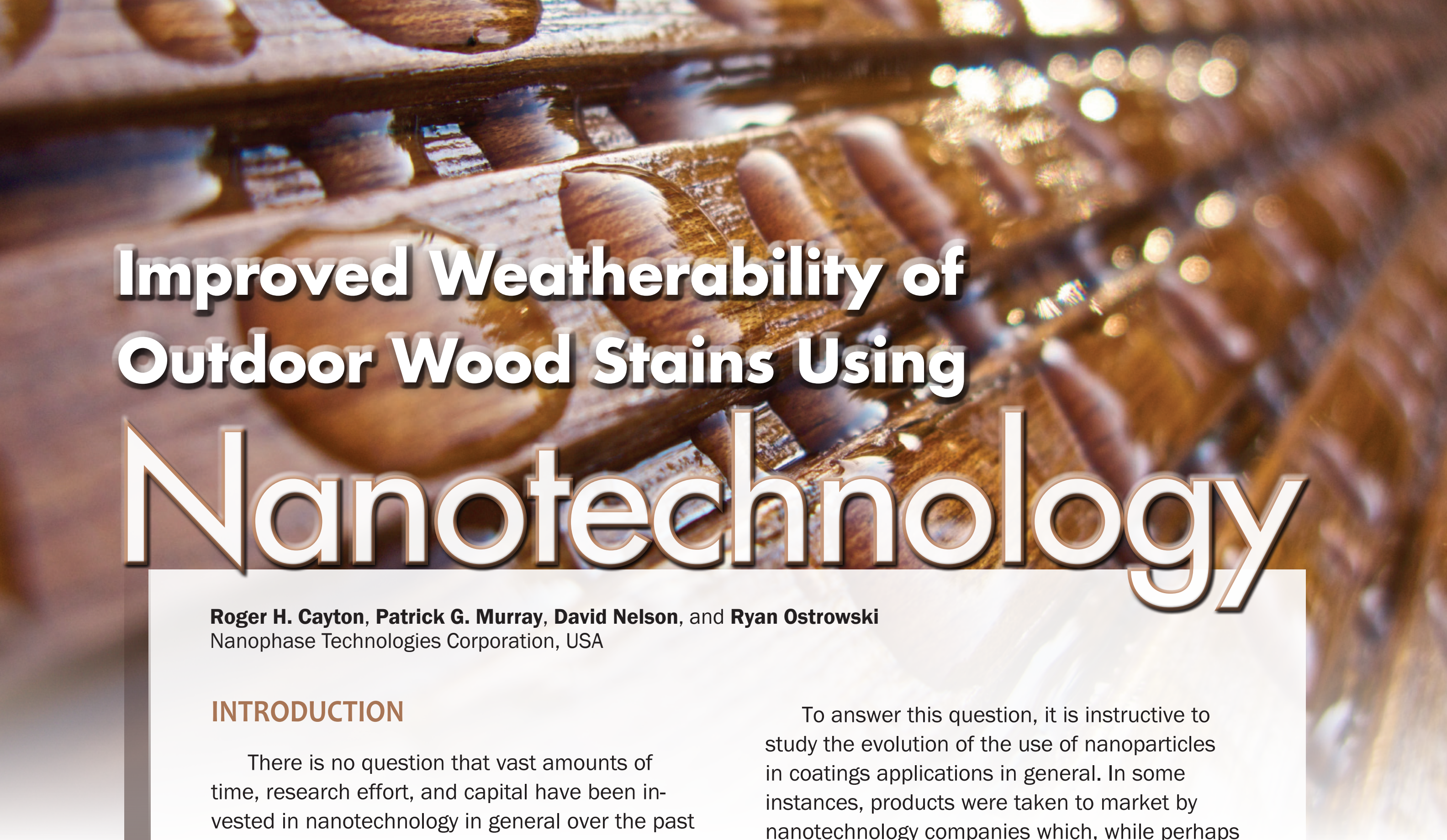

Improved Weatherability of Outdoor Wood Stains Using Nanotechnology

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INTRODUCTION

There is no question that vast amounts of time, research effort, and capital have been invested in nanotechnology in general over the past 20 years. The majority of this effort has been expended by government laboratories, academia, and industry, and a diversity of new nanomaterials, new routes to nano-versions of existing materials, and improved metrology and analytics have emerged as a consequence.

Indeed, hundreds of tons of nanoparticulate zinc oxide and titanium dioxide are sold into topical human sunscreens and daily wear cosmetics every year. That the benefits these materials (particularly zinc oxide) bring to sunscreens and cosmetics might be useful in other areas which require UV protection, such as coatings for outdoor wood, seems obvious. Despite this, commercial adoption of these materials for UV protection in exterior coatings has been less rapid than some forecasts had originally suggested it might be, despite well-known deficiencies in the existing organic UV absorbers. In fact, in many instances, innovative stain and finish developers investigated powders or newly developed dispersions of UV-absorbing metal oxides such as zinc oxide, titania, or ceria and discovered that the promised value (high performance, transparency) simply did not exist. It appears that assumptions about “drop in” performance in the end-use applications for nanoparticle containing additives may have simply been too optimistic. Why is this?

To answer this question, it is instructive to study the evolution of the use of nanoparticles in coatings applications in general. In some instances, products were taken to market by nanotechnology companies which, while perhaps expert in the synthesis and manipulation of nanomaterials, had little technical, marketing, or sales expertise in the coatings area. In other cases, large well-known chemical additives companies with a strong existing presence in coatings but little knowledge of nanomaterials attempted to invent or purchase nanotechnology and rapidly deploy it through existing channels to market. Neither of these approaches has been especially successful commercially; many small nanotechnology companies have simply disappeared, and at least one large specialty chemical company has exited the nanoadditives business altogether. The authors have identified what they believe to be the primary barriers to technical and commercial success in this application, and have assembled a model which has allowed several customers to realize commercial coatings products based on nanotechnology solutions. Although the model is general, examples will be selected from the area of outdoor wood protection, showing the performance improvements possible in both clear and semi-transparent systems.

DISCUSSION: A PRESCRIPTIVE THREE-STEP MODEL FOR SUCCESS

Dispersion of Particles: Owing to the very high surface areas, the stabilization of nanoparticulate metal oxides, such as zinc oxide, can be challenging and often requires both specialized chemistry and process technology. If the nanoparticles are

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not (or cannot be) dispersed down to their primary particle size, transparency in coatings will not be achieved except in the unlikely event that the refractive index of the coating exactly matches that of the particle. Because of this, most users of nano metal oxides, even those experienced with pigment dispersions, will fail to achieve the desired result when attempting to work with nanomaterials in powder form. Incomplete or improper dispersion will result in high viscosities, rapid gravimetric settling, and large particle agglomerates.

Compatibility of the Dispersion: In addition to having a stable dispersion of primary particles to begin with, it is also necessary that the dispersion be compatible with whatever coating formulation in which it is to be blended. Because of the wide variety of coating ingredients (resins, additives, biocides, etc.) and the number of variables typically present (resin type, solvency, pH, solids loadings, etc.), the effective use of nanoparticle additives is not a "one size fits all" situation, and companies that attempt to market nanoparticle dispersions with only a limited repertoire of formulation tools are likely to be unsuccessful. Failure to achieve compatibility with the target formulation will result in opacity and poor UV protection. It is primarily for this reason that nanomaterials additive companies, who simply "throw samples over the wall" without the means to ensure compatibility with customers' formulations will, in most instances, disappoint those customers.

Optimal Loading Level: Given that stable dispersion of primary particles are available and that compatibility with the target coatings formulation has been achieved, it is also necessary to empirically determine loading levels of the oxide using accelerated and outdoor weathering. The amount of zinc oxide (for example) which optimally satisfies requirements for performance, cost, and transparency simultaneously will differ from formulation to formulation and may well optimize at a different point for specific customers. If one of these parameters is not satisfied, it is unlikely that value will be realized over conventional UV-absorber technology.

In the remaining pages, the authors provide examples of each of these steps and demonstrate how the successful application of the three-step model can lead to step-change performance in outdoor wood coatings.

RESULTS

Clear, transparent, and semi-transparent exterior wood coatings require the incorporation of UV light absorbers and/or light stabilizers to protect both the coatings themselves, and the wood substrates, from degradation resulting from photochemical attack of ultraviolet radiation. A variety of organic chemistries have been used to absorb UV light and to scavenge radicals that may result from photochemical reactions. These organic systems are attractive for many clear and transparent coatings because the additives do not contribute color or haze to the system. However, because these additives are themselves subject to degradation from UV light exposure, once their concentration is reduced in the coating, rapid breakdown of the coating resins and weathering of the wood substrate ensues.

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Oxides of metals such as iron, zinc, titanium, and cerium also have UV absorption or scattering properties, and as such may also be used in coatings to protect them from UV radiation. These materials have the advantage that they do not decompose from photochemical attack, and therefore remain active for the lifetime of the coating. However, each of these oxides has other potential drawbacks including color (iron), photoactivity (titanium), and haze from light scattering. The contribution to haze arises from the inherent light scattering properties of the metal oxide particles embedded in the coating. The degree of light scattering varies according to the relationship shown in equation (1), where I_s = scattering intensity, N = number of particles, d^6 = particle size, and $\Delta\eta$ = the difference in refractive index between the particle and the coating matrix.

$$I_s = (N)(d^6)(\Delta\eta)^2 \qquad (1)$$

As can be seen in equation (1), the dominant contributor to light scattering is the size of the metal oxide particles. To minimize the contribution to haze, and to allow the use of metal oxides in clear wood coatings, it has been found that the particle size must be <100 nm. Furthermore, the scattering is mitigated as the difference in refractive index between that of the particle and that of the resin is minimized. Titanium dioxide has a relatively high refractive index (2.7) which results in substantial scattering in coatings, even for particles in the sub-100 nm range.

We have found that zinc oxide, when prepared with a primary particle size of <100 nm, provides the best combination of broad UV absorbance, no contribution to color, stability, and minimal impact on coating haze. The UV/visible spectrum of zinc

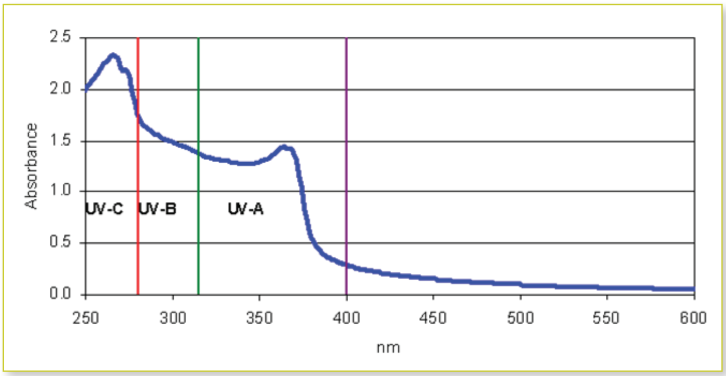

Figure 1—UV/Visible spectrum of zinc oxide with an average particle size of 20 nm dispersed at 0.013 wt% in mineral spirits.

Table 1—UV Absorbance and Haze of a Polyurethane Clearcoat (2 mil dry film thickness) Containing a Dispersion of 20 nm Zinc Oxide Particles

ZnO, wt% on Resin	% UV Absorbed at 375 nm	% Haze
1.0	81	1.4
2.0	96	2.1
3.0	99+	5.7

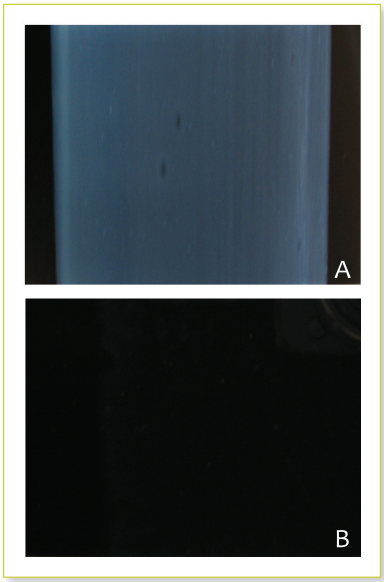

Figure 3—2.0 wt% zinc oxide nanoparticles in a water-based coating, 1 mil dry film thickness on glass over a black background. A is a flocculated formulation resulting in high film haze, B is a compatible formulation and very little film haze.

oxide with an average particle size of 20 nm is shown in *Figure* 1. The zinc oxide particles have a strong absorbance band at 375 nm (providing good coverage of the UV-A range) and exhibit relatively little scattering at wavelengths greater than 400 nm, producing but a minimal contribution to haze.

The UV absorbtive properties of zinc oxide were measured by varying the loading level of a 20 nm dispersion in a solvent-based polyurethane clearcoat. The results are shown in *Table* 1. As can be seen in *Table* 1, at a zinc oxide loading sufficient to absorb essentially all of the UV, the contribution to haze is acceptable for coatings on wood substrates.

A zinc oxide powder with a primary particle size of <100 nm is a necessary, but not sufficient, requirement to ensure high clarity in a coating formulation. It is also imperative that the zinc oxide powder be dispersed down to the primary particles, stabilized at that particle size to prevent any agglomeration, and made compatible with the coating formulation to prevent any potential for flocculation, viscosity change, reactivity, etc. that would adversely affect the performance properties. In the authors' experience, achieving dispersion stability and formulation compatibility is often the most challenging hurdle to overcome in the successful performance of zinc oxide nanoparticles in a coating application. Coating formulations cover a wide range of resin chemistries and contain numerous additives, requiring the compatibility package used for zinc oxide nanoparticle dispersions to be specific for the coating formulation being evaluated. The inability to compatibilize the zinc oxide dispersion with the coating formulation chemistry invariably leads to poor performance in the system. Examples of incompatibilities between nano zinc oxide dispersions and a representative coating formulation are shown in *Figure* 2. In these examples, water-based dispersions of zinc oxide nanoparticles featuring different stability packages were incorporated into a water-based coating formulation at 2 wt% zinc oxide (on total formulation). In picture A, one zinc oxide dispersion remains stable in the formulation whereas the zinc oxide in the second sample has flocculated and settled. In the picture B, one zinc oxide dispersion is stable in the formulation whereas the other has caused the formulation to crosslink and gel.

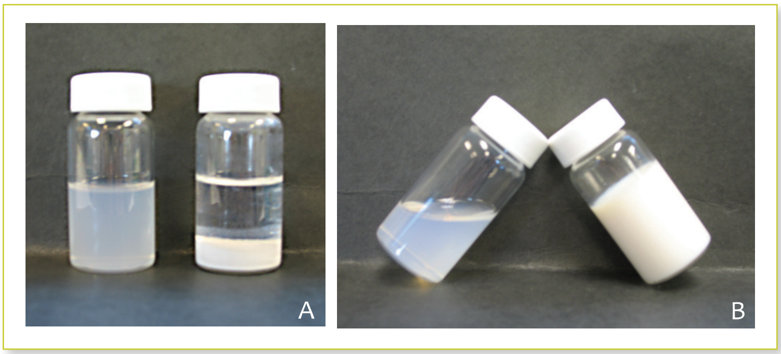

Figure 2—2.0 wt% zinc oxide nanoparticles in a water-based coating. A shows stable and flocculated formulations, B shows stable and gelled formulations.

Nano zinc oxide incompatibility in a coating can also be observed by measuring the haze in the coating. *Figure* 3 shows films of a water-based clearcoat applied over a glass surface, then photographed on top of a black background. The film in A was prepared with a coating in which the zinc oxide nanoparticle dispersion was incompatible, leading to flocculation of the particles into larger agglomerates that produce light scattering (haze). The film in B was prepared from the same coating, with the same zinc oxide concentration, but in this case with a zinc oxide nanoparticle dispersion that was fully compatible with the formulation. This film shows very little haze because the zinc oxide nanoparticles remain well dispersed.

The performance of zinc oxide nanoparticles in improving the weatherability and longevity of exterior wood coatings was evaluated using a combination of accelerated testing (QUV) and outdoor exposure in Florida. Two exterior coatings were evaluated: a water-based cedar-tone semi-transparent formulation and a water-based totally clear coating.

The protocol used in the accelerated QUV studies involved an eight-hour cycle with UV exposure for four hours at 50ºC (340 nm), followed by one minute of water spray, then four hours of condensation at 50ºC. In each study, a series of variables was evaluated including wood type, coating thickness, zinc oxide level, and zinc oxide stability packages. Delta E results for three panels from the QUV evaluation of the semi-transparent coating formulation are shown in *Figure* 4. The sample containing no UV absorber or light stabilizer (only the trans iron oxide pigment) darkened rapidly upon exposure to UV radiation. The addition of a traditional UVA/HALS combination to the stain reduced the rate of darkening, but it still exhibited considerable color change over the course of the exposure study. The sample containing 4 wt% zinc oxide on resin solids as the UV protection package showed the least color change over the accelerated exposure test. In this particular sample, the zinc oxide had an average particle size of 60 nm. Photographs of the three panels after 1280 hours of exposure in the QUV are shown in *Figure* 5.

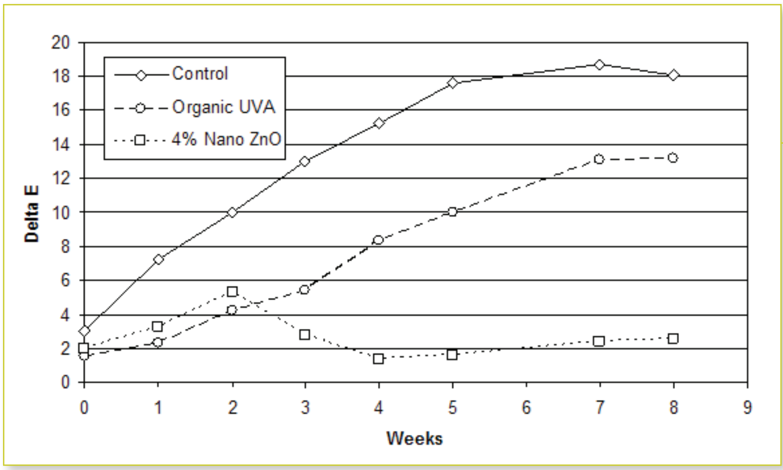

Figure 4—Delta E variation during accelerated weathering in a QUV of water-based semi-transparent stain on cedar panels.

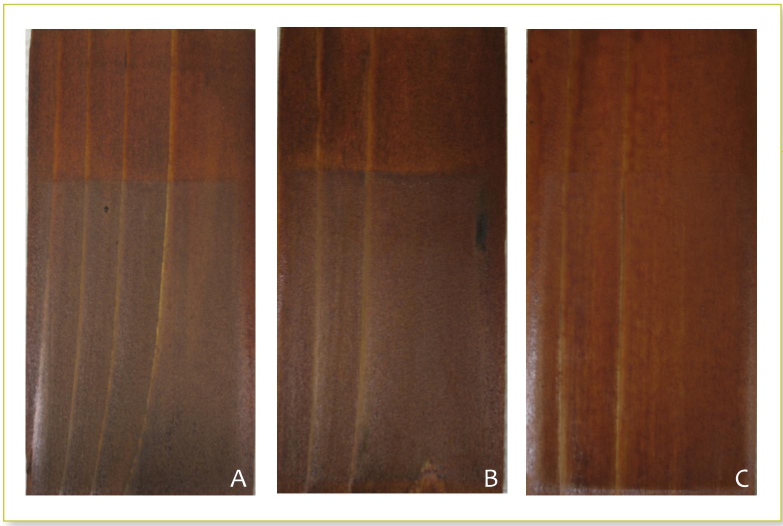

Figure 5—Cedar panels with semi-transparent stain after 1280 hr exposure in the QUV. A = stain with no UV absorber package; B = stain with organic UVA and HALS package; C = stain with 4 wt% 60 nm zinc oxide on resin solids.

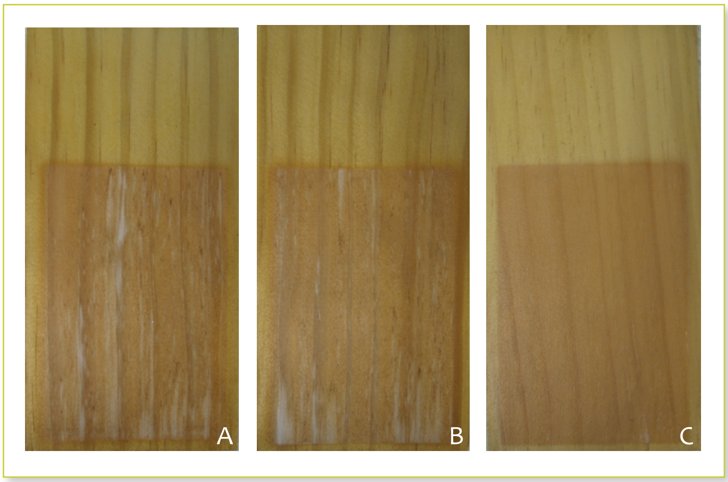

Figure 6—Pine panels with totally clear deck coating after 1600-hr exposure in the QUV. A = coating with no UV absorber package; B = coating with organic UVA and HALS package; C = coating with 4 wt% 60 nm stabilized zinc oxide on resin solids.

The pictures confirm the delta E measurements in the samples with either no UV package or a traditional UVA/HALS combination (A and B) underwent considerable darkening, whereas the sample with the zinc oxide nanoparticles (C) was virtually unchanged in appearance. These results indicate that when zinc oxide nanoparticles are properly dispersed and formulated to be fully compatible with the coating formulation, they can impart long-lasting UV protection while contributing essentially no haze or color to the stain.

A totally clear water-based exterior wood coating was also evaluated in an effort to improve its UV durability through the incorporation of nano zinc oxide particles. *Figure* 6 contains photographs of three wood samples from the matrix of formulations evaluated in a QUV study. After 1600 hr of exposure, the sample without any UV stabilizer package (A) experienced considerable bleaching, cracking, and coating degradation. The addition of a traditional UVA/HALS combination (sample B) improved the durability of the coating somewhat, but was not sufficient to prevent extensive damage. However, the incorporation of a stabilized dispersion of zinc oxide nanoparticles at 4 wt% on resin solids was particularly effective at providing long-term UV protection for the coating and the wood substrate (sample C).

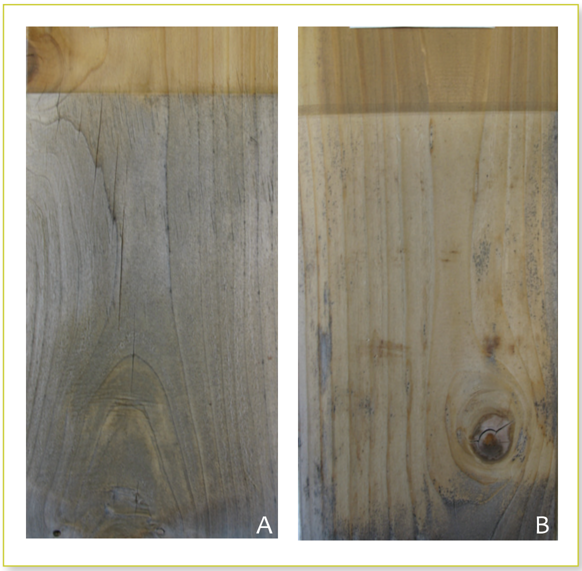

Figure 7—Cedar boards with totally clear deck coating after six months outdoor exposure in Florida. A = coating with organic UVA and HALS package; B = coating with 4 wt% 60 nm stabilized zinc oxide on resin solids.

The formulations containing a traditional UVA/HALS combination and the compatibilized zinc oxide nanoparticle package in the clear coating were also evaluated in an exterior exposure study in Florida. *Figure* 7 shows photographs of two cedar boards after six months' exposure. Sample A with the traditional UVA/HALS package underwent essentially complete degradation of the coating, causing the wood to gray. Sample B, featuring the stabilized nano zinc oxide package, showed only minimal coating loss and much better protection for the wood substrate. These data validate the utility of nano zinc oxide as a long-term UV absorber for exterior wood coatings, but only when properly dispersed and stabilized for compatibility in the coating formulation.

CONCLUSIONS

Nanometric metal oxide nanoparticles can enable completely transparent and semi-transparent outdoor wood finishes which have substantial longevity relative to those formulated with conventional UV absorber technology. Examples of commercial products in which this has been achieved are beginning to appear in the marketplace at the time of this publication.

Successful incorporation of nanometric metal oxides in coatings formulations requires adherence to a three-step process: (1) Beginning with a liquid dispersion of primary particles; (2) Ensuring compatibility of the nanoparticle dispersion with the target coating, and (3) Optimizing the nanoparticle loading versus performance attributes and cost through application testing. CT

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