Colloids and Surfaces A: Physicochem. Eng. Aspects 520 (2017) 736–742

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

High hiding power and weather durability of film-coated titanium dioxide particles with a yolk-shell structure

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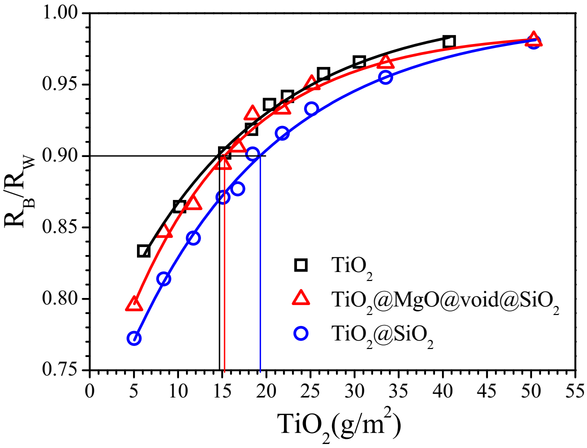
HIGHLIGHTS

- TiO_2@void@SiO_2structurewaspreparedbysurface-protectedetching.
- The void in the yolk-shell structure increased the refractive index difference.
- TiO_2@void@SiO_2 has high hiding power and low weather durability.
- TiO_2@MgO@void@SiO_2 was prepared to increase weather durability.
- TiO_2@MgO@void@SiO_2 structure saves TiO_2 consumption 21.2%.

GRAPHICAL ABSTRACT



Yolk-shell TiO_2@MgO@void@SiO_2 pigment exhibited high hiding power and weather durability. Compared with the same coating amount of 20% in dense film, the consumption of coated TiO_2 is reduced over 20%.

ARTICLE INFO

Article history:
Received 18 January 2017
Received in revised form 17 February 2017
Accepted 18 February 2017

Keywords:
Titanium dioxide
Coating
Yolk-shell structure
Hiding power
Weather durability

ABSTRACT

High hiding power and weather durability are the key characteristic indices of the high-performance pigmentary titanium dioxide (TiO_2). The film-coated TiO_2 particles with a yolk-shell structure of silica were prepared by surface-protected etching with polyvinyl pyrrolidone. The hiding power of the TiO_2 particles with the yolk-shell structure was 90.6, which is significantly higher than the hiding power of 87.7 for the dense film-coated TiO_2 particles with the same amount of coating (20%). However, the TiO_2 particles with the yolk-shell structure have low weather durability. The apparent degradation rate constant K_{app} for rhodamine-B had a high value of 13.2. An improvement was made by coating a dense MgO film on the TiO_2 particles first, and then coating a yolk-shell structure. The hiding power of the TiO_2 particles with the improved yolk-shell structure reached 90.6, and the weather durability was significantly increased as the apparent degradation rate constant K_{app} decreased to 2.2, reaching the excellent weather durability of the TiO_2 particles with 5 wt% dense film coating (Si3 + Al2), which is a common product in industry ($K_{app} = 1.8$). For the same indices of hiding power and weather durability, the TiO_2 particles with the improved yolk-shell structure obviously decreased the consumption of TiO_2, compared with the dense SiO_2-coated TiO_2 particles (TiO_2@SiO_2). It is inferred that the void in the yolk-shell structure increased

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http://dx.doi.org/10.1016/j.colsurfa.2017.02.046

the light reflectivity of the TiO_2 particles by increasing the difference of the refractive index between the core TiO_2 and the surroundings, and the dense MgO film increased the weather durability of the TiO_2 particles.

1. Introduction

Titanium dioxide (TiO_2) is the best white pigment due to its excellent optical properties, which is widely used in the paints, plastics, paper, ink and other industries. However, TiO_2 particles produce electrons and holes under UV light irradiation and generate radicals after reaction with water and oxygen, resulting in the degradation of the organic matter around the TiO_2 particles [1–4]. Hence, the TiO_2 particles need to be coated with the shield films of inert oxides, e.g., silica and alumina, to increase the weather durability [5–9].

Our previous work has confirmed that as the coating amount of the film-coated TiO_2 particles increased, the apparent degradation rate of rhodamine B by TiO_2 was reduced, i.e., the weather durability of the film-coated TiO_2 particles was increased [10,11]. However, as the coating amount increased, the hiding power of the film-coated TiO_2 particles decreased. The hiding power represents the ability of the TiO_2 particles in a paint layer to cover the background light from the matrix. The higher the hiding power of the TiO_2 particles was, the lower the amount of the TiO_2 was needed, i.e., the lower the cost.

The hiding power of titanium dioxide was not only affected by the particle dispersion in the organic matrix but also by the film refractive index coated on the titanium dioxide particles [12,13]. The hiding power of the film-coated TiO_2 particles was reported to increase as the film refractive index decreases in the range of 1.00–2.15, and the TiO_2 particles with a porous coating film have higher hiding power because the porous film has a lower apparent refractive index [14]. It is inferred that when the refractive index of the film is 1.00 (air), e.g., the yolk-shell structure, the film coated particle of titanium dioxide has the highest hiding power. The polymer yolk-shell structure containing TiO_2 particles in the centers of air void was obtained by using an emulsion polymerization [15]. The yolk-shell structure with air void was found to significantly enhance the pigment reflection in paint films. Compared with the same amount of the same titanium dioxide pigment used conventionally, the hiding power of the yolk-shell structure was increased from 38% to 66% [16]. However, the photocatalytic degradation of Rhodamine-B [17] and methylene blue [18] indicated that yolk-shell coated TiO_2 particles had higher photoactivity, i.e., worse weather durability. It is highly desired to fabricate an improved yolk-shell structure of the coating film on the TiO_2 particle surface to achieve high hiding power and weather durability.

Recently, many strategies for silica coating film with different morphologies on the surface of inorganic nanoparticles have been reported [19], especially for the preparation of a yolk-shell silica structure. Yolk-shell structure has exhibited many unique properties that are not accessible to core shell particles [20,21]. Templating strategies have been widely used for synthesizing yolk-shell structures, for example, the $TiO_2/C/SiO_2$ sample (core/template/shell) was prepared first, and then the sample was heated at 873 K for 3 h in air to remove carbon components and form the void [22]. This synthetic method is complex and time-consuming. The preparation methods of yolk-shell structures without templates have also been reported, a core shell particle was transformed into a yolk-shell particle directly by selective etching of the core particle [23] and by a surface-protected etching process with polyvinyl pyrrolidone (PVP) [24,25].

In this paper, TiO_2 particles were coated with a yolk-shell structure of silica by surface-protected etching, and the hiding power and weather durability of the coated TiO_2 particles were evaluated. The TiO_2 particles that were first coated with MgO film and then coated with the yolk-shell structure of silica were prepared to achieve high hiding power and high weather durability.

2. Experimental

2.1. Reagents

Commercial TiO_2 particles (technical pure, Jiangsu Hongfeng Titanium Company, China) having the rutile structure and an average diameter of 300 nm were used in the experiments. The TiO_2 particles were produced by the hydrolysis of $TiOSO_4$ and a subsequent calcination. They were pure without any preliminary treatment. All other chemicals used, namely, tetraethylorthosilicate (TEOS), polyvinyl pyrrolidone (PVP, MW ~ 10,000), sodium hydroxide (NaOH), $MgSO_4{\cdot}7H_2O$, ammonium hydroxide ($NH_3{\cdot}H_2O$, 28% by weight in water), ethanol, glycerol and rhodamine B, were analytical reagent (AR) grade.

2.2. Coating process

2.2.1. MgO coating on TiO_2 particles (TiO_2@MgO)

150 g TiO_2 particles were mixed with 300 g deionized water by an ultrasonic treatment for 30 min in a three-necked flask. Then $MgSO_4$ solution (1 mol/L) and NaOH solution (4.5 mol/L) were titrated into the TiO_2 suspension separately and simultaneously. The temperature was controlled at 60 °C by a constant temperature bath and the pH of the TiO_2 suspension was kept constant at 5 by adjusting the titration rate of the NaOH solution. After the titration, the suspension was aged for 2 h under stirring. Then, the suspension was filtered and dried at 105 °C for 24 h. The amount of MgO coating was set at 2.0 wt%.

2.2.2. SiO_2 coating on TiO_2 particles (TiO_2@ SiO_2), MgO and SiO_2 double layer coating on TiO_2 particles (TiO_2@MgO@SiO_2)

Ammonium hydroxide solution (10 mL), deionized water (40 mL), ethanol (100 mL) and TiO_2 particles (or TiO_2@MgO particles, 5 g) were mixed in a 250-mL three-neck flask with magnetic stirring. Then, a certain amount of TEOS was titrated into the TiO_2 suspension. The suspension was kept at room temperature under continuous magnetic stirring for 2 h. After aging, the suspension was centrifuged and washed 3 times, and dried at 105 °C for 24 h. The amount of SiO_2 coating was adjusted by controlling the amount of added TEOS.

2.2.3. Surface-protected etching

TiO_2@SiO_2 (5 g) (or TiO_2@MgO@SiO_2 particles) was added and dispersed in 100 mL PVP solution (10 g, MW ~ 10,000) under magnetic stirring. The suspension was heated to 100 °C and kept for 3 h to load PVP on the silica surface, and then cooled to room temperature. Under magnetic stirring, NaOH aqueous solution (30 mL, 0.20 g/mL) was added to the solution to etch the silica