Optimisation of the scattering efficiency of titanium dioxide can produce considerable cost savings. Ways to measure the efficiency of use of TiO₂ and to improve it are described. What is referred to as ‘highly treated’ TiO₂ can further improve opacity. This in turn can result in lower paint consumption, minimising environmental impacts.

One of the main functions of architectural paint is to hide a surface and improve its appearance. Hiding can be obtained either by scattering visible light or by absorbing it. For white paints, absorption is minimised, so that hiding in thin paint films can only be obtained by light scattering. Because of its high refractive index (RI), titanium dioxide (TiO₂) is the most efficient pigment for scattering visible light and its lack of absorption in the visible light range makes it the best white pigment available.

Since light scattering is the key parameter controlling hiding in white paint or whitening strength in tinted paints, more efficient use of TiO₂ can lead to improved hiding.

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Factors influencing hiding power in paints
Hiding or opacity in paints is controlled by light scattering and light absorption. Coloured pigments absorb light, but in the absence of absorption, white can only scatter visible light. Pigment light scattering is dependent on:
- The particle size of the scattering particle;
- The difference in refractive index between the particle and its surroundings;
- The proximity of the particles to one another.

TiO₂ is the most efficient pigment to whiten a surface as it does not absorb visible light, has one of the highest refractive indices available and the ideal particle size distribution for scattering visible light. Air voids in dry paint also contribute to light scattering because the refractive index of air is significantly lower than that of the surrounding medium.

Air voids can be introduced by formulating above critical pigment volume concentration (PVC) or by including opaque polymer (hollow spheres) in the paint. As with pigment particles, the light scattering of air voids depends on their size.

Determining the light scattering of paint
Kubelka and Munk published equations in 1931 which show the relationship between scattering (S) and absorption (K). These equations have been modified and simplified, and with today’s software programs S and K can be relatively easy determined from reflectance measurements over black and white surfaces [1, 2]. Typical methods used are a weighted hiding power method using laboratory draw down bars or a band viscometer to apply the paint to thin transparent “Mylar” film. Both methods produce both scattering coefficients, S_paint film, and absorption coefficients, K_paint film. Once these are determined, one has to separate the different scattering contributors (air voids, opaque polymers, TiO₂) from each other to determine the net scattering contribution of the TiO₂ pigment (Figure 1). The contribution of open air voids (above the critical PVC) can be assessed by measuring the opacity of oiled paint films. The oil used has a refractive index of 1.6, which is close to the average refractive index of a paint film.
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oil will fill the open air voids in the dry paint and therefore those will no longer contribute to light scattering. Subtracting the oiled hiding from the dry hiding allows the hiding contribution of air voids to be determined. For materials such as ZnO and opaque polymers, scattering can be determined from the volume fraction multiplied by the respective scattering coefficient [3].

Total scattering of the film measured from optical properties, $S_{\text{paint, film}}$ is the sum of scattering from materials of differing refractive index (including opaque polymer), the pore contribution and the TiO2 contribution. Assuming the scattering of inorganic fillers can be neglected in a dry paint film, the following equation can be used:

$$ S_{\text{paint, film}} = S_{\text{opaque polymer}} + S_{\text{pore}} + S_{\text{TiO2}} $$

Where $\chi_{\text{TiO2}}$ is the TiO2 weight fraction.

From Equation 1 it is clear that the scattering contribution of TiO2 ($S_{\text{TiO2}}$) can be calculated by measuring the total scattering of a paint film and subtracting the scattering contributions from opaque polymers and air voids. If $\chi_{\text{TiO2}}$ is known or measured, $S_{\text{TiO2}}$ (expressed as m²/g TiO2) can then be calculated. Equation 1 assumes that no other scattering pigments such as ZnO are present. Otherwise the equation needs to be corrected by including the contributions of these other scattering pigments as well.

Factors that limit pigment efficiency

The light scattering potential of a TiO2 particle is proportional to the square of the difference between the refractive index of the TiO2 and the average refractive index of the medium in which the TiO2 particle resides [4]. According to the effective medium theory [5] the refractive index of paint can be calculated from the paint composition by summing up individual component’s refractive index multiplied by their volume percent.

This explains why as TiO2 concentration increases, the average refractive index of a dry paint will increase and consequently the scattering efficiency per TiO2 particle will decrease. The reverse is true for increasing presence of air voids (RI = 1). This means that the maximum scattering of a TiO2 particle depends on the composition of the paint it is in.

Figure 2 illustrates the relationship between TiO2 scattering and paint refractive index for a large collection of matt white paints in Europe. The blue curve in Figure 2 indicates the highest possible scattering for TiO2 in paint of a certain refractive index. This curve can be used as a reference. It was calculated based on the highest $S_{\text{TiO2}}$ ever measured in Titanium Technologies Laboratories for paint with a certain refrac-

Results at a glance

- Because of its excellent light scattering capacity, titanium dioxide plays a key role in achieving opacity in architectural paints. Optimisation of this scattering efficiency is of considerable commercial importance.
- Ways to measure the efficiency of use of TiO2 and to improve it are described. In general, optimisation of efficiency is possible by improving the spacing of the pigment particles.
- Use of the right paint ingredients is important, but also the use of the right titanium dioxide grade in the right formulation space can have an important impact on paint opacity.
- What is referred to as ‘highly treated’ titanium dioxide can help to improve the opacity of high PVC paints by controlling pigment spacing. This in turn can result in lower paint consumption, minimising environmental impacts.

Figure 3: Correlation between light scattering per TiO2 particle (blue curve) and the total hiding power of the paint film (red curve)

Figure 4: Influence of filler particle size on $S_{\text{TiO2}, \text{CaCO3}(5)}$ and CaCO3(0.8) refer to CaCO3 fillers with average particle size of respectively 5 and 0.8 micrometres.

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Figure 5: Microscopy picture of highly treated TiO$_2$ (right) in comparison with standard (universal) TiO$_2$ pigment (left)

Figure 6: Spread rate as a function of TiO$_2$ concentration in paint for two different types of TiO$_2$

Figure 7: Comparison of light scattering of TiO$_2$ in resin, compared to air, showing that since scattering is proportional to the difference in refractive index between particle and paint, TiO$_2$ will scatter much more efficiently

How pigment spacing affects opacity

When optimising the light scattering of TiO$_2$ in paint, the opacity will increase. For the same amount of TiO$_2$, it is possible to obtain more hiding, or the same hiding with less TiO$_2$. Several factors can cause non-optimal TiO$_2$ scattering ($S_{TiO2}$, below the blue curve in Figures 2, 3 and 4). By influencing some of these factors, one can move $S_{TiO2}$ for a particular paint higher up in Figure 2 and hence improve $S_{TiO2}$ and opacity.

When two TiO$_2$ particles approach each other, their presence will start to diminish each other’s scattering ability. This phenomenon, also called crowding, cannot be avoided and is inherent in scattering physics. It means in practice that the scattering of TiO$_2$ particles per unit mass TiO$_2$ decreases with increasing concentration. Another process that adversely influences TiO$_2$ scattering is “non-ideal spacing”. This can be caused by a chemical process such as agglomeration or flocculation when a TiO$_2$ dispersion is ineffectively stabilised. It can, however, also be induced as a physical process when large filler materials or even resins are used (i.e. much larger than the average TiO$_2$ particle size).

These can push TiO$_2$ particles together and by doing so reduce their scattering efficiency. An example of non-ideal spacing is given in Figure 4. This graph shows the impact on $S_{TiO2}$ when replacing a large size CaCO$_3$ filler (5 µm) by a smaller size CaCO$_3$ (0.8 µm) in an acrylic matt wall paint with 10 PVC TiO$_2$ and total PVC 70. It can be clearly seen that $S_{TiO2}$ increases by more than 30 % because of improved TiO$_2$ spacing.

A pigment designed to maximise efficiency

The design of the TiO$_2$ pigment can also play a crucial role in enhancing TiO$_2$ scattering and hence opacity. The surface of TiO$_2$ pigments is almost always treated to improve properties such as photostability and dispersion [7]. In a newly designed TiO$_2$ pigment a new type of ‘engineered surface treatment’ was developed to create extra spacing between TiO$_2$ particles and hence reduce crowding [8]. The resulting pigment (Figure 5) will be referred to as ‘highly treated’ (HT) TiO$_2$ below.
Pigment efficiency

The engineered surface treatment influences the hiding potential in paints in two distinct ways. This is explained in Figure 6 where the blue curve shows the hiding of a paint (expressed as spread rate (m²/l) at contrast ratio 0.98) as a function of TiO₂ PVC.

At low PVC, hiding increases proportionally with TiO₂ PVC. Then it starts to flatten out and reaches a maximum around 20 to 25 % PVC due to increased crowding, as explained above. Beyond this maximum, hiding can even decrease when more TiO₂ is loaded in the paint.

It is however possible to take advantage of the presence of air voids when formulating above the critical PVC (cPVC). At higher pigment loadings, there will not be enough resin left to cover all dry pigment and fill the voids, so air voids will be formed. Air voids in an organic medium will also scatter visible light, when the right size, although much less efficiently than TiO₂ (Figure 7). This extra light scattering will increase hiding above the cPVC.

When using HT TiO₂ (red curve in Figure 6), there will be less crowding because of the spacing effect of the treatment. This results in a smaller loss of hiding beyond the maximum. The hiding, however, is a bit less than with universal TiO₂ since HT pigment contains less TiO₂ per gram compared to universal.

The engineered layer has a second effect. Because of the high surface area, the engineered layer will have much higher oil absorption and therefore absorb much more resin on the surface. As a result, critical PVC will be obtained at lower pigment concentration, allowing formation of air voids at lower PVC, so that the same amount of pigment will lead to more hiding (sum of TiO₂ and air void hiding).

Optimising formulations for opacity

The graph in Figure 6 describes paint containing only TiO₂. In reality paints above cPVC will contain mixtures of fillers and TiO₂ in order to limit costs. The right balance between TiO₂ and fillers needs to be found. Since fillers scatter little or no light, they can only give opacity via the creation of air voids above cPVC. Air is however much less efficient in scattering light than TiO₂. Therefore one will need much more air voids to obtain the same opacity as when using TiO₂.

Too many air voids (very high PVC) will harm the mechanical strength of the paint film. Therefore a fair amount of TiO₂ is necessary in order to limit the PVC and to retain acceptable paint quality.

Figure 8 illustrates the effect on hiding when using HT TiO₂. Both paints have a total PVC of 70, so both are above cPVC with TiO₂ PVC = 17. One paint is formulated with universal TiO₂, the other with HT TiO₂. SₜiO₂ of both paints was determined as well as the contribution of air voids to the dry hiding of the paint by oiling the dry paints. This comparison shows that SₜiO₂ is higher for HT TiO₂ (because of reduced crowding) and that there is more air void hiding. Increased SₜiO₂ leads also to higher tinting strength as shown in Figure 8.

In order to take advantage of HT TiO₂, it is important to work in the right formulation space. Design of experiment (DOE) allowed the proper formulation space for such grades to be identified [9]. This is shown in Figure 9 where the difference in dry hiding in paints formulated with HT TiO₂ compared to universal TiO₂ is shown. From
Figure 8: Comparison of hiding power and tinting strength of two paints; one formulated with universal TiO$_2$, the other with HT TiO$_2$.

Figure 9: Difference in hiding power (expressed as spread rate at contrast ratio 0.98) between paint with universal and HT TiO$_2$.

It is possible to observe that only at high TiO$_2$ concentrations (above 12 weight %) and above cPVC, there is a big enough advantage to justify using HT TiO$_2$. The same DOE approach was used to determine the effect on properties other than opacity e.g. wet scrub resistance, dirt pick up etc. It was observed that despite the presence of more air voids when using HT TiO$_2$, these properties are not necessarily adversely impacted. This is under investigation to improve understanding.

From what has been explained so far, it should be clear that when working in the right formulation space, the improved hiding of this highly treated TiO$_2$ can lead to more efficient coverage of walls with the same amount of paint (spread rate m$^2$/l) and hence a reduced environmental footprint per m$^2$ wall painted. This illustrates the importance of considering the environmental impacts of paints in use, rather than only considering the impact per litre of paint in the can.

Finally, however, it is important to remark that reformulating paints of course requires a broader evaluation of all quality-related properties (e.g. wet scrub resistance, rheology, application) but hiding power is identified as a key parameter by paint manufacturers and end-users alike.

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