100% Solids Aliphatic Polyurea Coatings for Direct-to-Metal Applications

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Sprayable polyurea coatings offer a unique combination of properties, such as rapid cure speed even at freezing temperatures, the ability to spray high build films in a single pass, and zero VOC. These features have allowed polyurea coatings to grow rapidly in the area of field-applied coatings, where low temperature cure and minimal down time are critical. New hindered amine adducts have been developed which yield aliphatic polyurea systems that have the potential to replace multiple coat systems with a single direct-to-metal exterior coating. The chemistry of the hindered amine adducts and in-depth coating performance, including effects of various formulating techniques, will be presented, with emphasis on PVC and UV packages.

INTRODUCTION

Polyurea spray elastomers offer a unique combination of properties, such as rapid cure speed—even at freezing temperatures—the ability to spray high-build films in a single coat, zero VOC, and low temperature flexibility. The majority of polyurea systems in use today are aromatic and based on diphenylmethane diisocyanate (MDI) prepolymers, polyoxypropylene amines, and aromatic amines. These aromatic systems have poor gloss and color retention which has limited their use in exterior topcoats where long-term aesthetics are important.[1] Polyurethane topcoats are commonly recommended to protect these systems in maintenance applications. Also, adhesion problems reported with early polyurea coatings have been overcome by a variety of measures, such as application of a primer coat, inclusion of ad-

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hesion promoters, and mechanical preparation of the substrates.[2] Another limitation is that the chemical resistance for this technology, especially to solvents and strong acids, can be poor, so immersion service is not recommended.

A new class of hindered amine adducts has been developed for use in aliphatic polyurea coatings that may be applied as a direct-to-metal (DTM) coating without the use of a primer or topcoat. These systems also have longer gel times than current aromatic systems, allowing for the flow and leveling needed to achieve the appearance required for topcoat applications. They also exhibit an excellent balance of UV resistance, chemical resistance, adhesion, corrosion protection, and low temperature cure down to -18°C. Although not as elastomeric as the aromatics, their flexibility is comparable to conventional polyurethanes and better than epoxies that are used in field maintenance applications. This paper describes the chemistry of the hindered amine adducts and the coating properties of the resulting aliphatic polyurea systems.

CHEMISTRY

Progress on the development of aliphatic polyurea coatings has been made through the use of secondary aliphatic amines[3] and aspartic ester amines.[1,4,5] The approach used in our work to develop a "slower polyurea" was the use of hindered amine adducts (HAAs). HAAs are based on sterically hindered primary amines, which are converted to secondary amines by reaction with acrylate oligomers and/or epoxy resins.[6] The chemistry used to prepare a typical HAA is shown in *Figure* 1, which is based on the reaction of one mole of trimethylol propane triacrylate (TMPTA) with three moles of tertiary-$C_{12\text{-}14}$ primary amine. The reaction of the primary amine with the acrylate groups proceeds via Michael addition under moderate conditions (60–100°C). Looking at the structure of the HAA in *Figure* 1, it is easy to see how the alkyl branches shield the secondary amine groups and reduce the reaction rate with isocyanates. In addition, the proximity of the amine group to the carbonyl group (two carbon separation) reduces the amine reactivity due to inductive effects. *Figure* 2 is an HAA using epoxy adduction where one mole of the diglycidyl ether of bisphenol A (DGEBPA) is reacted with two moles of t-$C_{12\text{-}14}$ amine. The t-$C_{12\text{-}14}$ amine used in this work is obviously a mixture, and the structure depicted in *Figure* 1 is a representation of a typical component of the amine mixture.

The basic properties of the TMPTA-based HAA, and the HAA based on epoxy adduction are shown in *Table* 1. The trends for gel time correlate closely with the degree of steric hindrance. Epoxy modification was considered to impart some of the positive features of this chemistry such as adhesion and corrosion protection. The DGEBPA adduct shown in *Figure* 2 is significantly higher in viscosity than the corresponding TMPTA adduct. The neat resin was a semi-solid and had to be reduced with xylene in order to prepare films. Also, the gel time of the DGEBPA adduct is considerably faster than the corresponding TMPTA adduct. The presence of the hydroxyls in the epoxy adduct is believed to be responsible for the increased reactivity compared to the acrylate adducts.

An HAA using a combination of the amine adducts described above was tailored to meet the needed gel time and hardness. This HAA will be referred to as "hybrid HAA." Compositionally, this HAA contains approximately 12% DGEBPA adduct and 88% TMPTA adduct.

Figure 1—HAA based on t-$C_{12\text{-}14}$ amine and TMPTA.

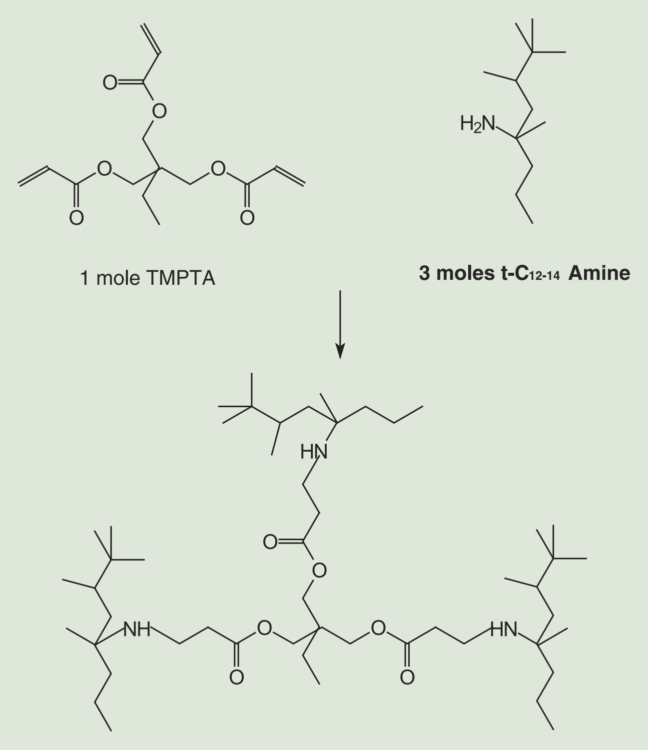

Figure 2—HAA based on t-$C_{12\text{-}14}$ amine and DGEBPA.

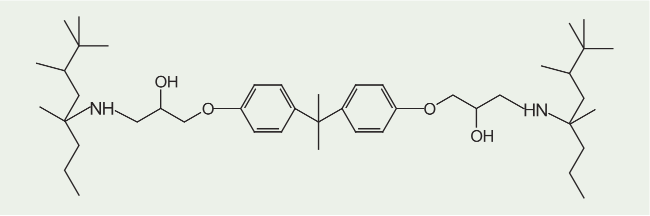

Table 1—Basic Properties of Hindered Amine Adducts

HAA Structure Amine/Reactant	Viscosity, cps at 25°C	Amine Eq Wt	Gel Time, Sec[a]	Shore D Hardness	Cured T_g, °C
t-C_{12-14} /TMPTA	1000	290	120	50	31
t-C_{12-14} /DGEBPA	Semi-solid	380	57[b]	66	51
Hybrid HAA	3500	306	40	68	43

(a) Gel time of HAA with HDI trimer, 1:1 eq ratio of amine: NCO, 20 gram mass.
(b) Gel time for 75% solution of HAA in xylene.

The TMPTA adduct uses a combination of amines in a molar ratio of 1.2 t-octyl amine to 1.8 t-C_{12-14} amine. The properties of the hybrid HAA are shown in *Table* 1. The coatings data presented in the following section are based on the hybrid HAA composition.

COATING PERFORMANCE DATA

Application Methods

Application of the polyurea coatings was performed using two methods. A static mixing technique was used in the laboratory as a screening tool.[7] Dual cartridges were loaded with the components, affixed with a static mixer and placed in a pneumatic gun. With this method, 15–20 mil films were drawn down on aluminum and steel panels or on polyester sheets for free films. The gel time of aliphatic coatings allowed this technique to be used; however, the aromatic systems used as controls could not be applied this way due to their extremely fast set times.

The second application method employed a Gusmer GX-7 impingement spray gun, which is the actual field method for applying polyurea coatings. The coatings were applied at a pressure of 2000+ psi and with temperatures between 150–180°F. At these temperatures and pressures, the polyurea can be applied with optimum mixing, atomization, and subsequent appearance. The two components are pumped to the impingement spray gun through needle-sized orifices into a mixing chamber. Here the two atomized streams are forced together (impinged), resulting in a very thorough mixing in a short time. The mixed material then exits the gun almost immediately.

Coating Formulations

Two formulations designed as direct-to-metal coatings are shown in *Tables* 2 and 3. The coatings have a 2:1 and 1:1 by volume mix ratio of pigmented amine to isocyanate prepolymer. The 2:1 formulation uses commercially available hexamethylene diisocyanate trimer with no modification.

Table 2—2:1 Aliphatic Polyurea Coating Formulation

Pounds	*Gallons*	*Material*
Isocyanate Component		
166.2	20.50	Hybrid HAA
1.0	0.12	Pigment dispersant
267.6	8.04	Titanium dioxide
High speed grind to 6 N.S., then let down with the following:		
577.4	71.30	Hybrid HAA
0.3	0.04	Defoamer
1012.5	*100.00*	**Total**
Isocyanate Component		
485.0	50.00	HDI Trimer, 195 NCO eq wt
1497.5	*150.00*	**Total, Both Components**
Properties		
	5.4	Pigment volume concentration, percent
	0.22	Pigment/binder ratio
	1.04	Isocyanate to amine index
	100	Percent solids, weight and volume
	10.0	Weight per gallon, mixed, pounds
	< 0.005	VOC, lb/gal, calculated

Table 3—1:1 Aliphatic Polyurea Coating Formulation

Pounds	*Gallons*	*Material*
Amine Component		
139.0	17.16	Hybrid HAA
3.1	0.40	Pigment dispersant
152.0	4.58	Titanium dioxide
57.0	2.36	Calcium metasilicate, amino silane treated
High speed grind to 6 N.S., then let down with the following:		
503.7	62.19	Hybrid HAA
4.8	0.70	Defoamer
47.5	5.43	Aspartic ester amine, 279 amine eq wt
57.0	7.18	Polyoxypropylene diamine, 118 amine eq wt
964.1	*100.00*	**Total**
Isocyanate Component		
930.0	100.00	Modifed HDI trimer, 268 NCO eq wt
1894.1	*200.00*	**Total, Both Components**
Properties		
	3.5	Pigment volume concentration, percent
	0.12	Pigment/binder ratio
	1.3	Isocyanate to amine index
	100	Percent solids, weight or volume
	9.5	Weight per gallon, mixed, pounds
	< 0.03	VOC, lb/gal, calculated

The amine component in the 1:1 formulation is modified with lower equivalent weight amines to adjust the stoichiometry and generate this mix ratio. The isocyanate component is based on hexamethylene diisocyanate trimer, which has been modified to increase the NCO equivalent weight, again to achieve a 1:1 mix ratio. The pigmentation is designed to provide improved corrosion protection by the inclusion of silane-treated calcium metasilicate. The pigment volume concentration is low at 3.5%, but provides adequate hiding in the thick films typical for polyurea systems. The VOC levels are virtually nil, with only a minor amount of solvent contributed by the dispersant and defoamer. Unless otherwise specified, the data presented is based on this 1:1 coating formulation.

Table 4—Cure Speed, Hardness Development, and Appearance Properties

Property	*1:1 Aliphatic Polyurea*	*Aromatic Polyurea A*	*Aromatic Polyurea B*
Gel time, lab mix, 25°C	45 sec	2–3 sec	2–3 sec
Gel time, field sag test	12–15 sec	3–4 sec	5–10 sec
Dry to handle	10 min	30+ min	1–2 min
Dry to touch (tack free)	25 sec	5–10 min	15–20 sec
Shore D hardness, 1 hour	62	Not tested	Not tested
Shore D hardness, 1 week	68	45-50	45-50
Gloss, sprayed, 60°/20°	80/50	90/54	85/53
Film thickness, mils	20	50	125

Aromatic Polyurea Controls

Spray applied films of two commercial aromatic polyurea systems were obtained from their manufacturers. These films were used as the aromatic controls in the performance comparisons.

Gel Times/Cure Speed

Gel times were measured using two methods. The first method involves hand mixing 20 g until it can no longer be stirred. The second method, which is the actual field technique, uses impingement spray equipment. The heated material is sprayed in one spot on a vertical surface until the mass begins to sag. Spraying is then discontinued and the gel time is recorded as the time when sagging stops.

As shown in *Table* 4, the aliphatic system based on the new hybrid HAA exhibits a much longer gel time, especially when measured using the room temperature test. It is noteworthy that even though the gel is extended, the tack free time of the applied coating is comparable to the commercially available aromatic products. Also, the hardness of the aliphatic system is higher than that of the aromatics, developing quickly within the first hour of cure.

Table 5 shows the effect of temperature on the cure speed of the 2:1 aliphatic polyurea formulation. As the temperature varies from -18°C to 50°C, there is relatively minimal effect on the dry time of the coating. This low temperature curability widens the painting season, allowing the system to be applied nearly any time of year.

Physical Properties

While the aromatic systems are usually described as elastomeric with high elongation characteristics, the aliphatic system is harder, as shown in *Table* 4, and has a much lower elongation. While the elongation of the aliphatic system is considerably less than the aromatics, it is superior to the epoxy and polyurethane systems used in industrial maintenance applications.

Adhesion

The hybrid HAA-based system was sprayed on various substrates as shown in *Table* 7. The adhesion was measured after a 14-day cure, using a pneumatic adhesion test according to ASTM D 4541 Type IV. Adhesion properties in general are excellent for the aliphatic polyurea over porous substrate, such as concrete and wood, with or without a primer. Even applied over frozen concrete and allowed to cure at 32°F, adhesion was essentially equal to the room temperature cure conditions.

Table 5—Cure Speed at Varying Temperatures[a]

Temp, °C	*Set Time*	*Tack Free*
-18	90 sec	< 3 min
0	60 sec	Not tested
25	50 sec	2.3 min

(a) 2:1 Aliphatic coating formulation.

Table 6—Physical Properties

Property	*1:1 Aliphatic Polyurea*	*Aromatic Polyurea A*	*Aromatic Polyurea B*	*Two-Component Epoxy*
Tensile strength, psi	2040	2300	2200	9600
Elongation at break, %	60	530	480	2.6
Tear strength, pli	336	500	210	Brittle

Figure 3—QUV-A340 Gloss retention: aliphatic vs aromatic polyurea.

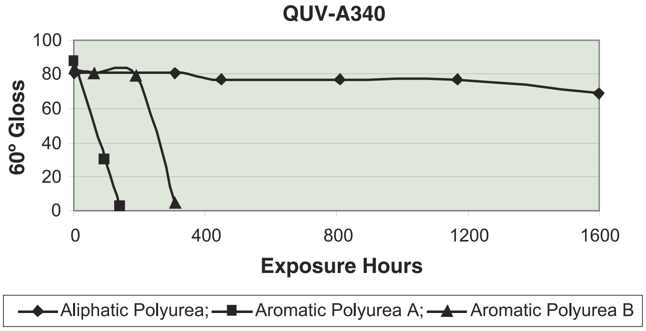

Figure 6—QUV-A340 gloss retention vs polyurethane and epoxy.

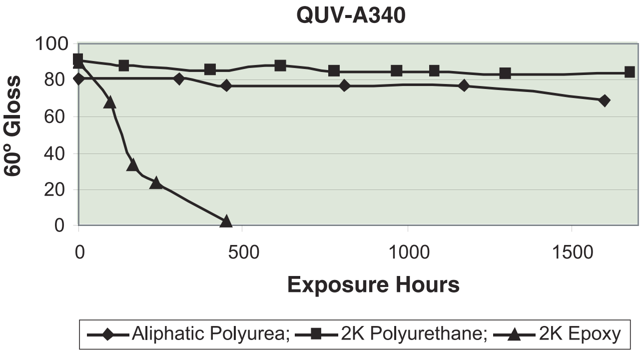

Table 7—Adhesion of Aliphatic Polyurea to Various Substrates

Substrate	*Adhesion, Psi at Failure*	*Method of Failure*
Concrete with aged epoxy sealer	876	Adhesive, intercoat
Bare concrete, 25°C	876	Concrete failure
Bare concrete, applied and cured at 0°C	836	Concrete failure
2 x 4 wood with latex sealer	815	Wood failure
2 x 4 wood with latex sealer (wet on wet)	958	Wood failure
Steel with zinc rich epoxy/urethane topcoat	1447	Adhesive, intercoat
Steel with flexible epoxy primer	937	Adhesive, intercoat
Steel with epoxy amine protective coating	>1835	No failure
Aluminum, smooth, untreated	692	Adhesive, from substrate
Blasted steel, 1.5 mil anchor profile	1672	Adhesive, from substrate

Figure 4—Color shift after QUV-A340 exposure.

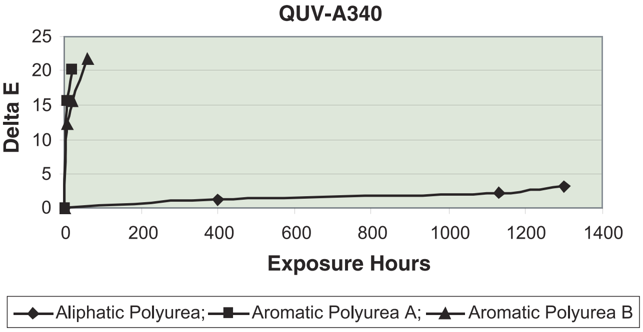

Figure 7—Effect of addition of UV package.

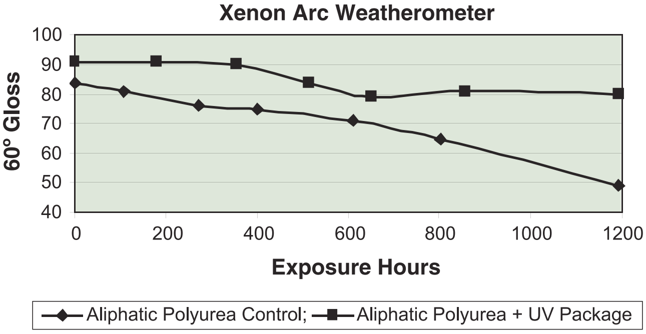

Figure 5—Color shift after exterior exposure.

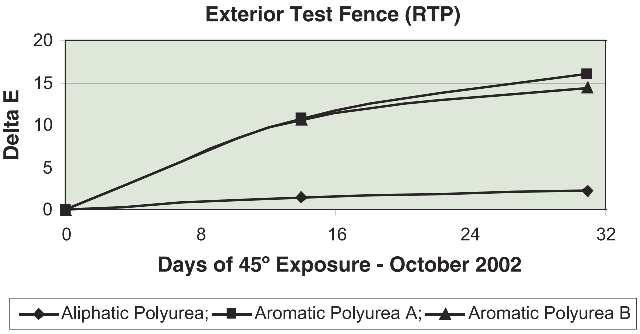

Table 8—Corrosion Resistance

	Salt Fog 1200 hr	*Prohesion 1300 hr*
Aliphatic Polyurea, 25–30 mils		
Field blisters	10	10
Scribe blisters	10	2F, 6M
Aromatic System A, 45–50 mils		
Field blisters	10	not tested
Scribe blisters	10	not tested

Corrosion Resistance

Since this system is intended for exterior use as a DTM coating, corrosion resistance is essential. Accordingly, this new system was tested in salt fog ASTM B117 and Prohesion ASTM G85. The coating was applied using an impingement spray to blasted steel panels with a 1.5 mil anchor profile. Resistance to corrosion in both accelerated tests proved to be excellent with minimal blister development and scribe creep.

Chemical Resistance

Resistance to several chemicals was measured using a 24-hour covered spot test, as shown in *Table* 9. The new aliphatic polyurea had superior overall chemical resistance to a high-solids epoxy system, especially in acids. The aromatic polyureas showed limited resistance to solvents, tending to swell and soften. The aliphatic system has the potential of meeting the requirements for the chemical splash and spill resistance necessary for tank or railcar coatings.

Table 9—Chemical Resistance[a]

	1:1 Aliphatic Polyurea	*Aromatic Polyurea A*	*Aromatic Polyurea B*	*HS Epoxy Polyamide*[b]
Coating film thickness, mils	20	50	125	12
10% sulfuric acid	5	5	3	1
10% acetic acid	5	5	4	1
10% hydrochloric acid	5	5	3	4
10% sodium hydroxide	5	5	4	3
Methanol	4	1	4	4
Ethanol	4	1	3	4
Xylene	4	1	4	4
Gasoline	3	2	3	4
Butyl Cellosolve	4	1	3	4
Skydrol LD-4	4	1	2	3
Water	5	5	5	5
Total	**48**	**33**	**38**	**37**

(a) 24-hour covered spot test rating: 5 = no effect, 4 = softening, 3 = soft, marred and/or yellow, 2 = extreme softening, 1 = destroyed.
(b) The epoxy system was based on liquid epoxy (EEW=190), cured with high-solids polyamide in a high-build epoxy mastic formulation.

Weatherability

The polyurea systems were tested in a xenon arc Weatherometer (SAE J1960), QUV-A340 (ASTM D 4587), and on exterior test fence. The results for the aliphatic system were far superior to the two commercial aromatic systems. *Figure* 3 shows results for 60° gloss in QUV-A340. The aliphatic system maintained approximately 85% of the original gloss after 1600-hr exposure, whereas the two aromatic systems were flat after less than 400 hr. *Figure* 4 shows the same trend with extreme color shift for the aromatic systems after less than 50 hr, while the aliphatic system maintained its color after 1300 hr of exposure. Exterior test fence exposure is shown in *Figure* 5 and follows the same trend seen in the accelerated tests, with the aromatic systems darkening in less than a month.

Gloss retention is compared with two-component epoxy and polyurethane systems in *Figure* 6. The aliphatic polyurea exhibits gloss retention just slightly below that of the two-component acrylic polyurethane and far superior to the epoxy system after 1500 hr of exposure.

A positive effect was seen with addition of UV stabilizers. As shown in *Figure* 7, the aliphatic polyurea with 2% UVA and 1% HALS (on resin solids) had a significant improvement in 60° gloss retention (30 units) after 1200-hr exposure when compared to the unmodified control.

SUMMARY

New hindered amine adducts have been developed which have utility in formulating aliphatic polyurea coatings that exhibit excellent adhesion, chemical resistance, corrosion protection, and UV durability. In addition, the extended gel time of the hindered amine adducts allows time for the flow and leveling needed for smooth and defect-free thin films. This combination of properties allows the possibility of replacing multi-coat systems with a single coat. The system maintains rapid cure at application temperatures as low as -18°C (0°F), extending the painting season into the winter months.

References

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(5) Huntsman Corp., "Method of Preparing an Aliphatic Polyurea Elastomer System," U.S. Patent 6,013,755.

(6) Reichhold, Inc., "Hindered Amine Adducts for Polyurea Systems," U.S. Patent 6,369,189.

(7) House, D.W. and Ilijevski, D., "Evaluating a Secondary Aliphatic Diamine Curative in Colorless, Light-Stable, IPDI-Based Polyurea Coatings Using a New, Low-Pressure, Static-Mixing Technique," Polyurea Development Association, December 2000.