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Effects of porous films on the light reflectivity of pigmentary titanium dioxide particles

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ABSTRACT

The light reflectivity of the film-coated titanium dioxide particles (TiO_2) as a function of the film refractive index was derived and calculated using a plane film model. For the refractive index in the range of 1.00–2.15, the lower the film refractive index is, the higher is the light reflectivity of the film. It is inferred that the lower apparent refractive index of the porous film resulted in the higher reflectivity of light, i.e., the higher hiding power of the titanium dioxide particles. A dense film coating on TiO_2 particles with different types of oxides, i.e., SiO_2, Al_2O_3, MgO, ZnO, ZrO_2, TiO_2, corresponding to different refractive indices of the film from 1.46 to 2.50, was achieved, and the effects of refractive index on the hiding power from the model prediction were confirmed. Porous film coating of TiO_2 particles was achieved by adding the organic template agent triethanolamine (TEA). The hiding power of the coated TiO_2 particles was increased from 88.3 to 90.8 by adding the TEA template to the film coating (5–20 wt%). In other words, the amount of titanium dioxide needed was reduced by approximately 10% without a change in the hiding power. It is concluded that the film structure coated on TiO_2 particle surface affects the light reflectivity significantly, namely, the porous film exhibits excellent performance for pigmentary titanium dioxide particles with high hiding power.

1. Introduction

Titanium dioxide (TiO_2) is an excellent white pigment that is widely used in paints, plastics, paper, rubber, ink and other industries. It has three crystal structures in nature, i.e., rutile, anatase and brookite. Rutile titanium dioxide has high hiding power because of its high refractive index. The hiding power represents the ability of TiO_2 particles in a paint layer to cover the background light from the matrix, which is contributed from a large number of TiO_2 particles. It is assumed that high reflectivity of a single TiO_2 particle indicates high reflectivity of the TiO_2 particles in the paint layer. The reflectivity of particles determines the hiding power of particles in the paint layer: high reflectivity corresponds to high hiding power.

However, titanium dioxide also has strong photocatalytic activity: it produces electrons and holes under UV light irradiation, which react with water and oxygen to generate radicals that catalyze and degrade the organic matter around the titanium dioxide particles [1–4]. This results in chalking and life shortening of the painting layer. To increase the weather durability of the TiO_2 particle, the surface needs to be coated with a shield film of inert oxides, e.g., silica and alumina. The co-precipitation method is usually used for the inorganic film coating. By titrating inorganic salts and acid/alkali solution into the TiO_2 suspension, an oxide or hydroxide film is coated on the TiO_2 particle surfaces, which increases the weather durability of TiO_2 particles [5–9].

In our previous work, it was confirmed that the apparent degradation rate coefficient of titanium dioxide with rhodamine-B was reduced as the amount of coating on the TiO_2 particle surface increased. In other words, the weather durability of coated TiO_2 particles increased [10,11]. However, the hiding power of the coated TiO_2 particles decreased as the coating amount increased. The factors affecting the hiding power of titanium dioxide particles were studied and reported in the literature. By using light scattering theory and numerical calculation, Fitzwater et al. [12] and Auger et al. [13] studied the effects of volume fraction of titanium dioxide and the painting thickness on the scattering efficiency of the painted layer to optimize the painting formulation. Veronovski et al. [14] found that TiO_2 particles have a better spatial distribution and scattering efficiency because the porous film-coated TiO_2 parti-

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cles have a thicker film structure compared with that of the dense silica-coated TiO_2 particles. This causes the TiO_2 particles coated with porous silicon oxide to have a lower transmittance and higher hiding power.

For TiO_2 particles, the light reflectivity is mainly affected by the difference in refractive indices between core TiO_2 particles and their surroundings. The higher the difference between the refractive indices is, the higher is the light reflectivity of the particles [15]. Theoretically, uncoated TiO_2 particles have high hiding power due to the high difference of refractive indices with their surroundings. However, for film-coated TiO_2 particles, the surrounding of the core TiO_2 particles is the inorganic oxide film (n_1) instead of an organic matrix (n_0), as shown in Fig. 1(a). Generally, the refractive index of the inorganic oxide film (n_1) is higher than that of the organic matrix (n_0), hence, the hiding power of the coated TiO_2 particles decreased because the difference in refractive indices decreased. For the same apparent hiding power, the higher the hiding power of the coated TiO_2 particles was, the lower was the amount of titanium dioxide needed, i.e., the lower the cost. Achievement of high weather durability and high hiding power by fabricating the coated film structure on the TiO_2 particle surface is desired.

The porous films are likely to increase the hiding power of coated TiO_2 particles because of their lower apparent refractive indices compared with the dense films. The preparations of porous alumina have been reported in the literature. Alphonse et al. [16] controlled the specific surface area, pore volume and pore size distribution of porous alumina by adding different organic templates and inorganic ions. Zhu et al. [17] added PEO template in the alumina synthesis process to produce a porous structure. Masoumeh et al. [18] prepared porous alumina with different pore size distributions using different aluminum sources and precipitating agents. Goparaju et al. [19] adjusted the film structure coated on the titanium dioxide particles by controlling the pH in the coating process. Porous alumina structures can be produced by adding different templates and adjusting the preparation process.

In this paper, the change in light reflectivity of the coated film with the film refractive index was calculated using a plane film model. Studies of TiO_2 particles coated with films of various oxides were conducted to verify the prediction of the effects of the refractive index from the model. The porous Si + Al composite film was prepared by addition of the organic template triethanolamine (TEA) and subsequent calcination. The relationship of the pore volume in the coated films on TiO_2 particles surface with the light reflectivity, i.e., hiding power of coated TiO_2 particles, was determined. A low-cost coated titanium dioxide product with high weather durability and high hiding power was prepared.

2. Reflectivity of film-coated TiO_2 particles

When incident light irradiates the surface of a single TiO_2 particle, light reflection, scattering, and absorption occur. For simplification of the analysis, only the reflection and transmittance was considered in the following discussion. Because the thickness of the coated film on the surface of TiO_2 particles is usually less than 20 nm, which is much lower than the TiO_2 particle diameter (approximately 300 nm in average), the spherical film model of a single coated TiO_2 particle was simplified to a plane film model. The reflectivities of coated films with various refractive indices were calculated, and the relationship between the film reflectivity and the film refractive index was determined through a plane film model. As shown in Fig. 1(b), the incident light from the surrounding environment irradiates the coated film surface at an angle of θ_0. The incident light vector is E_0, and the reflected light vectors are E_1, E_2, $E_3 \cdots$. The optical path difference of any two adjacent reflected lights from the surface of the coated film is $\Delta L = 2n_1 d_1 cos\theta_1$ [20], wherein n_1 is the refractive index of the coated film, d_1 is the coated film thickness, and θ_1 is the angle of refraction. To simplify the analysis, only vertically incident light is discussed below. Then, $\theta_0 = \theta_1 = 0^\circ$ and λ is the wavelength of the incident light, the phase difference is,

$$\delta = 2\pi/\lambda \times 2n_1 d_1 \tag{1}$$

Referring to Fig. 1(b), the reflection coefficients of light on the upper and lower surface of the coated film interfaces 1 and 2 are r_1^+, r_1^-, r_2^+, and r_2^-, respectively. The transmission coefficients are t_1^+, t_1^-, t_2^+, and t_2^-, respectively. Each of the reflected light vectors from the upper surface of interface 1 is,

$$\begin{aligned} E_1 &= {r_1}^+ E_0 \\ E_2 &= {t_1}^+ {r_2}^+ {t_1}^- e^{-j\delta} E_0 \\ E_3 &= {t_1}^+ {r_2}^+ {t_1}^- {r_1}^- {r_2}^+ e^{-j2\delta} E_0 \\ E_4 &= {t_1}^+ {r_2}^+ {t_1}^- \left({r_1}^- {r_2}^+\right)^2 e^{-j3\delta} E_0 \ldots \end{aligned} \tag{2}$$

According to Eq. (2), the sum of the reflected light vector from the upper surface of interface 1 is,

$$\begin{aligned} lE_R &= \sum_{i=1}^{\infty} E_i \\ &= {r_1}^+ E_0 + {t_1}^+ {r_2}^+ {t_1}^- e^{-j\delta} \left\{ 1 + {r_1}^- {r_2}^+ e^{-j\delta} + \left({r_1}^- {r_2}^+ e^{-j\delta}\right)^2 + \ldots \right\} E_0 \\ &= \frac{{r_1}^+ + {r_2}^+ ({t_1}^+ {t_1}^- - {r_1}^+ {r_1}^-) e^{-j\delta}}{1 - {r_2}^+ {r_1}^- e^{-j\delta}} E_0 \end{aligned} \tag{3}$$

According to the Fresnel formula [21], at interface 1,

$$ {t_1}^+ \cdot {t_1}^- = 1 - {r_1}^{+2} = 4n_0 n_1/(n_0 + n_1)^2 \tag{4}$$

$$ {r_1}^+ = \frac{n_0 - n_1}{n_0 + n_1}, \; r_1^- = -r_1^+ \tag{5}$$

At interface 2,

$$ {r_2}^+ = \frac{n_1 - n_2}{n_1 + n_2}, \; r_2^- = -r_2^+ \tag{6}$$

By combining Eqs. (3) and (4), the total reflection coefficient on the coating film of the upper surface is,

$$ r = \frac{E_R}{E_0} = \frac{{r_1}^+ + {r_2}^+ e^{-j\delta}}{1 + {r_1}^+ {r_2}^+ e^{-j\delta}} \tag{7}$$

The total reflectivity from the coated film of the upper surface is,

$$ R = |r|^2 = \frac{r_1^{+2} + {r_2}^{+2} + 2r_1^+ {r_2}^+ cos\delta}{1 + r_1^{+2} {r_2}^{+2} + 2{r_1}^+ {r_2}^+ cos\delta} \tag{8}$$

By combining Eqs. (1), (5), (6) and (8), the film reflectivity was calculated for various thicknesses and refractive indices of the coated film. The curves of coated film reflectivity versus film thickness were obtained, as shown in Fig. 2, by setting the refractive index of the organic matrix n_0 to 1.4; the refractive index of pure rutile titanium dioxide n_2 to 2.75; the film refractive index n_1 to 1.46 (corresponding to silica) or 1.76 (corresponding to alumina); and the wavelengths of incident light λ to 200, 500, and 800 nm. The curves of film reflectivity versus the film refractive index were obtained, as shown in Fig. 3, for a wavelength of the incident light λ at 500 nm; coated film thicknesses d_1 at 5, 10, 20, and 30 nm; and the film refractive index ranging from 1.0 to 2.8.

Fig. 2 shows that the reflectivities of the films corresponding to silica ($n_1 = 1.46$) and alumina ($n_1 = 1.76$) decrease with increasing film thickness under the irradiation of UV light (200 nm), visible