The Impact of Nano-Materials on UV-Protective Coatings

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ABSTRACT

Nanophase Technologies Corporation (NTC) has an integrated family of commercially scaled technologies that are required elements of nanocomposite manufacturing. First, NTC manufactures commercial quantities of metal oxide nanoparticles by vapor phase plasma synthesis techniques. Second, NTC developed a variety of commercially scaled, proprietary technologies to modify the surface of nanocrystalline powders. Third, NTC developed commercially scaled processes to disperse the surface treated nanocrystalline powders into a range of fluids and organic resins used in the manufacture of nanocomposite coatings.

UV-protective, nanocomposite coatings are made by embedding nanocrystalline zinc oxide particles in a polymer matrix. In March of 2004, Nanophase formed an exclusive partnership with Altana, BYK-Chemie, to develop and market nanoparticles for use in coatings, inks, and plastics. During the past year, the partnership has developed three zinc oxide-based nanoparticle additives for use in UV-protective coatings. The performance properties of these products will be presented, along with an overview of new nanoparticle-based additives under development.

***Keywords*:** nanoparticle, zinc oxide, absorbance, coatings

INTRODUCTION

During the past several years, advances in nanomaterials have allowed them to be formulated into numerous applications. The majority of these applications sought performance improvements that were previously unobtainable with conventional technology. Commercial products containing nanomaterials are now found in a wide range of areas including coatings, personal care, electronics, catalysis, polishing, and consumer products.

In the area of coatings and thin films, nanotechnology is being used to enhance or impart important properties such as UV protection, scratch and mar resistance, anti-graffiti, self-cleaning, conductivity, and gas diffusion prevention. A common type of nanotechnology used in coatings involves the incorporation of a nanomaterial that has been designed with a specific chemical or surface property into the film matrix, resulting in a change in the bulk properties of the film itself. Often these changes in film properties can be achieved with relatively low dosages of the nanomaterials.

Degradation of polymer-based coatings from UV light exposure is a widespread problem in the coatings industry. This issue is generally addressed through the use of organic materials specifically designed to absorb UV radiation. Such UV attenuation products have the advantage of being soluble in the film matrix, and thereby impart no loss of clarity when used in transparent coatings. However, these organic UV absorbers also tend to migrate out of the coating, and undergo UV degradation themselves, limiting their effectiveness over time. Certain inorganic fillers such as zinc oxide and ceria are also effective at absorbing UV radiation and could therefore be used in coatings as UV attenuators. Inorganic materials have the advantage of not migrating out of a coating or degrading over time. However, they also have the major disadvantage in that they contribute significant haze to coatings, even at relatively low dosages.

Maintaining transparency in a coating containing inorganic filler particles is a challenge. Many variables affect the ultimate degree of transparency in a composite material, including film thickness, filler concentration, particle size, particle shape, extent of particle aggregation, homogeneity of the particle dispersion, and the difference in refractive index between the bulk coating and the filler particle.

The recent availability of nano-scale inorganic fillers makes possible the use of these materials in coatings in which clarity is an important property. Based on this, a series of inorganic oxides having a mean particle size less than 100 nm were evaluated for their suitability in providing UV protection to coatings, as well as their impact on optical transparency of the system.

NANOPARTICLE SYNTHESIS

A number of processes can be used to synthesize inorganic oxide nanoparticles. Some of the better-known processes include precipitation, flame pyrolysis, fuming, and plasma technology. Nanophase Technologies uses a plasma process to manufacture metal oxide nanoparticles via a bottoms-up method starting from metallic feed. This process allows production of nonporous crystalline metal oxides having primary particle sizes less than 100 nm at economically viable rates with essentially no byproducts or waste streams.

These plasma-derived materials are unique in that they are comprised of loosely aggregated particles in the solid state, which can be readily dispersed to their primary nanoparticles and stabilized from re-agglomeration. This attribute makes these particles particularly suited for use in coatings applications.

Nanophase Technologies utilizes two plasma processes for the manufacture of nanomaterials, Plasma Vapor Synthesis (PVS), and NanoArc Synthesis (NAS). Both processes utilize a plasma to vaporize the feed and a quench to synthesize the oxide and control particle size and surface chemistry.

Nanophase Technologies manufactures zinc oxide by both the PVS and NAS processes, resulting in three different grades of the powder. These zinc oxide grades differ primarily in average particle size, with the PVS process used to produce material with average particle sizes of 60 nm and 40 nm, and the NAS process used to produce a 20 nm product. Cerium dioxide is manufactured exclusively by the NAS process, with average particle sizes ranging from 20 nm to 40 nm. A TEM image of the 60 nm PVS zinc oxide product is shown in Figure 1.

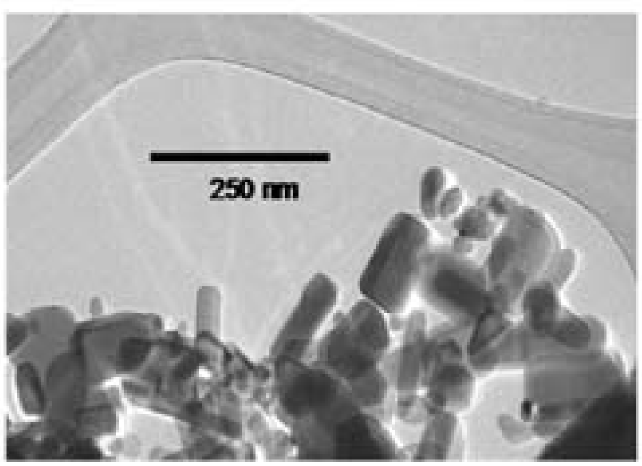

Figure 1: TEM image of 60 nm PVS zinc oxide.

The zinc oxide crystals are rectangular in shape with an aspect ratio averaging about 3:1. The 40 nm and 20 nm zinc oxide crystals feature a similar shape with the aspect ratio approaching 1:1 as the average particle size decreases. A TEM image of 40 nm NAS cerium dioxide is shown in Figure 2. The cerium dioxide primary particles feature a faceted cubic morphology. A common feature of the particles produced by the plasma processes is that they are not fused to neighboring particles, enabling them to be readily dispersed to their primary particles without aggregation.

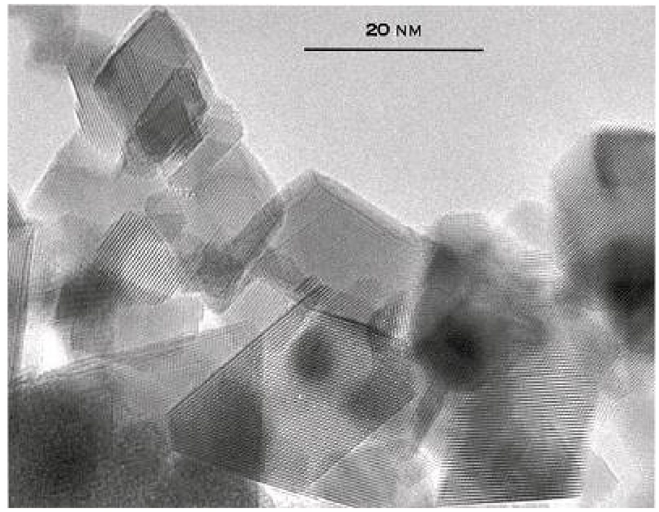

Figure 2: TEM image of 40 nm NAS cerium dioxide.

PARTICLE DISPERSION

Both zinc oxide and cerium dioxide can be dispersed directly in protic solvents; however, such dispersions tend to flocculate upon incorporation into coating formulations if the particles are not properly surface treated. Nanophase Technologies has developed specific surface treatments for both zinc oxide and cerium dioxide that allows the particles to remain well-dispersed in water or organic solvents, and prevents flocculation of the particles upon incorporation in either water-based emulsion coatings or solvent-based coating formulations. In addition, by employing size truncation processes, the mean particle size of these nanoparticle dispersions can be further tuned to meet the property requirements of the coating application.

The optical transparency of nanoparticle dispersions depends on the mean particle size of the nanomaterials and the refractive index of the oxide. Figure 3 shows the effect of particle size and refractive index for zinc oxide and cerium dioxide on the transparency of water-based dispersions. As can be seen, as the refractive index decreases going from cerium dioxide to zinc oxide, the transparency at a given particle size increases significantly. This property is critical with respect to the use of a UV absorbent nanoparticle in a transparent coating application.

SPECTROSCOPY

The performance of a metal oxide nanoparticle with respect to UV protection of transparent coatings depends on two critical factors: (1) The efficiency of absorption across the ultraviolet region, and (2) the degree of light scattering in the

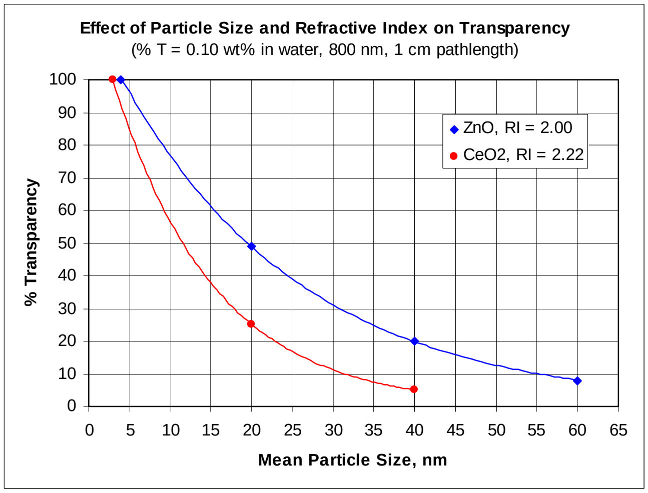

Figure 3. Impact of particle size on the % transparency of 0.10 wt% dispersions of zinc oxide and cerium dioxide measured at 800 nm with a 1 cm pathlength.

visible region. The goal is the design of a nanomaterial with has high UV attenuation and, is either sufficiently small in size or low in refractive index, to minimize scattering of visible light. Figure 4 shows the UV and visible spectra of zinc oxide at three different mean particle sizes (20, 40, and 60 nm) along with the spectra of 20 nm cerium dioxide particles. The spectra were measured at 0.005-wt%.

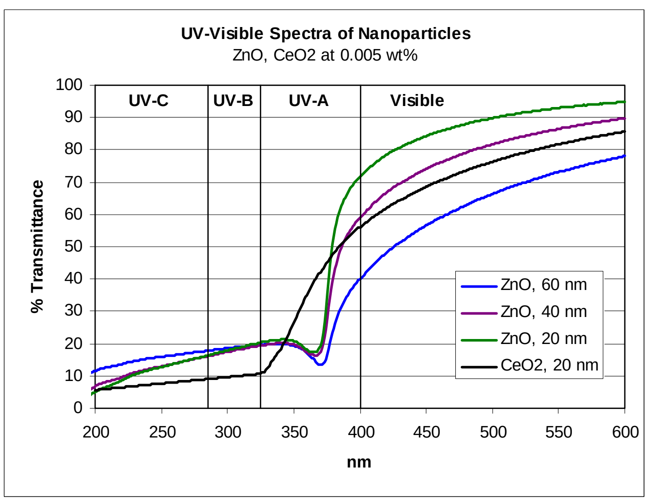

Figure 4: UV-Visible spectra of zinc oxide (0.005 wt%) and cerium dioxide (0.005 wt%) in water measured with a 1 cm pathlength.

The effect of particle size on performance is clear by comparing the spectra of the three grades of zinc oxide. As the mean particle size decreases from 60 nm to 20 nm, UV absorbance does not change but light scattering in the visible region is significantly diminished. The effect of refractive index is also apparent by comparing the spectra of zinc oxide with cerium dioxide, at equivalent particle size. In the visible region, 20 nm cerium dioxide results in greater light scattering than 20 nm zinc oxide. Based on these results, zinc oxide was chosen as the nanoparticle to pursue for UV protection in coatings.

A series of zinc oxide dispersions of different mean particle sizes were prepared in water using a surface treatment designed to provide compatibility of the zinc oxide with water-based emulsion coatings. These dispersions were post-added to a commercial water-based high-gloss polyurethane coating, and films prepared with a zinc oxide loading equivalent to that used for the UV spectra in Figure 4 (i.e. 0.005 wt% ZnO in a 1 cm pathlength equals 1 wt% ZnO in a 2 mil coating). After curing the % haze increase in the coating due to zinc oxide particles was measured and the results are shown in Figure 5.

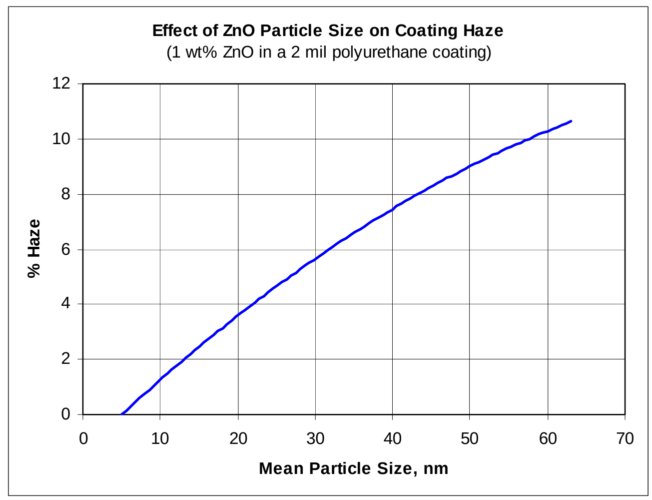

Figure 5. Effect of % transparency of zinc oxide dispersions on the haze imparted to a 2 mil water-based high-gloss polyurethane coating at 1 wt% loading.