Mixing ratio of zinc nitrate and phosphoric acid for preparation of zinc phosphate white pigments

(Mistura de nitrato de zinco e ácido fosfórico para preparação de pigmentos brancos de fosfato de zinco)

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Abstract

In this work, zinc phosphates were prepared from zinc nitrate and phosphoric acid at various Zn/P ratios as a novel white pigment for use in cosmetics. The chemical composition, powder properties, photocatalytic activity, color phase, moisture retention, and smoothness of the zinc phosphates were studied. Samples prepared at Zn/P = 2/1, 3/2, and 1/1 indicated XRD pattern of $Zn_3(PO_4)_2$•$4H_2O$. The plane particles were observed in SEM images of sample prepared at Zn/P = 2/1, 3/2 and 1/1. The photocatalytic activity of these zinc phosphate particles was too less to protect the sebum on the skin. The materials prepared at Zn/P = 2/1, 3/2 and 1/1 and their thermal products at 100 °C showed a high reflectance within the range of visible light. Samples prepared at high Zn/P ratio indicated small MIU value.
Keywords: white pigment, zinc phosphates, Zn/P ratio, photocatalytic activity, particle shape.

Resumo

Neste trabalho, os fosfatos de zinco foram preparados a partir de nitrato de zinco e ácido fosfórico variando Zn/P como um novo pigmento branco para utilização em cosméticos. A composição química, propriedades dos pós, atividade fotocatalítica, cor, humidade e textura dos fosfatos de zinco foram estudadas. Amostras preparadas de Zn/P = 2/1, 3/2, e 1/1 indicaram DRX de $Zn_3(PO_4)_2$•$4H_2O$. As partículas foram observadas por imagens de MEV das amostras preparadas de Zn/P = 2/1, 3/2 e 1/1. A atividade fotocatalítica destas partículas de fosfato de zinco foi muito menor para proteger o sebo da pele. Os materiais preparados de Zn/P = 2/1, 3/2 e 1/1 e os seus produtos térmicos a 100 °C mostrou uma alta reflectância na faixa da luz visível. Amostras preparadas em alta proporção de Zn/P indicaram pequeno valor MIU.
***Palavras-chave**: pigmento branco, fosfatos de zinco, proporção Zn/P, atividade catalítica, forma da partícula.*

INTRODUCTION

As white pigments, titanium dioxide and zinc oxide are used for cosmetic applications [1]. These oxides are well known to exhibit photocatalytic activity. Therefore, a certain amount of sebum on the skin is decomposed by the ultraviolet radiation in sunlight. To repress this effect, several kinds of technical processes have been investigated and used. In one such technique, composite particles with silicon oxide were utilized [2]. However, such particle materials are too hard for use on the human face. Instead, soft materials are required for use as a white facial pigment. In addition, one report stated that microfine oxide is absorbed through the skin [3]. Therefore, a novel white pigment that is not absorbed must be used.

Phosphates have been used as ceramic materials, catalysts, fluorescent materials, dielectric substances, metal-surface treatments, detergents, food additives, fuel cells, pigments, and so on [4, 5]. Phosphate materials are well known to have a high affinity for living organisms and are therefore expected to be useful as white pigments in cosmetics.

When used as a cosmetic pigment, the particle shape and size distribution of the phosphate are important. Spherical homogenized particles are expected to spread well on the skin. However, overly small particles are unsuitable because the pigments might enter the pores of the skin. Generally, the pigments with sub-micrometer size are used. In earlier studies [6-8], we prepared titanium and zinc phosphate pigments with no catalytic activity. The ratio of cation / phosphorus is important factor on the powder properties of phosphate materials [9]. Therefore, the present work was undertaken to obtain homogenized zinc phosphate particles by changing the mixing ratio of raw materials.

For this work, as a novel white pigment, zinc phosphate, was prepared from zinc nitrate and phosphoric acid at various Zn/P ratios. Their respective chemical compositions, powder properties, photocatalytic activity, color phases, moisture retention, smoothness of the

obtained precipitates, and thermal products were studied for application in cosmetics.

EXPERIMENTAL

0.1 mol/L of a zinc nitrate solution was mixed with 0.1 mol/L of a phosphoric acid solution in molar ratios of Zn/P = 2/1, 3/2, 1/1, and 2/3 at room temperature for more than 1 h. The precipitates were then filtered off, washed with water, and dried at room temperature over 3 days. All chemicals were of commercial purity from Wako Chemical Industries Ltd. (Osaka Japan) and used without further purification.

A part of the precipitates was dissolved in a hydrochloric acid solution. The ratios of phosphorus and zinc in the precipitates were also calculated based on the ICP results of these solutions using an SPS1500VR from Seiko Instruments, Inc. The chemical 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 monochromated Cukα radiation. The samples were heated at 100 °C in air to remove the adsorbed water, and the thermal products were analyzed according to their XRD patterns.

The particle shapes and sizes of the precipitates, as well as their thermal products at 100 °C, were estimated based on scanning electron microscopy (SEM) images and particle size distributions. The SEM images of the zinc phosphates 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, color phase, moisture retention, and smoothness. The photocatalytic activity of the samples was estimated through the decomposition of methylene blue using 365 nm radiation (sample; 0.01 g, methylene blue; $1x10^{-5}$ mol/L, 4 mL) [10, 11]. The residual ratio of methylene blue was calculated from the absorption at 660 nm with a UV2100, Shimadzu Co. The color of the phosphate pigments was estimated using ultraviolet-visible (UV-Vis) reflectance spectra from a UV2100, Shimadzu Co. For the moisture retention of the samples, 0.3 g per sample was mixed with 0.1 g of water, and the weight loss was then evaluated at 50 °C (MS-70 Moisture Analyzer, A and D Instruments Co. Ltd.). The same weight loss over longer time meant high water retention of samples. The particle smoothness was measured on artificial leather based on a KES-SE objective evaluation of the surface friction property (Kato Tech Co., Ltd.). The MIU and MMD values represent the slipping resistance and roughness of the powders, respectively. The sample powders were spread onto the leather, and a sensor was then run over the powders (scan speed; 1 mm/sec, area scanned; 3 cm). 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.

RESULTS AND DISCUSSION

Chemical composition and powder properties of zinc phosphates

Table I shows the Zn/P ratios of the samples prepared under various conditions. Sample prepared at Zn/P = 2/1 had high Zn/P ratio (1.63), on the other hand, sample prepared at Zn/P = 2/3 indicated low Zn/P ratio (1.18). Other samples had about a 1.5 Zn/P ratio, which corresponds to a composition of $Zn_3(PO_4)_2$. The Zn/P ratios in precipitates of the former samples were between Zn/P ratio in preparation and 1.5. Zinc phosphate, $Zn_3(PO_4)_2$, was easy to form in these conditions.

Table I - Zn/P ratios of precipitates prepared under various Zn/P ratios.
[Tabela I - Preparação de precipitados de Zn/P em várias proporções de Zn/P.]

sample	Zn/P ratio in preparation	Zn/P ratio in precipitates
A	2/1	1.63
B	3/2	1.51
C	1/1	1.50
D	2/3	1.18

Fig. 1 shows the XRD patterns of the samples prepared under various conditions (without heating). Samples prepared at Zn/P = 2/1, 3/2, and 1/1 indicated XRD pattern of $Zn_3(PO_4)_2•4H_2O$ (Fig. 1(a)(b)(c)) [12]. Because unknown peaks were observed in XRD pattern of sample prepared at Zn/P = 2/3, this material was the mixture of $Zn_3(PO_4)_2•4H_2O$ and other compounds (Fig. 1(d)). This ratio, Zn/P = 2/3, was too different with the Zn/P ratio in $Zn_3(PO_4)_2•4H_2O$ to form other compounds. The peak intensity was also affected from the preparation condition. Since samples prepared at Zn/P = 1/1 had strong peaks, the crystal structure was easy to grow in samples prepared at Zn/P = 1/1.

In terms of particle shape, spherical particles are suitable for cosmetic applications. Fig. 2 shows SEM images of the samples prepared under various conditions. The plane parts on particles were observed in samples prepared at Zn/P = 2/1, 3/2, and 1/1 (Fig. 2(a)(b)(c)). On the other hand, no specified shape was observed in sample prepared at Zn/P = 2/3 (Fig. 2(d)). The plate particles were related with the formation of $Zn_3(PO_4)_2•4H_2O$. Fig. 3 shows the particle size distribution of the samples prepared under various conditions. Sample prepared at Zn/P = 3/2 indicated high ratio of particles at 1.5 and 15 μm, other samples indicated high ratio at 15 μm. When the particles were aggregated, samples indicated smaller particle size in these distributions, because samples were dispersed and stirred in solution before the measurement of the particle size distribution. Since these

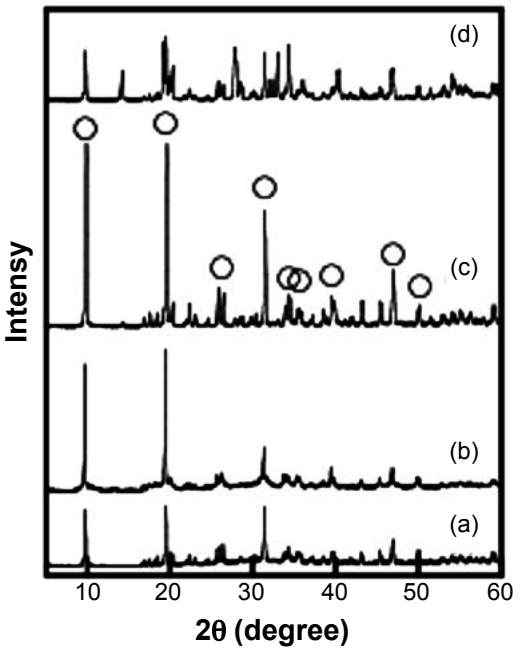

Figure 1: XRD patterns of samples prepared under various Zn/P ratio: (a) Zn/P=2/1, (b) 3/2, (c) 1/1, and (d) 2/3, ○; $Zn_3(PO_4)_2$•$4H_2O$.
[Figura 1: Difratogramas de raios X das amostras preparadas de Zn/P: (a) Zn/P=2/1, (b) 3/2, (c) 1/1, e (d) 2/3, ○; $Zn_3(PO_4)_2$•$4H_2O$.]

results in particle size distributions were corresponding with the above particle size in SEM images, the phosphate particles were considered to be not an aggregate.

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, the pigments with sub-micrometer size 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. Furthermore, overly large particles are inappropriate owing to a cracking of their coating on the skin. It is therefore important to control the particle sizes of the pigment.

Cosmetic properties of zinc phosphates

Fig. 4 shows the respective photocatalytic activities of the samples prepared under various conditions. Because zinc oxide is used as a white pigment in cosmetics, the compound was evaluated for a comparison with zinc phosphate [1]. Methylene blue decomposed with zinc oxide under UV irradiation (Fig. 4(e)). On the other hand, zinc phosphate, which is a mild material that can protect the

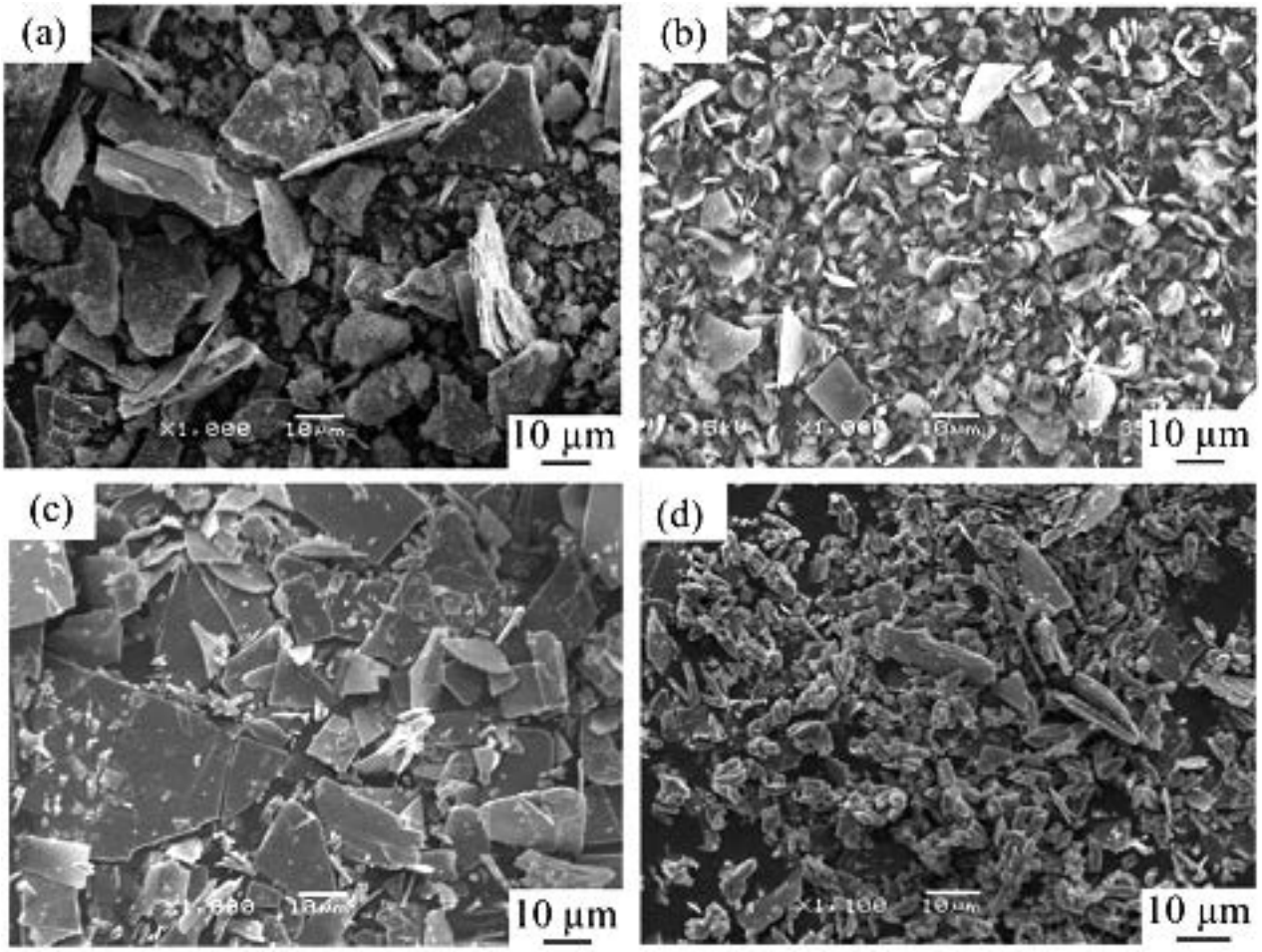

Figure 2: SEM images of samples prepared under various Zn/P ratios: (a) Zn/P=2/1, (b) 3/2, (c) 1/1, and (d) 2/3.
[Figura 2: Imagens de MEV das amostras preparadas Zn/P: (a) Zn/P=2/1, (b) 3/2, (c) 1/1, e (d) 2/3.]

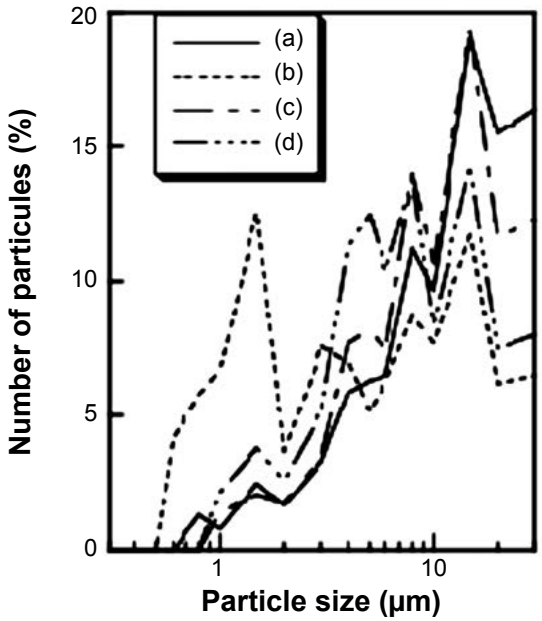

Figure 3: Particle size distribution of samples prepared under various Zn/P ratios: (a) Zn/P=2/1, (b) 3/2, (c) 1/1, and (d) 2/3.
[Figura 3: Distribuição de tamanho das partículas das amostras preparadas Zn/P: (a) Zn/P=2/1, (b) 3/2, (c) 1/1, e (d) 2/3.]

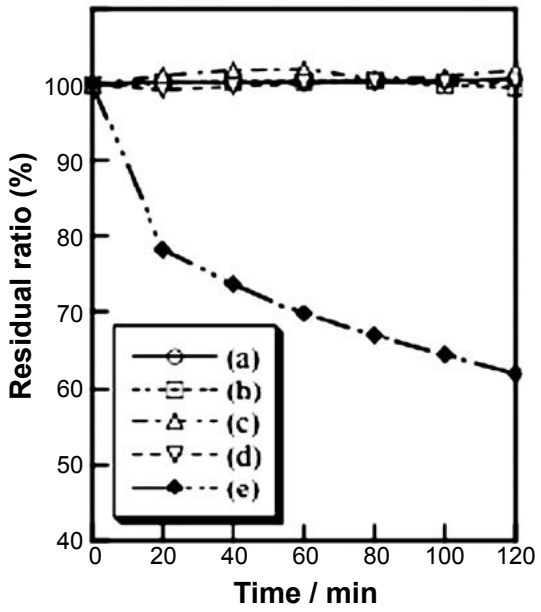

Figure 4: Photocatalytic activity of samples prepared under various Zn/P ratios: (a) blank, (b) Zn/P=2/1, (c) 3/2, (d) 1/1, and (e) ZnO.
[Figura 4: Atividade fotocatalítica das amostras preparadas Zn/P: (a) blank, (b) Zn/P=2/1, (c) 3/2, (d) 1/1, e (e) ZnO.]

sebum on the skin, had little photocatalytic activity (Fig. 4(b)-4(d)). Because sample prepared at Zn/P = 2/3 was easy to form the aggregations, the photocatalytic activity of this sample was difficult to be estimated. Fig. 5 shows the UV-Vis reflectance spectra of the zinc phosphates prepared under various conditions. Samples prepared at Zn/P = 2/1, 3/2, and 1/1 showed a high reflectance within the range of visible light (Fig. 5(a)(b)(c)). Sample prepared at Zn/P = 2/3 shows lower reflectance than other samples. Samples heated at 100 ºC had a high reflectance in spite of the Zn/P ratio in preparation (not shown). When sample prepared at Zn/P = 2/3 lost the adsorbed water by heating, the sample heated at 100 ºC indicated high reflectance.

Moisture helps to prevent the itchiness and damage to the skin. It is important that the pigments for use in cosmetics retain the moisture on the skin [11]. Fig. 6 shows the moisture retention of the samples prepared under various conditions. At the same retention time, a small weight loss indicates the high moisture retention of the phosphate pigments. For example, at 5 min, sample prepared at Zn/P = 2/1 indicated 22.3% of weight loss (Fig. 6(a)), on the other hand, sample

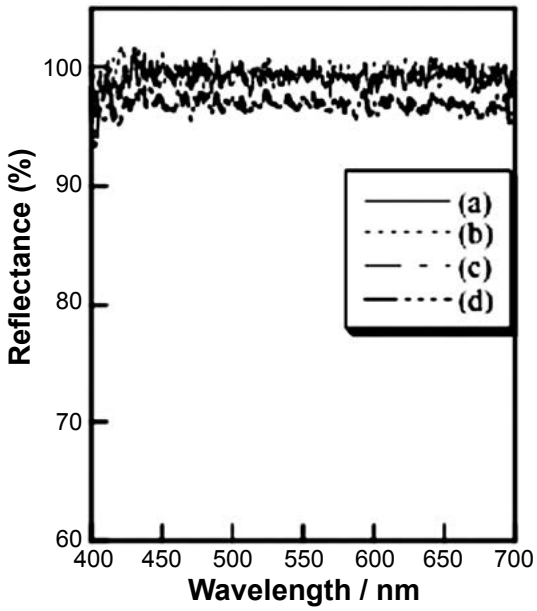

Figure 5: UV-Vis reflectance of samples prepared under various Zn/P ratios: (a) Zn/P=2/1, (b) 3/2, (c) 1/1, and (d) 2/3.
[Figura 5: Refletância UV-Vis das amostras preparadas Zn/P: (a) Zn/P=2/1, (b) 3/2, (c) 1/1, e (d) 2/3.]

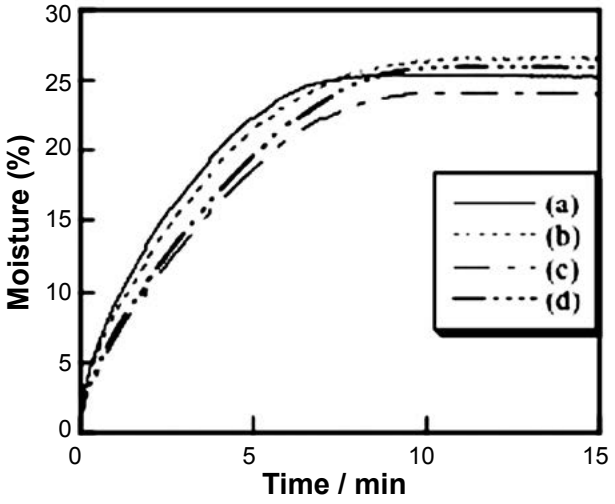

Figure 6: Water retention of samples prepared under various Zn/P ratios: (a) Zn/P=2/1, (b) 3/2, (c) 1/1, and (d) 2/3.
[Figura 6: Retenção de água das amostras preparadas Zn/P: (a) Zn/P=2/1, (b) 3/2, (c) 1/1, e (d) 2/3.]

Table II - Smoothness of samples prepared under various Zn/P ratios.
[Tabela II - Textura das amostras preparadas em várias proporções de Zn/P.]

sample	Zn/P ratio in preparation	MIU	MMD
A	2/1	0.356	0.006
B	3/2	0.586	0.016
C	1/1	0.623	0.008
D	2/3	-	-

prepared at Zn/P = 1/1 indicated 18.7% of weight loss (Fig. 6(c)). The samples prepared at Zn/P = 1/1 had a higher water retention than other samples.

As described above, a pigment with a high level of smoothness spreads well across the skin, and powder smoothness is also important for use in cosmetics [13]. Table II shows the smoothness of the samples prepared under various conditions. Because sample prepared at Zn/P = 2/3 was easy to form the aggregations, the MIU and MMD values of this sample could not be measured. Generally, for a cosmetic application, the suitable MIU and MMD values are smaller than 0.6 and smaller than 0.04, respectively. Samples prepared at high Zn/P ratio indicated small MIU value.

CONCLUSION

Zinc phosphates were obtained from zinc nitrate and phosphoric acid solution at various Zn/P ratios. Samples prepared at Zn/P = 2/1, 3/2, and 1/1 indicated XRD pattern of $Zn_3(PO_4)_2 \cdot 4H_2O$. The XRD peak intensity was varied from Zn/P ratio under preparation condition. The plane particles were observed in SEM images of samples prepared at Zn/P = 2/1, 3/2 and 1/1. The obtained zinc phosphates exhibit less photocatalytic activity, thereby protecting the sebum on the skin. The materials prepared at Zn/P = 2/1, 3/2 and 1/1 and their thermal products at 100 °C showed a high reflectance within the range of visible light. Samples prepared at high Zn/P ratio indicated small MIU value. The mixing ratio of zinc nitrate and phosphoric acid is important factor for preparation of zinc phosphate white pigments.

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