Isocyanate-Free Polyureth

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ane Technology FOR AUTOMOTIVE REFINISH APPLICATIONS

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Two-component polyurethanes are used in a variety of industrial coating applications due to their excellent weatherability, toughness, and chemical resistance. When formulated as ambient-cured systems, traditional two-component polyurethanes typically must balance cure speed for pot life. This article describes automotive refinish applications for a novel ambient-cure, two-component isocyanate-free polyurethane coating technology based on the reaction of polycarbamates with polyaldehydes. One significant benefit is the ability to decouple pot life from cure speed, facilitating the development of coating formulations with longer pot life without sacrificing fast hardness development and quick dry time. For the applicator, these attributes can offer faster return to service, higher production throughput, and less material waste. Additional coating benefits, including good chemical and humidity resistance and fast sandability, are described for automotive refinish primer surfacer coatings at conventional and low-VOC levels. Examples of isocyanate-free PU clearcoats are also presented.

INTRODUCTION

Industrial coating applications such as automotive refinish widely use aliphatic isocyanate-based polyurethanes due to their good solvent resistance, excellent mechanical properties, and weatherability, as well as their acceptable cure rates at ambient temperature.[1] Coating end users seek to improve dry times and hardness development as a means of improving productivity and providing faster return to service. In the auto refinish body shops, plural spray equipment and heat-assisted curing are often absent, and polyurethane coatings often suffer from longer time-to-sand after primer application

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and time-to-buff for topcoat applications. Typical approaches to fast cure times can often lead to formulations with a shorter pot life. An opportunity to improve cycle time in automotive refinish applications lies in accelerating the dry speed of polyurethane coatings under ambient conditions.

This article describes a novel, isocyanate-free technology that can provide fast ambient cure without the short pot life issues often observed with two-component (2K) polyurethane systems.[2,3] As described in *Figure 1*, the novel isocyanate-free chemistry developed for the preparation of polyurethane coatings at ambient temperatures results from the reaction of polyaldehydes with carbamate-functional polymers using an acidic catalyst. A primary alcohol (i.e., ethanol, n-propanol) is typically used as a cosolvent to enhance the pot life of the formulation. This crosslinking chemistry has the unique feature of decoupling pot life from coating dry time and hardness development under ambient conditions, leading to coatings with fast property development that is desirable to end users such as those in automotive refinish shops. An additional benefit of the new technology is that it does not suffer from irreversible reaction of the crosslinker with water, which can be problematic in the case of isocyanate-based coatings, especially in humid environments. Furthermore, there is interest from the coatings industry to find alternative routes to coatings with polyurethane properties. Exposure to isocyanates can cause potential health problems.[4]

Resins and crosslinkers based on this technology are being developed for markets where polyurethanes are currently the preferred product, such as primers and clearcoats for autorefinish; clearcoats for wood; topcoats for agricultural, construction, and earth moving (ACE) equipment; and industrial maintenance and protective coating (M&PC) applications. This article focuses on the features and benefits of this technology for 2K primers in automotive refinish applications.

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

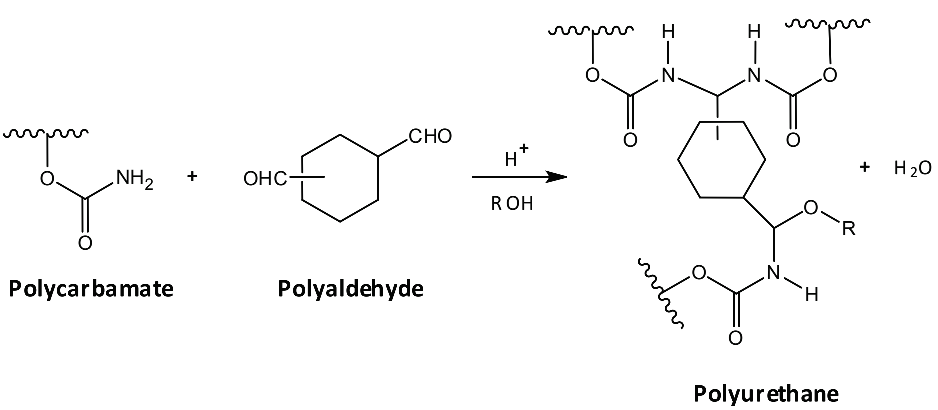
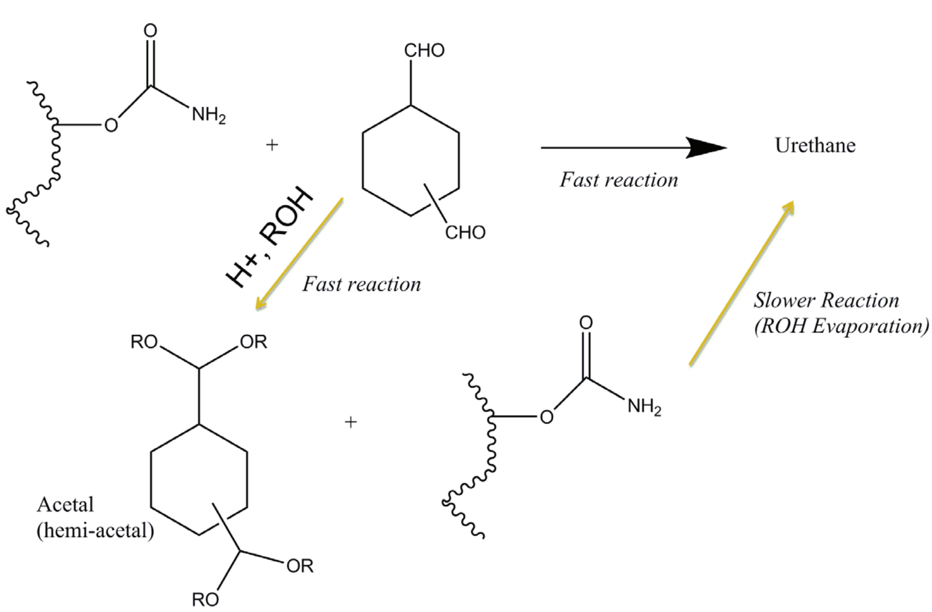


FIGURE 2—Reaction scheme for the isocyanate-free reaction pathways to produce PU.



EXPERIMENTAL MATERIALS AND METHODS

Raw materials used in this study were commercially available unless otherwise noted. The alkyd polycarbamates used were prepared from the corresponding alkyd polyol using a carbamylation process with ~60% conversion of hydroxyl functional groups to carbamate groups. For iso-free PU primer formulations #1 and #2, the equivalent weight of the alkyd carabamate is 589 as supplied at a 56.7 wt% solids solution in xylene. For iso-free PU primer formulation #3, the equivalent weight of the alkyd carbamate is 477 as supplied at a 70 wt% solids solution in Oxsol 100/acetone (70/30 wt% blend). A 1,3-cyclohexanedicarboxaldehydes and 1,4-cyclohexanedicarboxaldehydes (CHDA) mixture was prepared using a process previously described.[5] The equivalent weight of the CHDA is 79.5.

Film thickness of the coating was determined using a Positector 6000 dry coating thickness gauge and taking an average of five readings. Crosshatch adhesion was measured and rated (scale 0B to 5B with 5B being the best adhesion) according to ASTM-D3359-09.

Crosscut adhesion was measured and rated (scaled 0A to 5A with 5A being the best adhesion) according to ASTM-D3359-09. Solvent resistance using methyl ethyl ketone (MEK) was determined using a semi-automated MEK rub test machine (DJH Designs, Inc.) similar to ASTM D5402. Gloss measurements were made with a BYK Labotron Gloss Unit following ASTM D523-08 (Standard Test Method for Specular Gloss, 2008) and at the indicated angle of gloss measuring unit to substrate. Distinctiveness of Image (DOI) was measured using a BYK-Gardner wave scan dual meter.

Coating Application

The primer surfacer coatings were applied to cold rolled steel (CSR) panels sanded with 80 grit sandpaper. For panels with basecoats and clearcoats, commercially available solventborne basecoats and clearcoats were applied after the primed panels were sanded. A commercial solventborne black basecoat was then applied after the panels were sanded according to manufacturer's recommendations. A commercial clearcoat (two coats sprayed) was applied over the basecoat according to the manufacturer's recommendations. The coatings were cured at room temperature and properties were measured after 24 h and 7 d.

RESULTS AND DISCUSSION

2K Primer Formulation Development

The automotive refinish process generally involves filling and sanding of the surface to be refinished, application of an undercoat (a primer or a primer surfacer) followed by applications of an optional primer sealer then a pigmented basecoat and clearcoat to achieve the desired appearance. Multiple coats of primer surfacer are typically applied by spraying, then allowed to cure, followed by sanding and cleaning, before the final painting process begins. An opportunity for improvement of the primer surfacer would be a decrease in the dry time and the time to sand without sacrificing final coating performance. This would significantly improve the turnaround time for a refinish paint job and thereby increase a shop's productivity.[6]

A primer surfacer application of isocyanate-free PU coatings from an alkyd polycarbamate and 1,3/1,4- cyclohexanedicarboxaldehydes (CHDA) was previously reported.[3] In the pigmented primer, Part A of the coating was comprised of polycarbamate, pigments, and solvent, whereas Part B was the CHDA crosslinker. To avoid potential catalyst adsorption onto the pigment or neutralization problems with the catalyst, three components, including a separate acid component, were mixed prior to application of the coating. In the current study, the required components of a polycarbamate resin, CHDA crosslinker and acid catalyst were added as a two-component system. The reaction of polycarbamates with CHDA under acidic conditions occurs rapidly at room temperature. In most applications, the reaction is slowed down by the addition of a blocking agent, a primary alcohol such as ethanol. As shown in *Figure 2*, the alcohol reacts with CHDA to form acetals. Upon spray application, the volatile alcohol evaporates, driving the regeneration of the CHDA from its acetal, and allowing the CHDA to react with the carbamate. Based on this mechanism, a 2K system can be prepared where Part A comprises polycarbamate, solvents, pigments, and dispersants and Part B comprises a primary alcohol, such as ethanol, with CHDA and an acid catalyst.

Table 1 details autorefinish primer surfacer formulations based on the 2K isocyanate-free PU technology. The primer surfacer was formulated with a pigment volume concentration (PVC) of 25. A grind was prepared using the alkyd carbamate, xylene, toluene, a dispersant, and several pigments including corrosion-inhibiting pigments. Once the grind reached a Hegman of 5.5 or higher, the material was let down by adding the remaining solvents including toluene, MEK, ethanol, and diacetone alcohol, in addition to a silane epoxy additive (for the primer formulation #1). The material constituted "Part A" of the primer surfacer. Separately, "Part B" was mixed in the following order: CHDA was added to the ethanol with stirring and mixed for 10-15 min. The acid catalyst was then added to the CHDA and ethanol solution and stirred for an additional 10-15 min. For primer formulation #1, dinonylnapthalenedisulfonic acid (DNNDSA) was the catalyst used. For primer formulation #2, an experimental, hydrophobic sulfonic acid catalyst was used. The primer surfacer formulation was designed to be mixed at a 4:1 ratio by volume of Part A to Part B.

TABLE 1—Iso-Free PU Primer Surfacer Formulations #1 and #2

	PRIMER #1	PRIMER #2
PART A—POLYCARBAMATE COMPONENT	**WEIGHT (G)**	**WEIGHT (G)**
ALKYD CARBAMATE (56.7 WT % IN XYLENE)	34.15	34.40
XYLENE (SOLVENT)	2.01	2.02
TOLUENE (SOLVENT)	15.23	15.34
MEK (SOLVENT)	7.41	7.46
BYK-110 (DISPERSANT)	0.94	0.95
TIONA 595 TITANIUM DIOXIDE (PIGMENT)	4.16	4.19
NICRON TALC 665 (PIGMENT)	4.16	4.19
GRACE CS311 ION EXCHANGED SILICA (PIGMENT)	6.76	6.81
HALOX 650 ORGANIC DIACID (ADDITIVE)	1.47	1.48
BARYTES BARIUM SULFATE (PIGMENT)	4.76	4.79
DIACETONE ALCOHOL (SOLVENT)	1.97	1.99
EPOXY SILANE SILQUEST A-187 (ADDITIVE)	0.65	0.00
TOTAL PART A	**83.67**	**83.63**
PART B—CROSSLINKER COMPONENT		
ETHANOL (SOLVENT)	10.37	9.97
CHDA	4.29	4.32
DNNDSA (40% ACTIVE IN ISOBUTANOL)	1.67	0.00
EXPERIMENTAL SULFONIC ACID CATALYST (50% ACTIVE IN ISOBUTANOL)	0.00	2.08
TOTAL PART B	**16.33**	**16.40**
TOTAL FORMULATION	**100.00**	**100.00**
VOC (LB/GAL)		**4.75**
WEIGHT SOLIDS (%)		**47**
VOLUME SOLIDS (%)		**36**

Direct-to-Metal Primer Performance

The performance of primer formulations #1 and #2 was evaluated as primers only direct-to-metal (DTM) (cold rolled steel sanded with 80 grit sandpaper) and with two commercial systems of basecoat and clearcoat. The iso-free PU primer formulations were also

TABLE 2—Sand Times for the Primer Surfacers

PRIMER SURFACER	FLASH TIME (MIN)[a]	TIME TO SAND (MIN)
ISO-FREE PU DTM PRIMER #1 FORMULATION	10	40
ISO-FREE PU DTM PRIMER #2 FORMULATION	10	40
COMMERCIAL 2K PU PRIMER #1	10	180
COMMERCIAL 2K PU PRIMER #2	10	180

(a) Flash and drying conditions: 23°F/50% relative humidity

TABLE 3—Solvent Resistance and Adhesion Performance of PU Primer Surfacers

	ISO-2K PU #1				ISO-2K PU #2				ISO-FREE 2K PU #1						ISO-FREE 2K PU #2					
	PRIMER SURFACER		FULL SYSTEM		PRIMER SURFACER		FULL SYSTEM		PRIMER SURFACER		PRIMER + SYSTEM 1 BASE/ CLEAR		PRIMER + SYSTEM 2 BASE/ CLEAR		PRIMER SURFACER		PRIMER + SYSTEM 1 BASE/ CLEAR		PRIMER + SYSTEM 2 BASE/ CLEAR	
THICKNESS (MIL)	3.56	3.92	4.53	5.12	4.08	4.11	4.92	6.26	3.8	4.32	5.43	6.1	6.06	4.88	2.83	3.37	5.27	4.6	4.9	5.4
MEK RESISTANCE																				
24 H 25% FILM LOSS	>200	>200			>200	>200			192	>200					>200	>200				
7 D 25% FILM LOSS	>200	>200			>200	>200			173	>200					>200	>200				
CROSSHATCH ADHESION																				
24 H	5B	5B	5B	5B	5B	5B	5B	4B	4B	4B	5B	5B	5B	5B	5B	5B	5B	5B	5B	5B
7 D	5B	5B	4B	3B	5B	5B	4B	4B	4B	4B	5B	5B	5B	5B	5B	5B	4B	5B	5B	5B
24 H X CUT			3A	2A			5A	2A			4A	5A	5A	4A			5A	5A	5A	4A
7 D X CUT			5A	5A			4A	3A			5A	5A	5A	5A			5A	5A	4A	4A

TABLE 4—Gloss and DOI Performance of Full Automotive Refinish Coating System

	ISO-2K PU #1 FULL SYSTEM		ISO-2K PU #2 FULL SYSTEM		ISO-FREE 2K #1 PU WITH BASE/CLEAR #1		ISO-FREE 2K #1 PU WITH BASE/CLEAR #2		ISO-FREE 2K #2 PU WITH BASE/CLEAR #1		ISO-FREE 2K #2 PU WITH BASE/CLEAR #2	
24 H GLOSS												
20 DEGREE	85.9	85.6	88.8	89.1	86	88.2	88.8	86	86.9	87	88.6	88.4
60 DEGREE	90.7	90.8	92.7	92.9	90.8	93.1	93.1	90.7	91.9	91.9	93.4	93.9
85 DEGREE	99.6	99.4	99.7	99.6	99.4	99.7	99.8	99.6	100	100	100	100
7 D GLOSS												
20 DEGREE	84.5	84.7	87.9	88.5	85.1	88.5	87.4	85.7	86.5	86.5	88.7	87.9
60 DEGREE	90	90.2	92.3	92.9	90.5	93	92.6	90.6	91.1	91.2	92.7	93.2
85 DEGREE	99.5	99.8	99.6	100	99.2	100	99.6	99.9	99.5	98.8	100	100
24 H DOI	84.5	84.7	86.4	84.6	84.8	81.6	80.3	85.1	84.9	80.4	86.1	82
7 D DOI	80	82.2	85	83.5	80.9	80.4	80.1	81.4	81.2	86	82	79.9

compared to two commercial, DTM 2K polyisocyanate-based primer surfacers. The primer surfacers were evaluated for time to sand, adhesion to metal, solvent resistance, and humidity resistance. In combination with commercial base- and clearcoats, the iso-free PU and commercial primer surfacers were evaluated for intercoat adhesion performance along with gloss, DOI, and humidity resistance.

Time to Sand

The iso-free PU, alkyd carbamate-based primer surfacer formulations were spray applied directly to CRS panels (sanded with 80 grit) in two coats with a 10-min flash time after each application. The time (after the last 10-min flash) required for the primer to be sanded is summarized in *Table 2*. The coated panels were stored in a controlled temperature and humidity chamber during the drying process. The carbamate-based primers had a short time to sand (40 min). By comparison, commercial isocyanate-PU primers required longer times (180 min). The sandability was determined by the time required for the coating to be hand sanded with a 320 grit sandpaper without caking the paper, and any residual material on the paper was easily shaken or knocked off.

Solvent Resistance and Adhesion

Table 3 summarizes the solvent resistance and adhesion data of the iso-free primers #1 and #2 versus the commercial primers. The iso-free PU primers demonstrated very similar MEK solvent resistance performance compared to the commercial DTM iso-based primers. MEK double rubs reached nearly 200 or greater in 24 h for the iso-free PU primers, indicating fast early property development. The adhesion direct to metal as measured by crosshatch adhesion for the iso-free PU primer #1 is slightly lower at 4B than the iso-free PU primer #2 at 5B. The commercial primers give 5B adhesion direct to metal. The adhesion of full coat systems including primer, basecoat, and clearcoat was measured by crosshatch and crosscut. The iso-free PU primers #1 and #2 were evaluated in combination with two different commercial base- and clearcoat systems. Both iso-free primers with the basecoat and clearcoats gave excellent adhesion performance at 5B with both base- and clearcoat systems, and better adhesion versus the commercial primer with the basecoat and clearcoat. Crosscut adhesion was also measured as some of the film builds exceeded 5 dry mils, per the ASTM-D3359-09 recommendation. Similarly, the adhesion as measured by crosscut of the iso-free PU primers outperformed the commercial primers in a full coat system with base- and clearcoat. The excellent adhesion results of the primer suggest that the iso-free PU system is compatible with commercial solventborne basecoats and clearcoats, as there was no loss of intercoat adhesion or loss of adhesion direct to metal.

Gloss and DOI Data

DOI is a measurement of the sharpness of a reflection from a coating surface. The DOI value is dependent on the color family being used (dark/light metallic or dark/light solid color). Light metallic finishes are expected to have a DOI above 70 and dark solid colors should be over 85.[7] *Table 4* summarizes the DOI and 20-, 60-, and 90-degree gloss measurements of the iso-free PU and commercial primers with commercial black base- and clearcoats. Though the gloss and DOI are measured directly for the commercial clearcoat, it is important that the iso-free PU primers are compatible with existing commercial base- and clearcoats and do not affect the appearance properties of the clearcoat. In particular, if the DOI changes significantly with time, this could indicate that the primer is shrinking with time, causing defects in the topcoat. The high DOI values were maintained after 7 d for most of the iso-free PU primers. The results were similar to the panels primed with commercial controls. The gloss obtained for the clearcoats over the iso-free PU primers is very similar to the commercial controls, with the gloss of all coatings in the mid to high 80s. The gloss did not drop after 7 d for the iso-free PU panels. Overall, the gloss and DOI values of the iso-free PU primers are very similar to commercial benchmarks.

TABLE 5—Humidity Resistance Performance of PU Primer Surfacers

96 H HUMIDITY PERFORMANCE	ISO-2K PU #1		ISO-2K PU #2		ISO-FREE 2K PU #1			ISO-FREE 2K PU #2		
BAKED 3 H AT 140°F	PRIMER	FULL SYSTEM	PRIMER	FULL SYSTEM	PRIMER	FULL SYSTEM #1	FULL SYSTEM #2	PRIMER	FULL SYSTEM #1	FULL SYSTEM #2
THICKNESS (MIL)	3.57	4.17	3.87	5.64	3.45	5.04	5.46	3.23	4.4	4.73
OBSERVATIONS	<1-1 mm blisters on the entire panel	<1 mm blisters on 80% of the panel	No blisters	No blisters	No blisters	No blisters	No blisters	No blisters	No blisters	No blisters
7 D AMBIENT	PRIMER	FULL SYSTEM	PRIMER	FULL SYSTEM	PRIMER	FULL SYSTEM #1	FULL SYSTEM #2	PRIMER	FULL SYSTEM #1	FULL SYSTEM #2
THICKNESS (MIL)	3.55	4.4	3.78	4.91	3.33	5.4	4.77	3.2	5.07	5.13
OBSERVATIONS	<1mm blisters on 80% of the panel	<1 mm blisters on 60% of the panel	No blisters	No blisters	No blisters	No blisters	No blisters	No blisters	No blisters	No blisters

Humidity Resistance Performance

A critical performance feature for new DTM primer surfacer formulation development is the ability to pass the humidity and corrosion testing for automotive refinish applications. The protocol for the humidity testing requires the panels to cure for 7 d prior to being placed in a Cleveland humidity chamber for 96 h at 38°C with 100% condensing humidity. It is critical that the panels with primer only, as well as panels with primer coated with basecoat and clearcoat, both pass humidity testing by showing no signs of blistering or delamination of the films after 96 h of exposure to humidity. The iso-free PU primers were evaluated on a series of panels cured for 7 d under ambient conditions and also on a series of panels that were cured overnight then baked for 3 h at 140°F.

As summarized in *Table 5*, the iso-free PU primers #1 and #2 applied directly to sanded CRS for both sets of panels did not blister or delaminate. Both iso-free PU primer surfacers outperformed commercial iso-based primer surfacer #1 and had similar performance to the commercial iso-based primer surfacer #2. For the primer/base/clear panels, the iso-free PU primer surfacers #1 and #2 with both commercial basecoats and clearcoats #1 and #2 performed very well and comparable to commercial system #2 and outperformed commercial system #1 when applied in a full system.

The humidity resistance performance data shows further support that the novel iso-free PU based chemistry is compatible with existing technology for commercial base- and clearcoats. The humidity performance results show that the iso-free PU primer surfacers formulated with the appropriate ion-exchanged silica corrosion inhibitors and hydrophobic sulfonic catalysts effectively meet the humidity performance requirements for a DTM primer surfacer formulation.

Pot Life Study

One of the key performance features of the iso-free PU technology is the ability to decouple pot life and cure speed. Longer pot life vs traditional 2K isocyanate-based systems is desired without compromising property development. The iso-free PU primer surfacer formulations #1 and #2 were activated and sprayed almost immediately to obtain the results previously discussed. Retainers of both activated primers were saved in a sealed spray cup, and the primers were sprayed ~24 h later to evaluate the pot life of the material. Both primer formulations were able to be sprayed without a noticeable increase in spray viscosity as determined by visual observation (not actually measured). The primers were also sandable in 40 min, similar to the sandability of the primers when sprayed immediately after being activated.

As highlighted in *Table 6,* both DTM iso-free PU primer surfacers #1 and #2 resulted in good MEK double rubs performance after 24 h, with the DTM iso-free PU primer surfacer #2 containing the experimental hydrophobic sulfonic acid catalyst being slightly lower after 24 h (although the film builds were also slightly lower). After 7 d, the MEK double rub values of the two primer surfacers were comparable to one another and similar to the respective primer surfacer coatings that were sprayed immediately after activation (*Table 3*). In addition, both primer formulations gave excellent adhesion to the sanded CRS after 24 h and 7 d.

TABLE 6—Iso-Free PU Primers #1 and #2: Pot Life Study

	ISO-FREE PU PRIMER #1 SPRAYED 24 H AFTER MIXING PART A AND PART B		ISO-FREE PU PRIMER #2 SPRAYED 24 H AFTER MIXING PART A AND PART B	
THICKNESS (MIL)	2.93	3.12	2.33	2.31
MEK RESISTANCE				
24 H 25% FILM LOSS OR 200 RUBS	165	176	80	106
7 D 25% FILM LOSS OR 200 RUBS	>200	193	171	>200
CROSSHATCH ADHESION				
24 H	5B	5B	5B	5B
7 D	5B	5B	5B	5B

TABLE 7—Iso-Free PU Primer #2: Full System Performance With and Without Delayed Primer Application

	ISO-FREE 2K PU #2 SPRAYED IMMEDIATELY AFTER MIXING OF PART A AND PART B				ISO-2K PU #2 SPRAYED 24 H AFTER MIXING OF PART A AND PART B			
	PRIMER		PRIMER WITH SYSTEM #1 BASE AND CLEAR		PRIMER		PRIMER WITH SYSTEM #1 BASE AND CLEAR	
THICKNESS (MIL)	3.13	3	5.23	5.37	2.47	3.3		
MEK RESISTANCE								
24 H 25% FILM LOSS	143	186			133	112		
7 D 25% FILM LOSS	>200	>200			124	175		
CROSSHATCH ADHESION								
24 H	4B	4B	4B	4B	5B	5B	3B	4B
7 D	4B	4B	5B	4B	5B	5B	4B	4A
24 H X CUT			5A	5A			4A	5A
7 D X CUT			5A	5A			4A	5A

TABLE 8—Iso-Free 2K PU Primer Surfacer #2 Performance Cured under High Heat and Humidity

	ISO-FREE 2K PU PRIMER SURFACER #2					
	PRIMER		PRIMER #2 +SYSTEM # 1 BASE/ CLEAR		PRIMER #2 +SYSTEM #2 BASE/CLEAR	
THICKNESS (MIL)	2.7	3.3	4.87	5.6	4.9	5.3
MEK RESISTANCE						
24 H 25% FILM LOSS	162	168				
7 D 25% FILM LOSS	>200	>200				
CROSSHATCH ADHESION						
24 H	5B	5B	5B	5B	5B	5B
7 D	5B	5B	4B	5B	5B	5B
24 H X CUT			5A	4A	5A	3A
7 D X CUT			5A	5A	5A	5A
96 H HUMIDITY						
THICKNESS (MIL)	2.63	4.23	5.1			
BAKED (3 H,140°F)	No blistering	No blistering	No blistering			
THICKNESS (MIL)	2.57	5.43	4.43			
7 D AMBIENT	No blistering	No blistering	No blistering			

To further study the pot life effect on total system properties, panels with the iso-free PU primer #2 were prepared with commercial system #2 black base- and clearcoats. The iso-free PU primer was sprayed immediately after activation and again ~24 h after activation. Performance data on the primer alone and in combination with the commercial black basecoat and clearcoat is summarized in *Table 7.* The comparison of coating properties further illustrates that the iso-free PU primer formulation gives good properties even when applied 24 h after activation.

Effect of Temperature and Humidity on Cure

For industrial spray applications such as automotive refinish, coating application and cure temperature and humidity conditions are often uncontrollable. The primer formulations were sprayed at room temperature and cured under room temperature and 50% relative humidity (RH). To replicate high temperature and high humidity conditions that could be possible in a paint shop, the iso-free primer surfacer #2 was sprayed and allowed to flash under room temperature and then cured in a temperature controlled chamber at 90°F and 85% RH. Similar to the panels cured at controlled room temperature (68°F, 50% RH), the primed panels sanded easily after 40 min. Furthermore, the property development as measured by MEK resistance and adhesion at 24 h and 7 d (*Table 8*) was also comparable to the primed panels cured at room temperature and 50% RH (*Table 3*). The good property development as observed at 24 h suggests that the cure profile was not significantly affected when the coating was cured under high humidity conditions. The humidity resistance performance was also consistent with the panels cured at room temperature and 50% RH where no blistering or paint delamination was observed. The solvent resistance, adhesion, and humidity resistance performance data of the iso-free PU-based primer suggests that the novel 2K, iso-free PU chemistry is robust under high temperature and humidity for refinish primer applications.

Low-VOC Primer Surfacer

The 2K iso-free primer surfacers #1 and #2 were formulated at conventional VOC, approximately 4.8 lb/gal. In certain regions of North America, lower VOC formulations are required for primer surfacers. In many cases, these types of lower VOC formulations often require the use of exempt solvents to meet the requirement. *Table 9* summarizes an iso-free primer surfacer formulated at low VOC (2.05 lb/gal) at PVC = 25 with exempt solvents in a 3.5:1 mix ratio by volume of Part A to Part B.

The iso-free PU primer surfacer was applied in two coats with a flash time similar to the conventional VOC primer formulation and sanded easily in 40 min. The iso-free PU primer surfacer #3 had excellent solvent resistance and adhesion at 24 h and 7 d, as shown in *Table 10*. The humidity performance of the primer surfacer-only panels and those with primer surfacer in combination with commercial solventborne base- and clearcoat system #1 was also excellent (*Table 11*). No blistering or delamination was observed. Adhesion by crosshatch was measured immediately after removal of the panels from the humidity chamber and once again after a 24-h period of recovery. For both sets of panels (7 d ambient cure and overnight ambient cure followed by 3 h at 140°F bake), the primer surfacer only panels showed excellent adhesion post 96 h humidity exposure and maintained an excellent adhesion of 5B after 24 h. For the primer surfacer panels topcoated with base- and clearcoat, a loss of adhesion (measured at 2B) was observed upon immediate removal of the panels from the humidity chamber. However, the adhesion did recover after a 24-h period, with adhesion measured at 4B and 5B for the baked and ambient-cured panels, respectively.

CONCLUSION

A new ambient-cure, 2K isocyanate-free polyurethane technology has been developed and evaluated in automotive refinish primer surfacer formulations. Key performance features of the iso-free PU primer surfacers include fast primer sandability, excellent solvent resistance, adhesion and humidity resistance,

TABLE 9—Low-VOC Iso-Free Primer Surfacer Formulations #3

PRIMER #3	WEIGHT (G)
PART A—POLYCARBAMATE COMPONENT	
ALKYD CARBAMATE (70 WT % IN 70:30 OXSOL 100/ACETONE BLEND)	34.40
XYLENE (SOLVENT)	7.28
METHYL ACETATE (SOLVENT)	5.20
OXSOL 100 (SOLVENT)	14.04
BYK-110 (DISPERSANT)	1.03
TIONA 595 TITANIUM DIOXIDE (PIGMENT)	4.55
NICRON TALC 665 (PIGMENT)	4.55
GRACE CS311 ION EXCHANGED SILICA (PIGMENT)	7.38
HALOX 650 ORGANIC DIACID (ADDITIVE)	1.61
BARYTES BARIUM SULFATE (PIGMENT)	5.20
DIACETONE ALCOHOL (SOLVENT)	2.08
TOTAL PART A	**83.17**
PART B—CROSSLINKER COMPONENT	
ETHANOL (SOLVENT)	9.88
CHDA	4.69
EXPERIMENTAL SULFONIC ACID CATALYST (50% ACTIVE IN ISOBUTANOL)	**2.26**
TOTAL PART B	**16.83**
TOTAL FORMULATION	**100.00**
VOC (LB/GAL)	**2.05**
WEIGHT SOLIDS (%)	**50**
VOLUME SOLIDS (%)	**40**

TABLE 10—Solvent Resistance and Adhesion Performance of Low-VOC Iso-free Primer Surfacer Formulation #3

	ISO-FREE 2K PU PRIMER #3			
	PRIMER		PRIMER WITH SYSTEM #1 BASE AND CLEAR	
THICKNESS (MIL)	4.23	4	5.83	6.2
MEK RESISTANCE				
24 H 25% FILM LOSS	>200	194		
7 D 25% FILM LOSS	>200	>200		
CROSSHATCH ADHESION				
24 H	5B	5B	5B	5B
7 D	5B	5B	5B	5B
24 H X CUT			5A	5A
7 D X CUT			5A	5A

TABLE 11—Humidity Performance of the Low-VOC Iso-Free PU Primer Surfacer Formulation #3

	ISO-FREE 2K PU PRIMER #3	
96 H HUMIDITY	**PRIMER ONLY**	**PRIMER WITH SYSTEM #1 BASE AND CLEAR**
OVERNIGHT CURE 3 H @ 140° F		
THICKNESS (MIL)	3.2	5.6
OBSERVATION	No blisters	No blisters
ADHESION (IMMEDIATE)	5B	2B
ADHESION (24 H RECOVERY)	5B	4B
7 D AMBIENT CURE		
THICKNESS (MIL)	3.47	5.75
OBSERVATION	No blisters	No blisters
ADHESION (IMMEDIATE)	5B	2B
ADHESION (24 H RECOVERY)	5B	5B

as well as primer compatibility with commercial solventborne basecoat and clearcoat systems. A significant benefit of the iso-free PU technology is the ability to decouple pot life and cure speed, resulting in coatings with faster return to service and higher throughput at room temperature—both key benefits to the refinish market. Application of the iso-free PU chemistry to low-VOC formulations using exempt solvents was demonstrated and offered excellent performance versus conventional VOC formulations and isocyanate-based PU primer surfacers. ❊

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Benchmark studies for new isocyanate-free polyurethane technology show comparable results to commercial system for corrosion resistance and multi-substrate adhesion

Several important and favorable performance attributes of the new ambient cure, 2K isocyanate-free polyurethane technology—the ability to decouple pot life from cure speed, good chemical and humidity resistance, fast sandability, and good adhesion—were presented at the 2016 American Coatings Conference. These results demonstrated the benefits of using this novel technology for automotive refinish applications. At the time, results from tests that measure this technology's performance for other beneficial characteristics, including corrosion resistance and adhesion to substrates beyond cold rolled steel (CRS), were not available.

As part of ongoing testing to validate and enhance this technology for use in automotive refinish coating applications, recent benchmarking studies were conducted to determine performance related to corrosion resistance, adhesion, and other characteristics.

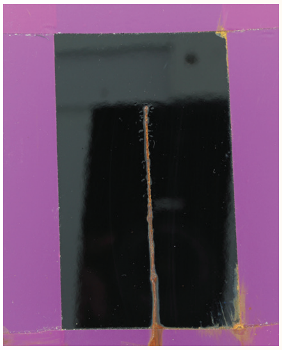
To obtain exceptional corrosion protection, automotive refinish polyurethane primer surfacers are often used in combination with etch primer. These recent studies evaluated the performance of the isocyanate-free polyurethane primer surfacer over a commercial etch primer versus a commercially available primer surfacer. The benchmark commercially available primer surfacer product was a speed primer designed for spot and panel repairs with outstanding film build, fast dry-to-sandability, and excellent resistance to film shrinkage.

Corrosion resistance for both primer surfacers was evaluated on panels of CRS that were coated with a full commercial automotive refinish coating system and exposed to a 1000-h salt fog test. In the first benchmark test, two CRS panels were sanded with 80-grit sandpaper and primed with a commercially available etch primer. Each panel was then coated with two coats of a primer surfacer—one was formulated with the new isocyanate-free polyurethane technology with the Nacure XC-315 catalyst from King Industries, and one with a commercially available primer surfacer. The primer surfacers were spray-applied and flashed for 10 min per coat. After about 50 min, both primer surfacers were sanded with 320 grit sandpaper. After sanding, a commercially available sealer, black solventborne basecoat and clearcoat were then applied per the manufacturer's instructions to complete the full system coating.

The panels were exposed to a salt fog for 1000 h and observed for blistering, delamination, and rust. Results, as shown in *Figure 1,* show no blistering or delamination on any of the coated CRS panels, and minimal differences in rust along the scribe. These results indicate similar corrosion resistance performance for the primer surfacer formulated with the new isocyanate- free polyurethane technology and the commercially available primer surfacer, when they are used as part of a full automotive refinish coating system. A second study repeated this benchmark test and indicated similar results.

FIGURE 1—Corrosion panels after 1000h of Salt Fog Testing.

Iso-free PU Primer Surfacer



Commercial PU Primer Surfacer

The primer surfacers were also evaluated for adhesion to several diverse substrates. Per ASTM 3359 guidelines and following the same coating application process used in the corrosion resistance tests, various metal panels—including CRS, aluminum, and galvanized steel panels—were coated with a full automotive refinish coating system. After conducting 24-h and 7-d crosshatch and crosscut tests, results showed comparable adhesion performance for both primer surfacers across the metal substrates tested.

These studies further validate the benefits of using the new ambient cure, 2K isocyanate-free polyurethane technology in automotive refinish coatings applications that require durability and versatility. Additional research and development will continue for this novel technology to further enhance corrosion resistance and adhesion performance. ❊