

Effect of Particle Size Distribution on the Performance of Two-Component Water-Reducible Acrylic Polyurethane Coatings Using Tertiary Polyisocyanate Crosslinkers

Denise E. Fiori, David A. Ley, and Richard J. Quinn—Cytec Industries Inc.*

INTRODUCTION

With the increasing regulatory pressure to reduce environmentally undesirable emissions of volatile organic compounds (VOCs), the coatings industry is developing two-component waterborne systems. Over the past five years, two-component waterborne polyurethane coatings have been developed for a number of applications.¹⁻⁵

There are generally three approaches to developing viable two-component waterborne polyurethane systems. The first two approaches involve the use of polyisocyanate crosslinkers that contain primary or secondary isocyanate groups. The disadvantage of these polyisocyanates is that they are so reactive with the water in the system that the formulator must use an excess of isocyanate to compensate for the loss of NCO to reaction with water. This competing water reaction generates carbon dioxide that causes foaming in the formulation and pinholing in the applied coatings. The high water reactivity also leads to short pot life and makes it difficult to obtain defect-free thick films. The first approach involves the use of hydrophilically modified polyisocyanates. However, problems with this technique are that these modifications require tight control over mixing due to the size and viscosity differences between the dispersed polyisocyanate and the polyol,^{6,7} and the hydrophilic modification makes the films more susceptible to water. Blistering can be difficult to avoid as film thickness reaches 60-80 μm . Another problem with this approach is that the end of usable pot life is not always clear because the polyisocyanate and polyols are dispersed in separate particles.

The second approach is to use a water-reducible polyol to disperse an unmodified polyisocyanate.⁸ This approach reduces the water susceptibility and eliminates the need for careful control over shear while reducing with water. However, it can shorten the usable pot life because the isocyanate and polyol are dispersed in the same particles. Neither of these approaches eliminates

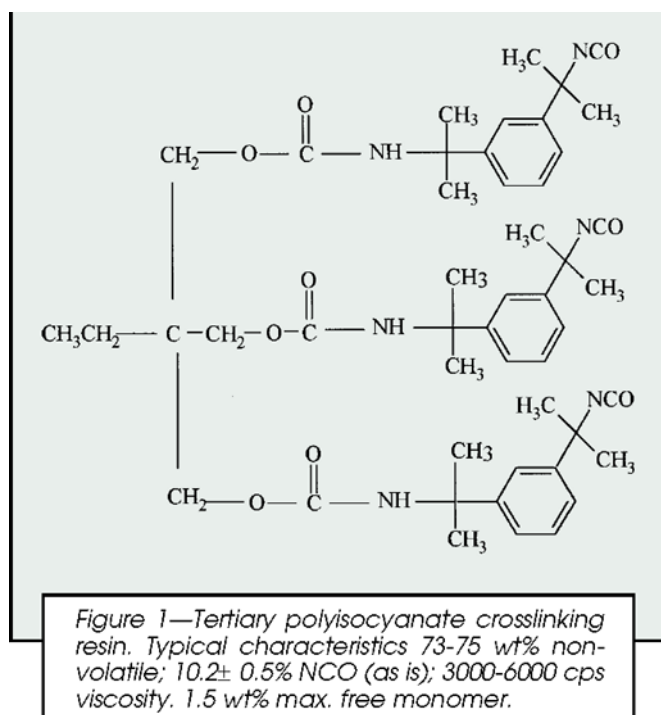
A two-component waterborne polyurethane system with a 250 g/l VOC has been formulated to meet the performance requirements of the automotive refinish market.

This paper discusses an experimental study to develop a two-component water-reducible polyurethane coating using a tertiary aliphatic polyisocyanate crosslinker with dry times, appearance, and reactivity equivalent to a two-component solventborne system. The effects of acrylic polyol monomer composition, glass transition temperature (T_g), and hydroxyl concentration on drytime and ambient cure film performance have been determined. The effects of particle size distribution of the formulated coating on performance were examined. It was found that smaller particle size provides overall improved film properties, i.e., faster dry time, increased hardness, and faster development of solvent resistance. The relationships of both acrylic polyol composition and formulation variables on the particle size distribution are discussed.

carbon dioxide generation due to over-indexing the isocyanate or the film build problems that this causes. The third approach, which avoids the problems of hydrophilic modification and over-indexing of isocyanate, is the use of a tertiary polyisocyanate crosslinking agent.^{9,10}

The tertiary polyisocyanate crosslinking agent used in this work is the adduct of meta-tetramethylxylene

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*1937 West Main Street, Stamford, CT 06904.



diisocyanate and trimethylol propane; it is commercially available as Cythane® 3174 (Cytec Industries) polyisocyanate resin. Previously published work¹¹ with this adduct in two-component solventborne coatings showed that its higher rigidity (Figure 1) relative to HDI and IPDI trimers required acrylic polyols with T_g of 0°C or lower, containing primary unhindered hydroxyls, to obtain acceptable reactivity and good film performance. Similar findings have been published on waterborne systems;⁹ low T_g acrylics containing primary hydroxyls are required. The waterborne work showed that when coating systems with tertiary polyisocyanate crosslinkers are properly formulated, performance properties equivalent to a solventborne system with an eight-hour pot life are easily achieved. Film properties were excellent, with 20° gloss at 87 and DOI at 98. Coatings passed 28 days of condensing humidity with no blistering or loss of 20° gloss. Stabilized coatings have now been on Florida exposure for two years (5° south black box) with 100% DOI retention and 95% 60° gloss retention.

Two-component polyurethanes have dominated the clear topcoats for automotive refinish paints because of their excellent combination of ambient cure capability with exterior durability, chemical resistance, and appearance. The ideal waterborne refinish paint system will be self-dispersing with fast dry time and rapid development of hardness and solvent resistance. A practical consideration in developing a commercial waterborne two-component polyurethane clearcoat is the ease of formulating the system. For the hydrophilic and hydrophobic primary and secondary polyisocyanates, development efforts have been mainly in the area of optimizing the mixing process by using unique two-component spray equipment.¹² Contrary to the careful control over mixing that is required for pre-formed acrylic emulsions or dispersions and self-dispersing polyisocyanates, the use of a water-reducible acrylic polyol as the dispers-

ing agent for the hydrophobic tertiary polyisocyanate eliminates the need for a high-shear mixing system. In laboratory work, hand mixing of the water into the polyol-polyisocyanate solution provided sufficient shear for a stable dispersion to be formed.

In addition to the automotive refinish market, the two-component water-reducible polyurethane systems described in this paper are useful for a variety of other application areas including transportation coatings, truck fleet coatings, interior and exterior maintenance coatings, and wood coatings.

But even though much attention has been focused on certain aspects of the development of two-component waterborne polyurethane coatings, little has been done to understand the relationship of resin structure to coating performance. In a previous paper, a statistical study of the optimization of acrylic polyols for use with tertiary polyisocyanate crosslinkers was discussed.¹³ This paper presents a continuation of that study by investigating the effects of acrylic polyol composition and formulation variables on the particle size distribution of the formulated system. It also discusses how the particle size distribution affects coating performance properties such as appearance, dry time, and reactivity.

EXPERIMENTAL

Polymer Synthesis

The acrylic polyols were prepared by free radical polymerization of vinyl monomers. Except where otherwise indicated in the tables, the acrylic polyols consisted of butyl acrylate, methyl methacrylate, 2-hydroxyethyl acrylate, and acrylic acid. The acrylic acid content was typically held constant at 6.4 wt%, and the other components adjusted to change the T_g or hydroxyl content. Polymerizations were carried out at 85% solids in methyl amyl ketone (MAK). Upon completion of the polymerization, sufficient triethylamine was added to neutralize 85% of the carboxylic acid groups, and water was added to make approximately a 48 wt% solids solution of the polyol. The resulting solutions contained nominally 40% water and 12% volatiles. It is critical that the polyol remain a clear, homogeneous solution and not phase invert to an oil-in-water dispersion prior to the addition of the tertiary polyisocyanate crosslinker.

Polymer Characterization

Molecular weight was determined by HPSEC on a Waters Model 150C liquid chromatography using a calibration curve prepared from polystyrene standards and a 10,000 Mn (Pd 1.1) polystyrene sample as a control.

The T_g of each polyol was measured on a Mettler TA-4300 DSC using the midpoint of the thermal curve (ASTM E-1356) at a heating rate of 10°C per min.

The viscosity of the polyol at 48% solids was measured at 25°C using a Brookfield Model RVT cone and plate viscometer.

The hydroxyl content of the polymer was calculated using the amount of each monomer charged to the reaction.

Coating Formulation

Coatings were formulated by first adding 0.5 wt% (total resin solids basis) of a 10 wt% solution of dimethyl tin dicarboxylate (Fomrez® UL-28, Witco) in methoxypropyl acetate to the acrylic polyol solution. The appropriate amount of tertiary polyisocyanate crosslinker was added to give a 1:1 NCO:OH ratio. It is critical that the water content of the polyol be such that the system remains a homogenous clear solution of crosslinker in polyol at this point. Water was added with hand mixing to bring the solids to an acceptable spray viscosity. The solids content was typically around 30-35 wt% as applied in this work. The coatings prepared in this manner have a VOC of 250 g/l as determined by EPA Method 24.

Unpigmented films were prepared on 4 in. × 12 in. Bonderite® (Parker & Amchem) ED-5050 primed cold-rolled steel panels using a 76 µm wet film thickness wirecator. Films were cured at two different schedules. They were either allowed to cure at 25°C, 50% RH; or they were force-dried for 40 min at 60°C. Film properties were determined at one, three, and seven days for coatings on the ambient cure schedule, or after removal from the oven for coatings on the force-dry schedule.

Coating Test Procedures

Particle size distribution of the formulated systems was measured on a Horiba LA-700 particle size analyzer. Samples were diluted with water to an appropriate concentration as indicated by the instrument.

NCO consumption was determined by casting a film on a ZnSe crystal and measuring the decrease in NCO stretch over time by FTIR.

Solvent resistance was measured using an MEK soaked cloth wrapped around a 0.91 kg hammer. The number of double rubs required to mar the surface and to begin to remove the coating was recorded.

Dry times were determined using a BYK dual speed drying time recorder. The time recorded is that for achievement of a tack-free coating.

RESULTS AND DISCUSSION

In our previous work, we had seen that appearance, as well as other performance properties such as dry time, of formulations prepared from acrylics with high T_g ($>0^\circ\text{C}$) and high OH (1.8 and 2.1 wt%) often differed from the bluish opalescent appearance of the standard low T_g ($<0^\circ\text{C}$) 1.5 wt% OH acrylic.¹³ In general, these formulations have appeared milky and sometimes even gritty. Particle size measurements to quantify these

differences in appearance showed a gradual increase in median particle size from 0.14 to 0.47 µm as appearance changed from bluish to milky. The dispersions with bluish appearance, which is indicative of a small particle size, usually had the shortest dry times (Table 1). Analysis of temperature and relative humidity during drying showed that neither could account for these differences in dry times, since waterborne systems tend to have shorter dry times with lower relative humidity.

The larger median particle size observed with the high T_g or high OH content acrylic polyols is thought to be due to increasing differences between the hydrophilicity of the polyol and the hydrophobicity of the crosslinker. Increasing either the hydroxyl content or methyl methacrylate/butyl acrylate ratio (higher T_g) appeared to make the acrylic polyol too hydrophilic to effectively disperse the tertiary polyisocyanate. To separate the effect of T_g and OH content, three polyols were synthesized with increasing OH content (1.5, 1.8, and 2.1 wt%) while holding T_g constant ($<0^\circ\text{C}$). Polyol composi-

Table 1—Variation in Dry Time as a Function of T_g or % OH and Appearance of the Formulated Coating System

Polyol Characteristics			Appearance	Time to Tack-Free, hr	°C/% RH
T_g , °C	% OH	Mn			
11	1.5	4020	Milky	4.0	24/33
11	1.5	4020	Bluish	1.0	22/77
14	1.5	3000	Milky	4.25	23/30
14	1.5	3000	Bluish	1.5	20/80
16	1.5	3310	Milky	4.25	24/30
16	1.5	3310	Bluish	1.25	20/80

Table 2—Effect of 2.1, 1.8, and 1.5 wt% OH Acrylic Polyol Composition and % Neutralization on the Median Particle Size of the Acrylic/Tertiary Polyisocyanate Dispersion

Acrylic Composition (Wt% Monomer)					T_g , °C	Mn	% Neutr.	Median Particle Size (µm)
MMA	BA	HEA	AA					
18.1	43.5	32.0	6.4	-4	3270	85	0.457	
						43	0.198	
19.6	47.0	27.0	6.4	-8	3050	85	0.290	
						47	0.160	
21.1	50.5	22.0	6.4	-8	2890	85	0.153	
						49	0.302	

Acrylic Composition: MMA/BA/HEA/AA

Table 3—Reproducibility of Effect of Polyol Composition and % Neutralization on Appearance and Median Particle Size of Formulated Systems

ID	Acrylic Characteristics			T_g (°C)	Appearance	Median Particle Size (µm)
	% OH (On Solution)	% Neutr.	Mn			
A	1.5	85	3110	-9	Bluish	0.143
B	1.5	49	3110	-9	Bluish	0.225
C	1.8	85	3260	-7	Milky, gritty	0.256
D	1.8	45	3260	-7	Bluish	0.199
E	2.1	85	3490	-6	Milky, gritty	0.355
F	2.1	45	3490	-6	Bluish	0.169

Acrylic Composition: MMA/BA/HEA/AA; Acid Number 50 Based on Solids

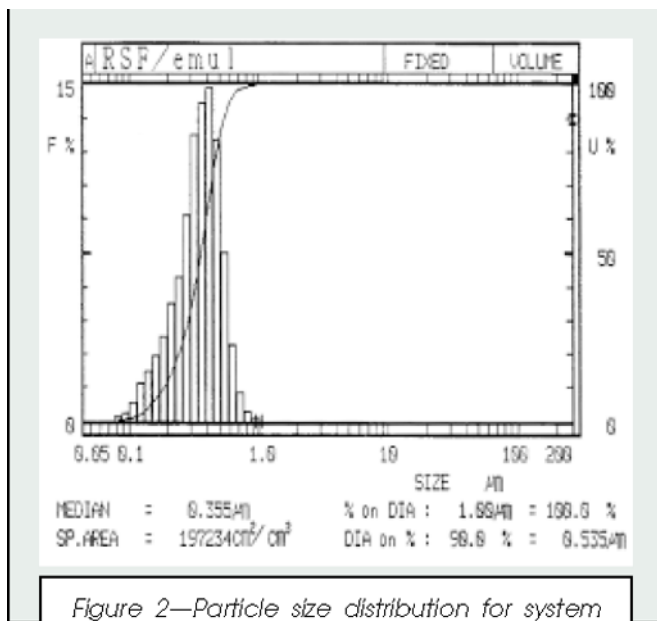


Figure 2—Particle size distribution for system containing 2.1 wt% OH, 3490 Mn, -6°C T_g polyol and hydrophobic tertiary polyisocyanate crosslinker at 85% neutralization.

tions and T_g are given in Table 2. The appearance of the 1.5 wt% OH polyol was bluish opalescent with a particle size of 0.14 μm, while the 1.8 and 2.1 wt% OH polyols appeared milky to gritty with particle sizes of 0.29 and 0.46 μm, respectively. To evaluate whether the hydro-

phobic/hydrophilic balance between the polyol and the hydrophobic tertiary isocyanate crosslinker was a factor, the hydrophilicity of the polyol was decreased by reducing the neutralization of the carboxylic acid from 85 to 43-49%. The relationship between the degree of neutralization of the polyol and the resulting particle size distribution is complex. Reducing the level of neutralization increased the median particle size for the 1.5 wt% OH polyol. This is similar to our unpublished observations in tertiary isocyanate-based polyurethane dispersions, where particle size of the dispersion is inversely related to carboxylate content. Interestingly, the opposite effect was observed for the higher OH containing polyols (1.8 and 2.1 wt%). Here, the median particle size decreased as the level of neutralization was lowered (Table 2). This result is not completely unexpected since the higher OH polyols are more hydrophilic and require less neutralization in order to be more compatible with the hydrophobic tertiary isocyanate crosslinker.

These results suggest that as the acrylic polyol becomes more hydrophilic, the ability of the acrylic to yield a stable dispersion of the hydrophobic crosslinker decreases. Other observations indicated that particle size of the formulated coating was a critical factor in dry time. It was thought that fast reactivity and good film performance could be maintained by adjusting the acid number and/or percent neutralization. This should yield small particle size dispersions with good dispersibility of the hydrophobic crosslinker in the acrylic polyol. To test the validity of this reasoning, the series of low T_g

Table 4—Effect of Formulated Coating Median Particle Size on Film Performance and Reactivity. Catalyst: 0.5% UL-28 Based on Total Resin Solids. The Acrylic ID Numbers Refer to the Polyols Described in Table 3

Acrylic ID	A	B	C	D	E	F
Particle Size, μm	0.143	0.225	0.256	0.199	0.355	0.169
One-Day Ambient						
Film thickness, μm	43	38	43	43	43	36
Knoop hardness	2.4	1.1	4.1	1.4	4.4	1.0
MEK resistance ^a	10/50	10	10/150	20	10/150	20
% NCO reacted	41	36	35	25	36	29
Three-Days Ambient						
Knoop hardness	6.2	4.6	8.0	6.8	9.3	6.9
MEK resistance ^a	50/200+	50/200+	10/150	10/200+	10/150	10/200+
% NCO reacted	70	68	62	52	60	57
Seven-Days Ambient						
Knoop hardness	6.2	7.3	8.0	11.0	7.8	11.4
MEK resistance ^a	200+	150/200+	10/200+	200+	10/200+	200+
% NCO reacted	90	89	80	76	75	77

(a) MEK double rubs to mar film/breakthrough film.

Table 5—Effect of Acid Number on Median Particle Size in Styrene-Modified Acrylic Polyol/Tertiary Polyisocyanate Dispersions

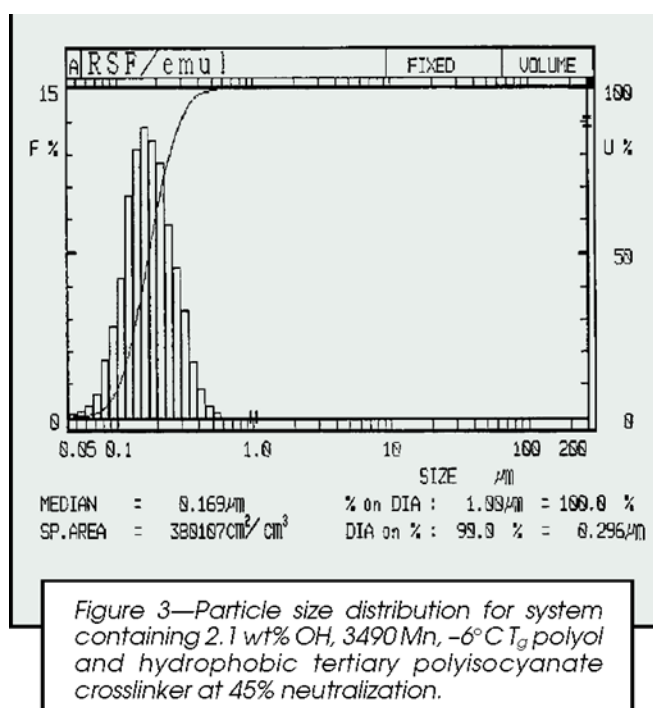
Acrylic ID	Acrylic Composition (Wt% Monomer)					Acid No. (on solids)	Mn	Median Particle Size, μm
	MMA	BA	HEA	Styrene	AA			
G	14.9	49.9	22.0	10.0	3.2	25	3570	8.288
H	13.8	49.9	22.0	10.0	4.3	35	2970	0.135
I	11.6	50.0	22.0	10.0	6.4	50	3320	0.136
J	9.7	49.9	22.0	10.0	8.4	65	4220	0.159
K	7.1	49.7	22.0	10.0	11.2	87	2430	0.229

T_g = -3°C, 1.5% OH based on solution, 85% neutralization.

resins with OH contents of 1.5, 1.8, and 2.1 wt% was prepared again. The acid number was maintained at 50 and neutralization varied between 45 and 85%. The results show that the effect of neutralization on particle size and appearance is very reproducible, and controlling percent neutralization is an effective method of improving crosslinker compatibility with inherently hydrophilic polyols (Table 3). Figures 2 and 3 show the particle size distributions for the 2.1 wt% OH polyol at 85 and 45% neutralization. Although both distributions are smooth curves, the appearance of the formulated coatings was different. The 85% neutralized system appeared milky and gritty while the 45% neutralized system had the desired bluish opalescent appearance. The film properties of the two systems also showed significant differences (Table 4). The lower level of neutralization does not materially change the stability of the system since the acrylic polyol at 45% neutralization remains as a solution until the tertiary polyisocyanate crosslinker is added and the system is let down with water. The pot life is also minimally affected by the lower neutralization.

The effect of neutralization and particle size distribution on film performance is complex as shown in Table 4. At all three levels of OH, the lower neutralization leads to an apparent early inhibition of cure as evidenced by slower development of hardness, solvent resistance, and NCO reactivity in the first 24 hr. At three days, solvent resistance has caught up but not film hardness. After seven days the lower neutralization systems are harder, and the solvent resistance in the 1.8 and 2.1 wt% OH polyols surpasses the more highly neutralized systems. At this time it is not understood what factor(s) may be causing this retardation of early cure and it is an area of continued research. A subsequent study of lower acid number polyols suggests that the cure "inhibition" is not simply due to reducing the amount of tertiary amine in the system.

The previous study¹³ showed that replacing some of the MMA with the more hydrophobic styrene provided a number of advantages in formulating small, narrow particle size systems. The impact of acid number and degree of neutralization was studied in a series of resins with polyols containing 10 wt% styrene with acid numbers of 25, 35, 50, 65, and 87. No significant performance differences were observed between 85 and 100% neutralization. The data for the 85% neutralized polyols is shown in Table 5. Optimum median particle size, reactivity, and film performance were obtained at an acid number of 50 (Table 6). The median particle size of the dispersed formulation goes through a minimum at acid numbers 35-50. There is an apparent lower limit to the amount of carboxylate groups required to obtain a good dispersion with these hydropho-



bic polyols. Similar to observations in non-styrene polyols, increasing carboxylate groups above acid number 65 leads to compatibility problems between the increasingly more hydrophilic polyol and the hydropho-

Table 6—Effect of Acid Number on Particle Size and Film Performance of Styrene-Modified Acrylic Polyol/Tertiary Polyisocyanate Formulated Systems

Acrylic ID	G	H	I	J	K
Particle Size, μm	8.288	0.135	0.136	0.159	0.229
One-Day Ambient					
Film thickness, μm	36	33	31	31	31
Knoop hardness	2.0	2.1	4.1	5.7	5.8
MEK resistance ^a	10/150	10/150	10/150	10/150	10/150
% NCO reacted	21	21	42	49	47
Three-Days Ambient					
Knoop hardness	6.9	7.1	9.8	8.6	6.5
MEK resistance ^a	30/200+	50/200+	150/200+	40/200+	30/200
% NCO reacted	51	52	68	71	65
Seven-Days Ambient					
Knoop hardness	12.6	12.0	13.0	11.0	8.0
MEK resistance ^a	150/200+	200+	200+	50/200+	30/200
% NCO reacted	70	71	80	81	73
40°/60°C					
Film thickness, μm	33	33	33	36	33
Knoop hardness	1.9	2.2	6.0	6.5	7.1
MEK resistance ^a	20/150	30/200+	100/200+	80/200+	30/200
40°/60°C+One-Day Ambient					
Knoop hardness	4.9	5.5	9.5	10.6	10.5
MEK resistance ^a	30/200+	30/200+	200+	200+	30/200
Full Cure					
Knoop hardness	14.0	13.7	13.0	10.7	8.3

Catalyst: 0.5% UL-28 Based on total resin solids. The acrylic ID numbers Refer to the polyols described in Table 5.
(a) MEK double rubs to mar film/breakthrough film.

Table 8—Characteristics of Acrylic Polyols Containing HBA or Styrene

Acrylic ID	Acrylic Composition (Wt% Monomer)					Mn	T _g (°C)
	MMA	BA	HBA	HEA	AA		
O	24.9	40.8	27.9	—	6.4	4140	-2
P	11.6	50.0	—	22.0	6.4	3320	-3

Acid number 50 based on solids; 85% neutralization.

bic crosslinker. It is interesting to note that the solvent resistance under both force dry and ambient cure goes through a maximum in the same acid number range as the particle size minimum. Smaller particle size of the dispersed polyol/crosslinker may lead to better coalescence of the film. This improves inter-diffusion of the polymer chains prior to crosslinking. Similar observations have been reported for other systems.¹⁴ The rate of NCO loss in the coating during the first 24 hr correlates with increasing carboxylate content of the polyol while the development of solvent resistance is unaffected. For both ambient and force-dry cure systems, early film hardness values are not predictive of the ultimate hardness of the coating. High acid number polyols provide early hardness while low acid number polyols afford better ultimate hardness. The factors that control early and ultimate film hardness are not fully understood. The higher acid content polyols may absorb more atmospheric water, which can plasticize the coating and soften it. The increased loss of NCO may be due to the presence of more water in the higher acid number polyols. Unlike the non-styrene polyols, a reduction of the amine content in the 25 and 35 acid number polyols did not adversely affect solvent resistance at 24 hr.

Early hardness development is an important consideration in the development of a practical refinish system. The effect of styrene content on the development of early hardness was studied. The data shows that 10 wt% styrene affords the best overall development of hardness, solvent resistance, reactivity, and formulated appearance. Solvent resistance is maintained when the styrene content is reduced to 5 wt% but film hardness is reduced. Increasing the styrene level to 20 wt% provides harder films but with an unacceptable sacrifice in solvent resistance and reactivity (Table 7). As the styrene content is increased to provide higher hardness and faster physical drying, it also decreases the reactivity of the rigid tertiary polyisocyanate crosslinker by increasing the steric hindrance in the system. Data on these systems showed no yellowing problems at 10 wt% styrene when properly stabilized. As a practical matter, there is also an upper limit to the amount of styrene that can be added to the polyol while main-

taining non-yellowing characteristics required for some exterior applications. We have not investigated what the upper limit of styrene is for exterior applications with this system.

The increased steric hindrance of the tertiary polyisocyanate crosslinker can be compensated for by adjusting the hydroxyl containing monomer. Increasing the distance of the OH group from the backbone chain reduces the steric hindrance associated with the polyol. Replacing 2-hydroxyethyl acrylate with 4-hydroxybutyl acrylate led to a significantly faster disappearance of NCO (40% vs. 30%) after one-day cure at ambient conditions. More importantly, the faster disappearance of NCO in this system correlated with a faster development of solvent resistance under force-dry conditions. The advantages of both monomers can be obtained (Tables 8 and 9) by physically blending the styrene/HEA and styrene-free HBA polyols. Blending 25% of the HBA polyol with 75% of the styrene/HEA polyol provided complete solvent resistance one day after force-dry cure with a minimal effect on hardness.

Table 9—Effect of HBA and Styrene Blends on Particle Size, Reactivity, and Film Performance of Acrylic/Tertiary Polyisocyanate Coating Formulations

Acrylic ID	O/P	O/P	O/P	O/P	O/P
Blend ratio	100/0	75/25	50/50	25/75	0/100
Particle Size, μm	0.168	4	41	45	0.136
One-Day Ambient					
Film thickness, μm	33	36	36	33	33
Knoop hardness	1.8	1.3	2.7	2.7	3.0
MEK resistance ^a	100/200+	30/200+	50/200+	50/200+	100/200+
% NCO reacted	38	48	42	39	32
Three-Days Ambient					
Knoop hardness	4.1	2.4	5.3	6.1	8.3
MEK resistance ^a	200+	200+	200+	200+	200+
% NCO reacted	59	82	76	75	61
Seven-Days Ambient					
Knoop hardness	5.5	3.4	5.3	8.0	10.6
MEK resistance ^a	200+	200+	200+	200+	200+
% NCO reacted	91	96	92	92	86
40°/60°C					
Film thickness, μm	33	33	33	33	33
Knoop hardness	3.9	3.6	3.5	4.1	4.5
MEK resistance ^a	200+	150/200+	100/200+	80/200+	100/200+
40°/60°C+One-Day Ambient					
Knoop hardness	6.9	5.6	5.8	7.1	8.5
MEK resistance ^a	200+	200+	200+	200+	120/200+

Catalyst: 0.5% UL-28 Based on total resin solids. The acrylic ID numbers refer to the polyols described in Table 8.

(a) MEK double rubs to mar film/breakthrough film.

CONCLUSION

Proper selection of monomers and formulation variables can provide a polyol with sufficient cure speed and hardness development to be used with tertiary polyisocyanate crosslinking agents. The selection of styrene as a polyol component provides hydrophobicity and hardness to the coating. The selection of 4-hydroxybutyl acrylate provides increased cure speed to match the low reactivity of tertiary isocyanates. The use of either of these monomers as a component of the polyol makes these systems ideally suited for use in two-component waterborne urethane coatings. Physical blends of a styrene/HEA polyol with a HBA polyol provide benefits of both polyols to coating performance.

The effect of particle size on film performance for a self-dispersing acrylic polyol/tertiary polyisocyanate is an important coating formulation variable. The polyol's hydrophobic/hydrophilic balance must match that of the tertiary polyisocyanate to obtain the desired 0.13-0.15 μm median particle size. Increasing the hydrophilicity of the polyol by increasing the MMA or hydroxyl content must be compensated for by reducing the percent neutralization. An apparent initial cure inhibition was observed with lower neutralization in simple MMA/BA/HEA/AA polyols.

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