Future Coating Designs for Enhanced Optics – Taking Lessons from Nature

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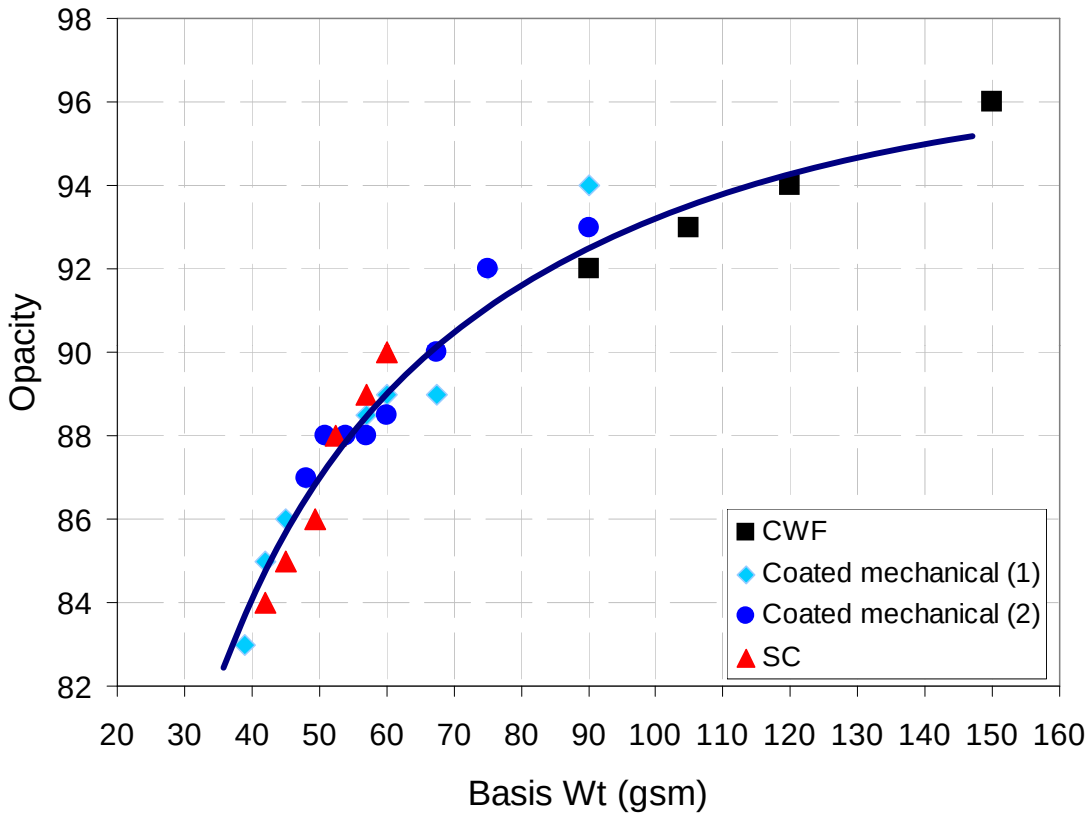
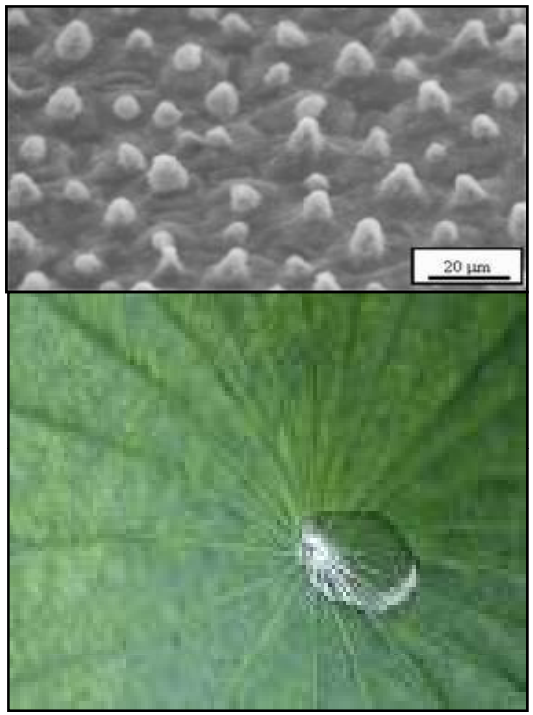
RETHINK PAPER:
Lean and Green

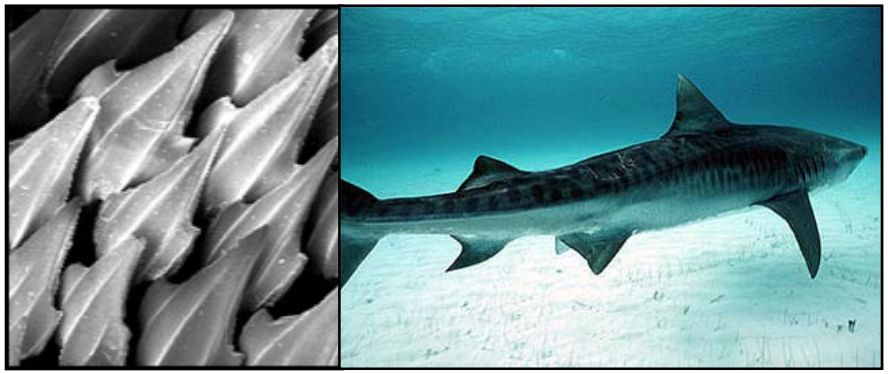
How Do You Make a 50gsm Paper Perform Like a 100gsm Paper?



- As transportation and raw material costs grow, reducing weight/material volume becomes desirable
- However, reducing weight also lowers optical performance
- To break this trend, new concepts are required
- Bio-mimetic studies of white species in Nature could give useful ideas on how scattering structures may be optimised for performance against weight

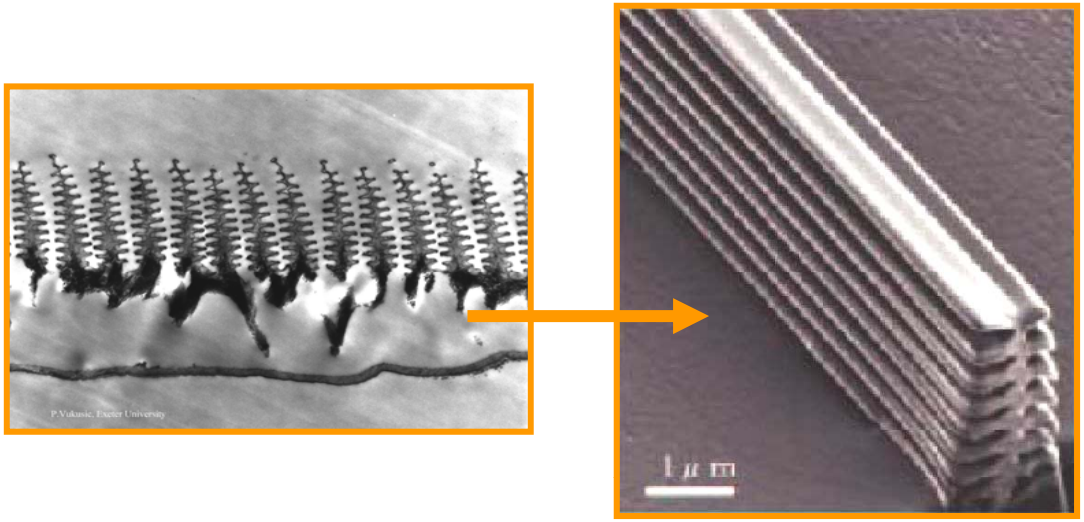
What is Biomimetics?



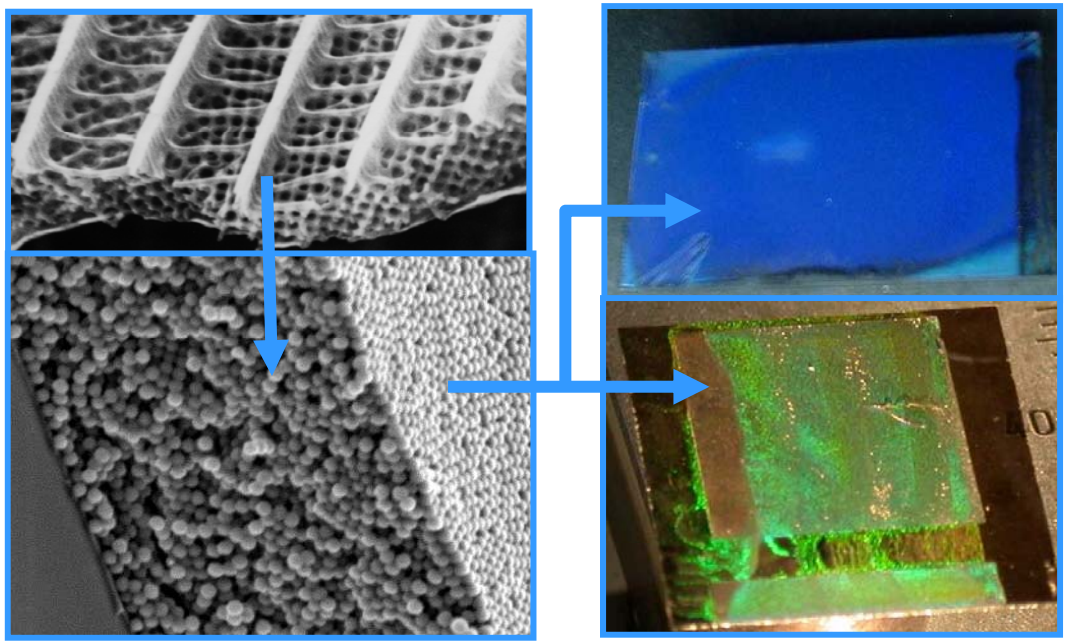


- **Biomimetics is an enabling discipline which looks at Nature for ideas that may be adapted and adopted for commercialisation**
- **Countless iterations of form, driven by function, offer us natural "products" which have undergone extensive development though the process of evolution**

Biomimicry – Optical Solutions



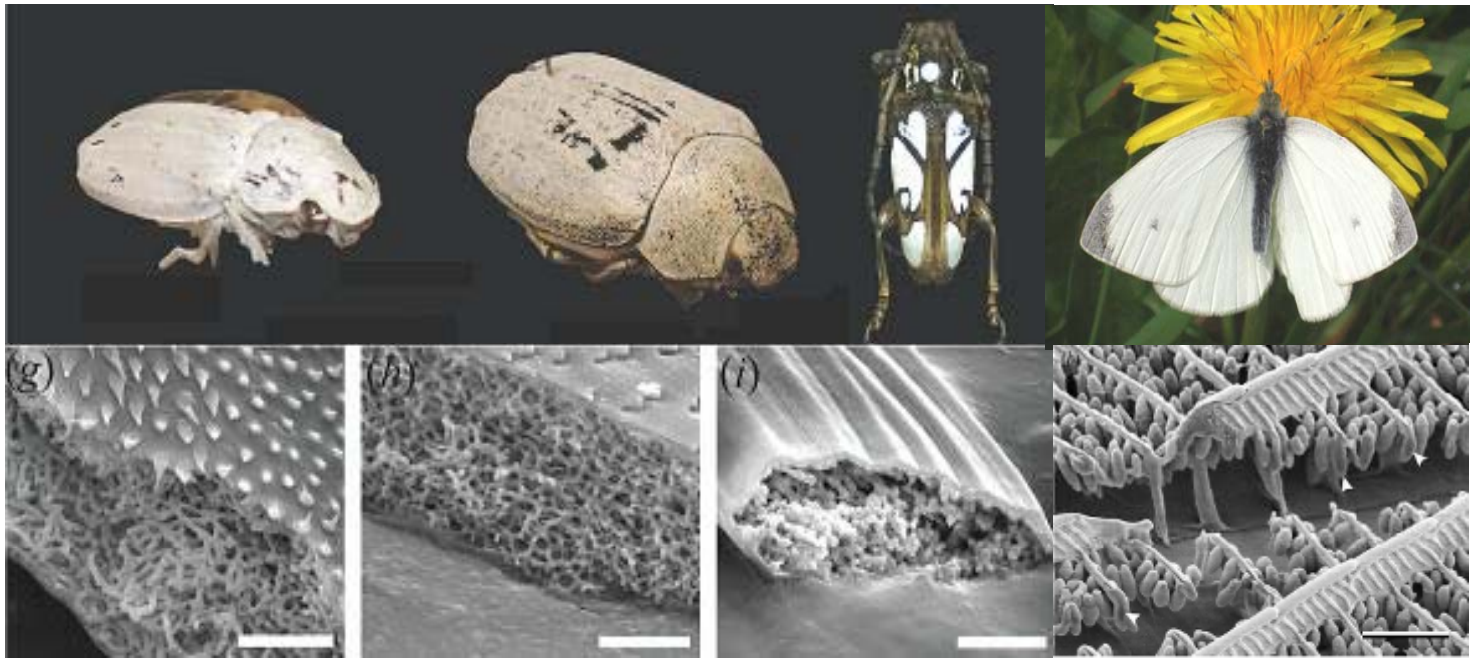
- **Morpho spp. butterfly: high luminance structural colour over wide angle range**
- **K Watanabe *et al.*, Jpn J. of Appl. Phys., 44, L48-L50 (2005)**
- **Fabricated by FIB-CVD**



- **Green Hairstreak butterfly: high luminance structural colour over medium angle range**
- **H Xu *et al.*, Materials Lett., 58 27-28, 3419-3423 (2004)**
- **Fabricated with sol-gel process**

But What About Biomimetic Structural White?

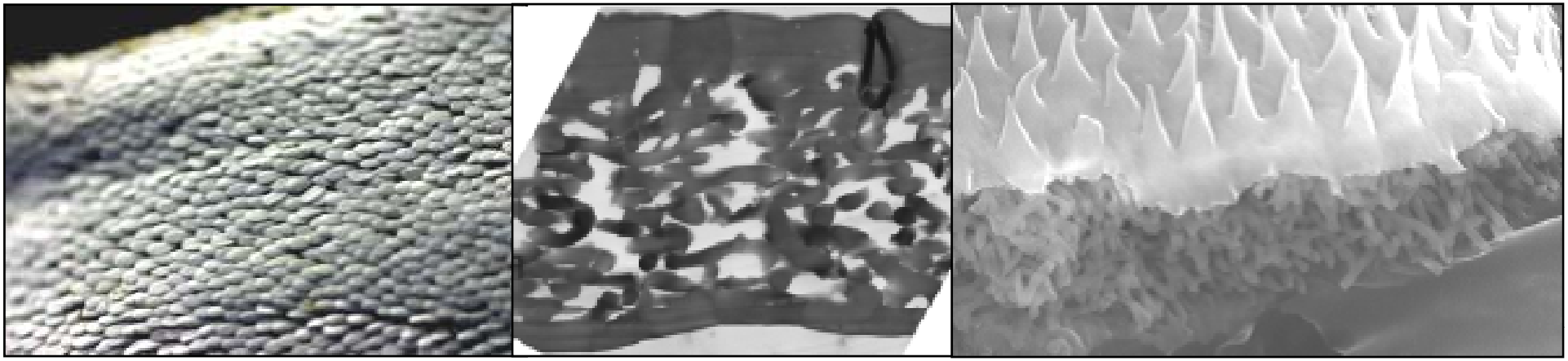
- Nature provides a wide variety of white systems to study
- It is our belief that some of these systems have evolved to produce white in very efficient, lightweight structures
- A number of design concepts are found in Nature:
  - Optimising the size and number density of scattering centres
  - Anisotropic scatter
  - ‘Double-pass’ systems
- Here we present one of the concepts on optimising scattering centres



Optimising the Size and Separation of Scatterers

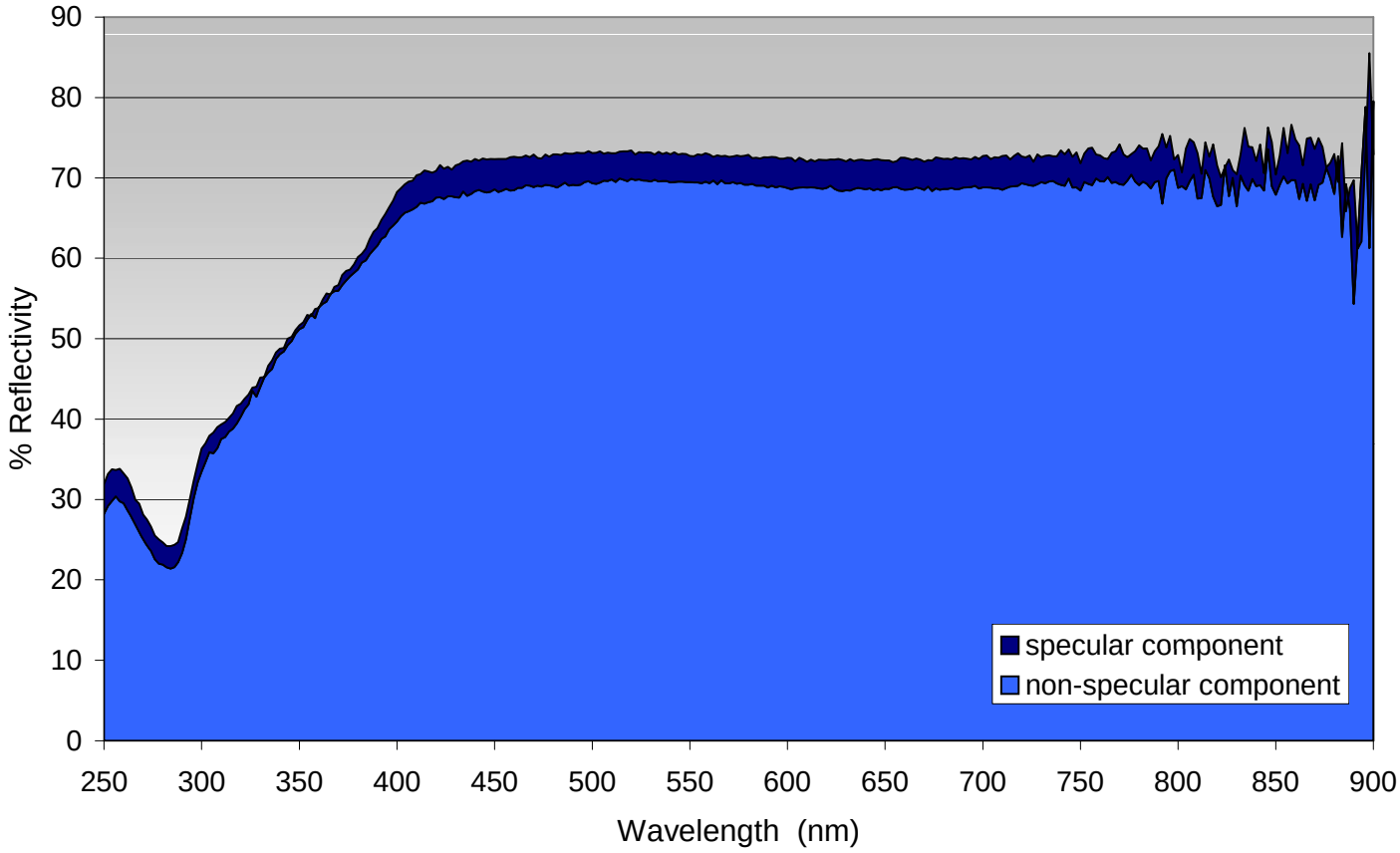
- **S. East Asian beetle (*Cyphochilus spp.*) is covered with a white surface structure**
- **Underneath, it is black**

Cyphochilus spp



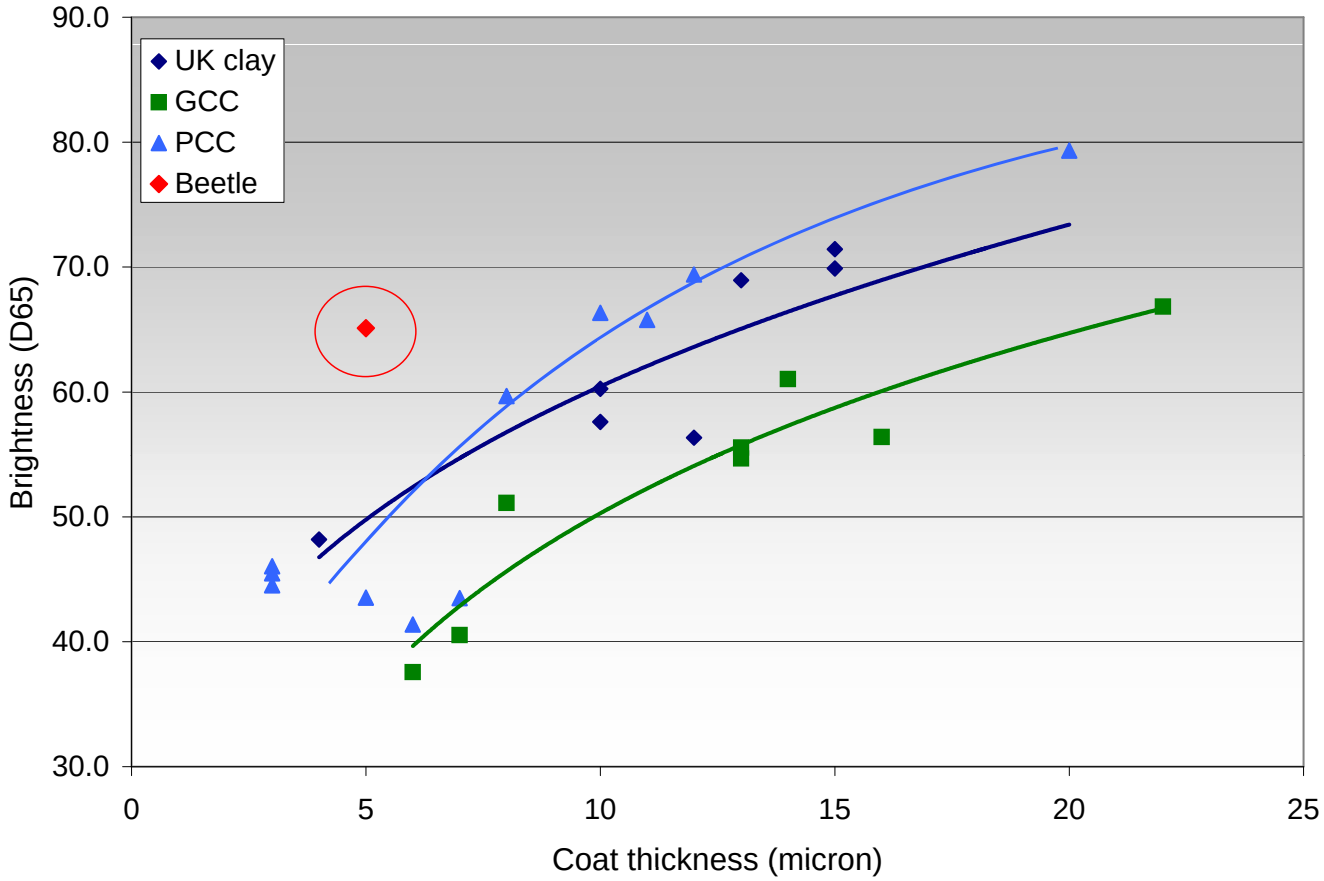
- **Surface covered by small scales**
- **Scales contain a random lattice of interwoven ‘fibrils’ c.250nm diameter**
- **Only 5 µm thick, making it interesting for understanding optical performance/weight relationship**
- **Void volume is ca. 30%, which is high compared to typical paper coating layers (5-10% for 100% clay and 10-20% for 100% CO_3)**

Spectral Response



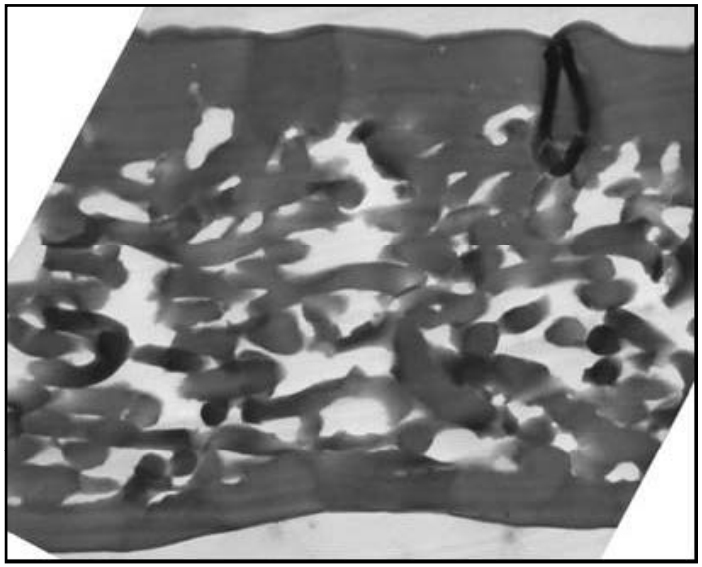
- **UV/VIS spectrometry shows scatter is not biased towards the specular direction (matt, not glossy)**
- **Scatter is also very flat-banded across visible waveband (good physical white)**

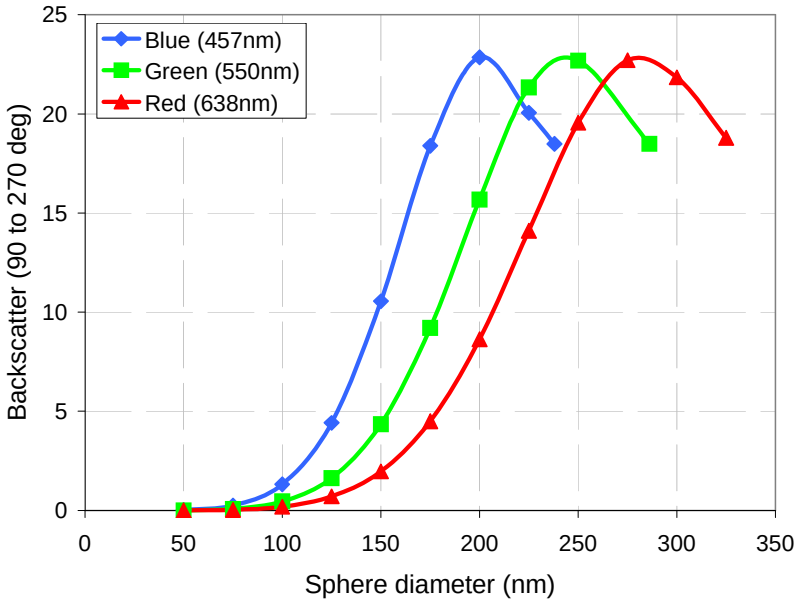
Comparison with Mineral Coatings



- **Beetle outperforms mineral coating layers at same coating caliper**
- **Requires twice the thickness of PCC to match the beetle's optical performance**

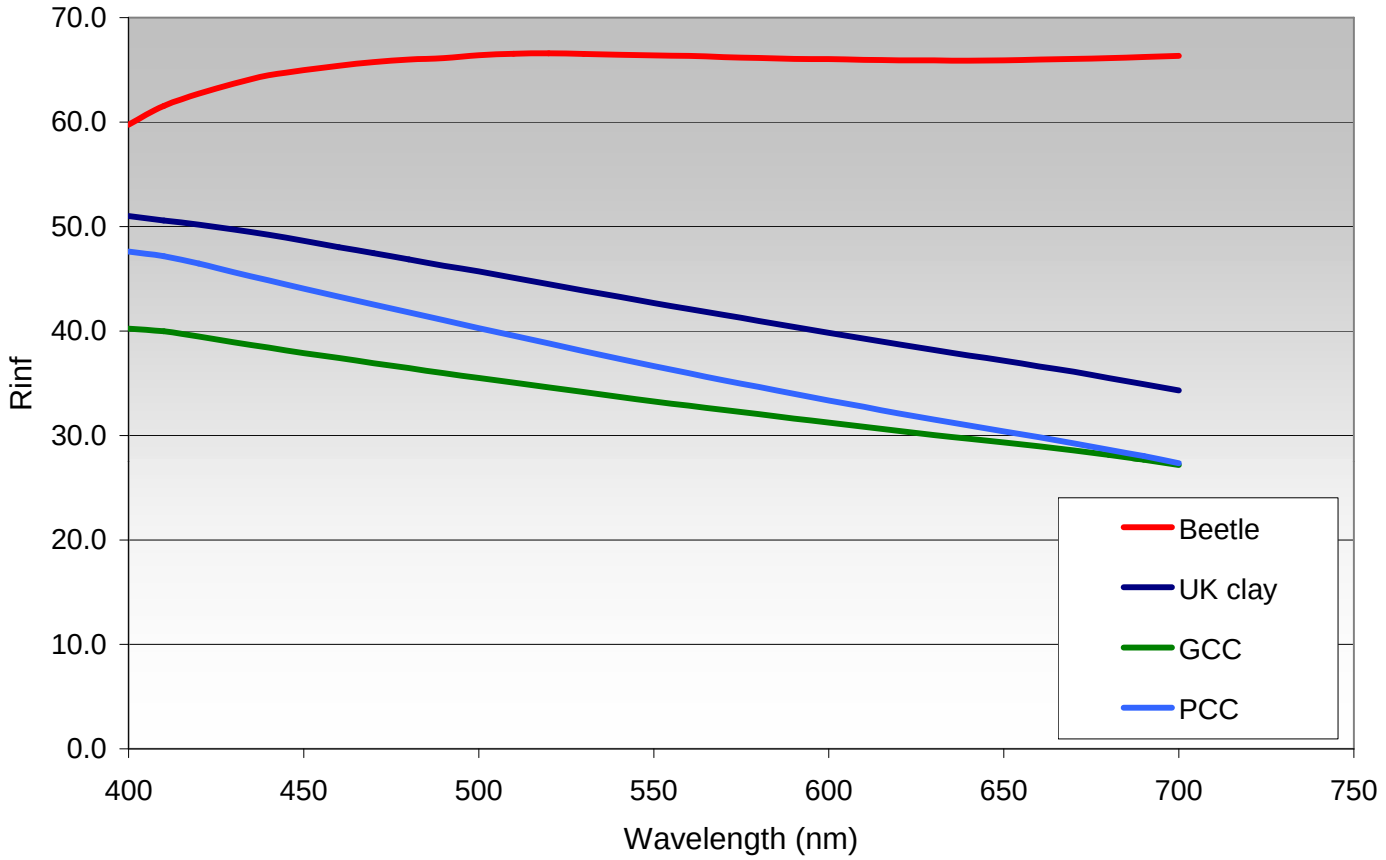
Optimised Size (1/2)





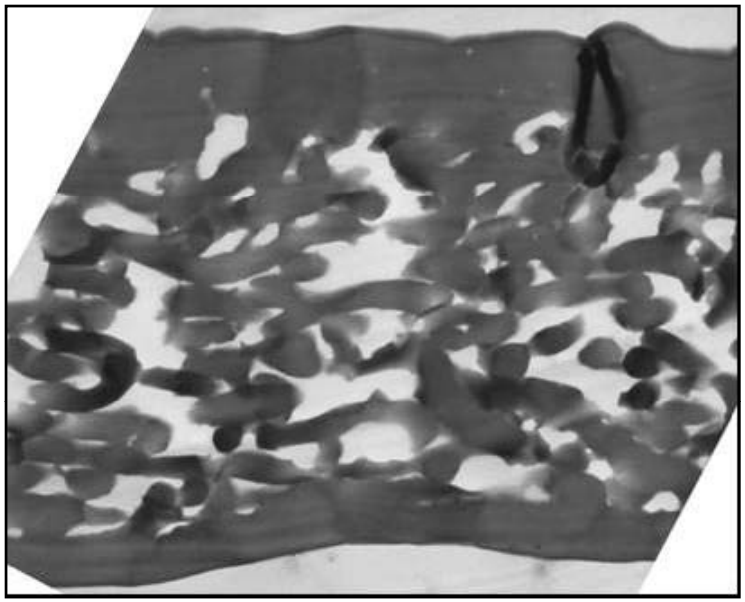
- **TEM cross-sections suggest:**
  - **Fibril diameter = 250+/-50nm**
- **Mie calculations for spherical particles suggest that this fibril cross-section is optimised for 'reflected' light scatter from individual fibrils**
- **Interestingly, larger 'sister' beetle has larger fibrils and gives lower reflectivity**

Optimised Size (2/2)



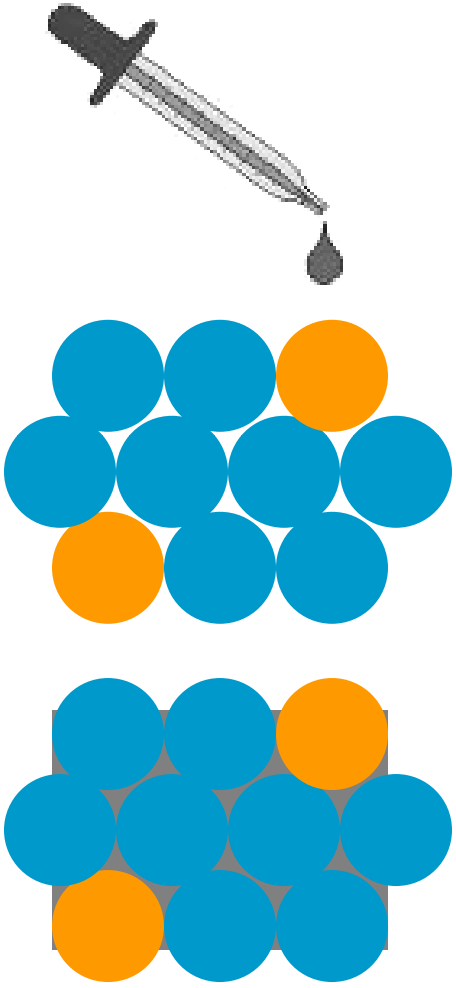
- **The beetle's reflection (D65/10) spectrum shows very different behaviour to the mineral coating layers**
- **Mineral coatings demonstrate wavelength-dependent scatter – suggesting that the pores in coating structure are too small**

Optimised Spacing (1/2)



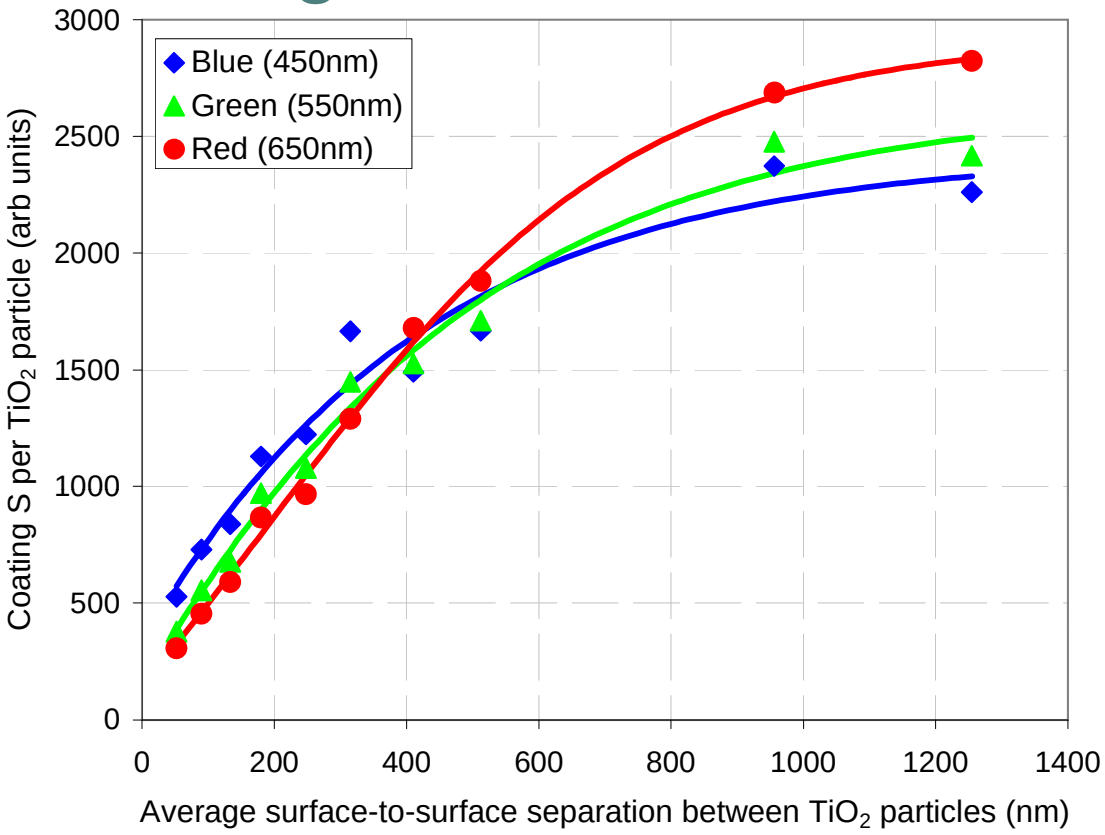
- **TEM cross-sections also suggest:**
  - **Inter-fibril spacing = 600+/-260nm**
- **What is the significance of this dimension?**

Optimised Spacing (2/2)



- **Solid plastic pigment with similar D50 to TiO_2 was selected and blended at known volume concentrations**
- **A refractive index matching mineral oil was applied to optically remove the air/plastic pigment boundary - yielding discrete TiO_2 particles in an otherwise homogenous sheet**
- **With matching D50, and very narrow PSDs, the particle packing may be approximated to hexagonal close packing (at least in local domains)**
- **This enables the average separation of adjacent TiO_2 particles to be modelled while including the impact of the 12 nearest neighbours in the packing structure**

Optical Crowding

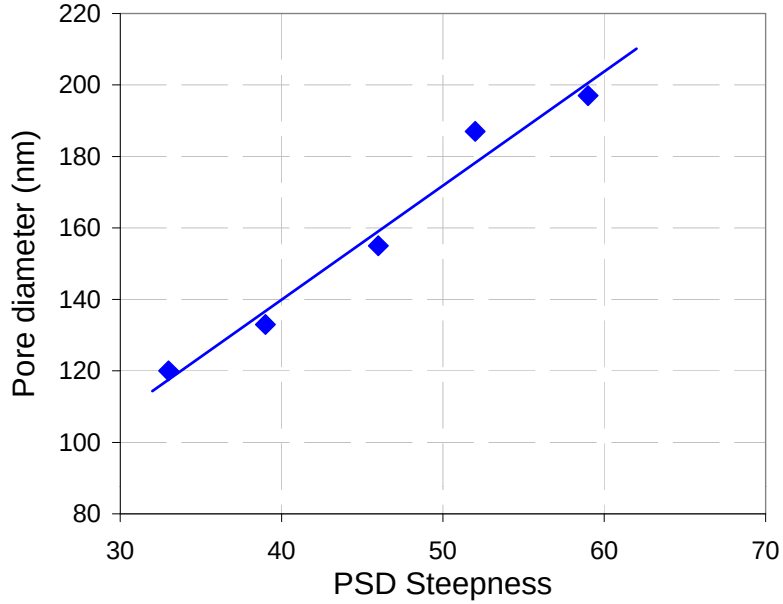


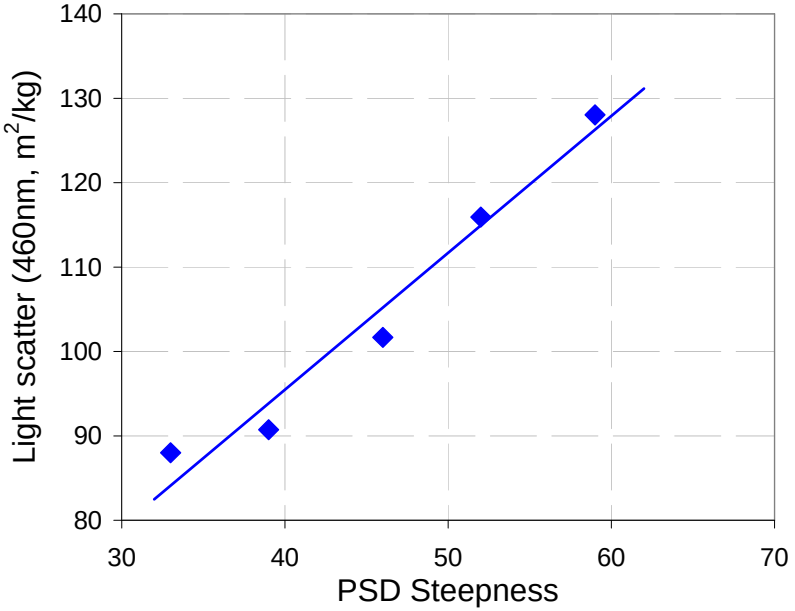
- **As the separation between individual TiO_2 particles becomes smaller, the light scatter contribution from the individual particles diminishes**
- **This process is called 'optical crowding'**
- **The beetle structure is well optimised with inter-fibril spacing of ~600nm; this maximises the number density of scattering elements without compromising their individual contribution to light scatter**

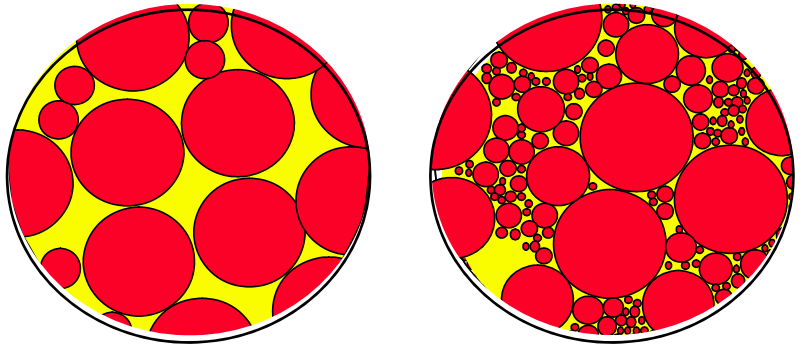
Lessons

- As with all scattering systems, optimisation requires a balance between maximising the number density of scattering units and avoiding ‘optical crowding’
- It is commonly considered that spacing between particles of ca. one wavelength is sufficient to avoid optical crowding
- This requires large void volumes
- What does this mean for pigment design? Narrow pigment size distributions is one way to introduce greater void volumes, but there are others....

Narrow PSD Pigments



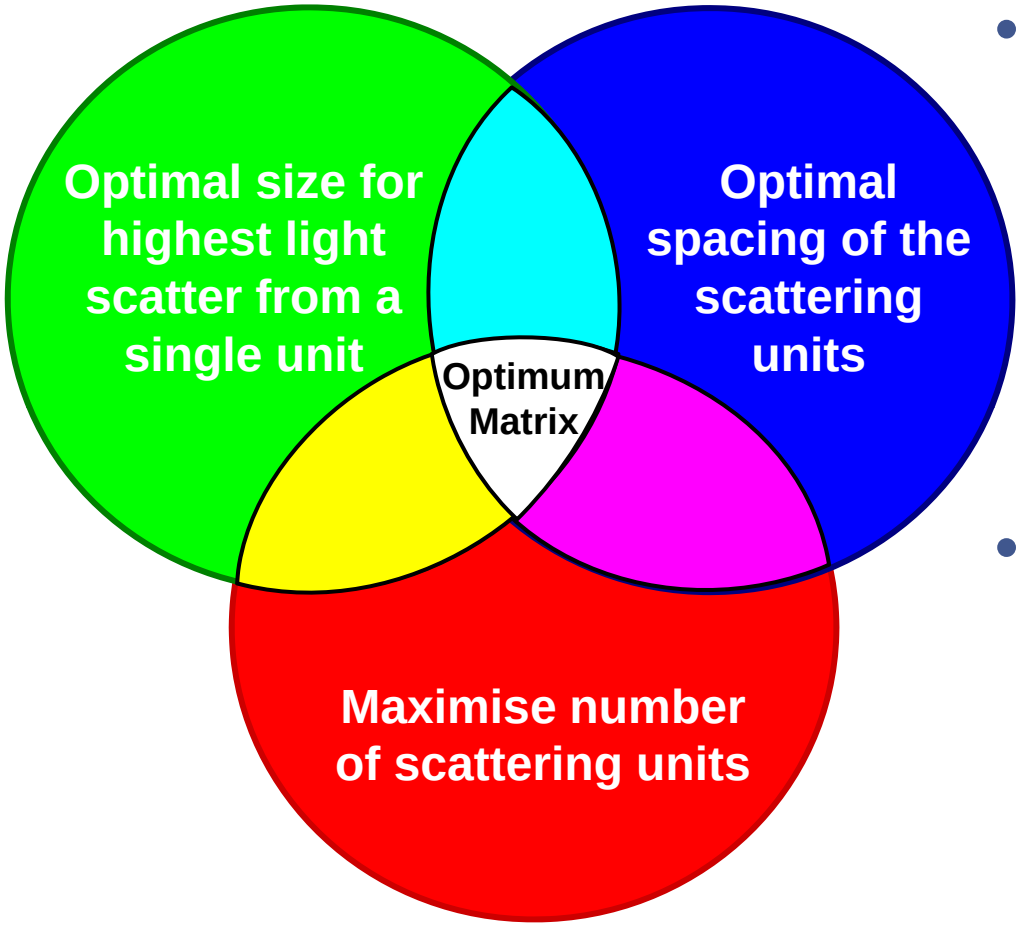




Steeper (narrower) PSD

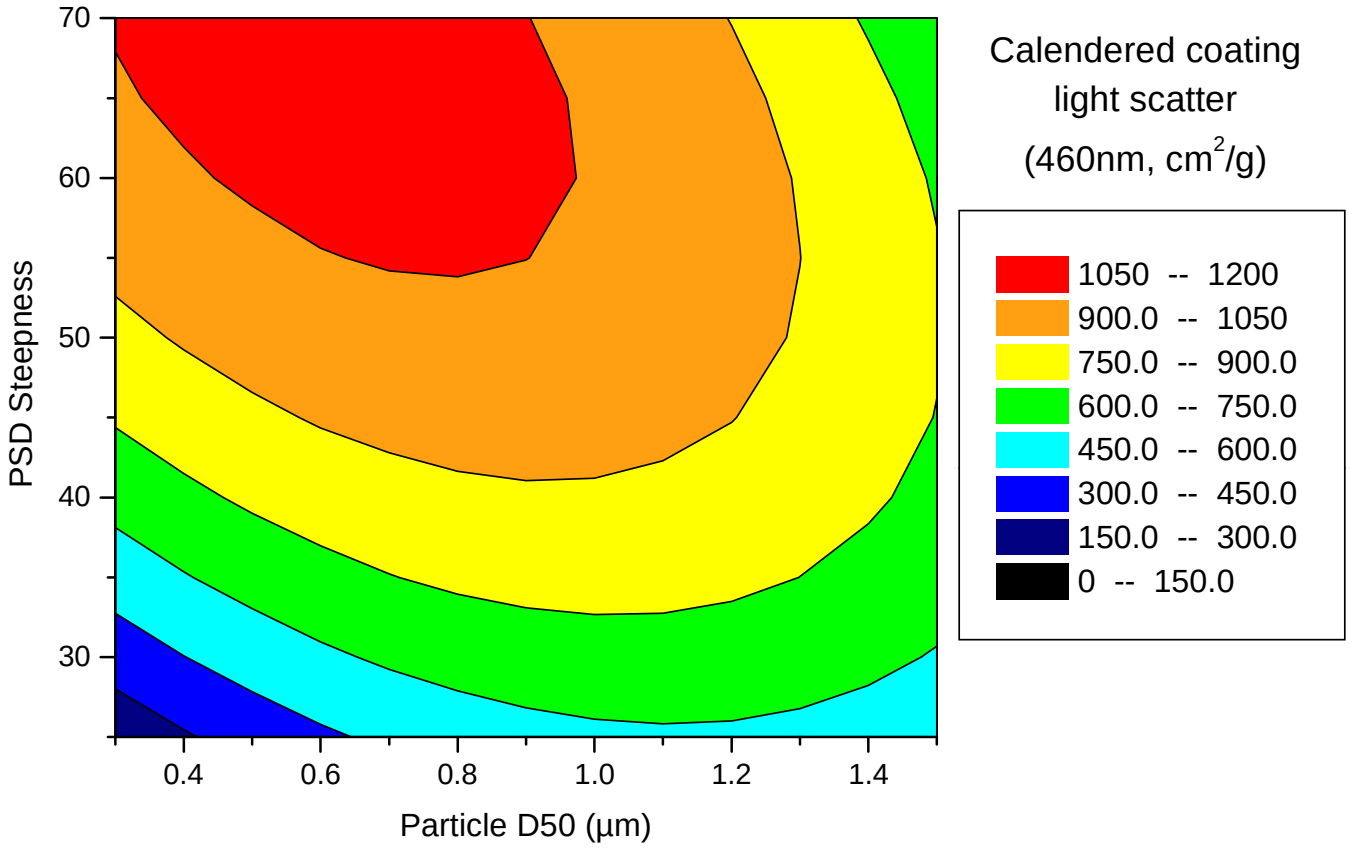
- PSD Steepness is a measure of the range of particle sizes included in a mineral product:
  - A high steepness value means the product contains fewer different particle sizes
  - In mineral coatings, fewer different particle sizes usually means that the particles will pack together to produce larger air pores between adjacent pigment particles
  - Larger air pores tends to generate greater light scatter (and hence optical performance) in the finished sheet

Optimising Light Scatter



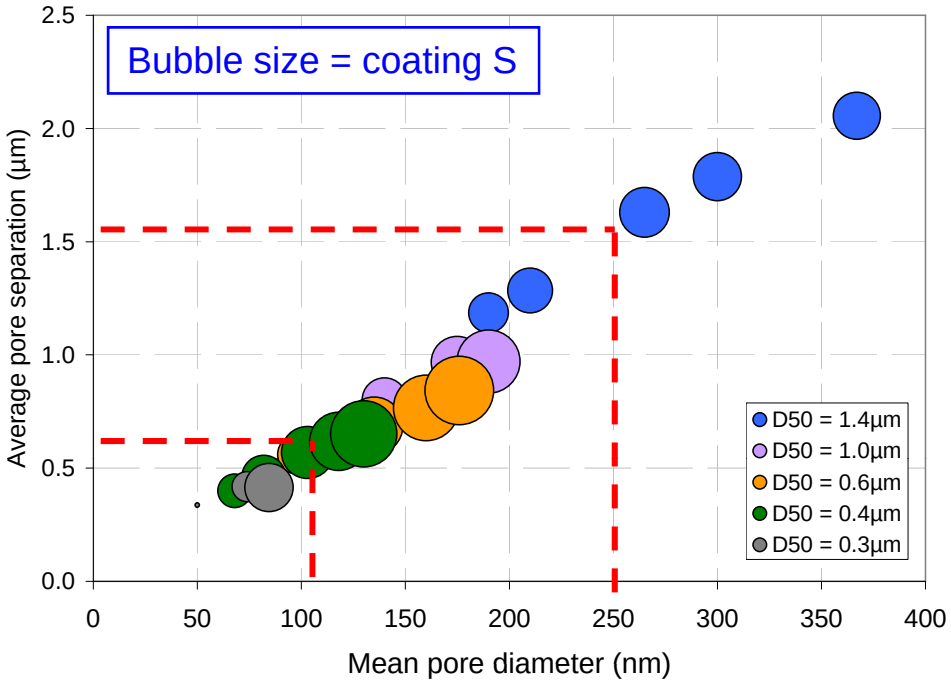
- However, the mineral system becomes more complex
  - Dense packing makes the air voids the scattering unit within a mineral matrix
  - Controlling the void size therefore also changes the spacing and number density
- Optimising scatter in a coating matrix requires a delicate balance between:
  - Getting the pore size right
  - Maximising the number of scattering units
  - Minimising optical crowding

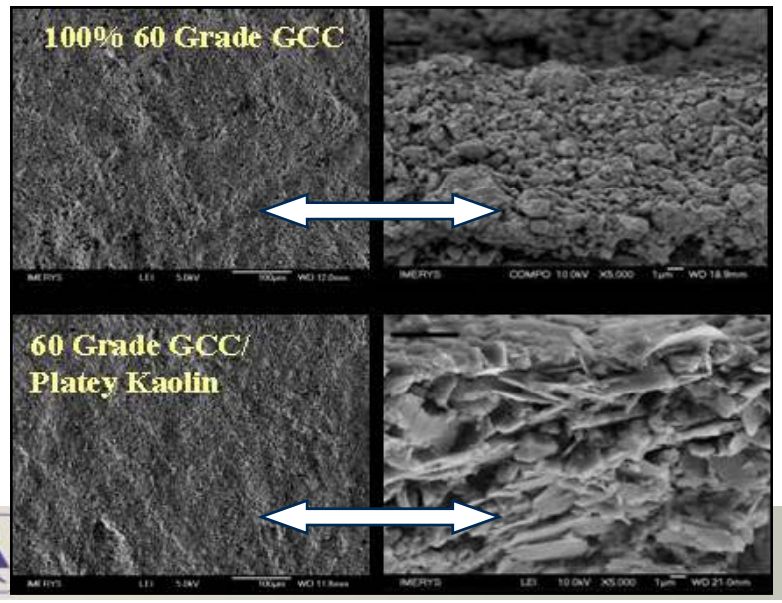
Optimising Light Scatter – Pigments



- **Balancing all of these factors in a mineral coating requires compromise**
- **Truly optimised optics requires the size and spacing of the scattering unit to be separated (as in the beetle), enabling each to be optimised independently – but shape gives us one more parameter**

Optimised Structure Gives Optimised Light Scatter





- **Since the mineral size and PSD control both pore size AND separation in mineral coatings, varying one tends to also vary the other simultaneously**
- **For this reason:**
  - **At 250nm void diameter, S is not optimised because pores are too far apart (not many per unit volume)**
  - **At 600nm inter-void separation, S is not optimised because individual pores are too small**
- **Blending with the correct non-isometric pigments (kaolin) could shift this paradigm**

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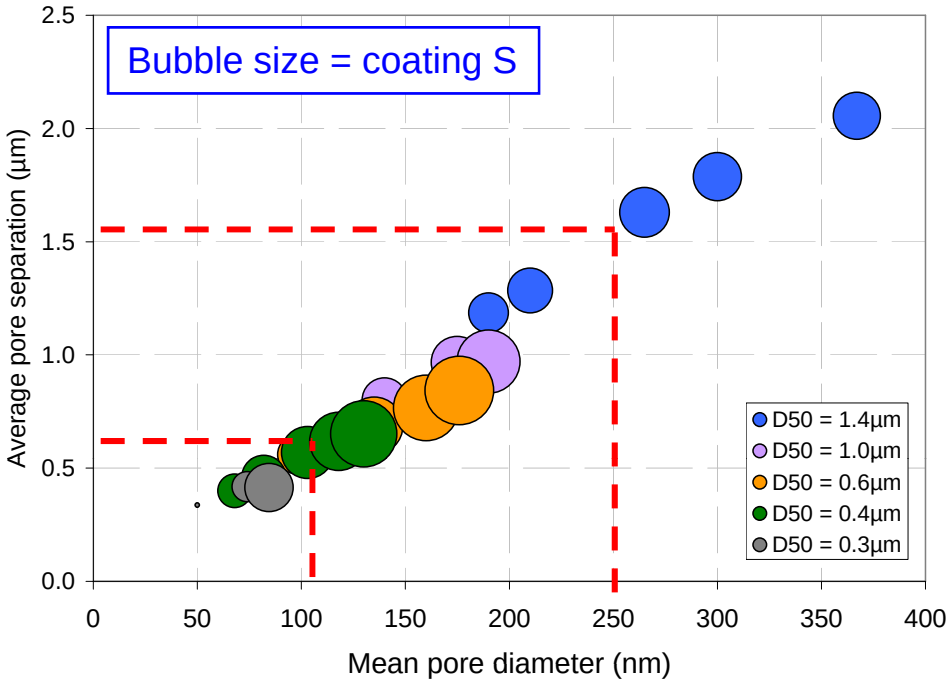

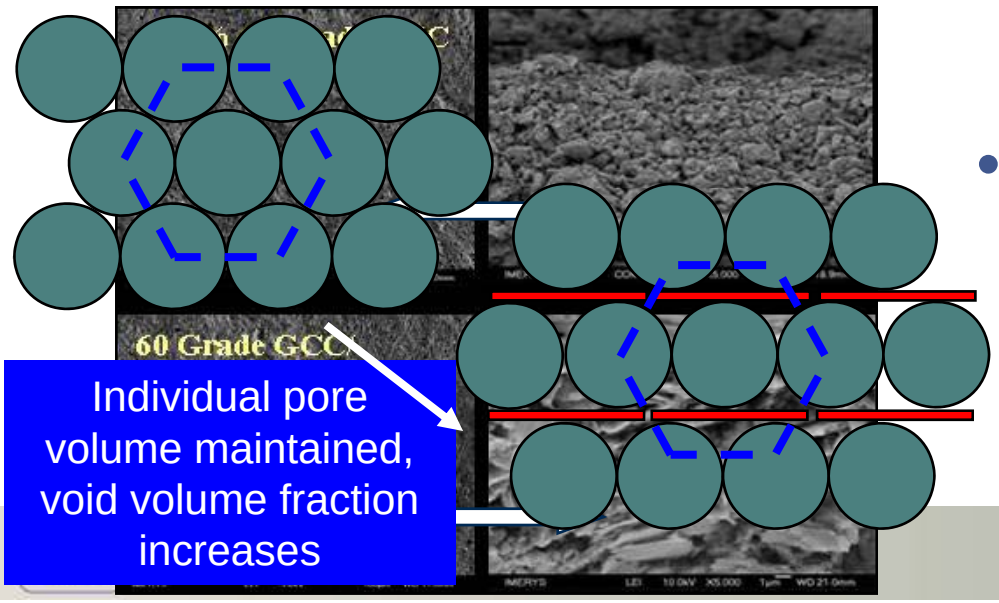

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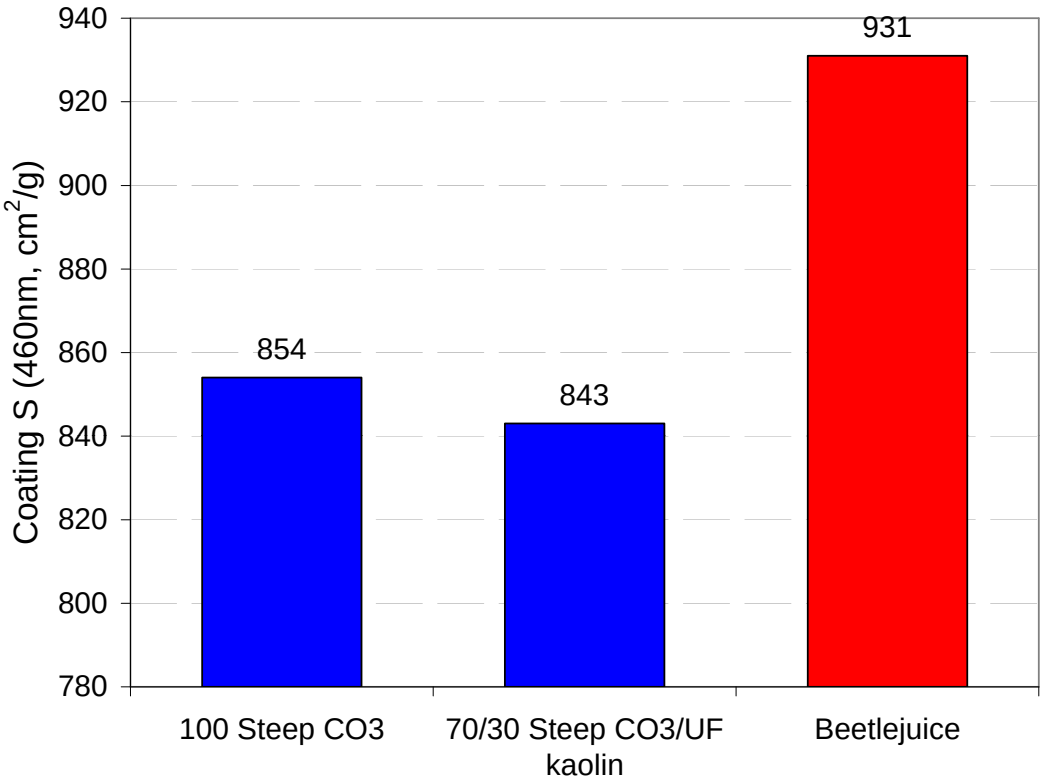
Beetlejuice



- **The optimal partner kaolin is very important. Specific crude must be selected and processed to give the necessary physical attributes**
- **The results show an optimised 'Beetlejuice' formulation which contains 70pph of the steep (narrow-PSD) carbonate. The other 30pph come from the optimised multi-pigment strategy**

HeliCoated at 800m/min, WF base, 8/4 latex/starch, 10gsm

Conclusions

- **Structural optics in Nature provides an interesting insight into advanced photonic systems and gives design cues for future coating ideas**
- **The key to highly efficient white scatter systems seems to be in de-coupling the scattering element from the matrix that surrounds it, enabling size and spacing to be optimised as independent parameters**
- **Achieving this will enable a disconnect in the current performance/weight relationship**
- **Structuring these elements into organised, or random architectures must then be addressed**
- **Work continues in this field that will offer ideas for cost-optimisation in troubled market conditions and out-performance in buoyant times**