



*The miracles of science™*

## **TiO<sub>2</sub> Scattering Optimization and Not-In-Kind Opacity Alternatives**

*Dr. Michael Diebold, Robert Kwoka, David Mukoda,  
DuPont Titanium Technologies, USA*

### **Abstract**

With TiO<sub>2</sub> in short supply, many coatings manufacturers are specially formulating their paints to optimize TiO<sub>2</sub> effectiveness and/or turning to not-in-kind alternative options for opacity. These strategies include adding free or attached spacer particles that prevent TiO<sub>2</sub> particles from closely approaching one another, minimizing the loss in scattering due to crowding. Additionally, air incorporated into a paint film can improve opacity by two mechanisms, which will be detailed. In this presentation we review several of these concepts and report results from our lab work that test these strategies, both in terms of the effectiveness to improve opacity as well as the effects that are seen in other important paint film properties.

### **Introduction**

With titanium dioxide (TiO<sub>2</sub>) in short supply, many coatings manufacturers are re-evaluating their paint formulas to optimize TiO<sub>2</sub> 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 paper.

1. Incorporating air voids into a coating, either by formulating above Critical Pigment Volume Concentration (CPVC) or by using hollow sphere opaque polymers, can provide good dry film optical performance at reduced TiO<sub>2</sub> 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<sub>2</sub> light scattering efficiency, allowing some reduction in TiO<sub>2</sub> loadings, but this is not likely a result of the smaller extenders preferentially "spacing" the TiO<sub>2</sub> particles.
3. Targeted spacing technologies, like the use of highly coated TiO<sub>2</sub> products, can improve TiO<sub>2</sub> efficiency, allowing a reduction in TiO<sub>2</sub> pigment loading in appropriate coating formulations.

### **Background**

The primary property that TiO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> to scatter light in a coating depends on:

- Particle size
- The difference in refractive index of the TiO<sub>2</sub> particle and its surroundings, and
- Proximity of the TiO<sub>2</sub> particles to one another.

For the purposes of this paper we will assume that commercial TiO<sub>2</sub> grades produced for coatings are more or less optimally sized and this attribute will not be discussed further.

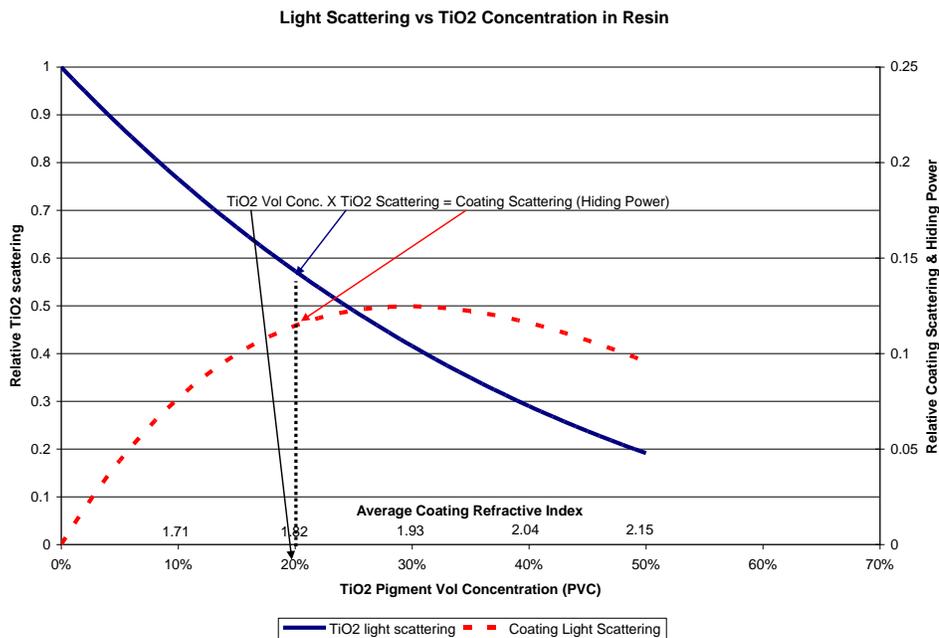


The miracles of science™

The light scattering potential of a TiO<sub>2</sub> particle is proportional to the square of the difference between the refractive index of the TiO<sub>2</sub> and the average refractive index of the medium in which the TiO<sub>2</sub> particle resides. [1] While the refractive index of the TiO<sub>2</sub> particle remains constant (Rutile TiO<sub>2</sub> R.I. = 2.73), the average refractive index of its surroundings changes depending on the 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). So 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<sub>2</sub> in a coating affects the average refractive index of the coating, affecting the difference in refractive index between the TiO<sub>2</sub> particle and its surroundings, and thereby affecting the light scattering efficiency of the TiO<sub>2</sub>.

This effect is illustrated in Figure 1, which represents the simple case of TiO<sub>2</sub> dispersed in resin. The x-axis shows the effect of increasing the TiO<sub>2</sub> volume concentration on the average refractive index of the coating. For example, increasing the TiO<sub>2</sub> 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<sub>2</sub> light scattering efficiency as the TiO<sub>2</sub> content and average refractive index of the coating increase as predicted by Mie Theory. [2] This effect is often referred to as the “TiO<sub>2</sub> crowding effect”.

Figure 1



The light scattering or hiding power contribution of TiO<sub>2</sub> in a coating is the product of the TiO<sub>2</sub> scattering efficiency at a specific average coating refractive index (or TiO<sub>2</sub> volume concentration in this simple example) times the TiO<sub>2</sub> volume concentration. This total light scattering contribution is represented by the dashed red line in Figure 1. At low TiO<sub>2</sub> concentrations, say less than 15% TiO<sub>2</sub> by volume, the coating light scattering / hiding power



The miracles of science™

increases almost linearly with  $\text{TiO}_2$  concentration. As  $\text{TiO}_2$  concentrations increase further, the incremental increase in coating light scattering / hiding power per increment of  $\text{TiO}_2$  volume concentration diminishes. Eventually the point is reached where additional increases in  $\text{TiO}_2$  content actually reduce the total coating light scattering / hiding power. Obviously, this is a very inefficient space to formulate coatings.

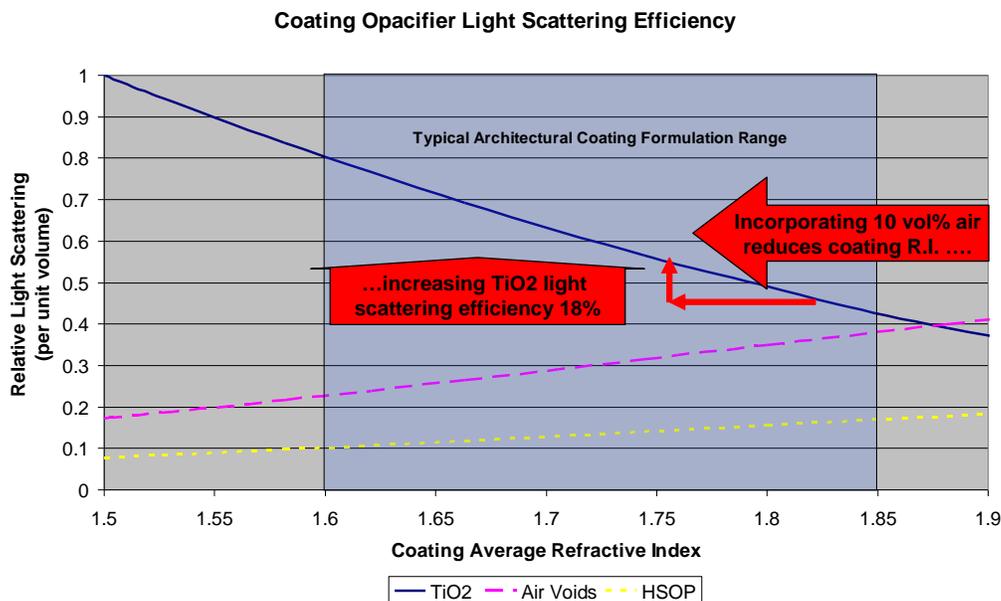
### Formulating Above Critical Pigment Volume Concentration (CPVC)

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  $\text{TiO}_2$ , 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 increases the difference in refractive index between the  $\text{TiO}_2$  particles and their surroundings, increasing the light scattering efficiency of the  $\text{TiO}_2$ . Because the  $\text{TiO}_2$  is more efficient, the  $\text{TiO}_2$  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%  $\text{TiO}_2$  reduces the average refractive index of the coating from 1.82 to 1.76. As a result, the  $\text{TiO}_2$  light scattering efficiency increases by 18%, meaning that the  $\text{TiO}_2$  concentration can be reduced by 18% while maintaining equal coating light scattering and hiding power.

Figure 2





*The miracles of science™*

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  $\text{TiO}_2$  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  $\text{TiO}_2$  particles. The selection of extender pigments in coatings formulated above CPVC can have 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.

Of course, 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 can not exist in the wet coating and therefore they 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 negative effects 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 non film forming synthetic pigments that are supplied as emulsions and are added to the wet paints. In the wet state, each HSOP particle consists of spherical styrene/acrylic bead with a void filled with water 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  $\text{TiO}_2$  light scattering efficiency as creating air voids by formulating above CPVC. The encapsulated air voids created by the HSOPs increase  $\text{TiO}_2$  light scattering efficiency by reducing the average refractive index of the paint film and increasing the difference in refractive index between the  $\text{TiO}_2$  particle and its surroundings.

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  $\text{TiO}_2$  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 increases with increasing average coating refractive index (i.e. increasing  $\text{TiO}_2$  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 of paints containing both  $\text{TiO}_2$  and HSOP,  $\text{TiO}_2$  is 3 to 5 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  $\text{TiO}_2$  reduction in coatings where the  $\text{TiO}_2$  content (and therefore the average refractive index of the coating) is high.

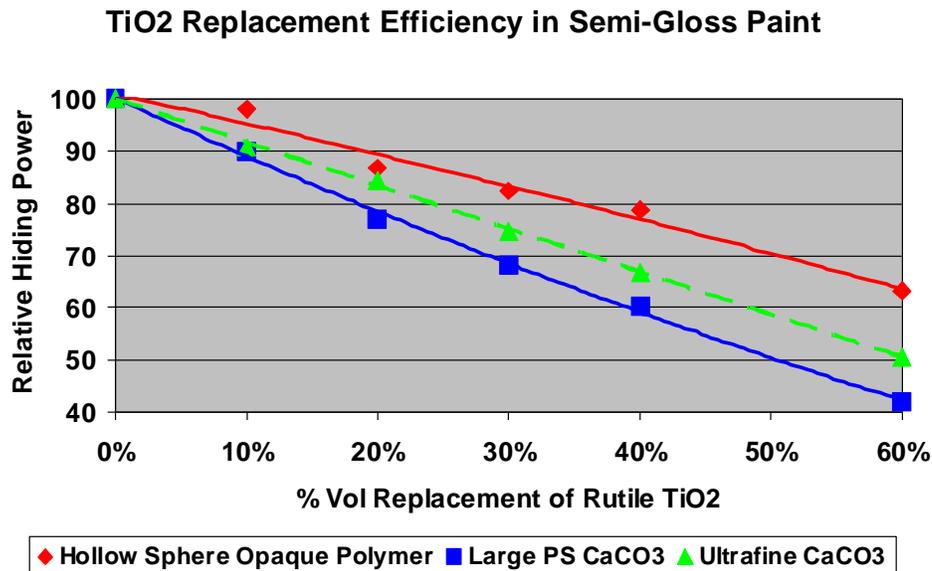
An example of the efficacy of HSOPs as a  $\text{TiO}_2$  replacement in a high  $\text{TiO}_2$  content semi-gloss paint is shown in Figure 3. Figure 3 shows the effect on coating hiding power resulting from one-for-one volume replacements of rutile  $\text{TiO}_2$  with commercially available HSOP, a



The miracles of science™

large particle size  $\text{CaCO}_3$  and an “ultrafine”  $\text{CaCO}_3$ . Though clearly more effective in maintaining hiding power than replacing  $\text{TiO}_2$  with  $\text{CaCO}_3$ , HSOPs are not a one-for-one replacement for  $\text{TiO}_2$ . Based on the relative light scattering efficiencies shown in Figure 2, HSOP would need to replace  $\text{TiO}_2$  at a 3 - 5 to 1 volume ratio to maintain equal dry hiding, and, in fact, one supplier of HSOPs recommends replacement at precisely these ratios. Insights into the differences between the hiding power efficiency of the two  $\text{CaCO}_3$  products will be discussed in the next section.

Figure 3



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  $\text{TiO}_2$  content, so any replacement of  $\text{TiO}_2$  with HSOPs will diminish the wet hiding power of the coating. HSOPs also have a high specific volume when dry and therefore have 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. Also, care needs to be taken to manage gloss and sheen of the coatings through use of extenders. In short, the use of HSOPs to reduce  $\text{TiO}_2$  content of a coating needs to be balanced with managing other important coating properties.

### Mineral Fillers

We next turn our attention from HSOP particles 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 above, the slight differences in

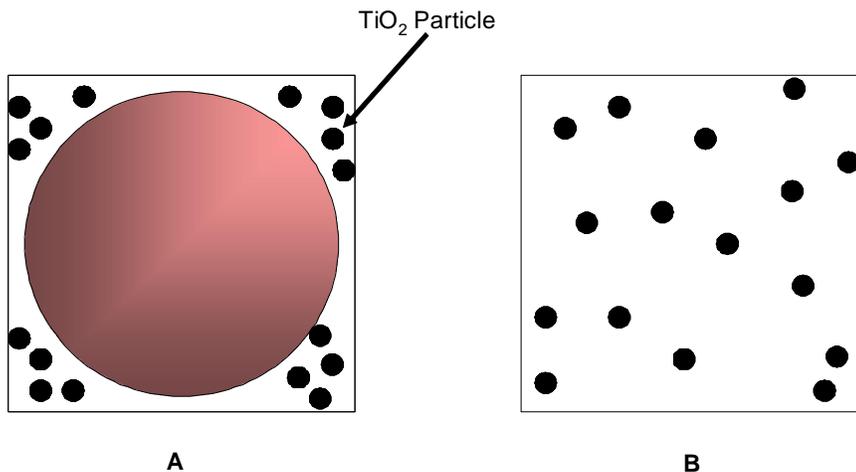


The miracles of science™

refractive indices between organic resin and most of these extender particles results in their providing negligible light scattering in the dry paint. That said, they can influence the white opacity of a paint by altering the scattering efficiency of the  $\text{TiO}_2$  pigment. In some cases the influence is positive; in other cases it is negative.

Among the negative influences of extender on  $\text{TiO}_2$  scattering is the crowding effect associated with extender particles that are large compared to  $\text{TiO}_2$  particles.[6] For most extenders, particles are significantly larger than  $\text{TiO}_2$  pigment particles, and, when present in a paint film, restrict the location of pigment particles to the interstitial regions between the large particles (Figure 4a). This has the effect of crowding the  $\text{TiO}_2$  particles together, 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 ten percent or more.

Figures 4a, 4b

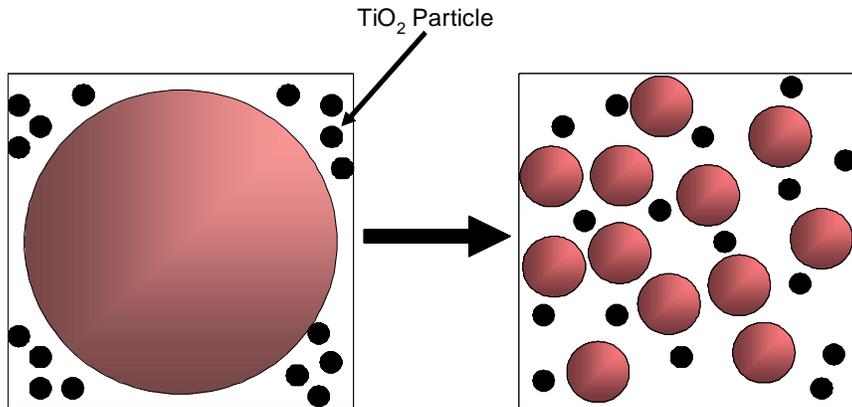


The decrease in opacity due to crowding from large particle extenders can be partially remediated by replacing the large particles with an equal volume of small particle size extenders (that is, extender size ranges on the same order as the quarter micron  $\text{TiO}_2$  particles). In the presence of small extender particles, the space available to the  $\text{TiO}_2$  particles is much less restricted, and, as shown in Figure 5, the pigment particles can approach a random distribution within the paint film.



The miracles of science™

Figure 5



By this mechanism, small extender particles return the  $\text{TiO}_2$  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 extender. The effect of replacing large extenders with small extenders can be seen by referring back to Figure 3. The hiding powers of coating films of identical coating PVC but with increasing one-for-one volume replacement of  $\text{TiO}_2$  by different sized extender particles and by hollow sphere opaque polymers are shown. Clearly, replacing large extender with smaller extender improves hiding, but even small extenders are not as effective as hollow sphere opaque polymer (HSOP), which in turn is not as effective as  $\text{TiO}_2$  at equal volume concentrations.

In addition to the boost in  $\text{TiO}_2$  efficiency seen when large extender particles are replaced with small ones, there is a second mechanism often cited by which extender particles smaller than  $\text{TiO}_2$  particles can increase opacity. In this mechanism nano sized extender particles randomly get in-between  $\text{TiO}_2$  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 positions. One of us has reported a theoretical resolution of this debate wherein a Monte-Carlo simulation approach was used to determine the extent to which  $\text{TiO}_2$  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  $\text{TiO}_2$  spacing. Instead, the results showed that  $\text{TiO}_2$  positioning within a paint film is indifferent to the presence of nano particles.

While *randomly* positioned nano particles do not enhance  $\text{TiO}_2$  spacing, *targeted* positioned nano particles can. By targeted positioning we mean that the nano particles are attached directly to the surface of the  $\text{TiO}_2$  pigment particles. By doing this we greatly increase the probability that one or more nano particles will get in-between  $\text{TiO}_2$  pigment particles that might otherwise be touching. 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 determined not by their composition, but rather to their physical size and ability to stick onto  $\text{TiO}_2$  particles rather than remain unattached in the film matrix.



The miracles of science™

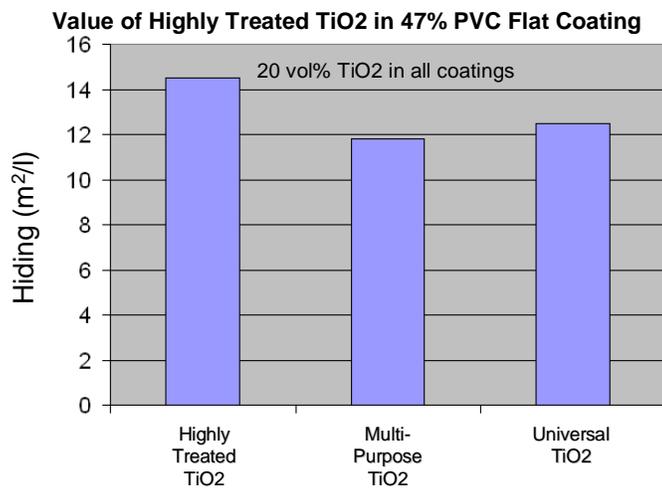
### Highly Coated TiO<sub>2</sub> Grades

There is a second route for improving TiO<sub>2</sub> light scattering efficiency that is closely related to targeted spacing, and that is the encapsulation of the TiO<sub>2</sub> particles by a thick, porous material. This coating material, which in practice is aluminosilicates, needs to be thick enough to effectively prevent close contact of the TiO<sub>2</sub> portion of these pigments and highly porous because a solid coating would unnecessarily dilute the TiO<sub>2</sub> content of the pigment. Even with high porosity, these coatings dilute the weight percent TiO<sub>2</sub> in the pigment to roughly 80%, decreasing the number of TiO<sub>2</sub> 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<sub>2</sub> particles to spread out, with only the occasion random close contact between the pigment particles. At higher PVC, where crowding is high and TiO<sub>2</sub> – TiO<sub>2</sub> contacts are inevitable, targeted spacer particles or a thick porous coating on the pigment particles can significantly increase TiO<sub>2</sub> scattering efficiency.

The effectiveness of porous coatings is shown in Figure 6. Here we compare the spread rates of three paints that are identical except for the TiO<sub>2</sub> pigment used. Each paint has a total PVC of 46% and a TiO<sub>2</sub> pigment content of 20%, and the pigments examined were a multi-purpose grade (93% TiO<sub>2</sub>), a universal grade (also 93% TiO<sub>2</sub>) and TiO<sub>2</sub> pigment coated with 18% porous aluminosilicate (82% TiO<sub>2</sub>). As can be seen in Figure 6, the highest spread rate is seen for the pigment with the porous coating, despite the fact that there are 11% fewer TiO<sub>2</sub> particles per pound of pigment than for the other two grades.

Figure 6



Based on these results, we undertook a larger study to quantify the benefits of a highly coated TiO<sub>2</sub> grade in a range of formulations, with the intention of identifying the formulation space over which such a grade would offer clear opacity advantages over multi-purpose and universal TiO<sub>2</sub> pigments. In this study we looked at sixty formulas encompassing five TiO<sub>2</sub> PVCs, three total

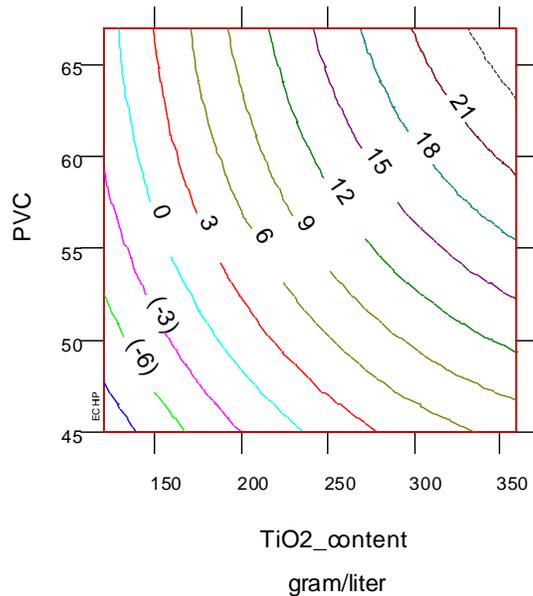


The miracles of science™

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<sub>2</sub> grade allowed for a reduction in TiO<sub>2</sub> PVC while holding total film hide constant (Figure 7). TiO<sub>2</sub> pigment savings of up to 21% are possible by replacing universal TiO<sub>2</sub> with a highly treated TiO<sub>2</sub> grade in a high TiO<sub>2</sub> loading, high PVC application.

Figure 7

Potential % TiO<sub>2</sub> Savings with Highly Treated TiO<sub>2</sub>



As with the other optimization technologies discussed, there are also constraints to the use of highly treated TiO<sub>2</sub> pigments. First, the dilution of the TiO<sub>2</sub> particles with the aluminosilicate surface coating reduces the number of TiO<sub>2</sub> particles per pound of pigment. As seen in Figure 7, these highly treated TiO<sub>2</sub> grades will be less efficient than universal grades in coatings where the TiO<sub>2</sub> content is low and TiO<sub>2</sub> particle spacing is not an issue. This dilution effect also reduces the wet hiding performance of the pigment. The porous aluminosilicate coating also increases the oil absorption of the highly treated TiO<sub>2</sub> grade which will lower the Critical Pigment Volume Concentration (CPVC) of the coating. Finally, these highly treated TiO<sub>2</sub> grades will diminish the gloss of the coating which is why they are sometimes referred to as "flat grades".



*The miracles of science™*

## Conclusions

With  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{TiO}_2$  and the film matrix, which in turn increases the scattering intensity of light as it enters and exits the  $\text{TiO}_2$  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 a 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  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{TiO}_2$  scatters light, and to the extent possible 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  $\text{TiO}_2$  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  $\text{TiO}_2$  efficiency. Thus we recommend that in high PVC applications the formulator should consider  $\text{TiO}_2$  grades specifically designed to prevent close  $\text{TiO}_2 - \text{TiO}_2$  particle contacts, such as those grades that have a thick, porous aluminosilicate coating.

---

The information set forth herein is furnished free of charge and based on technical data that DuPont believes to be reliable. It is intended for use by persons having technical skill, at their own risk. Since conditions of use are outside our control, we make no warranties, expressed or implied and assume no liability in connection with any use of this information. Nothing herein is to be taken as license to operate under or a recommendation to infringe any patents.

---



The miracles of science™

## References

1. Fitzwater, S., and Hook, J. W., "Dependent Scattering Theory: A New Approach to Predicting Scattering in Paints," *J. Coat. Technol.* **57**, 39 (1985).
2. Mie, G., "Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen," *Leipzig, Ann. Phys.* **330**, 377 (1908).
3. Ross, W. D., "Theoretical Light-Scattering Power of TiO<sub>2</sub> and Microvoids", *Ind. Eng. Chem. Prod. Res. Dev.*, **13**(1), 45 (1974).
4. Patton, T. C., "Paint Flow and Pigment Dispersion: A Rheological Approach to Coating and Ink, 2<sup>nd</sup> Ed.", Wiley-Interscience, Hoboken, NJ (1979).
5. Mussard, I., "25 Years of Hollow-Sphere Hiding Technology." *Paint Coat, Ind.*, **21**(9), 96 (2005)
6. Stieg, F. B., "Dilution Efficiency of Extenders." *J. Coat. Technol.*, **53** (680), 75 (1981)
7. Stieg, F. B., "Effect of Extender on Crowding of Titanium Pigment." *J. Coat. Technol.*, **61** (778), 67 (1989).
8. Dietz, P. F. "The Effect of Fine-Particle-Size Extenders and Entrapped Air on TiO<sub>2</sub> in Emulsion Paint." *Paint Coat, Ind.*, **9** 2 (2003).
9. Gittins, D, Gadson, M, Skuse, D, "Mineral Blends for Low-Titania Coatings." WO 2010/143068 A1, 2010.
10. Stewart, D, "An End to Overcrowding: Hydrous Kaolin Optimizes Paint Opacity by Improving TiO<sub>2</sub> Spacing." *Eur. Coat. J.*, **5** 178 (2007).
11. Hirani, H, Dighe, A, Patel, C, "Staying Apart: TiO<sub>2</sub> Pigments can be Partly Replaced by Calcium Aluminium Silicate Extenders." *Eur. Coat. J.*, **3** 24 (2007).
12. Braun, J. H., "Crowding and Spacing of Titanium Dioxide Pigments." *J. Coat. Technol.*, **60** (758) 67 (1988).
13. Temperley, J, Westwood, M. J., Hornby, M. R., Simpson, L. A., "Use of a Mathematical Model to Predict the Effects of Extenders on Pigment Dispersion in Paint Films." *J. Coat. Technol.*, **64** (809) 33 (1992).
14. Ashek, L, "New Generation Kaolin-Based Pigment Extenders." *Paint Coat. Ind.*, **19** (3) 80 (2003).
15. Ashek, L, "New Generation Kaolin-Based Pigment Extenders." *Surf. Coat. Int. Part A: Coat. J.* **85** (6) 223 (2002).
16. Kaye, B. H., Clark, G. G. "Computer Aided Image Analysis Procedures for Characterizing the Stochastic Structure of Chaotically Assembled Pigmented Coatings." *Part. Syst. Charact.*, **9** 157 (1992).
17. Fellers, A, Christian, H-D, "Filling Up Paint." *PPCJ*, **195** (4484), 26 (2005).
18. Stieg, F. B., "Ending the 'Crowding/Spacing Theory' Debate." *J. Coat. Technol.*, **59** (748), 96 (1987).
19. Hook, J., "Conclusions on 'Crowding/Spacing Theory' Clarified." *J. Coat. Technol.*, **58** (742), 81 (1986).
20. Cutrone, L., "Influence of Fine-Particle Size Extenders on the Optical Properties of Latex Paints." *J. Coat. Technol.*, **58** (736), 83 (1986).
21. Diebold, M. P., "A Monte Carlo Determination of the Effectiveness of Nanoparticles as Spacers for Optimizing TiO<sub>2</sub> Opacity", *JCT Research*, **8** (5), 541 (2011).
22. Bolt, J. D., "TiO<sub>2</sub> Light Scattering Efficiency when Incorporated in Coatings", US 5,650,002 (1997).
23. Adamson, L., Fasano, D., "Polymeric Hiding Technologies That Make TiO<sub>2</sub> Work Smarter", *PCI Magazine*, June (2011).