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Influence of the seed layer on photoactivity inhibition of mica–titania pigments

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Abstract

The influence of the seed layer on the phase composition and photoactivity inhibition of mica–titania pigments was investigated. The prior deposition of MnO_2 or SnO_2 as a seed layer resulted in a complete rutile TiO_2 coating without calcinations, while the prior deposition of ZnO led to a mixture of anatase and rutile. The rutile promoting effect of MnO_2 and SnO_2 could be ascribed to the small lattice mismatch (< 5%) between the seed layer and the rutile TiO_2. Moreover, the seed layer had a great influence on the photoactivity inhibition of mica–titania pigments. A seed layer of MnO_2 inhibited the photoactivity of the pigments, whereas a seed layer of SnO_2 or ZnO enhanced the photoactivity of the pigments. The degradation rate constant of mica–MnO_2–TiO_2 was approximately 72.7% that of mica–TiO_2, while the degradation rate constant of mica–SnO_2–TiO_2 was approximately 4.5 times as high as that of mica–TiO_2. The influence of the seed layer on the photoactivity of mica–titania pigments depended on the transfer process of electron–hole pairs between the seed layer and TiO_2.

Keywords: D. TiO_2; Pearlescent pigment; Photoactivity inhibition; Seed; Degradation

1. Introduction

Due to the lustrous and iridescent appearance and the angle-dependent optical effects, pearlescent pigments have a growing economic significance for functional [1–3] and decorative purposes [4,5]. Pearlescent pigments are based on a substrate as the mechanical support of a thin optical layer. The best known substrate is mica, which can be natural or synthetic. The most common optical layers consist of titanium oxide, iron (III) oxide, mixed titanium–iron oxides, and chromium (III) oxide [5–7].

The most important pearlescent pigment is mica–titania pigment. Mica–titania pigments are typically produced by the deposition of TiO_2 on the mica in aqueous suspension followed by a calcination process [8]. TiO_2 is a polymorphous compound that crystallizes as rutile, anatase, or brookite [9]. Due to the higher refractive index of rutile, a better colour and lustre effect can be achieved when the rutile form of TiO_2 is coated on mica [10].

To obtain the rutile phase, generally, a seed layer is first deposited on the mica surface, followed by precipitation of TiO_2. The most used seed layer includes SnO_2, MnO_2 or ZnO [11,12]. As is known, TiO_2, SnO_2, MnO_2 and ZnO are typical semiconductor materials exhibiting photocatalytic activity that exert strong oxidizing power and can produce highly reactive free radicals [13]. Oxidation of the surrounding polymeric binders is the reason for the degradation of the materials, which manifests itself with a decreased mechanical strength, and impairment of the appearance by losing its gloss, changing its colour, or chalking in outdoor weathering [14–16]. For pigment applications that require low photocatalytic activity, the ability to inhibit the photoactivity would be of great value. This research was aimed at obtaining mica–titania pigments with low photoactivity.

Several papers have studied the effect of the seed layer on the phase composition of a TiO_2 coating [17,18]. However, very few studies have reported the effect of the seed layer on the photoactivity inhibition of a mica–titania pigment. In this study,

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the effect of SnO_2, MnO_2 or ZnO as a seed layer on the photoactivity inhibition of a mica–titania pigment was first reported.

2. Experimental

2.1. Materials

Synthetic mica was used as the substrate. The mica particles had an aspect ratio of 5.1 and were less than 1 μm thick. Analytical grade titanium tetrachloride ($TiCl_4$), manganese chloride ($MnCl_2$), stannic chloride ($SnCl_4$), zinc chloride ($ZnCl_2$), absolute ethanol (C_2H_5OH), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were used in the experiments, throughout which distilled water was used. The starting material in this study to deposit TiO_2 layer on mica was $TiCl_4$ ethanolic solution.

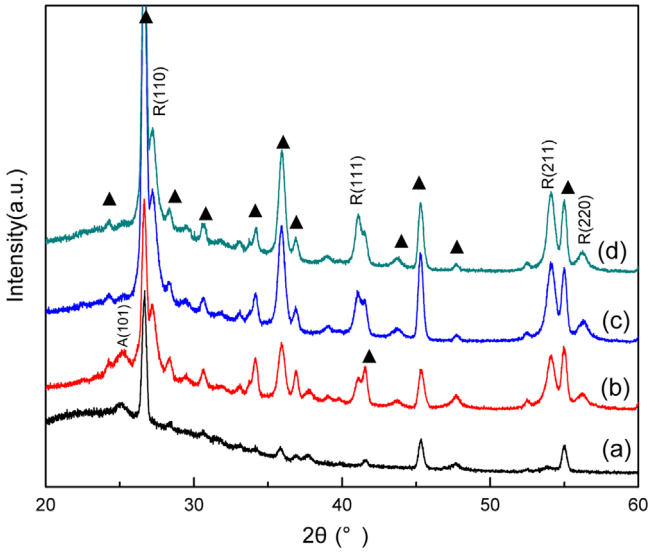

Fig. 1. XRD patterns of mica–titania pigments: (a) mica–TiO_2, (b) mica–ZnO–TiO_2, (c) mica–SnO_2–TiO_2, (d) mica–MnO_2–TiO_2.

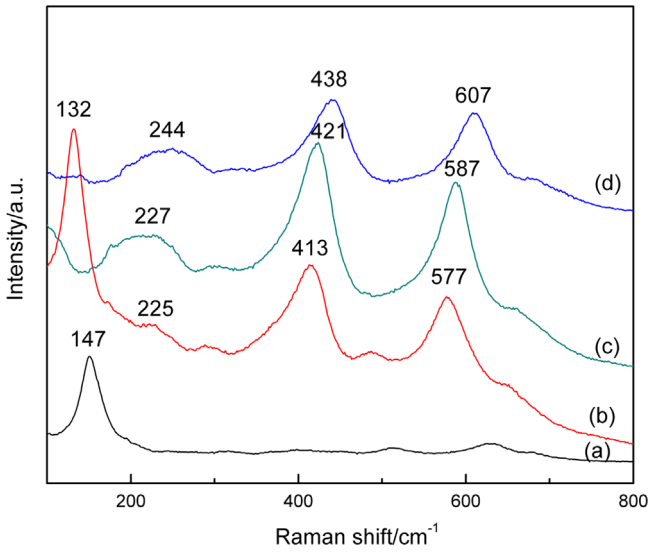

Fig. 2. Raman spectra of mica–titania pigments: (a) mica–TiO_2, (b) mica–ZnO–TiO_2, (c) mica–SnO_2–TiO_2, (d) mica–MnO_2–TiO_2.

2.2. Preparation method

2.2.1. Preparation of mica–titania pigments without a seed layer

To prepare the pigments, 1 L of distilled water containing mica particles was heated to 70 ℃ under stirring. The pH value of the batch was adjusted to 1.0 with diluted hydrochloric acid. Next, 0.12 L of $TiCl_4$ ethanolic solution was slowly dropped into the above suspension. The pH value of the slurry was kept constant by simultaneous addition of NaOH solution. After the addition was completed, the mixture suspension was aged for 1 h and then allowed to settle and cool to room temperature. Last, the product was separated from the mother liquid and then dried at 70 ℃ for 24 h. This sample was labelled as mica–TiO_2.

2.2.2. Preparation of mica-titania pigments with a prior deposition of a seed layer

The introduction of a seed layer to deposit the rutile phase of TiO_2 onto a mica substrate was achieved using a $SnCl_4$, $MnCl_2$, or $ZnCl_2$ solution. First, mica was suspended in distilled water and heated to 70 ℃, and the pH value of the slurry was adjusted to 2.0–3.0 using HCl. Next, the $SnCl_4$, $MnCl_2$, or $ZnCl_2$ solution (15 g/L) was added dropwise while the pH value was held constant by simultaneous addition of NaOH solution for 1 h. The weight ratios of $SnCl_4$, $MnCl_2$, or $ZnCl_2$ to mica were 3%. Next, the pH value was adjusted to 1.0, and then the TiO_2 coating was deposited onto mica by the addition of precursor in the same manner as described in 2.2.1.

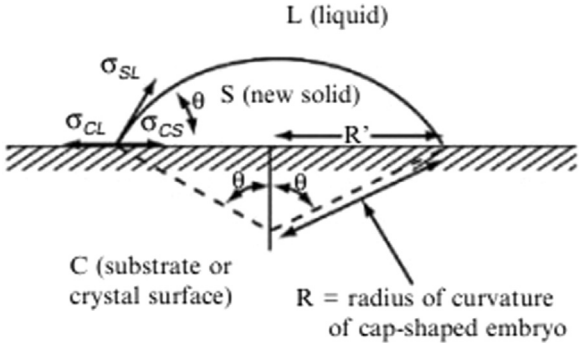

Fig. 3. Model geometries for idealized nucleation at the solid-water interface.

Table 1
Lattice parameters and lattice mismatch of the phases.

Phase	Lattice parameters (Å)		Lattice mismatch[a]
	a	*c*	
Rutile	4.5933	2.9592	–
Cassiterite (SnO_2)	4.7200	3.1700	2.8%
Pyrolusite (MnO_2)	4.3999	2.8740	4.2%
Zincite (ZnO)	3.2498	5.2066	29.2%

[a]Lattice mismatch = *a* (seed) − *a* (rutile)/*a* (rutile).