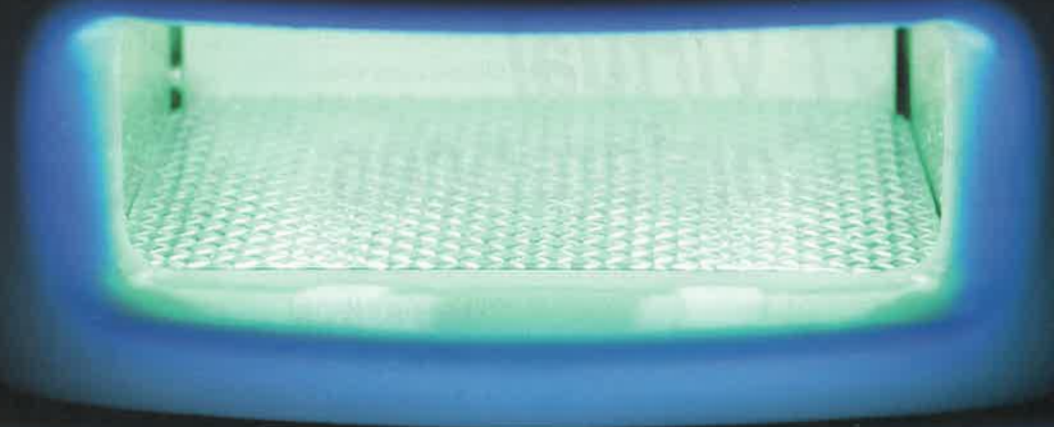


Zinc Oxide Nanoparticle Dispersions



as Unique Additives for Coatings

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The growing availability of reliable sources of nanoparticles has resulted in significant technological advances in numerous applications, including exterior coatings with extended weatherability. However, the difficulty of dispersing nanoparticles and integrating them into polymer systems has limited the commercialization of nanoparticle-enabled products. When nanoparticles are not effectively dispersed and integrated into a formulated polymer, the desired properties can not be fully achieved. We have developed novel dispersion technology for metal and metal oxide nanoparticles that enables their incorporation into polymer systems. This article illustrates the use of this dispersion technology and the effectiveness of nano-zinc oxide as a UV absorber in organic coatings. We also have uncovered that nano-zinc oxide can improve other properties such as chemical and humidity resistance with apparent crosslinking of the polymer. Formulating with nano-zinc oxide has resulted in shelf-stable, one-component self-crosslinking coatings with significantly improved properties.

INTRODUCTION

The effects of UV exposure on coatings and other polymer systems are well documented.¹⁻⁶ Photodegradation occurs when polymer systems absorb photons causing the molecules to become excited. Excitation leads to chemical reactions which cause degradation.^{6,7} Degradation mechanisms may include chain scission of covalent bonds, formation of free radicals, and abstraction of hydrogen. Oxygen can enhance degradation by reacting with free radicals to form peroxy radicals and hydroperoxides. At this point, many reactions can occur to produce even more free radicals leading to further degradation of the coatings.^{6,7} In general, shorter wavelengths of light, such as ultraviolet light, have the ability to break many polymer covalent bonds.⁶ In some cases, such as when clearcoats and stains are applied, underlying

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substrates also can be degraded by exposure to UV, especially with wood and plastic substrates.

To minimize such failures, coatings that are exposed to UV during their service life are formulated with UV-resistant polymers, such as acrylics and aliphatic polyurethanes. Although these systems are resistant to UV, they provide minimal UV protection to the underlying substrate. Coatings used in more demanding applications, such as automotive, aerospace, and exterior wood, also contain additives which absorb UV to assist in protection. These additives not only protect the coating, but they also can protect the substrate, which may be vulnerable to UV degradation (e.g., wood, plastics, and textiles). Typically, these additives are included in

coating formulations at concentrations of <5%. Some of the more common chemical classes of organic UV absorbers are benzophenones, benzotriazoles, triazines, malonates, and oxalanilides.⁹ However, due to their relatively low molecular weight, these additives can migrate out of applied coatings, either to the coating surface or into the substrate.¹⁰⁻¹² Also, because they are organic, they are susceptible to a number of degradation mechanisms.

Many metal oxides also are known to absorb UV radiation; the most common of these are zinc oxide (ZnO) and titanium dioxide (TiO₂). With the development of nano-particle technology, nano-particle ZnO has the ability to offer UV protection while also being

Table 1—Epoxy Clearcoats Evaluated in Phase 1

Formulation Designations	22A	22B	22C	22D	22E	22F	22G	22H	22I
Additive Package	No additive	2% ZnO	4% ZnO	7% ZnO	2% UVA	1% HALS	UVA & HALS	ZnO w/ UVA	2% ZnO w/ UVA & HALS
PART A									
EPOR 828	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Toluene	44.80	32.00	19.20	0.00	44.80	44.80	44.80	32.00	32.00
BYK-333	0.60	0.60	0.60	0.60	0.60	0.50	0.60	0.60	0.60
ZnO dispersion (S41Z)	—	16.00	32.00	56.00	—	—	—	16.00	16.00
Total Pre-Mix	145.40	148.60	151.80	156.60	145.40	145.40	145.40	148.60	148.60
PART B									
Ancamine 2143	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00
Tinuvin 292	—	—	—	—	—	1.60	1.60	1.60	1.60
Tinuvin 1130	—	—	—	—	3.20	—	3.20	—	3.20
Total	205.40	208.60	211.80	216.60	208.60	207.00	210.20	210.20	213.40

(a) Formulation 22A also used as a basecoat in Phase 2.

Table 2—Hybridur Clearcoats Evaluated in Phases 1 and 2

Formulation Designations	21A	21B	21C	21D	21E	21F	21G	21H	21I
Additive Package	No additive	2% ZnO	4% ZnO	7% ZnO	2% UVA	1% HALS	UVA & HALS	ZnO w/ UVA	ZnO w/ UVA & HALS
PRE-MIX									
DPnB	9.83	9.83	9.83	9.83	9.83	9.83	9.83	9.83	9.83
BYK-346	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44
Tinuvin 292	—	—	—	—	—	0.32	0.32	0.32	0.32
Tinuvin 1130	—	—	—	—	0.64	—	0.64	—	0.64
Total Pre-Mix	10.27	10.27	10.27	10.27	10.91	10.59	11.23	10.59	11.23
LETDOWN									
Hybridur 570	74.23	74.23	74.23	74.23	74.23	74.23	74.23	74.23	74.23
Dec Fo PI 4	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22
ZnO dispersion (S44Z)	—	3.50	7.01	12.27	—	—	—	3.50	3.50
Water	15.28	12.41	9.53	5.22	15.28	15.28	15.28	12.41	12.41
Total	100.00	100.63	101.26	102.21	100.64	100.32	100.96	100.95	101.59

Figure 1—One-coat system with epoxy clearcoat.

Epoxy (828/2143) clearcoat
2K polyurethane topcoat gloss white
Substrate: Zn phosphated steel

Figure 2—One-coat system with Hybridur clearcoat.

Hybridur 570 clearcoat
2K polyurethane topcoat gloss white
Substrate: Zn phosphated steel

Figure 3—Two-coat system with epoxy clearcoat and Hybridur clear overcoat.

Hybridur 570 clearcoat
Epoxy (828/2143) clearcoat
2K polyurethane topcoat gloss white
Substrate: Zn phosphated steel

transparent in the visible spectrum. Particles with diameters less than 100 nm can be included into a polymer matrix (e.g., coatings) to yield visibly transparent materials. The transparency is possible due to the particle size being considerably less than the wavelengths of visible light (400–800 nm). As a result, nano-ZnO particles have become an option as a formulating material for UV protection. Due to the fact that they are inorganic and particulate, they have added advantages of being stable and non-migratory within an applied coating, thus allowing them to potentially offer better effectiveness and a longer service life.

The objective of this work was to assess the effectiveness of nano-ZnO to protect coatings and underlying substrate from UV degradation, as well as determine the effects on other common coating properties.

EXPERIMENTAL

This effort was performed to assess nano-ZnO as an additive to enhance UV protection of coatings and underlying substrates, as compared to traditional organic UV absorbers (UVA) and hindered amine light stabilizers (HALS). The work was completed in two phases. In the first phase, nano-zinc oxide dispersions were evaluated and compared to a traditional organic UVA and a HALS in a UV exposure chamber. In this phase, nano ZnO dispersions also were formulated with the UVA and HALS to determine the effects of combining these additives. The second phase was an assessment of the effects of these additives on other coating properties, such as adhesion, hardness, flexibility, and chemical resistance.

Phase 1: Nano-ZnO Compared to and with Organic UVA and HALS

The additive packages were assessed in two clearcoat polymer systems: a cycloaliphatic amine (Auramine 2143)/epoxy (Epon 828) high solids system, and a polyurethane-acrylic hybrid latex system (Hybridur 570). The epoxy represents a polymer that photo-degrades and severely yellows upon exposure to UV.⁶ The

Hybridur is fairly weather resistant without addition of UV absorbers.¹³ The following additive packages were assessed in both the epoxy and Hybridur 570, respectively:

- No additive (control)
- 2 wt% ZnO based on total resin solids (0.4% by volume on total solids)
- 4 wt% ZnO (0.8% by volume on total solids)
- 7 wt% ZnO (1.3% by volume on total solids)
- 2 wt% UVA (Tinuvin 1130)
- 1 wt% HALS (Tinuvin 292)
- 2 wt% UVA/1 wt% HALS
- 2 wt% ZnO/1 wt% HALS
- 2 wt% ZnO/2 wt% UVA/1 wt% HALS

The epoxy and Hybridur formulas were prepared as described in Tables 1 and 2, respectively. Note once again that in addition to comparing nano-ZnO to the traditional UVA and HALS additives, it also was assessed when combined with these additives.

In addition to the UV absorbers being assessed in the epoxy and Hybridur coatings separately (noted as one-coat systems and illustrated in Figures 1 and 2), another set of specimens was prepared that consisted of the Hybridur clearcoats with the additives noted above applied over top of the epoxy clearcoat containing no UV additives. This is noted as the two-coat system, referring to the epoxy and Hybridur clearcoats (Figure 3). This configuration allows assessment of any UV absorbers in the Hybridur clearcoat to shield underlying coatings and substrate.

UV exposure test panels were prepared by applying a highly weather resistant two-component gloss white polyurethane topcoat (Rustoleum High Performance Industrial Low-VOC Urethane 9700 system gloss white) to zinc phosphated steel panels (Bonderite 952) to a dry film thickness of approximately 2 mils. Previous studies demonstrated that this coating does not change appearance during long-term exposure to accelerated weathering (e.g., QUV-A). After allowing the polyurethane white coating to cure for a suitable period (e.g., seven days at room temperature, or some equivalent cure schedule at elevated temperature), the

epoxy and Hybridur coatings from *Tables 1 and 2* were applied as described below.

PREPARATION OF ONE-COAT SYSTEMS (*Figures 1 and 2*): the epoxy coatings described in *Table 1* and the Hybridur coatings noted in *Table 2* were applied over the polyurethane basecoat to form "one-coat systems." The epoxy coatings listed in *Table 1* were applied using an RDS rod number 44 to an approximate wet film thickness of 4 mils. This coating was cured at room temperature for approximately 16 hr, followed by curing for approximately 16 hr at 43°C. The ultimate dry film thickness of the epoxy coatings was 3 mils. Hybridur coatings listed in *Table 2* were applied using a wire wound rod manufactured by RDS (rod number 70), which provides a wet film thickness of approximately 6.3 mils. The Hybridur coating systems were dried for 5 hr at room temperature, followed by approximately 16 hr at 43°C. Dry film thickness for the Hybridur coatings was approximately 1.4 mils. *Figure 4* illustrates scanning electron micrographs of the 4% ZnO-Hybridur coating, which demonstrates the size of the nano-ZnO particles (~50 nm diameter) and that they are well dispersed throughout the polymer system.

PREPARATION OF TWO-COAT SYSTEMS (*Figure 3*): a second series of panels were prepared by applying and curing the control epoxy clearcoat formula (no additives, 22A in *Table 1*) to the polyurethane topcoat as described above. At this point, the Hybridur clearcoats listed in *Table 2* were applied and cured over top of the epoxy coating using the same methods as the one-coat hybrid system.

After allowing these coatings to dry and cure, a series of specimens was placed in a QUV-A 340 cabinet with UV exposure (continuous UV 340 A bulb exposure with irradiance of 0.89 W/m²). The specimens were removed periodically to measure color and gloss. From these measurements, color change (ΔE) and gloss retention were calculated versus pre-exposed samples.

Figure 4—SEM of Hybridur coating with 4% nano-ZnO.

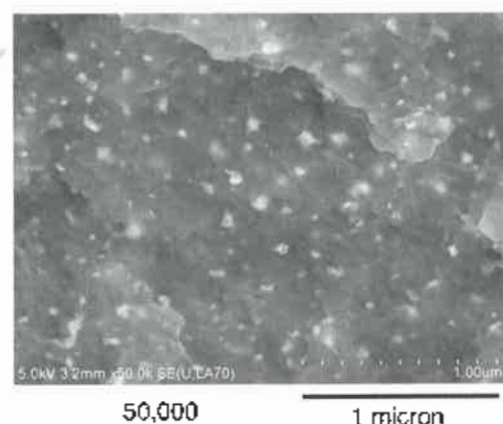


Table 3—Test Properties and Methods

Property	Method
Gloss—White Leneta (20°)	ASTM D 523
Gloss—White Leneta (60°)	ASTM D 523
Gloss—White Leneta (85°)	ASTM D 523
Gloss—Black Leneta (20°)	ASTM D 523
Gloss—Black Leneta (60°)	ASTM D 523
Gloss—Black Leneta (85°)	ASTM D 523
Contrast ratio (y black/y white)	—
Dry scrape	ASTM D 2197
Wet scrape (24 HR/RT)	ASTM D 2197
Dry tape	ASTM D 3359
Wet tape (24 HR/RT)	ASTM D 3359
Water immersion (24 HR/RT)	—
Humidity (100°F/100% RH)	ASTM D 4585
IPA double rubs	ASTM D 4752
Initiator double rubs	ASTM D 4752
MEK double rubs	ASTM D 4752
Gardner impact (in./lb) Direct	ASTM D 2794
Gardner impact (in./lb) Reverse	ASTM D 2794
Pencel hardness	ASTM D 4366/ANSI/ISO 1522
Pencil hardness	ASTM D 3363

Phase 2: Assessment of Effects on Other Coating Properties

In addition to QUV-A exposure evaluations, an unexposed set of epoxy and Hybridur-based coatings were tested for a number of common coating properties. Epoxy and Hybridur coatings for this phase were applied directly onto steel panels and cured as described above. The properties evaluated and associated test methods are listed in *Table 3*.

RESULTS AND DISCUSSION

Phase 1: Nano-ZnO Compared to Organic UVA and HALS

Color change of the one-coat epoxy clearcoats as a result of QUV-A exposure duration is presented in *Table 4* and *Figure 5*. As is common with epoxy-amine systems, these coatings yellowed quickly and severely upon UV exposure. This yellowing is caused by the formation of conjugated chromophores during polymer degradation.⁷ After just 20 hr of exposure, ΔE color change values ranged from 3 to 5.7, which is quite considerable for such a short duration. After one week, ΔE values were 16–19 and after six weeks (1000 hr) they were 32–39, at which time the test was suspended. There was minimal differentiation between coatings with the various additive packages, probably because of the extreme susceptibility of these systems to yellow, and the quick and extensive extent of yellowing. The

Table 4—Color Change of Epoxy One-Coat Systems During QUV-A Exposure

COLOR L,a,b Exposure Time	ΔE 20 hr	ΔE 1 wk	ΔE 2 wk	ΔE 3 wk	ΔE 4 wk	ΔE 5 wk	ΔE 6 wk
Control—no additives	2.99	15.96	28.87	36.18	37.41	37.45	37.92
2% ZnO	3.63	18.00	31.33	37.24	38.16	38.13	38.36
4% ZnO	4.05	18.84	31.41	37.38	38.05	38.07	38.17
7% ZnO	5.01	19.49	30.20	35.99	36.71	36.53	36.65
UVA	5.04	18.17	28.72	32.69	32.86	32.67	33.08
HALS	3.00	16.32	29.99	35.55	35.91	35.97	36.58
UVA/HALS	4.50	16.02	24.37	31.09	32.84	32.06	31.99
2% ZnO/HALS	3.56	16.05	29.70	36.55	38.17	38.46	38.69
2% ZnO/UVA/HALS	5.73	16.98	26.34	32.39	33.28	33.28	33.58

Figure 5—Color change of epoxy coatings during QUV-A exposure.

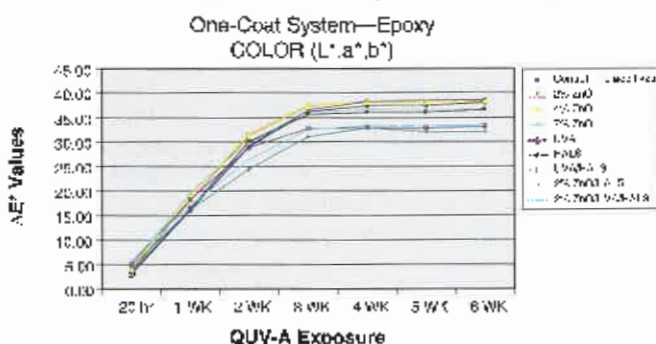


Figure 6—Color change of Hybridur coatings during QUV A exposure.

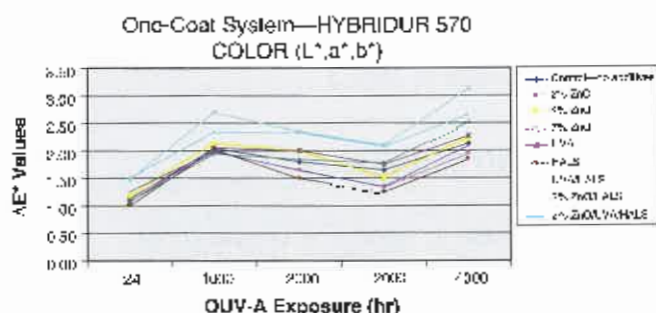


Table 5—Color Change of Hybridur One-Coat Systems During QUV-A Exposure

COLOR L,a,b Exposure Time (hr)	ΔE 24	ΔE 500	ΔE 1000	ΔE 2000	ΔE 3000	ΔE 4000
Control—no additives	1.12	1.62	2.04	1.79	1.65	2.22
2% ZnO	1.14	1.53	1.97	1.64	1.34	1.95
4% ZnO	1.18	1.64	2.13	1.99	1.52	2.23
7% ZnO	1.46	2.00	2.69	2.34	2.10	3.12
UVA	1.06	1.59	2.05	1.99	1.75	2.27
HALS	1.00	1.48	2.02	1.49	1.25	1.84
UVA/HALS	1.07	1.57	1.94	1.84	1.77	2.31
2% ZnO/HALS	1.26	1.43	1.98	1.63	1.35	2.09
2% ZnO/UVA/HALS	1.51	1.92	2.33	2.32	2.08	2.65

coatings industry has desired a “weatherable” epoxy coating for some time and there have been numerous attempts to provide such performance through polymer chemistry changes and additive packages. These attempts generally have been unsuccessful. This evaluation indicates that incorporating nano-ZnO as a formula

tion additive dispersed throughout the applied coating is an approach which also will not provide the desired level of UV protection to epoxy-amine systems.

However, as will be discussed later in this article, it is possible that improvement may be obtained by formulating such that ZnO concentrates at the surface of the applied coating.

Color change in the Hybridur 570 clearcoat system is presented in Table 5 and Figure 6. Hybridur 570 is known to be a fairly weatherable system and has been used in commercial coatings for exterior (UV exposure) applications.¹² As opposed to the epoxy system, color change in the Hybridur clearcoats is quite low. After 24 hr, ΔE values range from 1 to 1.5 and after this time they increase only slightly over a 4000-hr exposure. At 4000 hr, ΔE 's range from 1–3, which is quite amazing for such a long exposure period to QUV-A (24 weeks). Again, there was little differentiation in color change between coatings and additive packages.

Another potential effect of weathering is gloss reduction due to roughening of the coating surface from polymer degradation and erosion. Twenty degree gloss results for Hybridur coatings over the 4000-hr exposure are presented in Table 6 and Figure 7. Initial 20° gloss for the control with no additives is 79, with gloss for most of the other systems being 78–80. Therefore, in-

corporation of the nano ZnO at concentrations up to 7% does not adversely affect gloss. The only formulations which displayed a slight reduction in gloss are those containing 2% ZnO/HALS and 2% ZnO/UVA/HALS. There was no obvious visual cause for this gloss reduction, but it may be due to an incompatibility between these additives, causing surface roughness and/or haze. Throughout the QUV-A

Table 6—20° Gloss of Hybridur One-Coat Systems During QUV-A Exposure

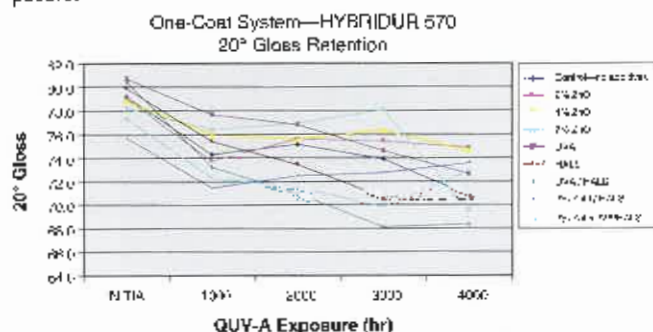
20° Gloss	Avg.	Avg.	Avg.	Avg.	Avg.	Avg.	Gloss
Exposure Time (hr)	Initial	500	1000	2000	3000	4000	Ret. (%)
Control—no additives	79.2	78.4	74.3	75.1	73.9	70.8	89.4
2% ZnO	79.0	76.9	73.7	75.6	75.4	74.8	94.7
4% ZnO	78.8	76.3	75.9	75.5	76.3	74.5	94.5
7% ZnO	78.2	75.9	76.4	76.9	78.1	69.5	88.9
UVA	80.7	78.1	77.7	76.8	74.6	72.6	90.0
HALS	79.9	77.0	75.4	73.4	70.6	70.7	88.5
UVA/HALS	80.4	76.5	73.2	70.9	68.1	68.3	85.0
2% ZnO/HALS	75.7	74.1	71.4	72.4	72.7	73.5	97.1
2% ZnO/UVA/HALS	77.3	73.7	72.3	71.5	69.8	72.8	94.2

exposure period, the control reduces gloss from 79.2 to 70.8, an 89% gloss retention, certainly good performance for such an extended exposure. However, formulations with ZnO, UVA, and HALS, respectively, have even higher gloss retentions. In fact, the 2% and 4% ZnO formulations have gloss retentions of 94.7% and 94.5%, respectively. This is remarkable, especially considering that 20° gloss readings are severe and discriminating; any degradation or roughening of the coating surface will result in a considerable reduction in 20° gloss. These results clearly indicate nano-ZnO is providing benefits during this exposure duration.

The two-coat systems (i.e., epoxy clearcoat with Hybridur clear overcoat) were prepared to assess the ability of the UV absorbers in Hybridur to protect the underlying epoxy. Color change and gloss data for the two-coat systems are presented in Tables 7 and 8 as well as Figures 8 and 9. As expected based on the epoxy one-coat results, the control system with no additives has rapid and severe yellowing, with a ΔE at 4000 hr of 53. Coatings with 2% ZnO, UVA, and HALS, both separately and combined, also display considerable color change with ΔE s of 49 or higher. The 4% ZnO has a ΔE of 43 after 4000 hr, which is improved over the control and the traditional organic UVA/HALS additives. The 7% ZnO coating provides exceptional color retention, with a ΔE of only 6.1 after 4000 hr. In fact, color change for the 7% ZnO formulation was remarkable throughout the entire exposure duration. Figure 10 is a photograph of selected specimens after 4000-hr QUV-A exposure, illustrating the severe color change of the control versus exceptional color retention of the 7% ZnO specimen.

Similar trends, but with some differences, are observed with 20° gloss and gloss retention (Table 8 and Figure 9). Gloss of the control dropped considerably, with a gloss retention of only 57.1% after 4000 hr. The 2% ZnO and 2% ZnO/HALS systems also did not fair well. The UVA, HALS, and UVA/HALS systems had

Figure 7— 20° gloss retention of Hybridur coatings during QUV-A exposure.



gloss retentions of 85–90%, which is considerably good for this exposure duration. However, the 1% and 7% ZnO, as well as the 2% ZnO/UVA/HALS, had excellent gloss retention throughout the exposure time, with nearly 100% after 4000 hr.

The results of the two-coat systems clearly illustrate that the nano-ZnO is providing UV protection to Hybridur and also the underlying epoxy coating, even more so than the traditional organic UVA/HALS additives. This is indicated by excellent gloss retention of the Hybridur and minimal color change of the epoxy. It should be considered that ZnO is quite stable, both chemically and physically, especially compared to organic UVA and HALS additives. Previous reports^{10, 2} have documented that UVA and HALS additives can migrate out of coating systems to the surface, or to the substrate. Being organic in nature, they also are susceptible to degradation. Therefore, although they have been used extensively and are effective over shorter periods of time, they can be rendered ineffective over longer durations. In contrast, nano-ZnO particles are more prone to be anchored in these polymer systems and will not migrate. Also, they are chemically stable as dispersed in these polymer systems. So, as the results

Table 7—Color Change of Two-Coat Systems During Exposure in QUV-A

COLOR L,a,b Exposure Time (hr)	ΔE 24	ΔE 1000	ΔE 2000	ΔE 3000	ΔE 4000
HY570—no additives	2.84	41.30	46.33	49.91	52.77
2% ZnO	1.27	34.28	50.07	54.00	58.25
4% ZnO	0.51	7.36	23.09	34.80	43.07
7% ZnO	0.54	1.33	2.42	3.85	6.13
UVA	0.52	13.97	35.52	46.84	49.77
HALS	3.22	40.78	44.66	48.58	51.56
UVA/HALS	0.30	8.88	33.58	46.42	49.22
2% ZnO/HALS	1.43	35.71	48.56	51.70	54.73
2%ZnO/UVA/HALS	0.41	5.45	22.91	37.27	46.45

Figure 8—Color change of two-coat systems during QUV-A exposure.

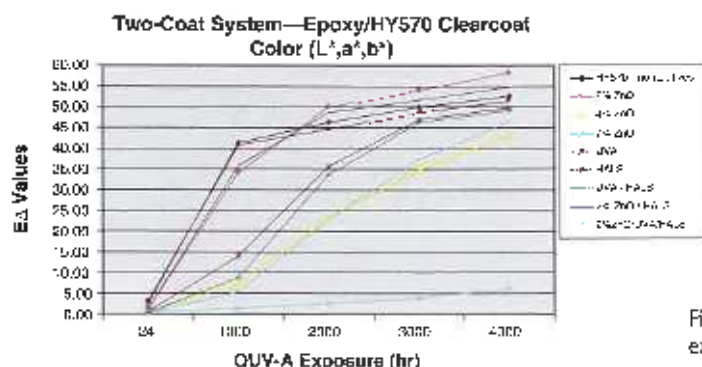


Figure 9—20° gloss retention of two-coat systems during QUV-A exposure.

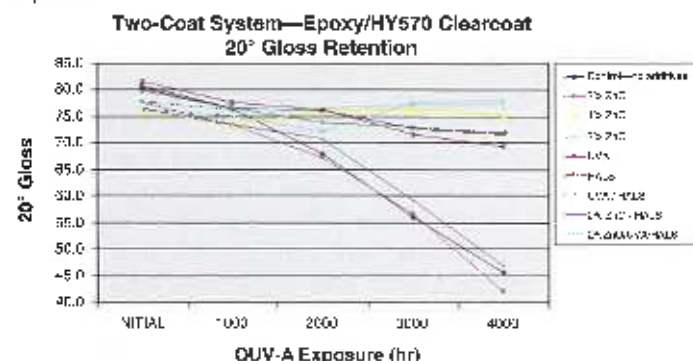
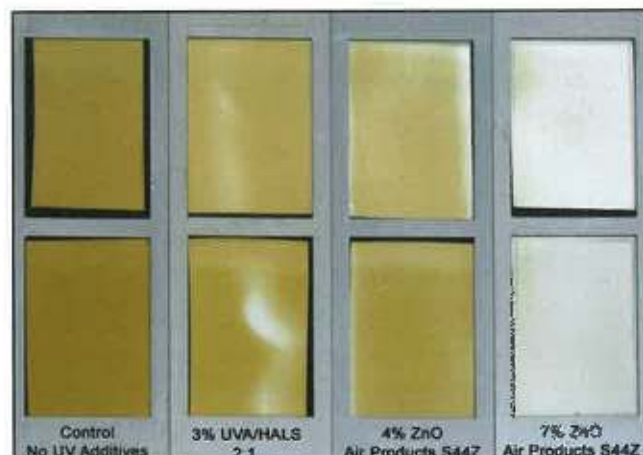


Table 8—20° Gloss of Two-Coat Systems During Exposure in QUV-A

20° Gloss	Avg.	Avg.	Avg.	Avg.	Avg.	Gloss Ret. (%)
Exposure Time (hr)	Initial	1000	2000	3000	4000	
HY570—no additive	80.3	76.4	67.9	56.0	45.7	57.2
2% ZnO	77.6	73.5	67.2	56.7	42.0	54.1
4% ZnO	76.3	73.5	76.1	76.5	75.2	99.6
7% ZnO	76.5	75.1	72.1	77.6	78.0	102
UVA	81.6	77.6	76.3	71.6	69.3	84.9
HALS	80.7	76.6	76.1	72.7	71.8	89.0
UVA/HALS	79.8	76.6	73.9	73.0	72.0	90.2
2% ZnO/HALS	76.6	73.5	70.7	59.2	46.8	61.1
2%ZnO/UVA/HALS	77.8	76.2	76.5	77.1	77.2	99.2

Figure 10—QUV-A two-coat system specimens after 4000-hr exposure.



herein illustrate, they are effective for much longer exposure periods.

It is interesting to compare ΔE results from the epoxy one-coat system to those from the two-coat system. As noted above, ΔE s for the epoxy one-coat system were all above 30, even after just three weeks (~ 500 hr) exposure, indicating that none of the UV absorbers were providing much protection in the formulation. In contrast, some of the two-coat systems had much less color change over this time, and the 7% system was remarkably better, even at 4000 hr. One main differentiation is that in the one-coat system, the UV absorbers are dispersed throughout the coating and therefore not concentrated at the surface. This allows UV rays to penetrate deeper into the coating where they can cause photodegradation of polymer chains closer to the coating surface where they are exposed to UV. In the two-coat system, the UV absorbers are in a coating above the epoxy, and therefore have the ability to absorb considerable UV radiation before penetrating into the epoxy coating. This is suspected to be the difference. If it is possible to formulate the epoxy coating, or any other coating, such that the UV absorbers (nano-ZnO in this case) rise to the surface of the coating and are concentrated there in the dry, applied coating, this may provide substantial absorption of incident UV radiation and thereby protect the underlying polymer even further.

In order to understand the fundamental cause for the protection observed during the QUV-A exposures, some of the Hybridur coatings were evaluated for transmission through the UV-visible spectrum. These results are illustrated in Figures 11 and 12. Figure 12 magnifies transmission in the UV region. The control with no additive has well over 20% UV transmission at wavelengths greater than 230 nm. The UVA/HALS coatings at

both 3% and 8% total concentration have a large spike in the 240 to 290 nm range. The 4% ZnO coating has a transmittance of $<2\%$ throughout nearly the entire UV spectrum; the 7% ZnO system has virtually no transmittance over this range, which explains such exceptional UV protection in the coating systems evaluated.

Phase 2: Assessment of Effects on Other Coating Properties

The second phase of this effort focused on determining if other coating properties are affected by incorporation of nano-ZnO. Tables 9 and 10 list results for the epoxy and Hybridur systems, respectively. For the epoxy system, nearly all of the properties remain consistent, with the exception of scrape adhesion and especially wet scrape adhesion. The dry scrape adhesion values range from 6.5 kg for the control to 8.5 and 9.5 kg for the coatings containing 4% and 7% ZnO. From these results, it appears that the nano-ZnO is improving the toughness and/or adhesion of the coating. In the wet scrape adhesion, almost all of the adhesion values decrease considerably relative to the dry scrape, with most

Figure 11—UV-Vis transmission of Hybridur coatings.

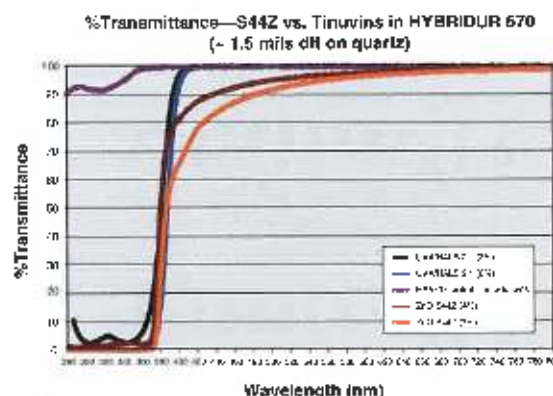


Figure 12—UV transmission for Hybridur coatings.

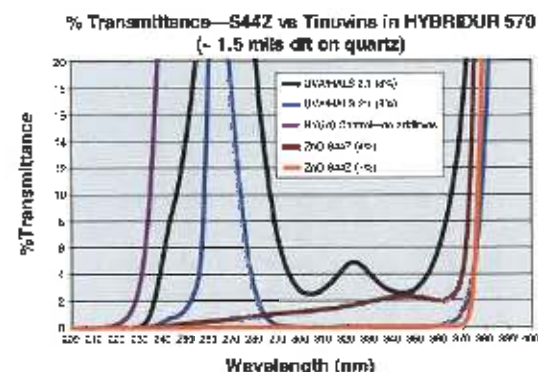


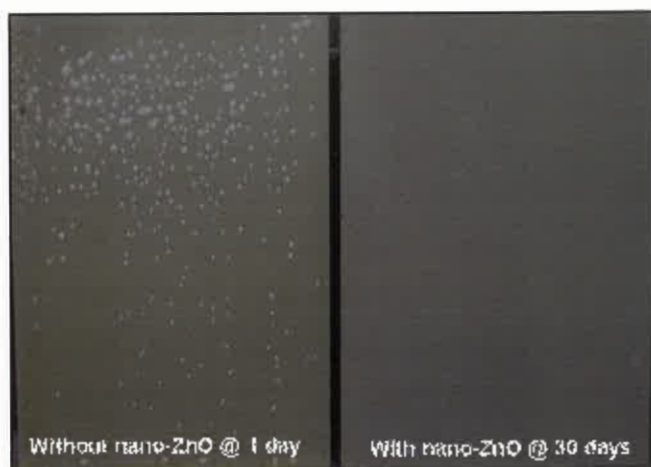
Table 9—Properties of Epoxy Based Coating Systems

Formulation Designations	22A	22B	22C	22D	22E	22F	22G	22H	22I
Additive Package	No additive	2% ZnO	4% ZnO	7% ZnO	2% UVA	1% HALS	UVA HALS	2% ZnO w/ UVA	2% ZnO w/ UVA & HALS
Dry scrape (kg)	pass 6.5	pass 7.5	pass 8.5	pass 9.5	pass 7.5	pass 7.5	pass 7.5	pass 8.0	pass 8.0
Wet scrape, 24 hr/70 F (kg)	pass 3.5	pass 4.0	pass 7.0	pass 8.5	pass 3.5	pass 4.0	pass 4.5	pass 4.0	pass 5.5
Dry tape	5A	5A	5A	5A	5A	5A	5A	5A	5A
Wet tape, 24 hr/70 F	4A	5A	4A	4A	5A	4A	5A	5A	5A
Water immersion, 24 hr/70 F	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Humidity—30 days(100°F/100% RH)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
IPA double rubs	200	200	200	200	200	200	200	200	200
Toluene double rubs	200	200	200	200	200	200	200	200	200
MEK double rubs	200	200	200	200	200	200	200	200	200
Gardner impact (in./lb) Direct	84	108	88	88	92	84	76	84	112
Gardner impact (in./lb) Reverse	72	72	72	72	64	68	96	76	72
Pencil hardness	3H	3H	3H	3H	3H	3H	3H	3H	3H

Table 10—Properties of Hybrid-Based Coating Systems

Formulation Designations	21A	21B	21C	21D	21E	21F	21G	21H	21I
Additive Package	No additive	2% ZnO	4% ZnO	7% ZnO	2% UVA	1% HALS	UVA HALS	2% ZnO w/ UVA	2% ZnO w/ UVA & HALS
Gloss—white (20°)	67.7	65.9	59.5	63.4	62.8	63.3	63.4	61.4	60.6
Gloss—white (60°)	88.4	88.0	87.9	88.4	89.3	88.2	88.7	87.6	88.2
Gloss—white (85°)	97.3	97.3	96.8	97.1	96.4	96.9	97.1	96.8	97.1
Gloss—black (20°)	71.0	62.6	64.2	64.3	61.7	63.8	64.1	63.4	63.6
Gloss—black (60°)	86.6	85.7	85.8	85.9	85.8	86.0	86.2	85.8	86.5
Gloss—black (85°)	97.2	97.3	97.7	96.9	96.3	96.8	97.4	97.2	96.3
Haze—white (60°-20°)	20.7	22.1	28.4	25.0	26.5	24.9	25.3	26.2	27.6
Haze—black (60°-20°)	15.6	23.1	21.6	21.6	24.1	22.2	22.1	22.4	32.9
Contrast ratio (y black/y white)	0.0075	0.0082	0.0094	0.0112	0.0074	0.0076	0.0079	0.0083	0.0082
Dry scrape (kg)	pass 3.0	pass 3.0	pass 2.5	pass 2.5	pass 2.5	pass 2.5	pass 2.5	pass 2.5	pass 2.5
Wet scrape, 24 hr/70 F (kg)	pass 1.5	pass 2.0	pass 1.0	pass 1.0	pass 1.5	pass 2.0	pass 1.0	pass 1.5	pass 1.0
Dry tape	5A	5A	5A	5A	5A	5A	5A	5A	5A
Wet tape, 24 hr/70 F	5A	5A	5A	5A	3A	5A	4A	5A	5A
Water immersion, 24 hr/70 F	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Humidity—30 days(100°F/100% RH)	Fail	Pass	Pass	Pass	Fail	Fail	Fail	Pass	Pass
IPA double rubs	92	200	200	200	60	70	53	200	200
Toluene double rubs	200	200	200	200	200	200	200	200	200
MEK double rubs	200	200	200	200	200	200	200	200	200
Gardner impact (in./lb) Direct	160	160	160	152	160	152	140	160	144
Gardner impact (in./lb) Reverse	160	160	160	160	160	160	160	160	100
Pencil hardness	135	144	140	148	125	140	126	144	132
Pencil hardness (in./lb)	3B	B	HD	2S	B	2B	B	B	B
Pencil hardness (in./lb)	Control	12	+3	-1	-2	-1	+2	+2	+2

Figure 13—Hybridur specimens exposed in humidity chamber.



results being in the 3.5 to 4.5 kg range, which is approximately a 50% reduction. This is somewhat expected. In this test, a coated specimen is immersed in water for 24 hr at 70°F. Upon removal, the specimen is tested for scrape adhesion of the coating to the substrate. Water will plasticize and soften many coatings, as well as decrease adhesion, so it is expected to have lower values for the wet versus dry scrape adhesion. In general, the overall results for the epoxy coatings are quite good and somewhat expected due to the excellent hardness, adhesion, and water-resistance of epoxy coatings. However, even more notable is the dramatic improvement of wet scrape adhesion of the coatings with 4% and 7% ZnO (relative to those without ZnO), which have values of 7 and 8.5 kg, respectively. Not only are these coatings notably harder than those without nano-ZnO, there is only a minimal reduction in scrape adhesion due to water immersion (i.e., dry scrape versus wet scrape).

Results with the Hybridur coatings are presented in Table 10. In these tests, ZnO had the most notable effects with improved alcohol resistance (IPA double rubs) and humidity resistance. This polyurethane-acrylic, as with other polyurethane-acrylic hybrids and polyurethane dispersions (PUDs) in general, are susceptible to alcohols as observed with double rub tests, spot tests, and immersion. In many cases with these polymers, alcohols severely soften and sometimes actually dissolve the polymer. In these current evaluations, all of the coatings without nano-ZnO have IPA double rubs <100, while all of the Hybridur coatings with nano-ZnO have IPA double rubs of 200 or greater.

To assess alcohol resistance further, we performed spot tests by placing a 0.5 × 0.5 in. non-extractable towel, soaking the towel with IPA for 30 min, removing, and then assessing effects on the coatings. Again,

dramatic improvements were observed with coatings containing nano-ZnO. Coatings without ZnO softened dramatically and were easily removed from the substrate, while coatings with nano-ZnO softened and swelled only slightly and had a crosslinked character.

The other property that was substantially improved with inclusion of nano-ZnO was humidity resistance. As illustrated in Figure 13, the non-ZnO coatings formed blisters within 24-hr exposure in the humidity chamber, while the ZnO coatings lasted 30 days with no blisters or other coating defects. The coatings were removed from the chamber at 30 days.

To further study effects of nano-ZnO, other waterborne polymer systems were evaluated, including PUDs, other hybrids, acrylic, and vinyl acetate-ethylene co-polymers. All of the waterborne polymers tested that had carboxyl functionality displayed improvements in alcohol resistance.

Based on all of these test results and observations, it clearly appears that the nano-ZnO has a self-crosslinking effect on carboxy functional polymers, which significantly improves chemical resistance and humidity resistance from the properties tested, and possibly other properties which have not been evaluated to date.

The potential of self-crosslinking of these polymer systems led to a question of their shelf stability as a raw material and in a formulated coating. Sets of the prepared Hybridur formulations containing 4% and 7% of the S44Z nano-ZnO were placed in sealed containers and kept at room temperature (70°F) for six months and another set was placed in an oven at 129°F for four weeks. The containers were evaluated periodically for viscosity and pH, and the coatings were applied and tested for IPA double rub resistance. No substantial changes were observed in either the room temperature or elevated temperature coatings and all of the applied coatings containing nano-ZnO passed 200 IPA double rubs. These results provide evidence of shelf-stable, self-crosslinking polymer systems.

CONCLUSIONS

- Epoxy coatings (one-coat systems) yellow severely when exposed to UV without UV absorbers and also with UVA/HALS and nano-ZnO.
- Hybridur coatings (one-coat systems) maintain color and gloss very well without and with UV absorbers.
- Two-coat systems containing an epoxy clearcoat with a Hybridur clear overcoat yellow severely with no UV absorbers and with UVA and HALS. Coating systems with 4% nano-ZnO in the Hybridur clear overcoat have less yellowing, especially over extended durations (up to 1000 hr) in QUV-A. Coating systems with 7%

ZnO have exceptional color and gloss retention over the 4000 hr QUV-A exposure. UV transmission results indicate that this exceptional performance is due to nearly 100% absorption of UV, especially compared to the organic UVA additives.

• Hybridur coatings containing 4% and 7% nano-ZnO have dramatically improved alcohol and humidity resistance. Similar improvements were observed in other polymers such as polyurethane dispersions, acrylic latex, and polyurethane-acrylic hybrids. IPA double rub and spot test results provided clear indication that systems with nano-ZnO are self-crosslinking.

• The 4% and 7% Hybridur coatings were shelf stable at 70°F for >6 months and at 129°F for >4 weeks, indicating a shelf-stable, self-crosslinking polymer. 

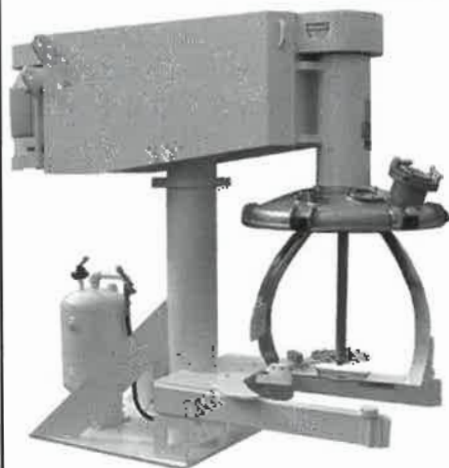
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