groups into the urethane linkage.

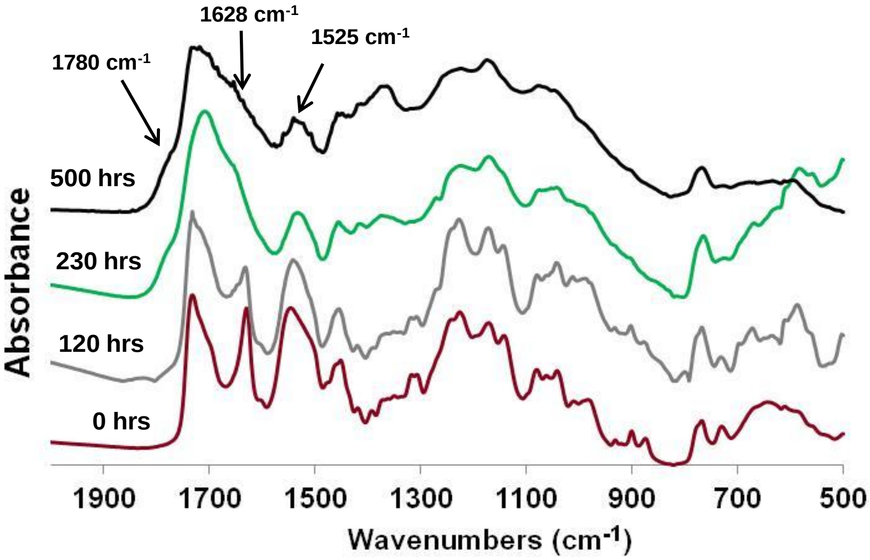

Figure 11. Progression of FTIR spectra with immersion time in water at 180 °F.

Figure 12 graphs these changes. The appearance of ether groups coincides with the decrease of the urethane links. Identical structures were identified for all seven coated fabrics studied in this report.

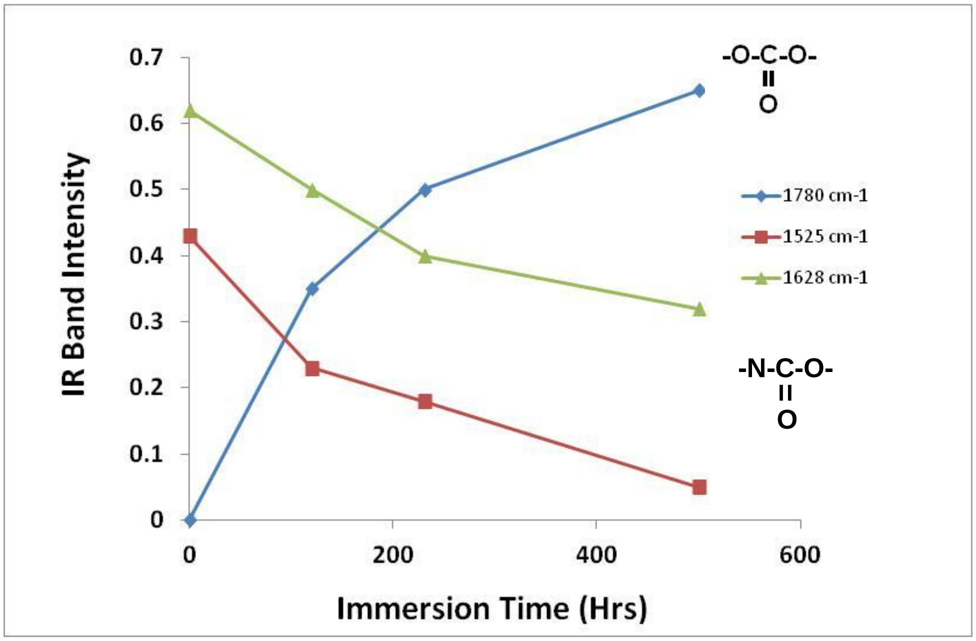

Figure 12. FTIR individual IR band changes with immersion time in water at 180 °F.

4. Conclusions

The urethanes studied in this work fall into two groups, those that underwent hydrolysis within the 72-h conditioning cycle and those that resisted hydrolysis during this time period. The polyurethane materials provided by Cooley and Reliance showed a vulnerability water attack, while all the materials provided by Seaman provided better resistance to water. The Cooley and Reliance exhibited no peel adhesion strength retention after 72 days in water at elevated temperatures, while the Seaman coated fabrics retained an average of 85% of original peel adhesion strength. It is expected that tanks made from these Cooley materials, and especially the Reliance materials, would have a shorter shelf life and service life in areas with hot, humid environments. Another problem could arise with tanks that have been used, cleaned, and returned to storage with some residual water. The picture of the Reliance-coated fabric after water immersion at 180 °F for 42 days is indicative of what the Cooley materials looked like after water immersion for 70 days at 180 °F.

5. References

1. Leggieri, J. A.; Perdue, W. Collapsible Petroleum Tanks: Past Present, and Future. *Army Logistician* **2000**, *32* (5), 12.
2. Feuer, H.; Touchet, P. *Failure Mechanism of Urethane Elastomer Collapsible Fuel Tanks;* BRDEC Report No. 2488; Belvoir Research, Development and Engineering Center: Fort Belvoir, VA, March 1990.
3. Gatza, P.; Touchet, P.; Feuer, H.; Teets, A. *Extending the Service Life of Urethane Fuel Tanks;* BRDEC TR No. 2519; Belvoir Research, Development and Engineering Center: Fort Belvoir, VA, March 1992.
4. Feuer, H.; Touchet, P. Effects of Extracting Hydrolytic Stabilizers on Urethane Performance. Presented at Rubber Division, American Chemical Society, Washington, DC, 9–12 October 1999.
5. MIL-T-52983G. *Performance Purchase Description ATPD 2266 for Tanks, Fabric, Collapsible: 3000, 10,000, 20,000, and 50,000 Gallon, Fuel* **2000**.
6. Sloan, J.; Flanagan, D.; Deschepper, D.; Pergantis, C.; Touchet, P.; Feuer, H. Environmental Aging of Coated Fabric Composites. *Proceedings of the 70th Annual Technical Conference,* Society of Plastics Engineers, Orlando, FL, 2–4 April 2012, pp 789–792.
7. Sloan, J.; Flanagan, D.; Deschepper, D.; Pergantis, C.; Touchet, P.; Feuer, H. Accelerated Environmental Aging of Materials Used for Collapsible Fuel Storage Tanks. *Proceedings of the 69th Annual Technical Conference & Exhibition,* Society of Plastics Engineers, Boston, MA, 1–5 May 2011, p 908.
8. Deng, Y.; Yu, T.; Ho, C. Effect of Aging Under Strain on Physical Properties of Polyester Poly-Urethane Elastomer. *Polymer Journal* **1994,** *26* (12), 1368.
9. Magnus, G.; Dunleavy, R. A.; Critchfield, F. E. Stability of Urethan Elastomers in Water, Dry Air, and Moist Air Environments. *Rubber Chem Tech* **1966,** *39,* 1328.
10. Deng,Y. W.; Yu, T. L.; Ho, C. H. Effect of Aging Under Strain on the Physical Properties of Polyester-Urethane Elastomer. *Polymer J.* **1994,** *26,* 1368–1376.
11. Seymour, R. W.; Allegrazza, A. E.; Copper, S. L. Segmental Orientation Studies of Block Polymers. I. Hydrogen-Bonded Polyurethanes. *Macromolecules* **1973,** *6*, 896.
12. Singh, A.; Saxon, R. Moisture-Resistant Urethanes. *Rubber Age* **1975,** *107,* 53.

13. Desper C. R.; Schneider, N. S.; Jasinski, J. P.; Lin, J. S. Deformation of Microphase Structures in Segmented Polyurethanes**.** *Macromolecules* **1985,** *18,* 2755.

14. ASTM D751 Standard Test Method for Coated Fabrics. *Ann. Book ASTM Stand.* **2004.**

15. ASTM D413 Standard Test Method for Rubber Property – Adhesion to Flexible Substrate, *Ann. Book ASTM Stand.* **1996.**

16. Irusta, L.; Fernandez-Berridi, M. J. Photooxidative Behaviour of Segmented Aliphatic Polyurethanes. *Poly. Deg. & Stab.* **1999,** *63,* 113.

17. Wilhelm, C.; Gardette, J. L. Infrared Analysis of the Photochemical Behaviour of Segmented Polyurethanes: Aliphatic Poly(ether-urethane)s. *Polymer* **1998,** *39,* 5972.

18. Yilgor, I.; Yilgor, E.; Guler, I. G.; Ward, T.; Wilkes, G. L. FTIR Investigation of the Influence of Diisocyanate Symmetry on the Morphology Development in Model Segmented Polyurethanes**.** *Polymer* **2006,** *47,* 4105.

19. Thompson, D.; Osborn, J.; Kober, E.; Schoonover, J. Effects of Hydrolysis-Induced Molecular Weight Changes on the Phase Separation of a Polyester Polyurethane. *Poly. Deg. & Stab.* **2006,** *91,* 3360.

.

1 (PDF)	DEFENSE TECHNICAL INFORMATION CTR DTIC OCA
2 (PDF)	DIRECTOR US ARMY RESEARCH LAB RDRL CIO LL IMAL HRA MAIL & RECORDS MGMT
1 (PDF)	GOVT PRINTG OFC A MALHOTRA
1 (PDF)	DIR USARL RDRL WMM G J SLOAN

INTENTIONALLY LEFT BLANK.