

LOW TEMPERATURE PHOSPHORIC ACID TREATMENT OF ZINC OXIDE FOR NOBEL WHITE PIGMENTS

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Zinc oxide that has the photocatalytic activity is used as white pigment for cosmetics. A certain degree of sebum on the skin is decomposed by the ultraviolet radiation in sunlight. In this work, zinc oxide was shaken with phosphoric acid to synthesize a white pigment for cosmetics. Zinc oxide was set with $0.1 \text{ mol} \cdot \text{l}^{-1}$ of phosphoric acid at $P/Zn = 1/1$ and $1/2$, and then shaking in water at 30, 40, 50 °C for 1, 3, 6 hours. The chemical composition, powder properties, photocatalytic activity, color phase, and smoothness of the obtained powder were studied. The P/Zn ratio in preparation had influence on the reaction between phosphoric acid and zinc oxide. The photocatalytic activity of zinc oxide was inhibited by phosphoric acid treatment. The treated samples at 50 °C had enough high reflectance at the visible light region.

INTRODUCTION

As a white pigment, zinc oxide is used for cosmetic applications [1]. This oxide is well known to have photocatalytic activity [2]. 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 dioxide have been used [3]. However, these particle materials are too hard for use on a human face. Mild materials are required for use as a white pigment on a human face. In addition, the microfine zinc oxide is adsorbed through the skin [4]. A white pigment that is not adsorbed must be used.

Phosphates have been used for ceramic materials, catalysts, adsorbent, fluorescent materials, dielectric substances, biomaterials, for metal surface treatment, as fertilizer, detergents, food additives, in fuel cells, pigments, and in other applications [5, 6]. Phosphate materials are well known to have high affinity for living organisms [7]. Therefore, as a white pigment, phosphates are expected to be useful as cosmetics.

When used as a cosmetic pigment, the particle shape and size distribution of the phosphate particles are important. Homogeneous spherical particles are expected to spread well on the skin [8]. However, overly small particles are unsuitable because the pigments might enter the pores of the skin. Generally, sub-micrometer size pigments are used. The standard size of white pigment particles used in cosmetics is

difficult to determine because the pore sizes of the skin are affected by such factors as age, gender, and climate [9]. Furthermore, overly large particles are inappropriate owing to a cracking of their coating on the skin [10]. It is therefore important to control the particle sizes of the pigment. In earlier studies [11, 12], we prepared zinc phosphate pigments with no catalytic activity. However, zinc phosphates had particle sizes larger than 1 μm . Because these particles were too large, the novel process was required to produce the smaller particles as a white pigment. The zinc phosphate without photocatalytic activity had too much large particles, on the other hand, zinc oxide in small particle size had a photocatalytic activity. In previous work, to obtain the zinc oxide particles with zinc phosphate coating, zinc oxide was shaken in phosphoric acid at 60, 70, and 80 °C [13]. The target particles have the core-shell structure, which core part is zinc oxide and shell part is zinc phosphate without photocatalytic activity. However, the obtained zinc oxide with zinc phosphate coating included larger particles than 10 μm . Because of high temperature in phosphoric acid treatment, zinc phosphate was much formed on the surface of zinc oxide. Our purpose in this work was to obtain the white pigment in sub-micrometer size without photocatalytic activity by the control of the reaction between zinc oxide and phosphoric acid.

In this work, zinc oxide was shaken with phosphoric acid at lower temperatures, 30, 40, and 50 °C. The chemical compositions, powder properties, photocatalytic activity, color phases, and smoothness of the obtained samples and their thermal products were studied for application to cosmetics.

EXPERIMENTAL

Zinc oxide was set with $0.1 \text{ mol} \cdot \text{l}^{-1}$ of phosphoric acid (50 ml) at molar ratios of $\text{P}/\text{Zn} = 1/1$ and $1/2$ in a glass tube, and then this glass tube was shaking in hot water at 30, 40, and 50 °C for 1, 3, and 6 hours (rate of shaking; 100 times/min) [13]. The solutions were decanted off, and the powder samples were washed with water, and then dried at 50 °C over 3 days. 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., Akishima, Japan) using monochromated $\text{CuK}\alpha$ radiation. The IR spectra were recorded on a HORIBA FT-IR 720 (Horiba Ltd., Kyoto, Japan) using the KBr disk method. A part of the samples was dissolved in a nitric acid solution. The ratios of phosphorus and zinc in the precipitates were also calculated based on the inductively coupled plasma optical emission spectrometry (ICP-OES) results of these solutions using a Thermo Scientific iCAP7000 from Thermo Fisher Scientific (Waltham, USA).

The particle shapes and sizes of the precipitates were estimated based on scanning electron microscopy (SEM) images and particle size distributions. The SEM

images of the sample powders were observed (JSM-5510LV; JEOL, Akishima, Japan). The particle size distributions of these materials were measured using a centrifugal precipitation particle-size distribution (SA-CP3L, Shimadzu Corp., Kyoto, Japan).

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 [14, 15]. The 0.01 g of sample was placed in 4 ml of methylene blue solution ($1.0 \times 10^{-5} \text{ mol} \cdot \text{l}^{-1}$), 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., Kyoto, Japan) (reference compound; BaSO_4). The whiteness was also estimated in $L^*a^*b^*$ color space with TES135 plus color analyser (TES Electrical Electronic Corp., Taipei, Taiwan) (average of 5 times).

As the smoothness of sample powders, the static friction resistances were estimated on artificial leather with Portable Friction Meter 94i-II (SHINTO Scientific Co., Ltd., Tokyo, Japan). The sample powders were spread on the leather, and then a sensor was run over the powders.

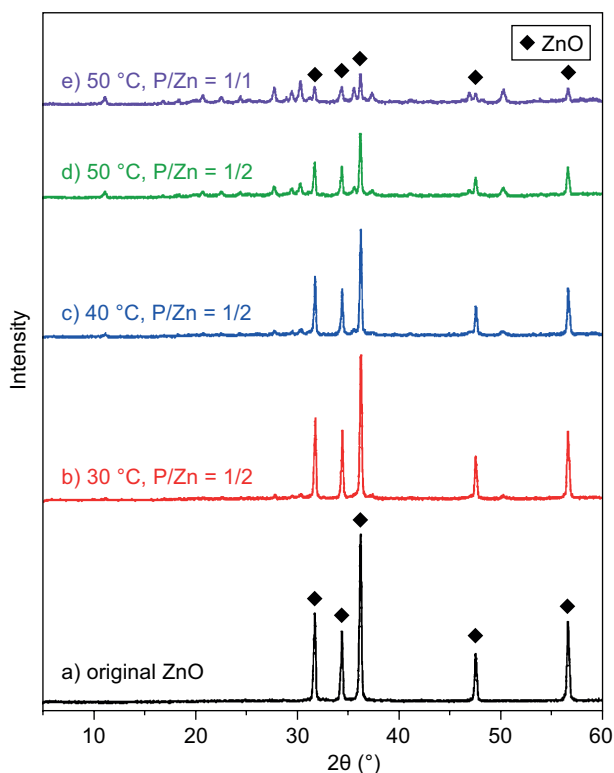


Figure 1. XRD patterns of samples prepared under various conditions (6 h).

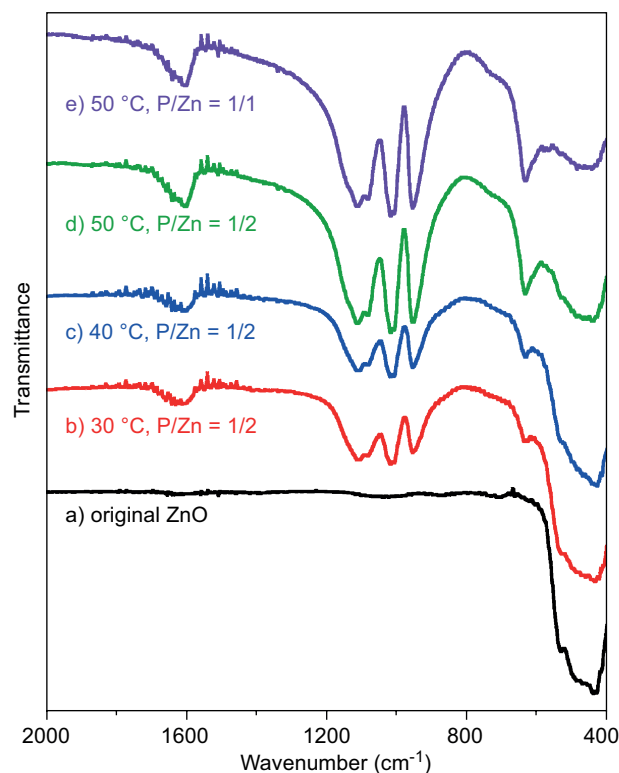


Figure 2. IR spectra of samples prepared under various conditions (6 h).

RESULTS AND DISCUSSION

Chemical composition

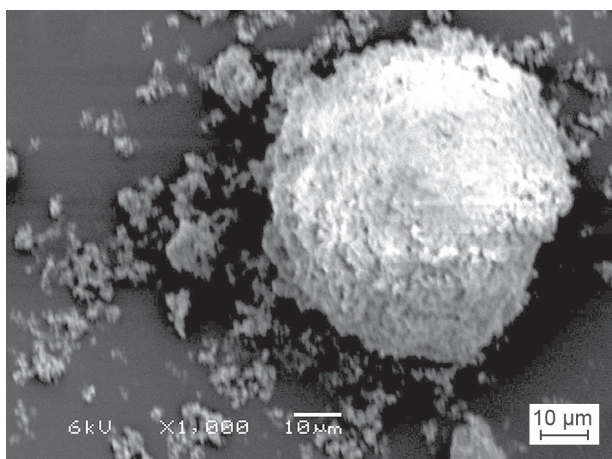
Figure 1 presents XRD patterns of samples treated in various conditions. By phosphoric acid treatment at higher temperature, the peak intensity became weaker. Samples treated at $P/Zn = 1/1$ indicated weaker peaks of zinc oxide than those at $P/Zn = 1/2$. Nobel weak unknown peaks appeared in the XRD patterns of samples treated at $P/Zn = 1/1$. These changes were corresponding with the reaction between zinc oxide and phosphoric acid.

Table 1. P/Zn ratio of samples prepared under various conditions.

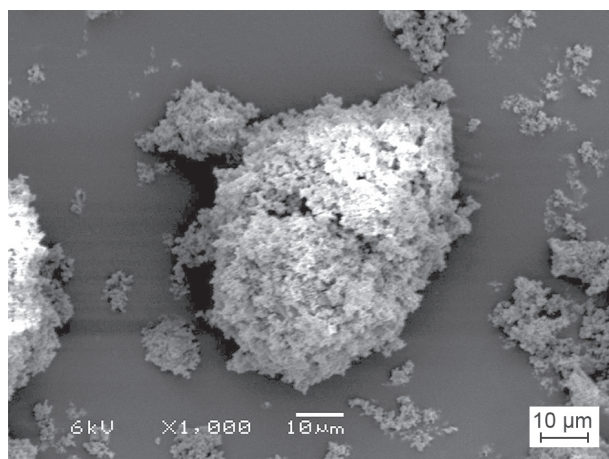
Temp. (°C)	Preparation P/Zn	Time (h)		
		1	3	6
30	1/2	0.228	0.215	0.183
40	1/2	0.270	0.257	0.340
50	1/2	0.285	0.355	0.438
50	1/1	0.540	0.573	0.650

Figure 2 shows IR spectra of samples treated in various conditions. Original zinc oxide had no absorption at $1110-950\text{ cm}^{-1}$, on the other hand, samples prepared in this work had some peaks at this region, due to zinc phosphate. The formation of zinc phosphate in the phosphoric acid treatment of zinc oxide was confirmed from IR results. The peaks at $400-550\text{ cm}^{-1}$, due to zinc oxide, became weaker by phosphoric acid treatment.

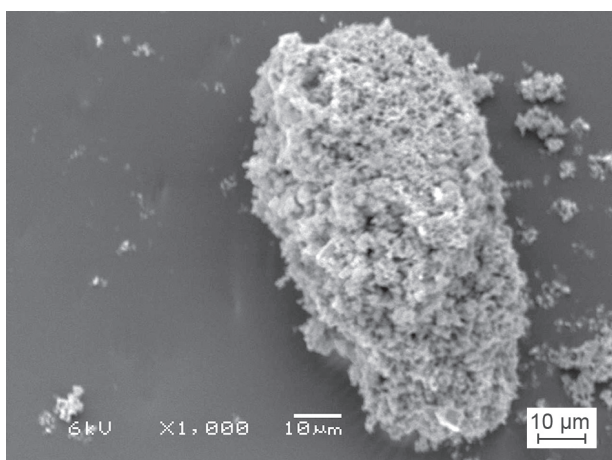
Table 1 shows P/Zn ratio in samples prepared under various conditions. The P/Zn ratio of starting zinc oxide and zinc phosphate, $Zn_3(PO_4)_2$, is 0 and 2/3, respectively. Samples treated at higher temperature indicated higher P/Zn ratio. Samples treated at $P/Zn = 1/1$ had high P/Zn ratio. The high P/Zn ratio of samples means that samples contained large amount of zinc phosphate. Shaking higher temperature and high P/Zn preparation ratio promoted the reaction with phosphoric acid. When sample was the mixture of zinc oxide and phosphate in the molar ratio of $ZnO / Zn_3(PO_4)_2 = 2/1$, the P/Zn ratio became 2/5. The mixture of zinc oxide and phosphate in the molar ratio of $ZnO / Zn_3(PO_4)_2 = 7/1$ was $P/Zn = 2/10$. The molar ratio of $ZnO / Zn_3(PO_4)_2$ was much inferred from these P/Zn ratio of samples.



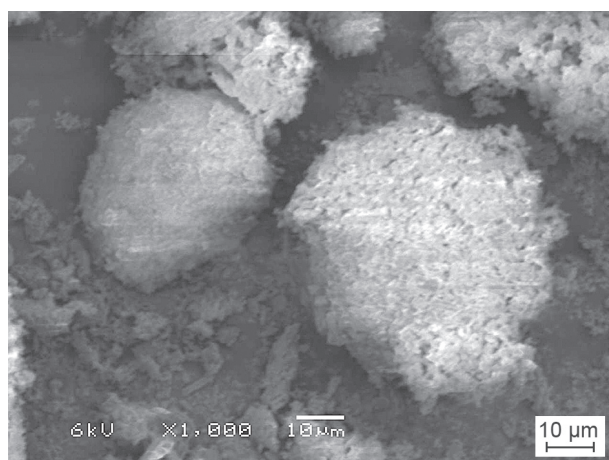
a) 30 °C, $P/Zn = 1/2$



b) 40 °C, $P/Zn = 1/2$



c) 50 °C, $P/Zn = 1/2$



d) 50 °C, $P/Zn = 1/1$

Figure 3. SEM images of samples prepared under various conditions (6 h): a) 30 °C, $P/Zn = 1/2$; b) 40 °C, $P/Zn = 1/2$; c) 50 °C, $P/Zn = 1/2$; d) 50 °C, $P/Zn = 1/1$.

Powder properties of samples

From the viewpoint of particle shape, spherical particles are suitable for cosmetic applications [16,17]. Figure 3 portrays SEM images of samples prepared in P/Zn = 1/1 and 1/2 at various shaking temperatures. All samples had no specified shape in particles and large aggregates. The particle shape of samples had no change from P/Zn ratio in preparation and shaking temperatures.

Figure 4 presents the particle size distribution of samples prepared at 50 °C in P/Zn = 1/2 for various shaking hours. The ratio larger than 1 μm became high by phosphoric acid treatment for 6 hours. Because zinc phosphate had larger particle size than zinc oxide [11, 12], the formation of zinc phosphate produced large particle size.

Cosmetic properties

Figure 5 shows the photocatalytic activity of samples prepared with shaking at various temperatures. Methylene blue was decomposed with zinc oxide using UV radiation (Figure 5b). The photocatalytic activity of zinc oxide was inhibited by the phosphoric acid treatment (Figure 5c-f). Because zinc phosphate, expected as a product on the surface of particles, had no photocatalytic activity [11, 12], the inhibition of photocatalytic activity was related with the reaction between zinc oxide and phosphoric acid. Sample prepared at 50 °C for 3 or 6 hours indicated enough weak photocatalytic activity. The temperatures; 30 °C and 40 °C were too low to react

between zinc oxide and phosphoric acid, and the shaking time; 1 hour was too short. The shaking temperature and hours had influence on the photocatalytic activity of samples.

Figure 6 shows UV-Vis reflectance spectra of samples prepared at 50 °C in P/Zn = 1/1 for various shaking hours. All samples indicated high reflectance at visible light region. Sample treated for 6 hours indicated higher reflectance at ultraviolet region than others. Because zinc phosphate had the high reflectance at ultraviolet region [6], samples treated in this work indicated higher reflectance than zinc oxide at this region. From the above ICP results (Table 1), sample treated for 6 hours included higher ratio of zinc phosphate than those for 1 and 3 hours.

The color of sample powder was also estimated by L*a*b* color space. Table 2 shows the whiteness of samples prepared in various conditions. These values were L* value in L*a*b* color space. Because samples treated 50 °C in P/Zn = 1/2 indicated over 95, these samples were suitable as a white pigment. These results were corresponding with the UV-Vis reflectance spectra of samples.

As described above, pigment with high smoothness spreads well on the skin. The powder smoothness is also important for cosmetics [18]. Table 3 shows the smoothness of samples prepared under various conditions. All samples indicated lower static friction resistance than zinc oxide (0.607). The samples obtained in this work were suitable to use as a novel white pigment for cosmetics from the viewpoint of smoothness.

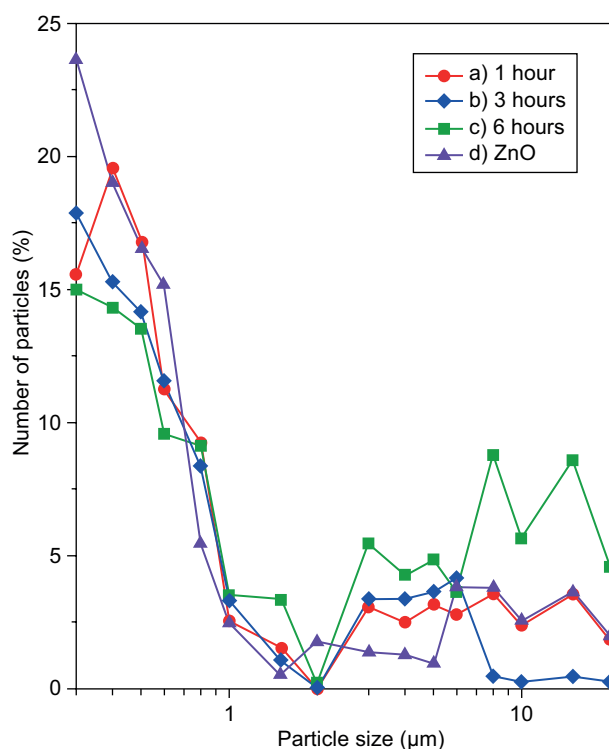


Figure 4. Particle size distribution of samples treated for several hours (50 °C, P/Zn = 1/2).

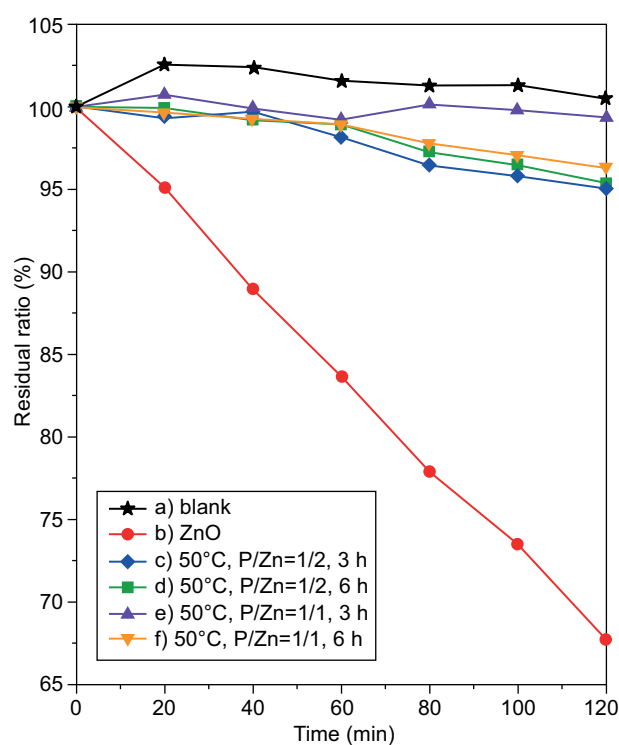


Figure 5. Photocatalytic activity of samples prepared under various condition.

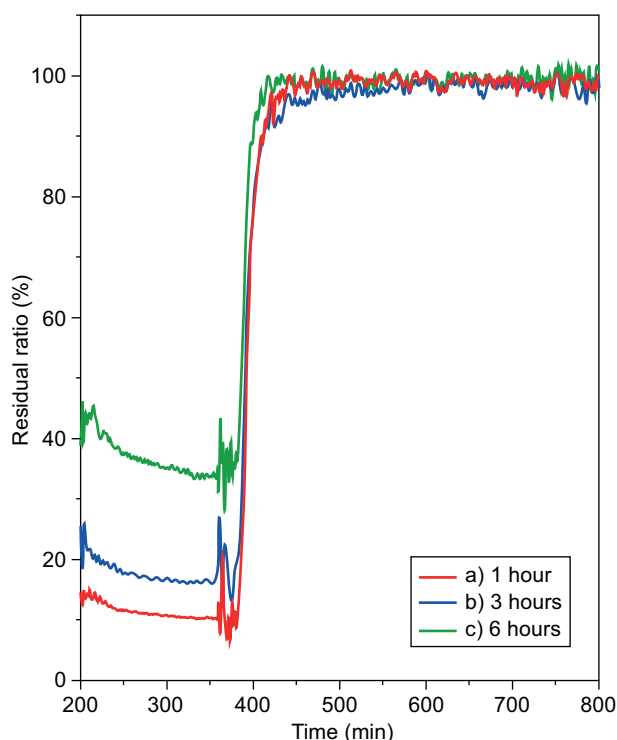


Figure 6. UV-Vis reflectance spectra of samples treated for several hours (50 °C, P/Zn = 1/1).

Table 2. Whiteness of samples prepared under various conditions.

Temp. (°C)	Preparation P/Zn	Time (h)		
		1	3	6
30	1/2	79.9	84.0	80.5
40	1/2	91.1	90.5	97.3
50	1/2	97.6	98.2	97.9
50	1/1	89.4	88.3	86.2

Table 3. Smoothness of samples prepared under various conditions.

Temp. (°C)	Preparation P/Zn	Time (h)		
		1	3	6
30	1/2	0.303	0.323	0.463
40	1/2	0.285	0.281	0.431
50	1/2	0.451	0.311	0.242
50	1/1	0.250	0.386	0.307

CONCLUSION

Zinc oxide was shaken in phosphoric acid under various conditions. A part of zinc oxide reacted to zinc phosphate in this process. The P/Zn ratio in preparation had influence on the progression of this reaction. The treated samples for 6 hours had a certain degree of larger particles than 1 μm . The photocatalytic activity of zinc oxide was inhibited by this phosphoric acid treatment at

50 °C for 3 and 6 hours. The treated samples at 50 °C had enough high reflectance at the visible light region. This phosphoric acid treatment at 50 °C for 3 hours is the effective method to obtain a novel white pigment for cosmetics.

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