Preparation of novel cosmetic white pigments by mechanochemical treatment of zinc oxide with phosphoric acid

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ABSTRACT
Zinc oxide has a photocatalytic activity, but in cosmetics it is used as a white pigment. When used in cosmetics, this photocatalytic activity causes some of the skin’s sebum to be broken down by the ultraviolet rays contained in sunlight. In this study, we attempted to mill zinc oxide with phosphoric acid to react the powder surface to zinc phosphate. Since zinc phosphate has no photocatalytic activity, the particles whose surface is replaced by zinc phosphate are expected to have little photocatalytic activity. The chemical composition, powder properties, photocatalytic activity, hue (visible light reflectance, L*ab* value), and smoothness of the obtained powder materials were examined. A portion of the zinc oxide was reacted to zinc phosphate by milling with phosphoric acid. In some samples, the reaction to zinc phosphate was observed to be too advanced, resulting in larger particles. The photocatalytic activity of zinc oxide was successfully eliminated through milling. Although the samples in this study had sufficient whiteness, the whiteness of some of the samples decreased due to contamination by milling. The smoothness of the pigment powders produced in this study was improved by milling, especially by prolonged treatment and the use of low concentrations of phosphoric acid.

1. Introduction
Zinc oxide is used in cosmetics as a white pigment [1]. On the other hand, it is well known that this oxide has photocatalytic activity [2]. Therefore, with the use of cosmetics, the sebum of the skin is broken down to some extent by the ultraviolet rays of the sun. Several types of technological processes have been studied and used to reduce this effect. For example, particles composited with silicon dioxide have been used as one such technique [3]. However, these composite particles are too hard to be used on the human face. To use them as white pigments on the human face, we need softer materials. In addition, ultrafine particle zinc oxide is absorbed by the skin [4]. A white pigment of a size that will not be absorbed is needed.

Phosphates have been used in applications such as ceramic materials, catalysts, adsorbents, fluorescent materials, dielectrics, biomaterials, metal surface treatment, fertilizers, detergents, food additives, fuel cells, and pigments [5,6]. It is well known that phosphate materials have high affinity for living organisms [7]. Therefore, phosphates are expected to be useful as white pigments for cosmetics.

The particle shape and size distribution of phosphate particles is important when used as cosmetic pigments. Homogeneous spherical particles are expected to spread well on the skin [8]. Excessively small particles, however, are inappropriate because the pigments may penetrate into the skin pores. In general, sub-micrometer sized pigments are used. The standard size of white pigment particles used in cosmetics is difficult to determine because the size of skin pores varies with age, gender, and climate [9]. Furthermore, if the particles are too large, the coating will break on the skin, which is inappropriate [10]. Therefore, it is important to control the particle size of the pigment. In previous studies [11,12], zinc phosphate pigments were prepared and it was found that these did not have photocatalytic activity. These pigments, when prepared with additives used in cosmetics, constituted spherical, uniform particles. However, the particle size of the zinc phosphate was greater than 1 µm. The zinc phosphate particles were too large and a new process was needed to produce smaller particles as white pigment. In summary, the particles of zinc phosphate were too large without photocatalytic activity; conversely, zinc oxide with a small particle size had photocatalytic activity.

In a previous study, zinc oxide was shaken in phosphoric acid at various temperatures to obtain zinc phosphate-coated zinc oxide particles [13]. As a result, target particles with a core-shell structure, where the core is zinc oxide and the shell is zinc phosphate without photocatalytic activity, were obtained. However, the obtained zinc phosphate-coated zinc oxide contained particles larger than

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10 μm. The purpose of this study was to obtain white pigments with sub-micrometer size without photocatalytic activity by controlling the reaction between zinc oxide and phosphoric acid. Therefore, we studied the mechanochemical reaction between zinc oxide and phosphoric acid. Mechanochemical treatment is known to reduce the size of particles in the reaction of powder materials.

In this study, novel white pigments were prepared by milling zinc oxide with phosphoric acid. The chemical composition, powder properties, photocatalytic activity, hue, and smoothness of the obtained samples were investigated for the purpose of application to cosmetics.

2. Experimental

Zinc oxide was added to phosphoric acid (0.1 or 0.3, 0.5 mol/L, 40 mL) under various molar ratios of P/Zn = 1/2 or 1/5, 1/10 in a polypropylene pot (65 mL) with 12 mullite balls (average weight 1.693 g, diameter 8.85 mm). The pot was rotated by Ball Mill ANZ10S (Nitto Kagaku, Co Ltd, Nagoya, Japan) for 10, 30, and 60 minutes (330 rpm). 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, and were obtained from FUJIFILM Wako Pure Chemical Corp. (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 CuKa radiation (30 kV, 15 mA, 3°/min, step size: 0.02°). The IR spectra were recorded on a HORIBA FT-IR 720 (Horiba Ltd., Kyoto, Japan) using the KBr disk method. To estimate the ratios of phosphorus and zinc in the samples, a portion of the sample was dissolved in a nitric acid solution. These ratios were calculated from the results with Agilent 4200 Microwave Plasma Atomic Emission Spectroscopy (MP-AES). The particle size distributions of these materials were measured using a centrifugal precipitation particle-size distribution (SA-CP3L, Shimadzu Corp., Kyoto, Japan). The approximate particle size distribution of samples was evaluated using the density of zinc oxide, although exact measurement was not possible because the ratio of zinc oxide to zinc phosphate in the sample was not clear.

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 x 10⁻⁵ mol/L), 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; BaSO₄). The whiteness was also estimated in L*a*b* color space with TES135 plus color analyzer (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.

3. Results and discussion

3.1. Chemical composition and powder properties

Figure 1 presents XRD patterns of samples prepared in various conditions. All samples indicated the XRD peak patterns of zinc oxide and zinc phosphate. It was confirmed that a part of zinc oxide reacted to zinc phosphate. Sample prepared at P/Zn = 1/2 had relatively weak peaks due to zinc oxide, and it was found that the reaction was relatively advanced (Figure 1(a)).

Figure 2 shows IR spectra of samples prepared in various conditions. Zinc oxide had strong absorption at 400–550 cm⁻¹ and no absorption at 600–2000 cm⁻¹ [16]. On the other hand, zinc phosphate had the peaks at 625, 950, 1010, and 1110 cm⁻¹ [17]. Samples

![Figure 1. XRD patterns of samples prepared in various conditions (0.1 mol/L, 60 min), (a) P/Zn = 1/2, (b) 1/5, (c) 1/10, ▼; ZnO, ▽; Zn₃(PO₄)₂.](attachment:image.png)
prepared at P/Zn = 1/5 and 1/10 showed the absorption peaks of zinc oxide and zinc phosphate. Sample prepared at P/Zn = 1/2 showed strong peaks due to zinc phosphate and weak peak due to zinc oxide. These IR results indicated that the P/Zn ratio in preparation process influenced the progress of the reaction between zinc oxide and phosphoric acid.

Table 1 shows the P/Zn ratio in samples prepared under various conditions. The P/Zn ratios of all samples were higher than the P/Zn ratios of the raw materials, because part of zinc oxide was dissolved in phosphoric acid. The high P/Zn ratio in samples indicated the possible formation of ZnHPO₄ and Zn(H₂PO₄)₂. It was found that the phosphoric acid concentration did not significantly affect the P/Zn ratio in samples (Table 1 (D)-(F)). Similarly, the changes in milling time within the scope of this study did not significantly affect the P/Zn ratio (Table 1(C)(G)(H)). On the other hand, when the P/Zn ratio at the preparation was small, the P/Zn ratio of sample tended to be small (Table 1(C)(F)(L)).

Figure 3 presents the particle size distribution of samples prepared in various P/Zn ratios. The original ZnO indicated high ratio of smaller particles than 1 µm. On the contrary, zinc phosphate for comparison had a high proportion of large particles. Sample prepared with P/Zn = 1/2 contained relatively large particles compared to the other samples. This was due to the fact that zinc phosphate tended to increase in size, which corresponded to the high P/Zn ratio in this sample described above.

### 3.2. Cosmetic properties

Figure 4 shows the photocatalytic activity of samples prepared in various P/Zn ratios. Methylene blue was decomposed with original zinc oxide under UV light radiation (Figure 4(d)). On the other hand, samples prepared in this study did not decompose methylene blue (Figure 4(a-c)), which confirmed that they did not have the photocatalytic activity. Since zinc phosphate, which is assumed to be a product on the particle surface, has no photocatalytic activity [11,12], the inhibition of photocatalytic activity indicated that the surface of zinc oxide reacted with phosphoric acid by milling.

Figure 5 shows UV–Vis reflectance spectra of samples treated in various P/Zn ratios. All samples indicated high reflectance at visible light region, and it was confirmed...
conditions are shown in Table 2. Some samples showed $L^*$ values below 90. In previous studies of white pigment preparation by shaking, few samples had $L^*$ values below 90 [13]. This decrease in $L^*$ value was considered to be due to contamination during milling.

As described above, pigment with high smoothness spreads well on the skin. The powder smoothness is also important for cosmetics [18]. Table 2 shows the static friction resistance of samples prepared in various conditions. The low static friction resistance means high smoothness. Zinc oxide measured in this condition was 0.664. Sample prepared for longer milling time showed lower static friction resistance (Table 2 (C)(G) (H)(F)(I)(J)). It was also found that low concentration conditions produced samples with low resistance (Table 2 (A)(B)(C)(D)(E)(F)). Previous studies have shown that zinc phosphate is smoother than zinc oxide [19]. However, there were some samples that did not match this trend, which was thought to be related to the fact that the occurrence of a few large particles can cause a significant decrease in smoothness. High smoothness was produced by the mild change of surface to zinc phosphate at low concentrations.

Since it is required to be smooth and have small particles, it was considered that low phosphoric acid concentration, low $P/Zn$ ratio in preparation, and long-term treatment were suitable to produce white pigment for cosmetics.

### 4. Conclusions

Zinc oxide was treated with ball mill in phosphoric acid under various conditions. A part of zinc oxide reacted to zinc phosphate by milling. Samples prepared in $P/Zn = 1/2$ had larger particles due to the influence of zinc phosphate’s tendency to grow. The photocatalytic activity of zinc oxide was almost eliminated by mechanical treatment. Samples in this study had sufficient whiteness, however some samples showed a decrease in whiteness due to contamination by milling. The smoothness of the pigment powder was improved by milling, and it became smoother by long-term treatment and the use of low concentration of phosphoric acid.
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Disclosure statement

No potential conflict of interest was reported by the author(s).

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