Isocyanate-Free Urethane Coating *for* Industrial Metal Applications

by **Paul Popa**,
John Argyropoulos,
Yanxiang Li,
Nahrain Kamber,
and **Jeff Anderson**
The Dow Chemical Company

Two-component polyurethane coatings are used in a wide variety of applications, including maintenance and protection of industrial infrastructure; agriculture, construction, and earthmoving equipment; automotive refinishing; and wood furniture, cabinetry, and joinery. These coating systems offer excellent weatherability, toughness, chemical resistance, and stain resistance. When formulated for ambient curing, however, traditional 2K polyurethane coating systems sacrifice cure time for pot life unless plural component application equipment is employed. This article describes a novel urethane technology that is isocyanate-free, cures at ambient temperature, and decouples pot life from cure speed. In addition to an improved environmental, health, and safety profile, this novel technology offers multiple end-user benefits such as higher throughput in original manufacturing applications and faster return-to-service in field applications. Performance attributes such as good weatherability and chemical resistance in various industrial metal applications are also highlighted.

INTRODUCTION

Introduced in the 1970s, isocyanate-based polyurethanes are widely used in industrial coating applications as a result of their exceptional mechanical properties, good chemical resistance, excellent weatherability (when using aliphatic polyisocyanates), and the ability of the coatings to cure at acceptable rates under ambient conditions.[1] Today, many coating applicators have expressed a need for faster drying and hardness development than can be achieved with current isocyanate chemistry, which is limited, in part, by a need to balance cure speed with acceptable pot life. There is also ongoing interest in finding alternative routes to polyurethane properties without the use of isocyanates in order to improve the environmental, health, and safety profile of the formulated coating.[2]

Although a number of technologies have been developed that lead to the formation of polyurethanes without the use of isocyanates, these approaches lack the ability to cure under ambient temperatures. For example, the methoxymethyl groups of melamine-formaldehyde (MF) resins have been shown to react with primary carbamate groups and secondary carbamate (urethane) groups at elevated temperatures (greater than 120°C) to provide polyurethane coatings with exceptional properties such as improved acid rain resistance, weatherability, and scratch resistance.[3,4] The reaction of primary amines with cyclic carbonates at elevated temperatures (greater than 70°C) can also provide polyurethane coatings with good properties.[5–7] However, these technologies are not amenable to coatings that are applied under ambient conditions (20° to 30°C), and hence are limited to original equipment manufacturer (OEM) applications where the coating can be cured at elevated temperatures. A new technology developed by Dow offers an alternate route to urethane chemistry that is both isocyanate-free (manufactured without the intentional addition of isocyanate) and cures under ambient conditions. It also offers the additional benefit of decoupling pot life from coating dry time and hardness development.

As a result, this novel technology can provide fast, ambient cure, without the short pot-life issues of traditional two-component (2K) polyurethane systems. Additionally, the enhanced technology does not suffer from an irreversible reaction of the crosslinker with water. Formulations can be applied under ambient conditions that lead to coatings with fast property development, including excellent mechanical properties, good chemical resistance, and exceptional weatherability.

TECHNOLOGY OVERVIEW

As demonstrated in *Figure* 1, the novel isocyanate-free chemistry developed for the preparation of urethane coatings at ambient temperatures results from the reaction of polyaldehydes with carbamate functional polymers using an acid catalyst.[8] The polycarbamate polymer can be prepared from a variety of polyols (i.e., acrylics and alkyds). The preferred polyaldehyde is 1,3/1,4-cyclohexanedicarboxaldehyde. A primary alcohol (i.e., ethanol, n-propanol) is typically used as a cosolvent to enhance the pot life of the formulation.

Resins and crosslinkers based on this technology are being developed for applications where polyurethanes are currently the preferred system, such as primers and clearcoats for auto refinish; clearcoats for wood; topcoats for agricultural, construction, and earthmoving (ACE) equipment; and industrial maintenance and protective coating (M&PC) applications. This article focuses on the features and benefits of the technology for topcoats in M&PC and ACE applications.

EXPERIMENTAL MATERIALS AND TESTING METHODS

This study employed two acrylic carbamate functional polymers with a molecular weight of ~15,000 in n-butyl acetate at ~70% solids by weight. The polymers differed only in glass transition temperature (T_g) and relative hardness of the resulting coatings: the T_g was ~5°C for Polycarbamate A and ~25°C for Polycarbamate B.

Coating dry times were determined using a straight line dry-time recorder following ASTM D5895; T2 represents tack-free time and T3 represents dry-hard time. Film thickness of the coating was determined using a Positector 6000 dry coating thickness gauge and taking the average of five readings. Crosshatch adhesion was determined following

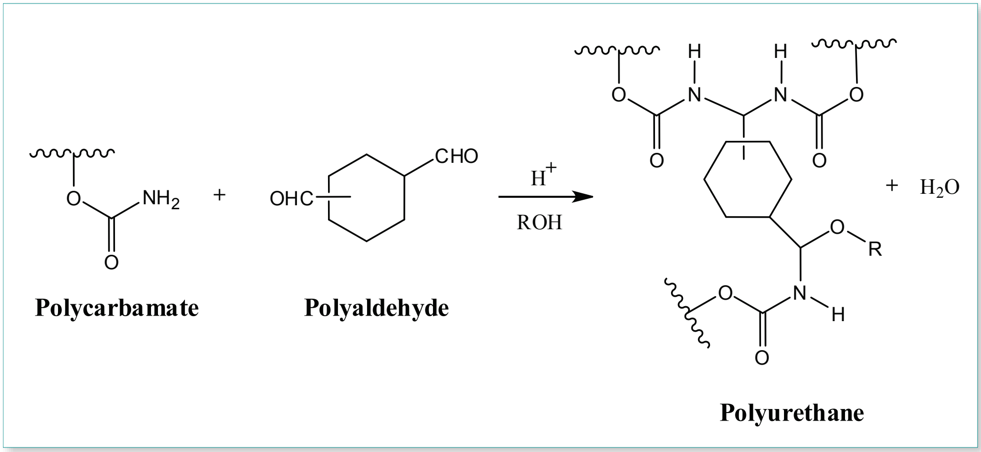

Figure 1—Formation of a polyurethane from the reaction of a polycarbamate and polyaldehyde.

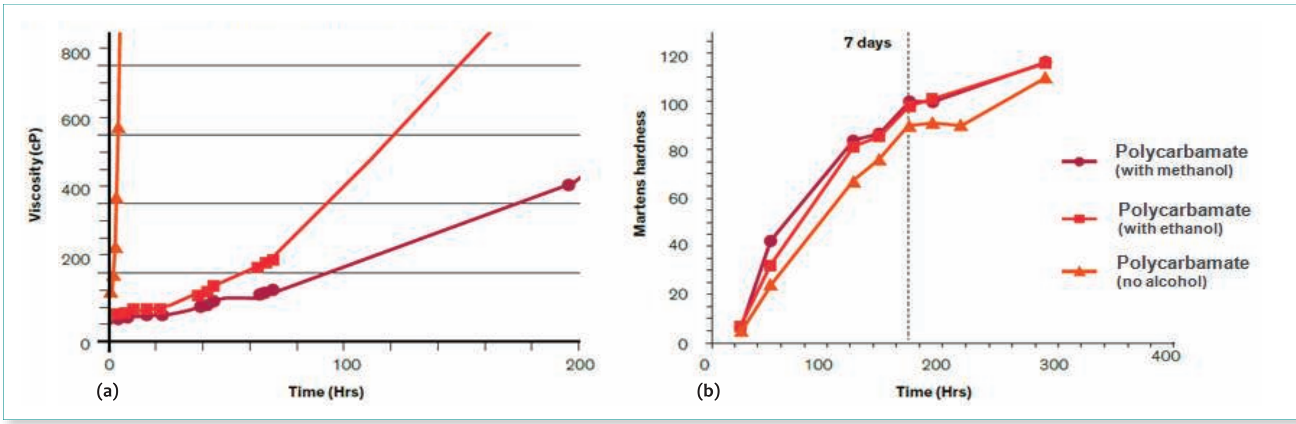

Figure 2—Viscosity development over time (a) and Martens hardness over time (b).

ASTM D3359. Solvent resistance was determined following ASTM D5402, using methyl ethyl ketone, and stopping at an upper limit of 100 double rubs. Pendulum hardness of the coating was measured according to ASTM D4366 and reported in seconds. Martens hardness measurements were performed in triplicate using an automated Fisherscope HM2000 XYp indenter equipped with a Berkovich tip. Mandrel bend measurements were performed according to ASTM D522 using the cylindrical mandrel test apparatus. Gloss measurements were performed according to ASTM D523. Accelerated weatherability was performed according to ASTM D4587, using cycle number 4. Color change was performed according to ASTM D2244.

RESULTS AND DISCUSSION

Decoupling Pot Life from Cure Time

To demonstrate the decoupling of pot life from cure time, three formulations were prepared that differed only with the presence or type of alcohol used as a blocking agent (BA). *Figure* 2a shows the viscosity development over time of the three formulations. With no BA present, the viscosity increased rapidly, while the addition of 5% by formulation weight of either methanol or ethanol showed a dramatic inhibition of viscosity increase, in effect extending the usable pot life of the formulation from minutes to days. Conversely, the cure rate was not affected, as can be seen in *Figure* 2b, where the Martens hardness shows similar trends with or without the presence of the BAs over time.

Polycarbamate A Coating Formulations

Coatings prepared using Polycarbamate A were formulated to a pigment volume concentration (PVC) of 10% using titanium dioxide (TiO_2); a 1:1 carbamate:aldehyde stoichiometry; 1.2 wt% solids

Figure 3—Structure of HALS for acid catalyzed paint formulation.

Table 1—Properties of Coatings Based on Polycarbamate A

Formulation	A1	A2	A3	A4
HALS Level	0%	1%	2%	3%
Beck & Koller dry time: T2 (hr)	0.6	1.1	1.9	2.4
Beck & Koller dry time: T3 (hr)	1	1	3.7	4.3
Pot life (hr)–gel	27	36	48	60
Film thickness (µm)	58	57	56	54
60° gloss	88	88	89	89
Pendulum hardness (sec)–7 day	58	46	41	34
X-hatch adhesion	5B	4B	4B	4B
MEK resistance (double rubs)	>100	>100	>100	>100
Mandrel bend (0.5 in.) Pass/Fail	Pass	Pass	Pass	Pass

Table 2—Increased Catalyst Levels

Formulation	A5	A6
HALS level	3%	3%
Catalyst level	1.8%	2.4%
Beck & Koller dry time: T2 (hr)	1.3	0.6
Beck & Koller dry time: T3 (hr)	2.2	1.1
Pot life (hr)–gel	24	8
Film thickness (µm)	71	69
60° gloss	89	87
Pendulum hardness (sec)–7 day	45	54
X-hatch adhesion	4B	4B
Mandrel bend (0.5 in.) Pass/Fail	Pass	Pass

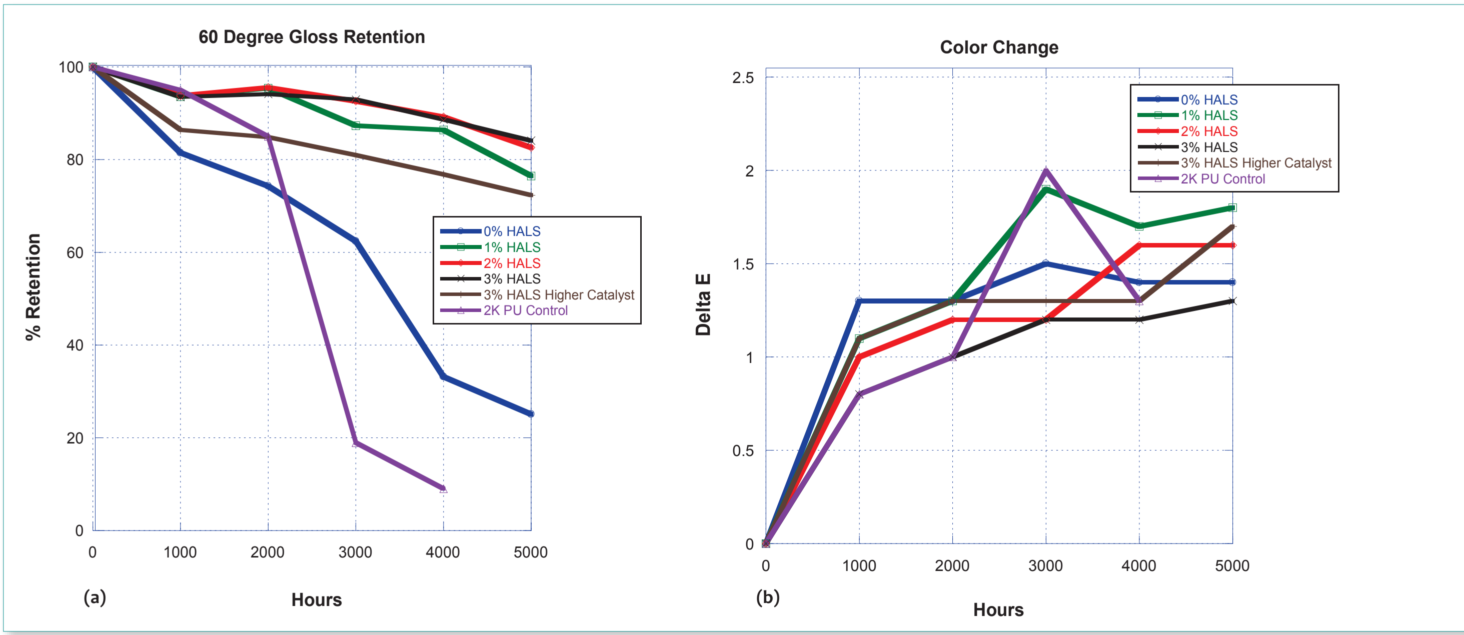

Figure 4—Gloss retention (a) and color change (b) after 5,000-hr QUV-A exposure.

p-toluenesulfonic acid (PTSA) on binder solids; and with different levels of a hindered amine light stabilizer (HALS)—0, 1, 2, and 3 wt% based on binder solids. The formulations were applied to pre-cleaned chromate-treated aluminum (Al) Q-panels to a target dry film thickness of 50–60 µm and cured for a minimum of seven days at approximately 22°C and 50% relative humidity (RH).

As demonstrated in *Table* 1, the incorporation of HALS slightly impacted the rate of cure as indicated by the increased T2 and T3 times. The pot life, defined in this study as the gel point, also increased with increased levels of HALS. In addition, pendulum hardness decreased with increased levels of HALS, further indicating a slight effect on cure development.

Although the HALS used in this study is recommended for acid catalyzed systems (structure shown in *Figure* 3), it could potentially affect the catalytic activity of the acid catalyst (PTSA). To better understand the potential effects, additional formulations (labeled A5 and A6) were prepared using 3% HALS at increased catalyst levels: 1.8% and 2.4% solids based on total binder solids.

The PVC, stoichiometry, application, and cure conditions were held constant; results are shown in *Table* 2.

Increasing the level of catalyst decreased both T2 and T3 time, thus overcoming the slight cure inhibition previously observed. The formulation containing 2.4% solids PTSA had a similar hardness to the formulation without HALS, indicating that the effect on catalytic activity can be overcome through formulation.

Accelerated weathering (QUV-A) was evaluated for Formulations A1–A4 and A6. The coatings were prepared, applied, and cured as described above.

As demonstrated in *Figures* 4a and 4b, the 60° gloss retention after 5000-hr QUV-A exposure was >75% for all formulations containing HALS and the ΔE values <2, demonstrating the excellent weatherability of this new isocyanate-free technology.

Table 3—Isocyanate-Free Coating Properties Over Primer

Formulation	A1	A2	A3	A4	A6
HALS level	0%	1%	2%	3%	3%
Catalyst level	1.2%	1.2%	1.2%	1.2%	2.4%
Topcoat film thickness (µm)	71	68	76	79	85
60° gloss	89	89	89	89	87
Pendulum hardness (sec)–7 day	60	47	41	33	49
X-hatch adhesion	5B	5B	5B	5B	4B

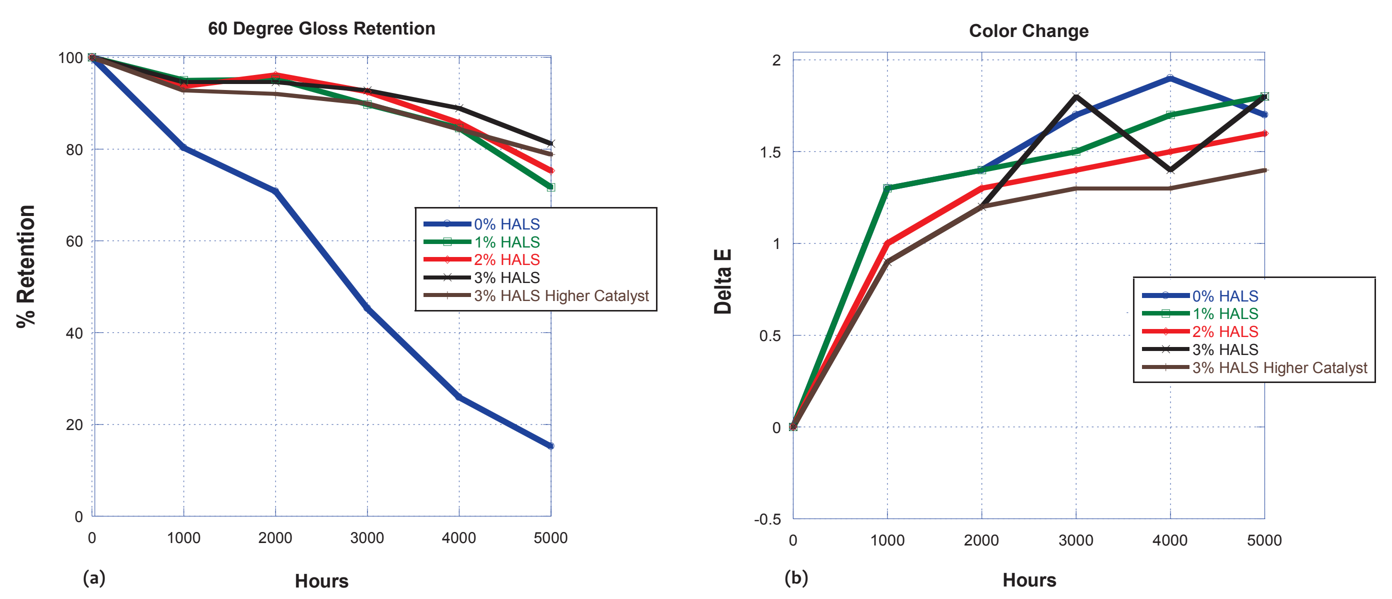

Figure 5—Excellent 60° gloss retention (>70%) (a) and color stability (ΔE values <2) (b) were observed after 5000-hr QUV-A exposure for all formulations containing HALS.

Table 4—Polycarbamate Blend Coating Formulation Properties

Formulation	AB-1	AB-2	AB-3	B
Blend ratio (A/B)	75/25	50/50	25/75	0/100
Film thickness (μm)	66	65	65	70
60° gloss	89	88	90	90
Pendulum hardness (sec)–7 day	89	93	96	102
X-hatch adhesion	4B	4B	4B	4B
MEK resistance (double rubs)	>100	>100	>100	>100
Mandrel bend (0.5 in.) Pass/Fail	Pass	Pass	Pass	Fail

Polycarbamate A Coating Formulations Applied on Epoxy Primer

Formulations A1–A4 and A6 were applied to primed panels. The primer was epoxy-based and cured using a low free amine containing hardener. The primer was applied to pre-cleaned chromate-treated Al panels targeting a dry film thickness of 50–60 μm. The primer was allowed to cure for 24 hr at ambient conditions before applying the isocyanate-free topcoat.

As demonstrated in *Table* 3, the topcoat properties achieved on the primed panels were similar to those when applied direct to metal. Accelerated weathering (QUV-A) was also evaluated on this set of formulations; results are plotted in *Figures* 5a and 5b.

Formulations of Polycarbamate Polymer Blends

A higher T_g polycarbmate polymer (Polycarbamate B) was developed for applications requiring higher hardness. Coating formulations based on blends of Polycarbamates A and B were prepared at the following ratios based on weight solids: 75/25, 50/50, 25/75, and 0/100. These paints were formulated at a 10% PVC using TiO_2; a 1:1 carbamate:aldehyde stoichiometry; and 1.2% solids PTSA on binder solids. The formulations were cured for seven days at approximately 22°C and 50% RH.

As demonstrated in *Table* 4, the compatibility of the polycarbamate polymers was excellent based on the gloss values. The hardness of the coatings increased slightly with an increasing amount of Polycarbamate B, the higher T_g polymer.

The same blend formulations were prepared with the addition of 3% HALS solids on total formulation. The panels were applied direct to metal (chromate-treated Al panels) and epoxy primed panels as described previously. Accelerated weathering (QUV-A) was evaluated on the topcoats applied direct to metal and on the primed panels.

As shown in *Figure* 6, all of the formulations based on the polycarbamate blends exhibited excellent UV resistance with >80% gloss retention.

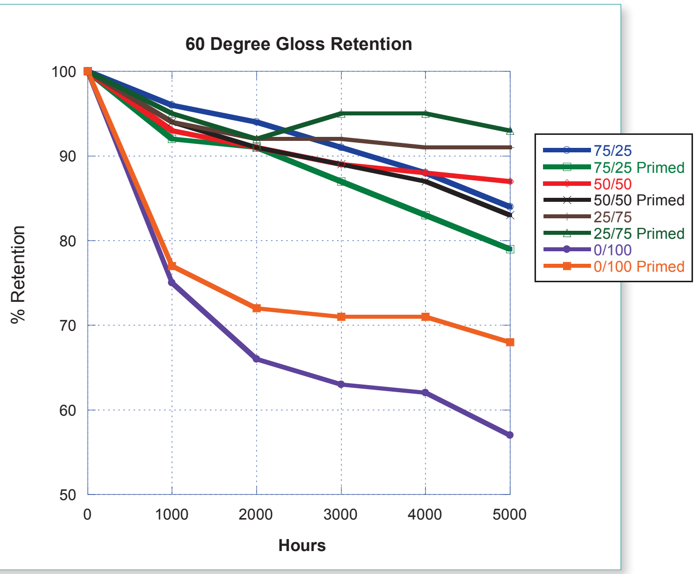

Figure 6—QUV-A data on polycarbamate polymer blend coating formulations.

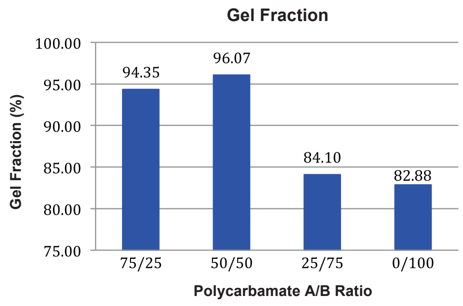

Figure 7—Gel fraction data.

The formulation based on Polycarbamate B did not have the same gloss retention as the blended formulations.

Gel fraction and dynamic mechanical analysis (DMA) of the cured films was performed to determine if the coating adequately cured (*Figure* 7 and *Table* 5).

As demonstrated in *Figure* 7, gel fractions were higher for the compositions containing 50% or greater Polycarbamate A. The crosslink density[9] of the coating film based solely on Polycarbamate B was notably lower than the blended formulations. These data suggest a lower degree of crosslinking with increased levels of Polycarbamate B. This could be attributed to the higher T_g coating film vitrifying faster during the curing process, therefore limiting its crosslink density. Formulation optimization is ongoing to further understand and improve the crosslinking of the coating.

CONCLUSIONS

To meet multiple needs in polyurethane coatings, a 2K, isocyanate-free urethane technology has been developed that cures at ambient temperature and decouples pot life from cure speed. These features offer faster cure time; longer pot life; and an improved environmental, health, and safety profile. This technology has demonstrated excellent weatherability in accelerated testing. Additional benefits include faster return-to-service in field applications and higher throughput in OEM applications.

Table 5—DMA Data

Polycarbamate A/B Ratio	T_g (°C)		Crosslink Density (mol/L)	
	1st DMA Cycle	2nd DMA Cycle	1st DMA Cycle	2nd DMA Cycle
75/25	58.0	76.7	1.53	1.84
50/50	63.4	85.0	1.34	1.72
25/75	60.6	85.3	1.33	1.59
0/100	61.8	85.0	1.16	1.17

TA instruments Q100 DMA
Temperature -10°C to 160°C; 5°C/min ramp
Frequency of 1 Hz

ACKNOWLEDGMENTS

Special thanks to Marty Beebe, Chloe Lu, and Daryoosh Beigzadeh for resin synthesis and characterization and Ben Schaefer, Jessica Kaake, and Mike Christy for preparation, application, and evaluation of the coatings.

References

1. Shaffer, M., Stewart, R., Allen, K., Wylie, A., and Lockhart, A., “Two-Component Polyurethane Coatings: High Performance Crosslinkers Meet the Needs of Demanding Applications,” *JCT CoatingsTech, 6* (1), 50-55 (2009).
2. Takas, T.P., “100% Solids Aliphatic Polyurea Coatings for Direct-to-Metal Applications,” *JCT CoatingsTech, 1* (5), 40-45 (2004).
3. Green, M.L., “Low VOC Carbamate Functional Coatings Compositions for Automotive Topcoats,” *J. Coat. Technol., 73* (198), 55-62 (2001).
4. Higginbottom, H.P., Bowers, G.R., Ferrell, P.E., and Hill, L.W., “Cure of Secondary Carbamate Groups by Melamine-Formaldehyde Resins,” *J. Coat. Technol., 71,* 49-60 (1999).
5. Webster, D.C. and Crain, A.L., “Synthesis and Applications of Cyclic Carbonate Functional Polymers in Thermosetting Coatings,” *Prog. Org. Coat., 40,* 275-282 (2000).
6. Webster, D.C., “Cyclic Carbonate Functional Polymers and Their Applications,” *Prog. Org. Coat.*, *47,* 77-86 (2003).
7. Guan, J., et al., “Progress in Study of Non-Isocyanate Polyurethane,” *Ind. Eng. Chem. Res., 50,* 6517-6527 (2011).
8. Anderson, J.R., et al., “Ambient Temperature Curable Isocyanate-Free Compositions for Preparing Crosslinked Polyurethanes,” U.S. Patent 8,653,174, February 18, 2014.
9. Peppas, N.A., et al., “Poly(vinyl alcohol) Hydrogels: Reinforcement of Radiation-Crosslinked Networks by Crystallization,” *J. Polym. Sci., 14,* 441-457 (1976).

AUTHORS

Paul Popa, **John Argyropoulos**, **Yanxiang Li**,
Nahrain Kamber, and **Jeff Anderson**,
The Dow Chemical Company, Midland, MI USA