Nanocrystalline Alumina in Transparent UV Coatings

Roger H. Cayton
Nanophase Technologies Corporation, www.nanophase.com

Abstract

Nanocrystalline alumina has been dispersed as primary particles into reactive acrylate monomers to form stable, low viscosity, concentrated dispersions. These dispersions have been used to incorporate nano-alumina into a variety of UV coating formulations. At low alumina loading levels (< 5 wt%), transparent films have been produced that exhibit superior scratch resistant properties. Data will be presented showing significant improvement in steel wool scratch and mar resistance of UV coatings containing the nano-alumina particles.

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 a goal 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 have the potential to overcome many of these detriments because of their inherent small size and particle morphology.

Maintaining transparency in a coating containing inorganic filler particles is a challenge. Four properties dictate the degree of transparency in a composite material: Film thickness, filler concentration, filler particle size, and the difference in refractive index between the bulk coating and the filler particle. Mie theory describes the relationship between particle size, concentration, refractive index, and light scattering for spherical particles dispersed in a bulk phase as shown in equation 1.

$$I_s \; \alpha \; (Nd^6/\lambda^4) \; \{[(n_p/n_c)^2-1]/[(n_p/n_c)^2+2]\}(I_i) \qquad (1)$$

I_s = Intensity of scattered light
N = Number of particles
d = Particle diameter

λ = Wavelength
n_p = Particle refractive index
n_c = Coating refractive index
I_i = Intensity of incident light

As is evident in equation 1, the magnitude of light scattering in a particle/coating composite is strongly influenced by the particle size. In addition, the greater the difference between the refractive indices of the particle and that of the bulk coating, the greater the degree of light scattering.

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 high refractive index coatings, such as the melamine-formaldehyde resins used in laminate production, can use sub-micron alumina for scratch resistance and maintain transparency.

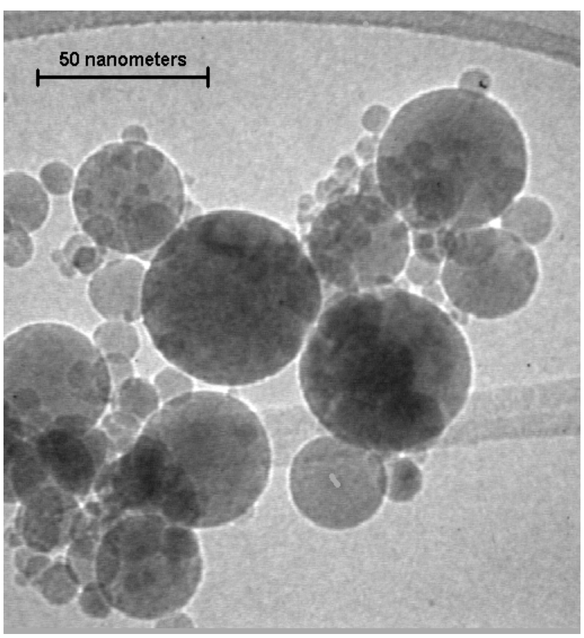

Figure 1: TEM image of NanoTek™ aluminum oxide.

Nanoparticle Production

To use alumina as scratch-resistant filler in transparent coatings, the particle size must be sufficiently small to overcome its refractive index mismatch. Nanophase Technologies Corporation (NTC) has developed the Plasma Vapor Synthesis (PVS) process that is capable of producing 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.

NTC produces two grades of aluminum oxide using the PVS process: NanoTek™ and NanoDur™ alumina. Both grades feature a mixture of γ and δ crystal phases and are spherical in shape, but the grades differ in terms of primary particle size. NanoTek™ alumina has a surface area of 35 m^2/g corresponding to a mean particle size of 48 nm, whereas NanoDur™ alumina has a surface area of 45 m^2/g with a mean particle size of 37 nm. A TEM image of NanoTek™ alumina is shown in Figure 1.

Nanoparticle Dispersion

For nanoparticles to be of use in transparent coatings, it is critical that the aggregates present in the powder form be dispersible to their primary particle size in the coating formulation in order to avoid rapid settling and excessive light scattering. In addition, it is critical that the dispersed primary particles avoid re-aggregation during the coating curing process.

NTC has developed a proprietary particle dispersion/stabilization process that involves specific surface treatments designed to yield nanoparticles that are compatible with a variety of different coating formulations. For example, stable dispersions of metal oxide nanoparticles can be prepared in solvents such as water, alcohols, polar and nonpolar hydrocarbons, plasticizers, and even directly in acrylate monomers with the appropriate surface treatment process. These surface treatments allow solids levels of up to 60 wt% to be dispersed and yet maintain a sufficiently low viscosity for ease of blending.

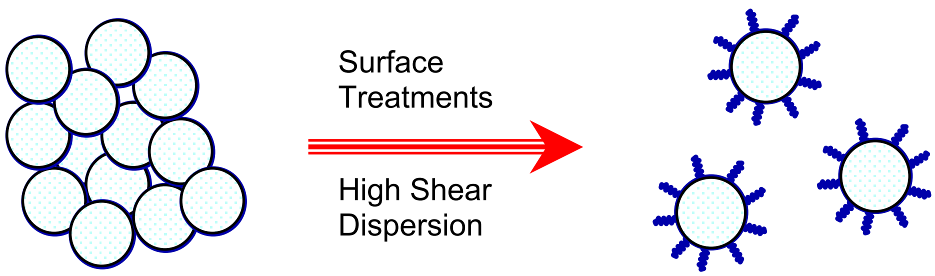

Figure 2: Dispersion of weakly agglomerated nano-powders to discrete particles.

The use of highly concentrated, completely deaggregated, nanoparticle dispersions allows incorporation of the nanoparticles into a coating formulation without substantial dilution of the formulation with the dispersion liquid. This feature is particularly important in 100% solids coating formulations wherein the nanoparticle is dispersed in one of the reactive monomers.

Alumina Incorporation in UV-Curable Coatings

NanoDur™ alumina powder was dispersed into 1,6-hexanedioldiacrylate (HDDA) at 35 wt%, and this concentrated dispersion was used to formulate UV-curable coatings containing dispersed alumina nanoparticles. The base coating formulation used for the alumina study was a urethane acrylate with the composition shown in Table 1.

Table 1. UV-Curable Urethane Coating Formulation.

Component	Wt%
Urethane oligomer (SR-368)	30
1,6-hexanedioldiacrylate (SR-238)	30
Propoxylated(6)trimethylolpropanetriacrylate (CD-501)	30
Ethoxylated(4)pentaerythritoltetraacrylate (SR-494)	10

Alumina nanoparticles were incorporated into the formulation at loadings up to 5 wt% by substituting the HDDA component with the appropriate amount of the 35 wt% alumina/HDDA dispersion, and blending by high speed mixing. Coatings were prepared on glass slides at 1 and 2 mil thickness and irradiated at 0.6 J/pass using a combination of benzophenone and Irgacure 651 as curing agents. Light scattering resulting from the alumina nanoparticles was measured by film haze as shown in Figure 3. The small size of the alumina particles limits the extent of light scattering, and at loading levels up to 5 wt%, only 2% haze is generated at 1 mil coating thickness.

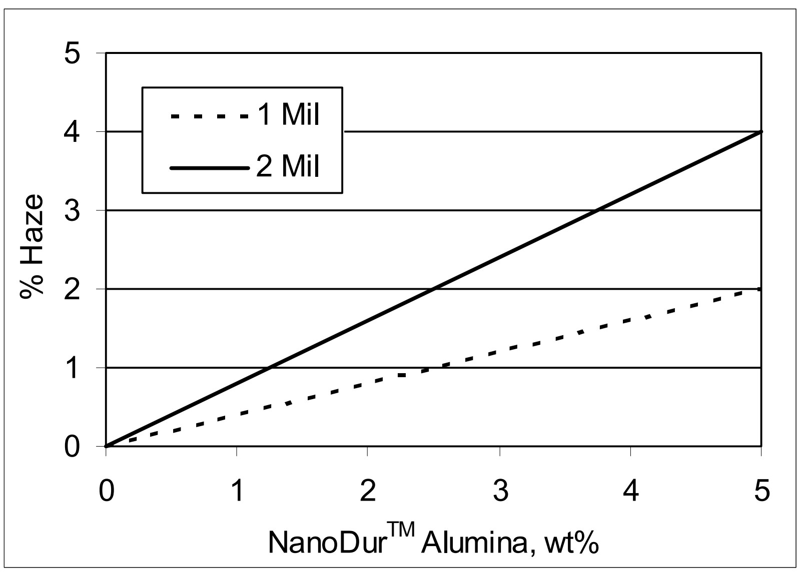

Figure 3: % Haze of 1 and 2 mil urethane coatings containing NanoDur alumina nanoparticles.

Scratch-Resistance of UV-Curable Coatings Containing Alumina Nanoparticles

The performance of alumina nanoparticles with respect to scratch resistance was also evaluated using the UV-curable formulation in Table 1. Again, the alumina/HDDA dispersion was used as the method of incorporation into the formulation, and loading levels up to 5 wt% were studied. The performance of the alumina nanoparticles was compared to that of a commercial silica nanoparticle product incorporated into the UV-curable formulation in an analogous manner.

The oxide-containing coatings were subjected to a scratch test involving 200 double rubs with a 0000 grade steel wool pad and 40 g/cm^2 pressure, and the level of scratching was quantified by measuring the increase in % haze due to the scratches. In each case, the scratch resistance of the oxide-containing coating was normalized to that of the neat coating by the ratio of the haze generated from steel wool scratching as indicated in equation 2. If the scratch resistance of the particle-containing coating is improved relative to the neat coating, less haze is generated by the scratch test and the Relative Scratch Resistance will be greater than 1.0. The results of scratch tests conducted on the alumina and silica nanoparticle coatings are shown in Figure 4.

$$\text{Relative Scratch Resistance} = \%\text{Haze}_{(\text{Neat Coating})}/\%\text{Haze}_{(\text{Particle Coating})} \quad (2)$$

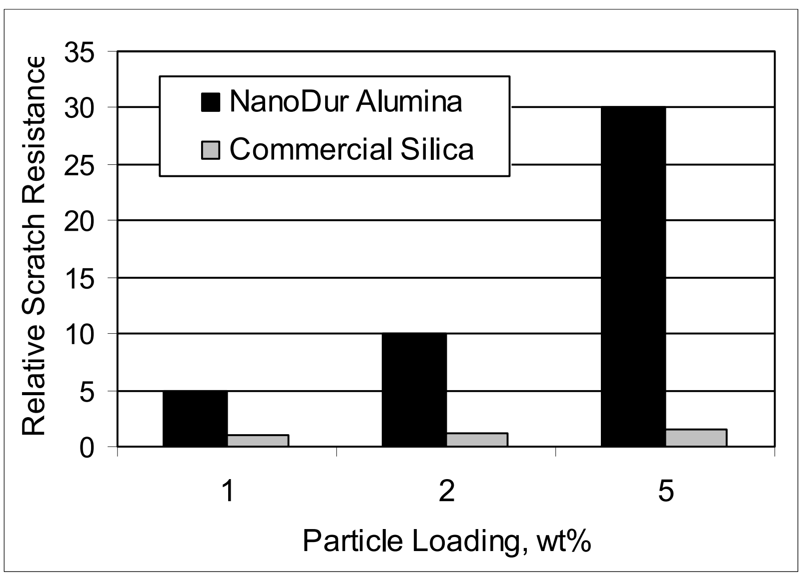

Figure 4: Comparison of the scratch-resistance performance of NanoDur™ alumina particles and commercial silica particles in a UV-curable urethane coating.

As is evident in Figure 4, the improvement in scratch resistance resulting from relatively low levels of alumina incorporation in the urethane coating is quite dramatic. By comparison, the softer silica particles are much less effective at preventing scratches.

Summary

Due to the past unavailability of aluminum oxide that was less than 100 nanometers in average size, improvements in scratch resistant coatings were limited. As demonstrated in the above examples the use of nanoparticles in coating formulations can significantly improve scratch resistance. These improvements can be used in clear top coats, ink over print varnishes and pigmented finishes. The commercial availability of nanoparticles will allow coating formulators to obtain new properties that were unachievable in the past, not only in scratch resistance but many other physical performance attributes.