USE OF OPTICAL DENSITY AND TiO$_2$ LIGHT SCATTERING TO IDENTIFY OPTIMIZATION POTENTIAL IN ARCHITECTURAL COATINGS

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ABSTRACT

Optical density is a technique that evaluates the amount of light scattered by particles in a suspended paint sample. After developing an improvement in it, it is now possible to understand the titanium dioxide (TiO$_2$) light scattering efficiency without knowing the complete paint formulation. Spreading rate analyses take into consideration the TiO$_2$ amount to define this material scattering coefficient in the dry paint film.

With these analyses it was possible to identify how well the TiO$_2$ was dispersed in the liquid paint and how evenly distributed in the dry paint film it was (reflecting dispersion/flocculation problems or crowding effect during drying process), which we called the TiO$_2$ dispersion efficiency and formulation efficiency. Some paints presented an opportunity to improve the TiO$_2$ usage efficiency by almost 20% and the formulation (extenders/fillers, resin, etc.) by 55%. After defining the TiO$_2$ usage efficiency it was possible to compare paints from different countries in Latin America.

KEYWORDS

Properties optimization; architectural coatings; titanium dioxide; artificial neural networks

INTRODUCTION

Titanium dioxide (TiO$_2$) is the most important white pigment in several industries due to its ability to facilitate light scattering and white color (1-4). However, to achieve adequate performance, coatings that use TiO$_2$ pigments must have good dispersion of individual particles (5).

In this study, a direct measurement of TiO$_2$ dispersion in dry film was studied using electron microscopy. The image was broken into sub-images, and then the sub-images were compared to one another (6). Spatial point statistics methodologies were used, such as those developed by Clark-Evans and Ripley, as well as the neighborhood distribution function (7).

Not all paint producers have access to equipment like electron microscopes, so the purpose of this work was to understand the final coatings’ formula TiO$_2$ dispersion – how well the TiO$_2$ stays dispersed in dry film and how this directly affects its final properties – using a combination of theoretical and empirical methodologies.

TiO$_2$ DISPERSION IN DRY FILM

The light scattering provided by TiO$_2$ is strongly influenced by several factors, including particle size, crystal phase, refractive index of the binder or surrounding medium, and degree of isolation from other TiO$_2$ particles. This degree of isolation is also referred to as the degree of dispersion or lack of crowding (8-11).

To achieve the best possible performance, TiO$_2$ particles must be separated with a particle to particle distance of at least 400 nm (8). For instance, agglomerated pairs of particles exhibit a
20% decrease in the scattering parameter associated with the hiding power of a paint film relative to a single particle.

Another way of looking at this is demonstrated in Figure 1, which depicts the impact of particle-to-particle spacing on the efficiency of a paint’s hiding power. The Figure shows electron micrographs of three different paints with different particle dispersions. It can be seen that good particle spacing increases the hiding power performance of the paint in this case by 30%.

![Figure 1 - Impact of particle-to-particle distance on the paint’s hiding power.](image)

To achieve the condition in which the particles are separated or isolated from each other, the dispersion process and stability of the suspension must be carried out such that when the coating film is drying or curing, the particles remain dispersed and isolated from each other.

A proper TiO\(_2\) dispersion in the dry film can be achieved by combining a good dispersion of the TiO\(_2\) with a proper formula for keeping the TiO\(_2\) apart after the film is formed (12). On the one hand, previous studies have shown that the de-agglomeration process is influenced by the wetting ability of the pigmentary TiO\(_2\) (13-14) and the mechanical forces applied by the equipment design (15). On the other hand, Diebold (16) demonstrated that TiO\(_2\) spacing is effective for scattering light and that its crowding is influenced by other coatings of raw materials.

There are several theories for explaining the interaction of a light beam with a particle (see, for example, the work of Mie, Rayleigh, and Fraunhofer - 17). Mie developed a basic theory for spherical particles that is useful when particles with more complex shapes are under evaluation. Rayleigh’s scattering theory applies when particles are smaller than the wavelength of the incident beam, and Fraunhofer’s theory can be applied when the particles are larger than the wavelength of the incident beam.

In the case of pigmentary TiO\(_2\), optimal scattering is seen for particles that are about half the size of the visible light wavelengths (400 nm to 750 nm). Therefore, the particles range between 200 nm and 350 nm. Bigger particles are sometimes found due to the particular requirements of the application. Therefore, Rayleigh’s and Mie’s solutions for Maxwell’s equation were used in this study to calculate the particle size based on light scattering.

According to Rayleigh’s and Mie’s theories, the scattering pattern (I) is independent of the particle’s shape, but it takes into account the distance from each particle to the detector (r), the incident light intensity (I\(_0\)), and the wavelength (\(\lambda\)) as shown in Equation 1:

\[
I = I_0 \alpha^2 \left( \frac{2\pi}{\lambda} \right)^4 \frac{1 + \cos^2 \theta}{2r^2},
\]

Equation 1
where $\alpha$ is the light polarization or the parameter of the equation that contains the relative refractive index ($m$) and the volume of the particle ($V$) as presented in Equation 2:

$$\alpha = \frac{3(m^2 - 1) V}{m^2 + 2 - 4}.$$  

**OPTICAL DENSITY**

Optical density originated from the Lambert-Beer law, which was derived from the first-order Taylor expansion of Maxwell’s equations and is depicted by Equation 3 (18).

$$OD = -\log \left(\frac{I(t)}{I_0}\right),$$  

where $I(t)$ is the light transmitted through the media of interest and $I_0$ is the incident light; e.g., the optical density is the attenuation of light when passing through the media under investigation. Since the main function of TiO$_2$ is to scatter light, measuring attenuation is equivalent to measuring the light scattering efficiency of this TiO$_2$. Measuring particle size could be an alternative option, but the different refractive index of each particle makes it harder to understand and interpret the output data.

The problem of optical density is to define a reference of the optimized dispersion. By dividing the sample into two and sonicating one of these halves, we can create the reference that we are looking for. Sonication might break some extenders and resins down into smaller particles, but the TiO$_2$ particles will remain intact - only any particle agglomerates that remain from the poor dispersion process are broken down, rather than the individual particles themselves. The ratio of the sonicated and nonsonicated samples gives us the dispersion efficiency of that sample of TiO$_2$ ($\epsilon_{\text{Disp}}$).

**SPREADING RATE**

The weighed hiding test method is a form of ASTM D2805-11, Hiding Power of Paints by Reflectometry. The ISO equivalent is the ISO 6504-1:1983. The Kubelka-Munk hiding power method can be applied to white and light-colored paints. Both test methods include a means to perform the calculations presented by the Kubelka-Munk theory (Equation 4 to Equation 11).

$$R = f(SX, R_s, R_o) = \frac{1 - R_a b \text{ctgh} h SX}{1 - R_s + b \text{ctgh} h SX}$$  

and

$$SX = f(R_s, R_o) = \frac{1}{b} \arctgh \frac{1 - a R_s}{b R_o},$$  

where

$$a = \frac{1}{2} \left[ R + \frac{R_o - R + R_s}{R_s} \right],$$  

$$b = (a - 1)^{\frac{3}{2}},$$  

$$R_a = a - b,$$  

$$S = \frac{H_{\text{abs}}}{2B} \left( \frac{1 - R_o R_s}{1 - R_s R_o} \right),$$  

and

$$K = \frac{S}{R_o}.$$  

where $R$ is the reflectance of film applied to the substrate, $R_g$ is the substrate reflectance, $R_s$ is the reflectance of a film so thick that increasing its thickness has no effect on $R$, $R_o$ is the reflectance of the film applied to an ideal black substrate ($R_g = 0$), $X$ is the thickness of the film, $S$ is the scattering coefficient of the film, and $K$ is the absorption coefficient of the film.
Basically, in the ASTM test method the dry film thickness is measured whereas the and wet film thickness is back-calculated using an additional measurement (i.e., nonvolatile content). The ISO test method and the ASTM test methods are similar in this regard.

Using the scattering coefficient of the film and the TiO₂ amount, it is possible to calculate the scattering coefficient of TiO₂ ($S_{TiO2}$). The TiO₂ concentration determines the average refractive index of the coating film, since resin, fillers, and extenders all have about the same refractive index (1.56 to 1.6). The average refractive index will determine the TiO₂ scattering efficiency in dry film.

If a single particle of TiO₂ (refractive index 2.73) is surrounded by resin (with a refractive index of 1.5), the refractive index ratio would be of 1.82. This is the highest value that this ratio can reach for a TiO₂ resin mix – adding more TiO₂ to the resin increases the average refractive index rises and reduces the TiO₂ scattering efficiency. If arbitrary values are given to the scattering value, then the curve of light scattering as a function of TiO₂ concentration would be described as in Figure 2.

The curve in Figure 2 assumes that the TiO₂ is fully dispersed into the resin or dry film, meaning that this would be the maximum value possible for achieving each TiO₂ concentration. It is possible to compare the opacities of paints with different TiO₂ concentrations by simply comparing their overall scattering values. However, it is better to compare them by using the theoretical curve as a reference point. For example, in Figure 3 the TiO₂ efficiency of Paint 1 is 85%, while it is 90% for Paint 2. We see that the better scattering value for Paint 1 is due to its lower average refractive index and that the pigment in this paint is actually more poorly dispersed than the pigment in Paint 2.
As previously mentioned, poor TiO₂ dispersion efficiency in paints may be a result of dispersion or formulation, and the STiO₂ efficiency is an intensive property that basically ignores formulas differences, looking to the TiO₂ scattering efficiency alone. To calculate the formulation efficiency of a paint ($\varepsilon_{\text{Form}}$), the dispersion efficiency ($\varepsilon_{\text{Disp}}$) must be excluded from the overall efficiency and calculated from the STiO₂ ($\varepsilon_{\text{STiO}_2}$), as shown in Equation 11.

$$\varepsilon_{\text{Form}} = 1 - (\varepsilon_{\text{Disp}} - \varepsilon_{\text{STiO}_2}).$$

**Equation 11**

**SAMPLES**

For this study, 208 paint samples from different Latin American countries were collected. Colombia, Argentina, Brazil, Chile, Ecuador, Peru, Venezuela, and Mexico were the most dominant countries. The samples were collected from producers that controlled at least 50% of their markets to assure that they are representative. As many of these countries do not have regulations regarding paint quality, this was determined according to the perception of our representatives in these countries.

**RESULTS AND DISCUSSIONS**

An average dispersion efficiency boxplot for each of the paints from the different countries is presented Figure 4. It can be seen that most of the countries have a dispersion efficiency above 90%, meaning that the dispersion is primarily efficient. Since, there was no way to increase dispersion before these paints are used, these dispersion efficiencies directly affect the paint quality.
In Figure 4, it is also possible to see which paints have poor dispersion, such as the low-quality paints from Mexico whose dispersion efficiency is about 60%. Our investigation showed that this poor dispersion was a mix of poor TiO₂ quality and direct use of the pigment without pre-dispersing it.

Figure 5 shows paint efficiency for each country. This efficiency is primarily determined by the mix of resin and extenders, since these particles push the TiO₂ into a crowding state, reducing the TiO₂ efficiency in the dry paint film. If the TiO₂ particles were more evenly separated from each other, the paint would have better opacity.

The reason that the Mexican low-quality paint appears as one of the top performers is that the crowding effect due to a lack of dispersion of the pigment does not allow the TiO₂ particles to be pushed to the available space between the other particles. This means that it does not matter what extenders and resins are used, the TiO₂ dispersion cannot be improved (or in other words, a bad initial dispersion cannot be worsened by a bad choice of extenders and resins).
A different way of looking at the same data above is the graph in Figure 6, which combines the dispersion and formulation efficiencies with TiO₂ content (i.e., bubble size). A different perspective is then presented, showing that the Latin American region’s average dispersion efficiency is 93% and that its average formulation efficiency is about 70%.

When looking to specific cases (in Figure 6), the Brazilian Coating 18 shows good performance regarding formulation of the paint - the proper fillers and extenders are used - and the success of this paint maker to disperse the TiO₂.

![Bubble Plot of Average of Dispersion ef vs Average of Fromula Effic](image)

Figure 6 – Formula and dispersion efficiency combined with TiO₂ amount (i.e., bubble size).

When looking at the individual qualities, like the high-end coatings (Figure 7), it is clear that Brazilian coatings have lower TiO₂ amounts (i.e., smaller bubble sizes), but most of them are well dispersed (with dispersion efficiency of more than 90%). The range of formulation efficiency spreads throughout all the existing ranges, meaning that good dispersion is achieved, but not used well by the combination of ingredients, like in Brazilian Paints 2 and 3. On the other hand, the Mexican coatings have an impressive formulation efficiency but lack dispersion efficiency. At this point, one can only assume that this is probably caused by Mexico’s habit of not pre-dispersing the TiO₂.
This coating’s dispersion average is perfectly dispersed in the liquid paint, suggesting formula and process variations.

Figure 7 – Top-quality coatings’ dispersion and formula efficiency.

Figure 8 adopts the perspective of a single paint maker to determine if he is facing batch-to-batch variations and to allow the targeting of specific paint lines and grades. For example, this customer has selected a particular paint as being top quality (Top 1); it uses a good amount of TiO₂, but lacks dispersion. This coating’s dispersion average is below the other coatings average from this same customer (that ranges about 96%). It is also possible to see variations in the same paint lines, such as Top 3, where a difference of almost 20% is found between two samples, or in the Mid paint, where no sample is close to any of the others (which is the same for the Top 2 paint), suggesting formula and process variations.

Figure 8 – Customer-specific perspective.

CONCLUSIONS

Through the analyses described in this paper, it was possible to identify how well TiO₂ is dispersed in the liquid paint and if it is evenly distributed in the dry paint film (i.e., if there are dispersion/flocculation problems or a crowding effect during the drying process, which are
referred to as TiO₂ dispersion efficiency and formulation efficiency in this study). Almost 20% of the paints showed a need to improve the TiO₂ dispersion, and 55% of the paints demonstrated a need for improved formulation (extenders/fillers, resin, etc.). When combined, the optical density and the scattering efficiency of the dry film can also guide improvement projects where the most benefit can be extracted from the TiO₂ particles.

It is also possible to use the same basis to compare TiO₂ use and performance in paints produced by different companies, even those from different countries.

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REFERENCES

