

Developing optical efficiency through optimised coating structure

BT Hallam and A G Hiorns

⊕ KAOLIN

⊕ GCC

⊕ PCC

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IMERYS Minerals Ltd,
Par Moor Centre,
Par Moor Road,
Par, Cornwall,
PL24 2SQ, UK

Benny.hallam@imerys.com

ABSTRACT

Controlling the optical performance of coated papers requires detailed understanding of the coating structure in the finished paper. Careful design of the particle size distribution (PSD) of the constituent pigments enables very different pore structures to be created within the mineral matrix. It is this complex mineral/void matrix which dictates the interactions with incident illumination and gives the visual appearance to the finished sheet. In this work we vary parameters that underpin coating structure in a very controlled manner in order to explore in detail how coated paper optics can be controlled through suitable pigment choice. We concentrate on structures comprising calcium carbonate pigments, which are broadly isometric in dimension, in order to simplify the understanding and include a wide gamut of sizes and PSD widths to cover the likely industrial workspace. The work highlights that different pigments give rise to very different optical efficiencies, suggesting that equal optical performance may be obtained in lighter sheets through suitable pigment choice.

INTRODUCTION

Mineral coating layers are used extensively in the paper industry to control the visual appearance of paper and the interaction of printing inks with the substrate.

The optical appearance is a result of a combination of factors. These include the particle size distribution (average size and width of distribution) and shape of the mineral which affects the ability of the coated paper to scatter light across the visible waveband. Additionally, mineral choice and the presence of impurities might affect the light absorption profile of the finished sheet [1]. While light absorption enables sheet opacity to be generated, it can be detrimental to sheet brightness, whiteness and shade since photons are removed from the composite system and can no longer form part of the integrated reflectance from the paper.

Light scatter, by comparison, enables opacity to be generated by preventing photons from passing through the sheet. Since these photons may be scattered into the observer half-space they also contribute to the resultant sheet brightness, and whiteness. Light scatter provides versatility to the paper maker since he is able to target additional brightness or trade some of the additional reflectance for opacity and/or colour shade through the use of dyes. For this reason, light scatter, rather than absorption, is a key target for the development of paper optics.

In practice this means engineering the coating structure to provide the most efficient light scatter generation [2-6]. For pigment additives such as TiO_2 , which are used sparingly at low volume concentrations, this is a relatively easy process (in theory) since it is purely a matter of optimising particle size for the given material index of refraction [7, 8]. There are plenty of theoretical models available [9] that will enable the light scatter from discrete particles to be calculated, and the optimisation in practise becomes purely a commercial balance between the cost performance and ease of manufacture. For pigments such as ground calcium carbonate (GCC), precipitated calcium carbonate (PCC) and kaolin the picture is more complicated. This is because these pigments are used in much greater concentrations and actually form the basis of the mineral/void coating matrix. As such they dictate the size and spacing of the scattering units, the air voids [10-14], as inter-dependent parameters. As a result, optimisation becomes a delicate balance between defining the most efficient light scattering units in terms of size, number density and separation.

For the paper maker, a decision must be made in balancing the idealised performance of the speciality additive against the less expensive, but slightly compromised, performance of the bulk pigment.

For the bulk pigments, conventional wisdom might suggest that the optimisation process should still centre on defining the optimal size of the scattering unit. In the coating matrix, it is the air voids which become discrete units surrounded by a matrix of pigment. However, making larger air voids also requires coarser pigments, which leads to a lower number density of scattering sites. An alternative approach is to compromise on optimising the size of the scattering unit and instead target the largest number density of scattering sites. In practise this means reducing the separation between coating pores. However, it has long been known that reducing the separation between scattering sites can introduce the problem of ‘optical crowding’ where adjacent sites no longer act as discrete entities, but interact with the incident radiation as a paired, or composite system [15-17]. Such an effect acts to reduce the optical efficiency of the individual elements since the combined system is not optimised in terms of size.

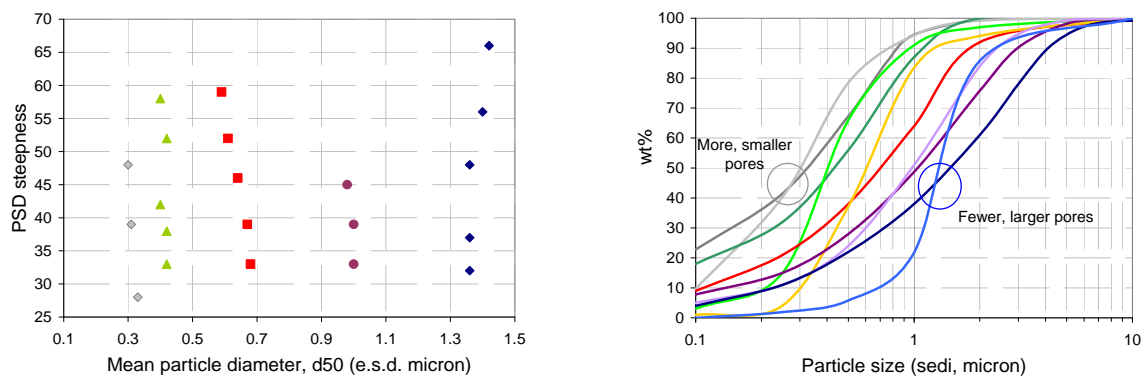


Figure 1 (a) – matrix of pigments coated in the study, allowing the effect on coating structure of changes of D50 and PSD steepness ($D_{30}/D_{70} \times 100$) to be studied independently; (b) by blending broad and narrow distribution pigments with matched D50 enabled the matrix of coating pigments to be controlled

In this paper, the fine balancing act between scattering centre size, separation and number density is investigated, including examination of the onset of optical crowding. Model pigment sets with controlled median particle size (D50) and PSD widths have been developed and coated onto a paper base sheet. Through suitable blends of broad and narrow distribution carbonates, an extensive set of pigment system parameters has been investigated, enabling the effect on coating structure of PSD steepness (parameter associated with the width of the size distribution) and D50 to be evaluated while keeping other pigment parameters constant. By blending with carefully selected PCC particles, narrower width PSD systems have also been included, as shown in Figure 1(a) and (b).

In a complimentary study, the onset of the phenomenon of ‘optical crowding’ has been investigated. As part of the process involved with optimising light scatter, it is important to achieve a balance between maximising the number density of scattering sites and keeping adjacent centres sufficiently separated so that they do not take on the characteristics of a single, larger, particle. This process is often termed optical crowding.

For the papermaker, an often disparate set of additional performance targets such as gloss generation and print performance must also be balanced against that of achieving optimal light scatter. Gloss, for example, becomes a balance between ensuring good coverage of the base fibres and obtaining a locally micro-smooth surface. The former condition requires pigments that may be coarser or platy in nature, while the latter may require relatively fine particles. It is the combination of these varied requirements that usually determine the papermaker’s ultimate requirements.

EXPERIMENTAL DETAILS

Broad and narrow distribution pigments were carefully selected so that they had near equal pigment D50 by Sedigraph™. By blending these partner pairs in carefully controlled ratios, a wide range of PSD steepness ($D_{30}/D_{70} \times 100$) was experimentally accessible, all with matched average particle size. By means of reference, standard commercial GCCs tend to exhibit steepness values of approximately 34, while commercially available engineered-PSD GCC with a similar 2-micron count has a steepness value of approximately 45. The steepness range of 28 to 66 assessed in this study, therefore, represents a full range of values. In practice this meant selecting a broad distribution GCC and a narrow distribution rhombic PCC for the blends. For systems in which no PCC was available, it was replaced with an engineered-PSD GCC with the specified D50 for the purposes of blending. Such an example may be observed for the blends at $D_{50} = 1.0\mu\text{m}$, with the obvious draw-back on the limit of accessible steepness values.

By carefully selecting pigment pairs with strongly different average particle sizes (the range employed in this study covered 300nm to $1.5\mu\text{m}$), very different coating structures are produced, enabling the effect of critical parameters to be studied. For example, for similar pore volume systems, a coarse D50 system will contain a smaller number of larger individual pores, while a fine D50 system will contain a larger number of finer individual pores.

The pigments were formulated with 10pph Dow 920 latex and 0.5pph FF10 CMC to make the coating colour. A HeliCoater™ with a pond head was used to apply a range of coat weights for each coating colour at 800m/min onto a 52gm^{-2} woodfree base. The application was performed using a 0.381mm thick blade set with a 2cm extension, at 45° . Some of the coated papers were calendered using a Perkins laboratory calender with steel (20cm diameter) and cotton (30cm diameter) rolls for 10 nips at 87Kgcm^{-2} pressure and 65°C at $36\text{m}\cdot\text{min}^{-1}$.

The calendered and uncalendered papers were conditioned at 50% relative humidity and 23°C for 24 hours before measuring their optical characteristics using an Elrepho 3300 spectrophotometer with D65/10 illumination. The data were later interpolated to a common coat weight of 11gm^{-2} . Kubelka-Munk theory [18, 19] was used to calculate the coating layer light scattering coefficient (S) and light absorption coefficient (K).

A Pascal 140/240 mercury porosimeter was used to characterise the pore structure of the calendered and uncalendered coating layer for each different coating colour, by analysing the papers exhibiting a coat weight closest to the target 11gm^{-2} (examples existed for all colours which had a coat weight of $11 \pm 0.5\text{gm}^{-2}$). The pressure range employed during the characterisation was 0-190MPa. Corrections for compression of the mercury, glassware and oil phase were made by running a blank. A curve fitting program was then employed to extract the signal corresponding to coating layer pores.

The coating pore structure measured by mercury porosimetry was characterised in terms of total coating pore volume and average pore diameter by fitting the data to theory [20]. By modelling the total measured pore volume as an array of discrete cylinders with a diameter equal to the measured average pore diameter enables the number density of pores to be ascertained [21].

Optimising the Size of the Scattering Unit

By assuming that the principle light-scatter units in the coating layer are in fact the voids (or pores) within the pigment matrix [10-14], it is possible to calculate the average light scatter contribution from each individual void. Examining the light scatter contribution from individual voids removes the confusion associated with differences in the number of scattering sites between different pigment sets. Plotting the individual light scatter contribution from individual pores as a function of pore size enables the optimal individual pore size to be elucidated. Figure 2 shows the excellent trend between different pigment systems and leads to conclusive evidence that the optimal void size for individual pores is approximately 420nm, in agreement with simple Mie theory [22].

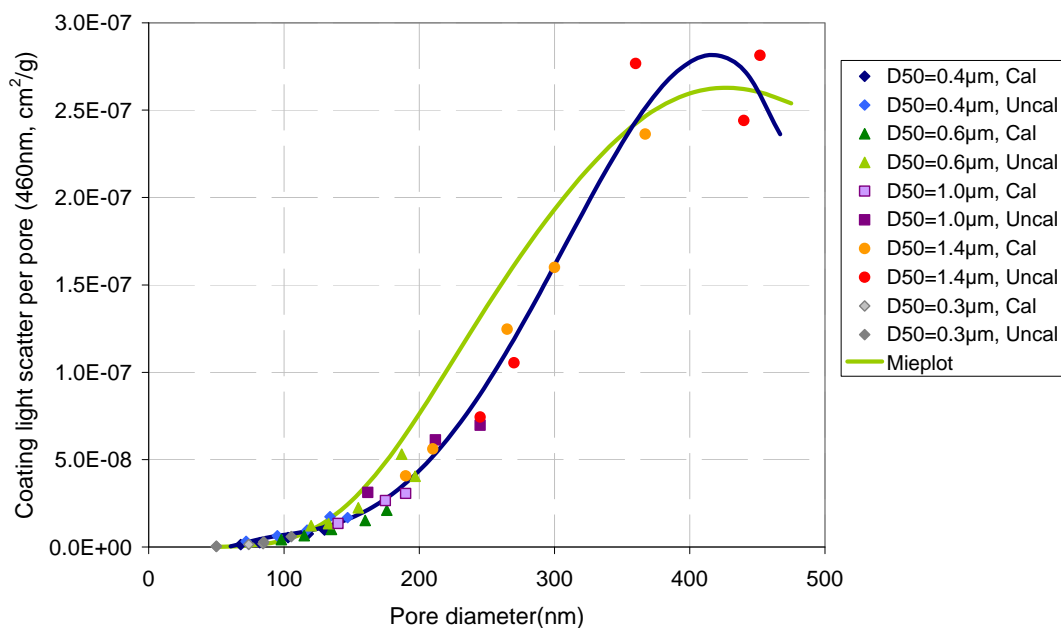


Figure 2 – Light scatter contribution per air void; data points show experimental data, solid blue line is a fourth-order polynomial fit to the experimental data and is included as a guide the eye, solid green line is the predicted response according to Mie Theory (scattered intensity, arb. units) and gives fit to data with $R^2 = 0.94$

In order to compare the experimental data shown as points in Figure 2 with theoretical predictions, the light back-scattered from discrete air voids in a matrix of solid calcium carbonate was calculated using Mie Theory. The air voids were modelled as having a log-normal distribution of sizes about the average pore size, the calcium carbonate was modelled with a refractive index of 1.5, and the incident illumination was set to 460nm. The scattered radiation was calculated as a function of collection angle and the portion back-scattered into the observer's half-space (90° to 270°) was integrated and plotted. This modelling represents only light that was scattered back towards the observer and would hence constitute the reflected signal, assuming only single scatter interactions.

The excellent agreement with theory (fit to data demonstrates $R^2 = 0.94$) which peaks for voids of 425nm diameter is, perhaps, rather surprising. The model assumes that each void is suitably spaced from its neighbours so as to act as an independent entity, and that no multiple scattering events occur, which is not representative of the real system. The model also assumes (as does the treatment of the experimental data) that the pigments themselves provide a much smaller contribution to the observed sheet light scatter potential. Perhaps the promising nature of the comparison with theory provides further evidence that this assumption is valid. Previous work by Gate [11] has shown that a maximum in light scatter for narrowly-cut particle size fractions of kaolin give a peak in light scatter for pore diameters between 300 and 440nm depending on incident wavelength, while Climpson and Taylor [23] showed that voids in the range 300nm to 700nm gave the largest contribution to light scatter, also in kaolin films. While both these studies give broad agreement with the current work, no attempt was taken to control the inter-particle spacing between the sample sets, introducing the possibility of differences in number density of scattering centres.

Optimising the Number Density of Scattering Units

However, the individual void volume is only part of the complexity in such composite systems. In order to achieve such large independent void diameters in carbonate systems, a relatively steep and coarse pigment system must be employed. The coarser D50 associated with such systems inevitably leads to a lower number density of scattering sites since there is a greater spacing between voids (the physical dimensions of the separating pigment is larger).

Indeed, as shown in Figure 3, the number density of voids can be seen to diminish with increasing individual pore diameter as a power law. The line of best fit to the data gave an $R^2 = 0.97$ with an exponent equal to -2.8 .

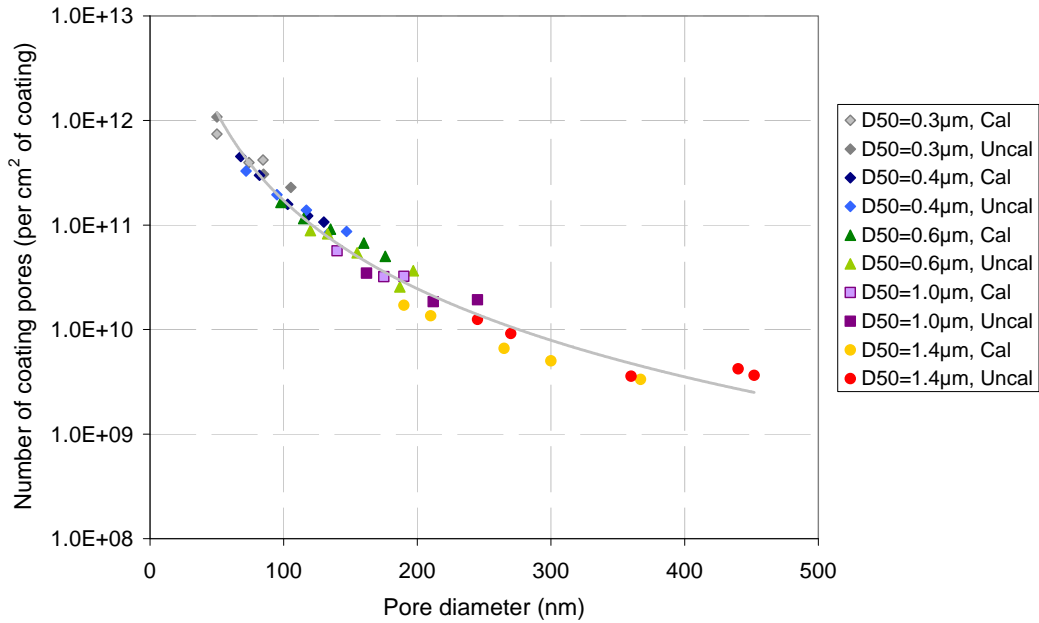


Figure 3 – Number density of scattering sites as a function of average scatter site diameter; data points show experimental data, solid grey line is a power law fit to the data with the equation: $y = (7 \times 10^{16}) x^{-2.8014}$ and $R^2 = 0.97$

Indeed, Figure 4 demonstrates that the number density of scattering units is maximised for very fine pigment systems with a broad PSD. The data has been fitted using a curved surface of the form given in the figure caption.

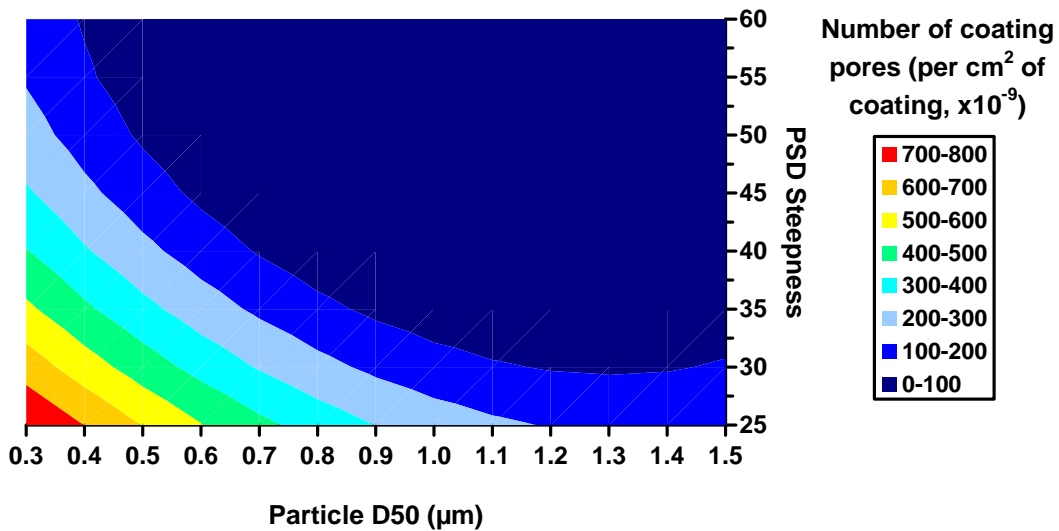


Figure 4 – Number density of scattering sites as a function of typical pigment parameters, data is fitted with $z = Ax + Bx^2 + Cy + Dy^2 + Exy + F$ (with A – F constants), which gives an $R^2 = 0.81$

Optical Crowding

By assuming the pore structure in the mineral coating layer may be described as an array of discrete cylinders, the average spacing between pores may be calculated by comparing the average individual pore volume with the measured porosity of the coating layer. This approach demonstrates that the system complexity is further complicated by the possibility of optical crowding. Indeed, those systems that demonstrated the highest number density of voids also demonstrate very small average separation between pigments, as shown in Figure 5.

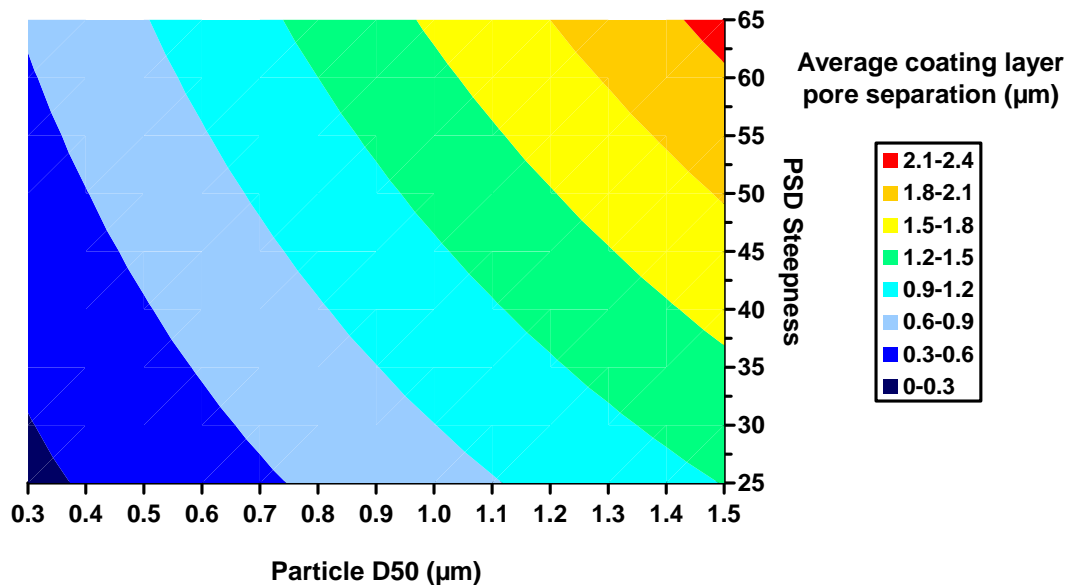


Figure 5: Average pore separation (μm) as a function of typical pigment parameters, data has been fitted to a curved surface defined by $z = Ax + Bxy + Cy + D$ (with A-D constants), which gives an $R^2 = 0.96$

To understand better the importance of optical crowding in paper coating systems a complimentary coating exercise has also been undertaken. To remove system complexity, blends of TiO_2 (DuPont RPS Vantage) with a solid plastic pigment (Dow 722HS) were coated in different blend ratios. The plastic pigment was carefully selected to ensure that it had a D50 that closely matched that of the TiO_2 (average D50 = $0.42 \pm 0.03 \mu\text{m}$). Since the plastic pigment was almost mono-sized, and the TiO_2 has a very steep PSD, the system may be considered as a reasonably close approximation to a set of mono-sized spheres, in which different blend ratios are characterised by greater or lesser displacement of one species by another.

Pigments were formulated with 10pph Dow 920 latex to make the coating colour. Coating was performed by draw-downs of the suitably diluted (typically 40-50% solids) coating colour with a wire-wound draw-down bar onto Yupo plastic paper (Yupo Europe, GMBH). In practise, colours were diluted until smooth, ripple-free coatings were obtained and were dried by blowing warm air across the coated surfaces. Again, a range of coat weights were prepared to enable interpolation of results to a common coat weight of 10gsm.

To remove the complexity due to air voids within the coating layer, the coated papers were immersed in a suitably mixed index-matching fluid to optically match the plastic pigment, leaving the TiO_2 pigments in an otherwise homogenous medium. The fluid was a blend of mineral oils, carefully mixed to minimise the reflection from the fluid-saturated sheet as measured in an ATI Unicam UV4 uv/visible spectrometer. The point of minimum reflection occurs when the fluid fills the pore structure in the paper coating and is optically-matched to the coating minerals. The different blend ratios effectively act to provide different spacing for the TiO_2 particles in a controlled manner according to the pigment volume fractions. By modelling the system as a hexagonally-close-packed (HCP) system of spheres and randomly filling the available sites with TiO_2 according to the volume fractions specified by the blend ratios, the average separation of individual TiO_2 particles can be calculated by taking into account the packing

co-ordination number and the number of nearest neighbours at each ‘lattice’ point. Such an approach is considered reasonable in this instance given the relatively close D50 values of the partner pigments and near mono-sized nature of the system.

This study enables the light scatter contribution from individual TiO₂ particles to be calculated as a function of average adjacent particle separation. Average particle separation was calculated by considering the volume concentration of the first complete particle as modelled using the randomly-populated HCP lattice. The data in Figure 6 shows clearly the separation at which optical crowding occurs and the light scatter contribution from individual scattering units starts to diminish. Comparing this separation with those calculated from the carbonate blends suggests that optical crowding is likely to be an issue with some of the coating systems studied.

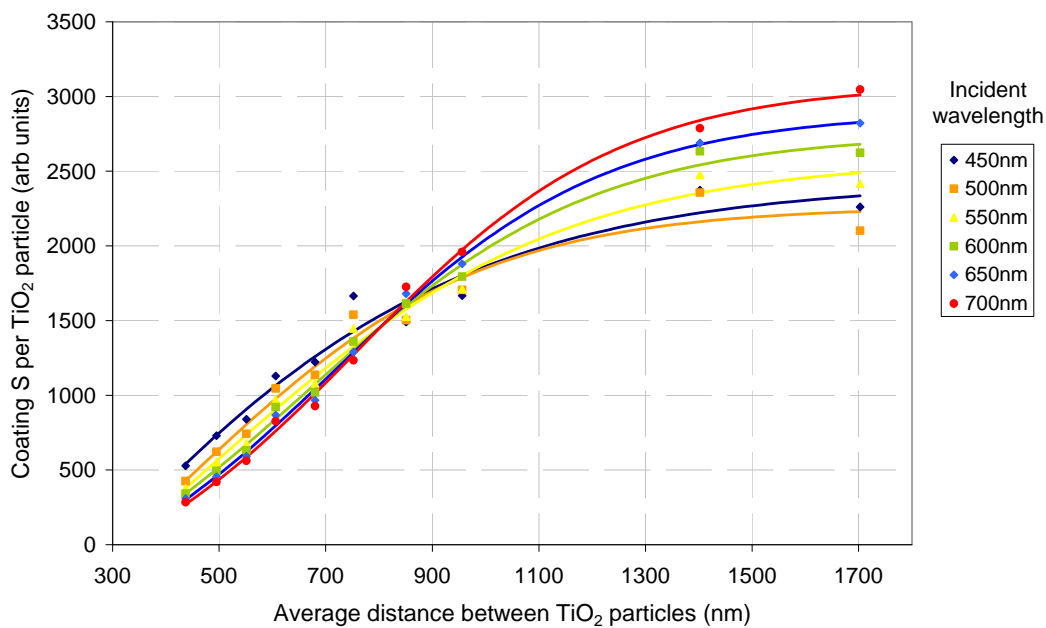


Figure 6 – The light scatter contribution from individual TiO₂ particles as a function of average particle separation for a series of different incident wavelengths

Figure 6 clearly shows that when the separation between individual TiO₂ particles becomes too small, the light scatter contribution from individual particles diminishes due to optical crowding. The point at which this occurs is for particle separations of less than approximately 0.9-1.3 μ m depending on incident wavelength. This distance is the equivalent of approximately 2.0 free-space wavelengths in the middle of the visible waveband (of course this corresponds to approximately 3.1 wavelengths within the surrounding material, assumed to be $n=1.57$). This value is approximately 20% higher than theoretical modelling reported in [15] which suggests that the on-set of optical crowding occurs when the surface-to-surface distances between particles falls lower than the wavelength of light within the medium. Comparing this result with the data presented in Figure 5 suggests that all but the very steep and coarse pigment systems will be subject to some degree of optical crowding. Obtaining good light scatter from such systems requires a balance to be struck between the degree of optical crowding and the large number of scattering pores available.

Optimising the Coating System

In order to optimise a full coating system, all the above factors must be carefully balanced. Figure 7 shows how pigment parameters affect the final coating performance.

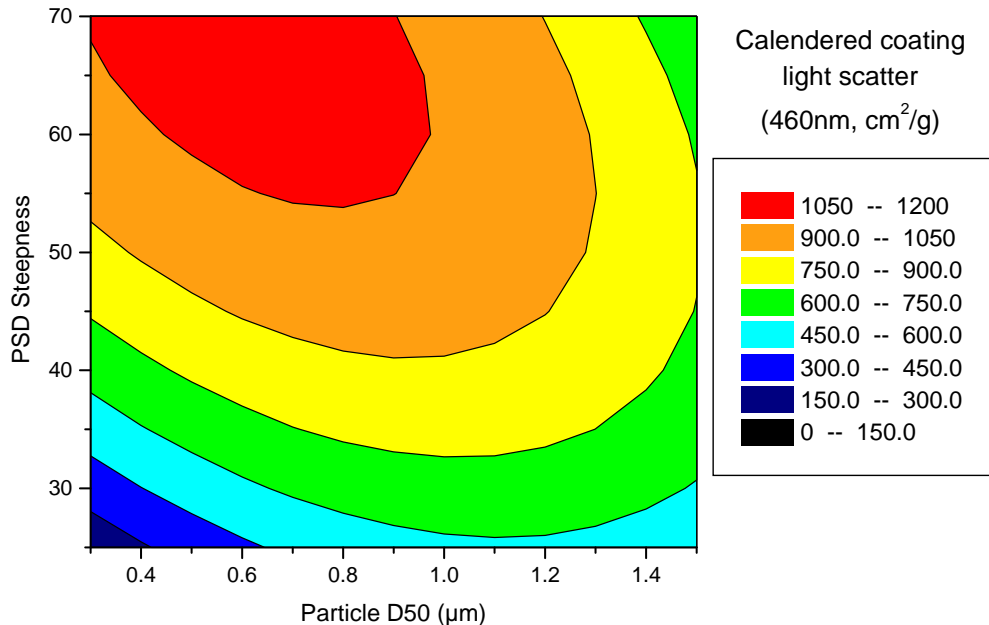


Figure 7 – Calendered sheet light scatter (at 460nm) as a function of typical pigment parameters; experimental data is fitted to a curved surface defined by $z = Ax + Bx^2 + Cy + Dy^2 + Exy + F$ (with A-F constants), which gives an $R^2 = 0.94$

Figure 7 shows the finished sheet light scatter potential as a function of pigment D50 and PSD steepness. The data clearly show the interplay between number density, size and separation of the scattering units created. There is a penalty to pay in terms of light scatter for going too fine in particle size, as the contribution from each individual void becomes so small that it can not be compensated by the increase in the void number. Likewise, the more optimally sized voids created by the steep, coarse pigments also suffer in finished sheet light scatter, this time due to the low number density of voids.

The data also show that there is a complex relationship between the development of pore size and structure with PSD steepness and D50, as the optimum D50 for light scatter tends to shift depending on PSD steepness – presumably due to subtleties in the shape of the size distribution. It is interesting to note that coatings comprising 100pts solid latex spheres have been shown [24] to provide maximum light scatter with particle diameters equal to 500nm. This qualitatively agrees with our findings as such systems would represent very high PSD steepness as the particles are essentially mono-sized.

CONCLUSIONS

In this paper, the parameters underpinning light scatter generation in mineral coatings for papers have been examined. The work has highlighted the interplay between the size, number and separation of the scattering units – and how optimising the balance between these parameters is necessary for optimising finished sheet optics. These parameters have been linked to pigment parameters which are routinely controlled during manufacture. While this work necessarily concentrates on the generation of light scatter, a functional paper must also satisfy other wide-

reaching technical criteria such as glossibility and print performance. This data has also been recorded, but has not been presented here.

In order to move outside the space examined in the current work (i.e. that corresponding to dimensionally isometric pigment building blocks), it is necessary to consider multi-pigment solutions where more optimised pore sizes located at smaller void separations may be envisaged, enabling a new pore size/separation to be accessed. Such a system might conceivably be accessed by mixing steep carbonate with platy kaolin which would preserve the large void volume, but might reduce the void separation by virtue of being highly anisometric.

ACKNOWLEDGMENTS

The authors are grateful to Matthew Cheeseman and Ian Soper for technical assistance. We also thank the board of Imerys Minerals Ltd for permission to publish this work.

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✦ **Europe**
Tel: +44 1726 818000

✦ **Asia Pacific**
Tel: +65 67 99 60 60

✦ **N. America**
Tel: +1 770 594 0660

✦ **S. America**
Tel: +55 11 2133 0055

Email
paper@imerys.com