

Development of Organometallic and Metal-Organic Catalysts for Polyurethane Applications

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Abstract

A variety of organometallic and metal-organic catalysts have been developed employing organotin, inorganic tin, bismuth, and zinc metals. The selected catalysts were evaluated for catalytic activity, physical property development, and catalyst shelf life in both MDI/HDI elastomers and 2K waterborne/solventborne polyurethane formulations.

The catalysts of interest demonstrated excellent catalytic activity and a range of performance levels providing “tunable” reactivity based on catalyst selection and loading. While offering “tunable” reactivity, the catalysts also offered high levels of hardness, chemical resistance, and color/gloss property development. Additionally, catalyst selection was found to play a critical role in reactivity under high levels of humidity, selectivity towards the NCO/OH reaction, and polyol shelf life.

Based on these observations a library of catalysts have been developed that offer adjustable levels of catalytic reactivity, exceptional physical property development, enhanced reactivity and stability in aqueous environments, and improved polyol shelf life. Furthermore, the utilized inorganic Sn-, Bi-, Zn-based catalysts offer potential replacements for DBTL and related organotin-based catalysts as stricter environmental regulations on organotin use are enforced.

Background

While organotin-based catalysts, such as dibutyltin dilaurate (DBTL), have traditionally been used in polyurethane-based applications, recent regulatory changes have restricted their sustainability and driven a demand for environmentally friendlier versions of current products and practical non-organotin replacements such as inorganic Sn-, Bi-, and Zn-based materials.¹ Moreover, while previous delayed-action (long-induction period and sharp back-end curing) industrial benchmarks, such as phenyl mercuric acetate, have been phased out due to toxicity concerns, suitable substitutes have been elusive and viable alternatives are essential.²

In most polyurethane applications a catalyst that provides a high level of reactivity, good versatility and stability, excellent physical property development, and a high level of selectivity towards the polyol-isocyanate reaction is ideal, however, this “universal catalyst” has eluded researchers for many years and no suitable material has yet been identified.³ DBTL has been generally accepted as the most effective catalyst as a result of its generally balanced and versatility. Unfortunately, DBTL does not typically afford the delayed cure demonstrated by traditional mercury-based materials, a high degree of selectivity towards the polyol-isocyanate reaction, and catalyst stability may often become a concern in waterborne formulations or upon exposure to water. Furthermore, DBTL and related materials have come under intensifying scrutiny as a result of environmental and toxicity concerns, increasing the demand for viable substitutes. Catalysts based on alternative metals, such as inorganic Sn, Bi, Zn, and Zr have been viewed as promising replacements since they possess lower toxicity levels, high catalytic activity, and greater levels of selectivity.^{4,5,6}

An additional concern, that is particularly relevant to waterborne applications and environments possessing high levels of relative humidity, is the selectivity of the polyol-isocyanate reaction, which is often highly dependent on the nature of the catalyst being utilized. The water-isocyanate side reaction can be extremely detrimental to a 2K WB PU coating as it often results in foaming/CO₂ generation, which can lead to pinholes, low gloss, and other film defects (**Figure 1**). Moreover, undesired reactivity between the isocyanate and water may also result in reduced pot life. However, selection of an appropriate catalyst may help to greatly increase the drying speed, pot-life, and polyol-isocyanate selectivity of the coating.⁶⁻⁷ As a result, the design of hydrolytically stable, water-soluble, 2K WB PU catalysts that possess exceptional catalytic activity and impart a high level of selectivity is of great importance.

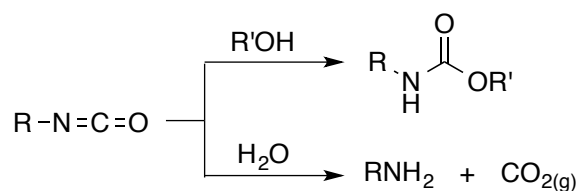


Figure 1. Production of CO₂ as a result of NCO/H₂O reactivity.

While catalytic activity, selectivity, and property development are vital characteristics when selecting the best catalyst for a polyurethane-based application, the stability and shelf life of a catalyst can play an equally critical role in catalyst selection. Whereas catalysts such as DBTL provide balanced reactivity and good versatility, its long-term stability in a polyol (“part A”) or aqueous environment in the case of a waterborne formulation can often lead to decreased levels of reactivity and even decomposition of the catalyst.^{3,7} The development of stable catalysts with

improved shelf lives and enhanced hydrolytic stability in aqueous environments places a greater demand for high performance catalysts that meet all of the desired requirements.

This study showcases the utility of a variety of organotin-, inorganic tin-, Bi-, and Zn-based catalysts in both MDI/HDI elastomers and 2K waterborne/solventborne polyurethane formulations. The library of catalysts demonstrates “tunable” catalytic activity, excellent color/gloss, and physical property development and offers novel non-organotin alternatives for the traditionally used DBTL.

Experimental

Investigated Catalysts

A variety of commercial and experimental organotin-, inorganic Sn-, Bi-, and Zn-based catalysts were utilized in this study (Table 1).

Table 1. Library of Utilized Catalysts

Inorganic Tin Catalysts		Bismuth Catalysts	
C109	Stannous Octoate/Plastizicer Blend	C716	Bismuth Neodecanoate
C114	Stannous Oleate	C717	Proprietary Bismuth/Zinc Blend
C125	Stannous Neodecanoate	C723	Bismuth Oleate
C129	Stannous Octoate	C726	Bismuth Octoate
		C739 E50	Proprietary
		C739 W50	Proprietary
Organotin Catalysts		Zinc Catalysts	
C216	Diocetyl tin Dilaurate	C620	Zinc Octoate
C218	Dibutyltin Dilaurate	C622 W78	Proprietary
C226	Dibutyltin Diacetyl Acetonate	C717	Proprietary Bismuth/Zinc Blend
C228	Diocetyl tin Diacetate		
C311X	Dibutyltin Bis-(2-ethylhexanoate) Solution		
C320	Diocetyl tin Dilauryl Mercaptide		
C321	Dimethyltin Dilauryl Mercaptide		
C325	Dimethyl Dineodecanoate		
C331	Proprietary		
C333 E50	Proprietary		
C333 W50	Proprietary		

MDI Elastomer Formulations A and B

MDI elastomer formulation A was prepared using the desired catalyst ($1.0\text{--}2.0 \times 10^{-4}$ mol), a 98% polypropylene oxide-based triol and 2% 1,4-butanediol (by wt.) polyol blend (60.0 g), and a polymeric isocyanate based on diphenylmethane-diisocyanate (MDI) (8.0 g, 1.05:1 NCO/OH).

MDI elastomer formulation B was prepared using the desired catalyst (1.0×10^{-4} mol), a 80% polypropylene oxide-based triol, 17% propylene oxide-based triol and 3% ethylene glycol (by wt.) polyol blend (60.0 g), and a polymeric isocyanate based on diphenylmethane-diisocyanate (MDI).

HDI Elastomer Formulation

The HDI elastomer formulation was prepared using the desired catalyst (1.6×10^{-4} mol), a 98% polypropylene oxide-based triol and 2% 1,4-butanediol (by wt.) polyol blend (60.0 g) and an aliphatic isocyanate trimer based on hexamethylene diisocyanate (HDI).

Two-Component Waterborne (2K WB) Coating Formulations A and B

Waterborne coating formulation A was prepared using a hydroxyl-bearing, polyester polyol dispersion (205.5 g), rutile TiO₂ pigment (65.3 g), defoamer (3.8 g), dispersant (2.3 g), flow modifier (3.4 g), rheological modifier (0.9 g) and a 3:1 mixture of a water-dispersible, aliphatic polyisocyanate and ethyl-3-ethoxypropionate (9.0 g) to achieve a 1.1 NCO/OH ratio. Catalysts were added to achieve a final catalyst concentration of 0.1% by weight on resin solids.

Waterborne coating formulation B was prepared using a water-reducible polyester polyol (295.6 g), a silicone-based substrate wetting agent (4.4 g), a 10% aqueous ammonia solution (23.4 g), a water-dispersible polyisocyanate based on hexamethylene diisocyanate (HDI) (462.0 g), and water (641.3 g) to achieve a 1.4-1.5 NCO/OH ratio. Catalysts were added to achieve a final catalyst concentration of 0.2 or 0.4% by weight on resin solids.

Two-Component Solventborne Coating Formulation

The solventborne polyester urethane coating formulation was prepared using a branched, hydroxyl-bearing, polyester polyol dispersion (58.6 g), an aliphatic polyisocyanate resin based on hexamethylene diisocyanate (HDI) (12.7-13.3 g), rutile TiO₂ pigments (38.0g), dispersant (1.42 g), flow modifier (2.36 g), ethyl-3-ethoxypropionate (71.2 g), and 1-methoxy-2-propanol acetate (18.22 g) to achieve a 1:1-1:2 NCO/OH ratio. Catalysts were added to achieve a final catalyst concentration of 0.1% by weight on resin solids.

Determination of MDI/HDI Elastomer Gelation

The desired catalyst and polyol blend were mixed at 2000 rpm for 15 s using a high-speed mixer. The isocyanate was then added and the formulation was mixed at 2000 rpm for an additional 15 s. The mixture was then poured into a gel time apparatus and the time required to achieve gelation was reported. All experiments were performed at room temperature. All data is reported as the average of 3 trials with the reported error being the standard deviation of those trials.

Determination of Shore A Hardness

Using MDI elastomer formulation A the desired catalyst (1.0×10^{-4} mol) and polyol blend were mixed at 2000 rpm for 15 s using a high-speed mixer. The isocyanate was then added and the formulation was mixed at 2000 rpm for an additional 15 s. The mixture was then cast into an

aluminum book mold (5 cm diameter, 8 mm thickness) and post-cured at 60 °C for 1 h. Following post-curing the mold is allowed to cool to room temperature and the samples are removed. Shore A hardness was determined using an ASTM Shore A durometer. All data is reported as the average of 3 trials with the reported error being the standard deviation of those trials.

Catalyst Shelf Life Studies

Using MDI elastomer formulation A the desired catalyst (1.0×10^{-4} mol) and polyol blend were mixed at 2000 rpm for 15 s using a high-speed mixer. The blend was then stored at room temperature in a plastic container for a set amount of time. The isocyanate was then added and the formulation was mixed at 2000 rpm for an additional 15 s. The mixture was then poured into a gel time apparatus and the time required to achieve gelation was reported. All experiments were performed at room temperature. All data is reported as the average of 3 trials with the reported error being the standard deviation of those trials.

FT-IR ATR Curing Profile

Reaction monitoring was performed using Fourier Transform Infrared (FTIR) spectroscopy (Jasco FT/IR-4100). Waterborne coating formulation A was drawn down onto aluminum foil to provide a thickness of ~2 mm and aluminum stripes were removed at various time points for analysis. Disappearance of the NCO peak (2270 cm^{-1}) was monitored over time and compared against an internal C-H reference peak (2935 cm^{-1}) to compensate for wavelength film penetration as the refractive index of the material changed during curing.

2K Waterborne/Solventborne Coating Physical Property Development

Pot life was determined by measuring 60° gloss as a function of time after mixing using a gloss meter in accordance with ASTM D523. A sharp, linear decline in gloss was taken as an indication of pot life.

Dry time was determined following ASTM D5895. The coating was applied to a 12 x 1 inch glass substrate and placed beneath a dry time recorder at a rate of 1 inch per minute. As the coating dries the dry time recorder stylus produces characteristic markings associated with the 4 stages of drying (set-to-touch, tack-free, dry-hard, and dry-through).

Coating hardness was determined using pencil hardness as described in ASTM D3363. Pencil hardness ranged from 6H (hardest) through H, F, HB, B, and 6B (softest). Solvent resistance (MEK double-rub) was determined as described in ASTM D4752.

Coating adhesion was measured according to ASTM D3359 method B using the cross-cut tape adhesion test. A lattice pattern of incision was created through the coating, pressure sensitive tape was applied, and then rapidly removed. Adhesion values were based on the area

of coating removed from 5B through 0B (5B – no coating removed, 4B - <5% removed, 3B – 5-15% removed, 2B – 15-35% removed, 1B – 35-65% removed, and 0B - >65% removed).

Results and Discussion

Catalyst selection plays an enormous role in many polyurethane applications and was examined in MDI elastomer formulation A (**Figure 2**). Several organotin-, inorganic Sn-, Bi-, and Zn-based were evaluated and demonstrated a range of catalytic activity as reflected by the gelation times. Catalysts such as C726, C226, and C320 exhibited faster gelation than C218 (DBTL) while others such as C114, C723, C620, and C331 revealed slower or delayed curing when compared to C218. This data demonstrates a “tunable” reactivity or ability to dictate curing time based on the selection of catalyst.

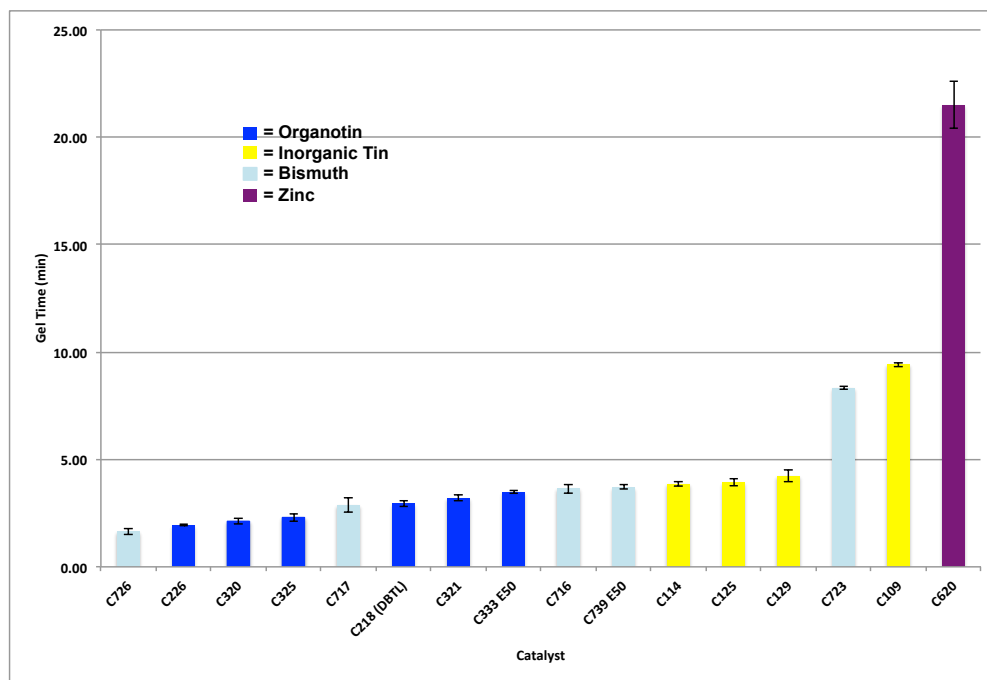


Figure 2. Catalyst activity as determined by gelation time in MDI formulation A.

A similar trend is observed in **Figure 3** when evaluating catalyst selection in a HDI elastomer formulation. While many catalysts, such as C233 and C325, remained more active than C218, others like C716, C739E50, and C333E50, drastically shifted in terms of reactivity. In the MDI formulation C716 was comparable to C218 in terms of reactivity but in the HDI formulation C716 was found to be substantially faster than DBTL. Likewise, C739E50 and C333E50 were similar in reactivity to C218 in the MDI system but were found to possess a delayed cure in the HDI formulation.

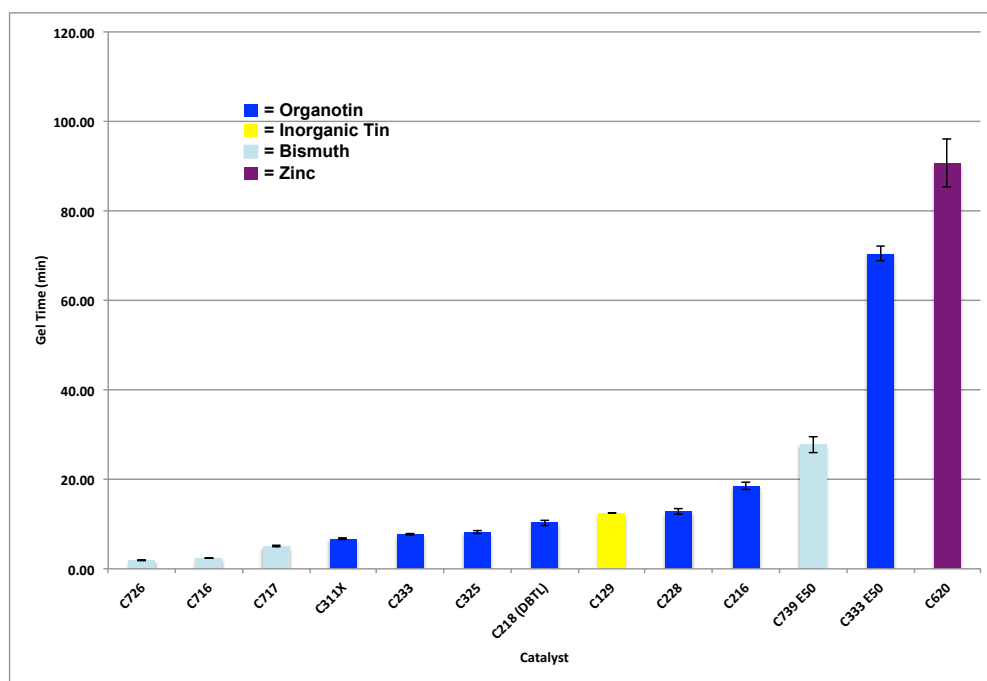


Figure 3. Catalyst activity as determined by gelation time in HDI formulation A.

In addition to studying the effect of catalyst selection we also wanted to elucidate the effect of catalyst loading on gelation time in MDI elastomer formulation A. **Figure 4** displays the gel time of several non-organotin alternatives at various catalyst loadings. Increasing the catalyst loading led to decreased gelation times for all catalysts studied, however, it should be noted that

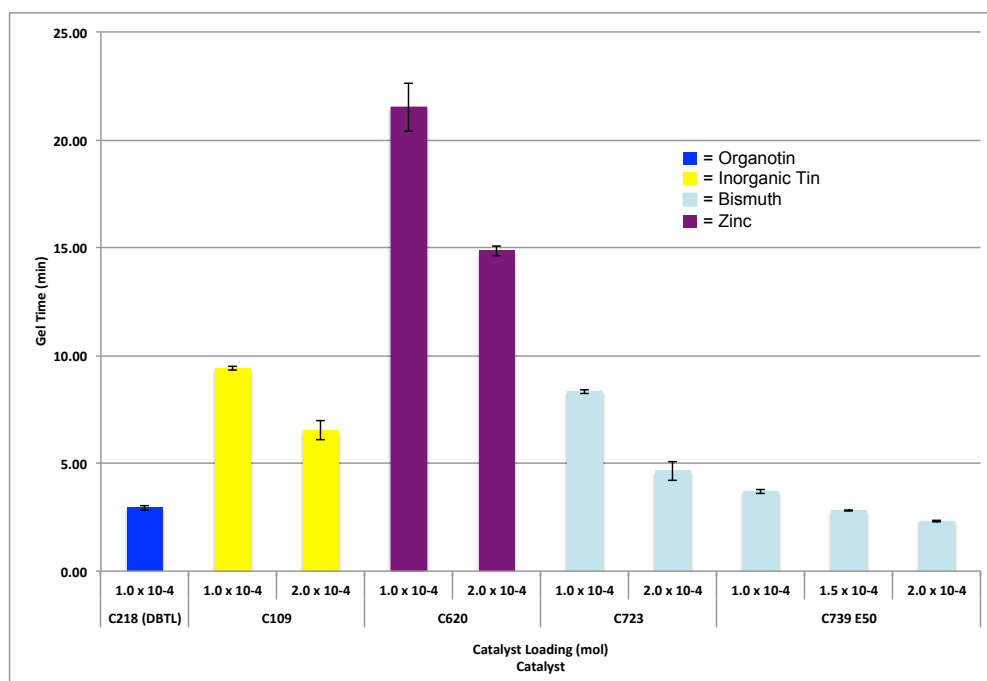


Figure 4. Effect of catalyst loading on gel time in MDI formulation A.

doubling the loading of both C723 and C739 E50 resulted in gel times comparable to that obtained using C218 at a normal loading. This observation is of particular interest as while Bi-based catalysts are sometimes scrutinized for lower levels of activity, increasing the catalyst loading provided reactivity similar to that observed when using DBTL.

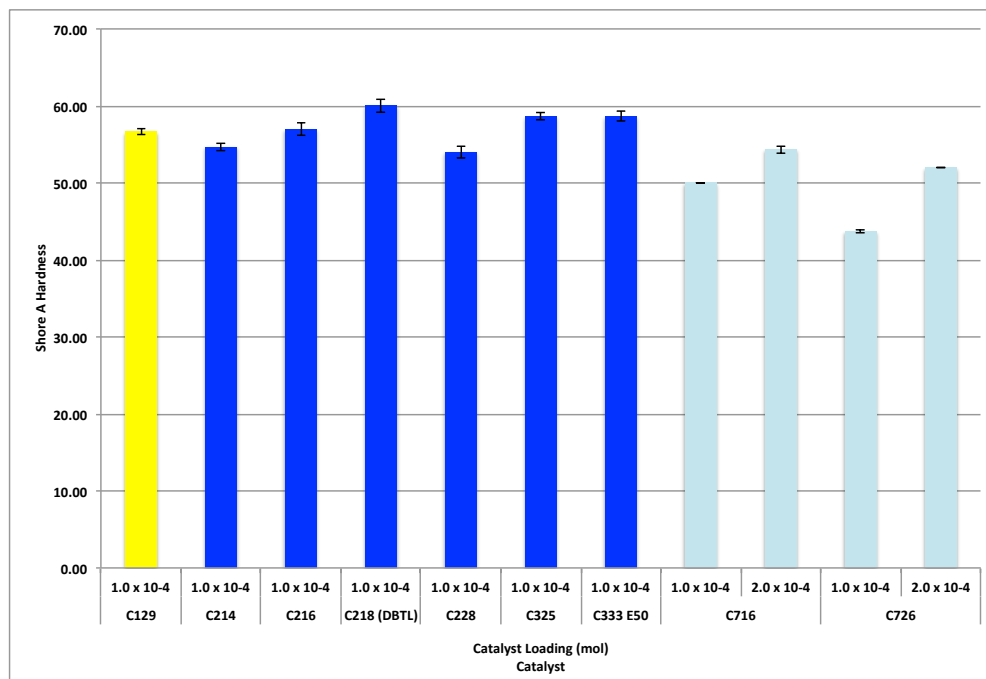


Figure 5. Shore A hardness using various catalysts in MDI formulation B.

While catalyst activity and cure time play a paramount role in polyurethane applications, physical property development such as material hardness, chemical resistance, adhesion, and color/gloss development can also be extremely important properties to consider. **Figure 5** displays the effect of catalyst selection on Shore A hardness development in MDI formulation B. Many of the catalysts provided relatively similar levels of hardness; however, C716 and C726 displayed slightly lower hardness levels. Increasing the catalyst loading of both C716 and C726 provided an increase in hardness; implying that increasing catalyst loading may provide enhanced performance and hardness development.

Although much of the work in the field of catalysis is based on optimizing reactivity, selectivity, and physical property development, the stability of a catalyst often ultimately determines the viability of a potential new catalyst. We evaluated the shelf life of several catalysts in MDI formulation A in order to determine some of the major factors that impact the stability of a catalyst (**Figure 6**). The literature suggests that the main influences on catalyst stability are the steric environment around the metal center and the nature of the metal's ligands.⁷⁻⁸ When comparing the shelf life C320 and C321 we find that C320 loses less reactivity over time and

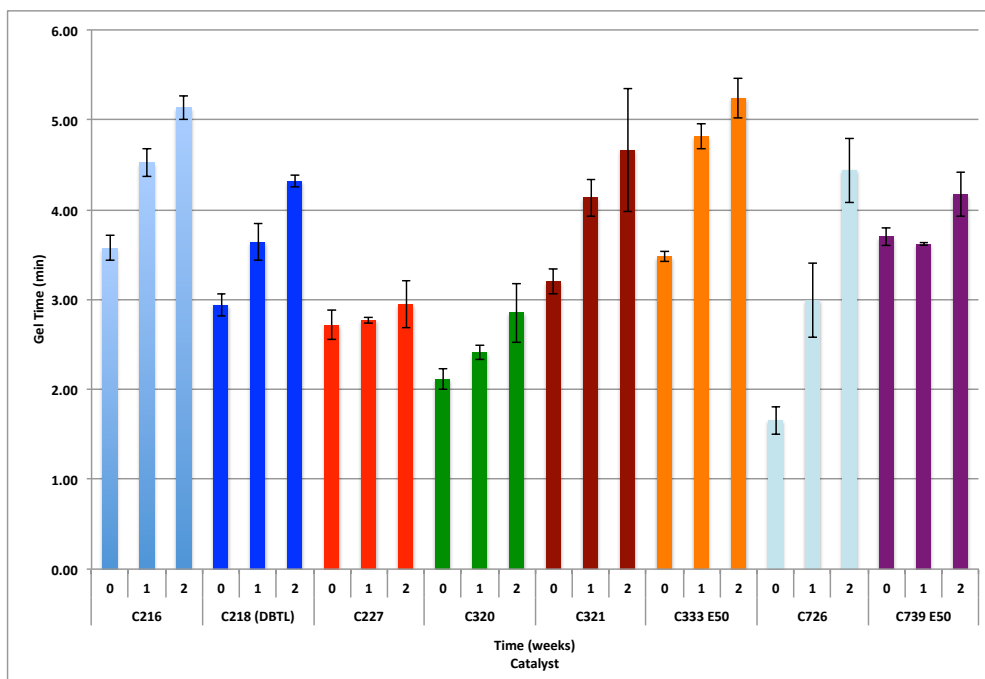


Figure 6. Catalyst polyol shelf life in MDI formulation A.

demonstrates an improved shelf life (**Figure 7**). In this case, the increased steric hindrance surrounding the metal center (**Figure 8**) seems to provide increased catalyst stability. Similarly, C227 possesses more steric interactions around the metal center when compared to C333E50 and also displays better shelf life. Although sterics play a significant role in catalyst stability the nature of the metal center ligands are also vital. From the data in **Figure 6** and **7** we find that in

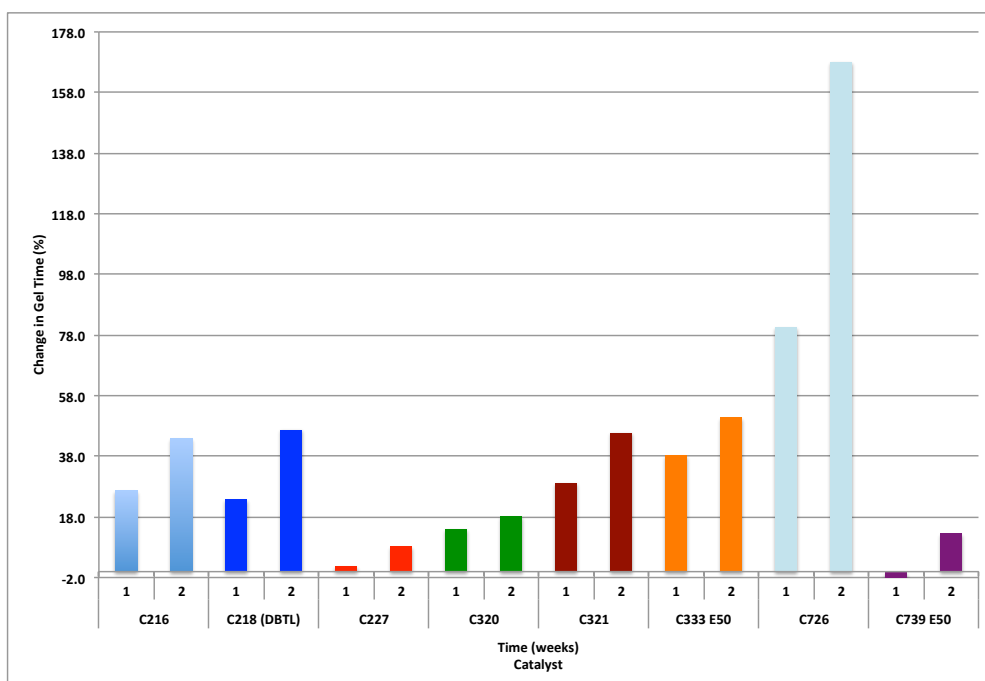


Figure 7. Catalyst polyol shelf life in MDI formulation A evaluated as % change in gelation time

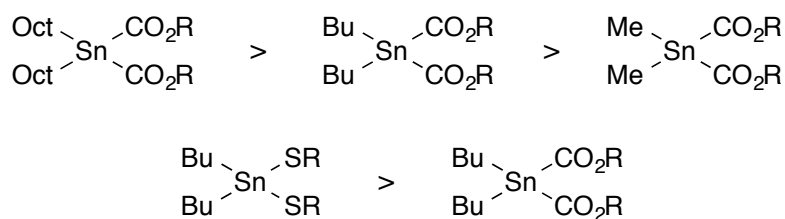


Figure 8. Factors generally influencing catalysts stability and shelf life.

general mercaptide containing catalysts, such as C320 and C321, possess better stability than their carboxylic acid counterparts, such as C218. Maybe the most interesting observation from the shelf life data is the stability demonstrated by C739 E50. While Bi catalysts have shown much promise as viable organotin alternatives they sometimes lack the desired polyol stability offered by other materials. In this case C726 displays less stability than the other the catalysts, which were evaluated, however, C739 E50 demonstrates the best stability and shelf life of all catalysts in the study. Based on this observation C739 E50 may be considered an excellent organotin alternative that also demonstrates improved stability and shelf life when compared to both traditional organotin catalysts and typical Bi-based materials. While we are able to take away general information regarding factors that affect catalyst stability, the specific application/formulation can also drastically affect catalyst shelf life and must be taken into consideration when discussing catalyst stability.

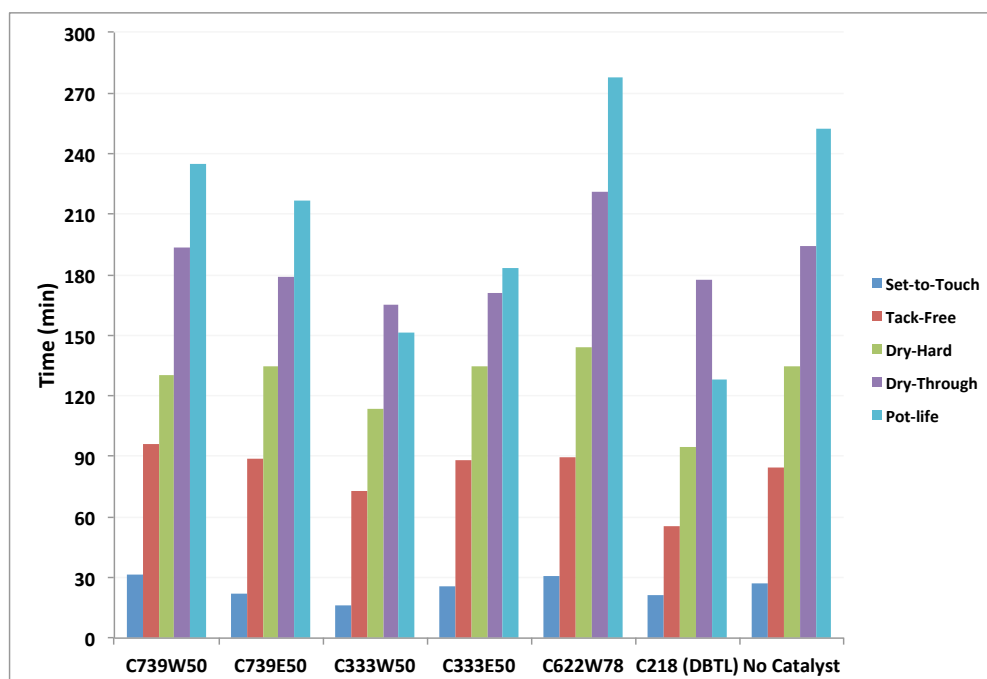


Figure 9. Curing profile and pot-life of select catalysts in waterborne formulation A.

One of the increasingly important issues in the production of polyurethane coating applications is the compatibility and stability of catalysts in waterborne formulations. We evaluated several novel, water-soluble, hydrolytically stable catalysts (C333W50, C739W50, and C622W78) in two separate 2K WB PU coating formulations. In waterborne formulation B C333W50, C218, and C739E50 demonstrated the shortest set-to-touch times, 16.5, 21.5, and 21.9 min respectively, while C62278, C739W50, and the control (no catalyst) displayed slightly slower set-to-touch times (**Figure 9**). C218 and C333W50 provided the fastest tack-free times (<73 min), whereas the remaining catalysts revealed similar tack-free times. C333W50 and C333E50 provided the best dry-through times (165.4 and 171.3 min) while C739E50, C739W50, and C218 afforded similar values. C739E50, C739W50, and C622W78 demonstrated the longest pot-life of the catalysts tested. In summary, while C333W50, C333E50, and C218 all provided faster overall rates of curing, they also resulted in shorter pot-lives whereas C739W50, C739E50, and C622W78 afforded slightly slower curing rates and prolonged pot-lives.

Table 2. Physical Property Development in Waterborne Formulation A

Catalyst	Pencil Hardness	Cross-Cut Tape Adhesion	MEK Double Rubs
C739W50	F	5B	68
C739E50	3H	4B	68
C333W50	B	3B	54
C333E50	HB	3B	52
C622W78	HB	4B	52
C218 (DBTL)	HB	5B	48
No Catalyst	HB	5B	38

In addition to investigating the curing properties of the coating formulation we also evaluated the formulation's physical property development (**Table 2**). C739E50 provided by far the highest hardness value (3H) followed by C739W50. The remaining catalysts demonstrated similar hardness values with C333W50 resulting in a slightly softer coating. C739W50 and C218 provided the best adhesion properties (5B) while the remaining catalyst afforded similar adhesion properties. C739W50 and C739E50 showed considerably better solvent resistance (68) when compared to that of C218 and the control, whereas C333W50, C333E50, and C622W78 resulted in slightly better solvent resistance than C218.

The effect of catalyst selection on color and gloss development was also studied (**Table 3**). Each catalyst afforded a glossy, white industrial coating with gloss levels greater than 78 gloss units at 60° in addition to exceptional color development. While color and gloss development is often highly dependent on the composition and additives of the formulation it should be noted that the utilized catalysts showed no detrimental effects and resulted in excellent film properties.

Table 3. Color and Gloss Properties of Waterborne Formulation A

Catalyst	Color			Gloss	
	L*	a*	b*	20°	60°
C739W50	90.85	-1.23	1.17	46.1	79.7
C739E50	91.05	-1.10	1.41	59.1	82.4
C333W50	90.54	-1.36	0.84	59.7	84.2
C333E50	90.77	-1.23	1.19	60.3	84.4
C622W78	90.94	-1.17	1.30	41.3	78.2
C218 (DBTL)	91.22	-1.12	1.35	64.1	80.3
No Catalyst	90.68	-1.16	1.35	50.9	81.6

We then examined an additional waterborne coating formulation to determine the effect of different catalyst loadings (**Figure 10**). In general, the higher catalyst loading (0.4% wt.) demonstrated faster overall curing than the lower loading (0.2% wt.) of the same catalyst. In this formulation C333E50 and C218 displayed the fastest set-to-touch (5.0 and 12.2 min) and tack-free times while C333W50 afforded slightly slower curing using a catalyst loading of 0.4%. However, it should be noted that C218 provided faster dry-through times (24.4 min at 0.4% wt.) than any of the other catalysts studied. C739E50 and C739W50 both showed very similar rates of curing and were slightly slower than C333W50, C333E50, and C218. C622W78 demonstrated excellent catalytic activity when compared to the control sample though was still slower to cure than the other catalysts in the study (39.4 min at 0.4% for set-to-touch). An especially interesting observation is that using either C739E50 or C739W50 at a loading of 0.4% weight provided a very similar curing profile to that of C218 at a loading of 0.2%; suggesting that using a slightly higher loading of the C739W50 or C739E50 may act as a “drop-in” replacement for C218. While not shown in **Figure 10**, a control study (no catalyst) showed curing times requiring >6.5 h to

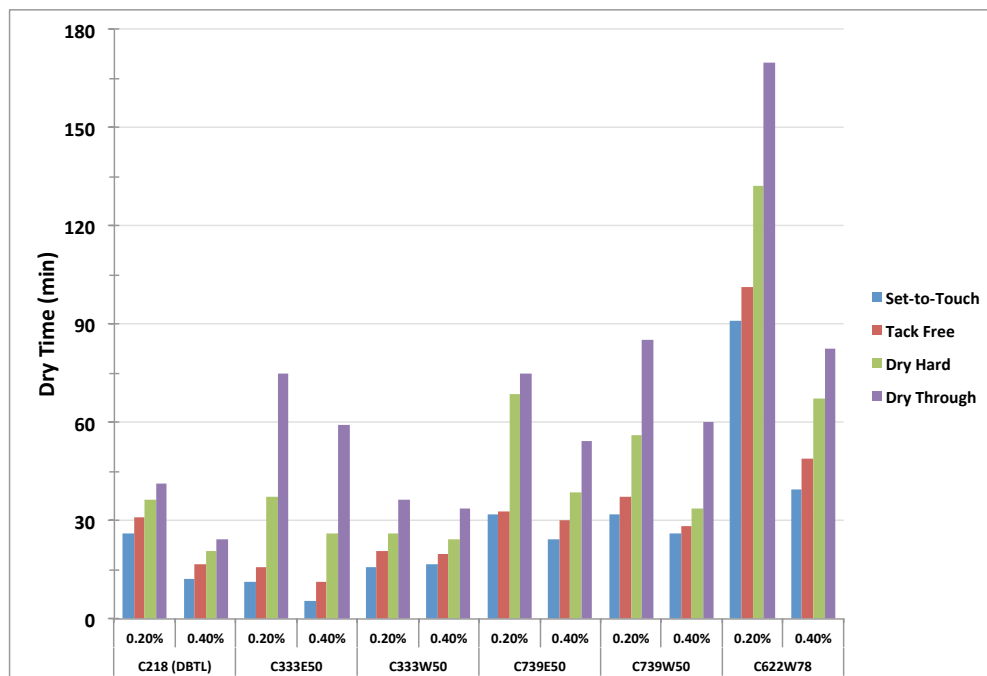


Figure 10. Curing profile of select catalysts in waterborne formulation B.

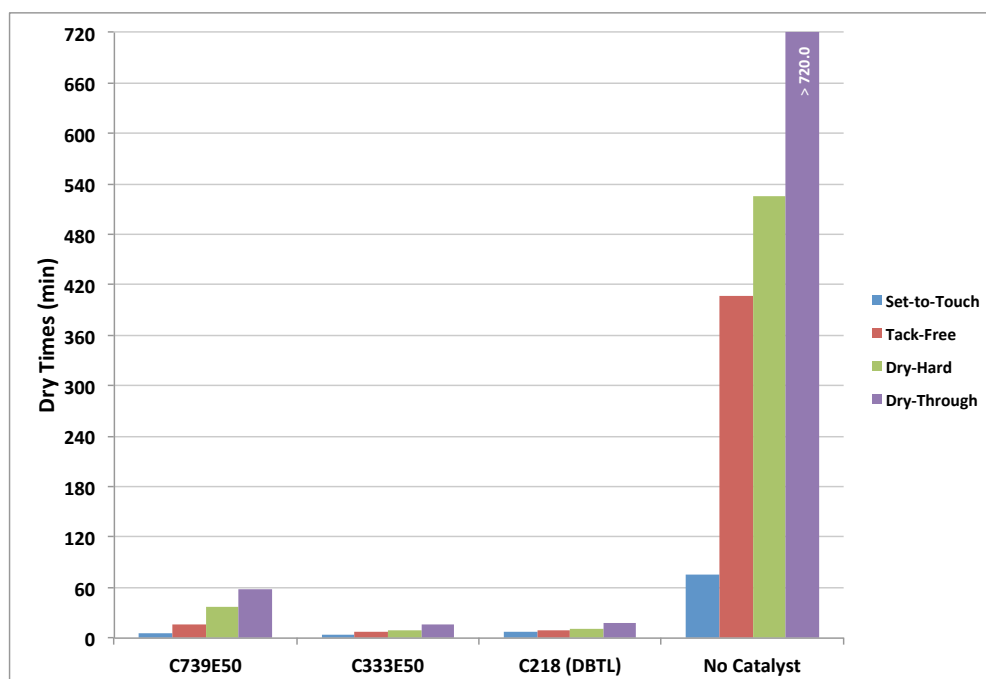


Figure 11. Curing profile of select catalysts in a solventborne formulation.

even achieve set-to-touch requirements.

Additionally, the reactivity of catalysts in a solventborne coating formulation (**Figure 11**) was investigated. C333E50 and C218 both demonstrated very fast set-to-touch (6.8 and 9.8 min), tack-free, dry-hard, and dry-through times. C739E50 provided slightly slower set-to-touch and tack-free times and considerably longer dry-hard (39.5 min) and dry-through (60.9 min) values.

As with waterborne formulation B we investigated the color and gloss properties generated in the solventborne system (**Table 4**). Analogous to the waterborne system, the solventborne formulation resulted in glossy, white industrial coatings with gloss levels >78 gloss units at 60° and excellent color development.

Table 4. Color and Gloss Properties of the Solventborne Formulation

Catalyst	Color			Gloss	
	L*	a*	b*	20°	60°
C739E50	92.34	-0.77	3.16	65.1	88.9
C333E50	92.61	-0.70	3.25	46.5	78.2
C218 (DBTL)	92.71	-0.64	3.43	63.1	83.6
No Catalyst	92.47	-0.62	3.39	80.3	87.3

In addition to investigating the curing speed and property development in several waterborne and solventborne coating formulations we also were interested in the effect that relative humidity has on catalyst activity. **Figure 12** compares the curing times of waterborne formulation A using C333 W50 and C218 under elevated levels of relative humidity. The data

shows that while both catalysts exhibited elongated drying times under higher levels of relative humidity, C333 W50 provided faster curing at all levels of humidity and demonstrated less “drop-off” in reactivity at higher amounts of humidity. We wanted to further explore this observation and next studied the NCO/OH selectivity of C333 W50.

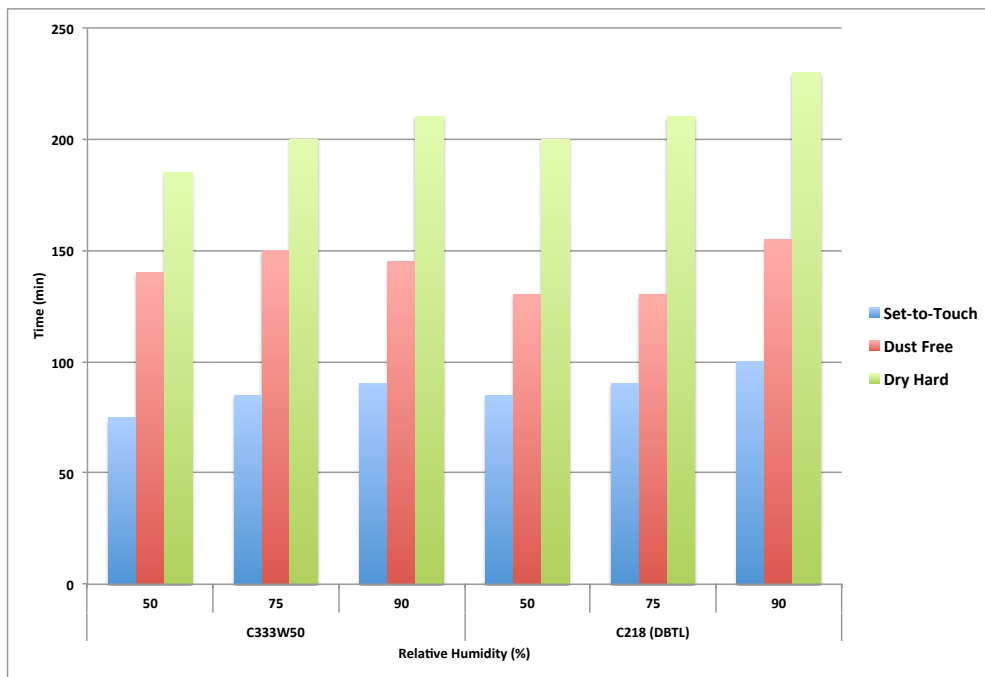


Figure 12. Effect of relative humidity on curing using C333 W50 and DBTL in waterborne formulation A.

In order to determine the selectivity of C333 W50 towards the NCO/OH reaction we compared the reaction of butanol and water in waterborne formulation C (**Figure 13**). The data shows that the reaction rate of butanol with the isocyanate is nearly 7-fold faster than that of water; demonstrating that the NCO/OH is highly favored over the NCO/H₂O when using C333 W50. Given the impressive reactivity, under both ambient and conditions of high relative humidity, the enhanced levels of selectivity towards the NCO/OH reaction likely plays a key role in the effectiveness of C333 W50 as a catalyst for waterborne formulations. Furthermore, the hydrolytic stability and high selective of the catalyst makes is a prime candidate for any system where the undesired NCO/H₂O reaction and CO₂ formation is problematic.

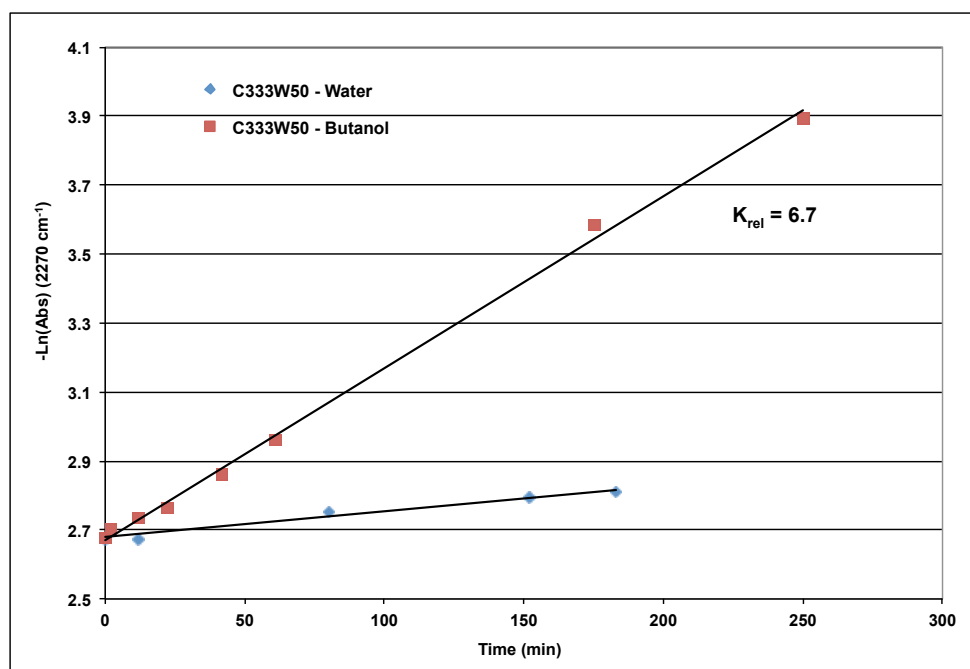


Figure 13. Selectivity of C333 W50 towards the NCO/OH reaction in model waterborne formulation C.

Conclusions

This work showcases a library of organotin-, inorganic tin-, Bi-, and Zn-based catalysts that display a range of “tunable” reactivity, excellent physical property development, and improved shelf life. Furthermore, a series of novel, water-soluble, hydrolytically stable catalysts exhibit exceptional catalytic activity, physical property development, and color/gloss development in both 2K waterborne and solventborne coating formulations. C333W50 was found to demonstrate enhanced reactivity under high levels of relative humidity when compared to DBTL, which may be a result of its high level of selectivity towards the NCO/OH reaction. Consequently, this work has demonstrated the importance of selecting the appropriate catalyst for polyurethane elastomer applications and as regulatory restrictions on commonly used organotin-based catalysts tighten a number inorganic tin-, Bi-, and Zn-based catalysts have shown tremendous potential of viable organotin alternatives.

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