



New Low-Viscosity Acrylic-Urethane Prepolymers and Their Acrylated Oligomers for Moisture and UV-Curable Coatings

by Daniel B. Pourreau
Lyondell Chemical Company*

and
Scott Smyth
Resin Chemists LLC†

This article describes a new class of urethane acrylate oligomers for weatherable UV-curable systems. Unlike commercial urethane acrylates that are based on polyether or polyester polyols, this new class of urethane oligomers is based on acrylic polyols. These new acrylic polyols are unique in that they produce low-viscosity, nongelling urethane prepolymers with isophorone diisocyanate. These prepolymers can be further treated with hydroxy-functional acrylates such as hydroxyethylacrylate (HEA) or caprolactone acrylate (CA) to yield low-viscosity acrylated urethane acrylic oligomers.

By replacing the polyester and polyether backbone in urethane acrylates with an acrylic backbone, this chemistry opens the door to more weatherable UV-curable coatings, with properties that approach two-component urethane systems. These new urethane acrylates were formulated into sprayable UV-curable coatings with properties that rival two-component urethanes. The influences of diluent monomer type and content, hydroxy acrylate, and solvents on coating viscosity, VOC content, and properties were evaluated.

INTRODUCTION

The majority of commercial urethane prepolymers are based on polyether or polyester polyols and aromatic polyisocyanates, such as toluene diisocyanate (TDI) or diphenylmethane diisocyanate (MDI).¹ Polyester prepolymers based on isophorone diisocyanate (IPDI) are often used for weatherable coating applications. Aliphatic isocyanates such as IPDI are less susceptible to yellowing and UV-induced photodegradation than their aromatic counterparts, and polyesters are also more resistant to UV degradation than polyethers.

Reports of urethane prepolymers based on acrylic polyols are virtually non-existent and the authors are aware of no such commercial products. We believe this is in part because, unlike condensation polymers, the

Presented at the 82nd Annual Meeting of the Federation of Societies for Coatings Technology, October 27-29, 2005, in Chicago, IL.

*1601 West Chester Pike, Newtown Square, PA 19073. For additional information, email acryflow@lyondell.com or visit acryflow.com.

†Moorestown, NJ.

functionality of acrylic polyols cannot be readily controlled to 2 or 3. Also, in conventional acrylic polyols, the OH functionality is randomly distributed throughout the polymer and in many cases the OH functionality is primary. Consequently, treating acrylic polyols with diisocyanates usually causes rapid crosslinking of the polymer chains and produces highly viscous or gelled products which are not suitable for high-solids coatings.²

However, by using isophorone diisocyanate, allyl-based acrylic polyols with all secondary OH functionality,³ and carefully controlling the reaction conditions, low-viscosity aliphatic urethane prepolymers were obtained in quantitative yield. The prepolymers were used to formulate moisture-curable coatings and prepare acrylated urethane acrylic oligomers for highly weatherable UV cured coatings.

EXPERIMENTAL

Raw Materials

ACRYFLOW[™] acrylic polyols were obtained from Lyondell Chemical Co. Joncryl[®] 920 was obtained from Johnson Polymer. Darocur[®] 4265 was obtained from Ciba Specialty Chemicals. UV monomers were obtained from Sartomer Co. and used as received. Solucote[™] 373 MA was obtained from Soluol, Inc.

Attempted Preparation of an Acrylic Urethane Acrylate Oligomer with a Conventional High-Solids Acrylic Polyol

Joncryl 920 acrylic polyol (850 g, 80% solids in MAK) was charged into a 2-L glass resin kettle equipped with a stirrer, addition funnel, air inlet, thermometer, and heating mantle. Dibutyltin dilaurate (0.88 g) and 2,6-di-*t*-butyl-4-methylphenol (2.0 g, BHT) were added to the reactor and the reaction temperature increased to 40°C. Isophorone diisocyanate (125 g) was added to the reactor over a period of one hour under air sparge. The addition rate was controlled to keep the reaction temperature at 40°C. The reaction contents gelled after 89 g of IPDI had been added.

Preparation of an Acrylated Urethane Acrylic Oligomer

ACRYFLOW P120 acrylic polyol (680 g, OH# 120 mg KOH/g) was dissolved in acetone (170 g) and charged to the same apparatus as above. Dibutyltin dilaurate catalyst (0.88 g) and 2,6-di-*t*-butyl-4-methylphenol (2.0 g, BHT) were added to the reactor and the temperature increased to 40°C. Isophorone diisocyanate (125 g) was added to the reactor over a period of one hour under air sparge. The addition rate

was controlled to keep the reaction temperature at 40°C. Hydroxyethyl acrylate (78.5 g) was added to the reactor over 30 min at 40°C. The temperature was raised to 60°C and maintained for four hours. The reaction was monitored by the disappearance of the NCO stretching frequency at 2,265 cm⁻¹ in the infrared spectrum. A clear product (1,018 g, 97% yield) with the following properties was collected: OH#: 59.4 mgKOH/g; solids%: 83.0; acrylated P120: 72.2%; IPDI diacrylate: 10.8%; Mn 4370; Mw 24200; viscosity: 4,090 cps; residual NCO content: 0.040 meq/g.

Preparation of an Acrylic Urethane Acrylate Oligomer for UV-Curable Coatings

A reactor was charged under air sparge with 128 g of IPDI monomer, 132 g of diluent (*n*-BuAc), and 1.02 g of DBTDL. To this mixture were added three 120.53 aliquots of ACRYFLOW M100 acrylic polyol (80% solution in *n*-BuAc) one hour apart. Hydroxyethylacrylate (HEA), 56.6 g, was added over 20 min. The mixture was then heated to 40°C and stirred for one hour. The resulting mixture was a 70% solids solution of M100-IPDI-acrylate with a Brookfield viscosity of 19,300 cps (*n*-BuAc).

Preparation of a Flexible Acrylic-Polyester Urethane Acrylate Oligomer for UV-Curable Coatings

A quart-sized round amber bottle was charged with 111 g of IPDI monomer and 0.8 g of DBTDL. To this bottle were added 325 g of ACRYFLOW M100 acrylic polyol (80% solution in *n*-BuAc) diluted with 100 g of *n*-BuAc in three parts, one hour apart. The bottle was rolled to mix the contents between each addition. Caprolactone acrylate (CA) (SR 495 from Sartomer), 182 g, was then added. The mixture was then placed in a 50°C oven for two hours, then rolled overnight. The resulting mixture was a 70% solids solution of M100-IPDI-caprolactone acrylate in *n*-BuAc with a Brookfield viscosity of 1,941 cps.

Preparation of Acrylic Urethane Acrylate Oligomers for UV-Curable Coatings and Adhesives

A reactor was charged under air sparge with 100 g of IPDI monomer, 100 g of diluent (*n*-BuAc or HDDA), 0.04 g of MEHQ and 0.8 g of DBTDL. To this mixture were added three 146.67 aliquots of ACRYFLOW P60 acrylic polyol (90% solution in *n*-BuAc or HDDA, hexanediol diacrylate), one hour apart. Hydroxyethylacrylate, 57 g, was added over 20 min. The mixture was then heated to 40°C and stirred for one hour. The resulting mixture was an 80% solids solution of P60-IPDI-acrylate oligomer with a Brookfield viscosity of 3,900 cps (*n*-BuAc) or 38,800 cps (HDDA). The P60

Table 1—Relative Rate Constants of the Isocyanate Reaction with Primary OH

Isocyanate	k1	k2	k1/k2
TDI.....	400	33	12.1
MDI	320	110	2.9
IPDI.....	0.62	0.23	2.7
HDI.....	1	0.5	2.0
H ₁₂ MDI	0.57	0.4	1.4

acrylated oligomer solution in n-BuAc was stable indefinitely at room temperature, whereas the HDDA solution gelled after approximately one week.

Preparation of UV-Curable Acrylic Urethane Clearcoats

The acrylated oligomers were dissolved in acrylate monomers and treated with 4% by weight on total resin solids of Darocur 4265 photoinitiator. The resulting formulations were reduced to spray viscosity with acetone and applied to steel panels coated with Bonderite 1000 and a white basecoat. Coatings were irradiated after a 30-min flash-off period. Physical property tests were performed on the coated steel panels. Appearance tests were performed on the white basecoated panels.

UV Equipment and Cure

The panels were UV-cured using a Fusion UV Model LC-6B Benchtop Conveyor equipped with a mercury vapor lamp ("H" bulb). The conveyor belt speed was set at 16 ft/min. Actinometry was performed using a Power Puck® from EIT, Inc. All coatings were tack and print free in one pass which corresponds to 1.65 J/cm² and were subjected to three more passes to insure full cure.

RESULTS AND DISCUSSION

Preparation of Acrylic Urethane Prepolymers

Attempts to prepare acrylic urethane prepolymers with conventional acrylic polyols or with isocyanates other than IPDI produced gels. We attribute this in part to the higher reactivity of conventional polyols that are usually based on hydroxyethyl acrylate (HEA) or methacrylate (HEMA). Primary OH groups react two to four times faster with isocyanates than secondary ones. In addition, isocyanates can have very different reactivities, even in the same molecule (Table 1).

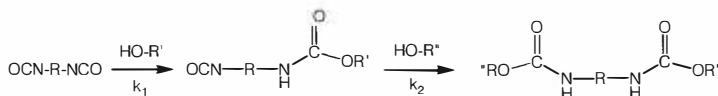


Table 2—Physical Properties of Acrylic Aliphatic Urethane Prepolymers

Acrylic urethane prepolymers.....	UP60	UM100
Nonvolatile content	77%	80%
Viscosity @25°C cps	11,050	5,000
Viscosity 70% in MAK, cps.....	—	530
Viscosity 60% in MAK, cps.....	400	—
% NCO of nonvolatiles	4.9	6.1
% Free IPDI in nonvolatiles	0.22%	0.18%

By using IPDI—a slow-reacting isocyanate with a reactivity ratio of 2.7—we were able to produce low viscosity acrylic aliphatic urethane prepolymers by controlled addition of acrylic polyols to IPDI monomer at ambient temperature (Table 2). The reaction proceeds rapidly at, or slightly above, room temperature, and in quantitative yield. Adding an alcohol at the end of the reaction prevents gel formation and improves storage stability.

UM100 produced fast-drying coatings without amine accelerators compared to a commercial aliphatic urethane prepolymer (Figure 1). This marked increase in cure speed is in part due to the higher functionality of the acrylic polyol and, presumably, to the higher T_g of the acrylic polyol. It is not due to a higher NCO content as the commercial product has an NCO content of 7.2% versus 6.1% for the acrylic based prepolymer.

UM100 gives hard films with limited flexibility. Adding a flexible diluent like the uretidione of hexamethylene diisocyanate (HDI dimer) yields coatings with higher solids, improved chemical resistance, and flexibility. Blending UM100 with a polyester-based prepolymer is also expected to improve the coating flexibility and abrasion resistance. The effect of adding these diluents on the cure speed of the coating is illustrated in Figure 2. Weatherability and other performance evaluations of these coatings are underway.

Figure 1—Hardness development of moisture-curable coatings based on acrylic and polyester aliphatic urethane prepolymers.

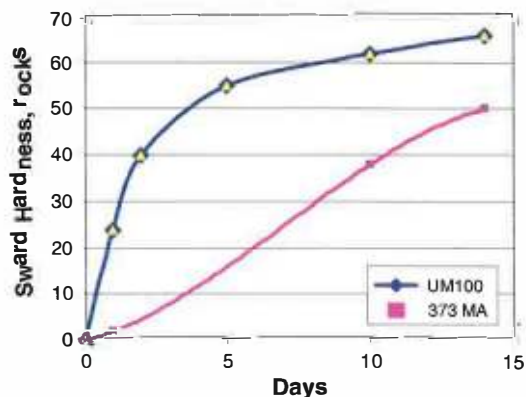


Figure 2—Hardness development of moisture-curable coatings based on blends of UM100 and isocyanate-functional diluents.

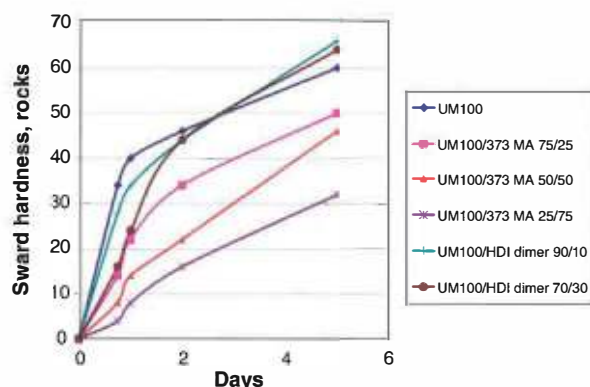
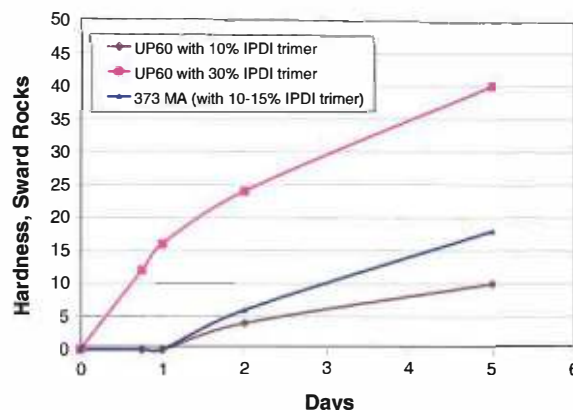


Figure 3—Effect of added IPDI trimer on the hardness development of moisture-curable coatings based on UP60 vs. a polyester aliphatic urethane prepolymer.



UP60, on the other hand, cured very slowly in the absence of added isocyanate trimer and yielded soft, tacky films. Adding IPDI trimer to UP60 had a positive effect on both cure speed and final coating hardness (Figure 3). UP60 behaves similarly to a polyester-based prepolymer. This is not surprising, since the OH functionality of the P60 polyol is only 2.4 per polymer chain and its T_g is -48°C . This is in contrast to M100, which has a T_g of 5°C and an average OH functionality of 4.5 per polymer chain. The commercial polyester-based prepolymer also contains 10–15% IPDI homopolymer to improve cure speed and ultimate coating hardness.

Acrylated Acrylic Urethane Oligomers for UV-Cured Coatings

Low-viscosity acrylated acrylic urethane oligomers were prepared by addition of HEA or CA to UM100 and UP60. Oligomer and coating properties are listed in Table 3.

UV-curable coating formulations were obtained by adding 4% of a blend of bis-acylphosphine oxide/ α -hydroxyketone photoinitiators. The P60 urethane acrylate (P60 UA) and caprolactone acrylate of UM100 yielded soft films following UV irradiation, whereas the HEA of UM100 yielded a hard film with good adhesion to pretreated metal

and good chemical resistance. The diluent had an effect on film properties. P60 UA in HDDA yielded a harder film with greater chemical resistance than P60 UA in n-BuAc. However, its adhesion and impact resistance were reduced.

Formulation of UV-Curable Coatings

Traditional UV formulations do not contain solvents and are relatively viscous compared to solventborne formulations. That is because acrylate monomers are relatively weak solvents for the acrylated oligomers resins. High coating viscosity makes spray application difficult if not impossible. Hence, UV-curable coatings are usually applied by roll, curtain, or vacuum techniques.

Table 4 lists several starting UV-formulations and their coating properties. The formulations have VOC contents ranging from 120–200 grams VOC/liter and most can be sprayed with conventional spray equip-

Table 3—Physical Properties of Acrylated Acrylic Urethane Oligomers and UV-Cured Coatings

Oligomer properties.....	P60 UHA	P60 UHA	M100 UHA	M100 UCA
Hydroxy acrylate used.....	HEA	HEA	HEA	CA
Diluent.....	HDDA	n-BuAc	n-BuAc	n-BuAc
% Nonvolatile content.....	100%	80%	70%	70%
Viscosity, cps.....	38,800	3,900	2,620	1,941
Mn.....	800	3,057	2,081	3,442
Pd.....	26.4	8.3	8.0	18.8
Coating Properties, 3 mils wet on Bonderite® steel				
Photoinitiator.....	4% Darocur 4265			
Koenig hardness.....	28	18	109	17
Impact resistance.....				
Front.....	60	160	20	160
Reverse.....	<20	160	<20	160
MEK rubs.....	69	20	90	60
% Crosshatch adhesion.....	0	20	95	95

Table 4—Starting Formulations and Coating Properties of UV-Curable, Acrylic Urethane Coatings

Formulation Components	1008816	1008817	1008818	1008819	1008820	1008821	1008822	1008823
M100 UHA (70% in BuAc).....	86	86	86	86				
P60 UHA (80% in BuAc).....					75	75	75	75
IBOA (SR 506).....			20		10	20		30
Isobutyl acrylate (SR 440).....	10	20		30			20	
TMPTA (SR 351).....		20	20		30			10
EO6 TMPTA (SR 499).....	30			10		20	20	
Darocur 4265.....	4	4	4	4	4	4	4	4
Acetone.....	20	20	20	20	15	15	15	15
Total grams.....	150	150	150	150	134	134	134	134
Formulation Constants								
% Solids.....	69%	69%	69%	69%	78%	78%	78%	78%
Grams VOC/liter.....	218	196	192	199	134	122	124	123
Lb VOC/gal.....	1.82	1.63	1.61	1.66	1.12	1.02	1.04	1.03
% Photoinitiator on TRS.....	4%	4%	4%	4%	4%	4%	4%	4%
Brookfield viscosity, cps.....	235	185	169	130	95	89	52	50
Coating Appearance, 3 mils wet on white basecoat								
60° Gloss.....	94	94	93	92	88	88	88	88
20° Gloss.....	87	87	87	86	80	80	80	81
DOI.....	60	50	70	60	90	90	90	100
Yellowness index.....	5.1	4.1	6.5	2.3	2.5	2.5	3.1	3.1
Coating Properties, 3 mils wet on Bonderite steel								
Dry film thickness, mils.....	2.1	2.2	2.2	2.2	2.4	2.5	2.3	2.3
Koenig hardness, swings.....	112	121	135	84	90	37	14	80
Impact Resistance in./lb								
Front.....	50	30	30	70	30	160	160	70
Reverse.....	10	10	10	60	10	100	100	40
MEK double rubs.....	200	200	200	200	200	200	200	200
Crosshatch adhesion.....	0	0	0	0	0	20%	30%	0

ment. These formulations were applied to pretreated and basecoated steel panels and UV-cured to yield glossy, solvent-resistant coatings with poor adhesion to pretreated steel. The coating hardness varied with the hardness of the acrylic backbone and the nature of the reactive diluents.

To improve the impact resistance and adhesion of these coatings, we replaced IIEA with caprolactone acrylate in the oligomer synthesis. Polyesters such as caprolactone are known to improve the flexibility of two-component acrylic urethane coatings. We also added a proprietary adhesion promoter described by the manufacturer as a mono-functional acid ester (Table 5). Since M100 UCA, the CA-modified urethane prepolymer, gave a soft coating without acrylate diluents (Table 3), we selected isobornyl acrylate (IBOA) and trimethylolpropane triacrylate (TMPTA)—two high- T_g monomers—as the diluents.

Table 5—Starting Formulations and Coating Properties of UV-Curable, Acrylic-Polyester Urethane Coatings

Formulation Components	1008825	1008827	1008828	1008829
M100 UCA (70% in BuAc).....	86	86	86	86
IBOA (SR 506).....	40	20		20
TMPTA (SR 351).....		20	20	
Adhesion promoter (CD 9050).....	5	5	5	5
Darocur 4265.....	4	4	4	4
Acetone.....	10	10	20	20
Total grams.....	145	145	135	135
Formulation Constants				
% Solids.....	75%	75%	66%	66%
Grams VOC/liter.....	188	192	226	220
Lb VOC/gal.....	1.57	1.61	1.88	1.83
% Photoinitiator on TRS.....	4%	4%	4%	4%
Brookfield viscosity, cps.....	85	122	54	59
Coating Appearance, 3 mils wet on white basecoat				
60° Gloss.....	90	93	93	93
20° Gloss.....	85	86	86	86
DOI.....	90	90	90	90
Yellowness index.....	3	6.84	9.21	3.33
Coating Properties, 3 mils wet on Bonderite steel				
Dry film thickness, mils.....	2.8	2.8	2.4	2.4
Koenig hardness, swings.....	115	117	109	95
Impact resistance, in./lb				
Front.....	30	40	40	160
Reverse.....	10	10	10	160
200 MEK double rubs.....	scratch	OK	OK	OK
Crosshatch adhesion.....	100%	95%	95%	100%

A couple of trends are evident from these results. Using TMPTA—a trifunctional acrylate monomer—negatively affected the coating's adhesion and color. Reducing the IBOA/oligomer ratio from 40% (1008826) to 25% (1008829) resulted in improvement in impact resistance and abrasion resistance (MEK double rubs). We attribute the improvement in adhesion and flexibility to a reduction in shrinkage during the UV-cure process. The coating with less IBOA also showed improved scratch resistance when subjected to 200 MEK rubs. We attribute this to an increase in the coating's crosslink density and a reduction in hardness as evidenced by the lower Koenig swing value.

Based on these results, we developed optimized formulations based on M100 UHA, an all-acrylic urethane oligomer, and M100 UCA, a caprolactone-modified acrylic urethane resin (Table 6). We added a flow aid to improve gloss and distinctness of image (DOI) and a hindered amine light stabilizer (HAL) and UV-screener package to two of the formulations. The two formulations without HAL and UV-screensers yellowed slightly more than the other two when UV-cured, but otherwise had identical properties.

Film thickness had an effect on impact resistance and surface hardness. The thicker the film, the softer it was and the lower its impact resistance. Overall, film properties were excellent for both formulations, although the caprolactone-modified acrylic urethane has superior impact resistance and DOI. These formulations were sprayable at 66% solids and less than 1.9 lb VOC/gal.

These results also illustrate that using solvents in UV-curable formulations offers several benefits. First, the amount of acrylate monomer used can be substantially reduced while achieving spray viscosity. This has a positive effect on coating adhesion because UV-induced shrinkage is reduced and the solvent cleans the surface. Second, the coating viscosity is reduced, which also has a positive effect on adhesion and appearance. Contrast, for example, the DOI values between the coatings in Tables 4 and 5. Third, coating sag resistance is improved because the solvent evaporates quickly be-

Table 6—Optimized UV-Curable Coatings for Weatherable Applications

Formulation Components	1008830	1008831	1008832	1008833
M100 UHA (70% in BuAc)	86.0		86.0	
M100 UCA (70% in BuAc)		86.0		86.0
Isobornyl acrylate (SR 506)		20.0		20.0
Isooctyl acrylate (SR 440)	20.0		20.0	
BYK 358 N (Flow Aid)	1.0	1.0	1.0	1.0
Adhesion promoter (CD 9050)	5.0	5.0	5.0	5.0
Darocur 4265 (photoinitiator)	3.0	3.0	3.0	3.0
Hostavin PR-25 (50% in acetone)	1.65	1.65	0.00	0.00
Tinuvin 292 (50% in acetone)	3.35	3.35	0.00	0.00
Acetone	17.5	17.5	20.0	20.0
Total grams	137.5	137.5	135.0	135.0
Formulation Constants				
% Solids	66%	66%	66%	66%
Grams VOC/liter	219	215	224	220
Lb VOC/gal	1.83	1.80	1.87	1.84
% Photoinitiator on TRS	3%	3%	3%	3%
Brookfield viscosity, cps	36	130	34	103
Coating Appearance, 3 mils wet on white basecoat				
60° Gloss	94	93	94	93
20° Gloss	87	86	87	85
DOI	90	100	95	100
Yellowness index	1.4	1.4	2.8	3.0
Coating Properties, 3 mils wet on Bonderite steel				
Dry film thickness, mils	2.3	1.7	1.7	2.3
Koenig hardness, swings	75	95	91	70
Impact resistance, in./lb				
Front	30	160	120	160
Reverse	5	160	160	160
200 MEK double rubs	pass	pass	pass	pass
Crosshatch adhesion	100%	100%	100%	100%

fore UV cure, leaving a semi-solid coating with little tendency to flow.

Clearly, fast solvents are preferable so that the flash-off time is relatively short and productivity is not significantly affected. In this study, we chose n-Butyl acetate to prepare the acrylated oligomers and acetone to reduce the coating to spray viscosity. N-BuAc is non-HAP and acetone has the added advantage of being VOC exempt in the United States. Tail solvents are not needed as the acrylate monomers help with flow and leveling.

Choosing acrylate monomer diluents can be confusing, with literally hundreds available. However, careful consideration of the intended application and the properties of the acrylated oligomer can significantly reduce the number of viable options. Our goal in this study was to develop weatherable coatings for spray application. To reduce potential respiratory and skin hazards, we chose relatively nonvolatile monomers such as isobornyl and isooctyl acrylate, and TMPTA and its ethoxylated version. Although weatherability data are not yet available on these latest formulations, we are confident that they will weather as well as our earlier acrylic urethane coating formulations.⁴

CONCLUSIONS

By careful selection of raw materials and reaction conditions, low-viscosity, storage-stable acrylic aliphatic urethane prepolymers were prepared. Addition of hydroxy-functional acrylates such as HEA and caprolactone acrylate to these prepolymers produced acrylated acrylic urethane oligomers suitable for UV-curable coatings and, potentially, adhesives.

Moisture-curable coatings with superior curing speed were prepared from M100, an acrylic polyol with mid-range hardness and OH functionality and IPDI. P60, a liquid acrylic polyol with an average of 2.4 OH groups per polymer chain, produced a slow curing urethane prepolymer. Addition of IPDI trimer to the P60 urethane prepolymer improved the coating's cure speed and chemical resistance properties.

These new acrylic urethane polymers are expected to find use in applications where polyester- or polyether-based prepolymers or acrylated urethanes have insufficient weatherability, hardness, or cure speed. These applications include industrial maintenance, automotive, and wood coatings. **CT**

ACKNOWLEDGMENTS

The authors wish to thank Bob Good for expert technical assistance.

References

- (1) Szycher, M., *Szycher's Handbook of Polyurethanes*, CRC Press, 1999.
- (2) Wang, W. and Pourreau, D.B., U.S. Patent 6,696,593, Feb. 24, 2004.
- (3) Guo, S.-H., Wang, W., Harris, S.H., Patel, S., Junker, L.J., Blackwell, R., Fadakar, F., and Pourreau, D.B., *Paint & Coatings Industry*, June 2002.
- (4) Arndt, L.W., Junker, L.J., Patel, S., Pourreau, D.B., and Wang, W., *Paint & Coatings Industry*, page 42, February 2004.

Go to
www.coatingstech.org
for updates on
all FSCT activities!