

Bio-based ester polyols for flexible foam applications

Emery Oleochemicals LLC, through its new eco-friendly polyols platform, offers Emerox renewable content polyols. Emerox polyols are produced from dibasic acids that are a product of Emery Oleochemicals' proprietary ozonolysis technology. These polyols possess all the structural design freedom of a petrochemical-based polyol, but with a high renewable content and often with superior performance properties. Emerox 14060, a bio-based azelate (C₉) ethylene glycol polyester polyol developed by Emery Oleochemicals, targets "click-able" flexible ester foams and CASE applications. In this investigation, we compare flexible foam performance properties of Emerox 14060 versus an adipate (C₆) diethylene glycol polyester polyol in 32 kg/m³ (2 pcf) foam formulations. Foam "click-ability" (i.e. smooth cut as opposed to a pinched foam edge when die cut) and polyol/polyurethane hydrophobicity aspects are compared as well. Overall Emerox 14060, an azelate (C₉) ethylene glycol polyester polyol, exceeds the performance criteria for typical adipate (C₆) diethylene glycol polyester polyols for many applications and should be considered an attractive renewable alternative.

1 Introduction

Ester foams, while somewhat regionally dependent, account for approximately 5–7 % of the flexible slabstock foam market. Ester foams are used in a broad range of applica-

tions outside of typical home furnishings and/or automotive markets where better mechanical properties, consistent pore size control, and/or increased solvent resistance are desired/required.

1.1 Emerox bio-based polyols

Emerox polyols are based on dibasic acids produced via Emery Oleochemicals' ozonolysis technology (**fig. 1**). Emery Oleochemicals' ozonolysis technology and process was first developed in the 1950s to produce azelaic and pelargonic acid (C₉ dibasic and C₉ monobasic acid respectively) from oleic acid and is a well-established large-scale commercial production process.

The process begins with natural oils that are hydrolyzed (split) to produce glycerin and fatty acids. Next, the fatty acids are sepa-

rated into saturated (e.g., stearic) and unsaturated (e.g., oleic) fatty acids. Oleic acid is a C₁₈ mono-functional acid with unsaturation between the C₉ and C₁₀ positions. When reacted with ozone, the unsaturation is cleaved, forming acid groups on both sides of the unsaturated site. 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 (trade name Emerox) by reaction with diols, glycerin, or higher functional alcohols via esterification. This oleochemical process provides all the design freedom of building polyol structures similar to a petrochemical process with the key benefit of high bio-based content from these feed streams. This enables bio-based polyols that can be better optimized for specific applications by controlling functionality, hydroxyl placement (primary or secondary), and hydrophobicity. Additionally, the ozone process is robust over a broad range of natural oils with high unsaturation and eliminates seasonality effects that can be present in more traditional (e.g., castor and/or modified soy) natural oil polyols.

Emerox polyols are well-suited for a broad range of applications:

- Flexible foams: low hydroxyl number/ slightly branched polyols
- Rigid foams: high hydroxyl number/highly branched polyols
- CASE (coatings, adhesives, sealants, elastomers): low to high hydroxyl/linear polyols

Typically, Emerox polyols have renewable contents in the 70–100 % range.

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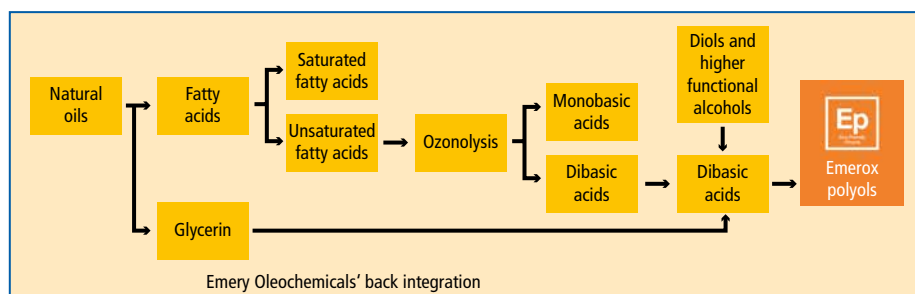
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All figures and tables, unless otherwise stated, have been kindly provided by the authors.

▼ Fig. 1: Process flow chart for Emerox polyols



2 Experimental

2.1 Overview

Flexible TDI ester foam (density: 32 kg/m³; 2 pcf) performance properties (including foam “click-ability”; e.g. smooth cut as opposed to a pinched foam edge when die-cut) are compared between Emerox 14060, an

azelate (C₉) ethylene glycol polyester polyol and a typical adipate (C₆) diethylene glycol polyester polyol. We attempted to keep the formulation as consistent as possible, with the exception of the surfactant. An alternative surfactant was required for Emerox 14060 due to its enhanced hydrophobicity. Respective ester polyol water miscibility comparisons are shown in **figure 2**.

Comparative polyester polyol structures are shown in **figure 3** and physical property comparisons for Emerox 14060 and a traditional adipate diethylene glycol are shown in **table 1**.

2.2 General procedure

The foam formulations used in this comparison study are shown in **table 2**. The reference formulation is typically used for producing a 32 kg/m³ (2 pcf) TDI ester “click-able” foam. However, due to the unique chemical structure of Emerox 14060, it is substantially more hydrophobic than typical adipate DEG polyols and therefore an alternative surfactant/emulsifier blend (i.e. surfactants commonly used in semi-rigid and/or viscoelastic applications) is required as opposed to typical surfactants utilized in ester formulations.

To prepare the foams, the side A components (polyol) were mixed (drill mixer at 1,500 min⁻¹) for 10 s, the side B (TDI 80) was added and further mixed for 10 s and then the mixture was poured into a 30.5 cm × 17.8 cm × 17.8 cm mold.

Common observations of the foam mixture are the cream time (when the mixture goes from a translucent liquid to a creamy state), the rise time (the moment when the foaming mass stops rising) and time to the appearance of “health bubbles” at the surface of the foam at approximately the time of full rise, which signifies a proper reaction balance.

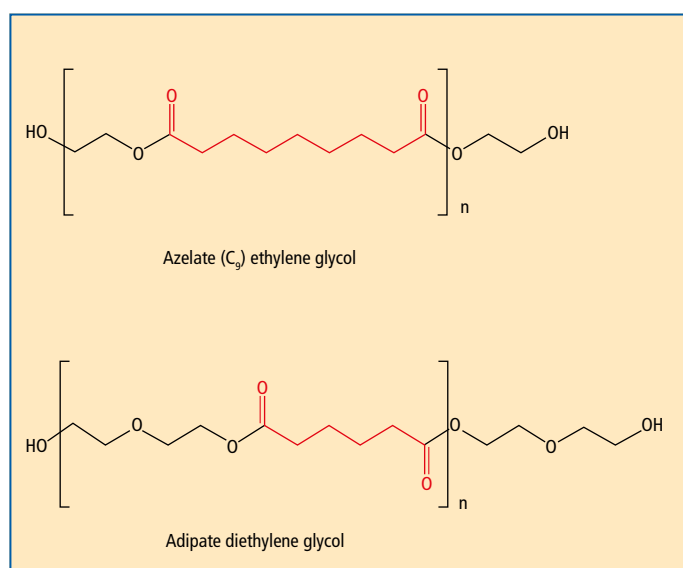
3 Results

All physical testing was done in accordance with ASTM 3574-11. The results are summarized in **table 3**.

Foam density was relatively consistent for hand mixing formulations. While no differences were observed in compression force deflection at 25 %, reduced CFD at 65 % is observed for Emerox 14060, but this may be offset with machine mixing and/or surfactant optimization. Also reduced resiliency



◀ **Fig. 2:**
(a) Emerox 14060 + 4 pphp water;
(b) adipate diethylene glycol + 4 pphp water



◀ **Fig. 3:**
Comparative polyester structures

Physical properties	Emerox 14060	Adipate/DEG
Hydroxyl value in mg KOH/g	60	60
Functionality (calculated)	3.1	2.9
Acid value in mg KOH/g	1.0	1.6
Moisture content in %	0.01	0.05
Viscosity at 25 °C (77 °F) in mPa·s	24,600	27,700
Specific gravity at 25 °C (77 °F) in g/cm ³	1.17	1.19
Gardner index color	4	2
Primary hydroxyl content in %	100	100
USDA certified bio-based content in %	82	Not applicable

◀ **Tab. 1:**
Physical property comparison

was observed for Emerox 14060, which again might be mitigated by machine mixing and/or surfactant optimization.

Compression set (50 %) was significantly improved for Emerox 14060, dry compression set (18 %) as well as wet compression set (71 %). The reduced air flow that was observed with Emerox 14060 might be improved by choosing optimized surfactants and/or machine mixing parameters.

Use of Emerox 14060 led to a significant increase of tensile strength by 21 % as well as of tensile tear strength (32 %). Despite these significant differences, the elongation changed only slightly. Emerox 14060 provided almost no foam edge welding (high “foam click-ability”) compared to a traditional adipate diethylene glycol polyol.

The solvent resistance of Emerox 14060 based foam was significantly better (less weight gain) as compared to a typical adipate diethylene glycol foam for both, aliphatic as well as aromatic hydrocarbons.

4 Summary and conclusions

The following results with Emery Oleochemicals’ bio-based ester polyol, Emerox 14060, have been observed for ester flexible foam applications:

- Greater hydrophobicity, exceeding properties obtained from adipate DEG polyols
- Significantly improved dry and wet compression sets compared to adipate DEG polyols
- Increased tensile and tear strength properties compared to adipate DEG polyols
- Better die cut foam click-ability perfor-

mance compared to adipate DEG polyols

- Superior hydrocarbon (aliphatic and aromatic) resistance, compared to adipate DEG polyols

In conclusion, Emerox 14060, an azeolate (C₉) ethylene glycol ester polyol, exceeds the performance criteria for traditional adipate (C₆) DEG ester polyol for many

applications and should be considered an attractive renewable alternative.

5 Acknowledgements

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Reagents	Emerox 14060	Adipate/DEG
Surfactant “18” *	2.0	
Surfactant “30” **		1.5
Blow reaction catalyst	0.4	0.4
Balanced reaction catalyst	0.25	0.25
Water	4	4
Toluene diisocyanate, TDI 80	47.35	47.97
Index	100	100
Properties		
Cream time in s	25	21
Rise time in s	154	140
Comments: “health bubbles”	Present	Present
Cell structure	Predominately fine	Fine

*Polyether-modified polysiloxane; **Mixture of polyether-modified polysiloxane and surfactants

Tab. 2: Ester TDI formulations (in pph)

Tab. 3: Comparison of mechanical foam properties

Mechanical properties	Emerox 14060	Adipate/DEG
Foam density in kg/m ³ (pcf)	27.1 (1.69)	27.4 (1.71)
Compression force deflection (CFD) at 25 % in kPa (psi)	3.17 (0.46)	3.45 (0.50)
Compression force deflection (CFD) at 65 % in kPa (psi)	5.17 (0.75)	7.65 (1.11)
Resiliency, ball rebound in %	18	25
Dry compression set (50 %) in %	10.8	13.2
Wet compression set (50 %) in %	12.8	43.6
Air Flow in m ³ /min (SCFM)	1.02 (36)	1.36 (48)
Tensile strength in MPa (psi)	0.123 (17.9)	0.102 (14.8)
Tear strength in N/m (pli)	473 (2.7)	350 (2.0)
Elongation in %	281	275
Foam click-ability / Edge-weld in %	2	10
Aliphatic hydrocarbon swelling*: weight gain in %	33	71
Aromatic hydrocarbon swelling**: weight gain in %	8	17

* Naphtha (VM & P) at 25 °C (77 °F): 64 h exposure / 24 h drying
 ** Xylene at 25 °C (77 °F): 64 h exposure / 24 h drying