

Light-scattering efficiency of white pigments: an analysis of model core-shell pigments vs. optimized rutile TiO_2

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THE HIGH REFRACTIVE INDEX, HIGH brightness, and inert chemical properties of titanium dioxide have made it the premium opacifying pigment in paper as well as paints and plastics. Since TiO_2 is more expensive than pulp and other mineral pigments like kaolin clay and calcium carbonate, it must be used as efficiently as possible. For paper applications, the cost-effective approach is to optimize the use of non- TiO_2 components and then add TiO_2 as required to achieve target opacity. Strategies for optimizing both paper furnish and coating formulations have been outlined in the literature (1-4).

The next level of optimization involves selecting the most cost-effective TiO_2 pigment for the application under study. Opacification by titanium dioxide is due primarily to scattering of visible light. It is well documented that the efficiency of TiO_2 for light scattering is strongly dependent on the refractive index of the pigment relative to that of the surrounding medium and on the size of the TiO_2 particles (5-6). The rutile crystalline form of TiO_2 has higher intrinsic scattering efficiency than the anatase crystal because of its higher refractive index (2.74 vs. 2.56) at the center of the visible light spectrum. Efficiency is maximized by generating narrow particle size distributions near the optimum diameter. The width of TiO_2 particle size distributions can be characterized by geometric standard deviation (GSD).

GSD is calculated from d84 (diameter for 84% finer) and d16 (diameter for 16% finer).

$$\text{GSD} = (\text{d84}/\text{d16})^{0.5}$$

The minimum GSD of 1.0 is achieved when all particles are the same size. **Figure 1** compares scattering efficiency vs. GSD for rutile and anatase TiO_2 in a typical paper coating formulation. Particle size measurements were made using laser light-scattering technology with multiple angle detectors to measure particles as small as 0.04 μm . Light-scattering coefficients were determined by applying paper coatings to Mylar base at precise coat weights and measuring reflectance and transmittance. The data clearly show the benefits for commercial pigments with a narrow size distribution (low GSD). The higher efficiency of the new rutile pigment relative to commercial anatase pigments is due to a combination of higher refractive index and narrower particle size distribution.

Another approach to increase the efficiency of TiO_2 is to create novel pigment structures that might compete with conventional TiO_2 pigments. Recently, it has been proposed that scattering efficiencies can be improved by coating a shell of titania on spherical silica particles (7-9). The lower TiO_2 content of such particles suggests their potential as a higher-value pigment than pure TiO_2 . However, fundamental light-scattering

TITANIUM DIOXIDE

ABSTRACT

The light-scattering efficiency of a white pigment is strongly dependent on its refractive index and particle size. Rutile TiO_2 is an effective opacifier because of its high refractive index. Its efficiency can be further optimized by generating narrow particle size distributions near the optimum diameter. Recently, an alternative core-shell pigment was proposed as a means of increasing the light-scattering efficiency of TiO_2 . The proposed hybrid pigment would be prepared by coating a shell of titania on spherical silica particles or some other low-refractive-index material. Theoretical calculations of the light-scattering efficiencies of these core-shell particles and solid TiO_2 particles show that core-shell particles are substantially less efficient light-scattering materials than pure rutile, especially in the domain of titania coating thickness that can be realistically applied to a core material.

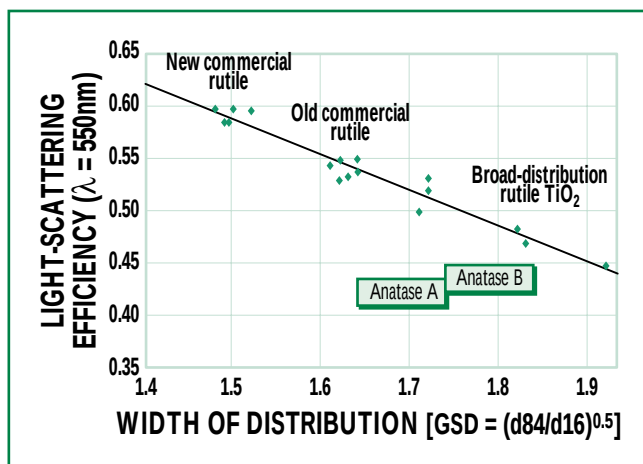
Application:

A theoretical comparison of the light-scattering efficiency of titania-coated silica spheres and pure rutile. Results demonstrate that the coated spheres are substantially less efficient than pure rutile.

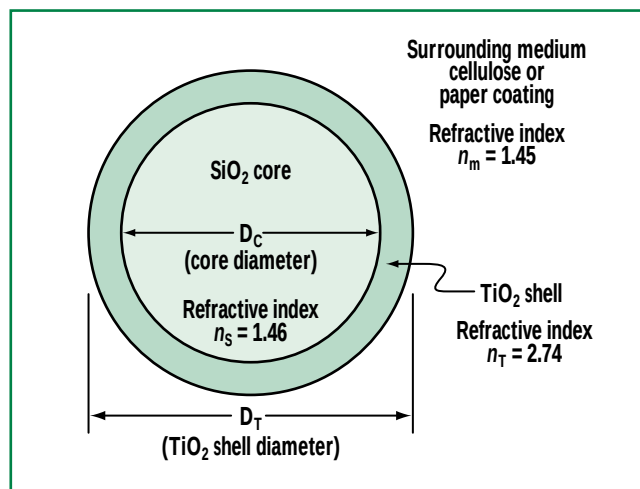
theory predicts that core-shell structures have significantly lower scattering efficiency than particles of pure rutile. After a brief review of Mie theory, examples are presented for the general case of a titania shell over cores with refractive index ranging from 1.0 (hollow TiO_2 spheres) up to 2.74 (solid TiO_2 spheres). This is followed by a more detailed comparison of the light-scattering performance of titania-coated silica vs. pure titanium dioxide.

MIE THEORY

Mie theory provides rigorous solutions for light scattering by an isotropic sphere embedded in a homogeneous medium (10-13).



1. Light-scattering efficiency of TiO_2 in a typical paper coating as a function of the width of its particle size distribution. Efficiency is optimized by narrowing the width of the distribution.



2. Titania-coated silica sphere

Extensions of Mie theory include solutions for core-shell spheres (14) and gradient-index spheres (15). Although the theory deals with perfect spheres, the results provide insight into the scattering and absorption properties for a wide variety of pigment systems, including nonspherical pigments (16). In most paper applications, where TiO_2 concentrations are relatively low (<15% by volume), theoretical calculations predict the relative effects of particle size, particle composition, composition of the surrounding medium, and wavelength of light. These trends correlate well with experimental data (17). In applications with TiO_2 concentrations greater than about 15% by volume, near-field optical interactions between neighboring particles become significant and can dramatically impact macroscopic optical properties. The optical theories applied in the present study describe the light-scattering properties of an isolated spherical particle. Thus they cannot be applied to systems in which the particles are crowded together, where near-field interactions between particles are significant.

The concepts of geometric optics (refraction by lenses and reflection by mirrors) that are familiar in the macroscopic world do not fully describe the interactions of particles with light when the particle size is comparable with the wavelength of the light.

Rigorous optical theories such as Mie theory address the full complexity of vector electromagnetic quantities interacting with a particle. The mathematics of Mie theory is fairly straightforward but tedious, requiring the computation of a potentially large number of series expansions. Digital computers are ideally suited to this task. In the present study, computer codes (BHMie and BHCoat) developed by Bohren and Huffman (13) were used to compute the scattering results. The computations were made after slight modification to incorporate computation of the asymmetry parameter (13).

In general, when the light wavelength is similar to the particle diameter, light interacts with the particle over a cross-sectional area that is larger than the geometric cross section of the particle. The Mie calculation output provides this scattering cross section, C_{sca} . Often this parameter is divided by the geometric cross-sectional area to give a dimensionless scattering-efficiency parameter, Q_{sca} .

$$Q_{\text{sca}} = C_{\text{sca}} / \pi r^2$$

However, in pigment applications, the formulation properties and costs depend on particle volume rather than cross-sectional area. Therefore, a more meaningful efficiency parameter is the scattering coefficient per mi-

cron (SCPM), defined as the scattering cross section divided by particle volume.

$$\text{SCPM} = C_{\text{sca}} / (4\pi r^3/3) = 3 Q_{\text{sca}} / 4r$$

Since the intensity of scattered light varies with the scattering angle, the asymmetry parameter ($\cos \theta$) must be considered (5) to give the scattering coefficient, $S(\mu\text{m}^{-1})$, which is the preferred parameter for correlations with experimental data for systems on which multiple scattering is predominant. The relationship is

$$S(\mu\text{m}^{-1}) = 0.75(1 - \overline{\cos \theta}) \cdot \text{SCPM}$$

where

$\overline{\cos \theta}$ = average cosine of the scattering angle, weighted by the intensity of the scattered light as a function of angle

SCATTERING OF TITANIA-COATED CORE-SHELL PIGMENTS

Figure 2 is a schematic diagram of the configuration for the titania-coated silica particles. All critical parameters are indicated. The silica core is a sphere of diameter D_c . The titanium dioxide coating forms a shell with outside diameter D_T . The reported calculations include particles with shell diameters up to 1 μm and consider the full range of 100% TiO_2 (core diameter = 0) to 100% core material ($D_c = D_T$).

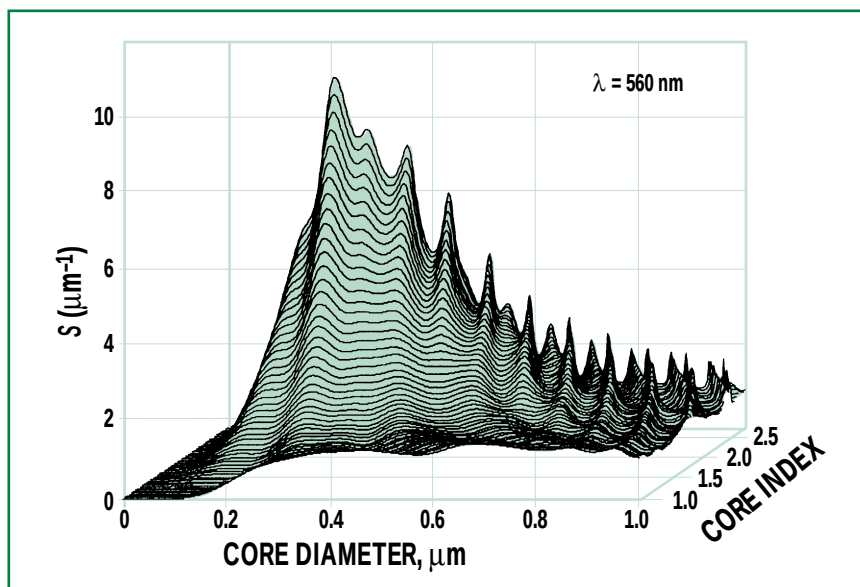
In the case of silica cores, it is not practical to deposit more than 40 wt.% titania on the core. Since the volume percent TiO_2 is related to the cube of D_c/D_T —and since titania is more dense than silica—40 wt.% titania corresponds to a thin shell around the silica cores. The shell diameter would be only 10% larger than the core diameter, and D_c/D_T would range from 0.9 to 1. For clarity, the schematic in Fig. 2 illustrates a particle with a shell diameter about 20% larger than the core diameter. This represents an impractical case with a TiO_2 content of 64 wt.%. For practical cases, the thickness of the titania layer would be much thinner than illustrated.

The other key parameters in Fig. 2 are the refractive indices of the components. The value of 2.74 for TiO_2 is the average refractive index for rutile in the center of the visible spectrum. For generality, the refractive index of the core can be left as an independent value. A core index of 1.0 (air) represents a hollow titania shell. The index for a silica core is 1.46. Finally, a core with a refractive index equal to that of rutile TiO_2 (2.74) represents a solid rutile particle.

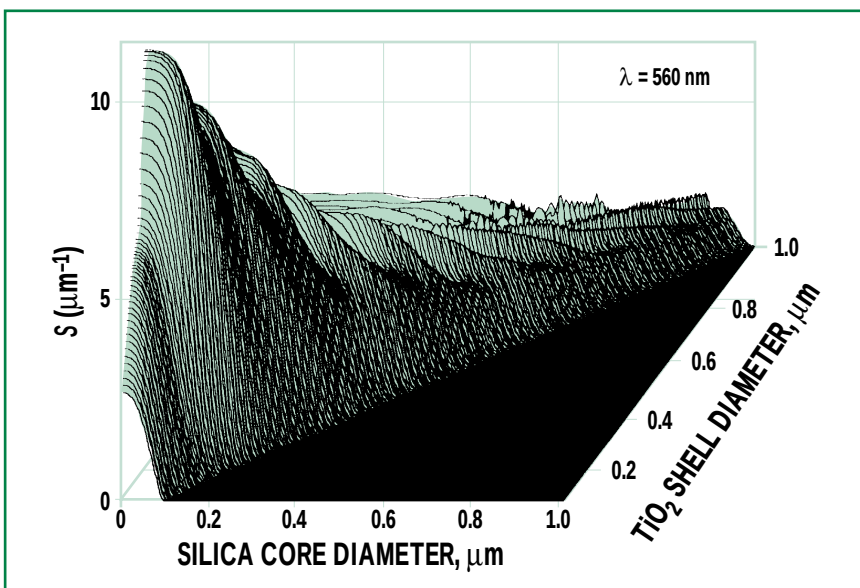
The refractive index for the surrounding medium is more difficult to define uniquely. The value of 1.45 used in these calculations is representative of the average refractive index of typical paper coatings composed of a mixture of clays/calcium carbonates (index of 1.6), starch or latex binders (index of 1.5), and air voids (index of 1.0). Uncoated papers are composed of cellulose fiber (index of 1.45), clays/calcium carbonates, and air voids. Thus a refractive index lower than 1.45 should be used to represent the surroundings for TiO_2 in filled sheets.

Refractive index of surrounding medium at 1.45

Figure 3 shows a plot of scattering coefficient, $S(\mu\text{m}^{-1})$, for the general case of a rutile-titania-coated cores in a paper



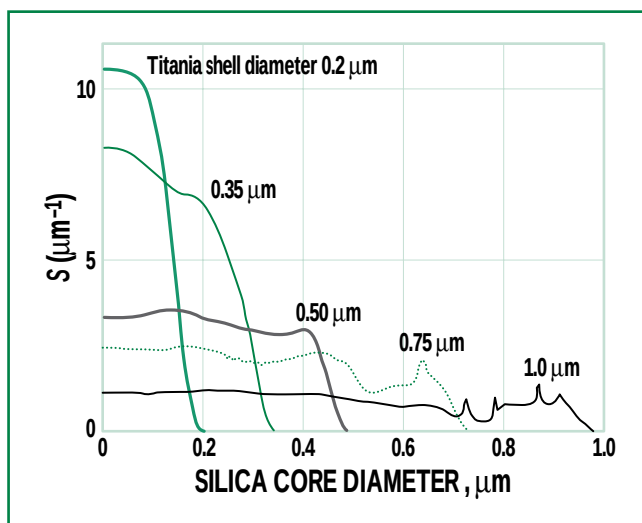
3. Light-scattering coefficient, $S(\mu\text{m}^{-1})$, vs. coated-particle diameter and refractive index of the core material for titania-coated particles with coating thickness equal to 10% of the particle radius. (Refractive indices: titania 2.74, surrounding matrix 1.45.)



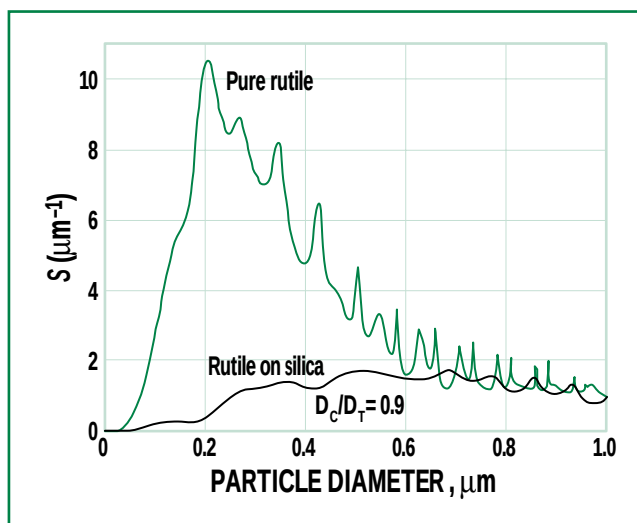
4. Light-scattering coefficient, $S(\mu\text{m}^{-1})$, vs. silica-core diameter and titania shell diameter for a coated particle. The global maximum of this plot corresponds to a solid titania sphere of 0.2- μm diam. (Refractive indices: silica 1.46, titania 2.74, surrounding matrix 1.45.)

coating or cellulose matrix. The results were calculated for green light of wavelength 560 nm, the center of the visible spectrum. This is the wavelength where the human eye is most sensitive and close to the center of the wavelength bands used for measurement of paper opacity. TAPPI Test Method T 425 uses

CIE illuminant A centered at 572 nm, while TAPPI T 519 uses CIE illuminant C centered at 557 nm. Absolute values of scattering coefficients are dependent on wavelength, but results calculated at 560 nm provide a sound representation of the light-scattering properties that affect opacity.



5. Light-scattering coefficient, $S(\mu\text{m}^{-1})$, for five particles with different outside diameters. The 0.2- μm curve corresponds to the cross-sectional slice through the global maximum peak (pure TiO_2) in Fig. 4. The other curves correspond to slices through Fig. 4 for particles with larger shell diameters.



6. Light-scattering coefficient, $S(\mu\text{m}^{-1})$, vs. particle diameter for a solid rutile sphere and a titania-coated silica particle with coating thickness equal to 10% of the particle radius (i.e., a coated particle with the highest practical titania content)

For the particles in Fig. 3, the ratio of the core diameter to total diameter, D_c/D_t , is fixed at 0.9. The three-dimensional plot shows the scattering efficiency for particles with outer diameter, D_t , from zero to 1 μm . Each contour line represents the dependence of $S(\mu\text{m}^{-1})$ on the diameter for a given core refractive index. Refractive index is incremented by 0.035 with each contour line, moving from 1.0 (air) to 2.74 (solid rutile). The global maximum indicating the most efficient particle structure corresponds to a solid rutile particle (i.e., a particle whose "core" and "shell" have the same refractive index of 2.74) with a diameter of 0.2 μm .

For the case of titania-coated silica, the refractive index for the core is 1.46. The data in Fig. 4 are plotted as a function of the diameters of both the silica core and the titania shell, both of which vary from zero to 1 μm . Each

contour line represents a 0.002- μm increment of outer-shell diameter. The global maximum corresponds to a solid rutile sphere (i.e., the silica-core diameter is zero). Variation of the core and shell diameters results in the series of hills and valleys of Fig. 4. The highest hill corresponding to a sphere that has substantial silica content occurs at a titania shell diameter of about 0.35 μm , with a silica-core diameter of about 0.2 μm . The S value associated with this coated silica particle is only about 64% relative to the most efficiently scattering solid rutile sphere.

For added clarity, five cases are extracted from the three-dimensional plot in Fig. 4 and presented in a two-dimensional format in Fig. 5. Figure 5 shows $S(\mu\text{m}^{-1})$ as a function of silica-core diameter for spheres with five different titania shell diameters. The sphere with titania shell diameter 0.20 μm —the one that has the highest S value—depicts the case of solid titania (no silica core). The decline in S of the particles as the diameter of the silica core increases is clear. Many of the titania-coated silica particles nearly match the scattering efficiency of pure TiO_2 particles with the same outside diameter, but they are deficient relative to pure TiO_2 near its optimum diameter.

For example, for particles with a titania shell diameter of 0.5 μm , the scattering coefficient is nearly constant as the silica core is increased from zero to 0.4 μm . But the scattering coefficients for these particles are 70% below the performance of 0.2- μm particles of pure TiO_2 . The sphere with a titania shell diameter of 0.35 μm is the particle with the highest S value among those spheres containing a substantial amount of silica (silica-core diameter 0.2 μm). Note that such a particle has a D_c/D_t value of $0.2/0.35 = 0.57$ and a TiO_2 content of 89 wt.%, which means that the titania coating is impractically thick from a synthesis standpoint. All other silica-containing particles exhibit even lower $S(\mu\text{m}^{-1})$ values.

As noted previously, practical cases are limited to those with a titania shell thickness that is less than or equal to 10% of the particle diameter ($D_c/D_t = 0.9$). This limiting case has been plotted in Fig. 6, which shows $S(\mu\text{m}^{-1})$ as a function of sphere diameter for solid titania and for coated particles with $D_c/D_t = 0.9$. The results for the two structures are strikingly different. The maximum $S(\mu\text{m}^{-1})$ value achieved by a solid titania sphere is 10.5, while the maximum value achieved by a coated

KEYWORDS

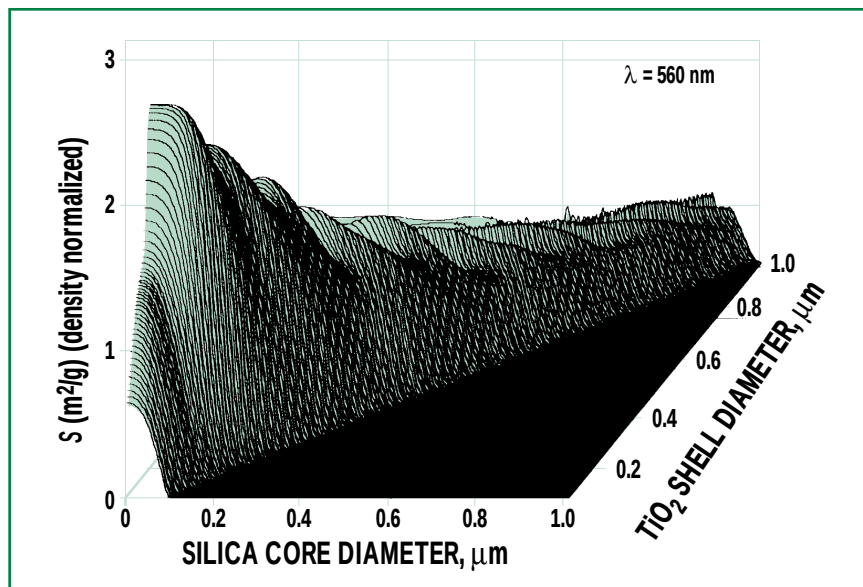
White pigments, optical scattering, rutile, titanium dioxide, particle size distribution, silica, refractivity, substitutes, theories, efficiency, coating, particles.

silica particle is only about 1.7. The two types of pigment are separated by a factor of six. The spikes observed in Fig. 6 are resonance effects that occur because of the inherent symmetry of a sphere. In practice, such spikes are not observed experimentally even for pigments with a narrow distribution of particle sizes.

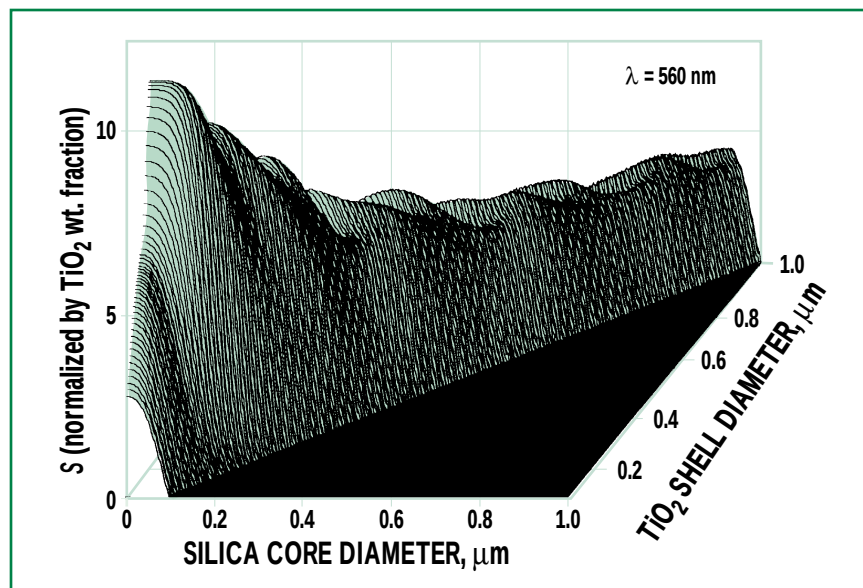
As previously noted, the optical theories applied in the present study describe the light-scattering properties of an isolated spherical particle and thus cannot be applied to systems in which the particles are crowded closely together. However, crowding can be viewed as an agglomeration of individual particles into clusters. If these clusters are represented by spheres of higher equivalent volume, the data in Fig. 6 at higher diameters suggest that optimized rutile particles will show more loss due to crowding than particles of titania-coated silica. However, this effect will not apply for most paper applications, where TiO_2 concentrations are below 15% by volume.

Alternative normalization schemes

One of the incentives for depositing titania coatings on a low-density and inexpensive material like silica is the hope that one can increase the light-scattering power per pound of material and/or reduce the price per pound of material. The scattering coefficients in Figs. 3–6 can be divided by the density of the coated particle, thereby expressing S on a weight basis, $S(\text{m}^2/\text{g})$. Using specific gravities of 2.2 g/mL for silica and 4.26 g/mL for titania (the value for rutile), the scattering coefficients with units of μm^{-1} in Fig. 4 were converted to the scattering coefficients with units of m^2/g in Fig. 7. While this normalization scheme does slightly increase the effective S values for the particles containing silica, the global maximum in Fig. 7 still corresponds to a solid titania sphere with no silica present.



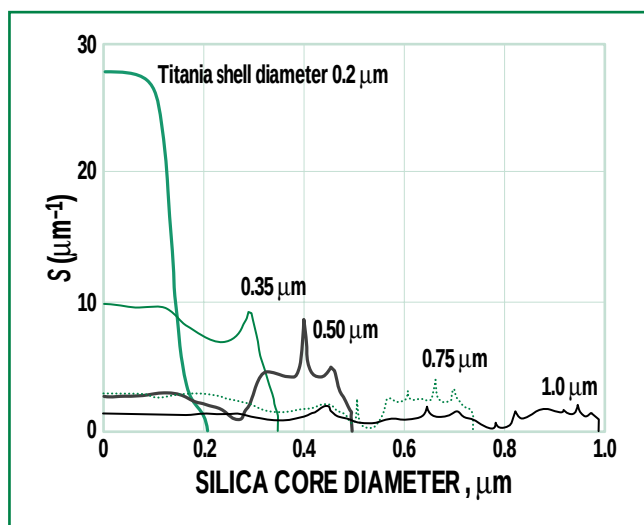
7. Light-scattering coefficient, $S(\mu\text{m}^{-1})$, of Fig. 4 divided by the density of the coated particle to give $S(\text{m}^2/\text{g})$. The global maximum of this plot corresponds to a solid titania sphere with no silica present.



8. Light-scattering coefficient, $S(\mu\text{m}^{-1})$, of Fig. 4 divided by the weight fraction of titania present on the coated silica sphere. The global maximum of this plot corresponds to a solid titania sphere with no silica present.

Another interesting approach is to weight the light-scattering data in Fig. 4 by dividing the $S(\mu\text{m}^{-1})$ value by the weight fraction of titania present in the particle. This approach is useful because it highlights the relative efficiency for the limiting case, where the titania-coated silica is valued based only on its TiO_2 content. The results of

this normalization are shown in Fig. 8. These data do not include the diverging values that resulted in cases where the titania coating thickness approaches zero. However, even with this normalization scheme, the global maximum in Fig. 8 still corresponds to a solid titania sphere, with no silica present.



9. Light-scattering coefficient, $S(\mu\text{m}^{-1})$, for the five particles shown in Fig. 5 for the case of a surrounding matrix of air (refractive index of 1.0) instead of cellulose (refractive index of 1.45)

Finally, core-shell pigments can be compared with a simple blend of the two pure pigments to evaluate any potential synergy. For the titania-coated silica particles in Fig. 6, D_c/D_t is 0.9, which translates to 27.1 volume percent TiO_2 . The highest scattering coefficient of $1.702 \mu\text{m}^{-1}$ occurs at a diameter of $0.687 \mu\text{m}$. For pure rutile, the optimum of $10.574 \mu\text{m}^{-1}$ occurs at a diameter of $0.203 \mu\text{m}$. The optimum for pure silica is very low because the refractive index is close to that of the surrounding medium. The optimum occurs at $0.20 \mu\text{m}$, but it is only $0.0005 \mu\text{m}^{-1}$. For a blend of optimized rutile and silica particles, the scattering coefficients are combined based on volume fraction v .

$$S_{\text{total}} = (v_{\text{TiO}_2} S_{\text{TiO}_2}) + (v_{\text{silica}} S_{\text{silica}})$$

For the core-shell particle with 27.1 volume % TiO_2 , v_{TiO_2} is 0.271 and v_{silica} is 0.729. Therefore, S_{total} for the blend of pure TiO_2 and pure silica is

Refractive index of surrounding medium at 1.0 (air)

White pigment particles in filled-papers are not surrounded completely by cellulose (refractive index 1.45) but, rather, by cellulose and air. To address this point, the calculations were modified to change the refractive index of the surrounding medium from 1.45 to 1.0 (i.e., to the refractive index of air). In a matrix of air, the difference in S between a solid titania sphere and titania-coated silica is even more pronounced. Figure 9 shows a plot of $S(\mu\text{m}^{-1})$ vs. silica-core diameter for the five particles that were displayed in Fig. 5, but with the refractive index of the surrounding medium set at 1.0 instead of 1.45. The $S(\mu\text{m}^{-1})$ value for a solid titania sphere with diameter $0.20 \mu\text{m}$ is about 28, while the value for a titania-coated silica sphere with outer diameter $0.35 \mu\text{m}$ and silica-core diameter $0.3 \mu\text{m}$ is about 10. This difference is much more pronounced than the values observed in Fig. 5.

$2.866 \mu\text{m}^{-1}$, which is 1.7-fold higher than the scattering coefficient for the same volumes of TiO_2 and silica in the core-shell structure. Similar evaluations of other cases also confirm no evidence of synergy in the core-shell structures.

Since pure rutile particles outperform titania-coated silica particles in both a cellulose matrix and an air matrix, it is clear that rutile particles will also be more efficient in porous paper substrates, which are a mixture of cellulose and air.

CONCLUSIONS

The light-scattering efficiency of white pigments is strongly dependent on the pigment's refractive index and its particle size. Rutile TiO_2 is an especially effective opacifier because of its high refractive index. The efficiency of commercial rutile TiO_2 can be further optimized by generating narrow particle size distributions near the optimum diameter.

The prospect of manufacturing a core-shell structure—a shell of titania coated on a core material with a lower refractive index—would appear to be a reasonable means of extending the usage of expensive TiO_2 . However, theoretical calculations of light-scattering efficiency based on Mie theory suggest otherwise. The calculated efficiencies for core-shell composites and solid TiO_2 particles show that core-shell pigments are substantially less efficient light-scattering materials than pure rutile, especially in the domain of titania coating thicknesses that can be realistically applied to a core material. **TJ**

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LITERATURE CITED

1. Houle, L. L., Boudreau, J., and Shukla, G., *TAPPI 1990 Coating Conference Proceedings*, TAPPI PRESS, Atlanta, p. 259.
2. Kwoka, R. A., *TAPPI 1990 Dyes, Fillers and Pigments Short Course Notes*, TAPPI PRESS, Atlanta, p. 21.
3. Kwoka, R. A., *TAPPI 1993 Coating Conference Proceedings*, TAPPI PRESS, Atlanta, p. 133.
4. Kwoka, R. A. and Logan, T. W., *Tappi J.* 77(10): 136(1994).
5. Ross, W. D., *J. Paint Technol.* 43(563): 51(1971).
6. Ross, W. D., *I&EC Prod. Res.* 13(1): 45(1974).
7. Hsu, W. P., Yu, R., and Matijevic, E., *J. Colloid Interface Sci.* 156: 56(1993).
8. Matijevic, E., Hsu, P., and Kuehnle, W., U.S. patent 5,248,556 (1993).
9. Otterstedt, J., Otterstedt, O., Sterte, P., et al., International patent application WO 94/21733 (1994).
10. Mie, G., *Ann. Physik* 25(4): 377(1908).
11. Van de Hulst, H. C., *Light Scattering by Small Particles*, Wiley, New York, 1957, Chaps. 9 and 10.
12. Kerker, M., *The Scattering of Light and Other Electromagnetic Radiation*, Academic Press, New York, 1969, Chaps. 3 and 4.
13. Bohren, C. F. and Huffman, D. R., *Absorption and Scattering of Light by Small Particles*, Wiley, New York, 1983.
14. Aden, A. L. and Kerker, M., *J. Appl. Physics* 22: 1242(1951).
15. Kai, L. and d'Alessio, A., *Particle and Particle Systems Characterization* 12: 119(1995).
16. Braun, J. H., *Introduction to Pigments*, Federation of Societies for Coatings Technology, Blue Bell, PA, 1993, p. 16.
17. Fields, D. P., Buchacek, R. J., and Dickinson, J. G., *JOCCA* 1993(2): 87(1993).