

Influence of concentration in phosphoric acid treatment of titanium oxide and their powder properties



Hiroaki Onoda*, Aki Matsukura

Department of Informatics and Environmental Sciences, Kyoto Prefectural University, 1-5, Shimogamo Nakaragi-cyo, Sakyo-ku, Kyoto 606-8522, Japan

ARTICLE INFO

Article history:

Received 4 August 2014
Received in revised form 9 October 2014
Accepted 13 October 2014
Available online 2 November 2014

Keywords:

Titanium oxide
Phosphoric acid treatment
Photocatalytic activity
Particle size

ABSTRACT

Titanium oxide that has the photocatalytic activity is used as a white pigment for cosmetics. A certain degree of sebum on the skin is decomposed by the ultraviolet radiation in sunlight. In this work, titanium oxide was shaken with various concentrations of phosphoric acid to synthesize a novel white pigment for cosmetics. Their chemical composition, powder properties, photocatalytic activity, color phase, and smoothness were studied. The obtained materials indicated XRD peaks of titanium oxide; however, these peak intensities became weak by phosphoric acid treatment. The photocatalytic activity of the obtained powders became weak by phosphoric acid treatment to protect the sebum on the skin. The high concentration of phosphoric acid was suitable to obtain a novel white pigment in the phosphoric acid treatment of titanium oxide.

© 2014 The Ceramic Society of Japan and the Korean Ceramic Society. Production and hosting by Elsevier B.V. All rights reserved.

1. Introduction

As a white pigment, titanium dioxide is used for cosmetic applications [1]. This oxide is well known to have a photocatalytic activity. Therefore, a certain degree of sebum on the skin is decomposed by the ultraviolet radiation in sunlight. To repress this effect, technical processes of several kinds have been investigated and used. For example, as one such technique, composite particles with silicon oxide have been used [2]. However, these particle materials are too hard to use on a human face. Mild materials are required to use as a white pigment on a human face. In addition, one report has described that microfine titanium dioxide is adsorbed through the skin [3]. A novel white pigment that is not adsorbed must be used.

Phosphates have been used to modify the surface of ceramic materials, catalysts, adsorbent, fluorescent materials, dielectric substances, biomaterials, metals, as fertilizer, detergents, food additives, in fuel cells, pigments, and in other applications [4,5]. Phosphate materials are well known to have a high affinity for living organisms. Therefore, as a novel white pigment, phosphates are expected to be useful as cosmetics.

In earlier studies [6,7], we prepared a titanium phosphate pigment with titanium chloride that had no catalytic activity. The weak

point of this preparation was that titanium chloride is difficult to treat because of its high reactivity, forming smoke and undesirable precipitates. Generally, starting compounds can influence the formation and properties of products. In the group of titanium compounds, titanium sulfate is also important intermediate in the production of titanium oxide. In previous work, titanium phosphate was prepared from titanium sulfate and phosphoric acid [8]. The obtained phosphates also showed no photocatalytic activity.

Small and homogeneous particles are suitable for cosmetic applications. However, overly small particles have a major shortcoming in that they enter the pores of the skin [3]. Generally, pigments with sub-micrometer size are used. The optimum size for white pigment particles used in cosmetics is difficult to determine because the pore sizes of the skin are affected by factors such as age, gender, and climate. Furthermore, overly large particles are inappropriate owing to cracking of their coatings on the skin. It is therefore important to control the pigment particle sizes. In the previous work [6–8], the titanium phosphates prepared from titanium chloride and sulfate gave particles larger than 10 μm . Because these particles were too large, the novel process was required to produce the smaller particles as a white pigment. The titanium phosphate particles without photocatalytic activity were too large; on the other hand, titanium oxide small particles were photocatalytically active. In this work, we proposed to make the titanium oxide particles with titanium phosphate coating. Our purpose in this work was to obtain a white pigment in sub-micrometer size without photocatalytic activity.

In this work, titanium oxide was shaken with various concentrations of phosphoric acid. Their respective chemical compositions,

* Corresponding author at: Department of Informatics and Environmental Sciences, Kyoto Prefectural University, 1-5, Shimogamo Nakaragi-cyo, Sakyo-ku, Kyoto 606-8522, Japan. Tel.: +81 757035653; fax: +81 75 703 5653.

E-mail address: onoda@kpu.ac.jp (H. Onoda).

Peer review under responsibility of The Ceramic Society of Japan and the Korean Ceramic Society.

powder properties, photocatalytic activity, color phases, and smoothness of the obtained precipitates and their thermal products were studied for application to cosmetics.

2. Experimental

The 0.1, 0.2 and 0.5 mol L⁻¹ of phosphoric acid were adjusted to pH 7 with sodium hydroxide. Titanium oxide was set with the phosphoric acid (50 mL) at molar ratios of P/Ti = 1/1 and 1/2 in a glass tube, and then this glass tube was shaken in hot water at 80 °C for 1 h. The powder samples were decanted, washed with water, and dried at 50 °C for about 1 week. All chemicals were of commercial purity from Wako Chemical Industries Ltd. (Osaka Japan) and used without further purification.

The crystalline phase compositions of these materials were analyzed using X-ray diffraction (XRD). The XRD patterns were recorded on an X-ray diffractometer (MiniFlex; Rigaku Corp.) using monochromatic CuK α radiation. Samples were heated at 100 °C, 200 °C, and 400 °C in air for 1 h with electric furnace. These thermal products were also analyzed according to their XRD patterns.

The particle shapes and sizes, as well as their thermal products at 100 °C, 200 °C, and 400 °C, were estimated based on scanning electron microscopy (SEM) images and particle size distributions. The SEM images of the sample powders were observed (JGM-5510LV; JEOL). The particle size distributions of these materials were measured using a centrifugal precipitation particle-size distribution (SA-CP3L, Shimadzu Corp.).

The cosmetic properties were estimated according to the photocatalytic activity, the color phase, and the smoothness. The photocatalytic activity of samples was estimated with the decomposition of methylene blue by 365 nm radiation [9,10]. The 0.01 g of sample was placed in 4 mL of methylene blue solution (1.0 \times 10⁻⁵ mol L⁻¹), and then this solution was radiated. The decrease of the absorption at about 660 nm was estimated for 120 min. The color of phosphate pigments was estimated using ultraviolet–visible (UV–Vis) reflectance spectra with a spectrometer (UV2100; Shimadzu Corp.) (reference compound; BaSO₄). The whiteness was also estimated with TES135 plus color analyser (TES Electrical Electronic Corp). The particle smoothness was measured on artificial leather with KES-SE objective evaluation of surface friction property (Kato Tech Co. Ltd.). The values of MIU and MMD respectively represent the slipping resistance (coefficient of kinetic friction) and roughness of powders (dispersion on coefficient of kinetic friction). Sample powders were spread on the leather. Then a sensor was run over these powders. The values of MIU and MMD were calculated respectively from the power to move a sensor and the pitching of a sensor. The values of MIU and MMD have no unit because these values are related with coefficient of friction and scattering, respectively.

3. Results and discussion

3.1. Chemical composition and powder properties of precipitates

Fig. 1 presents XRD patterns of samples prepared at various conditions (without heating). All samples treated with phosphoric acid indicated the same peak pattern with original titanium oxide. However, the peak intensity became a little weak by the phosphoric acid treatment. A part of titanium oxide was considered to react with phosphoric acid. By changing from titanium oxide to titanium phosphate on surface of particles, XRD peaks due to titanium oxide became weak. In previous works [6–8], titanium phosphate, expected product from titanium oxide and phosphoric acid, was easy to form amorphous phase. Therefore, no novel peaks appeared in XRD patterns. Table 1 shows the ratios of XRD peak intensities of

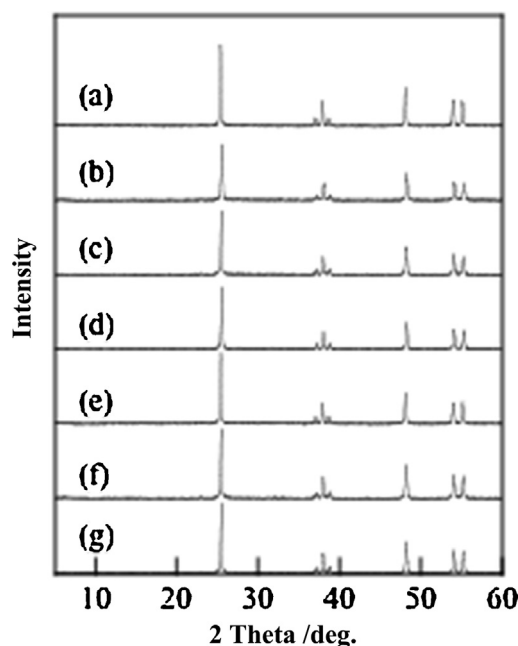


Fig. 1. XRD patterns of samples prepared at various conditions (without heating), (a) original TiO₂, (b) P/Ti = 1/1, H₃PO₄ 0.1 mol L⁻¹, (c) 1/1, 0.2 mol L⁻¹, (d) 1/1, 0.5 mol L⁻¹, (e) 1/2, 0.1 mol L⁻¹, (f) 1/2, 0.2 mol L⁻¹, and (g) 1/2, 0.5 mol L⁻¹.

samples prepared under various conditions. These ratios were calculated from the peak intensities of samples and original titanium oxide. The value “100%” meant the same intensity with original titanium oxide, namely titanium oxide had no change by the phosphoric acid treatment. The lower ratio was corresponding with the reaction between titanium oxide and phosphoric acid. Samples treated at P/Ti = 1/1 indicated lower XRD peak ratio than those at P/Ti = 1/2, because the high ratio of phosphoric acid was easy to react with titanium oxide. Further, the condition with 0.5 mol L⁻¹ of phosphoric acid indicated the lower XRD peak ratio than others. The heating temperature had less influence on the ratio of XRD peaks.

From the viewpoint of particle shape, spherical particles are suitable for cosmetic applications. Fig. 2 portrays SEM images of samples prepared under various conditions (without heating). All samples had no specified shape and had particles larger than 10 μ m. The small particles were observed in these large particles. Fig. 3 presents the particle size distribution of samples prepared at P/Ti = 1/1. Because all samples had particles smaller than 1 μ m, the large particles in SEM images dispersed by stirring before the measurement of particle size distribution. The original titanium oxide had the maximum ratio at 0.4 μ m; on the other hand, samples treated with phosphoric acid had the ratio at 0.3 μ m. The average particle size was reduced by the phosphoric acid treatment. Especially, samples treated with 0.5 mol L⁻¹ of phosphoric acid indicated high ratio at 0.3 μ m in the particle size distribution. Generally, pigments with sub-micrometer average sizes are used

Table 1
Ratios of XRD peak intensities of samples prepared under various conditions/%.

	P/Ti	Conc. (mol L ⁻¹)	Heating temperature (°C)			
			R.T.	100	200	400
a	1/1	0.1	69.6	85.1	65.0	80.5
b	1/1	0.2	80.0	88.0	83.3	87.0
c	1/1	0.5	78.0	72.7	71.8	72.3
d	1/2	0.1	88.7	81.7	82.5	80.2
e	1/2	0.2	86.4	85.2	85.8	79.9
f	1/2	0.5	86.8	82.0	77.4	67.1

Download English Version:

<https://daneshyari.com/en/article/1473294>

Download Persian Version:

<https://daneshyari.com/article/1473294>

[Daneshyari.com](https://daneshyari.com)