

Cracking of titania nanocrystalline coatings

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Abstract

Cracking of wet-chemically precipitated nanocrystalline TiO₂ films deposited on different platelet-like substrates is investigated. The thicknesses of the films are also in the nanometric range: 60, 140 or 300 nm. Scanning electron microscopy, X-ray diffraction and nitrogen adsorption are employed to determine layer thickness, grain size, and porosity. The synthesis of TiO₂ films through an aqueous route affords very good reproducibility of these properties (layer thickness ± 5 nm). Mica, SiO₂ and Al₂O₃ platelets are used as substrates, providing different properties with regard to surface charge, structure and roughness. The drying step is found to be responsible for the cracking of some of the TiO₂ layers and the evolution of the cracks during sintering is related to shrinkage of the substrate. Film thickness as well as the chemical nature of the substrate influences the cracking of nanocrystalline TiO₂ films during the drying step.

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1. Introduction

Titanium oxide-coated platelet-like substrates are largely used in the industry of pearlescent pigments. The most common substrate used for the precipitation of the titanium oxide layers in pigments is the muscovite mica, due to its availability. Synthetic substrates, like SiO₂ platelets, Al₂O₃ platelets, glass platelets and synthetic mica have been developed during the last two decades. These substrates allow, for example, a better control of the thickness and/or of the impurities. Nevertheless, TiO₂-coated natural mica remains commercially by far the most important family because of low cost of the mica substrate in comparison to synthetic substrates.^{1,2} TiO₂-coated mica studied in this work was obtained using the chloride process in which a TiOCl₂ solution is slowly added to a mica platelet suspension at low pH and temperatures of 60–90 °C. The synthesis of TiO₂-coated platelet-like substrates produced by Merck has already been optimised in terms of TiO₂ precipitation, lustre and chroma. Nevertheless, the presence of cracks

can still be observed at the surface of some of the pigments. In order to continuously improve the quality of the pigments, crack formation at the surface of inorganic pigments needs to be understood.

Cracking of inorganic films has repeatedly been reported in the literature.^{3–14} Depending on the systems studied, several reasons have been proposed for crack formation. The drying of porous material, like sol–gel bodies^{3,4,8,13} or granular ceramics^{5–7,9–12,14} is often seen as a decisive step for the appearance of cracks at the surface of these materials. In these cases, drying stresses develop which are linked to the tension forces that exist in the liquid inside the pores of the drying body. Crack formation is also reported to occur during sintering of ceramic films for cases with differential sintering leading to strain incompatibilities.^{5–7,11} During sintering, cracks favourably develop from intrinsic defects. Finally, problems of crack formation and decohesion can also develop during cooling of annealed ceramic films deposited on a substrate due to differences between the thermal expansion coefficients of the substrate and the coated film.^{15,16}

An improved understanding of the cracking of TiO₂ nanolayers deposited on platelet-like substrates is presented in this study. The effects of the drying step and the calcination step on cracking are treated. Moreover, the influence of layer thickness

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as well as of the underlying substrate has been examined, with respect to their acido-basicity, crystallinity and roughness.

2. Experimental

2.1. Synthesis of the samples

Titanium oxide layers were deposited on different platelet-like substrates via an aqueous liquid deposition process (LDP).^{1,2,17} It corresponds to controlled precipitation, at low pH (~ 2), of titanium chloride within an aqueous suspension containing the substrates. The TiO_2 rutile structure leads to a higher refractive index than the TiO_2 anatase structure.² Therefore, a process has been developed at Merck to create a TiO_2 rutile layer on mica by precipitating first a very thin SnO_2 layer on the substrate, which acts as a template for the TiO_2 rutile. The preparation of the samples used in this publication has been described in the literature.¹⁷ The thickness of the TiO_2 layers can be accurately controlled (± 5 nm) by varying the amount of titanium chloride solution. The precipitates were filtered off, washed completely with deionized water and dried at 110°C for 12 h. The dried pigments were then sintered at 850°C for 30 min.

The TiO_2 layer thickness deposited on the substrates were equal to 60 nm, 140 nm and 300 nm after sintering. Natural mica, SiO_2 platelets and Al_2O_3 platelets were utilized as substrates. To describe the samples studied in this work, the following type of notation will be used: “Ti-140-mica” with “Ti” for TiO_2 layer, “140” for TiO_2 -thickness layer equal to 140 nm after sintering and “mica” for the substrate used.

2.2. Substrates

The titanium oxide layers were precipitated on three different substrates: mica platelets (Merck, diameter 10–50 μm , thickness range 300–800 nm, mean thickness 400 nm), SiO_2 platelets (Merck, diameter 10–50 μm , thickness 450 ± 10 nm) and Al_2O_3 platelets (Merck, diameter 10–50 μm , thickness 200 ± 10 nm). The mica employed is the natural dioctahedral muscovite $\text{KAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$.¹⁸ The surfaces of the mica muscovite platelets are oriented along the (001) plane.¹⁹ The synthetic SiO_2 platelets are produced by a web-coating process.²⁰ These substrates are amorphous. Al_2O_3 platelets (α - Al_2O_3 , corundum) were produced using a controlled crystal growth process in molten sodium sulfate.²⁰ The surface of the platelets is preferentially orientated according to the (001) plane of α - Al_2O_3 corundum. There is no correlation between the lattice parameters of mica or Al_2O_3 platelets (corundum) with the lattice parameters of SnO_2 and TiO_2 rutile or anatase. The points of zero charge (PZC) values, given in the literature, for the oxides constituting the substrates are the following: $\text{PZC}_{\text{SiO}_2} \sim 2$ and $\text{PZC}_{\text{Al}_2\text{O}_3(001)} \sim 5 - 6$.^{18,21} Since the main plane developed at the surface of mica is close to SiO_2 , the PZC of mica can be considered close to the SiO_2 value.

Most of the experiments have been carried out with the three previously quoted substrates: natural mica, SiO_2 and Al_2O_3 platelets. Nevertheless, some experiments have been performed

using synthetic mica and glass platelets. In fact, the surfaces of SiO_2 , Al_2O_3 and glass platelets are smoother than those of natural and synthetic mica. Also, the chemical nature of synthetic and natural mica (respectively fluorophlogopite and muscovite) is different.

2.3. Characterization of pigments

The layers consist of oxide particles, which are called grains throughout this publication to make a clear distinction from the whole pigment particles themselves that consist of these films attached to substrates. In a given sample, not all pigment particles contain cracks. Therefore, the average percentage of pigment particles exhibiting cracks in a sample has been determined, using light microscopy. For ease of reading, the term “crack percentage” is used in the following instead of “average percentage of pigment particles”. Micrographs of the samples were taken using an Eclipse ME 600 (Nikon GmbH) under reflection conditions. It has also been used to determine the evolution of the cracks between the drying and the sintering steps. For this purpose, dried pigment particles were deposited on a sapphire holder on which markers had been inscribed. The dried particles were observed through the optical microscope; then the system composed of the dried particles on the sapphire holder was sintered at 850°C for 30 min. Thanks to the markers on the sapphire holder, the pigments previously observed in their dried state were identified and characterized after sintering.

The morphology of the TiO_2 layers and of the substrates was studied by scanning electron microscopy (SEM) (LEO 1530 Gemini). SEM was also used to measure the layer thickness on micrographs of fractured pigments. The pigments were mixed with a lacquer and dried. The lacquer, containing the pigments, was then broken in such a way that some of the particles were also fractured which allowed the thickness of the coating film to be measured.

The Brunauer–Emmett–Teller (BET) specific surface areas and the pore volumes were measured using a Micromeritics ASAP 2400 apparatus with nitrogen at 77 K. Assuming that the surface area of the substrates is negligible and that the TiO_2 grains attached to them are spherical, the particle size G_{BET} of dried TiO_2 layers was evaluated. (The specific area of mica, SiO_2 platelets and Al_2O_3 platelets are 2.8, 3.05, and $1.8\text{--}3.0\text{ m}^2/\text{g}$, respectively.) The weight percentage of TiO_2 in the pigments is taken into account for determination of the grain size:

$$G_{\text{BET}}(\text{nm}) = \frac{6000 f_{\text{TiO}_2}}{S_{\text{BET}} \times \rho_{\text{TiO}_2}}$$

Here f_{TiO_2} is the TiO_2 weight oxide fraction, S_{BET} is the BET surface area (m^2/g) and ρ_{TiO_2} is the theoretical density of titanium oxide (4.26 g/cm^3 (for rutile) and 3.85 g/cm^3 (for anatase)). The relative densities ρ_{rel} of the TiO_2 layers were also deduced from nitrogen adsorption measurements. Finally, the average pore radius $\bar{r}_p$ of the sample is also calculated from the nitrogen adsorption analyses according to the following formula

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