Two-Component Aliphatic Polyurea Coatings for High Productivity Applications

Beau Catcher Tunnel in North Carolina protected with polyurea for fast-track renovation (Mirror image shown here). Photos courtesy of Bayer Corporation

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This article decribes the development of a new class of aliphatic polyurea polymer systems. These systems are based on the reaction of polyaspartic ester compounds (a type of secondary aliphatic amine with aliphatic polyisocyanate). Polyaspartic ester-based polyurea topcoats are non-yellowing and exhibit good outdoor weathering and long pot life. The moderately fast reactivity, combined with the relatively low viscosity of the polyaspartic ester compounds, allows for a broader range of applications in two-component coatings.

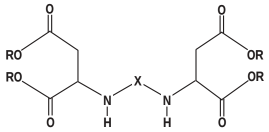
Additionally, it is possible to use the polyaspartic ester technology in combination with polyurethane technology to form polyurethane/polyurea hybrids. This may be advantageous when trying to achieve the highest levels of coating chemical resistance and/or owner-specific properties.

Characteristics of Polyaspartic Esters and Their Chemistry

The development of polyaspartic esters is fairly recent, with the initial work being reported in 1990. Zwiener, et al., first showed the applicability of polyaspartic esters as co-reactants for polyisocyanates.[1,2] This patented technology[3] was initially used in two-component polyurethane solvent-borne coating formulations because the polyaspartic esters are excellent reactive diluents for high-solids polyurethane coatings. They can be blended with hydroxyl functional polyester and polyacrylate co-reactants, thus allowing for reduction of volatile organic compounds (VOC) in relatively high solvent-containing coating systems.[4,5]

More recent developments have concentrated on achieving low or near-zero VOC-containing polyurea coatings where the polyaspartic ester is the main component of the co-reactant for reaction with a polyisocyanate. Because of the moderately fast curing feature, these coatings can offer productivity improvements, along with high-build, low-temperature curing, and abrasion and corrosion resistance.[6]

Polyaspartic Ester Products



Raw Materials

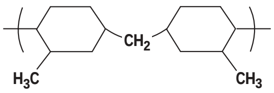
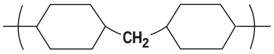
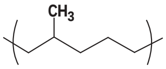
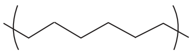
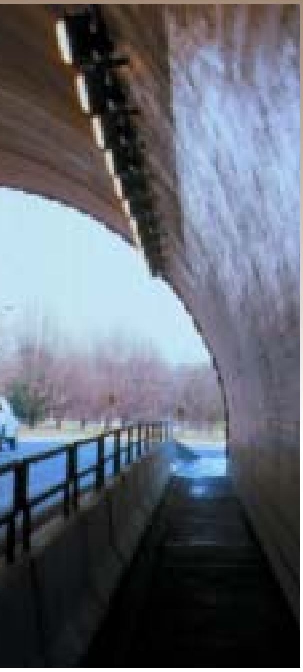
X	Diamine	Maleate	Designation
	cycloaliphatic	DEM	A
	PACM	DEM	B
	2-methylpentane diamine	DEM	C
	HDA	DEM	D

Fig. 1: Structures of polyaspartic esters



Reactivity

A polyurea can be defined as a reaction product of an aliphatic or aromatic isocyanate component, which is composed of *amine-terminated polymer resins and/or amine chain extenders.*

Polyaspartic esters have a unique reactivity with polyisocyanates because of their unique chemical structure. It is possible to provide a whole family of products based on structural variations that result in different reactivity with a polyisocyanate (Fig. 1).

The unique structural feature of the polyaspartic ester is a sterically crowded environment around the nitrogen. Additionally, the ester portion of the structure provides inductive effects. These features both act to slow down the reaction of the amino group of the polyaspartic ester compound and the isocyanate group of a polyisocyanate. Practically speaking, slower reaction speed between the isocyanate and an aliphatic diamine results in longer gel times, and thus, a longer application window.

The reaction speed of the polyaspartic ester compound and the polyisocyanate can be altered by changing the structure of the polyaspartic ester. For example, as we decrease the steric crowding in the structure of the polyaspartic ester (going down the column in Fig. 1), the reaction speed with a given isocyanate increases. Thus, the polyaspartic ester compound designated A is slower reacting than compound B, etc.

Table 2: Gel Time Reactivity Data for Aromatic Polyurea Clears

Polyaspartic Ester	Aromatic Polyisocyanate*	Gel Time @ 72 F (22 C)	Gel Time @32 F (0 C)
B	MDI Prepolymer 16% NCO	1 min.	4 min.
B	MDI Prepolymer 8% NCO	5 min.	Did not test
C	MDI Prepolymer 8% NCO	<0.5 min.	ca. 0.5 min.
B	TDI Prepolymer 3% NCO	40–60 min.	>90 min.
C	TDI Prepolymer 3% NCO	5 min.	9 min.

* The MDI prepolymers are high in 2,4-isomer content and based on polypropylene oxide-based polyols. Solvent-free, linear isocyanate prepolymer based on toluene diisocyanate (TDI); monomeric TDI content is less than 0.5%.

Some specific data illustrating the gel times of different polyaspartic ester products and a polyisocyanate are shown in Table 1. Additionally, it is possible to blend polyaspartic ester products to obtain mixtures with intermediate gel times.

For comparative purposes, we also conducted these gel tests with some aromatic polyisocyanates, both MDI (diphenylmethane diisocyanate)- and TDI (toluene diisocyanate)-based prepolymers/adducts. These data are shown in Table 2. The time to gel is, as expected, much shorter for the mixtures of aromatic MDI polyisocyanates and polyaspartic esters compared to the aliphatic polyisocyanate based on HDI (hexamethylene diisocyanate).

Table 1: Gel Time Reactivity Data for Aliphatic Polyurea Clears Based on HDI Trimer

Polyaspartic Ester	Gel Time @ 72 F (22 C)	Gel Time @ 32 F (0 C)
A	40 min.	Did not test
B	20 min.	23 min.
C	1–2 min.	2 min.
D	1–2 min.	Did not test

It is interesting to note the catalytic effect of water on the gel times of polyaspartic ester/aliphatic polyisocyanate mixtures (Table 3). It is a dramatic effect that can be used to further tailor the pot life/dry time of a given system. This also has the potential to provide the unusual combination of rather long pot life and fast dry time: the dry time of a coating system can be decreased dramatically because of humidity in the atmosphere.

Polymer Film Properties

Coating films derived from polyaspartic esters and a common aliphatic polyisocyanate crosslinker, the isocyanurate trimer of HDI, are hard, color-stable, and weather- and abrasion-resistant. Additionally, they can be formulated to provide good corrosion protection properties on steel.

Some film properties of clear coatings are illustrated in Table 4. In general, the data show that these coatings are of moderate tensile strength and, as expected, of very low elongations. Once again, the aliphatic polyisocyanate used in these gel studies is an HDI-based adduct with a 1,000 cps (@ 25 C) viscosity product with an NCO content of 20.5%. Other commercially available HDI-based

Table 3: The Catalytic Effect of Water on Reactivity*

Polyaspartic Ester	Water Content (%)	Gel Time @ 72 F (22 C)
B	0.08	65 min.
B	0.12	31 min.
B	0.17	21 min.

* Polyurea clears based on an HDI-based polyisocyanate adduct: NCO 21.5%, viscosity ca. 3000 cps @25 C (77F)

products with higher functionalities and viscosities may vary the tensile/elongation data somewhat.

The aliphatic polyureas based on polyaspartic esters yield hard, tough coatings that are clear and for the most part bubble-free, making them suitable for thin-film coating applications, more so than elastomeric membranes. This is because the hard block/soft block nature of the aliphatic polyaspartic ester-based polyureas is expected to be very different than typical aromatic polyureas, which are based on MDI prepolymers and polyether backbones.

Table 4: **Property Data for Aliphatic Polyurea Clear Films Based on HDI Trimer**

Polyaspartic Ester	Tensile (psi)	Elongation
A	6,875	4%
B	6,650	4%
C	2,290	23%
D	1,800	84%

Curing Characteristics of Polyurea Coatings Based on Polyaspartic Esters

The curing characteristics of polyaspartic ester-based polyurea coatings are somewhat different than traditional polyurethane coatings. They have a curing profile that shows a dependency on both temperature and humidity.

Generally, higher temperatures accelerate the curing speed of coatings by increasing the kinetics of the chemical reactions needed to form a polymeric film. If solvents are present in the coating, increasing temperature also works to speed up solvent flash-off, thus resulting in faster drying of a coating.

Table 5: **Curing Characteristics of Fast-Curing Polyurea Topcoat (Acrylic)**

Relative Humidity	Temp. F(C)	Dry Time (Minutes)
40% RH	45(7)	Set to touch: 225; tack free: 465; hard dry: 1020
90% RH	45(7)	Set to touch: 45; tack free: 105; hard dry: 180
65% RH	45(7)	Set to touch: 45; tack free: 60; hard dry: 115
40% RH	95(35)	Set to touch: 30; tack free: 60; hard dry: 90
90% RH	95(35)	Set to touch: 10; tack free: 15; hard dry: 20

Table 5A: **Curing Characteristics of a Traditional Polyurethane Topcoat (Acrylic)**

Relative Humidity	Temp. F(C)	Dry Time (Minutes)
40% RH	45(7)	Set to touch: 60; tack free: 195; hard dry: 435
90% RH	45(7)	Set to touch: 90; tack free: 210; hard dry: 435
40% RH	95(35)	Set to touch: 45; tack free: 45; hard dry: 75
90% RH	95(35)	Set to touch: 30; tack free: 45; hard dry: 60

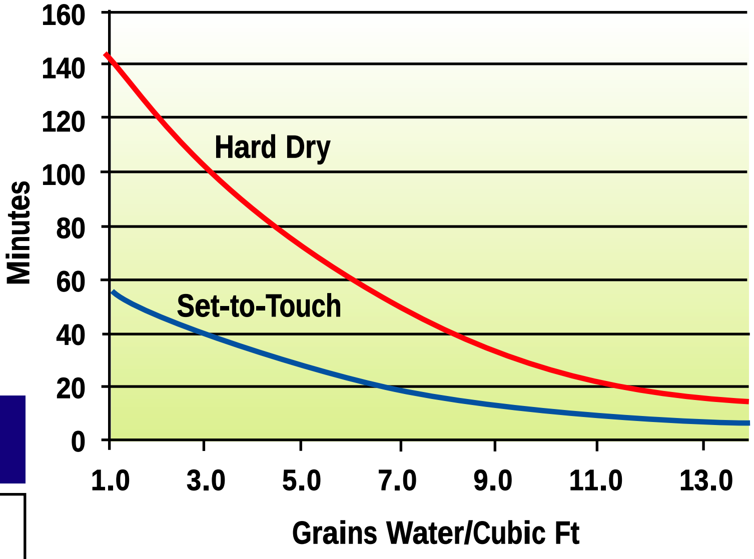


Fig. 2: Effect of ambient moisture on dry times of fast-curing aliphatic polyurea topcoat

Humidity, on the other hand, normally has minor effects on the curing characteristics of solvent-borne and solvent-free coatings. The curing characteristics of aliphatic polyurea coatings based on polyaspartic esters, however, exhibit a rather dramatic dependency on humidity, which in a catalytic manner accelerates the curing/drying process (Fig. 2). This provides the opportunity to develop some unique fast cure coatings with relatively long pot life, thus fulfilling special curing performances and productivity requirements.

The effect of temperature and humidity on the dry times of the polyaspartic ester-based polyurea coating are presented in Table 5. A traditional polyurethane topcoat, e.g., acrylic polyurethane, is also presented (Table 5A) for comparison purposes; as expected, it does not show much of a dry time dependency related to humidity in this study.

Fast-Curing, Corrosion Protection Coating System

Coating films derived from polyaspartic esters and a common aliphatic polyisocyanate crosslinker, the isocyanate trimer of HDI, are hard, color-stable, and weather- and abrasion-resistant—all good characteristics for use as a topcoat in a corrosion-resistant coating system on steel.

To illustrate this point, a fast-curing aliphatic polyurea topcoat formulation was spray-applied to abrasive blasted steel panels already primed with a moisture cure urethane (MCU) zinc primer and tested in accelerated weathering devices. The MCU primer and aliphatic polyurea topcoat together make a coating system with the characteristics suitable for enhancing productivity. They are fast-curing and, as two coats instead of the typical three, enhance productivity by eliminating a layer of paint.

After the coated steel panels cured for two weeks at 23 C and 50% relative humidity, they were subjected to a variety of testing criteria—cyclic weathering (ASTM D5894), adhesion (ASTM D4541-85), wet adhesion, and salt fog (ASTM B117). The cyclic weathering data are presented in Table 6.

Two sets of three coated panels were evaluated by ASTM D714-87, Standard Test Method for Evaluating Degree of Blistering of Paints. In one set, the topcoat was applied at a dry film thickness (dft) of approximately 6 mils (150 microns); in the second set, the topcoat was applied to a dft of 10 mils (250 microns).

Results of the testing indicate that this fast-curing two-coat system is very effective as a corrosion-resistant coating system. Minimal blistering was observed for both sets of coated panels after 1,000 hours of cyclic weathering. The Delta E test showed essentially no yellowing of the topcoat with some loss of gloss under these testing conditions. It should be noted that this formulation was not optimized with regard to additive packages that could help preserve coating gloss.

The results indicate that the two-coat, fast-cure coating system has adequate tensile adhesion—surpassing the value of 600 psi (40 MPa) minimum for failure accepted by the Northeast Protective Coating Committee (NEPCOAT). The failure results compare favorably with typical three-coat corrosion protection polyurethane coating systems. The averages for the two systems are 912 and 831 psi. The location of the failures was primarily cohesive coating failure at the primer. This is not unusual for zinc-rich coatings, which, because of the very high zinc pigment loading, have minimal film integrity.

Table 6: **Cyclic Weathering (ASTM D5894) of MCU Primer/Polyurea Topcoat System Gloss (60) Initial**

		9Z7A 6DFT			9Z7A 10DFT	
	Panel #1	Panel #2	Panel #3	Panel #1	Panel #2	Panel #3
Gloss(60) initial **1,000 Hours**		40.4			62.3	
Gloss	33.5	25.9	31.7	63.5	38.5	30.5
Delta E	1.041	1.16	1.125	1.186	0.945	1.103
Rusting (field)	10	10	10	10	10	10
Rusting (scribe)	10	10	10	10	10	10
Blistering (field)	10	10	10	10	10	10
Blistering (scribe)	10	10	8M	10	8M	10

Millerbernd Manufacturing Case Study

Millerbernd Manufacturing is a leading producer of steel poles for applications ranging from highway lighting to communication towers. The company demands a high-performance coating system for its products, which must withstand highly corrosive environmental conditions.


Light pole supports protected with polyurea

For years, Millerbernd engineers searched for a system that would provide the required toughness and durability without the inefficiencies inherent in the application of powder-based and acrylic enamel coatings.

A new aliphatic polyurea is providing Millerbernd with savings in energy and time. In addition, the non-yellowing, good weathering, and high corrosion protection characteristics of the polyurea topcoat meet or exceed the requirements of Millerbernd's customers.

The powder and liquid coating systems that had been used previously required heating in ovens and a long cooling time on the line. Before the company switched to the aliphatic polyurea coating, poles were heated to an average of 300 F to 350 F (149 to 177 C). The varying thicknesses of the metal made uniform heating difficult and increased the amount of energy required.

The aliphatic polyurea system has enabled Millerbernd to shut down its natural gas-fired infrared ovens. As a result, energy consumption at the facility has been reduced by 75%. Time savings have been impressive as well, with poles being moved off the line nearly 70% faster.

The surface of the poles, which reach 90 ft (27 m) in length and weigh up to 1,000 lb (450 kg), is prepared by steel shot blasting and then moved immediately into the two-part coating process. The powder coating system Millerbernd had used previously required additional pre-coating of caustic baths and washes using harsh chemicals.

After shot blasting, an acrylic urethane primer coat is applied at 3.5 mils (88 microns) dft, followed in 15 to 30 minutes by the topcoat of the aliphatic polyurea at 2–3 mils (50–75 microns) dft. On average, the topcoat is dry to the touch in five minutes. The topcoat is formulated in a variety of pigments and gloss ranges to meet specific customer needs.


Spray application of polyurea to steel pole

The rapid surface hardening provides immediate impact resistance, so the pole can be moved from the line in just 30 minutes. The coating system's latent inner-cure properties, meanwhile, also offer another benefit after the coating process is complete. Millerbernd is able to bend the poles, as required by some of the company's most popular designs, without cracking or otherwise damaging the coating.

The aliphatic polyurea coating system has been engineered to provide excellent ultraviolet (UV) protection. In addition, the system's abrasion resistance is critical for a product that is subjected to harsh conditions, particularly in the Northeast, where the combination of sand, road salt, and wetness creates a highly corrosive abrasive blasting effect from fast-moving traffic.

North Carolina Highway Tunnel Case Study

The Beau Catcher Tunnel is approximately 1,050 ft (319 m) in length and stands approximately 40 ft (12 m) tall. Since its original completion over 50 years ago, the tunnel has been adversely affected by graffiti and has accumulated dirt and residue caused by carbon monoxide, diesel fumes, and other environmental effects.

The purpose of the Beau Catcher Tunnel renovation was two-fold: to seal the tunnel to stop leakage and reduce the risks of rock slides; and, second, to improve the appearance of the tunnel by adding a high-gloss coating that would resist graffiti and environmental pollutants.

The walls of the tunnel are made up of concrete over rock. Prior to the application of the coatings, the surface was abrasive blasted, general patchwork was completed, and a base primer was applied. Next, a conventional 100% solids polyurea (light buff color) was spray-applied to approximately 50 mils (1.25 mm) dft using a plural-component spray system. Then, a coating of polyaspartic ester-based aliphatic polyurea was roller-applied to 16 mils (400 microns) dft to a height just below the tunnel lights, providing an anti-graffiti coating that is easy to clean and maintain.

A key reason polyaspartic ester-based aliphatic polyurea coatings were selected for this project is because the materials can be applied in low temperatures without problems. As is typical in all structures, when the tunnel is subject to higher temperatures, the substrates expand; and when the tunnel is subject to lower temperatures, the substrates contract. These environmental effects cause the joints to move anywhere from 25–30%.

The coating system provides elasticity between the joints, allowing movement. The two-component aliphatic polyurea topcoat, which provides "weather-proofing" (keeping rain, snow, wind, etc., from the structure's panels), is ideal for tunnel applications because it bonds to a variety of substrates, including metal, brick, and concrete, to name just a few.

Other attractive features of the polyaspartic ester-based aliphatic polyurea coatings are that they contain near zero VOCs and their reaction times can actually be slowed to 15–45 minutes' gel time for rolling or brushing.

San Mateo Bridge Case Study

Completed in 1929, the original San Mateo-Hayward Bridge was the longest bridge in the world at the time, extending more than seven miles across the San Francisco Bay.

As part of a $113 million widening project by the California Department of Transportation (CalTrans), the bridge is receiving a protective coating on new concrete structures that officials expect will prolong the bridge's life by 25 percent. The approach is intended to prevent


Concrete girder with aliphatic polyurea topcoat being placed on substructure for San Mateo-Hayward Bridge widening project

salt water and saline fog from penetrating the concrete and corroding the steel reinforcement bar (rebar) that strengthens the bridge.

The three-part coating system being used includes an epoxy primer coat, a polyurea intermediate coat, and a polyaspartic polyurea topcoat. The role of the polyaspartic topcoat is twofold. First, it provides an additional layer of protection against the destructive effects of salt water, and second, it prevents discoloration of the polyurea intermediate coat, which is sensitive to UV light. The coating has the environmental benefit of being nearly free of VOCs, thereby meeting local air quality standards.

The project will widen the bridge, that carries 29 million vehicles per year, from four lanes to six—three in each direction. It was part of a larger program underway in California to provide bridges throughout the state with additional seismic stability as protection against earthquakes. The San Mateo span is receiving a seismic retrofit in addition to the widening project.

To widen the flat trestle portion of the bridge, 120-foot (36-meter) concrete pilings are lowered into the bay, capped, and fitted with concrete trestles. Plates are installed on top of the trestles to hold the road surface.

The concrete elements are prefabricated and coated offsite. After curing for 30 days, the concrete sections are waterjetted at 6,000 psi (400 bar) in preparation for coating. The epoxy primer is spray-applied at a thickness of 10 mils (250 microns), followed by 50 mils (1.25 mm) of polyurea (MDI/amino polyether), and then 10 mils (250 microns) of the polyaspartic ester-based aliphatic topcoat.

A fast coating application is essential to keep pace with the construction schedule. The polyurea and polyaspartic coatings are sufficiently dry in a matter of minutes.

The epoxy provides an anchor for the polyurea, which adds durability and toughness to the concrete surface. The polyaspartic topcoat provides water resistance, chemical resistance, and protection from the discoloring effects of UV light.

Conclusion

Two-component aliphatic polyurea coatings based on polyaspartic esters are proving to be valuable alternatives to the standard solvent-borne polyurethanes. Through increased speed of cure, the polyaspartic ester-based polyurea coatings increase productivity in painting operations, which in turn generates additional value to a gallon of paint. They also provide the capability to increase film build as compared to the typical solvent-borne polyurethane topcoat. This allows one to use fewer coats of paint and adds to the improved productivity of a painting job.

The polyaspartic ester-based polyurea technology is often used in topcoat formulations because it is based on aliphatic polyisocyanates and aliphatic diamines (polyaspartic esters). In addition to good weathering charcteristics, the polyaspartic ester-based topcoats have fast cure times and can be applied up to 10 mils (250 microns) dft. Excellent corrosion protection properties are illustrated through accelerated weathering tests of a specific corrosion protective topcoat formulation. The curing characteristics of polyaspartic ester-based polyurea topcoats also include the accelerating effect of moisture/humidity on the pot life/drying time of a fully formulated topcoat paint.

From an applications perspective, this technology also simplifies some of the spray equipment issues associated with fast-curing coatings. The polyaspartic ester-based coatings, while fast-curing, are not so fast that they require the use of impingement mixing plural-component spray equipment. Less expensive and less complicated conventional spray equipment can be used in some cases depending on the specific formulation. And when plural-component spray equipment is dictated by the specific coating formulation, a long whip hose can often be used with mixing at the manifold, thus allowing for a conventional spray gun to be used.

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