Water Soluble Bismuth Based Curatives with Remarkable Activity and Shelf Life

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ABSTRACT

A new and inventive metal ligand technology gives rise to the first bismuth-based polyurethane curatives that are soluble in both water and hydrocarbons, offering high cure rates and long shelf life. Bismuth-based curatives have been of interest to the polyurethane industry for several decades because of their low toxicity. However, they have not achieved market penetration because of incompatibility with water-based resins for coatings, sealants and most notably, foams. As environmental and regulatory concerns eliminate HCFC blowing agents from formulation consideration, the replacement HFO blowing agents require reformulation with metal catalysts in order to achieve fast cures. If formulators choose toxic metal catalysts like organotin rather than bismuth, they should be prepared to address environmental and regulatory issues associated with such catalysts.

The Shepherd Chemical Company's new bismuth catalysts, BiCatTM 8840 and BiCatTM 8842 achieve fast cure profiles for all HFO polyurethane applications—including spray foam—while also supporting regulatory compliance, safer employee work conditions, and negligible impact to the environment. This has been achieved by inventive metalligand technology that balances acid-base and coordination chemistry. The curatives are U.S. EPA-approved and no components are restricted by REACh. Here, we report VOC measurements, cream, gel and tack-free times for these curatives vs. other metal catalysts. Foam rise profiles are presented for several formulations. We also provide foam characteristics such as thermal resistivity and density. Shelf life studies are ongoing and will be presented, to date.

INTRODUCTION

The negligible toxicity of bismuth has made it an interesting target for polyurethane curatives compared to other metal catalyst alternatives.¹ However, bismuth has never been sufficiently stabilized with respect to hydrolysis and formation of inert Bi₂O₃, impeding its widespread adoption in large polyurethane markets, particularly water bearing polyol formulations for various foam uses.² Addressing these challenges, our innovative BiCats[™] 8840 and 8842 provide water solubility to the bismuth while retaining polyol solubility and impressive cure rates. Figure 1 shows photographs of BiCats[™] 8840 and 8842 compared to BiCat[™] 8106 after the addition of water. The opacity of 8106, previously the most water-stable bismuth-based catalyst available from Shepherd Chemical, contrasts with the clarity and transparency of 8840 and 8842.

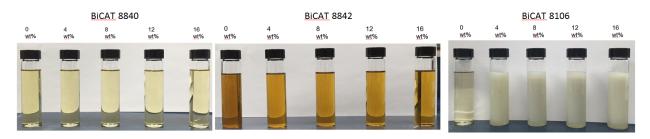


Figure 1. Water additions at varying w/w% concentrations as shown for (from left to right) BiCats[™] 8840, 8842 and 8106 reveal the miscibility of 8840 and 8842 and the precipitation of bismuth oxide from 8106. Photographs were taken 24 hours after the addition of water.

As a result of its stability in water-bearing polyol formulations, our new curatives allow formulators to address many important problems, including 1) reduction of VOCs as compared to amine catalysts; 2) negligible toxicity as compared to other metal catalysts; and 3) fast cures for reformulating spray foam polyol solutions with 4th generation

HFO blowing agents. The new BiCats'TM resistance to hydrolysis allows for pre-impregnated polyol foam formulations with unprecedented shelf lives, exceeding in some cases 15 months.

Prior to our innovation, it was impossible to use bismuth as a catalyst for water-bearing polyol formulations such as foams. While bismuth carboxylates clearly have a great affinity for the activated complex of alcohol and isocyanate— and catalyze reactions very well—they also have great potential to hydrolyze water, reprotonating the carboxylate and causing the bismuth to "fall out" as the oxide.³⁻⁷

Our insight was to use a bulky, lone-pair donating ligand, without significant potential for protonation, to protect the bismuth ion from water but allow displacement to make the biuret activated complex. It was also necessary that the ligands be compatible with the readily available bismuth carboxylates. To provide the needed coordination environment and chemistry, we focused on branched alkanolamines. As evident in Figures 2 and 3, we found the best performance in terms of hydrolytic stability and catalytic performance with two particular ligands, N,N,N',N',- tetrakis(2-hydroxyethyl)ethylene diamine (THEED, 1) and N,N,N',N'-tetrakis(2-hydroxypropyl)ethylene diamine (THPED, 2). BiCat 8842 uses THEED and BiCat 8840 uses THPED. The catalysts are also formulated with an ethylene glycol that seems to serve as a compatibilizer and phase transfer agent.¹

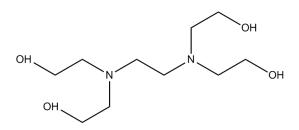


Figure 2. 1, THEED, N,N,N',N'tetrakis(2-hydroxyethyl)ethylene diamine

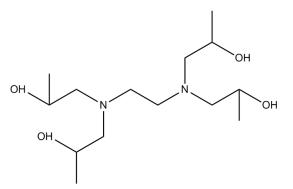


Figure 3. 2, THPED, N,N,N',N'-tetrakis(2hydroxyethyl)ethylene diamine

BiCats[™] 8840 and 8842 were formulated to address growing global concerns around chemical toxicity and environmental impact on made spaces and end users. REACh has placed pressures on manufacturers and many polyurethane catalysts are now registered or contain registered components. As the industry transitions to fourth generation HFO blowing agents, metal catalysts—like mercury, lead, organotin and bismuth—have been identified to potentially provide the necessary cure profiles. Some of these catalysts introduce employee safety, handling and regulatory issues including REACh restriction.⁸⁻¹⁰

In contrast, bismuth shows negligible toxicity to humans and other species, as well as the environment and presents an eco-friendly alternative for polyurethane formulations. BiCatsTM 8840 and 8842 were formulated with carboxylates that have been evaluated and found not to be Carcinogenic, Mutagenic, Reprotoxic (CMR) or Substances of Very High Concern (SVHC). The ligands used are similarly unregistered. Toxic Substance Control Act (TSCA) Pre-Manufacturing Notices (PMNs) have been submitted for both and approved by U.S. EPA.

Spray foams represent the largest market for polyurethanes, approaching 600 ktpy in the U.S.¹¹ These materials represent a breakthrough in building efficiency technology.¹² Regulatory phase-out of HFCs as foam blowing agents presents an opportunity and challenge for polyurethane foam formulators. Hydrofluoroolefins (HFOs) allow users to put together packages with almost no GWP and zero ozone depletion.^{13,14} However, amine catalysts that provide fast cures also react with the HFO, causing foam collapse. Replacement of the amines with, for instance, imidazole, allows foam stability, but does not provide fast enough cures for use in this application.¹⁵ Formulators have been searching for a curative that is both shelf-stable and "green," that is, low VOC, non-toxic and unencumbered by regulation. BiCatsTM 8840 and 8842 meet this need.

EXPERIMENTAL

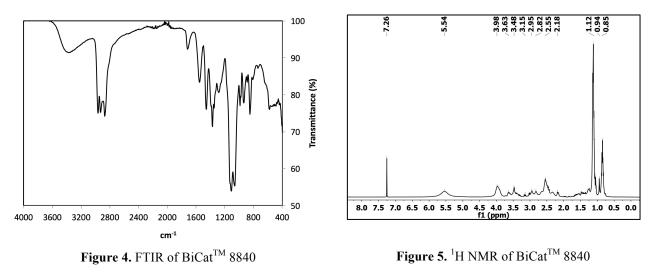
Abbreviations and Trade Names Cited

BiCatTM 8210: Bismuth octoate 28% BiCatTM 8106: Bismuth NDA / propylene glycol blend 20% Sn Oct: Tin (II) octoate DBTDL: Dibutyl tin (IV) Dilaurate TEDA: Triethylenediamine BDMAEE: Bis(2-dimethylaminoethyl)ether amine Terol® 469: Modified aromatic polyester polyol, Huntsman VoranolTM 470X: Mannich-based polyol, Dow

Preparation of BiCatTM 8840

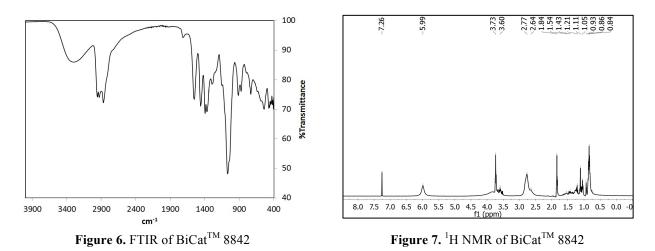
Voranol[™] 360: Polyether polyol, Dow Antiblaze® AB80: Chlorinated phosphate ester, Albermarle Dabco® DC193: Silicone surfactant, Air Products TOYOCAT® DM 70: Substituted imidazole, Toyo Dabco® K15: Potassium octoate, Air Products Solstice® LBA: Hydrofluoroolefin liquid blowing agent, Honeywell TDI: Toluene diisocyanate MDI: Methylene diisocyanate

To a 500 mL reaction flask with a nitrogen blanket, overhead stirrer, and temperature probe, is added 100 grams of BiCatTM 8106. Begin agitation and warm to 35°C. After temperature is reached, charge 60 grams N,N,N',N'- tetrakis(2-hydroxypropyl)ethylenediamine. After adding, a small exotherm is observed along with a color change from yellow to orange. After exotherm subsides, 40 g of diethylene glycol monoethyl ether is charged. Agitate at medium speed for one hour. Raise the temperature to 45°C and hold for one hour. The material is then poured into a sample cup with lid. Characterization, or "fingerprinting," of BiCatTM 8840 is conducted by FTIR, ¹H NMR, and metal concentration determination, as evident in Figures 4 and 5. BiCatTM 8840 is formulated to a bismuth concentration of 10.0 ± 1.0 wt%.



Preparation of BiCatTM 8842

To a 500 mL reaction flask with a nitrogen blanket, overhead stirrer, temperature probe, is added 50 grams of BiCatTM 8106. Begin agitation and warm to 35°C. After temperature is reached, charge 50 grams N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine. After adding, a small exotherm is observed along with a color change from yellow to orange. Using medium agitation speed, continue to mix for one hour. Raise the temperature to 45°C and hold for one hour. The material is then poured into a sample cup with lid. Characterization, or "fingerprinting," of the 8842 is conducted by FTIR, ¹H NMR, and metal concentration determination, as evident in Figures 6 and 7. BiCatTM 8842 is formulated to a bismuth concentration of 10.0 ± 1.0 wt%.



Polyurethane Applications of BiCatTM 8840 and 8842

Slabstock Foam Performance

To test the behavior and performance of BiCatTM in typical polyurethane applications, we made several tests of typical foam formulations. Table 1 features the formulations used for a foam study comparing the performance of BiCatsTM and tin catalysts in automotive slabstock foam. BiCatTM 8842 was used in a two-part polyurethane system (TDI) for slabstock applications. BiCatTM 8842 was added at 0.125 wt% to the polyol side (B-part). In addition, the polyol side contained 2.5 wt% water. The same dosage of stannous octoate curative was added to the TDI-tin-based control formulation. The test was run on a proprietary, industrial scale machine according to the owner's best practices.

Component	Weight, pphp
Polyester Polyol, OH # 60, F = 2	
TEDA	0.16
BDMAEE	0.12
Silicon surfactant	proprietary
Catalyst	0.125
Water	2.5
Index, TDI 80-20	100

Table 1. Formulation for foam study comparing tin and bismuth catalysts in an automotive slabstock foam

Spray Foam Performance and Accelerated Aging

BiCatsTM 8840 and 8842 were also tested in a spray foam formulation with HFO blowing agent. Table 2 features the formulation. Free-rise densities, cream time, string gel time, rise-free and tack free times were all collected with the fresh sample. The spray foam polyol resin was then stored at 50 °C for 1 week and retested for shelf-life stability. Thermal resistivities are measured for the foams using ASTM C518. Exotherm and foam height vs. time data were recorded on a Foamat Foam Qualification System instrument (Messtechnik, GmbH).

Table 2. Formulation for spray foam study comparing bismuth and tin catalysts with Solstice® LBA

Component	PBW
Terol® 469	60.0
Voranol [™] 470X	30.0

Voranol [™] 360	10.0
Antiblaze® AB80	10.0
Water	2.2
Dabco® DC193	1.5
TOYOCAT® DM 70	3.0
Dabco® K15	1.0
metal catalyst*	0.5
Solstice® LBA	12.0
MDI Index	110 TM

* The loading was 0.17% for BiCatTM 8210

All tests for cure rates and foam densities were performed according to method ASTM D7487 (Styrofoam Cup Test). VOC levels were measured in accordance with method VDA 277 (GC-MS) in the automotive slabstock formulation.

RESULTS and DISCUSSION

Slabstock Foam Performance

BiCatTM 8842 remained stable for many weeks in the presence of moisture, while a control formulation using bismuth neodecanoate at the same use level began to turn white after ~14 min, a sign of bismuth hydrolysis to the hydroxide. During the industrial test, 13 - 15 meters of polyurethane foam matrix in continuous mode had been produced and, from visual analysis, the BiCatTM 8842 foam matrix retained the same properties as did the stannous octoate. The cure rate and gel time were similar to that of the stannous octoate. Results are presented in Table 3.

Table 3. Foam performance characteristics for metal catalysts in an automotive slabstock foam

Catalyst	Cream Time (s)	Tack-free time (s)	foam density (kg/m ³)	
Sn Oct	14	89	35.4	
BiCat TM 8842	15	88	35.1	

Spray Foam Performance with HFO Blowing Agent

BiCats[™] 8840 and 8842 were tested in a spray foam formulation with HFO blowing agent and showed excellent performance. Table 4 and Figure 8 show the results in comparison to typical PU metal catalysts. Note that even though the metal concentration of BiCats[™] 8840 and 8842 are less than half of other bismuth-containing catalysts, their performance in this system is very similar. Also interesting is the equivalent or better performance with respect to the organotin catalysts. Finally, we note that BiCat[™] 8840 has the shortest tack-free time of all the catalysts tested, supporting increased back-end cure performance, a significant issue with bismuth polyurethane catalysts.

Table 4. Foam performance characteristics for metal catalysts in a wall foam system with Solstice® LBA

Catalyst	Free rise density (lb/ft ³)	Cream Time (s)	String gel time (s)	Rise-free Time (s)	Tack free time (s)	Thermal Resistivity (ft².°F·h/Btu)
BiCat [™] 8106	4.4 ± 0.5	7.0 ± 0.0	10.0 ± 0.7	18.0 ± 4.0	45.0 ± 1.0	2.41

BiCat [™] 8210	4.4 ± 0.1	7.0 ± 0.2	11.0 ± 1.0	22.0 ± 4.0	33.0 ± 0.2	2.15
BiCat [™] 8842	3.7 ± 0.3	7.0 ± 1.0	11.0 ± 0.7	20.0 ± 2.0	43.0 ± 2.0	1.95
BiCat [™] 8840	4.5 ± 1.0	8.0 ± 0.2	13.0 ± 0.5	22.0 ± 0.5	30.0 ± 1.0	2.30
Sn Oct	4.6 ± 1.0	7.0 ± 0.4	10.0 ± 0.2	17.0 ± 0.5	51.0 ± 6.0	2.03
DBTDL	4.7 ± 0.1	8.0 ± 0.4	17.0 ± 0.5	24.0 ± 1.0	31.0 ± 3.0	1.96

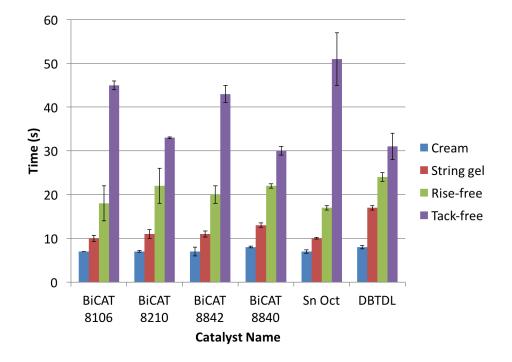


Figure 8. Foam performance characteristics for metal catalysts in a general wall foam system with Solstice® LBA

Shelf Life Stability with HFO Blowing Agent

The spray foam polyol resin was stored at 50 °C for 1 week and retested to give shelf-life stability. Results are shown in Table 5 and Figure 9. We again note that aged performance of BiCatsTM 8840 and 8842 is very similar to standard polyurethane catalysts. Importantly, the BiCatsTM 8840 and 8842 are equivalent or better to the organotin catalysts. Finally, we note the high shelf-life stability of BiCatsTM 8840 and 8842, giving equivalent performance after aging.

Catalyst	Free rise density (lb/ft ³)	Cream Time (s)	String gel time (s)	Rise-free Time (s)	Tack free time (s)	Thermal Resistivity (ft².°F·h/Btu)
BiCat TM 8106	4.8 ± 0.5	6.0 ± 0.1	10.0 ± 0.1	27.0 ± 2.0	32.0 ± 5.0	3.08
BiCat TM 8210	4.8 ± 0.2	7.0 ± 0.7	12.0 ± 0.3	21.0 ± 0.0	27.0 ± 0.0	2.45
BiCat TM 8842	5.0 ± 0.8	7.0 ± 1.7	13.0 ± 0.3	23.0 ± 1.0	29.0 ± 0.0	2.54

Table 5. Foam performance characteristics for metal catalysts after aging for 1 week at 50 °C.

BiCat TM 8840	4.6 ± 0.9	7.0 ± 0.4	13.0 ± 1.0	23.0 ± 1.0	42.0 ± 1.0	2.41
Sn Oct	4.4 ± 1.4	6.0 ± 0.6	13.0 ± 1.0	21.0 ± 3.0	29.0 ± 2.0	2.82
DBTDL	3.4 ± 0.2	8.0 ± 0.0	16.0 ± 0.0	22.0 ± 1.0	37.0 ± 1.0	2.81

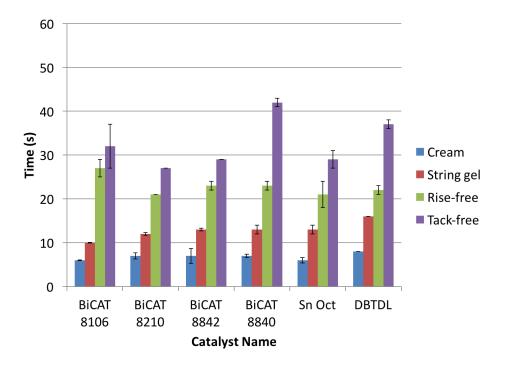


Figure 9. Foam Performance Characteristics for Metal Catalysts after aging for 1 week at 50 °C.

Maintenance of high cure rates and thermal resistivity after initial aging supports the stability of BiCat[™] 8840 and 8842 in this formulation. Foam rise and exotherm profiles are shown in Figures 10 and 11, respectively.

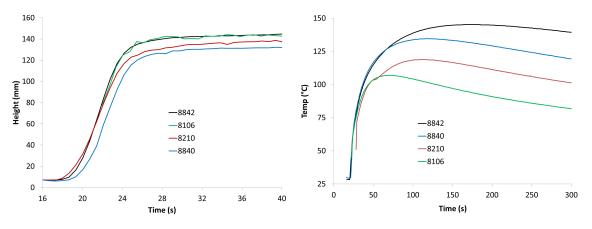


Figure 10. Foam height vs. time for BiCats

Figure 11. Foam temperature vs. time for BiCats

BiCatTM 8842 shows the highest rise and highest ultimate temperature. BiCatTM 8840 achieves the second highest temperature but does not rise as much as any of the other samples. The material catalyzed with BiCatTM 8106 rises as high as any of the samples, but reaches its highest temperature earlier with the lowest ultimate temperature of any of

the samples. BiCatTM 8210 is intermediate between 8840 and 8106 in both regards. It is noted again that the loading of BiCatTM 8210 is 1/3 of the other two catalysts because of its high bismuth content. These plots show that both 8840 and 8842 meet or exceed the performance of established bismuth based polyurethane curatives and can produce hot cures and high foam rises. Additional data on the foam rise is shown in Figure 12.

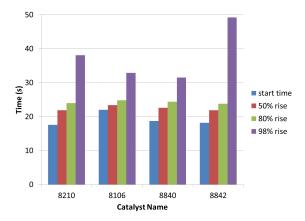


Figure 12. Foam Rise vs. Time for BiCatTM Catalysts

It is evident that while the initial rises are similar for all the BiCatsTM, 8840 achieves maximum rise much earlier than the two established catalysts, and that 8842 has a longer total rise time.

Extended Shelf-Life Stability with HFO Blowing Agent

The spray foam formulation with HFO and BiCat[™] 8842 in polyol was subjected to an extended shelf life study and measured performance showed no significant decrease after 15 months. The test was discontinued as the test material was exhausted (used up). Further tests of shelf life are ongoing.

VOC Levels

Finally, we studied the VOC levels (thermodesorption analysis according to VDA 277) from an automotive foam formulated with Sn Oct vs. BiCatTM 8842 and found values of 204 μ g/g vs. 94 μ g/g, respectively. This result has implications for fogging in automotive interiors.

CONCLUSION

The Shepherd Chemical Company has discovered and commercialized new bismuth complexes that are very active and soluble in both water and hydrocarbons, providing numerous benefits to the polyurethane industry, including:

- Negligible toxicity
- Freedom from regulation
- Unprecedented shelf life
- Low VOC
- Enabling HFC phase-out and HFO formulation

These technical advances and benefits to the market are enabled by application of The Shepherd Chemical Company's dedication to the polyurethane market, intimacy with consumer and regulatory concerns and particularly our deep and practical expertise in metal chemistry. It is now possible, with HFO LBA and BiCats[™] 8840 and 8842 to formulate spray foam resins that exceed customers' and regulators' demands for the foreseeable future.

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REFERENCES

- Duvall, T.; Eckert, N.; Sullivan, J. Novel Polyurethane Curatives. U.S. Patent Appl. WO2016114876 A1, July 21, 2016.
- 2. Nordberg, G.; Fowler, B.; Nordberg, M., Eds. *Handbook on the Toxicology of Metals*; Academic Press: Burlington, MA, **2007**.
- 3. He, Z.; Blank, W.; Picci, M. Catalyzing Cationic Resin and Blocked Polyisocyanate with Bismuth Carboxylate. U.S. Patent 6,353,057, March 5, 2002.
- 4. Arenivar, J. Bismuth Carboxylates for Polyurethane Catalysis. Polyurethanes. 1989, 89, 623-627.
- 5. Dammann, L.; Carlson, G. Tin or Bismuth Complex Catalysts and Trigger Cure of Coatings Therewith." U.S. Patent 4,788,083, November 29, **1988**.
- 6. Silva, A.; Bordado, J. Recent Developments in Polyurethane Catalysis: Catalytic Mechanisms Review. *Catalysis Reviews* **2004**, *46(1)*, 31-51.
- Luo, S.; Tan, H.; Zhang, J.; Wu, Y.; Pei, F.; Meng, X. Catalytic Mechanisms of Triphenyl Bismuth, Dibutyltin Dilaurate, and Their Combination in Polyurethane-Forming Reaction. *Journal of Applied Polymer Science*, 1997, 65(6), 1217-1225.d.
- 8. Cole, R.; Mills, G.; Parker, R.; Bolam, T.; Birchenough, A.; Kröger, S.; Fones, G. Trends in the Analysis and Monitoring of Organotins in the Aquatic Environment. *Trends in Environmental Analytical Chemistry.* **2015**, *8*, 1-11.
- Gumy, C.; Chandsawangbhuwana, C.; Dzyakanchuk, A.; Kratschmar, D.; Baker, M.; Obermatt, A. Dibutyltin Disrupts Glucocorticoid Receptor Function and Impairs Glucocorticoid-Induced Suppression of Cytokine Production. *PLOS One.* 2008, *3(10)*, e3545.
- **10.** Hoch, M. Organotin Compounds in the Environment—an Overview. *Applied Geochemistry*. **2001**, *16*, 719-743.
- 11. John, J. Spray Foam Market to Grow at 7% CAGR, Report Says. Sprayfoam.com. March 6, 2016. <u>http://www.sprayfoam.com/foam-news/spray-foam-market-to-grow-at-7-cagr-report-says-/2638</u>. (accessed June 16, 2016).
- 12. Chasar, D; Sherwin, J.; vonSchramm, V.; Chandra, S. Measured Performance of Side-by-Side South Texas Homes. In *DOE Buildings XI Conference Proceedings*, ASHRAE, December **2010**.
- 13. Honeywell Solstice® 1233zd(E) Technical Information. <u>https://www.honeywell-blowingagents.com/?document=solstice-lba-technical-brochure&download=1</u>. November 2013. (accessed June 17, 2016).
- 14. Bogdan, M.; Ross, M.; Gittere, C. Honeywell's Next Generation (LGWP) of Blowing Agents for Global Spray Foam Applications. In *CPI Polyurethanes 2011 Technical Conference Proceedings*. <u>https://www.honeywell-blowingagents.com/?document=cpi-2011-paper-honeywells-next-generation-lgwpof-blowing-agents-for-global-spray-foam-applications&download=1</u>. 2011. (accessed August 26, 2016).
- 15. Bogden, M. Honeywell International, Inc., Buffalo, NY. Personal Communication, 2016.

BIOGRAPHIES

Nathan Eckert



Nate was promoted to Project Leader for the Carboxylate-Organic Product Line with The Shepherd Chemical Company in 2015. He joined the company in 2007 as an R&D Chemist. He holds a B.S. in chemistry from the University of Cincinnati and a Ph.D. in inorganic chemistry from the University of Rochester. There he studied reactive, low coordinate transition-metal complexes with Professor Patrick Holland. As a postdoctoral research associate in the laboratory of Professor Charles Riordan at the University of Delaware, he studied the reaction mechanisms of organometallic systems. His interests include synthesis and characterization of organometallic compounds, as well as

organometallic mechanistic studies. Nate is the author of over 15 peer-reviewed papers and conference proceedings.

Robert Hart



DISCLAIMER

Rob has been the Head of R&D for The Shepherd Chemical Company since 2014. He came to Shepherd in 2005 as an R&D Chemist and has filled managerial roles in R&D and Manufacturing. He holds a B.S. in chemistry from University of Wisconsin and a Ph.D. in physical chemistry from Indiana University where he studied optically non-linear glasses with Professor Joe Zwanziger. As a postdoctoral research associate at Argonne National Laboratory with Professor Chris Benmore, he worked on quantum structure effects in supercooled water. His interests include new product development and commercialization and the role of the chemical industry in society. He is also the current leader of the ACC's Working Group on Catalysis. Rob is the author of over 25 peer-reviewed papers and conference proceedings.

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