The Impact of Nano-Materials on Coating Technologies

Roger H. Cayton*, Thomas Sawitowski**

* Nanophase Technologies Corporation
   Romeoville, IL 60446
** BYK-Chemie
   Wesel, Germany 46483

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. Examples of such applications containing nanomaterials that have been commercialized include scratch/abrasion resistant transparent coatings, sunscreen lotions to provide visible transparent UV protection, polishing slurries to provide pristine surfaces for optics, and environmental catalysts to reduce pollution.

The quest for improved scratch/abrasion resistant coatings is an on going project for many coating formulators. Thousands of scratch resistant coating applications are present in our everyday lives. Examples of these applications include coatings for wood floors, safety glasses, electronic displays, automotive finishes, and polycarbonate panels. Improving the mar, scratch and/or abrasion in these transparent coating applications is a major challenge, particularly with regard to not affecting the other performance attributes of the coating.

Incorporation of inorganic fillers into coatings to improve mechanical properties is well known. Drawbacks associated with this approach can include loss of transparency, reduced coating flexibility, loss of impact resistance, increase in coating viscosity, and appearance defects. To overcome these defects a filler material should impart improved scratch resistance without causing the aforementioned detriments. Nanomaterials, due to their small size and particle morphology, have the potential to overcome many of these detriments.

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.

Silica particles, colloidal or fumed, and clays are among the most widely studied inorganic fillers for improving the scratch/abrasion resistance of transparent coatings. These fillers are attractive from the standpoint that they do not adversely impact the transparency of coatings due to the fact that the refractive indices of these particles (fumed silica = 1.46, bentonite clay = 1.54) closely match those of most resin-based coatings. The drawback to silica-based fillers is that high concentrations of the particles are generally required to show a significant improvement in the scratch/abrasion resistance of a coating, and these high loadings can lead to various other formulation problems associated with viscosity, thixotropy, and film formation.

The use of alumina particles in transparent coatings is much more limited even though alumina is significantly harder than silica-based materials, and as a scratch and abrasion-resistant filler, higher performance at lower loadings is often observed. For alumina particle sizes greater than 100nm, the high refractive index (1.72) results in significant light scattering and a hazy appearance in most clear coatings. Currently, only coatings with a high refractive index, such as the melamine-formaldehyde resins used in laminates, can utilize micron-size alumina particles to gain scratch resistance and still maintain transparency.

NANOPARTICLE PRODUCTION

In order to utilize alumina as scratch-resistant filler in transparent coatings, the particle size must be sufficiently small to overcome its refractive index mismatch. Nanophase Technologies uses plasma processes to produce 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.

Nanophase Technologies produces three grades of aluminum oxide using the plasma process, two of which are commercial and one that is under development. All grades feature a mixture of \( \gamma \) and \( \delta \) crystal phases and are spherical in shape, but the grades differ in terms of primary particle size. NanoTek\textsuperscript{TM} alumina has a surface area of 35 m\textsuperscript{2}/g corresponding to a mean particle size of 48 nm, whereas NanoDur\textsuperscript{TM} alumina has a surface area of 45 m\textsuperscript{2}/g (37 nm), and the developmental NanoArc\textsuperscript{TM} alumina features a surface area ranging from 80 – 100 m\textsuperscript{2}/g (17 – 21 nm). A TEM image of NanoDur\textsuperscript{TM} alumina is shown in Figure 1. As is evident in the TEM, the primary particles are spherical.
and are not “necked” or fused together, rather they are loosely aggregated in the bulk powder. Figure 2 provides a comparison of the particle size distributions among the three plasma alumina grades.

Nanophase Technologies has developed a variety of commercially scaled, proprietary technologies to modify the surface of nanocrystalline powders as well as processes to disperse the surface treated powders into a range of fluids and organic resins used in the manufacture of nanocomposite coatings.

Nanophase has formed an exclusive partnership with Altana, BYK-Chemie, to develop and market nanoparticles for use in coatings, inks, and plastics. To date the partnership has commercialized two aluminum oxide-based nanoparticle additives for use in UV-curable coatings to reduce scratch and mar.

Figure 3 depicts the improvement in gloss retention of a UV-curable coating after the incorporation of the nano-alumina product, NANOBHK 3600. The improvement in scratch resistance is evident in the images shown in Figure 4 of the control coating and a coating containing the alumina nanoparticles.

Figure 3: Gloss retention following scrub test of a control coating, and coatings containing alumina nanoparticles, with and without a slip additive.

**NANOPARTICLE COATINGS**

Nanocomposite coatings are made by embedding nanocrystalline metal oxide particles in a polymer matrix. The benefits accrued by incorporating nanoparticles into a polymer matrix become economically driven when several advantageous properties are obtained simultaneously, compared with conventional materials, i.e., transparency with increased abrasion resistance and toughness.

Figure 1: TEM image of NanoDur™ aluminum oxide.

Figure 2: Particle size distributions of aluminum oxide produced by a plasma process.

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Figure 1: TEM image of NanoDur™ aluminum oxide.

Figure 2: Particle size distributions of aluminum oxide produced by a plasma process.
Figure 4A. Microscopic image of control coating following 500 scrub cycles.

Figure 4B. Microscopic image of a coating containing 2 wt% alumina nanoparticles and 0.1 wt% slip additive following 500 scrub cycles.