Waterborne Coatings Direct-to-Metal (DTM) Applications

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Waterborne coatings have promised much and have been accepted very cautiously over the last 30+ years in the industrial coatings market. Surface tension sensitivities and narrow application windows have hindered acceptance in some segments of the market. Advances in high and ultra-high solids technologies have competed successfully in many areas of this market. As a result, the formulator has had to wait for new developments in waterborne resin technology.

Solventborne polyurethane types have been available for many years. The continuing surge forward in the development of more environmentally friendly coatings has produced significant advances in polyurethane dispersion (PUD) waterborne chemistry.[1] It is the authors' belief that newly developed PUDs should be considered an important part of the formulator's toolkit.

This article focuses on advances made in the area of oxidatively curing PUDs which typify the rapid developments in waterborne polyurethane chemistry.[2] This curing mechanism finds its precedent in solventborne alkyd technology and has been adapted for use in waterborne resins.[3,4]

Our discussion deals with how oxidatively curing PUDs meet the needs of the general industrial market. Therefore, these key properties of PUDs are emphasized:

- Low solvent content or co-solvent free
- Low viscosity at high molecular weight
- Polyurethane networks formed during the polymer synthesis rather than after application onto the substrate
- Many options for 1K applications
- Low temperature drying
- "Polyurethane performance"
- Superior adhesion to a wide variety of substrates

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These oxidatively curing PUDs have several features that make them attractive to the industrial coatings formulator:

- Neutral to slightly basic pH, which affords good compatibility with a wide range of other aqueous resin systems
- Formulating latitude with film-forming co-solvents due to being solvent-free or near solvent-free
- High compatibility with other modifying additives
- Film-forming properties at room temperature allow for various types of application, such as dip or spray

CHEMISTRY AND CHOICE OF PUD

An oxidatively curing PUD that includes the features previously cited was used for this study (*Table* 1). It is an anionic PUD prepared using the acetone process.[5] Modified with a fatty acid for oxidative cure, it contains a polyester backbone with monomeric components chosen for their excellent exterior durability.[6]

It is important to remember that this type of PUD potentially can cure in at least two ways: (a) oxidative cure and (b) reaction with polyisocyanate or other crosslinking agent.

This type of resin chemistry is environmentally friendly since it is substantially free of organic solvent, anti-skinning agent, drier, and emulsifier. The formulator thus has the option of choosing anti-skinning agents, driers, and emulsifiers that meet specific regulatory requirements.

This chemistry is considered relevant to such markets as the agricultural construction equipment market. Coatings formulated with this class of PUDs can have the following properties:

- Direct-to-metal adhesion
- Reduced energy due to ambient or low temperature cure
- Rapid set-up (short tack-free times and rapid cure)
- Ease of field repair
- Colormatching to OEM finishes
- Durability
- Corrosion inhibition

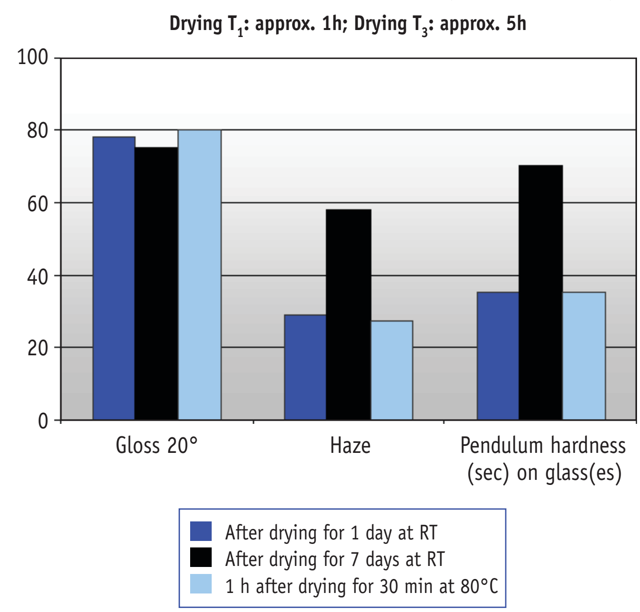
This particular example of oxidatively curing PUDs can be formulated into low- to high-gloss coatings by dispersing pigments directly into the PUD. An alternative approach that we have found attractive is the use of commercially available predispersed pigment pastes.

We cite examples of coatings data which illustrate (a) dry time, (b) chemical resistance, (c) weathering properties, and (d) potential use of water-dispersible polyisocyanates to enhance film properties.

Table 1—PUD Resin Properties

Form Supplied	45 wt% Solids in Water
Nonvolatile content (DIN EN ISO 3251)	~45 wt%
Viscosity (23°C, DIN EN ISO 3219/A.3)	~300 mPas
pH (1:4 in deionized water, DIN 53785)	~7.3
Acid value (DIN EN ISO 2114)	~12 mg KOH/g
Mean particle size (laser correlation spectroscopy)	~125 nm
OH-content (on resin solids)	~2.1%
Density (20°C, DIN EN ISO 2811)	1.0 g/ml

Figure 1—Film properties of white topcoat. (See *Appendix* A.)



PERFORMANCE PROPERTIES

It is possible to obtain desired film properties such as high gloss, low haze, and desired hardness by either curing at room temperature or curing at elevated temperatures, e.g., 80°C (see *Figure* 1).

In *Figure* 1, T_1 refers to the elapsed time to obtain a dust-free surface at room temperature. T_3 refers to the time elapsed to obtain a mar-free surface at room temperature by placing a 200 g weight on the coated panel for 60 sec and then removing the weight without marring the coated surface.

This coating example also developed chemical resistance with time. *Figure* 2 illustrates both the time and temperature effect as oxidative cure proceeded under either room temperature or elevated cure temperature conditions. Chemical resistance development will depend on ambient conditions of temperature and relative humidity during application and cure. Additionally, film properties will be affected by dry film thickness, dry time, and coating pigmentation.

This PUD provides the formulator with the ability to formulate coatings with excellent weathering properties (see *Figure* 3).

If increased hardness and chemical resistance are required, a technique can be used that has its precedent with solventborne fatty acid-modified polyesters (alkyds).[7] The hydroxyl content of the PUD can be utilized to further crosslink by the addition of a polyisocyanate such as a commercially available water dispersible IPDI trimer.[8]

Oxidatively curing PUDs can be formulated into corrosion-resistant primers. Properties of a guide formulation are given in *Figure* 5 and *Table* 2. (Note that the scoring for adhesion ranges from 0, which is "unchanged," to 5, which is "film destroyed.") In general, these PUDs are excellent candidates for direct-to-metal adhesion on substrates such as steel, aluminum, and zinc. It is possible to overcoat the primed part as soon as it has dried to the touch. Ultimate adhesion will develop over time, depending on film thickness, temperature, and solvent- or waterborne one or two component polyurethane topcoats.

Figure 2—Chemical resistance of white topcoat without additional crosslinker.

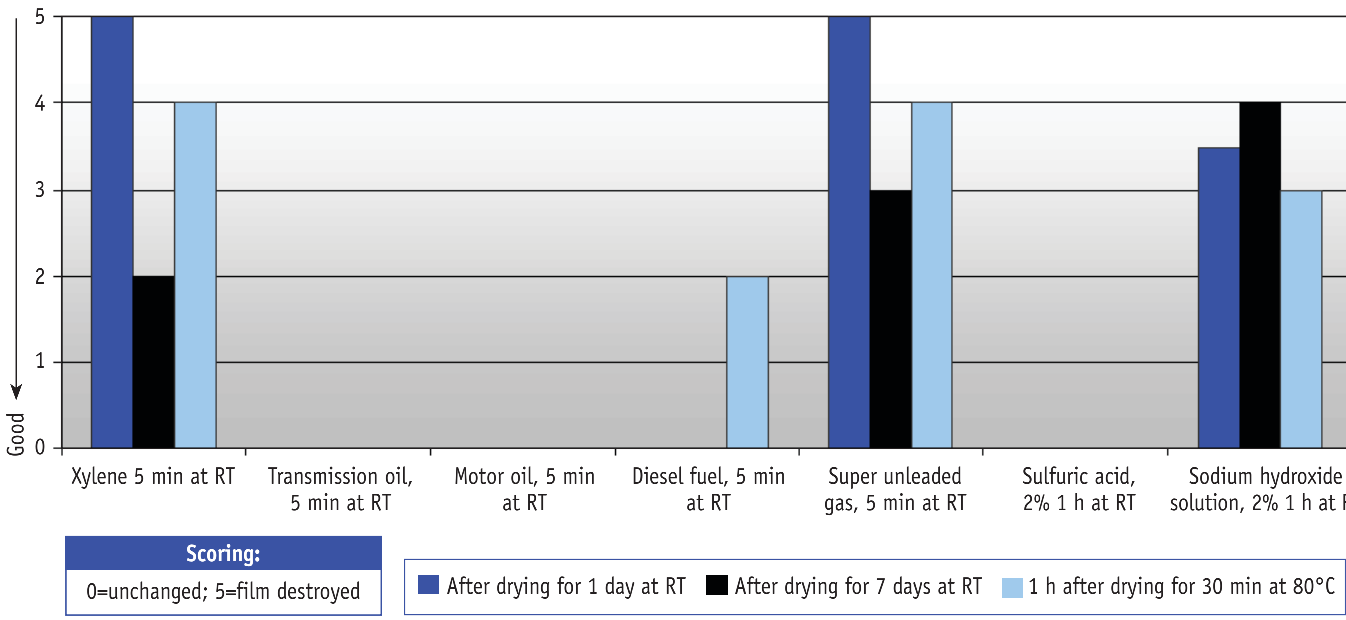


Figure 3—Weathering properties of white topcoat.

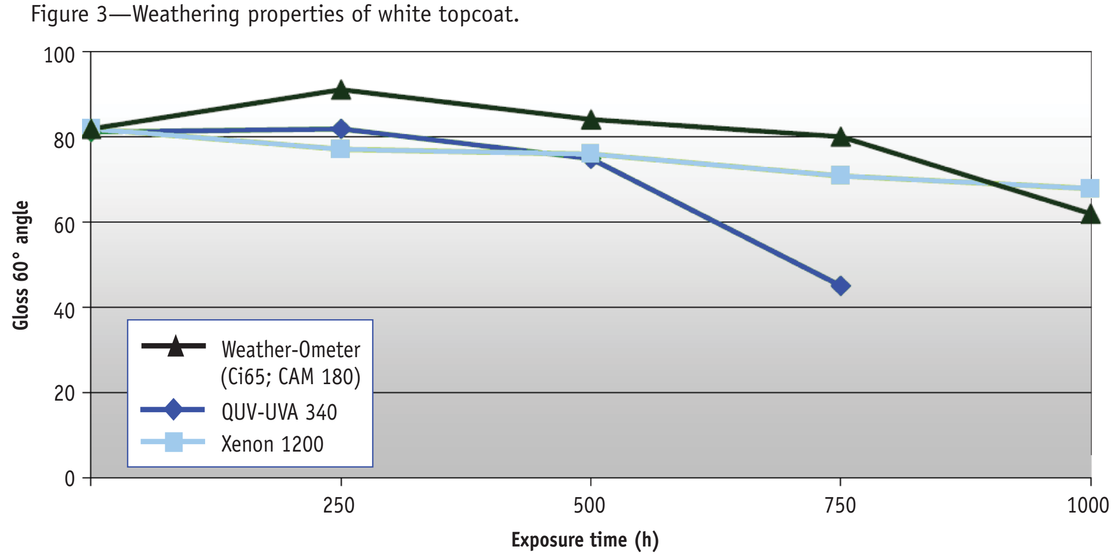


Figure 4—White topcoat with added water-dispersible polyisocyanate (IPDI)[9] (NCO/OH equivalency ratios of 0.31 and 0.62, respectively, for 5 and 10% additions).

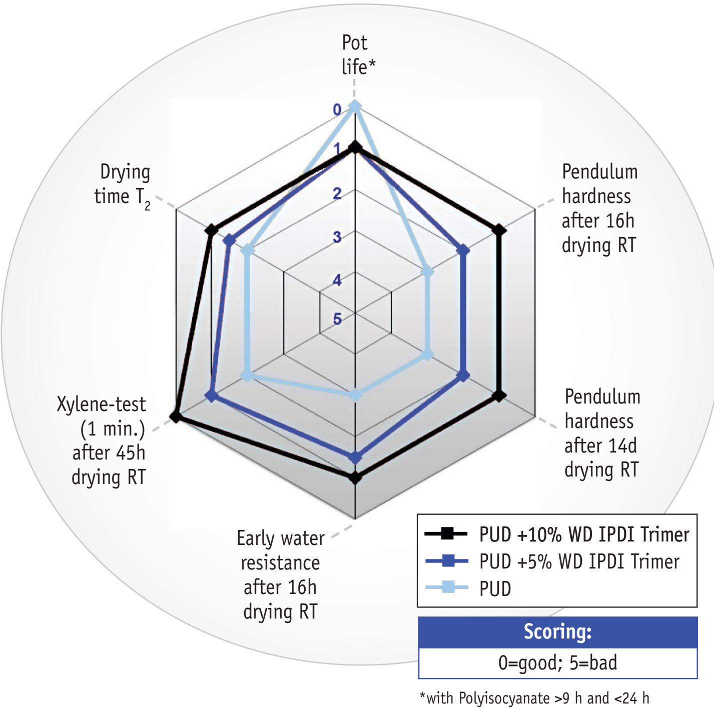


Figure 5—Film properties of gray primer (see *Appendix* B) on cold-rolled steel, DCo4/B, aluminum Al 99.5 hh, and hot-dip galvanized steel gardobond OE.

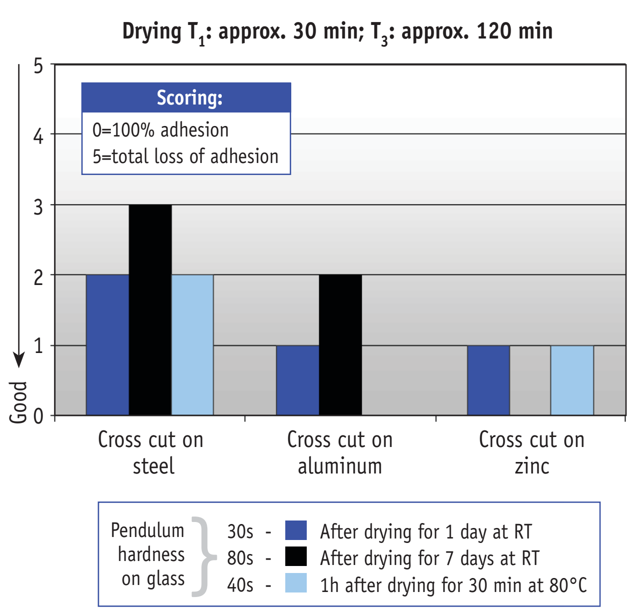


Table 2—Corrosion Protection of Gray Primer

	After drying for 7 days at RT	1 h after drying for 30 min at 80°C
Salt spray test on steel panel........ 240 h	Surface free of findings, max. 3 mm lost adhesion at cut, no rust creep	Max. 3 mm lost adhesion at cut, little rust cut
Humidity test on steel panel........ 240 h	Faded, no blistering	Faded, no blistering
Water resistance on steel panel........ 240 h	m3/g2, faded 2-3	No blistering, faded 2

Once dry, the primer can be over-coated at any time with all conventional solvent- and waterborne 1K or 2K topcoats. However, when the topcoat is applied shortly (<4 days) after the primer, it may take approx. 14 days until optimal topcoat adhesion is achieved. Overcoat ability should be carefully tested on a case-by-case basis.

CONCLUSIONS

Oxidatively curing PUDs are an excellent tool for use in the formulation of direct-to-metal coatings due to their rapid set-up and development of critical film properties. The proper choice of chemical composition enables their use as the sole binder or in combination with 1K or 2K polyol/polyisocyanate resin systems.

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References

(1) Online reference: www.bayermaterialsciencenafta.com/businesses/html.
(2) Wicks, Z.W. Jr., Jones, F.N., Pappas, S.P., Wicks, D.A., *Organic Coatings: Science and Technology, Third Edition*, John Wiley & Sons, p. 261-262, 322, 2007.
(3) Ibid., pp. 307-313.
(4) Mueller, B. and Poth, U., *Coatings Formulation*, Vincentz Network GMbH & Co., p. 83-94, 2006.
(5) Ibid., pp. 167-169.
(6) Bayer MaterialScience LLC internal technical literature, 2008. Available upon request.
(7) Wicks, Z.W. Jr., Jones, F.N, Pappas, S.P., Wicks, D.A., *Organic Coatings: Science and Technology, Third Edition*, John Wiley & Sons, p. 247, 315, 517, 672, 2007.
(8) Bayer MaterialScience LLC internal technical literature, 2008. Available upon request.
(9) Bayhydur® 401-70 water-dispersible polyisocyanate (9.4% NCO content as supplied at 70 wt% solids in propylene glycol monomethyl ether acetate/xylene).

APPENDIX A

Formulation RR 6158

			% by wt
1.	Bayhydrol® UH XP 2592, form supplied		21.49
2.	Butoxyethanol		1.95
	Dowanol® DPnB	(1)	1.95
3.	Ascinin® Anti Skin VP 0445	(2)	0.07
4.	Borchers® Dry 0347 aqua, 1:1 in water	(2)	1.75
5.	Water		2.00 (approx.)

Add an appropriate amount of water to offset severe thickening of Bayhydrol® UH XP 2592 during neutralization.

6.	N-ethyl diisopropyl amine, 50% in ethanol		0.30
7.	Tronox® R-KB-6 [or alternative Aquis White 0062 (Pigment paste from Heubach) Pigment/Binder ~0.7]	(3)	23.27
8.	Water		2.08

If needed, some more water can be used to adjust optimal viscosity for grinding.

9.	Bayhydrol® UH XP 2592, form supplied		43.16
10.	Water		1.98
			100.00

APPENDIX B

Formulation RR 6156

			% by wt
1.	Bayhydrol® UH XP 2592, supply form		30.84
2.	Butoxyethanol		1.85
	Dowanol® DPnB	(1)	1.85
3.	Ascinin® Anti Skin VP 0445	(2)	0.07
4.	Borchers® Dry 0347 aqua, 1:1 in water	(2)	2.78
5.	Nalzin® FA 179	(3)	0.17
6.	Foamstar® MF 330	(4)	0.18
7.	Aerosil® 300	(5)	0.27
8.	K-White 105	(6)	8.28
	Bayoxide® Z Active	(2)	0.82
9.	Water		1.30 (approx.)

K-White 105 and Bayoxide® Z active have to be stirred for approx. 5 min by 3000 rpm (without cooling) into XP 2592. Both pigments will reduce the viscosity of XP 2592 significantly.

10.	N-ethyl diisopropyl amine, 50 % in ethanole		0.50

Slowly drip N-ethyl diisopropyl amine in while agitating (viscosity increases).

11.	Water		0.50 (approx.)
12.	Tronox® R-KB-2	(7)	9.26
	Printex® 55	(5)	0.10
	Microdol® Super	(8)	5.89
	Microtalc AT extra	(8)	3.54

Add pigments while agitating (dissolver).

13.	Water		0.50 (approx.)

Add additional water to establish optimal grinding viscosity.

68.70

Let down

1.	Mill base, see above		68.70
2.	Bayhydrol® UH XP 2592, supply form		30.84
3.	Borchi Gel® PW 25 (supply form., 1:9 in water)	(5)	0.20 (approx.)

Use a stirrer to incorporate components 2 and 3 into the mill base one after the other. Use some of the thickener to initially set supply viscosity. Let the coating stand for approx. 16 hours. Defoaming and establishment of the neutralization equilibrium result in a decrease in viscosity.

4.	Byk® 346	(9)	0.10
5.	Borchi Gel® PW 25 (supply form, 1:9 in water)	(5)	0.16

Use a stirrer to incorporate components 4 and 5 into the mill base one after the other. Use thickener to establish the supply viscosity of approx. 60–100 s, DIN cup 4 mm, 23°C.

100.00