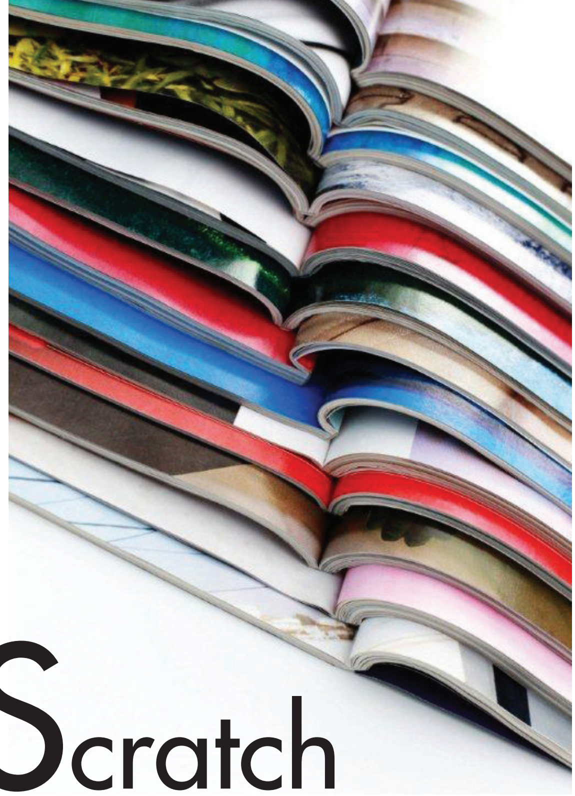

Scratch Resistant UV-Cured Coatings Containing Nano- and Sub-Micron Aluminum Oxide Additives

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Nanotechnology is a rapidly growing field and new nano-scale products continue to be commercialized in a wide range of markets, including personal care, precision polishing, electronics, energy, and textiles, to name but a few examples. One industry which has rapidly embraced nanotechnology as a source of innovation and product differentiation is coatings. The wide-ranging interest in nanotechnology by the coatings field is evidenced by the explosive growth in patent applications involving nanotechnology and various types of coatings—up by 25% in 2010 year-over-year, and up 100% over 2005. The increase in patent filings in this area is anticipatory of the commercial adoption of nanomaterials; according to the Global Industry Analysts, Inc. report—*Nanocoatings: A Global Market Report,* San Jose, CA, April 12, 2010—the global market for nano-enabled coatings is expected to be $6.5 billion by 2013 and to reach $11.7 billion by 2015.

UV-cured coatings are typically high value, high performance coatings which are gaining market share for a variety of reasons, including that they can be applied in solvent-free form and that they allow high throughput owing to their rapid cure rates. UV-cured coatings can be applied to a broad diversity of substrates including those used in flooring, furniture, plastics, electronics, graphic arts, packaging, and can coatings. These UV-cured coatings are often used as clear topcoats to protect substrates from degradation resulting from wear and abrasion.

Additives are commonly formulated into UV-cured coatings to improve their resistance to scratching and abrasion. Typical scratch-resistant additives include waxes and silicones, as well as inorganic particles such as silica and alumina. Each of the additives has its own advantages and drawbacks. For example, waxes and silicones concentrate at the coating surface

Photos (left, middle) courtesy of Nanophase.

where they can offer a degree of wear protection at relatively low addition levels while not contributing to coating haze, but their effectiveness can diminish over time as the additives wear away. Inorganic particles such as silica and alumina, on the other hand, increase the coating hardness and offer a greater and more permanent level of improvement in scratch and abrasion resistance. Silica has a relatively low refractive index, similar to that of most UV-cured acrylate coatings, and therefore does not contribute appreciably to opacity. Both fumed and colloidal silicas have been used as wear resistant additives. The use of fumed silica is limited in that it tends to increase the formulation viscosity, whereas colloidal silica is difficult to deliver in a solvent-free format to UV-cured formulations. Alumina, on the other hand, is significantly harder than silica and often provides the larger improvement in scratch resistance. However, because alumina has a slightly higher refractive index than the coating, these particles are capable of scattering light and contributing haze to the coating.

Recently, alumina products have become available in nano- and sub-micron particle sizes, which significantly reduce the degree of light scattering when these materials are well dispersed into a coating formulation. The equation for Mie scattering is shown below, where I_s = the intensity of the scattered light, N = the number of particles, d^6 = the diameter of the particle, and $\Delta\eta$ = the difference in refractive index between the particle and the matrix. In this article, the effects of both alumina particle size and loading level were evaluated with a view towards improving the scratch resistance of a UV-cured clear coating. It will be demonstrated that well dispersed, well stabilized, and highly compatible nano- and sub-micron sized alumina particles can be optimized for maximum performance in such systems.

$$I_s \approx Nd^6(\Delta\eta)^2$$

PARTICLE PROPERTIES

Nano-scale alumina particles can be prepared in commercial quantities using plasma arc methods. Alumina prepared in this way forms γ-phase alumina particles with a spherical morphology, as shown in the TEM image in *Figure* 1. The alumina particles synthesized in this fashion do not form durable agglomerates, and this lack of secondary structure allows them to be readily dispersed down to their primary particle size in subsequent processing steps. Since the particles are formed in a gas phase process (and not precipitated or milled), there are no by-products or solvents that need to be removed prior to dispersion. The process also yields particle surfaces that are very pure chemically.

ALUMINUM OXIDE DISPERSIONS

To realize the benefits of the small particle size of nano- and sub-micron scale alumina, complete dispersion of the particles to their primary particle size is required, and maintenance of this condition to prevent reagglomeration, flocculation, or settling becomes imperative in the application. This can be accomplished by applying a surface treatment to the particles that is specifically designed for the particular solvent and/or coating formulation into which the material is to be incorporated. For applications in UV-cured coatings, the aluminum oxide particles need to be surface-treated to allow dispersion directly in acrylate monomers such as tripropyleneglycol diacrylate (TPGDA). *Figure* 2 shows photos of aluminum oxide dispersions in TPGDA where two different surface treatments were used. The sample on the left has completely flocculated and settled whereas the sample on the right remains well dispersed. Choosing the correct surface treatment is critical for maintaining the nano-scale attributes of the particles and for ensuring compatibility between the particles and the fully formulated coating. Moreover, proper design of the surface treatment can allow the dispersion products themselves to be made at high alumina concentrations to minimize the amount of monomer carried into the coating formulation (if it is not already a component).

For the purpose of this work, stable dispersions of alumina were prepared over a range of

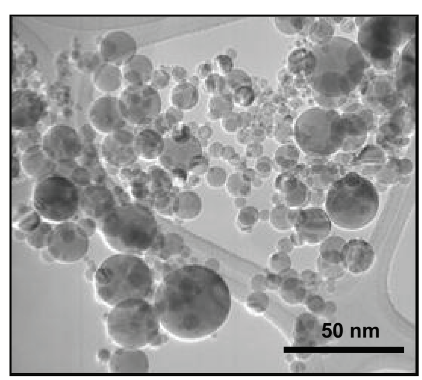

Figure 1—TEM image of alumina particles prepared via plasma arc synthesis with an average particle size of 20 nm.

Figure 2—Aluminum oxide dispersions in TPGDA with different surface treatments resulting in either poor dispersion and flocculation of the particles (left), or a stable and compatible dispersion of nano-particles (right).

Table 1—Nano- and Sub-micron Aluminum Oxide Dispersions in TPGDA

Product	Particle Size (nm)	Monomer	Al_2O_3, wt%
A	20	TPGDA	30
B	40	TPGDA	30
C	150	TPGDA	45
D	250	TPGDA	55
E	800	TPGDA	55

particles sizes, as shown in *Table* 1. In each case, the surface treatment was optimized for the particular particle size in order to ensure stability and compatibility with UV-cured coatings, as well as to maximize the alumina weight loading in the concentrated dispersion.

LIGHT SCATTERING

The effect of particle size on the light scattering of sub-micron particles in an organic matrix has been studied in some detail. At a constant weight loading, the degree of light scattering observed is a result of both the number of particles and the particle size. Larger particles exhibit greater scattering, but at a given concentration, there are also fewer particles present in the matrix. These two offsetting phenomena result in a scattering maximum for alumina particles at approximately 200 nm, as displayed in *Figure* 3. At dimensions below 200 nm, the particle cross-section dominates scattering and reduction of the particle size has a dramatic effect on the efficiency of light scattering. For particles larger than 200 nm, the number of particles in the matrix dominates light scattering and, as the particle size increases, the number of particles decreases (for a constant loading level), which lowers the degree of scattering. In addition, scattering and observed haze (versus measured haze) is also quite dependent on the substrate upon which the nanocomposite coating is applied. For a coating over a transparent substrate, the contribution to haze from alumina particles is much more apparent when compared with the same coating applied to an opaque substrate (transmitted haze versus reflected haze). For aluminas with an average particle size of greater than 100 nm, use in a clearcoat, even at loading levels of less than 2 wt%, would yield unacceptably high haze. However, on an opaque substrate, alumina with an average particle size between 100 nm and 1 µm has little impact on the haze or gloss of the coating, provided that the loading level is kept below 2 wt% and the film thickness is 1 mil or less.

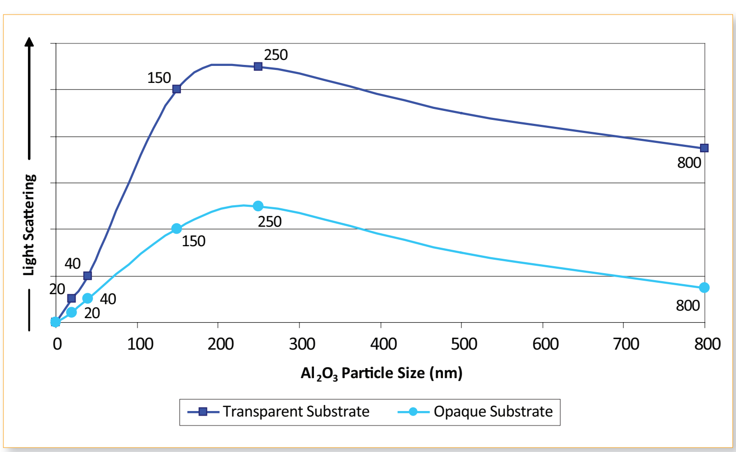

Figure 3—Scattering profile of nano- and sub-micron alumina on transparent and opaque substrates.

RESULTS

Effect of Aluminum Oxide Particle Size on Film Clarity and Scratch Resistance

The clarity and performance of coatings containing nano- and sub-micron aluminum oxide particles were evaluated in a commercial urethane acrylate clearcoat. Alumina with average particle sizes of 20, 40, 150, 250, and 800 nm were dispersed and stabilized at high weight loadings in TPGDA monomer (see *Table* 1). These dispersions were then added to the coating formulation at 0.5, 1.0, and 2.0 wt% alumina on total resin solids. The alumina-filled coating formulations were laid down on black acrylonitrile butadiene styrene (ABS) test panels at 0.3 mil thickness and cured under a high energy UV lamp (1.8 J/cm^2).

For the case of clear coatings applied to opaque substrates, reflected gloss is one method to determine the impact that alumina-based additives may have on the visual appearance of the coating. The 20° gloss measurements are shown in *Figure* 4 for the neat coating and for the alumina-filled coatings wherein the particle size and loading level were varied.

As anticipated, the larger particle size aluminas resulted in a greater drop in initial gloss. The 20 and 40 nm particles have little to no impact on the coating gloss while the 150 nm particle contributes only a slight gloss drop (<2%). The 250 nm and 800 nm particles have a greater impact on gloss reduction, particularly apparent at the higher loading levels. The significant gloss reduction at 2.0 wt% from the 800 nm particle may be the result of the impact on the micro-topography of the coating resulting from a relatively large particle in a thin coating layer (0.3 mil). This effect would not be expected in coatings >0.8 mil.

The scratch resistance of the coatings was measured using a steel wool scratch test. For this

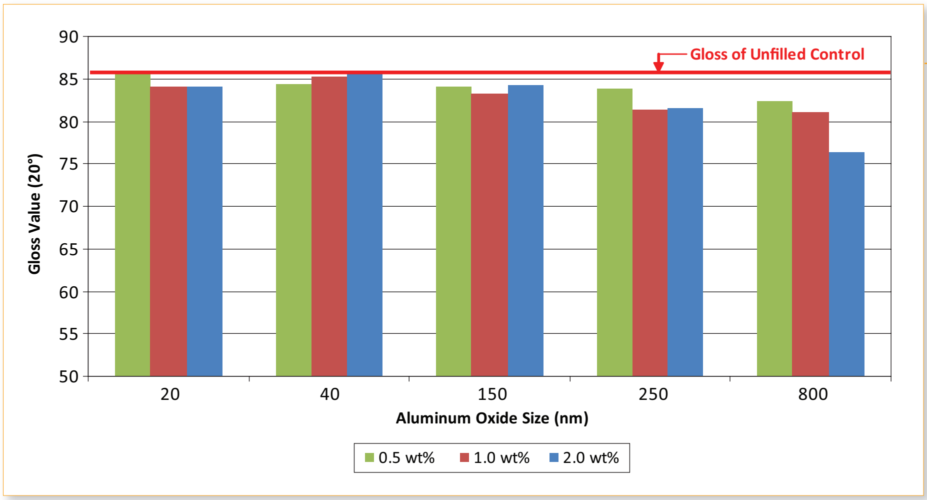

Figure 4—Effect of particle size and loading level on 20° gloss.

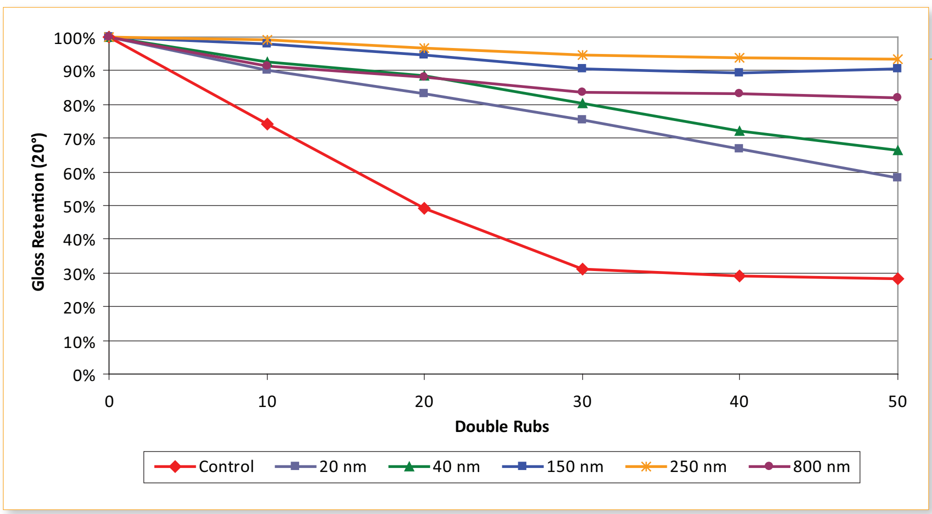

Figure 5—Gloss retention following steel wool scratching of a commercial UV-cured coating containing various particle size alumina at 1 wt%, and an unfilled control, on black ABS plaques.

test, the coatings were subjected to 50 double rubs with a #0000 steel wool pad at 8 g/cm^2 pressure and the resulting reduction in gloss was measured every 10 cycles (1 cycle = 1 double rub). The scratch resistance of each sample was determined by measuring the level of gloss reduction that resulted from the steel wool scratch test. A plot of gloss retention over the 50 scratch cycles is shown in *Figure* 5 for each of the alumina particle sizes at 1 wt% loading, as well as for the unfilled control.

All the alumina-filled coatings exhibited a significant improvement in scratch resistance compared to the unfilled control; however, there were clear performance differences among the various particle sizes. As a group, the sub-micron alumina additives (150, 250, 800 nm particle sizes) provided greater scratch resistance than the nano-alumina additives (20 and 40 nm particles), as evidenced by the greater gloss retention of such coatings following the scratch test. Coatings containing the 20 and 40 nm additives experienced gloss retentions of 60–70% after 50 cycles, compared to 30% gloss retention for the unprotected control coating. By comparison, the 800 nm particle size displayed greater than 80% gloss retention, and the 150 and 250 nm particles provided >90% gloss retention, after the same degree of scratching.

In addition, the visual appearance of the surface scratches varied with particle size. The unfilled control panel yielded a significant number of very deep, narrow scratches and their onset was apparent by the end of the first 10 double rubs. By contrast, the scratches observed on coatings containing the 20 and 40 nm particles were shallower and less numerous and thereby had less impact on the 20° gloss reduction. There were essentially no scratches on the coatings containing 150 and 250 nm particles; rather, only a slight marring of the surface finish which was barely perceptible at the 1 and 2 wt% loadings. The 800 nm alumina-filled coating had a similar surface appearance as the 150 and 250 nm coatings following the steel wool test, but with a slightly higher number of visible scratches.

A photo comparing the post-scratched panels of the unfilled control and a sample containing the

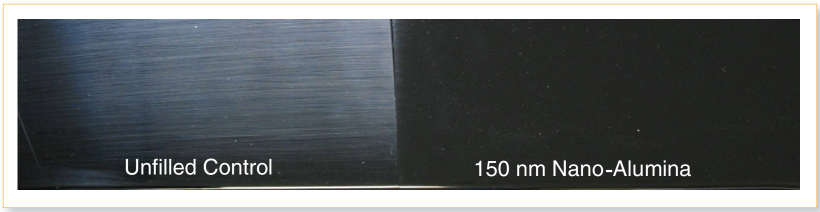

Figure 6—Unfilled control (left) and 150 nm nano-alumina (right) after 50 cycles with #0000 steel wool.

150 nm particles is shown in *Figure* 6. The panels were fastened together for the scratch test to ensure that both were subjected to the same steel wool pad and same conditions. The ability of the 150 nm alumina particles to enable this particular coating system to resist surface scratching was dramatic when compared to the unfilled coating.

The effect of alumina loading level on the scratch resistance was also evaluated by preparing coatings with each of the five particles sizes at three concentrations: 0.5, 1.0, and 2.0 wt%. The gloss retention results are shown in *Figure* 7.

As previously described, the unfilled control has only 30% gloss retention at the completion of the scratch test. For each alumina particle size, there is a significant improvement in the scratch resistance relative to the unfilled control sample with as little as 0.5 wt% loading. This effect appears to be unique to alumina particles as other conventional particulate scratch resistant additives such as silica typically call for much higher loading levels. Not unexpectedly, the larger (sub-micron) group of products outperforms the smaller (sub-100 nm) materials at each of the loading levels. Interestingly, the performance of the 40 nm particle continued to improve with loading levels such that at higher concentration its behavior was consistent with that of the sub-micron group.

The results shown above illustrate the importance of optimizing each coating application individually based on the resin type, clarity requirements, film thickness, and wear resistance needs of the system. The effect that alumina particle size exerts upon each of these parameters varies, and therefore the optimal solution (particle size and loading) must often be determined empirically for each system.

Performance of Conventional Additives vs. Sub-micron Alumina for Scratch Resistance

In addition to the obvious practical utility of the aforementioned observations, a comparison of the performance of small particle size alumina with more conventional scratch resistance additives is also of interest. Therefore, the performance of various common silicone, wax, and silica scratch-resistant additives was compared to the results achieved using the nano- and sub-micron aluminum oxide products. These additives were added to the same UV-cured urethane acrylate clear coating used for the experiments with alumina, and then evaluated using the same reciprocating steel wool test method. Commercially available versions of the non-alumina additives were used to facilitate homogeneous incorporation into the formulations. The loading levels employed were those recommended by the manufacturers and are listed in *Table* 2.

The gloss retention of the coatings containing the silicone, wax, and silica additives following the steel wool scratch test is shown in *Figure* 8, along with the performance of the 150 nm alumina product at 0.5 wt% for comparison. The silicone,

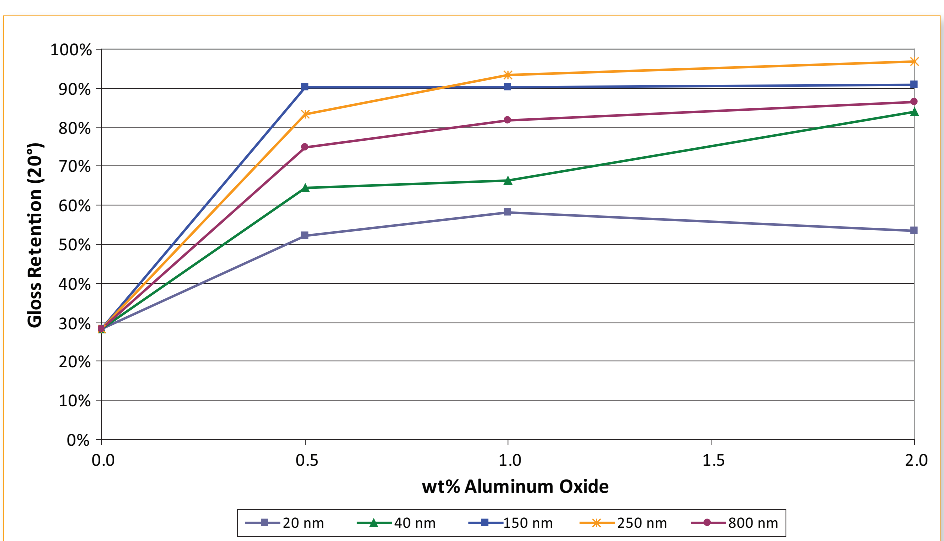

Figure 7—Gloss retention of a commercial UV-cured coating containing various particle size aluminas at 0.5, 1.0, and 2.0 wt% (after 50 test cycles).

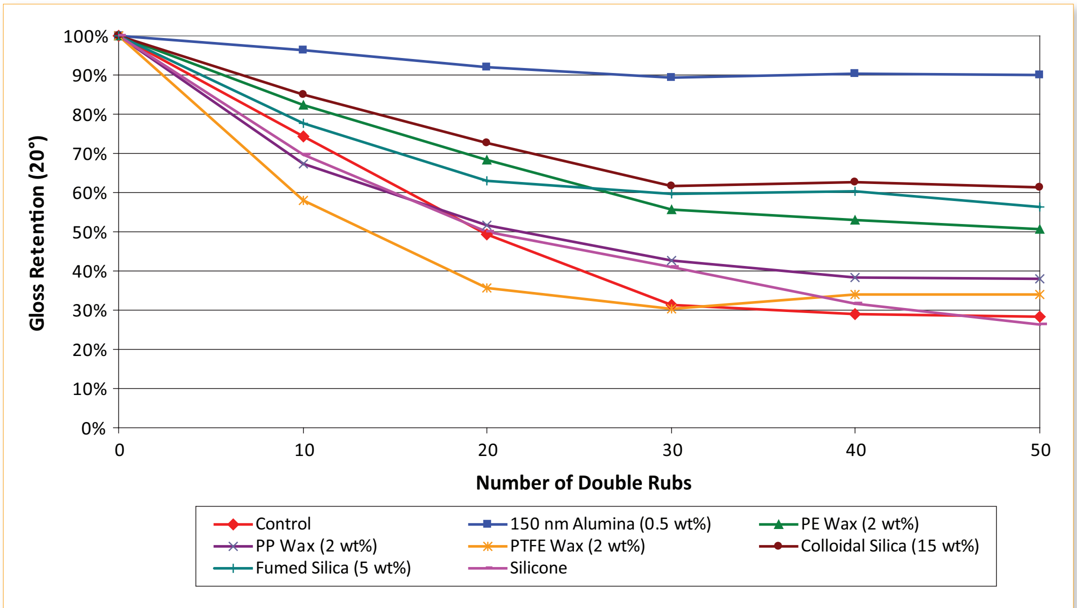

Figure 8—Gloss retention following steel wool scratching of a UV-cured coating containing silicone, wax, silica, 150 nm alumina, and an unfilled control on black ABS plaques.

PP, and PTFE waxes offered very little improvement over the unfilled coating in this system. The PE wax and the two silica products performed somewhat better with gloss retentions between 50 and 60% after 50 cycles. This level of enhancement is similar to that achieved with the 20 and 40 nm alumina particles, although for the silica products, much higher loadings were required to achieve this performance. None of the wax or silica products yielded scratch protection comparable to that which was achieved using the 150 nm alumina product at a usage level of 0.5 wt% or higher.

Table 2—Scratch Resistant Additives and Levels Used (actives basis)

Additive Type	Loading Level, wt%
Silicone	0.1
Polypropylene wax (PP)	2.0
Polyethylene wax (PE)	2.0
Polytetrafluoroethylene (PTFE)	2.0
Fumed silica	5.0
Colloidal silica	15.0

CONCLUSIONS

Various nano- and sub-micron particle size aluminas were dispersed in TPGDA monomer and incorporated into a urethane acrylate UV-cured coating to determine the impact of particle size and loading level on the clarity of the coating and the ability of these particles to improve scratch resistance over unfilled controls. The performance of the alumina products was also compared to that of conventional silica, wax, and silicone additives.

- All of the alumina dispersion products were effective in enhancing the scratch resistance of the coating, and, in most cases, as little as 0.5 wt% loading was required for substantial performance improvement.
- The 150, 250, and 800 nm particles were, as a group, more effective than the 20 and 40 nm particles, but this improvement came at the expense of a slight decrease in the initial gloss of the coating.
- The sub-micron alumina particles resulted in gloss retentions of >90% following a reciprocating steel wool scratch test, whereas the gloss retention in the unfilled coating dropped to 30% after the same treatment.
- None of the silicone, wax, or silica additives tested provided gloss retentions in excess of 60%, despite being utilized at higher loading levels relative to the alumina series.
- Selecting the optimum alumina particle size and loading level for a given coating system depends on the resin type, clarity requirements, film thickness, and type of wear resistance expected in application. Unlike conventional additives for scratch resistance, however, for effective use of nano- and sub-micron alumina particles, particle size and loading level are variables whose effect must often be elucidated empirically for each distinct UV-cured coating formulation for maximum benefit. CT

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