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The effects of particle size distribution on the optical properties of titanium dioxide rutile pigments and their applications in cool non-white coatings

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A B S T R A C T

The particle size distributions of three commercially available titanium dioxide pigments were measured, and their effects on the optical properties of the pigments were investigated. The Altiris 550 and 800 pigments possess larger median particle size and wider size distributions than those of the conventional titanium dioxide rutile. The visible (VIS) reflectance, the solar reflectance and the lightness of the films and coatings singly pigmented with any of these three pigments decrease as the pigment particle size increases. The VIS transmittance and near-infrared (NIR) reflectance both increase as the pigment particle size increases. The main reflection band of the coatings shifts farther into the NIR region with increasing pigment particle size. The partially VIS-transmitting Altiris pigments enable the NIR and the solar reflectance of cool non-white coatings to be improved, thereby yielding metameric matches to the desired colors.

1. Introduction

Cool-colored pigments play an important role in the manufacture of cool non-white coatings, which are desirable options for consumers from the esthetic and visual considerations [1–8]. In several related papers, cool-colored pigments were ambiguously termed near-infrared (NIR) reflective pigments [7–9], while in other papers, the cool-colored pigments were explicitly classified as “NIR-reflecting colorants” or “NIR-transmitting colorants” [10–13]. A coating pigmented with the former type of colorant is always cool over any substrate, but that pigmented with the latter type of colorant requires a background with moderate-to-strong NIR-reflectance to yield a cool non-white coating [10–12]. Apparently, the cooling principles of the coatings pigmented with these two types of cool pigments are different.

In a previous informative paper [14], the solar spectral optical properties of 87 predominately single-pigment paint films, with thicknesses ranging from 10 to 37 μm, were characterized with particular emphasis on the NIR properties. Most of the cool pigments were identified as NIR-transmitting colorants, but several pigments, such as titanium dioxide rutile white, were found to be NIR-reflecting colorants, showing both strong NIR backscattering and weak NIR absorption in a binder of refractive index 1.5 [3]. Conventional titanium dioxide rutile with a scattering power of 1.9 is one of the most hiding and the best visible scattering pigments [11]. If used to improve the NIR reflectance of cool non-white coatings, it will modify the reflectance curve [11] and the visual appearance of the coatings.

In addition to the NIR reflectance, color control is an equally important consideration in the manufacture of cool non-white coatings. For certain coating applications, such as building envelope coatings, the coating color is generally fixed. Therefore, significant adjustments in the amount of visible (VIS) light reflected or its wavelength is unlikely to be allowed; slightly modifying the visible absorption might be tolerated [11]. One way to make spectral irradiance-independent non-metameric colors with enhanced NIR reflectance is to use a pigment with high reflectance in the NIR region and high transmittance in the VIS region. An alternative way to produce metameric colors is to replace the absorptive visual color matching pigments with pigments that have similar absorptions in the VIS region but are highly reflective or transparent in the NIR region [11].

For a given value of the scattering power, the wavelength most efficiently scattered by a pigment positively correlates with the diameter of the pigment particles [11]. Therefore, large particle-sized pigment will effectively reflect NIR radiation with longer wavelengths. Commonly used commercial titanium dioxide rutile generally has a particle size ranging from 200 to 300 nm and it

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reflects well between 400 and 1700 nm, with a peak scattering intensity of 500 nm [11]. Titanium dioxide, with a mean particle size of 10 μm, reflects efficiently between 800 and 2300 nm but poorly between 400 and 800 nm [11]. When used as an extender pigment, it can greatly improve the non-white coatings' NIR reflectance, with little or no effect on their visual color. Larger particle-sized titanium dioxide rutile has been used in the manufacture of camouflage coatings; however, to the best of our knowledge, no papers to date have been published on its application in the manufacture of NIR-reflective coatings.

The optical properties of a conventional titanium dioxide rutile and two larger particle-sized commercial titanium dioxide rutile pigments were investigated in this study. In this paper, the measured particle size distributions of the three samples are presented. The spectral reflectance, transmittance and computed absorptance of three paint film samples and the spectral reflectance for coatings pigmented with the three pigments over white and black basecoats are compared. In addition, the effects of pigment concentration on the NIR reflectance of the three pigments are discussed. The applications of two larger particle-sized titanium dioxide pigments in preparation of cool non-white coatings are exemplified.

2. Experiments

2.1. Selection of materials

To study the effects of particle size distribution on the optical properties of titanium dioxide rutile pigments, the following commercial titanium dioxide samples with different particle size distributions were selected: a conventional titanium dioxide rutile, grade Ti-Pure R-902, purchased from DuPont Chemicals Co., Ltd., and two commercial dioxide rutile, grade Altiris 800 and 550, generously supplied by Huntsman Corporation.

To study the effects of the addition of Altiris pigments on the solar and spectral reflectances of cool non-white coatings, a nickel titanate yellow, a copper chromite black and a zinc iron chromite brown pigment, kindly supplied by Nanjing Pigments Tech. Co., Ltd., were selected.

To prepare the titanium dioxide rutile films and the cool non-white coatings, an ambient, self-curing, pure acrylic emulsion, purchased from Showa Highpolymer Co., Ltd., Shanghai, was used as a water-based binder. In addition, the following paint additives, purchased from Adeka Corporation, Tokyo, Japan, were used: a wetting agent, a dispersant, an antifoaming agent, a leveling agent and a coalescent.

2.2. Measurements of the particle size distributions

The particle size distributions of the three titanium dioxide rutile pigments dispersed in distilled water were measured by laser diffraction spectrometry (LDS) (BT-2003, Dandong Better Size Instruments, Ltd.). The dispersant was sodium henamephosphate. The refractive index of the TiO_2 particles and the surrounding medium are 2.81 and 1.333, respectively.

2.3. Measurements of the optical properties

The spectral reflectance and transmittance of the paint films and coatings were measured using a UV/VIS/NIR spectrophotometer (Perkin Elmer Lambda 750) equipped with an integrating sphere (150-mm diameter, Labsphere RSA-PE-19), following ASTM E903-96 (standard test method for solar absorbance, reflectance and transmittance of materials using integrating spheres). The solar reflectance and transmittance were computed by integrating the measured spectral data weighted with the air mass 1.5 beam normal solar spectral irradiance. The spectral absorptance was calculated as 1.00 – reflectance – transmittance.

The lightness of the coatings was measured using a color reader (CR-10, Konica Minolta Sensing, Inc.).

2.4. Measurements of the thermal emittance

According to ASTM C 1371 (Standard test method for determining the emittance of materials near room temperature using portable emissometers), a portable differential thermopile emissometer AE1 (Devices & Services Co., Dallas, TX) was used to measure the thermal emittance of the coatings. The instrument was calibrated using both high and low emittance standards placed on the flat surface of a heat sink. The emittance of the test specimen was determined via comparison with the emittances of the standards.

3. Results and discussion

3.1. Particle size and distributions of different TiO_2 samples

In general, particle size influences many properties of particulate materials. In the paint and pigment industries, particle size determines appearance, including gloss and tinctorial strength [15] and reflectance of coatings [11]. Therefore, it is of particular significance to measure and control the particle size distribution in the preparation of cool coatings.

Fig. 1 shows the cumulative and differential distributions of the conventional titanium dioxide rutile, the Altiris 550 and the Altiris 800 pigments. The median particle size, the volume median particle size, the area median particle size, D_{90} and D_{25} for the three samples are summarized in Table 1. The D_{25} particle size is listed in Table 1, instead of the D_{10}, to conveniently calculate the main reflection band of the pigments. Using Eq. (6) (as shown below) and the reported D_{10} and D_{16} to calculate the wavelength most efficiently scattered by the conventional titanium dioxide rutile results in values lower than 400 nm. However, it is known that all titanium dioxide pigments have strong absorption in the ultraviolet (UV) region. As shown in Fig. 1, the particle size of the conventional titanium dioxide rutile ranges from 0.04 to 1.832 μm; the particle size of the Altiris 550 pigment varies from 0.04 to 2.280 μm; and the particle size of the Altiris 800 pigment varies from 0.04 to 2.837 μm. The span of the conventional titanium dioxide rutile, the Altiris 550 and the Altiris 800 pigments is 1.81, 1.87 and 2.00, respectively. The Altiris 800 pigment has the widest particle size distribution, while the conventional titanium dioxide rutile has the narrowest particle size distribution.

As indicated in Table 1, the particle size values of the conventional titanium dioxide rutile, the Altiris 550 and the Altiris 800, reported in different ways, increase in the following sequence: $D_{TiO2} < D_{Al550} < D_{Al800}$. The measured median particle size of the above three samples is 0.28, 0.36 and 0.41 μm, respectively. Studies by microscopy confirmed that the optimum particle size for the conventional titanium dioxide rutile pigment ranges from 0.2 to 0.3 μm [16]. Generally, conventional titanium dioxide has a *mean* particle size of 0.20 μm [11]. As inferred from figures 2 and 3 in reference [15], for symmetric distributions, the median particle size is equivalent to the mean particle size, while for non-symmetric distributions, these two central values are different, with the median value being larger than the mean one [15]. Therefore, within the experimental error, the measured particle size for the conventional titanium dioxide rutile, the Altiris 550 and the Altiris 800 pigments are reasonable. The measured median particle size and particle size distributions of these three