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Low temperature preparation of Cr-doped rutile pigments with good colour properties

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A B S T R A C T

Cr-doped rutile pigments were prepared by calcination of doped rutile precursors resulting from the hydrolysis-precipitation method. The pigment properties were investigated by X-ray diffraction, Thermogravimetry–differential scanning calorimetry, scanning electron microscopy, energy dispersive spectroscopy, diffuse reflection spectroscopy, Raman spectroscopy, and colourimetry. The pigments were found to have a rutile phase composition. Rutile pigments with good colour properties can be acquired by calcination from 500 °C to 900 °C. The pigment with 1.25% dopant and calcination at 700 °C presented optimal colour properties ($L^* = 75.46$, $a^* = 15.24$, $b^* = 39.46$). The pigments presented high dispersion and could be dispersed directly into polyurethane paint and polyurethane epoxy resin without further modification.

1. Introduction

As yellow pigments, chromates of alkaline-earth metal ions (e.g., calcium, strontium, barium), naples yellow (lead antimonate), litharge (lead oxide), and cadmium yellow are restricted in terms of commercial use due to the toxicity of Cr, Cd, and Pb. Therefore, it is necessary to develop the environment-friendly pigments replace the toxic inorganic pigments. And some environment-friendly pigments have been developed [1–4]. Crystalline TiO_2, especially rutile TiO_2, has high chemical stability and is not dissolved by 10% hydrofluoric acid solution [5]. Rutile-based solid solutions doped with Cr or Ni present a yellow hue with red and green shades, respectively [3,6–10]. The toxic elements Cr and Sb exist in rutile-based solid solutions and are diffused into the rutile lattice for high chemical stability. The rutile phase presents one of the highest refractive indices among the three known crystalline polymorphs. Hence, rutile-based solid solutions with several expected properties satisfy most of the characteristics required for pigment application.

The inorganic pigments can be synthesized by solution processing [1–3,8,11,12] and solid-state reaction [4,6,8,10]. The solid-state reaction is generally used to prepare yellow rutile pigments. This traditional ceramic method must be performed at high temperature to ensure that the dopants are completely introduced into the rutile lattice and homogeneously dispersed into the rutile matrix [6]. Anatase or amorphous TiO_2 powders are used as precursors in this method but the final phase composition of the pigment is rutile because of its high thermal stability. The anatase-to-rutile transition induces the dopant to insert into the rutile lattice [6,13]. The colour of doped rutile pigments also develops during the anatase-to-rutile transformation [9,10,14]. However, this phase transition generally occurs at temperatures above 900 °C [13]. Thus, high-temperature calcination is necessary to prepare rutile-based yellow pigments by the solid-state method, requiring consumption of large amounts of energy. Milling and sieving must also be implemented to adjust the grain size of the pigment in the solid-state method [15,16] due to the coarsening of pigment particles caused by high-temperature calcination.

Cr ions have been reported to complete their diffusion in the rutile phase at about 750 °C [17]. Incorporating several counterions into the rutile phase can enhance dopant solubility to ensure lattice electroneutrality [18]. Rutile synthesis can be easily implemented by directly hydrolysing $TiCl_4$ solutions at low temperature [19,20]. Hence, yellow Cr-doped rutile pigments can be prepared by calcination of rutile precursors at temperatures lower than that in the conventional solid-state method. Few studies on the rutile phase as a precursor for yellow titania pigments have been published. Thus, in the present paper, a low-temperature method for synthesising

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yellow titania pigment by calcination of the rutile and dopants at temperatures from 500 °C to 900 °C is reported. The prepared pigment presented good colour properties.

2. Experimental section

2.1. Preparation of TiO_2 pigments

The Cr-doped rutile pigments were synthesised by firing mixtures of rutile precursors and doped ions at a low temperature. The rutile precursors were prepared according to the method by Nam [19]. In a typical synthesis, $TiCl_4$ (10 mL) (Sinopharm Chemical Reagent Co. Ltd., China) was added into ice blocks under vigorous stirring. Caution should be exercised as the reaction is rather violent and produces thick fumes. During the reaction, yellow solids formed. These solids were then taken and dissolved in melted ice water to form $TiOCl_2$ solution. The resulting solution was diluted with distilled water to obtain a $TiOCl_2$ concentration of 1 M. The rutile suspensions were prepared by refluxing 1 M $TiOCl_2$ aqueous solution at 60 °C–100 °C for 8 h. The precipitates were filtered and washed with distilled water.

The precipitates were either dried at 100 °C for X-ray diffraction (XRD) analysis or diluted to 20 wt% suspensions and mixed with chromium chloride. Approximately 2 mL of antimony chloride ethanol solution was dripped into the suspensions, and 10% aqueous ammonia solution was used to adjust their pH to 7. Green precipitates were obtained by filtration–washing cycles. The filtered precipitates were dried at 100 °C for 4 h to obtain green powders, which were calcined at different temperatures for 1 h to obtain the pigment products. The resulting samples were denoted as *Px–y*, where *x* refers to the atom ratio of Cr/Ti × 100 and *y* refers to the calcination temperature. The Cr ion content was equal to the Sb ion content in all samples. Thus, the value of *x* also refers to the atom ratio of Sb/Ti × 100. None of the samples were further milled or sieved.

2.2. Colouration of plastics and paint

The coloured paint was acquired by ultrasonicating 0.2 g of P1.25-700 pigments in 10 g of polyurethane (PU) paint (Dü Fang, Acryl PU-Klalack) for 2 min. This paint was then poured into a 9 cm Petri dish for curing into a coloured film.

Low-density polyethylene (LDPE, PetroChina Co. Ltd. of Lanzhou Petrochemical Company) was utilised as a base phase to fabricate the pigmented compact. LDPE (40 g) and 1.25-700 pigment (0.8 g) were mixed in a rheometer at 180 °C for 10 min. The mixtures were pressed in a flat vulcanising press at 180 °C for 5 min. After pressing at room temperature for 5 min, a 2 mm thick yellow polyethylene (PE) sheet was acquired.

2.3. Characterization techniques

The phases of the products were characterised by XRD using CuKα radiation ($\lambda = 0.15418$ nm) in a XD-3 diffractometer (Beijing Pgeneral). Morphological and elemental analyses were performed by scanning electron microscopy (SEM-EDS, Hitachi S-3700). Raman spectra were recorded on a Bruker RFS100 spectrometer with a resolution of 4 cm^{-1} using 1054 nm light as the excitation source. Ultraviolet–visible (UV–Vis) spectra were recorded on a spectrophotometer with an integrating sphere (Shmadzu UV-2550); $BaSO_4$ was used as a reference sample. The colour of the pigments was evaluated by measuring $L^*a^*b^*$ (L^*: 0 = black/100 = white, green ($-a^*$) to red ($+a^*$) and blue ($-b^*$) to yellow ($+b^*$)) parameters with a Konica-Minolta spectrophotometer CM-700d. Thermogravimetry–differential scanning calorimetry (TG–DSC) of the pigments was carried out in air at a heating rate of 10 °C/min using Netzsch instruments (NETZSCH STA 409 PC/PG). Tensile tests were performed on a universal testing machine (SANS CMT4104). The experiments were performed at room temperature with 10 mm/min to determine tensile strength.

The photocatalytic activities of the samples were evaluated by the degradation of methyl orange (MO) in an aqueous solution (20 mg L^{-1}). The light source was provided by a 450 W high pressure mercury lamp (Shanghai YaMin). Before the photocatalytic experiment, the suspension was stirred in the dark for 30 min, and this concentration was considered the original concentration (C_o) of MO. The sampled suspension was centrifuged at 5000 r/min at a given reaction time, and the clean upper solution was collected. The concentration (C) of the MO solution was monitored by measuring the maximum absorbance of MO using the UV–Vis spectrophotometer.

3. Results and discussion

The expected phase composition for yellow titania pigment is monophasic rutile. High-temperature calcination is indispensable to obtain rutile TiO_2 from anatase or amorphous TiO_2 precursors. Fig. 1 shows the XRD patterns of the precursors. The phase compositions of the samples present only the rutile phase. Nam et al. [19] reported that a pure rutile phase could be formed by hydrolysing $TiOCl_2$ solution just below 65 °C and that the rutile phase precipitates with the anatase phase at higher temperatures. This finding is somewhat different from our results. Fig. 1 indicates that a pure rutile TiO_2 can be fabricated by directly hydrolysing $TiOCl_2$ solution between 60 and 100 °C, and no anatase phase was observed in any of the samples. In our reaction system, 1 M $TiOCl_2$ solution was used as a precursor, twice as much as that used in the study by Nam. Therefore, a higher Cl anion concentration should be attained from the hydrolysis of $TiOCl_2$ solution in our reaction to suppress anatase phase formation [20]. The rutile precursor synthesised at 80 °C presented the most intense peak among the samples synthesised at three different temperatures.

Fig. 2 presents the XRD results of pigment products. As shown in Fig. 2(a), the products calcined from 400 °C to 900 °C always presented a pure rutile phase. The peaks became sharper and more intense as the calcination temperature increased, indicating improved crystallisation. This change was more obvious at lower temperature. When fired above 500 °C, especially at 700 °C or higher, the peaks of the products were sharp and intense, presenting little changes and indicating that stable rutile crystals were obtained. In the traditional solid-state method, obtaining a pure rutile phase is difficult in this temperature range [8,21]. Anatase-to-rutile transformation occurred at 900 °C for the ceramic method,

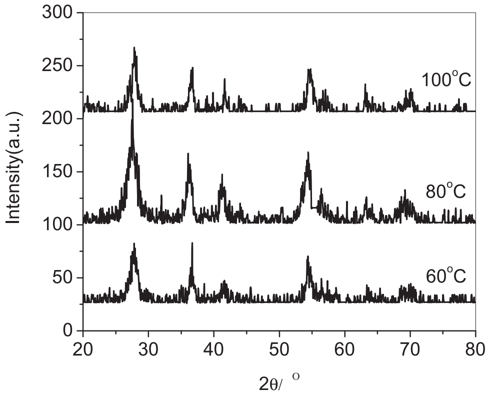

Fig. 1. XRD patterns of rutile precursors synthesised at different temperatures.