# Hydrolytically Stable Bismuth Catalysts – Extended Shelf Life and Performance Studies

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# ABSTRACT

Previously, we reported the discovery of bismuth polyurethane curatives that are stable and soluble in water. These curatives maintain the typically high performance seen with traditional bismuth carboxylate compounds, even in the presence of high levels of water over long storage periods. Bismuth-based curatives remain interesting to the polyurethane community because of their high reactivity and very low toxicity. In the 2016 CPI Conference Proceedings, we reported performance and toxicity results of our hydrolytically stable bismuth catalysts in systems with HFO blowing agents. It is important to note that these new blowing agents require metal catalysts due to their different reaction profiles when compared to HFC blowing agents. In this expanded report, longer term data suggest that our bismuth catalysts work well in HFO systems and are stable over long periods, up to 12 months in certain formulations.

In this paper, we expand on previous reactivity and shelf-life studies with our new bismuth catalysts in polyurethane foam formulations. We also share our initial investigation into the comparative kinetics of our new bismuth catalysts and industry standard metal-organic catalysts.

# INTRODUCTION

Spray polyurethane foams have a broad range of uses, from packing material to thermal insulation. In spray foam manufacturing, HFO blowing agents have been noted for their environmental and energy-efficient contributions. These HFO blowing agents require metal catalysts to achieve fast cures, but traditional curative catalysts contain mercury, lead, or organotin.<sup>1</sup> Concerns regarding catalyst toxicity have resulted in tightened regulations and a shift of focus toward environmental impact and end user safety. Due to its negligible toxicity, bismuth-based curatives have been sought after by the polyurethane industry as an alternative.

However, spray foam manufacturers using catalysts containing bismuth have long grappled with instability. On one hand, the affinity of bismuth carboxylates for the activated complex of alcohol and isocyanate results in excellent catalytic activity, but it also means that they are prone to hydrolysis.<sup>2</sup> When the bismuth carboxylate hydrolyzes water, the carboxylate is reprotonated and causes precipitation of bismuth oxide,  $Bi_2O_3$ .<sup>3-7</sup> It is for this reason that bismuth catalysts are often not used for water-bearing foams or other polyol formulations.

The Shepherd Chemical Company has overcome these challenges with the invention of two bismuth catalysts that are stable and exhibit water solubility with retained hydrocarbon miscibility. To resist bismuth protonation, we selected two branched alkanolamine ligands: N,N,N',N',-tetrakis(2-hydroxyethyl)ethylene diamine (THEED, 1) and N,N,N',N'-tetrakis(2-hydroxypropyl)ethylene diamine (THPED, 2), as shown in Figures 1 and 2. These lone-pair donating ligands protect the bismuth ion from protonation, while allowing displacement and formation of the activated biuret complex. Ethylene glycol serves as a compatibilizer and phase transfer agent for these formulations.<sup>1</sup>

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





These bismuth-based polyurethane curatives boast hydrolytic stability and seamless HFO blowing agent compatibility, while offering fast cure rates, long shelf lives, and reduced VOCs compared to amine catalysts. Since our original results were reported at the 2016 CPI Conference, ongoing testing was conducted for long-term performance and stability. This paper presents extended studies of the stability, turbidity, and performance of BiCAT 8840 and 8842 catalysts in polyurethane foam formulations.

Additionally, the remarkable stability and reactivity of these bismuth catalysts led to an interest in mechanism. We utilized NMR kinetics methods to gain a clearer understanding of the mechanisms supporting these catalysts, and to compare them mechanistically to other industry-standard catalysts, including other bismuth carboxylates, stannous octoate, zinc neodecanoate and organomercury. Preliminary results are featured in this paper.

### **EXPERIMENTAL**

#### **Abbreviations and Trade Names Cited** BiCAT<sup>TM</sup> 8210: Bismuth Octoate 28% Voranol<sup>™</sup> 360: Polyether polyol, Dow BiCAT<sup>TM</sup> 8106: Bismuth NDA / propylene glycol blend Antiblaze® AB80: Chlorinated phosphate ester, 20% Albermarle Sn Oct: Tin (II) Octoate Dabco® DC193: Silicone surfactant, Air Products DBTDL: Dibutyl Tin (IV) Dilaurate TOYOCAT® DM 70: Substituted imidazole, Toyo TEDA: Triethylenediamine Dabco® K15: Potassium octoate, Air Products BDMAEE: Bis(2-dimethylaminoethyl)ether amine Solstice<sup>®</sup> LBA: Hydrofluoroolefin liquid blowing Terol® 469: Modified aromatic polyester polyol, agent, Honeywell Huntsman TDI: Toluene diisocyanate Voranol<sup>™</sup> 470X: Mannich-based polyol, Dow MDI: Methylene diisocyanate

### Hydrolytic Stability of BiCAT 8840 and 8842

BiCATs 8840 and 8842 were subjected to water stability tests as determined by observation of precipitation and measured by turbidity. Water was dissolved in small samples of the BiCATs at concentrations up to 16 wt%. All the samples were prepared to a standard weight of 20 grams, hence the samples range from 20 grams of catalyst with 0 grams of water to 16.8 grams of catalyst with 3.2 grams of water. The samples were shaken for 20-30 minutes and allowed to sit at ambient temperature for 24 hours. Photographs were taken at the 24 hour mark to show their visible stability in water. Samples were then stored at ambient temperature for 6 months. The turbidity of each sample was measured at 24 hours after mixing, and then monthly for 6 months.

#### Spray Foam Performance with HFO Blowing Agent

The formulation used for spray foam performance testing is listed in Table 1. Exotherm and foam height vs. time data were recorded on a Foamat Foam Qualification System instrument (Messtechnik, GmbH). Additionally, the formulations were tested according to the industry-standard method ASTM D7487 (Styrofoam Cup Test). Cream times and string gel times were collected on fresh sample, then stored at 50°C for one week and retested for accelerated shelf-life stability.

For an extended study of resin stability, a master-batch of polyol resin was prepared for each catalyst. The masterbatch was then stored in a sealed vessel at ambient temperature for ten (10) months. Each data point was collected by removing an aliquot of the master-batch and performing the Styrofoam Cup Test with fresh MDI.

Table 1. Formulation for spray foam study comparing Bi and Sn catalysts in HFO systems

Component	PBW
Terol <sup>®</sup> 469	60.0
Voranol <sup>™</sup> 470X	30.0
Voranol <sup>™</sup> 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 <sup>®</sup> LBA	12.0
MDI Index	110

\* BiCAT 8210 was added at 0.25 wt% because reactivity was too high at 0.5%.

# <sup>1</sup>H NMR Kinetics Experiments

All <sup>1</sup>H NMR data was collected on a Varian AS400 MHz instrument. To a 5mm NMR tube was added 250  $\mu$ L of toluene- $d_8$  and 250  $\mu$ L of phenylisocyanate. For the catalyzed reactions, the isocyanate contained 0.01 wt% of catalyst. 25  $\mu$ L of 1-octanol was added to the tube, and then shaken. This event defined t = 0 for the reactions. The reaction was tracked by <sup>1</sup>H NMR. The lock signal and field shims were pre-optimized on a sample of phenylisocyanate and toluene- $d_8$ . The variable temperature air-stream was allowed to equilibrate at the experimental temperature before insertion of the sample for at least 10 minutes. Once the sample was inserted, the lock signal was allowed to stabilize and a spectrum was acquired from 14 to 2 ppm in 1 scan with a 1.2 s acquisition time. After the first scan, the lock and shim were re-optimized. Several spectra were acquired for each sample at time intervals until the alcohol protons were no longer resolvable from the noise, or 60 min had elapsed, whichever came first. The resulting FIDs were processed typically and the signals for alcohol and carbamate were quantified. The [OH] vs. time curves were tested for different reaction orders and it was found that first order was the best fit to the data.

The rate constants,  $k_{obs}$ , for each reaction were determined from the slope of the ln [OH] vs *t* plots. The rate constants for each system were determined at 3 or more temperatures and plotted using the Eyring equation. The Eyring plots were used to determine the activation parameters ( $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$ ) for each system. Finally, the activation parameters were used to calculate the Gibbs free energy of activation,  $\Delta G^{\ddagger}$ , using Gibbs' Equation.

 $\Delta G = \Delta H - T \Delta S$ 

**RESULTS and DISCUSSION** 

### Hydrolytic Stability of BiCAT 8840 and 8842

In 2016, we reported water stability data on BiCAT 8840 and 8842 out to two (2) months. Extended water stability results are reported here out to 6 months, as shown in Figures 3 and 4. The turbidity values are stable over this time for each sample, suggesting their resistance to hydrolysis.

Figure 3. Water-stability testing results for BiCATs 8840



**BiCAT 8840 Turbidity** 

Figure 4. Water-stability testing results for BiCATs 8842



BiCAT 8842 Turbidity

The stark difference in visual precipitation between the new BiCATs and the parent bismuth carboxylate, BiCAT 8106, can be seen in Figure 5 below. The murkiness of 8106, previously the most water-stable bismuth-based catalyst available from The Shepherd Chemical Company, contrasts with the clarity and translucency of 8840 and 8842.

**Figure 5.** Water additions at varying w/w% concentrations as shown for (from left to right) BiCATs<sup>™</sup> 8840, 8842 and 8106 reveal the miscibility of 8840 and 8842 and the precipitation of bismuth oxide from 8106 after 6 months. Photographs were taken 6 months after the addition of water.



#### Spray Foam Performance with HFO Blowing Agent

#### **Foamat Results**

FOAMAT data was collected for four bismuth-based catalysts: BiCATs 8106, 8210, 8840 and 8842. Results are shown in Figure 6. The lower concentration, BiCAT 8840 performs as well as or better than our traditional bismuth carboxylate catalysts, BiCAT 8106 and 8210. Although BiCAT 8842 has a longer time to full-rise height, there is considerably less foam shrinkage with this system than with the other catalysts, as indicated in Table 2.

Figure 6. FOAMAT Results for BiCATs 8106, 8210, 8840, and 8842



Table 2. Foam Shrinkage Results for BiCATs 8106, 8210, 8840, and 8842

Catalyst	8106	8210	8840	8842
Shrinkage	7.6%	1.6%	0.9%	0.4%

#### Extended ASTM D7487 (Styrofoam Cup Test) Results

Previously, we reported the remarkable performance of BiCATs 8840 and 8842 as catalysts for HFO spray foam systems. Figure 7 features gel times for a series of catalysts using the formulation given in Table 1. Gel times for each catalyst are provided at initial formulation (indicated by solid bar to the left) and after one week storage at 50 °C (indicated by diagonal stripe bar to the right).

It is worth noting that the formulation with "BiCAT 8106 + Ligand" represents the components of BiCAT 8842 added to the formulation as individual components. That is, the catalyst portion of the formulation was 0.25 wt% THEED and 0.25 wt% BiCAT 8106, added individually with mix time between the two additions. The stark difference in behavior between BiCAT 8842 and "BiCAT 8106 + Ligand" supports the formation of a new compound during synthesis of BiCAT 8842, rather than just a physical blend. The performance of the "BiCAT 8106 + Ligand" catalyst mixture is reminiscent of what one would expect with a very strong gelling catalyst, such as TEDA or BiCAT 8210 at 0.5 wt%. We hypothesize that the free ligand containing trialkylamine groups, behaves like a typical gelling amine catalyst, whereas this behavior is stifled when bound to the bismuth carboxylate in BiCAT 8842. That is, the ligand protects the bismuth from hydrolysis while also allowing the anticipated performance of a typical bismuth catalyst.

Figure 8 shows related cream time data for the same catalyst systems. Especially noteworthy is the lower concentration BiCATs 8840 and 8842 ( $10.0 \pm 0.5$  wt %Bi) are equivalent to other, higher concentration bismuth

carboxylates (BiCAT 8106 = 20 wt %Bi, BiCAT 8210 = 28 wt %Bi). All of the BiCATs performed as well as or better than the traditional tin catalysts: stannous octoate (Sn Oct) and dibutyltin dilaurate (DBTDL).





Figure 8. Cream Times: Initial vs. One Week



#### Extended Shelf Life Study (10 months)

Over the course of ten months, three BiCATs were tested for gel time and cream time stability. Results displayed in Figures 9 and 10 and suggest that BiCAT 8210 and 8842 show long-term stability. Gel times, while higher for 8842, are also more stable over time for 8842 than 8106 or 8210. The latter two catalysts have significant "bounce" in their gel time over the 10 months, while the 8842 is stable for the majority of the test. Future studies will examine the stability impacts of making a more economically viable system by potentially lowering the concentrations of HFO vs. water. Such studies would be possible thanks to the long-term hydrolytic stability of these compounds, and could support further comparison of the stability and reactivity of 8210 versus 8842.

# Figure 9. Gel Times for Extended Shelf Life Study



Figure 10. Cream Times for Extended Shelf Life Study



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### <sup>1</sup>H NMR Kinetics Experiments

The unique, hydrolytic stability of BiCATs 8840 and 8842 led us to investigate their reaction kinetics in a model system, allowing comparison to industry-standard catalysts, including other bismuth carboxylates, stannous octoate, zinc neodecanoate and organomercury. Preliminary results are shared here.

Each catalyst was used in approximately the same concentration under pseudo-first order conditions, with 1-octanol being the limiting reagent. The 1-octanol and phenylisocyanate system is particularly convenient because only one urethane bond is formed, allowing for the reaction to reach completion as well as easy monitoring by <sup>1</sup>H NMR spectroscopy. The  $\alpha$ -proton of 1-octanol is observed at 3.4 ppm in toluene- $d_8$  while the analogous proton in the resultant urethane, octyl-*N*-phenylcarbamate, is observed at 4.0 ppm (see Figure 11). That is, these two peaks are readily resolved.





Data was collected at four temperatures for each catalyst system: 15 °C, 25 °C, 35 °C and 45 °C. Determination of the rate constant for each catalyst at each temperature allowed for calculation of the enthalpy and entropy of activation for each system. An example of the [OH] vs *t* data is shown in Figure 12, while an example of the Eyring Plot is shown in Figure 13.

Figure 12. Plot of ln [OH] vs t for the BiCAT 8210 system at 25 °C



### Figure 13. Eyring plot for BiCAT 8106



Table 3 shows the enthalpies and entropies of activation ( $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$ , respectively) for the individual catalysts. The  $\Delta H^{\ddagger}$  values show the energy required for each catalytic system to work. The  $\Delta S^{\ddagger}$  values give insight into the transition state of each catalytic reaction. The negative entropies of activation support the associative pathway of combining two molecules, one alcohol molecule and one isocyanate molecule, into a single product: the carbamate. Interestingly, the mercury system is significantly different than the other catalyst systems. The mercury system has a substantially less negative  $\Delta S^{\ddagger}$  value than the other catalyst systems, while also having a significantly higher  $\Delta H^{\ddagger}$  value. This suggests that the transition state with a mercury catalyst is more dissociative (or less associative) than the other catalyst systems. Another way to think about the mercury catalyst is that the transition state is pre-formed.

Catalyst	$\Delta H^{*}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J/mol K)
none	28.7	-206
PhHgOAc	77.0	-26
Ph3Bi	47.2	-125
BiCAT 8842	46.2	-159
BiCAT 8210	38.8	-179
BiCAT 8106	37.4	-175
BICAT Z	35.1	-183
SnOct	50.9	-129

Table 3. Activation parameters for the catalyst systems used in this study.

Using the parameters in Table 3, we can extrapolate the temperature dependence of the activation barriers for the catalysis with different curing agents. These plots are shown in Figure 14. We see that mercury is an effective catalyst over the given temperature range. That is, the activation energy is effectively temperature independent. This supports the pre-formed transition state of this particular catalyst, which is very different than the other metal catalysts. The activation energies for the rest of the catalysts are clearly temperature dependent and resemble more closely the behavior of the non-catalyzed system. These catalysts vary in effectiveness as determined by the slope of the lines in Figure 14. Enthalpy is the dominant effect for the mercury catalyst, while significant rearrangement is required for the remainder. The mercury catalyst drives the arrangement, others require fortuitous molecular collisions. A molecular mechanism for this reaction remains to be determined.

Figure 14. Temperature dependence of activation energy for the catalysts used in this study



Activation Barrier ( $\Delta G^{\ddagger}$ )

# CONCLUSION

The Shepherd Chemical Company has invented two bismuth catalysts—BiCATS 8840 and 8842—that respond to environmental regulations while achieving water and hydrocarbon miscibility, high activity, and exceptional stability. The bismuth catalysts' stability with HFO blowing agents may play an important role in the global shift toward more sustainable HFOs. BiCATs 8840 and 8842 provide long-term stability in HFO spray foam systems, especially those formulations that contain higher than typical concentrations of water. BiCAT 8210 shows promise for HFO spray foam systems that consist of low water or require less than 6-month shelf-lives. <sup>1</sup>H NMR data reported in this paper suggest that BiCATs 8840 and 8842 portray similar reaction kinetics to other bismuth, tin and zinc catalysts. Mercury, however, has very different kinetics, with an activation energy that is essentially temperature independent. This result suggests that development of a mercury replacement catalyst may be unattainable. Further studies of structural and mechanistic differences could reveal additional insights into the unique capabilities of mercury catalysts. Overall, thanks to the low VOC levels and negligible toxicity of BiCATs<sup>TM</sup> 8840 and 8842, the extended shelf life results reported in this follow-on paper affirm that it is possible to formulate spray foam resins that exceed customers' and regulators' demands for the foreseeable future.

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# BIOGRAPHIES

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DISCLAIMER

Nate was promoted to Technical Manager for the Carboxylate-Organic Product Segment with The Shepherd Chemical Company in 2016. He joined the company in 2007 as a 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.

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.

Nickie graduated from Westminster College with her Bachelor's degree in Chemistry. After working for twenty years in the pharmaceutical industry as a medicinal chemist, she came to Shepherd Chemical in 2011.

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