

## Novel Bismuth Complexes for Polyurethane Catalysis

Water-tolerant. Carboxylate-free. Enhanced Selectivity.

As regulation drives a shift toward formulations with low VOC content and alternative metals, the development of catalysts that are hydrolytically stable is of great interest in the coatings, adhesives, sealants, and elastomers (CASE) industries as waterborne formulations grow in popularity. Bismuth-based catalysts are lower toxicity alternatives that provide comparable reactivity but require a significant amount of excess carboxylic acid to provide product stability and workable viscosities. The catalysts themselves are not stable in water, and the free carboxylic acids may neutralize amine co-catalysts in certain formulations.

To address these limitations, REAXIS has developed a family of water-soluble carboxylate-free bismuth catalysts for waterborne formulations, or, more generally, for formulations in which small amounts of water must be tolerated. This technical bulletin highlights the advantages of non-carboxylate, water-tolerant bismuth catalysts REAXIS® C3211, C3212, C739W50, and C739E50, in direct comparison with standard

bismuth catalysts and dibutyltin dilaurate (DBTL), a traditional go-to catalyst often employed as an emulsion in waterborne formulations.

Most bismuth catalysts that are widely available in the market are bismuth carboxylates (including REAXIS® C716, C3208, C3209, and C3210), which are low toxicity alternatives to tin and excellent reactivity in organic formulations. However, these catalysts are susceptible to hydrolysis and form insoluble bismuth hydroxides. This transformation results in rapid deactivation of the catalyst, resulting in shorter shelf-lives for formulations that contain water. Bismuth-centered catalysts containing certain non-carboxylate ligands are less common but offer improved hydrolytic stability and reactivity in aqueous systems. While traditional bismuth carboxylates can withstand virtually no exposure to water (Figure 1), REAXIS's family of neat bismuth non-carboxylates may be diluted by over 50% water before an equilibrium is achieved that produces insoluble bismuth hydroxides.

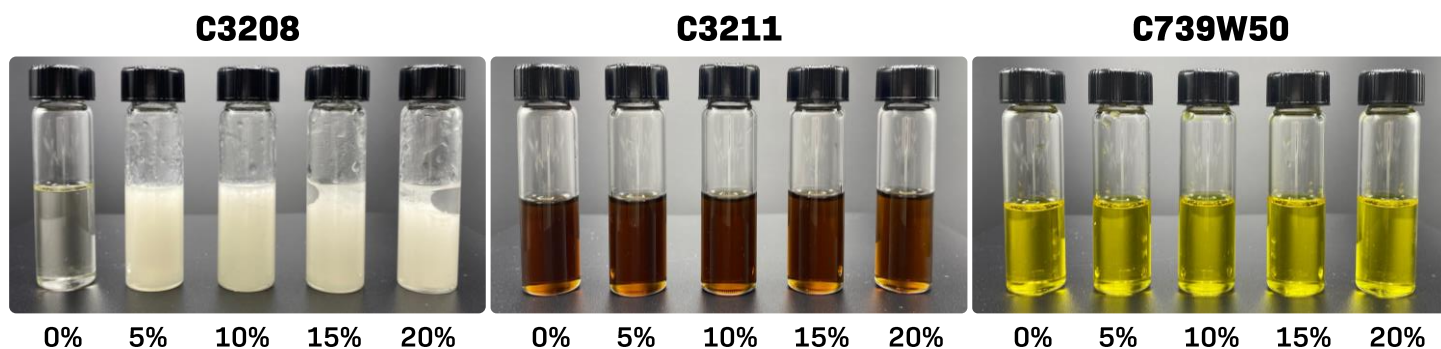


FIGURE 1. Photographs of bismuth carboxylate catalyst REAXIS® C3208 compared with water-tolerant non-carboxylate catalysts REAXIS® C3211 and C739W50 after being exposed to 0, 5, 10, and 20 wt% water for 24 h at 25 °C.

TABLE 1. Overview of bismuth-based catalysts.

Catalyst	Bi Content (%)	Diluent	Viscosity @ 20 °C (cPs)
<b>REAXIS® C3211</b>	16.3	Water	45
<b>REAXIS® C3212</b>	16.9	Diol	1830
<b>Standard A</b>	10.0	Neodecanoic acid	1250
<b>Standard B</b>	10.0	Neodecanoic acid	36,500
<b>REAXIS® C739W50</b>	19.5	Water	25
<b>REAXIS® C739E50</b>	19.5	Diol	175

As a whole, our water-compatible bismuth line offers higher metal content for superior reactivity without sacrificing shelf-life or workability in the form of high viscosities. As seen in Table 1, direct comparison shows >50% more bismuth metal within the REAXIS® C321X

series compared to Standard A and Standard B products without a significant elevation in product viscosity. In fact, Standard B's viscosity is well over 800X that of C3211. While Standard A and Standard B's products are prepared from precursors bearing carboxylate ligands,

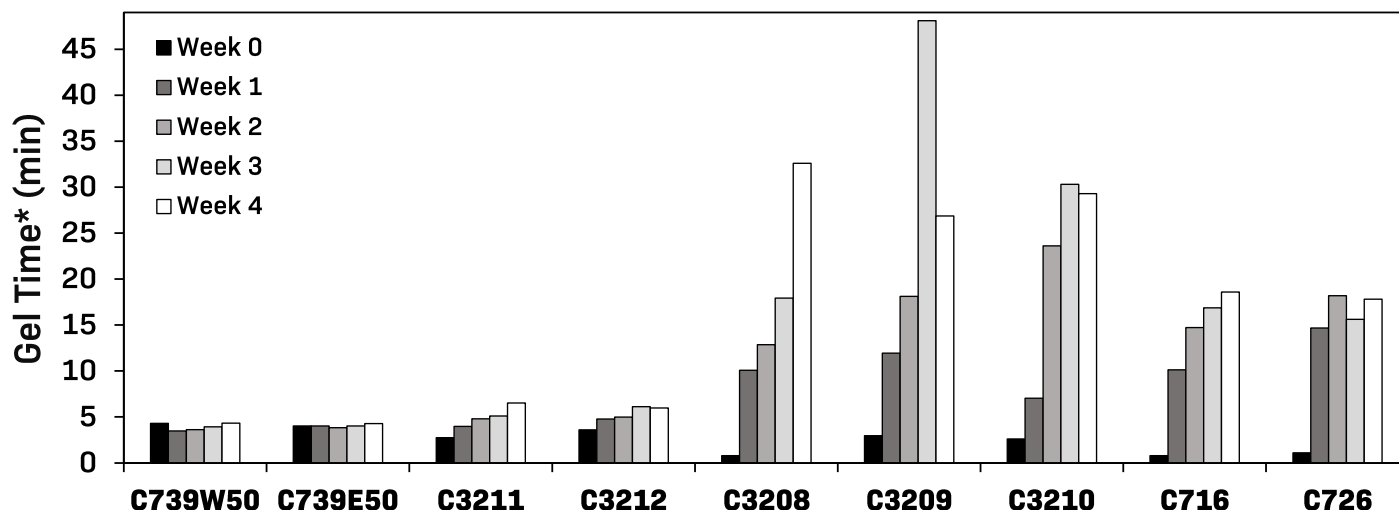


FIGURE 2. Accelerated shelf-life study of REAXIS water-soluble bismuth catalysts C3211, C3212, C739W50, and C739E50 alongside bismuth carboxylate catalysts C716, C726, C3210, C3208, and C3209 stored in polyol in a non-aqueous test formulation (NCO Content = 31.2%, OH Number = 238 mg KOH/g, Index 105, 0.1 wt.% catalyst, stored at 50 °C and cooled to room temperature before testing). \*Gel times determined according to ASTM D7997-15.

our synthetic approach allows the direct synthesis of an active bismuth complex, which can then be diluted to varying degrees in water or diols for tailored reactivity and formulation compatibility. Aside from reactivity, shelf-life must also be considered when choosing a catalyst for a formulation. As seen in Figure 2, bismuth non-carboxylates are not only potent catalysts in non-aqueous PU systems but retain original reactivity after being stored in polyol for four weeks at 50 °C. Bismuth carboxylates, however, being highly reactive initially, are prone to deactivation over time by trace amounts of water. Figure 2 highlights the trade-off between higher bismuth content/low free carboxylic acid (C3208/9/10) and lower bismuth content/higher free acid (C716 and C726) – while free carboxylic acid is not always compatible with formulations, the excess acid present in C716 and C726 provides accelerated gel times with slightly lessened deactivation over time.

With this shelf-life data in mind, we tested the reactivity of the water-soluble catalysts in a standard waterborne automotive coating formulation (Figure 3) and observed the reactivity of C3211 to be similar to that of DBTL. Films of 5 mil thickness were drawn down with a 17.5% water

letdown. Dry-through times with all catalysts at 0.1 wt% were less than one hour, whereas this exceeded 4 h in the uncatalyzed reaction. The importance of higher

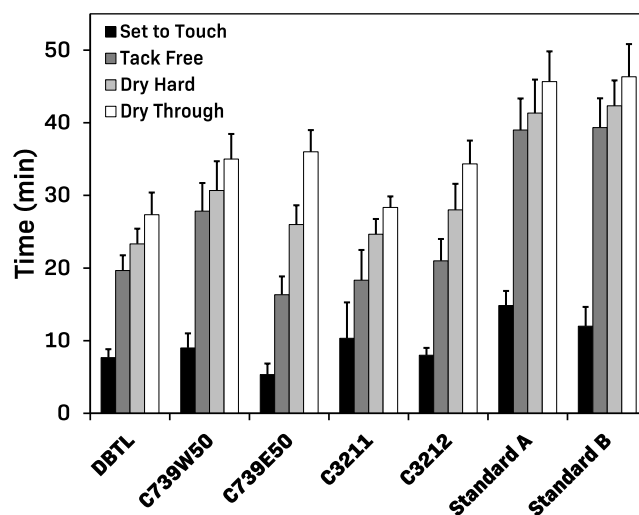


FIGURE 3. Catalyst evaluation in a standard waterborne automotive coating – Polyol Equivalent Weight = 969, NCO Content = 18.2%, 105 Index, 17.5% water letdown, 25 °C.



bismuth content for faster dry times is observed when comparing the performance between C3211/C3212 (~16% Bi) with Standards A/B (10% Bi). In a similar study (Figure 4), isocyanate consumption was monitored by FT-IR over the first two hours of reaction, revealing C3211 to be the most effective catalyst in this time frame with a steady rate of isocyanate consumption. The enhanced stability of bismuth non-carboxylate catalysts in aqueous media indicates these catalysts are not excessively reactive with water, and indeed this is observed in a model selectivity study in which isocyanate must compete with either an alcohol to produce a urethane linkage, or with water to produce a downstream urea linkage (Figure 4).

An equimolar amount of cyclohexylisocyanate was combined with a mixture comprising a 50:50 ratio of 2-methoxyethanol and water in tetrahydrofuran, such that the isocyanate has an equal probability of reacting with either, if hypothetically the reactivities between alcohol and water were identical. After two hours at 0.2 wt% catalyst loading, the reaction is complete and urethane or urea linkages are easily resolved by FT-IR. A term of "relative selectivity" is then calculated by taking the peak area ratio of urethane ( $1700\text{ cm}^{-1}$ ) to urea ( $1625\text{ cm}^{-1}$ ). As seen in Figure 4, bismuth non-carboxylate catalysts are generally found to be more selective toward urethane linkage formation, which may affect end properties of a formulation. In the example of coatings or elastomers, less reaction with water could result in less gassing during a cure as  $\text{CO}_2$  formation is limited.

As stated above, the REAXIS bismuth product portfolio includes water-soluble bismuth non-carboxylates (C739W50, C739E50, C3211, C3212) in addition to bismuth carboxylate catalysts (C716, C3208, C3209, C3210) with varying bismuth content and diluent concentration to tailor reactivity and physical properties. Bismuth/zinc carboxylate blends C708 and C717 are also available. Customized product design and sampling is available upon request.

JAMIE NOWALK, PhD and MICHAEL A. WASHINGTON, PhD  
 jamie.nowalk@reaxis.com  
 michael.washington@reaxis.com

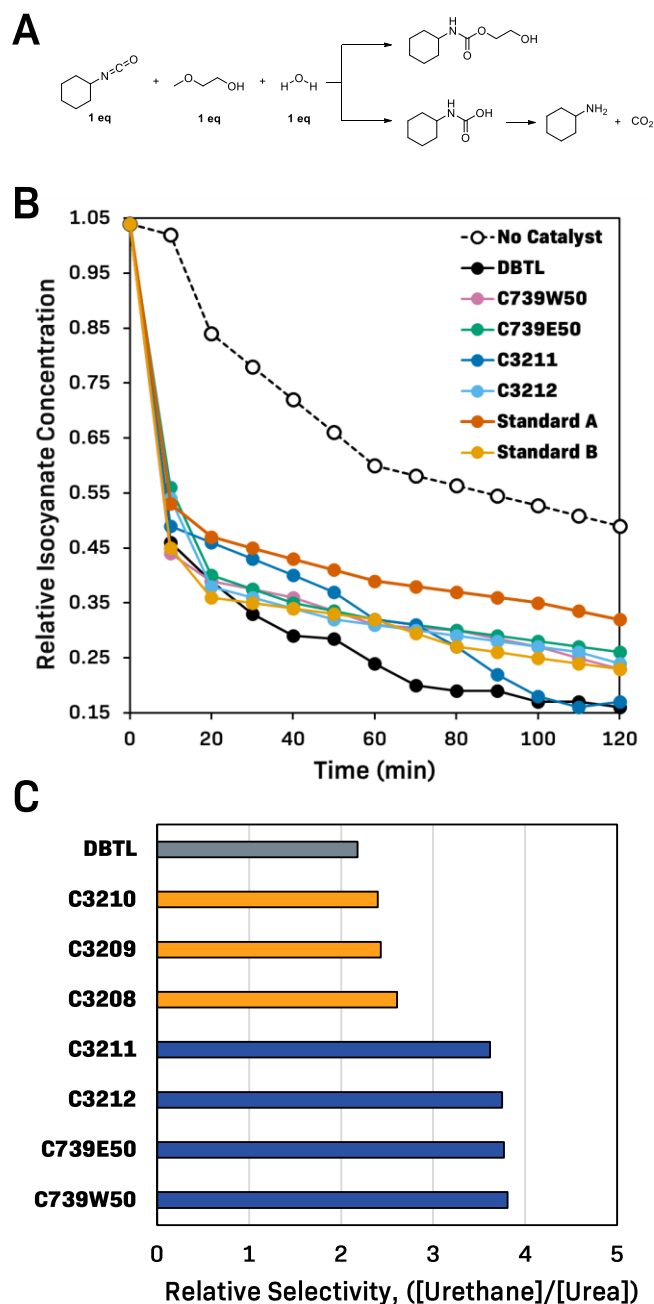


FIGURE 4. A) Model system for kinetics and selectivity study B) Monitoring isocyanate consumption by FT-IR spectroscopy after 10 min cure at 50 °C post-drawdown. Relative isocyanate concentration determined by the peak area ratio of alkyl region ( $\sim 2800\text{ cm}^{-1}$ ) to isocyanate peak ( $\sim 2200\text{ cm}^{-1}$ ). B). Relative selectivity of each catalyst, where relative selectivity = (Peak area  $1700\text{ cm}^{-1}$ ) / (Peak area  $1625\text{ cm}^{-1}$ ).

