

## PREDICTING PRESSURE IN PACKAGES CONTAINING POLYURETHANE FOAM

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### ABSTRACT

Small drum-type Type B shipping radioactive material packages often include materials such as polyurethane foam inside their containment vessels to cushion their contents. During the fire test of hypothetical accident conditions, the gas released from these materials can be a significant contributor to the pressure in the containment vessel.

We asked what the major constituents of the gas released from polyurethane foam were and how the pressure rise could be quantified. Our tests involved polyurethane foam samples from two vendors. One vendor provided multiple samples with differing chemistry in order to allow the contribution of different flame retardant additives and processing methods to be studied.

Samples were heated in a sealed container and the pressure monitored. At temperatures below 300°F (150°C) the pressure stabilized when the samples were held at constant temperature. Above this temperature the pressure continued to increase. Samples of gas from the test container were analyzed.

It was found that fire retardants had a small impact on the quantity of gas released. By far the largest contribution was from water vapor. Samples exposed to 0% humidity released almost no gas below 300°F (150°C) while samples exposed to 100% humidity released much more than samples stored at ambient conditions. Also found were strong dependencies on the relative amount of foam to available air in a container.

We found that to best predict the contribution of pressure rise inside a containment vessel, test parameters including sample preparation and the relative foam to test volume ratio must be controlled. Polyurethane foam chemistry and processing methods play a role in the quantity of gas released, but these contributions are small compared to the role of water.

No standard test methodology exists for predicting the pressure contributions of materials inside containment vessels. These studies show that the amount of gas released is sensitive to several parameters. Care is needed when using test results to predict pressure in containment vessels. An industry standard for conducting these tests could help ensure repeatability and allow meaningful sharing of test data.

### INTRODUCTION

Polyurethane foam is used in many shipping packages. It can both absorb impact energy and serve as a thermal insulator. Polyurethane is versatile in that it can be produced in many densities, be made to be either rigid or flexible, and be formed with open or closed cells. By carefully choosing parameters polyurethane foam can be made to serve many purposes in transportation packages.

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Polyurethane foam is generally produced by reacting isocyanate with polyol. A blowing agent is used to create gas bubbles and produce the cellular foam structure. Foam can be solvent blown or water blown. Solvent blown foams use volatile chemicals which boil during the foaming process. Water blown foams include a small amount of water which reacts with the isocyanate to produce carbon dioxide gas bubbles. Flame retardants, colors, and many other useful chemicals can also be used. Commercially available foam material is generally sold in two parts which contain all the necessary ingredients for producing a foam with the desired characteristics. These two parts are mixed right before pouring or molding a foam piece.

Y-12 has used flexible polyurethane foam for many years to surround the contents in small drum-type Type B Fissile material packagings such as the one shown in Figure 1. Such small drum-type containers generally consist of several layers. These can be seen moving from left to right in Figure 1. Outermost is a stainless steel drum. Inside this is an impact absorbing and thermal insulating material, such as the white painted fibrous insulation shown, which surrounds a strong inner vessel. This vessel is the containment boundary for the package. Inside the vessel, flexible polyurethane foam, such as the red pieces shown in the figure, are used to support and cushion the contents.



**Figure 1. Common components of small drum type package**

As Type B material packagings, small drum-type containers must maintain containment after regulatory testing including impacts from 30-ft and a 30-minute exposure to fire. The fire

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test causes the temperature inside the containment boundary to rise. At elevated temperatures the polyurethane foam can release gases which can also add to the build-up of pressure inside the containment boundary. Testing to determine the pressure inside the containment vessel is difficult as many parameters can influence the final pressure. The thermal response of the package also varies based on the damage from the impact tests. Testing each combination of impact angle and contents would be cost prohibitive, and so a method of calculating the pressure rise is needed. This calculated pressure can then be used to determine the acceptability and margin of containment.

In some container designs, polyurethane foam is used outside the containment boundary and can reach very high temperatures during the thermal test. There it decomposes producing much flame and char. In Y-12's use, however, the maximum temperature of the foam is generally less than 275° F (135° C), though hot spots have developed which led to small areas of localized decomposition of the foam in some packagings. In Y-12 applications, a large amount of foam is often used, with the apparent volume of the foam between ~66 and ~95% of the otherwise empty volume inside the containment boundary.

For this type of usage, we asked what the major constituents of the gas released from polyurethane foam were and how the pressure rise could be quantified. Of particular interest was which parameters had the greatest influence on the final pressure inside the boundary.

## **METHODS**

Several different tests were performed to study the pressure generation of polyurethane foam. Two foam types were studied.

### **Materials Tested**

The foam materials tested are described in Table 1. Foam S is solvent-blown foam and Foam W is water-blown foam. When cast, Foam W has a homogeneous nature, while cast specimens of Foam S develop a thick, dense, outer skin and a less dense inner core. Images of cast specimens are shown in Figure 2.

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**Table 1. Characteristics of foams tested**

	Foam S	Foam W
Blowing method	Solvent blown	Water blown
Free-rise density	8 lb/ft <sup>3</sup> (0.13 g/cm <sup>3</sup> )	8 lb/ft <sup>3</sup> (0.13 g/cm <sup>3</sup> )
As-cast density	~15 lb/ft <sup>3</sup> (0.24 g/cm <sup>3</sup> )	~15 lb/ft <sup>3</sup> (0.24 g/cm <sup>3</sup> )
Constituents (wt%) <sup>2</sup>		
Part A	4,4'-Diphenylmethane diisocyanate (40-60%) Modified MDI <sup>1</sup> (40-60%)	4,4' Diphenylmethane diisocyanate (50-75%) Modified MDIs and other oligomers (25-50%)
Part B	Polyether polyol mixture (75-95%) 1,1,1,3,3-Pentafluoropropane (HFC-245fa) (1-15%) Proprietary catalyst mixture (3-10%)	Polyether resins (70-95%) Brominated aromatic polyalcohol (18-24%) Tertiary amine (<1%) Polyether modified siloxane (<1%) Water (<.4%) <sup>3</sup>

<sup>1</sup> – Diphenylmethane diisocyanate.

<sup>2</sup> – From material safety data sheets.

<sup>3</sup> – From discussions with vendor.



**Figure 2. Foam S (red, left) and Foam W (white, right)**

**Pressure Rise Testing**

The intent of the pressure rise test is to quantify the amount of gas released from the foam per gram at different temperatures. Unfortunately, there is no known consensus standard on how to

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perform this test. This leads to difficulties in reproducing and applying test results to calculations.

Y-12 uses a method developed in the early 1990s. For this method, samples of the foam were cut and weighed. The samples were then placed in sealed containers. The sealed containers were placed inside temperature controlled ovens. The containers were connected to a pressure transducer located outside the oven by means of tubing. The total volume of the closed system was previously measured and known.

The temperature of the closed vessel was raised to a set point and held until the pressure stabilized. At some higher temperatures the pressure did not stabilize and the temperature was held for a set amount of time. An example of a heating profile used is shown in Table 2. Similar profiles were used for all experiments, though with varying hold

temperatures and times. From the known volume, the amount of air initially in the chamber can be calculated by assuming ideal gas behavior. An adjustment is included to account for the solid volume of the foam sample. Two methods have been used by Y-12 used for this adjustment. The first used the density of solid polyurethane to determine the density of the sample. The second compressed a sample of the same material and determined the compressed volume of a sample. The pressure in the container was then treated as an ideal gas. For each temperature, the amount of gas released into the container from the foam was then be calculated.

For this study, some of the testing was performed at Y-12, while others were performed at the University of Tennessee Space Institute in Tullahoma, Tennessee, under contract.

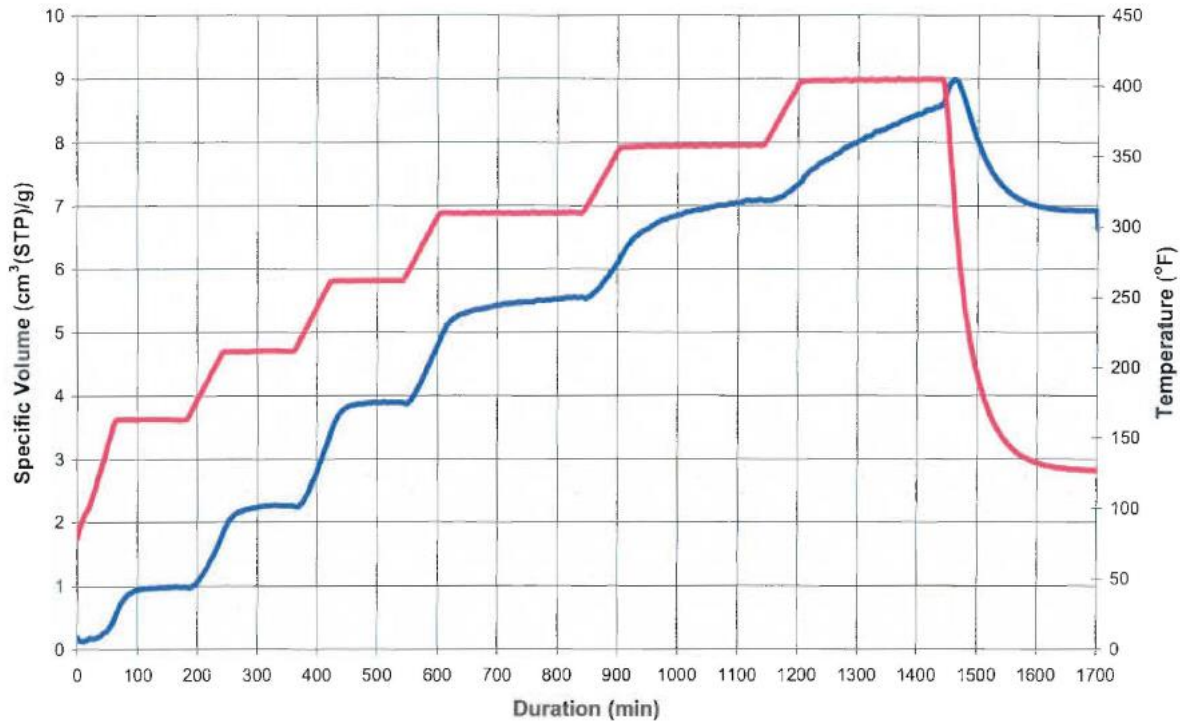
## RESULTS

Foam S was first tested by Y-12 in 1996. The results from this testing is shown in Figure 3. The units of the results are specific volume of gas released at each temperature in cm<sup>3</sup> of gas per gram of material at a standard temperature and pressure of 273 K and 1 atm. This test was of an 11.06-g specimen.

The curve shown is typical of the curves seen for all samples. At lower temperatures the pressure stabilizes at some value. At temperatures above ~300°F the pressure does not stabilize, even after a longer hold time.

**Table 2. Example heating profile**

Temperature Setting		Duration of ramp or hold
°F	°C	
77-150°	26-65°	1-hour ramp
150°	65°	2-hour hold
150-200°	65-93°	1-hour ramp
200°	93°	2-hour hold
200-250°	93-121°	1-hour ramp
250	121°	2-hour hold
250-300°	121-149°	1-hour ramp
300°	149°	4-hour hold
300-350°	149-177°	1-hour ramp
350°	177°	4-hour hold
350-400°	177-204°	2-hour ramp
400°	204°	4-hour hold
400-77°	204-25°	2-hour ramp



**Figure 3. Foam S test results from 1996 (red=temperature, blue=specific volume)**

Foam S and Foam W differ in many ways. One significant difference is the use of brominated polyol in Foam W. This material is used to make the foam flame retardant. When burned, bromine gas released can act to smother a small flame. This is useful in applications such as upholstery where a small source such as a cigarette may come into contact with the foam.

To determine the influence of the fire retardant, gas samples were taken at the end of a pressure test for both Foam S and Foam W. Also tested was a sample provided by the vendor which was similar to Foam W, but made without brominated polyol. Due to limitations with the experimental setup at the time of these tests, the test chambers for both samples were evacuated and backfilled to 0.1 atm with argon before heating. The gas samples were cooled to room temperature and analyzed using both gas chromatography and mass spectrometry. The results of these analyses are shown in Table 3.

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**Table 3. Analysis of gas samples from pressure tests**

	Foam S	Foam W	Foam W w/o brominated polyol
Gas chromatography (volume %)	CO <sub>2</sub> >20%	CO <sub>2</sub> >27%	CO <sub>2</sub> >30%
	Carbon monoxide <0.01%	Carbon monoxide <0.01%	
	Hydrogen, molecular 0.06%	Hydrogen, molecular 0.03%	Hydrogen, molecular <0.01%
	Methane <0.01%	Methane <0.01%	Methane <0.01%
	Nitrogen, molecular 2.5%	Nitrogen, molecular 0.15%	Nitrogen, molecular 0.13%
	Oxygen >45%	Oxygen >30%	Oxygen >20%
	Argon 8.79%	Argon 46.59%	Argon 23.21%
Mass spectrometry (volume %)	CO <sub>2</sub> 3.66%	CO <sub>2</sub> 27.01%	CO <sub>2</sub> 76.62%
	Helium <0.01%	Helium <0.1%	Helium <0.1%
	Hydrogen <0.01%	Hydrogen 0.01%	Hydrogen <0.1%
	Methane <0.01%	Methane <0.1%	Methane <0.1%
	Nitrogen 69.44%	Nitrogen 20.96%	Nitrogen <0.1%
	Oxygen 18.06%	Oxygen 5.37%	Oxygen 0.07%
			AMU 58, 0.03%

Samples of Foam W and Foam S were exposed to 0% humidity and 100% humidity conditions. The changes in weight after exposure to these conditions are shown in Table 4.

**Table 4. Changes in foam samples when exposed to extremes of humidity**

	Change in weight percent		
	0% humidity for 8 days	100% humidity for 5 days	Total
Foam S	-1.1%	+1.7%	2.8%
Foam W	-1.3%	+1.9%	3.6%

To determine the influence of humidity on pressure buildup, samples exposed to high and low humidity were tested. Figure 4 shows the specific gas volume generated by ~3.5 g Foam W samples exposed to different humidity levels. Figure 5 shows the equivalent for ~3.5 g Foam S samples. Note that these specific volumes are at 77°F and 14.7 psi.

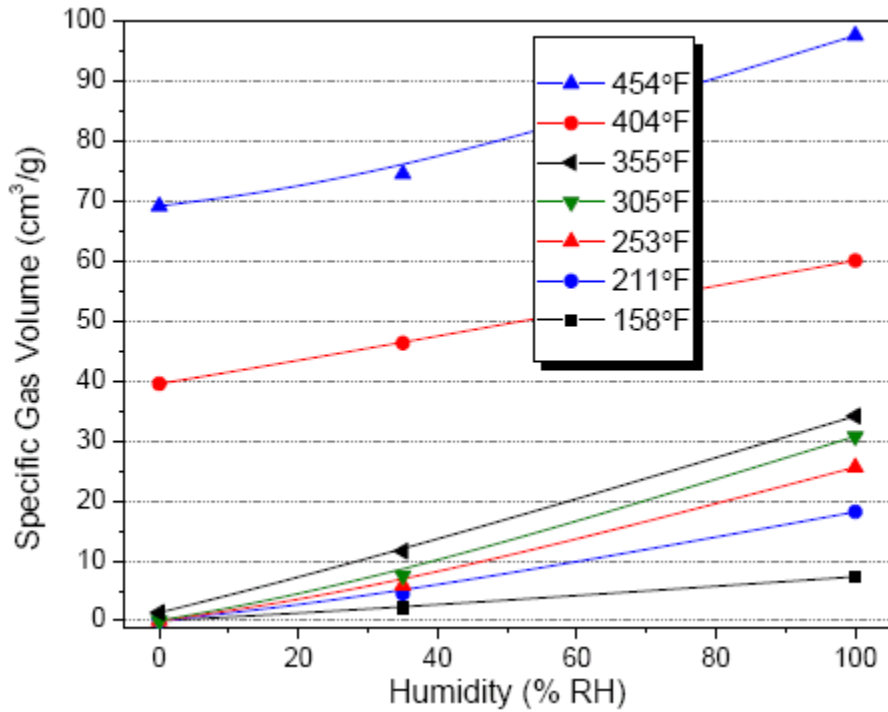


Figure 4. Effect of humidity on gas released from Foam W

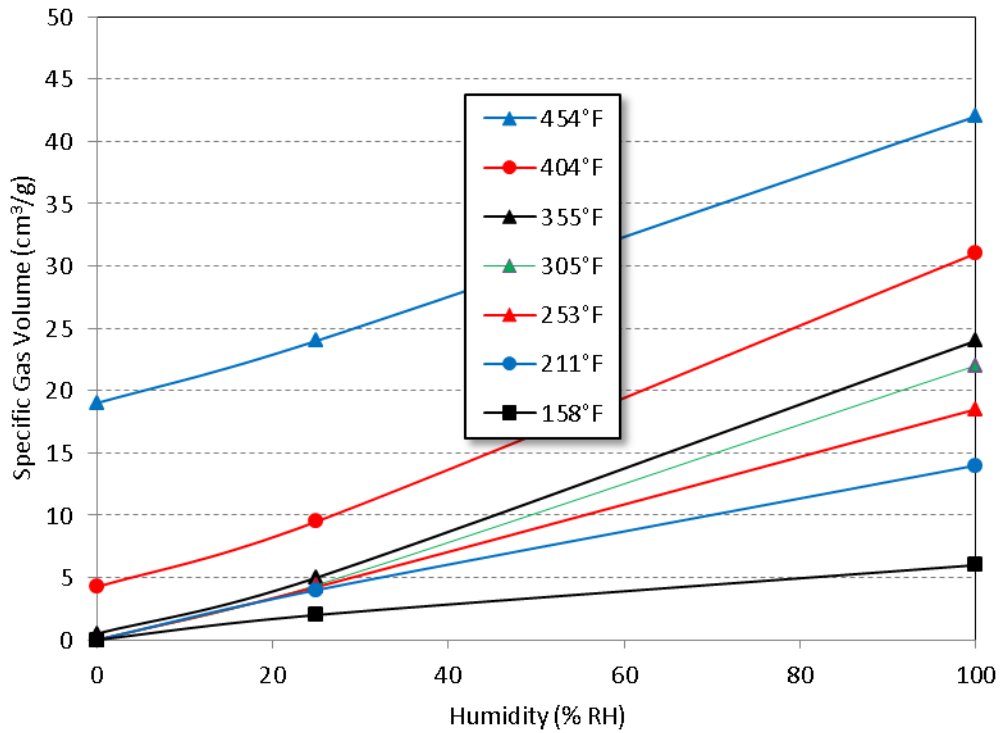


Figure 5. Effect of humidity on gas released from Foam S



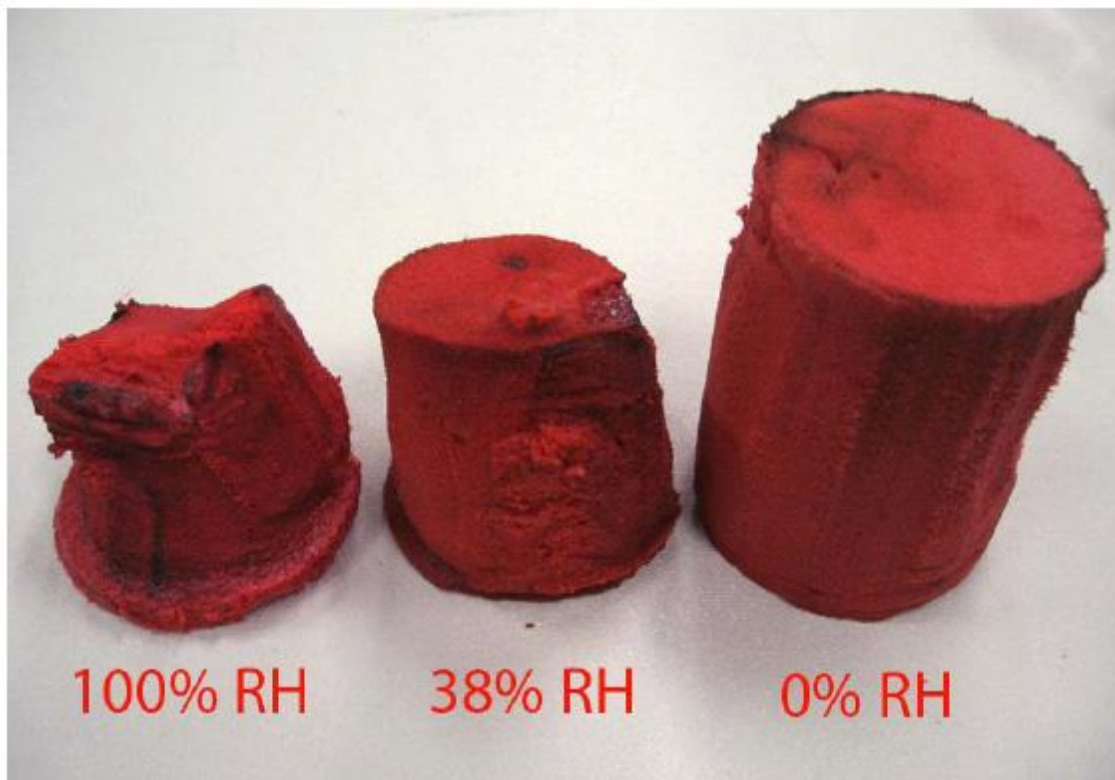
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Tests were also performed which varied the amount of foam relative to the test volume. As Foam S had produced less gas than Foam W in other tests, it was the focus of these tests. The fill ratio, or the proportion of the apparent foam volume (that is the volume of the uncompressed foam) to the test chamber volume was varied. Such a series of tests were performed to bound the humidity and fill ratio of Y-12 drum type packages. Table 5 shows an example of the specific offgassing of the Foam S material at a particular temperature under these varying conditions.

**Table 5. Specific offgassing (cm<sup>3</sup> per gram) of Foam S at 211°F for varying humidity and foam amounts**

		Test volume occupied by foam		
		~10%	~66%	~93%
Humidity (RH%)	0%	0	0	0.1
	~30%	3	0.8	0.4
	100%	14	4.4	2.4

Figure 6 shows the final appearance of Foam S samples after testing up to 350°F. All these samples were initially the same geometry.



**Figure 6. Foam S samples after being tested at 350°F with high loading ratios.**

## DISCUSSION

We found that the gas released from polyurethane foam and the resulting pressure rise in a shipping package is influenced by two main parameters: water content and fill ratio.

Testing of gas samples obtained after heating the foam showed no trace of flame retardant gases. Foam W was shown to both hold more water at ambient humidity and absorb more water at 100% humidity. As demonstrated by testing, when dried of water, no significant gas generation occurs below 355°F (Figure 4 and Figure 5) for either foam. Water appears to be not only a passive player, but to play an active role in the decomposition of the foam as demonstrated by the differing appearances of the foam samples in Figure 6.

The amount of gas generated is also found to decrease as more of the test volume is occupied by foam instead of air as demonstrated in Table 5.

The testing only provides empirical information on the release of gases by the polyurethane foam. The mechanisms behind the release of gases have not been positively identified. It is thought that adsorbed water is released from the foam as the temperature is raised. The more homogenous Foam W is thought to more readily adsorb water than the near solid skin and light core of Foam S.

According to *Reaction of polyurethane foam with dry steam: Kinetics and mechanism of reactions*, heating polyurethane in steam causes it to dissociate and starts a series of reactions which results in transforming the polyurethane and water into polyols, CO<sub>2</sub>, and amines. This could be the reason for the apparent decomposition of the polyurethane foam when water is available.

A weakness with the methodology used is the position of the pressure sensor outside of the heated area. In this cold location some gases (including water vapor) could condense and reduce the pressure. During testing long thin sections of tubing were used to connect the chamber to the pressure sensor. This tubing was in the heated area. The long tubing will slow the diffusion of gases from the test chamber, but not eliminate this possible source of error. Using a pressure sensor which could be heated along with the sample would remove this source of error. Though more expensive, such pressure sensors should be considered for future testing.

Future studies regarding polyurethane foam should be sure to control and bound the humidity levels and fill ratio expected in the packaging.

## CONCLUSIONS

Testing indicates that predicting the correct level of offgassing and therefore the final pressure in a small drum-type shipping package with polyurethane foam is dependent of correctly simulating the humidity and fill ratio experienced in the package.

The issues with polyurethane foam demonstrate the care which must be taken to understand the variables which affect the performance of a material in a shipping package. The characteristics which are important in a package are often not considered in other uses of commercial items and materials.

Performing testing of all the important characteristics is costly. Given the many parameters which can influence the results for something like polyurethane foam, it is difficult to ensure that results from testing performed in the past or by other organizations can be correctly understood and used. A central repository of packaging material test results and unified testing

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methods would allow for greater sharing of information and better predictions of package performance at a lower cost.

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