Optimizing Processing and Performance of Spray Polyurethane Foam Using BiCAT® Catalysts and Solstice® Blowing Agents

NATHAN ECKERT
Shepherd Chemical Company
4900 Beech St.
Norwood, Ohio 45212 USA

ROBERT HART
Shepherd Chemical Company
4900 Beech St.
Norwood, Ohio 45212 USA

JENNIFER HAGGARD
Shepherd Chemical Company
4900 Beech St.
Norwood, Ohio 45212 USA

DAVID WILKES
Honeywell
20 Peabody St
Buffalo, NY 14210 USA

DAVID WILLIAMS
Honeywell
20 Peabody St
Buffalo, NY 14210 USA

ABSTRACT

Growing concerns about emissive amines, the health and environmental impacts of tin catalysts, and accelerating adoption of hydrofluoroolefin (HFO) blowing agents are driving foam systems houses to reinvent their formulation technology, especially the catalyst packages. Traditional catalyst strategies often do not meet the strict performance and EH&S requirements in current and developmental spray polyurethane foam systems. Shepherd Chemical recognized the need for new catalysts to meet these requirements and developed a new generation of hydrolytically stable bismuth-based catalysts, BiCAT 8840 and BiCAT 8842. These catalysts have shown to be a critical component in spray foam catalyst packages, optimizing the performance of spray foam systems containing fourth-generation blowing agents, especially Solstice Liquid Blowing Agent (LBA).

This paper will address the common challenges and misconceptions around formulating with metal catalysts, particularly bismuth, for spray polyurethane foams (SPF). We will provide data demonstrating the high quality and efficiency of BiCAT catalysts for processing, adhesion, physical properties, and value in a model SPF wall foam formulation that is representative of commercial formulations used by systems houses.

INTRODUCTION

Spray polyurethane foams have a broad range of uses, from packing material to thermal insulation, critical for enhanced safety and energy efficiency. In spray foam manufacturing, HFO blowing agents have emerged as the greener and more energy-efficient alternative to the hydrofluorocarbon (HFC) blowing agents of the past. These HFO blowing agents require a new approach to catalysis as traditional reactive amines compromise blowing activity and tin has been associated with toxicity issues. Due to their negligible toxicity, high activity and stability, bismuth-based curatives are sought-after by the polyurethane industry as an innocuous alternative.

Bismuth-based polyurethane curatives have been in the market since the 1980's and, just as spray foam chemistries have evolved, so have the range and performance of bismuth catalysts. Today's bismuth-based curatives, particularly The Shepherd Chemical Company's BiCATs 8840, 8842, 8106 and 8210, are designed for and have been optimized in formulations to meet modern demands for reduced volatile organic compounds (VOC's), hydrolytic stability, solubility, cold substrate adhesion and uniformity of application.

The catalysts in a spray polyurethane foam (SPF) formulation have a significant impact on the rise profile of the polyurethane foam and the final foam properties. SPF formulations often contain multiple catalysts that serve different functions in the polyurethane reaction.

As the industry transitions from HFC to HFO technology, the change in the physical properties of the blowing agent and use of hindered and blocked amine gelling catalysts introduces a need for a stronger metal blowing catalyst. The focus of this study is to compare the impact of a commonly used tin catalyst, dibutyltin dilaurylmercaptide, to bismuth catalysts. Of specific interest is the catalysts' blowing effectiveness in initiating the front-end reactivity of the SPF system under hand mix and high-pressure spray conditions, the impact on finished foam quality, and the strength of adhesion to different substrates at various temperatures.

EXPERIMENTAL

Table 1. Bismuth Catalysts Technical Data

Catalyst	Bi, wt%	Ligand(s)	Viscosity @ 25 °C, Poise
BiCAT 8106	20.0 ± 0.5	Neodecanoic acid, polypropylene glycol	< 30
BiCAT 8210	28.0 ± 0.3	2-Ethylhexanoic acid	< 250
BiCAT 8840	10.0 ± 0.5	Neodecanoic acid, polypropylene glycol, *N,N,N,N*-tetrakis(2-hydroxypropyl)ethylenediamine	< 300
BiCAT 8842	10.0 ± 0.5	Neodecanoic acid, polypropylene glycol, *N,N,N,N*-tetrakis(2-hydroxyethyl)ethylenediamine	< 300

Hydrolytic Stability of BiCAT Catalysts

BiCAT 8840 and BiCAT 8842 catalysts have proven superior hydrolytic stability. Figures 1 and 2 below show stability in varying water concentrations for one day at ambient temperature for traditional BiCATs 8106 and 8210, and hydrolytically stable BiCATs 8840 and 8842. Water additions at varying concentrations (w/w%) reveal the miscibility of the hydrolytically stable BiCATs and the hydrolysis to bismuth oxide of traditional BiCATs after one day at ambient temperature.

Figure 1. Traditional BiCAT - Precipitation of Bismuth Oxide at Varying w/w% Water Concentrations

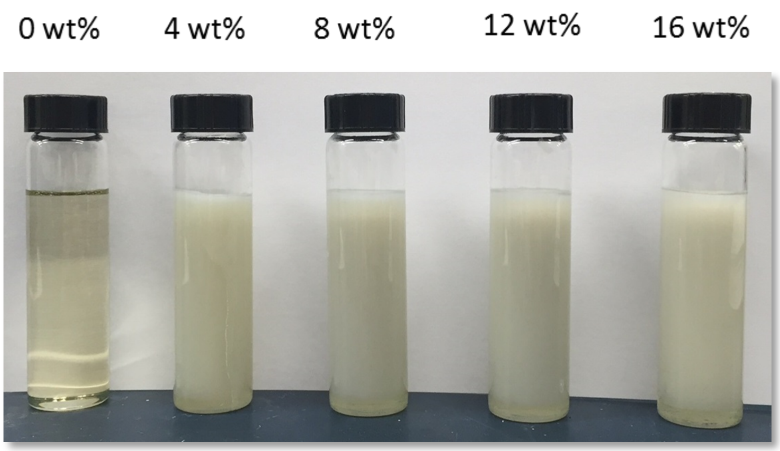
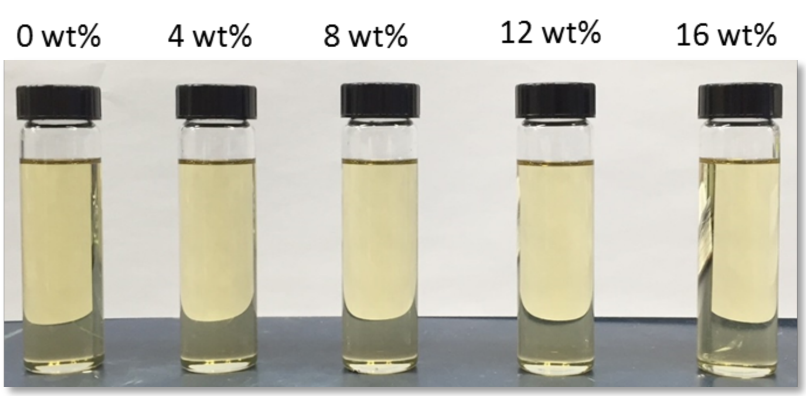


Figure 2. Hydrolytically Stable BiCAT - Water Miscibility at Varying w/w% Concentrations



Extended water stability results are shown in Figures 3 and 4. The turbidity values were stable over 6 months for each sample, exemplifying BiCATs 8840 and 8842 long-term resistance to hydrolysis.

Figure 3. Water-stability testing results for BiCAT 8840

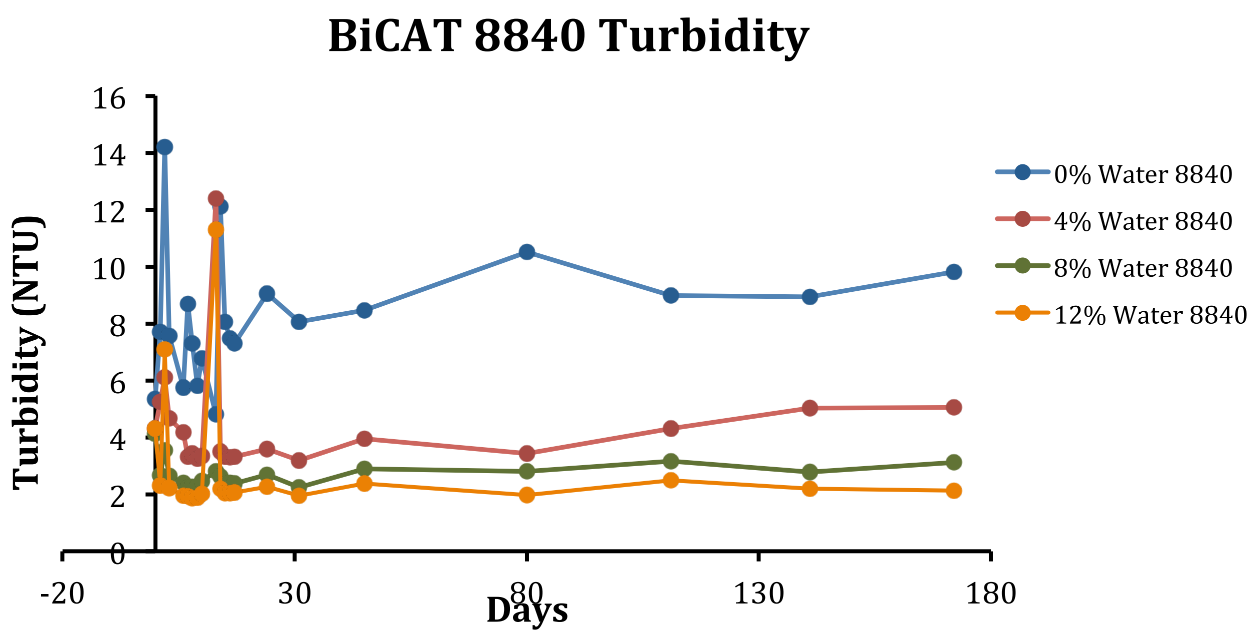
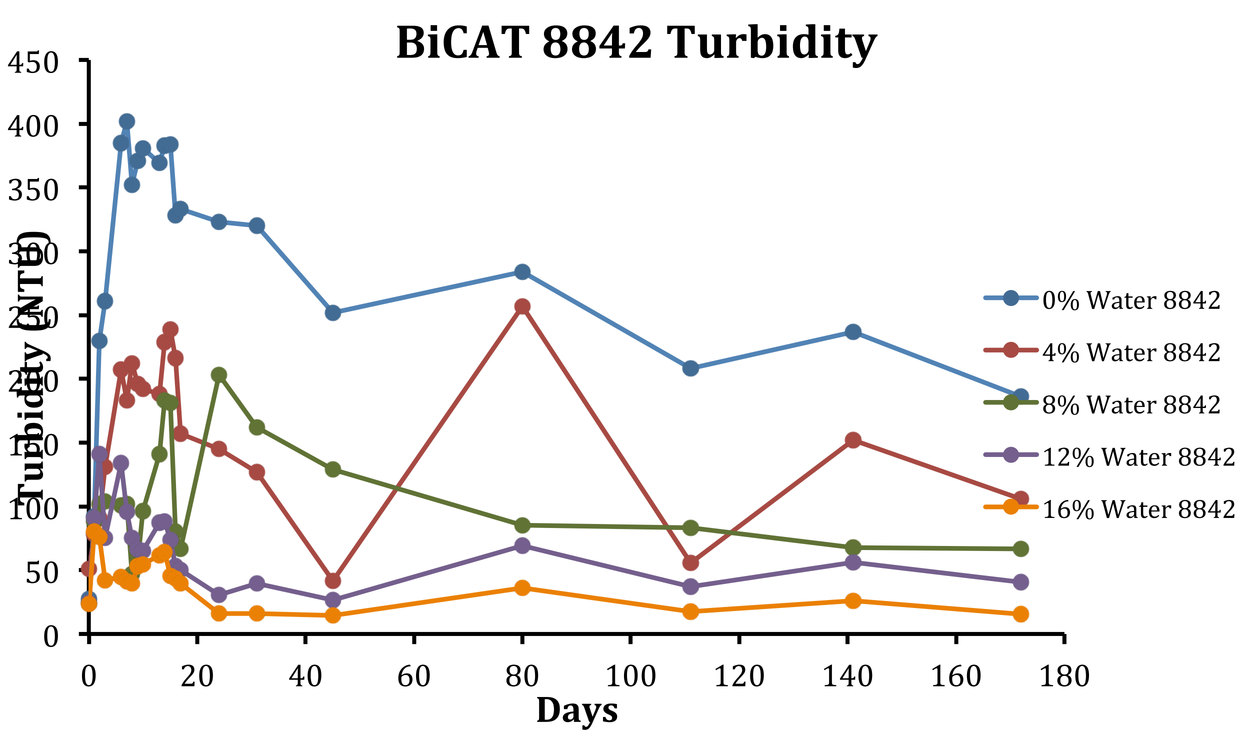


Figure 4. Water-stability testing results for BiCAT 8842



Experimental (SPF) Base Formulation

The model base formulation utilized in this study is representative of a commercial formulation. The formulation selected was for experimental purposes and not optimized for any specific catalyst or performance requirements. Table 2 contains the base formulation. All foams were prepared in Honeywell's Buffalo Research Laboratories.

Table 2. SPF Base Formulation

Raw Materials	phpp
Polyol Blend	100
Silicone Surfactant	1.5
Flame retardants	13.1
Water	2.5
Solstice LBA	18.9

Experimental Variables and Constants

Table 3 includes the constants and variables of this study. Key variables included the selection of hindered amine, tin and bismuths catalysts, catalyst concentrations, the sprayed substrates (wood and concrete) and the substrate temperatures, ranging from hot and humid to cold.

Table 3. Experimental Constants and Variables

Constants	Variables
Base SPF Formulation	Metal Catalysts
Amine Catalyst and Concentration	Metal Catalyst Concentrations
Blowing Agent and Concentration	SPF Substrates
Hand Mix Processing Conditions	Substrate Temperature
SPF Machine	
SPF Gun	
Foam Testing	

RESULTS and DISCUSSION

Impact of Metal Catalysts on Reactivity and Foam Properties

To understand the impact of metal catalysts on reactivity, specifically the rise profile and exotherm generated in the reaction, hand mix foams were tested. Metal catalysts were evaluated independently in this study to eliminate the effects of complementary amine catalysts. The polyol blend was at 50 °F and the isocyanate was at 70 °F. The polyol and isocyanate were mixed with a high shear mixer for 5 seconds. The reactivity, exotherm, rise height, rise speed and foam density were measured. While the reactivity and foam density were measured manually, the exotherm, rise height and rise speed were measured with the Foamat Foam Qualification System. The formulations are included in Table 4.

Table 4: Hand Mix Formulations

Raw Materials, g pphp	Dibutyltin dilaurylmercaptide	Bismuth		
		BiCAT 8210	BiCAT 8106	BiCAT 8842
Polyol Blend	100	100	100	100
Silicone Surfactant	1.5	1.5	1.5	1.5
Flame retardants	13.1	13.1	13.1	13.1
Water	2.5	2.5	2.5	2.5
Solstice LBA	18.9	18.9	18.9	18.9
Metal Catalyst	3	1.5*	3	3

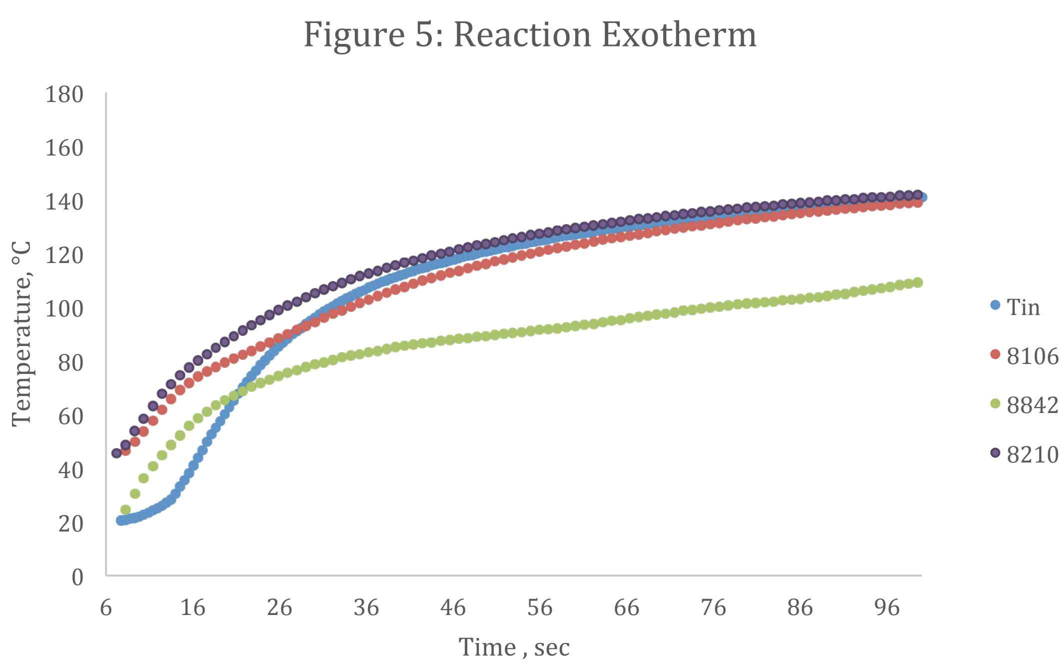
*Reduced catalyst concentration due to high Bi content in catalyst (28 wt%)/ Foam Index 107

Table 5 features the cream, gel and tack free times for each metal catalyst in the hand mix formulation. Bismuth catalysts, notably BiCAT 8106, were 2-3 times more reactive than tin with comparable foam densities.

Table 5: Hand Mix Reactivity and Foam Density

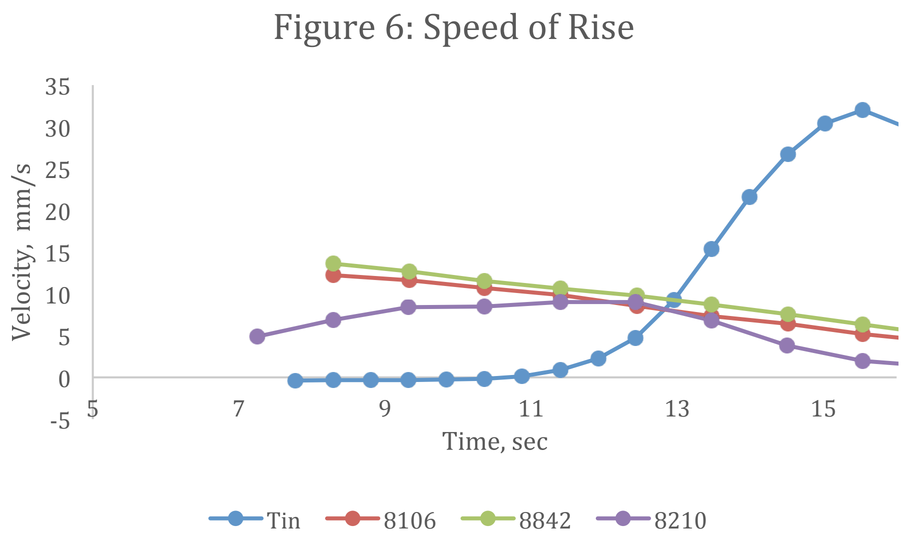
Test Data	Dibutyltin dilaurylmercaptide	Bismuth		
		BiCAT 8210	BiCAT 8106	BiCAT 8842
Reactivity, sec				
Cream	14	5	5	6
Gel	16	10	7	10
Tack Free	19	13	9	12
Foam Properties				
Density, pcf	2.19	2.23	2.23	2.32

Figure 5 shows the exotherm for each reaction. If the exotherm is too low, the reaction might not go to completion and, if the exotherm is too high, the foam could char at thicker foam applications. Exotherm is also an indication of the quality of front-end blowing catalysis. The considerably faster exotherm of bismuth versus tin exemplifies that bismuth is a stronger and more efficient front end blowing catalyst.

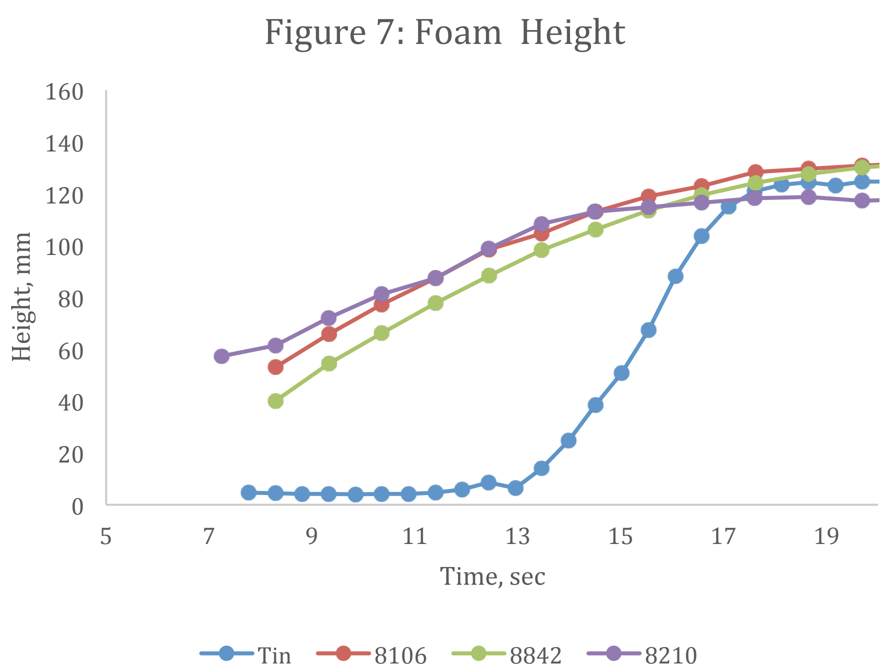


It is not only important to understand the exotherm of the reaction but also how quickly the foam rises and how long it takes to reach it maximum rise height. Figures 6 and 7 illustrate these phenomena. The ideal spray foam will rise and achieve its maximum foam height quickly. Since spray foam is applied in multiple layers and the operator does not want to spray into rising foam, rapid rise eliminates the need to wait for an extended period of time between layers.

Figures 6 shows that bismuth begins to rise almost immediately whereas the tin takes 11 seconds to begin rising. BiCAT 8210 demonstrated an immediate initiation of rise and the smoothest rise profile over time.



In parallel with quick rise, Figure 7 demonstrates that bismuth is also significantly faster in reaching maximum foam height. BiCAT 8210 reaches its maximum height at 14.5 seconds, 3.5 seconds faster than the tin catalyst. The data also shows that the bismuth catalyst provide a smoother rise profile, which is generally preferred in most SPF applications.



Spray Foam Performance

The hand mix data provided critical insight into the reactivity profile each metal catalyst provides. The next step of the study explores "real world" processing and conditions. In the SPF study, the amine catalyst was added to the formulation to provide a more realistic reaction profile and the foams were prepared on a typical spray foam machine. The formulation is in Table 6.

Table 6. Spray Foam Formulations

Raw Materials, g	Dibutyltin dilaurylmercaptide	Bismuth		
		BiCAT 8210	BiCAT 8106	BiCAT 8842
Polyol Blend	100	100	100	100
Silicone Surfactant	1.5	1.5	1.5	1.5
Flame Retardants	13.1	13.1	13.1	13.1
Amine Catalyst	9.0	9.0	9.0	9.0
Water	2.5	2.5	2.5	2.5
Solstice LBA	18.9	18.9	18.9	18.9
Metal Catalyst	3	1.5*	3	3

*Due to high 28% Bi content, a lower use level is required to achieve comparable performance.

Spray polyurethane foam formulations were prepared in bulk and sprayed under the conditions and processing parameters listed in Table 7. Processing was with a Graco H-40 proportioner and a Graco Fusion spray gun. A 4242 chamber and corresponding tip was used to spray all samples. Processing conditions were set to be consistent with field processing conditions. Although the same basic spray equipment was used throughout the study, processing parameters were adjusted to optimize spray pattern and foam quality for each formulation. Performance of catalysts vary because of the metal, chemistry of the catalyst and processing conditions. The bismuth catalyst is more forgiving to processing conditions.

Table 7: Spray Processing Parameters

Parameter	Tin Catalyst	BiCAT 8210	BiCAT 8106	BiCAT 8842
Proportioner	Graco H-40			
Chemical Processing Temp, °F				
Isocyanate	123	120	120	111
Polyol blend	126	120	120	116
Hose	122	120	120	109
Processing Static Pressure, psi				
Isocyanate	1400	1350	1510	1500
Polyol	1400	1400	1480	1500
Hydraulic	1550	1600	1675	1575
Spray Gun				
Spray Gun	Fusion AP			
Chamber	4242			
Spray Tip	Round			

Spray substrates and temperatures are listed in Table 8. Concrete was chosen as the substrate to test for cold adhesion performance. Samples were chilled to < 0 °F before spraying and, once cured, adhesion tested at ambient temperature.

Table 8: Substrates and Substrate Temperatures for Spray Foam Testing

Substrate / Temperature	Ambient Temperature	Cold, > -20 °F
Cardboard	Yes	No
Wood	Yes	No
Concrete	Yes	Yes

Table 9. Spray Foam Test Methods

Property	**Method, Instrument or ASTM Reference**	**Frequency/ Condition**
Density, lb/ft^3	ASTM D-1622-03	Initial, k-factor Sample
K- factor, $BTU.in/hr.ft^2.°F$	ASTM D-5935	12" x 12" x 1" Initial, 14 day @ 75 F
Compressive Strength, psi	ASTM D-1621-10	Initial, Parallel/ Perpendicular
Dimensional Stability, vol %	ASTM D- 2126-09	14 Day @ -29 °C 14 day @ 90 °C 14 Day @ 70 °C/ 95% RH
Closed Cell Content, %	ASTM D-6226	Initial
Adhesion, psi	Com-Ten Model # DFG1W1000	Initial
Surface	Visual	Visual

Table 10 contains the data on the finished spray foams including density, k-factor, compressive strength, dimensional stability and closed-cell content. All samples had desirable densities, 2.04-2.24 pcf. Initial and aged k-factors were all acceptable with expected deviations attributed to the un-optimized model system. Compressive strengths and dimensional stabilities were all in the suitable range with BiCAT 8842 showing particularly high dimensional stability performance under extremely cold and hot, humid conditions.

Table 10: Spray Foam Test Results

Method/ Catalyst	**Tin Catalyst**	**BiCAT 8210**	**BiCAT 8106**	**BiCAT 8842**
Density, lb/ft^3	2.04	2.17	2.24	2.08
K- factor@ 75 °F				
Initial	0.1466	0.1486	0.1444	0.1477
21 Day	0.1567	0.1570	0.1584	0.1573
Compressive Strength, psi				
Parallel	23.4	24.9	20.9	31.7
Perpendicular	15.8	13.0	15.6	11.5
Dimensional Stability, vol % @ 14 Day				
-29 °C	0.4	-4.2	0.6	-0.5
90 °C	-1.1	5.2	6.4	3.8
70 °C/ 95% RH	4.4	9.7	8.8	1.6

Beyond foam quality, the physical appearance of the processed foam samples was evaluated. For each catalyst and substrate, foam appearance, thickness and adhesion were measured. Table 11 and Figures 8-11 detail the results.

Although each formulation resulted in comparable foam thicknesses and excellent compressive strengths, there was a high degree of variation in physical appearance. The tin catalyst foams were consistently uneven with a popcorn-like appearance whereas the bismuth foams were smoother.

Table 11: Spray Foam Application and Adhesion Results

Observation/ Catalyst	**Tin Catalyst**	**BiCAT 8210**	**BiCAT 8106**	**BiCAT 8842**
Wood- RT				
Surface	Popcorn/Uneven	Smooth/Even	Smooth/Even	Slightly uneven
Thickness	~ 1 in.	~ 3 in.	~ 3 in.	~ 3 in.
Adhesion, psi	48	>64	>120	111
Concrete- RT				
Surface	Popcorn/Uneven	Smooth/Even	Smooth/Even	Slightly uneven
Thickness	~1.5 in	~1.5 in	~1.5 in	~1.5 in
Adhesion, psi	283	>179	>193	>234
Concrete- Cold				
Surface	Popcorn/Uneven	Smooth/Even	Rough/Uneven	Slightly uneven
Thickness	~1.5in.	~1.5in.	~1.5in.	~1.5in.
Adhesion, psi	>166	>121	>156	>173

Figure 8. BiCAT 8210 Spray Foam

Figure 9. BiCAT 8842 Spray Foam

Figure 10. BiCAT 8106 Spray Foam

Figure 11. Tin Catalyst Spray Foam

CONCLUSIONS

Bismuth-based catalysts, principally The Shepherd Chemical Company's BiCATs 8842, 8210 and 8106, tested in this study demonstrated industry-standard quality and efficiency for processing, foam properties, adhesion in a commercially representative SPF wall foam formulation. These model formulations demonstrate that these bismuth catalysts can be part of a commercially viable SPF foam system once optimized to achieve the specific performance requirements of each unique SPF system.

When tested under “real world” spray foam processing and conditions, the tin and bismuth catalysts resulted in foams with physical properties that meet or exceed industry standard values. The foam densities were all 2.10 ± 0.15 lb/ft^3. BiCAT 8842 contributed to foam with excellent dimensional stability over all conditions tested, while the remaining catalysts were in the acceptable range. The BiCAT 8842 SPF also had exceptional compressive strength. Visually, the spray foams formulated with bismuth were markedly smoother and more even, especially BiCAT 8210 when sprayed at both ambient and low temperatures.

In all tests, BiCAT 8210 was effectively used at a 50% loading level versus the tin and other bismuth catalysts.

Overall, the combination of Solstice LBA and BiCAT bismuth catalysts provides the manufacturer with a variety of formulation options that yield industry standard foam meeting the ultra-low GWP environmental demands of the industry.

BIOGRAPHIES

Nathan Eckert

Nate is the Technical Manager for the Carboxylate-Organic Product Segment, leading the technical group on innovations including the water-soluble bismuth catalysts, BiCAT™ 8840 and 8842, which won the 2016 Polyurethane Innovation Award. Nate’s tenure at Shepherd Chemical began in 2007 as a Research Chemist. Prior to that, he earned a B.S. in chemistry from the University of Cincinnati and a Ph.D. from the University of Rochester in New York. He spent his post-doctoral appointment at the University of Delaware studying cobalt complexes and how their reactivity could shed light on metalloenzyme behavior. Nate is the author of over 20 peer-reviewed papers and conference proceedings. He finds motivation from the great people at Shepherd, from the leadership all the way down, to enhance people’s lives and develop his individual skills in both chemistry and business.

Robert Hart

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. Rob is the author of over 25 peer-reviewed papers and conference proceedings. As he says, “It is my joy to lead our creative, hard-working research and development team. Everyday, I enjoy working with our scientists in building the future state of chemistry.”

Jennifer Haggard

Jennifer joined the Shepherd Chemical Company in September of 2017 as an International Account Manager for the Carboxylates and Organics business. She holds a B.S. in chemical engineering from Ohio University and an MBA from Belmont University. Prior to joining Shepherd, Jennifer spent her career in the food and beverage flavors industry with various roles including product management, global marketing and innovation.

David. J. Williams

Dave joined AlliedSignal (now Honeywell) in 1994 and is currently the Director of Technology for Honeywell's Blowing Agent business and Director of Technical Service for Honeywell's Fluorine Products. Dave has more than 43 years' experience in the rigid and flexible polyurethane, polyisocyanurate and extruded thermoplastic foam industry, holding a variety of research, product development, technical support, and management positions. Prior to joining Honeywell, Dave worked for 20 years at Upjohn, later Dow, and had technical responsibilities in both the polyurethane and polystyrene foam areas. Dave is the past chair of the Center for the Polyurethanes Industry (CPI) Rigid Foam Task Group and the CPI Management Committee and is currently the chair of the CPI Blowing Agent Issues Management Committee. Dave has been a member of the United Nations Environmental Program (UNEP) Flexible and Rigid Foam Technical Options Committee since 1997. Dave holds more than 45 patents, has authored more than 50 papers in rigid polyurethane and polyisocyanurate foam and was a contributing author to a textbook on polyurethane polymers (Reaction Polymers). Dave holds a B.S. degree in Chemistry from The University of New Haven, New Haven, CT, USA.

David Wilkes

Dave joined Honeywell in 2014 and is currently the Laboratory Manager and Research Scientist with the technology team for the Blowing Agent Technical Sales and Service Group. Prior to joining Honeywell Dave worked for 15 years as an analytical chemist on such projects as the Deep-Water Horizon Oil Rig spill remediation along the Gulf Coast. Dave holds a bachelor's degree in Biology from Buffalo State College.

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