TiO_2 Scattering Optimization and Not-In-Kind Opacity Alternatives

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With titanium dioxide (TiO_2) in short supply, many coatings manufacturers are re-evaluating their paint formulas to optimize TiO_2 effectiveness and/or incorporate not-in-kind alternative options for opacity. Applying optical theory to practical paint making leads us to the following conclusions, which will be explored more thoroughly in this article:

1. *Incorporating air voids into a coating, either by formulating above critical pigment volume concentration or by using hollow sphere opaque polymers, can provide good dry film optical performance at reduced TiO_2 loadings, but the use of air voids is constrained by other coating performance parameters.*
2. *Replacing large extender particles with small extender particles can improve TiO_2 light scattering efficiency, allowing some reduction in TiO_2 loadings, but this is not likely a result of the smaller extenders preferentially "spacing" the TiO_2 particles.*
3. *Targeted spacing technologies, like the use of highly coated TiO_2 products, can improve TiO_2 efficiency, allowing a reduction in TiO_2 pigment loading in appropriate coating formulations.*

BACKGROUND

The primary property that TiO_2 contributes to a coating is hiding power. Hiding power describes the ability of a coating to obscure a background of contrasting color. Hiding occurs when the penetration of incident light through a film is reduced, either by light scattering or by light absorption. TiO_2 contributes to hiding power by light scattering. Colored materials, whether they are colored impurities in the coating or intentionally added colored pigments, contribute to hiding power by light absorption.

The ability of TiO_2 to scatter light in a coating depends on particle size; the difference in refractive index of the TiO_2 particle and its surroundings; and the proximity of the TiO_2 particles to one another.

For the purposes of this article, we will assume that commercial TiO_2 grades produced for coatings are more or less optimally sized and this attribute will not be discussed further.

The light scattering potential of a TiO_2 particle is proportional to the square of the difference between the refractive index of the TiO_2 and the average refractive index of the medium in which the TiO_2 particle resides.[1] While the refractive index of the TiO_2 particle remains constant (rutile TiO_2 R.I. = 2.73), the average refractive index of its surroundings changes depending on the

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composition of the coating. Typical paint resins and filler particles (e.g., clay and calcium carbonate) have similar refractive indices (R.I. = 1.5–1.6). Fillers provide little light scattering and hiding power, and changing their relative composition does not significantly impact the average refractive index of the coating. However, changing the volume concentration of TiO_2 in a coating affects the average refractive index of the coating, influencing the difference in refractive index between the TiO_2 particle and its surroundings, and thereby impacting the light scattering efficiency of the TiO_2.

This effect is illustrated in *Figure* 1, which represents the simple case of TiO_2 dispersed in resin. The x-axis shows the result of increasing the TiO_2 volume concentration on the average refractive index of the coating. For example, increasing the TiO_2 volume concentration from 10% to 30% increases the average refractive index of the coating from 1.71 to 1.93. The solid blue line in the figure shows the diminishment of TiO_2 light scattering efficiency as the TiO_2 content and average refractive index of the coating increase as predicted by Mie Theory.[2] This is often referred to as the "TiO_2 crowding effect."

The light scattering or hiding power contribution of TiO_2 in a coating is the product of the TiO_2 scattering efficiency at a specific average coating refractive index (or TiO_2 volume concentration in this simple example) times the TiO_2 volume concentration. This total light scattering contribution is represented by the dashed red line in *Figure* 1. At low TiO_2 concentrations, say less than 15% TiO_2 by volume, the coating light scattering/hiding power increases almost linearly with TiO_2 concentration. As TiO_2 concentrations increase further, the incremental increase in coating light scattering/hiding power per increment of TiO_2 volume concentration diminishes. Eventually the point is reached where additional increases in TiO_2 content actually reduce the total coating light scattering/hiding power. Obviously, this is a very inefficient space to formulate coatings.

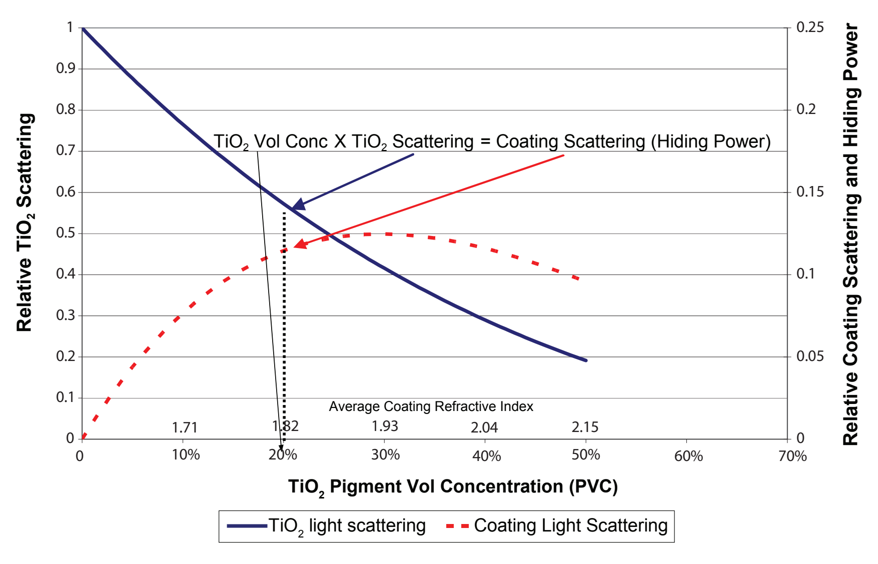

Figure 1—Light scattering vs. TiO_2 concentration in resin.

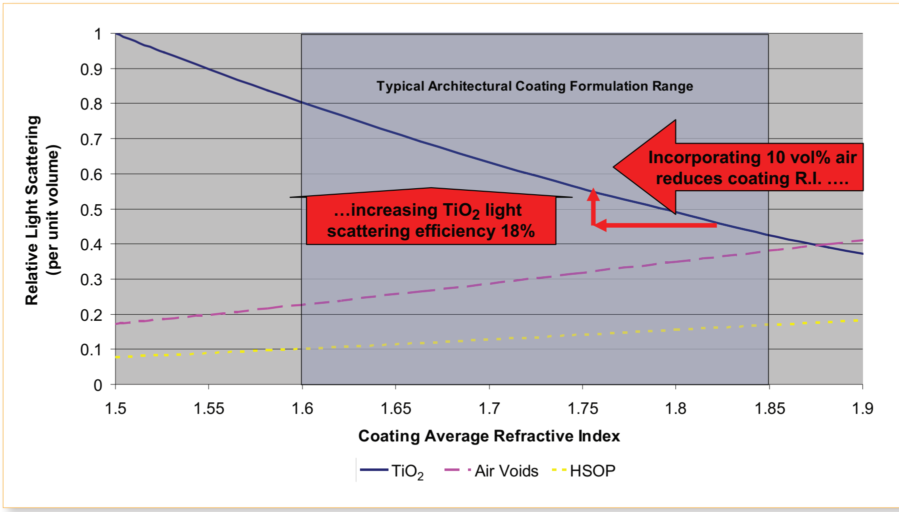

Figure 2—Coating opacifier light scattering efficiency.

FORMULATING ABOVE CRITICAL PIGMENT VOLUME CONCENTRATION

The critical pigment volume concentration (CPVC) is the formulation point at which there is just enough resin available to fill in the spaces between pigment particles, whether the pigment particles are TiO_2, clays, calcium carbonates, or other extenders. When the pigment volume concentration is increased beyond the CPVC, there is insufficient free resin to fill in the space between the pigment particles, and air voids are created within the coating matrix. Increasing the coating PVC further increases the volume of air voids incorporated.

Air has a refractive index of 1.0, so incorporating air into a coating film has a significant impact on coating light scattering and hiding power. The first effect is that the presence of air in the dried coating film reduces the average refractive index of the coating. This heightens the difference in the refractive index between the TiO_2 particles and their surroundings, increasing the light scattering efficiency of the TiO_2. Because it is more efficient, the TiO_2 content can be reduced while maintaining equal hiding power of the dried film.

An example of this effect is represented in *Figure* 2. Incorporating 10% air void volume into a coating with 20 vol% TiO_2 reduces the average refractive index of the coating from 1.82 to 1.76. As a result, the light scattering efficiency increases by 18%, meaning that the TiO_2 concentration can be reduced by 18% while maintaining equal coating light scattering and hiding power.

If the air voids in the dried coating are the right size, they provide additional value in terms of light scattering and hiding power, and additional opportunity for TiO_2 reduction. Because the air voids have a refractive index of 1.0 and are in a coating matrix with an average refractive index of 1.6 to 1.7, the voids can act as light scattering "particles" in their own right.[3] The optimum air void size for light scattering is about 0.23 microns, about the same optimum size of TiO_2 particles. The selection of extender pigments in coatings formulated above CPVC can have a significant impact on the size of air voids formed in the dried coating, and therefore on the light scattering efficiency of these voids. The relative light scattering efficiency of optimally sized air voids is represented by the pink dashed line in *Figure* 2.

The limitations of taking advantage of air voids by formulating above the CPVC are well known.[4] The primary drawback is that the air voids cannot exist in the wet coating and therefore provide no light scattering when the coating is wet, i.e., a loss of "wet hiding". When the coating dries, the air voids that provide so much benefit in terms of light scattering diminish the structural integrity of the coating and increase porosity. This generally has a negative impact on such important coating properties as washability, scrub resistance, stain resistance, and durability.

HOLLOW SPHERE OPAQUE POLYMERS

Air voids can also be incorporated into coatings formulated below CPVC by using hollow sphere opaque polymers (HSOPs).[5] HSOPs are nonfilm-forming synthetic pigments that are supplied as emulsions and are added to the wet paints. In the wet state, each HSOP particle consists of a spherical styrene/acrylic bead with a water-filled void in its center. As the paints dry, the water diffuses from the center of the beads and is replaced with air, resulting in encapsulated air voids dispersed uniformly throughout the dry paint film. The mechanism is irreversible.

Incorporating hollow sphere pigments into a coating has the same effect on TiO_2 light scattering efficiency as creating air voids by formulating above CPVC. The encapsulated air voids created by the HSOPs increase TiO_2 light scattering efficiency by reducing the average refractive index of the paint film, and increasing the difference in refractive index between the TiO_2 particle and its surroundings.

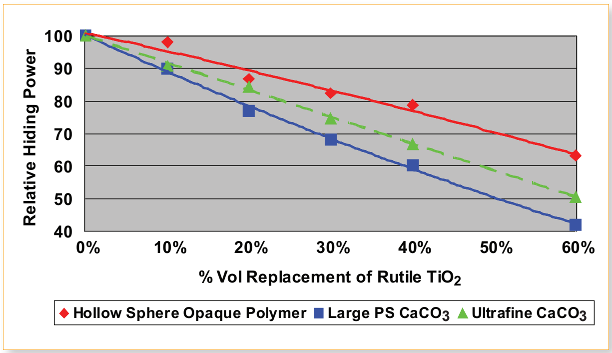

Figure 3—TiO_2 replacement efficiency in semigloss paint.

The encapsulated air void sizes provided by HSOPs are nearly optimized for light scattering and therefore are also light scattering sites in their own right. The relative light scattering efficiency of HSOPs compared to TiO_2 is shown by the yellow dotted line in *Figure* 2. The HSOP light scattering efficiency is lower than the air void light scattering efficiency because we need to account for the volume of the HSOP shell. It is assumed that the shell comprises 56% of the volume of the HSOP, so the HSOP light scattering efficiency is 44% that of a pure air void.

The HSOP light scattering efficiency rises with increasing average coating refractive index (i.e., increasing TiO_2 content), because the difference in refractive index between the entrapped air void and its surroundings increases. Within the normal range of average coating refractive index for paints containing both TiO_2 and HSOP, TiO_2 is three to five times more efficient in light scattering than HSOPs on an equal volume basis. HSOPs have the highest light scattering efficiency, and provide the highest potential for TiO_2 reduction in coatings where the TiO_2 content (and therefore the average refractive index of the coating) is high.

An example of the efficacy of HSOPs as a TiO_2 replacement in a high TiO_2 content semigloss paint is shown in *Figure* 3. The figure shows the effect on coating hiding power resulting from one-for-one volume replacements of rutile TiO_2 with commercially available HSOP, a large particle size $CaCO_3$, and an "ultrafine" $CaCO_3$. Though clearly more effective in maintaining hiding power than replacing TiO_2 with $CaCO_3$, HSOPs are not a one-for-one replacement for TiO_2. Based on the relative light scattering efficiencies shown in *Figure* 2, HSOP would need to replace TiO_2 at a 3–5 to 1 volume ratio to maintain equal dry hiding. In fact, one supplier of HSOPs recommends replacement at precisely these ratios. Insights into the differences between the hiding power efficiency of the two $CaCO_3$ products are discussed in the next section.

Again, there are limitations to formulating with HSOPs. First, since the HSOPs are filled with water when the coating is wet, they are essentially transparent, and therefore do not contribute to wet hiding. Wet hiding power is almost totally dependent on TiO_2 content, so any replacement of TiO_2 with HSOPs will diminish the wet hiding power of the coating. HSOPs also have a high specific volume when dry, and present a substantial impact on the coating PVC.

Care needs to be taken when formulating with HSOPs to manage coating PVC relative to CPVC to maintain scrub resistance. HSOPs can also diminish the burnish resistance of coatings. Care also needs to be taken to manage gloss and sheen of the coatings through the

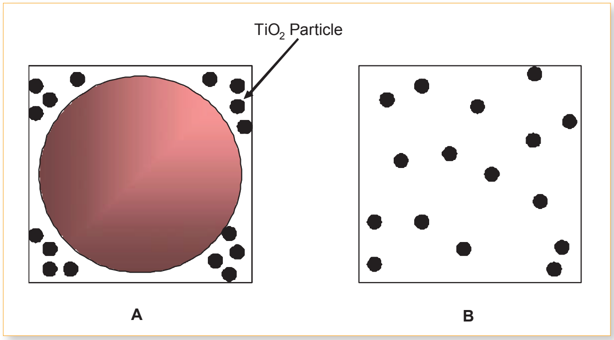

Figure 4—Crowding effect of extender particles. (a) Pigment scattering with large extender particles; (b) pigment scattering with no extender.

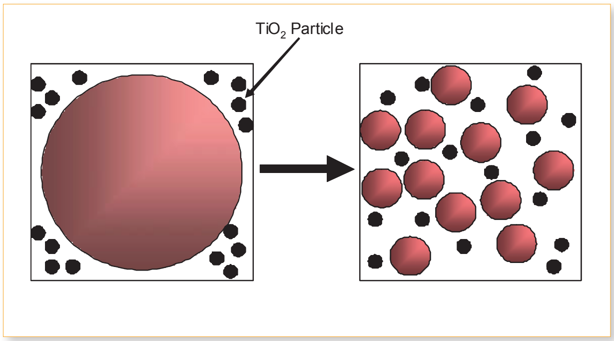

Figure 5—Crowding effect diminished by replacing large extender particles with smaller extender particles.

use of extenders. In short, the use of HSOPs to reduce TiO_2 content of a coating needs to be balanced with managing other important coating properties.

MINERAL FILLERS

We turn our attention to mineral extender particles (also known as fillers). These materials are ubiquitous in the coatings industry.[4] Their value proposition is that they are, on a volume basis, less expensive than resin, and so offer cost savings as a partial resin replacement. In addition, some fillers provide functionality to paints, such as decreasing sheen levels in dry paints or altering the rheology of wet paints. Mineral extenders are typically white powders in air, but, as noted previously, the slight differences in refractive indices between organic resins and most of these extender particles result in their providing negligible light scattering in the dry paint. However, they can influence the white opacity of paint by altering the scattering efficiency of the TiO_2 pigment. In some cases, the influence is positive; in other cases, it is negative.

Among the negative influences of extenders on TiO_2 scattering is the crowding effect associated with extender particles that are large compared to TiO_2 particles.[6] For most extenders, particles are significantly larger than TiO_2 pigment particles, and, when present in a paint film, they restrict the location of pigment particles to the interstitial regions between the large particles (*Figure* 4a). This crowds the TiO_2 particles, which decreases the scattering efficiency of the pigment.[7] By comparison, in the absence of large particles (*Figure* 4b), the available volume for pigment particles is significantly larger, and the pigment particles crowd one another much less. The detrimental effect of large particles on opacity can be quite significant, decreasing the pigment scattering efficiency in some cases by 10% or more.

The decrease in opacity due to crowding from large particle extenders can be partially remediated by replacing the large particles with an equal volume of small particle size extenders (that is, extender size ranges on the same order as the quarter micron TiO_2 particles). In the presence of small extender particles, the space available to the TiO_2 particles is much less restricted, and, as shown in *Figure* 5, the pigment particles can approach a random distribution within the paint film.

By this mechanism, small extender particles return the TiO_2 scattering efficiency to nearly that which would be seen if no resin had been replaced by extender particles, but not beyond the level seen in the absence of an extender. The effect of replacing large extenders with small extenders can be seen by referring back to *Figure* 3. The hiding power of coating films of identical coating PVC but with increasing one-for-one volume replacement of TiO_2 by different sized extender particles and by hollow sphere opaque polymers are shown. Clearly, replacing large extenders with smaller extenders improves hiding, but even small extenders are not as effective as HSOP, which, in turn, is not as effective as TiO_2 at equal volume concentrations.

In addition to the boost in TiO_2 efficiency seen when large extender particles are replaced with small ones, there is a second mechanism often cited by which extender particles smaller than TiO_2 particles can increase opacity. In this mechanism, nano-sized extender particles randomly get in between TiO_2 particles, increasing their spacing and thus enhancing their light scattering abilities.

Intuitively, this seems to be reasonable, and this mechanism is, in fact, widely accepted within the coatings industry.[8-17] However, there is some controversy about it,[18-20] with researchers on both sides of the argument citing experimental evidence that support their respective positions. A theoretical resolution of this debate has been reported wherein a Monte-Carlo simulation approach was used to determine the extent to which TiO_2 particle spacing is improved by the presence of small (nano-sized) extender particles.[21] The results of this study refute the proposition that such randomly placed nano-particles have a positive impact on TiO_2 spacing. Instead, the results showed that TiO_2 positioning within a paint film is indifferent to the presence of nano-particles.

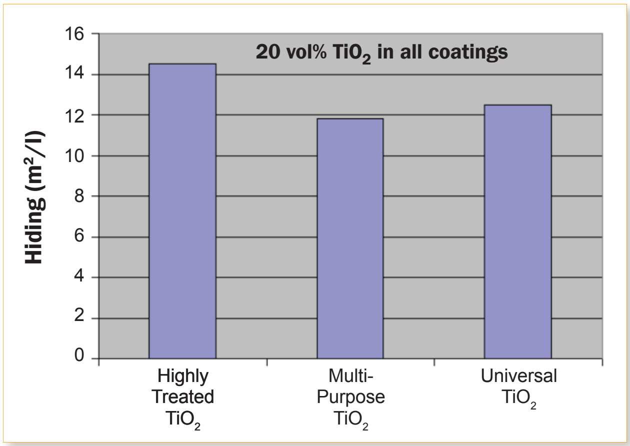

Figure 6—Value of highly treated TiO_2 in 47% PVC flat coating.

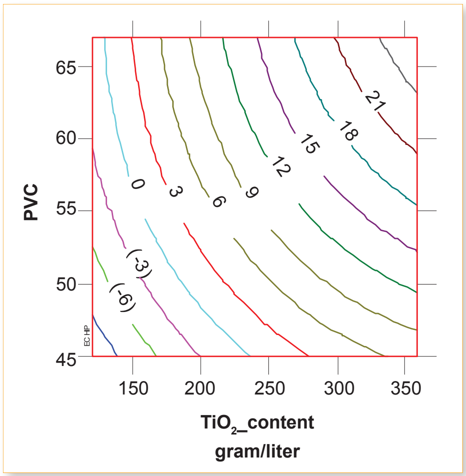

Figure 7—Potential percentage of TiO_2 savings with highly treated TiO_2.

While *randomly* positioned nano-particles do not enhance TiO_2 spacing, *targeted* positioned nano-particles can. By targeted positioning, we mean that the nano-particles are attached directly to the surface of the TiO_2 pigment particles. By doing this, the probability that one or more nano-particles will get in between TiO_2 pigment particles that might otherwise be touching is greatly increased. This creates a "stand-off" distance of similar dimensions to the nano-particle. Targeted spacer particles can be either inorganic [22] or organic.[23] Their effectiveness is determined not by their composition, but rather by their physical size and ability to adhere to TiO_2 particles rather than remain unattached in the film matrix.

HIGHLY COATED TIO_2 GRADES

There is a second route for improving TiO_2 light scattering efficiency that is closely related to targeted spacing—the encapsulation of the TiO_2 particles by a thick, porous material. This coating material, which is, in practice, aluminosilicates, needs to be thick enough to effectively prevent close contact of the TiO_2 portion of these pigments and highly porous, because a solid coating would unnecessarily dilute the TiO_2 content of the pigment. Even with high porosity, these coatings dilute the weight percent TiO_2 in the pigment to roughly 80%, decreasing the number of TiO_2 particles per pound of pigment.

Targeted spacer particles or thick porous coatings are most effective in high-PVC systems because, under low PVC conditions, there is plenty of room for TiO_2 particles to spread out, with only the occasional random close contact between the pigment particles. At higher PVC, where crowding is high and TiO_2–TiO_2 contacts are inevitable, targeted spacer particles or a thick porous coating on the pigment particles can significantly increase TiO_2 scattering efficiency.

The effectiveness of porous coatings is shown in *Figure* 6. In the figure, the spread rates of three paints that are identical except for the TiO_2 pigment used are compared. Each paint has a total PVC of 46% and a TiO_2 pigment content of 20%, and the pigments examined were a multipurpose grade (93% TiO_2), a universal grade (also 93% TiO_2), and a TiO_2 pigment coated with 18% porous aluminosilicate (82% TiO_2). As can be seen, the highest spread rate is seen for the pigment with the porous coating, despite the fact that there are 11% fewer TiO_2 particles per pound of pigment than for the other two grades.

Based on these results, a larger study was undertaken to quantify the benefits of a highly coated TiO_2 grade in a range of formulations. The intention was to identify the formulation space over which such a grade would offer clear opacity advantages over multipurpose and universal TiO_2 pigments. In this study, we looked at 60 formulas encompassing five TiO_2 PVCs, three total PVCs, and two pigment grades (a universal control and the highly coated grade). Within this formulation space, we found a distinct region where the highly coated TiO_2 grade allowed for a reduction in TiO_2 PVC while holding total film hide constant (*Figure* 7). TiO_2 pigment savings of up to 21% are possible by replacing the universal grade with a highly treated TiO_2 grade in a high TiO_2 loading, high PVC application.

As with the other optimization technologies discussed, there are also constraints on the use of highly treated TiO_2 pigments. First, the dilution of the TiO_2 particles with the aluminosilicate surface coating reduces the number of TiO_2 particles per pound of pigment. As seen in *Figure* 7, these highly treated TiO_2 grades will be less efficient than universal grades in coatings where the TiO_2 content is low and TiO_2 particle spacing is not an issue. This dilution effect reduces the wet hiding performance of the pigment. In addition, the porous aluminosilicate coating also increases the oil absorption of the highly treated TiO_2 grade which will lower the CPVC of the coating. Finally, these highly treated TiO_2 grades will diminish the gloss of the coating, which is why they are sometimes referred to as "flat grades."

CONCLUSIONS

With TiO_2 in short supply, it is critical that the paint formulator use this pigment as efficiently as possible. One way to increase paint opacity is by incorporating air voids into the dry film. This enhances the scattering efficiency of the TiO_2 pigment by decreasing the average refractive index of the film matrix and, in some situations, introduces light scattering centers from the air voids themselves. The decrease in average index results in a larger difference in refractive index between the TiO_2 and the film matrix, which, in turn, increases the scattering intensity of light as it enters and exits the TiO_2 particles.

Two methods of incorporating air voids have been identified. First, paints can be formulated above CPVC. While this is very economical (air is free), it can lead to degradation in the physical integrity of the paint film, resulting in poor stain resistance and scrub. Alternatively, hollow sphere opaque pigments can be used to bring air voids into the film. Like the voids present in paints formulated above the CPVC, these air voids increase the scattering efficiency of the TiO_2 particles by decreasing the average refractive index of the paint matrix. In addition, HSOP voids are of the appropriate size to scatter light in their own right, adding to the opacity of the film. However, these benefits are balanced by the fact that HSOPs do not offer any wet-hide, and can also result in higher PVC than is optimal for the desired paint performance.

In addition, the degree to which TiO_2 pigment particles crowd one another has a significant effect on the light scattering efficiency of this pigment and thus the opacity of the paint. Close particle–particle contacts interfere with the mechanism by which TiO_2 scatters light, and, to the extent feasible, paint formulators should provide conditions that allow these particles to remain as far from one another as possible. In high-PVC applications, however, this cannot always be done, and other strategies for maximizing light scattering should be considered. These include replacing large extender particles with smaller ones, and attaching small spacer particles or a thick layer of porous aluminosilicate onto the pigment surface. While this reduces the TiO_2 content of the pigment, and thus the number of scattering centers per pound, this dilution is more than made up for in crowded systems by the boost seen in TiO_2 efficiency. We recommend that, in high-PVC applications, the formulator should consider TiO_2 grades specifically designed to prevent close TiO_2–TiO_2 particle contacts, such as those grades that have a thick, porous aluminosilicate coating.

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