

# Development of a polyurethane rigid pour-in-place foam using Emerox polyols and ecomate blowing agent

In recent years, the demand and development of renewable source polyols has grown exponentially. As this field grows in terms of products and technology available, polyol manufacturers will have to work with formulators of polyurethane foam systems to continue to produce high quality foam systems. Although the high renewable content is appealing to many, any new system developed must still meet quality standards of today's established foams with lower amounts of renewable content polyols. These quality standards can be physical properties such as thermal aging and percent closed cell content or processing properties such as foam flowability and shelf life. In this paper, the work between Foam Supplies, Inc. and Emery Oleochemicals LLC in the development of a rigid polyurethane pour-in-place foam will be discussed. This includes a stepwise process of how both companies were able to work together to create a foam using 100 % Emery Emerox renewable source polyols and 100 % ecomate (VOC free, zero ODP, low GWP) blowing agent. There were some obstacles that needed to be overcome, and by working together, Foam Supplies and Emery Oleochemicals were able to work past them. Testing performed on the end product demonstrated that the foam had good flowability, good dimensional stability and excellent compression strength among other properties. In summary, the value of cooperation of Foam Supplies and Emery Oleochemicals was demonstrated when two companies work together toward the same end goal.

## 1 Introduction

For many years, renewable source polyols have been available for use in polyurethane foam systems. One such polyol is castor oil. It is a naturally occurring polyol ob-

tained from castor beans. Primarily it is composed of triglycerides with three units of ricinoleate. This gives a polyol with a functionality of 3 and a hydroxyl number of about 160 mg KOH/g. This chemical structure is shown in **figure 1**.

Since castor oil is already a polyol, it can be put in a polyurethane foam without the need for modification, but the low functionality and low hydroxyl number make it unsuitable for use as the sole polyol in a rigid polyurethane foam system. The unsaturated groups (carbon-carbon double bonds) found in castor oil

can also lead to degradation of the polyol or polyurethane foams made from the oil.

Many other natural oils exist, but do not have hydroxyl groups in their chemical structure. However, hydroxyl groups can be added to the oil by reacting the carbon-carbon double bonds found on their backbone. Traditionally, this is accomplished via a two-step reaction. First, the double bonds are reacted with a peroxy acid to form epoxides. Then, a nucleophile is added to the epoxide ring to form an alcohol group. This two-step reaction is shown in **figure 2**.

This two-step process is useful for making polyols out of natural oils, but the end polyol is still limited to the structure and seasonality of the original oil. The limited number of unsaturation groups and the long ligand chains will result in a polyol with a low hydroxyl number and low functionality, which in turn limits the amount that could be used in a pour-in-place rigid foam formulation. The addition of a nucleophile could also reduce the overall bio-based content of the polyol.

While the idea of making a polyurethane foam from a renewable source polyol is appealing, the end use foam must still have the same quality and processability of other foams that have less renewable content. Quality characteristics include dimensional stability, compression strength, thermal conductivity, and percent closed cell content. Processability characteristics include polyol viscosity, polyol compatibility (no separation or precipitation), foam flowability, and shelf-life stability. When formulating a rigid pour-in-place polyurethane foam, it is essential to use polyols with a high hydroxyl number (greater than 300 mg KOH/g) and high functionality

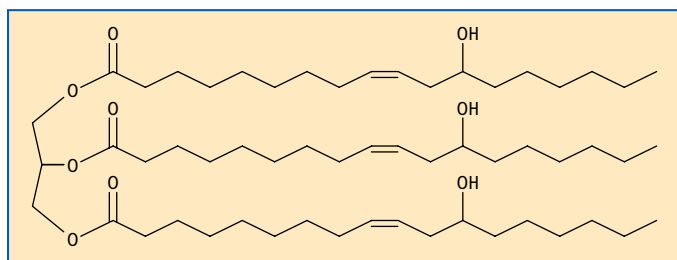
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**Fig. 1:**  
 Chemical structure of  
 castor oil



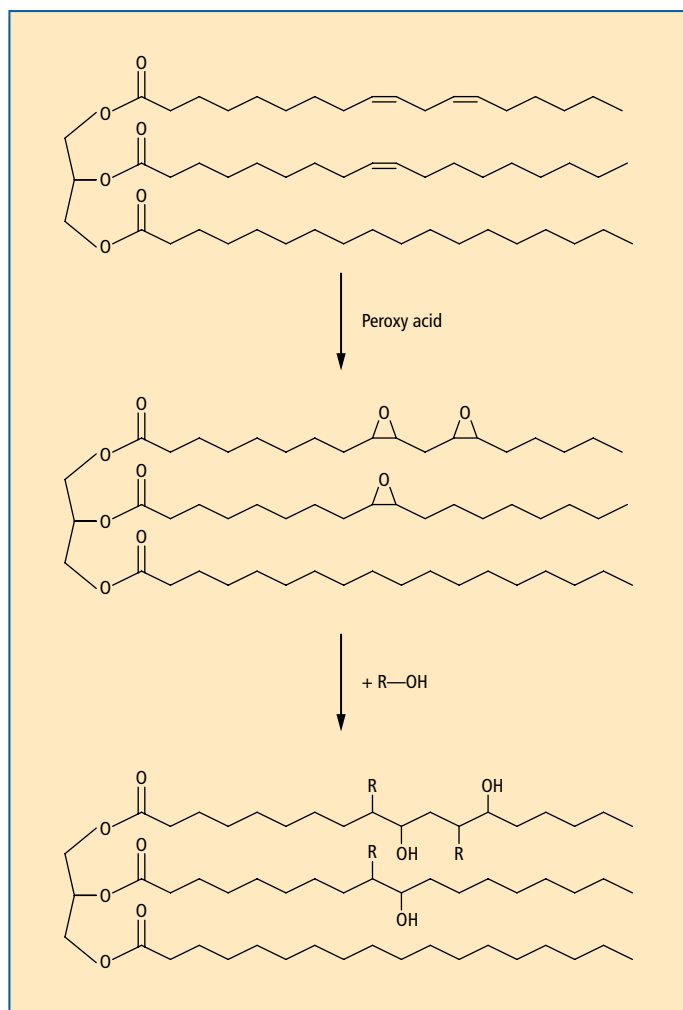
(greater than 3). Pour-in-place foams also generally have a significant amount of water in the resin blend to initiate foam rise. These characteristics of a pour-in-place foam tend to go against many natural oil polyols (NOPs). Most natural oil polyols have a hydroxyl number lower than 300 mg KOH/g and a functionality at or

less than 3. Since many NOPs are oils or modified oils, they tend to be very incompatible with water in the system. NOPs tend to have a viscosity substantially higher than petrochemical based polyols with the same functionality and hydroxyl number. These problems can be overcome by the addition of other polyols and/or other additives, but

this contradicts the end goal of this paper of formulating an ecomate blown pour-in-place foam using a 100 % renewable source polyol package. Thus, the renewable source polyol must have a hydroxyl number of at least 300 mg KOH/g and a functionality above 4. In addition, the polyol needs to be compatible and stable with water and other additives in the resin blend. This paper will show how a polyol was developed by Emery Oleochemicals for this application, and through collaboration with Foam Supplies, the polyol was engineered to work with an ecomate blown rigid pour-in-place foam formulation.

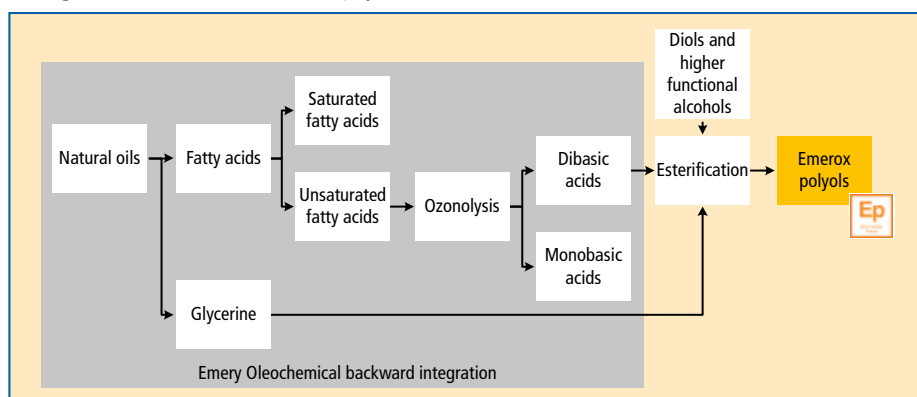
Emery Oleochemicals manufactures and sells polyols under the Emerox name. Emerox polyols are based on dibasic acids produced via Emery Oleochemicals' ozonolysis technology, as shown in **figure 3**. The ozonolysis oxidation process was developed in the 1950's to produce azelaic and pelargonic acid (C<sub>9</sub> dibasic and C<sub>9</sub> monobasic acid) from oleic acid and is a well-established large-scale production process.

The process starts with natural oils that are split into glycerin and fatty acids. The fatty acids are separated into saturated (e. g., stearic) and unsaturated (e. g., oleic) fatty acids. Oleic acid is C<sub>18</sub> monofunctional acid with an unsaturation between the C<sub>9</sub> and C<sub>10</sub> position. When reacted with ozone, the unsaturation is cleaved, forming acid groups on both sides of the cleavage. This reaction is shown in **figure 4**. The result is a mix of monobasic and dibasic acid compounds, which are separated and further purified. The dibasic acid streams from the ozonolysis process are converted to polyols (Emerox polyols) by reaction with diols, glycerin, or higher functional alcohols via esterification. The benefit is that, while there is high bio-based content from these feed streams, the chemist has all the polyol structure design freedom typical of a petrochemical ester polyol. This allows for bio-based polyols that can be better optimized for specific application needs than typical NOPs or bio-based polyols. Further, the ozone process is robust over a broad range of high unsaturation content natural oils and eliminates the seasonal-



◀ **Fig. 2:**  
Reaction of natural oils  
into polyols

▼ **Fig. 3:** Process flow chart of Emerox polyols



ity that can be present in more traditional NOP polyols.

The stepwise process designed by Emery Oleochemicals allows for polyols suited for pour-in-place foams. Polyols can be made with a broad range of functionalities and a broad range of hydroxyl numbers.

For over ten years, Foam Supplies, Inc. has produced and sold polyurethane rigid foam systems blown with ecomate blowing agent. Ecomate is a reduced environmental impact blowing agent having no ozone depletion potential, very low global warming potential, low MIR (smog value), and VOC free. Ecomate blowing agent has a boiling point of 32 °C (90 °F), making it ideal for a pour-in-place rigid foam system. Additionally, ecomate blowing agent is compatible with most polyurethane ingredients and will form shelf stable blends. Blowing agents may encounter issues with degradation at their double bond site, which can impact reactivity and cell structure. Differently, ecomate resin blends can be stored for extended periods of time without loss of reactivity or cell structure, and the resin blend will not separate during storage. A polyurethane rigid foam system blown with ecomate blowing agent and 100 % Emerox polyols would be an excellent combination of chemistries reducing environmental impact utilizing a 100 % bio-based, renewable source polyol package and a halogen free, VOC free blowing agent.

## 2 Collaboration

Foam Supplies, Inc. and Emery Oleochemicals LLC discussed using a 100 % bio-based polyol in an ecomate blown rigid pour-in-

place foam formulation. Foam Supplies began research using two of Emery Oleochemical's existing polyols for an ecomate blown polyurethane rigid pour-in-place formulation. Emerox polyol A and Emerox polyol B were selected based on their hydroxyl number and functionality, both of which were in the ranges suitable for rigid pour-in-place foams. A sample formulation, 14B96 was made for testing the two polyols. This formulation is given in **table 1**.

Two resin blends were made using the formulation 14B96, one using Emerox polyol A and the other using Emerox polyol B. The two resin blends were mixed with polymeric MDI at a weight ratio of 100 parts isocyanate to 70 parts resin blend. This gave the foams an isocyanate index of about 110. The foams were allowed to age 24 h to cure.

The following day, the foam made with Emerox polyol A was solid and dimensionally stable, but the foam made with Emerox polyol B was found to shrink. At this point, testing on polyol B was suspended. Although the foam made with Emerox polyol A looked preferable, there were three problems with the formulation. First, the foam had an excessive amount of growth after gel. This would result in excessive mold pressure when foaming parts and could lead to a high degree of damaged or defective parts. Second, the free rise foam, when cut open and tested, had a low percentage of closed cells, below 50 %. This would give foams with poor ther-

mal properties and could lead to high water absorption values. The third problem was seen after the resin blend sat on the counter for a week. A substantial amount of precipitate was seen on the bottom of the clear glass container. This would lead to storage problems as the storage container holding this material would build up precipitate over time.

The above results were shared by Foam Supplies with Emery Oleochemicals including the drawbacks experienced when using the polyol. Interpreting the results from Foam Supplies, Emery Oleochemicals then refined their process of synthesizing the polyol, producing new products, but with the same hydroxyl number and functionality. Three experimental polyol samples, each with varying degrees of modification, were sent to Foam Supplies for testing. All three experimental polyols were tested in formulation 14B96. The polyols are named A1, A2, and A3 based on their level of modification. All three polyols were tested in formulation 14B96 and observed for the following: post-gel growth, percent closed cell content, and precipitation in the resin blend. The results are summarized in **table 2**.

When using the Emerox polyol A1, all three previous problems were eliminated. The foam now had a high percent closed cell content, no precipitate formed in the resin blend, and a substantially reduced amount of post gel growth.

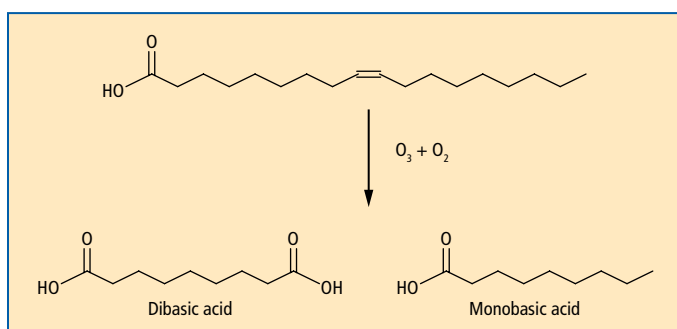
▼ **Tab. 1:** Formulation 14B96

Component	Parts
Emerox polyol (A or B)	100.0
Water	3.1
Silicone surfactant	2.8
Amine catalysts	1.8
Additive	1.0
ecomate	3.4

► **Tab. 2:** Results of modified Emerox polyols in formulation 14B96

Polyol	Post-gel growth	Percent closed cell	Precipitate formed
A1	Moderate	98.30 %	No
A2	High	94.80 %	No
A3	High	17.95 %	Yes

► **Fig. 4:** Ozonolysis of oleic acid



In these experiments, the polyol named Emerox polyol A1 is currently manufactured under the name Emerox 14270. It is a high functional, high hydroxyl polyol designed specifically for polyurethane rigid foams. It is engineered to give high crosslink density to rigid foams and can thus be used as the sole polyol in this system. Emerox 14270 is 100 % bio-based. Typical properties of this polyol are given in **table 3**.

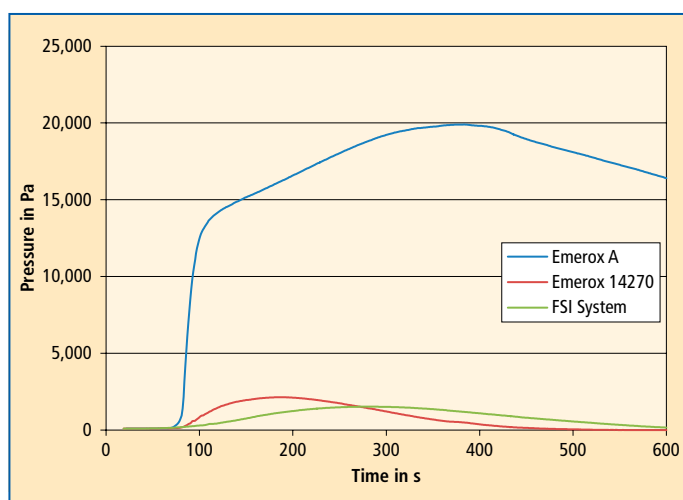
▼ **Tab. 3:** Properties of Emerox 14270

Property	Typical value/range
Bio-based content in wt%	100
Hydroxyl value in mg KOH/g	340–370
Water in wt%	max. 0.1
Acid value in mg KOH/g	max. 3.0
Viscosity at 25 °C in MPa·s	2,000–2,500
Specific gravity in g/cm <sup>3</sup>	1.09
Odor	Sweet, pleasant

▼ **Tab. 4:** Formulation 14B96-2

Component	Parts
Emerox 14270	100.0
Water	3.1
Silicone surfactant	2.8
Amine catalysts	1.8
Additive	1.0
ecomate	3.4

Test conditions	Volume change specification	Volume change result
Humid aging (70 °C and 100 % r. H.)	<7 %	3.75 %
Heat aging (90 °C)	<5 %	1.95 %
Freezer aging (-62 °C)	<5 %	0.08 %



◀ **Tab. 5:** Dimensional stability results (ASTM D2126)

◀ **Fig. 5:** Foamat plot of pressure vs. time

To further quantify the reduction in mold pressure seen when using Emerox 14270, both polyols, Emerox polyol A and Emerox 14270 were used in formulation 14B96 for testing in a Foamat machine. The Foamat apparatus is equipped with a pressure sensor, which measures pressure exhibited by the curing foam. The foam system 14B96 with the two Emerox polyols were tested in the Foamat machine as well as a standard foam system currently sold by Foam Supplies which will be called “FSI System” in this paper. The three systems were plotted on a pressure vs. time graph (**fig. 5**). In the graph, the reduction of mold pressure exhibited by 14B96 with Emerox polyol A vs. Emerox 14270 can be clearly seen. The mold pressure has been greatly reduced to a level more in-line with the standard Foam Supplies system.

### 3 Experimental

Using the formulation 14B96 with Emerox 14270, now called formulation 14B96-2 (**tab. 4**), a series of tests were performed to evaluate the system’s suitability for commercial use. These results were then compared to “FSI System”, a rigid pour-in-place foam system currently sold by Foam Sup-

plies. “FSI System” contains a sucrose/glycerin polyol with functionality of 4.5 and hydroxyl number of 360 mg KOH/g.

#### 3.1 Reactivity and density

First, the formulation 14B96-2 was checked for reactivity and density. The liquid components were brought to 25 °C (77 °F) for testing. When mixed at the proper ratio of 100 parts isocyanate to 70 parts resin blend by weight, the foam had a gel time of 85 s and a free rise density of 1.85 pcf (29.6 kg/m<sup>3</sup>). Both of these results are within the specification of the FSI System. During foam preparation, it was observed that the experimental foam, like the FSI System, had no friability observed on the surface. Surface friability in a foam system often gives poor foam-substrate adhesion resulting in substrate delamination.

#### 3.2 Dimensional stability

As with all polyurethane rigid foam systems, resistance to shrinkage is of utmost importance. Foams with substandard dimensional stability will deform when exposed to higher or lower temperatures causing damage or poor performance to the foamed part or appliance. Quality foam should resist shrink when exposed to higher or colder temperatures or high levels of humidity.

Cured foam samples of 14B96-2 were cut to 4 inch x 4 inch x 1 inch (10.2 cm x 10.2 cm x 2.5 cm) samples. Three samples each were placed in the following conditions: 90 °C, 70 °C and 100 % relative humidity, and -62 °C. The samples were conditioned for seven days, then removed and measured according to ASTM D2126 (**tab. 5**).

The rigid foam formulation 14B96-2 appears to have excellent dimensional stability, passing humid aging, heat aging, and freezer aging. All three results were well within specification set by Foam Supplies.

#### 3.3 Shelf life stability

Another important characteristic of polyurethane rigid foam systems is a long shelf life.

The resin must maintain its reactivity and cell structure over a long period of time so that the blended resin can be stored for months without compromising foam quality. Established specification is six months, but it is preferred that the product will last much longer. The FSI System is known to last over two years in ambient storage.

An accelerated shelf life stability test was performed on formulation 14B96-2. Enough of formulation 14B96-2 resin blend was made to run several hand mix tests in an accelerated shelf life aging test. First, the resin blend was mixed with polymeric isocyanate at 25 °C for an initial test. Then the resin blend was placed in an oven at 50 °C (122 °F) to be aged. At certain intervals the resin blend was removed from the oven, brought back to 25 °C and tested again. Testing at Foam Supplies estimates that one day (24 h) aged at 50 °C conditions is equivalent to seven days aged at ambient 25 °C. During each hand mix test, the reactivity gel time was recorded and an assessment of the cell structure was performed (tab. 6).

The resin blend appears to have excellent shelf life stability since even after 110 days aged at 50 °C (equivalent to over two years at ambient temperature), the foam has very little change in gel time and no change in cell structure or appearance. **Figure 6** shows a picture of the foam after 110 days aged at 50 °C showing the excellent appearance of the foam at the end of testing.

### 3.4 Water absorption and buoyancy change

The FSI System currently sold by Foam Supplies used for this comparison is approved for use as a flotation foam. To see if the new system, 14B96-2, will work in the same application, two water absorption tests were run on the foam. First, a test was performed to see how much water the foam absorbs in 24 h when submerged. Three cured foam samples measuring 4 inch x 4 inch x 1 inch (10.2 cm x 10.2 cm x 2.5 cm) were placed in a tote of water and submerged under a 2 inch (5.1 cm) head of water for 24 h. The

average amount of water absorbed was 0.011 psf (54 g/m<sup>2</sup>). The established specification is <0.1 psf, so the samples passed the test easily. The second test involves using a scale and cage apparatus that measures the buoyancy of foam. A foam sample 6 inch x 6 inch x 3 inch (15.2 cm x 15.2 cm x 7.6 cm) was submerged under water for 24 h. The buoyancy change of the foam was 0.405 %. A sample with less than 5 % buoyancy loss is considered passing, therefore this foam system passed the test easily. The results for both water absorption tests are found in **table 7**, showing that the foam system 14B96-2 appears to be well suited for flotation applications.

### 3.5 Compression strength and adhesion strength

Physical strength is critical to rigid pour-in-place foams. The foam must have a compression strength suitable for the application. In addition, the foam must also adhere well to the substrate being used. In the next set of tests, compression strength and tensile strength of adhesion were tested on both the standard Foam Supplies system and the new system 14B96-2. The tests were run side by side, using samples cut from the same place in each sample for compression and adhesion testing.

For compression, the samples were made by hand mixing foam and pouring into a cylinder. Then, samples were cut such that the foam would be compressed parallel to rise.

Five samples of each foam were compressed. The average compression strength of the Foam Supplies system was 30.26 psi (0.209 MPa). The 14B96-2 gave a compression strength of 30.62 psi (0.211 MPa).

For tensile strength, foam was hand mixed and poured on top of a sheet of fiberglass polyester, the same substrate used in boat hulls. Five samples of each were cut into 3 inch (7.62 cm) square sections and glued onto metal test platens. The samples were then pulled apart and the adhesion strength recorded. The average strength for the Foam Supplies system was 35.02 psi (0.241 MPa). The average strength for the 14B96-2 formulation was 31.09 psi (0.214 MPa). When pulled until the breaking point, all samples broke inside the foam (cohesive failure) instead of along the substrate (adhesive failure) so the adhesion strength of all samples is actually higher than the recorded strength. All results are shown in **table 8**.

### 3.6 Thermal conductivity

An essential aspect of all nominal two pound (32 kg/m<sup>3</sup>) rigid foams is a good insulation value. The thermal conductivity should be low, suitable for an insulation panel. Using a metal mold, small panel samples were made in a packed panel for k-factor testing. Then

**Fig. 6:** Foam made of resin blend 14B96-2 that was aged for 110 days at 50 °C



**Tab. 6:** Shelf life stability results (storage at 50 °C)

Storage time at 50 °C	Gel time in s
Initial test	85
Six days	93
Twelve days	88
26 days	95
110 days	93

**Tab. 7:** Water absorption results of 14B96-2

Test method	Specification	Result
Water absorption (ASTM D2127)	<0.1 psf	0.011 psf
Buoyancy change (ASTM D2842)	<5 %	0.405 %

samples were cut of each formula approximately 1.25 inch (3.2 cm) thick. The samples were then tested in a k-factor testing machine at two different median temperatures, 55 °F (13 °C) and 75 °F (24 °C). The results of 14B96-2 and the Foam Supplies system are given in **table 9**.

The results of the thermal conductivity tests show that the 14B96-2 foam has as good an insulation value as the current FSI system. This means that the foam could be used in panel insulation. It should be noted that the

foams tested here were not optimized for thermal insulation value. Improvements in insulation value could be made in several ways including, but not limited to, silicone surfactant choice/amount, blowing agent content, and reactivity profile.

A large battery of tests was performed on the system 14B96-2 (**tab. 5–9**). The tests were performed to ensure that the new foam formulation maintains the same quality and processability as the FSI System currently sold.

#### 4 Conclusions

Foam Supplies and Emery Oleochemicals have shown that a rigid pour-in-place polyurethane foam system using 100 % bio-based, renewable source polyols and ecomate blowing agent can be made. This rigid foam system had physical properties matching those of commercially available foam systems. The foam had good dimensional stability, low water absorption, high compression strength, and low thermal conductivity. The foam system is suited to a wide number of applications including, but not limited to, refrigeration, panel insulation, and flotation. The foam system also had good processability since it had an excellent shelf life, did not separate or precipitate, and had good flow properties. This foam system represents a great combination of chemistries with reduced environmental impact, combining an Emerox bio-based, renewable source polyol and ecomate, a halogen free, VOC free blowing agent. ■

Formulation	Compressive strength (ASTM D1621)	Adhesion strength to fiberglass polyester (ASTM D1623)
14B96-2	30.62 psi (0.211 MPa)	31.09 psi (0.214 MPa)
FSI System	30.26 psi (0.209 MPa)	35.02 psi (0.241 MPa)

◀ **Tab. 8:**  
Compression and adhesion results

Formulation	k-Factor at 55 °F (12 °C)	k-Factor at 75 °F (24 °C)
14B96-2	0.15 btu-in/(h-ft <sup>2</sup> ·°F) 21.62 mW/(m·K)	0.16 btu-in/(h-ft <sup>2</sup> ·°F) 23.06 mW/(m·K)
FSI System	0.15 btu-in/(h-ft <sup>2</sup> ·°F) 21.62 mW/(m·K)	0.16 btu-in/(h-ft <sup>2</sup> ·°F) 23.06 mW/(m·K)

◀ **Tab. 9:**  
Thermal conductivity results (ASTM C518)

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