MIXING RATIO OF ZINC CHLORIDE AND PHOSPHORIC ACID, AND ADDITION OF SODIUM LACTATE FOR PREPARATION OF ZINC PHOSPHATE WHITE PIGMENTS

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Submitted March 15, 2014; accepted July 25, 2014

Keywords: White pigment, Zinc phosphates, Zn/P ratio, Photocatalytic activity, Particle shape

In this work, zinc phosphates were prepared from zinc chloride and phosphoric acid at various Zn/P ratios with / without sodium lactate 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. All samples indicated XRD pattern of $Zn_3(PO_4)_2 \cdot 4H_2O$. The plane parts on particles were observed in SEM images of sample prepared at Zn/P = 3/2 with sodium lactate and samples prepared at Zn/P = 1/1. The photocatalytic activity of these zinc phosphate particles was too less to protect the sebum on the skin. The materials obtained and their thermal products at 100°C showed a high reflectance within the range of visible light. The slipping resistance of the powder decreased as a result of the addition of sodium lactate.

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 moisture retention of the materials used in cosmetics is also important for preventing dry skin. Sodium lactate and glycerin make it easy for water to remain in the materials, and these are therefore generally used in cosmetic products. The addition of sodium lactate was effective to obtain the spherical particles and moisture retention of zinc phosphates [8]. Further, 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 and addition of sodium lactate.

For this work, as a novel white pigment, zinc phosphate, was prepared from zinc chloride and phosphoric acid at various Zn/P ratios with and without the addition of sodium lactate. 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 chloride solution was mixed with 0.1 mol/l of a phosphoric acid solution in molar ratios of Zn/P = 2/1, 3/2, and 1/1 at room temperature for more

than 1 hour. Sodium lactate was added to 0.5 mol/l in the phosphoric acid solution before mixing [8]. 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 Cu Kα 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 [10, 11]. 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.

Table 1. Zn/P ratios of precipitates prepared under various Zn/P ratios with and without sodium lactate.

sample	Zn/P ratio in preparation	sodium lactate (mol l^{-1})	Zn/P ratio in precipitates
A	2/1	0.0	1.82
B	2/1	0.5	1.44
C	3/2	0.0	1.48
D	3/2	0.5	1.47
E	1/1	0.0	1.28
F	1/1	0.5	1.45

RESULTS AND DISCUSSION

Chemical composition and powder properties of zinc phosphates

Table 1 shows the Zn/P ratios of the samples prepared under various conditions. Sample prepared at Zn/P = 2/1 without sodium lactate had high Zn/P ratio (1.82), on the other hand, sample prepared at Zn/P = 1/1 indicated low Zn/P ratio (1.28). 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. By the addition of sodium lactate, the Zn/P ratio closed to 1.5. Zinc phosphate, $Zn_3(PO_4)_2$, was easy to form in these conditions.

Figure 1 shows the XRD patterns of the samples prepared under various conditions (without heating). All samples indicated XRD pattern of $Zn_3(PO_4)_2 \cdot 4H_2O$ [12]. However, the peak intensity was affected from the

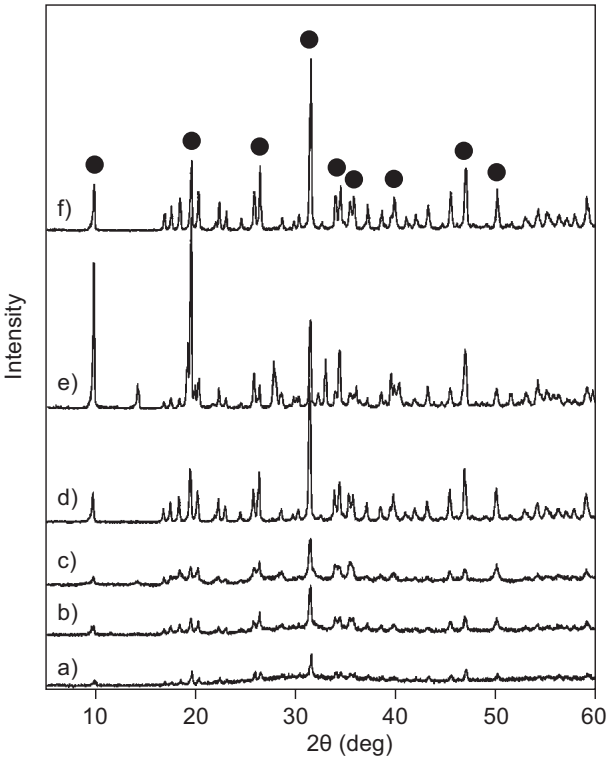
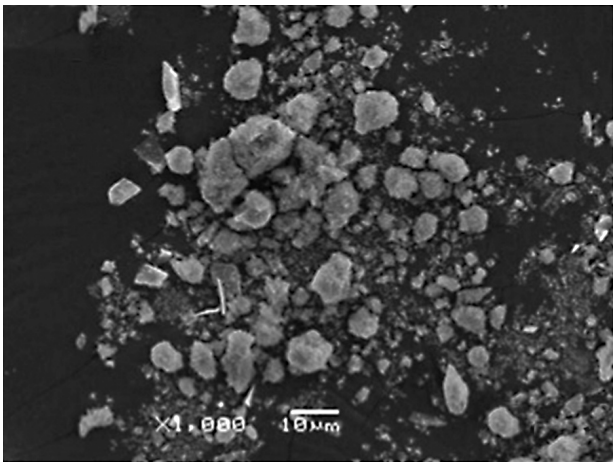


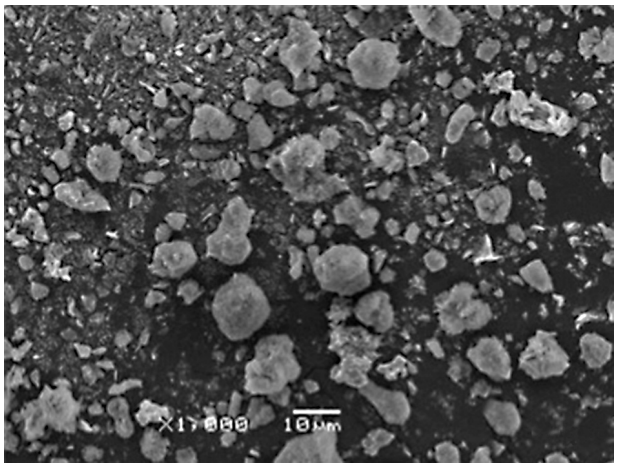
Figure 1. XRD patterns of samples prepared under various Zn/P ratios with and without sodium lactate: a) Zn/P = 2/1, without, b) 2/1, with, c) 3/2, without, d) 3/2, with, e) 1/1, without, f) 1/1, with; ● - $Zn_3(PO_4)_2 \cdot 4H_2O$.

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. By the addition of sodium lactate, the peak intensity became strong. XRD patterns of thermal products at 100ºC had little difference with those of samples without heating.

In terms of particle shape, spherical particles are suitable for cosmetic applications. Figure 2 shows some SEM images of the samples prepared under various conditions. The plane parts on particles were observed in sample prepared at Zn/P = 3/2 with sodium lactate and samples prepared at Zn/P = 1/1 (Figures 2d, e, f). Since



a)



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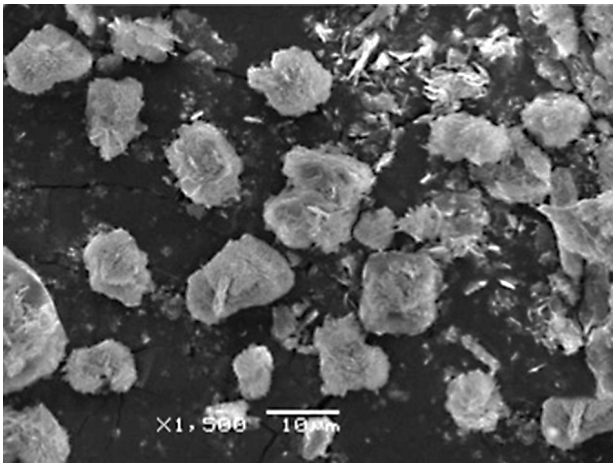

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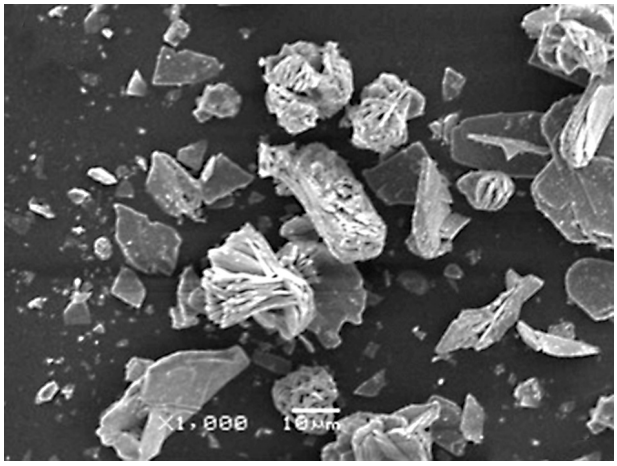
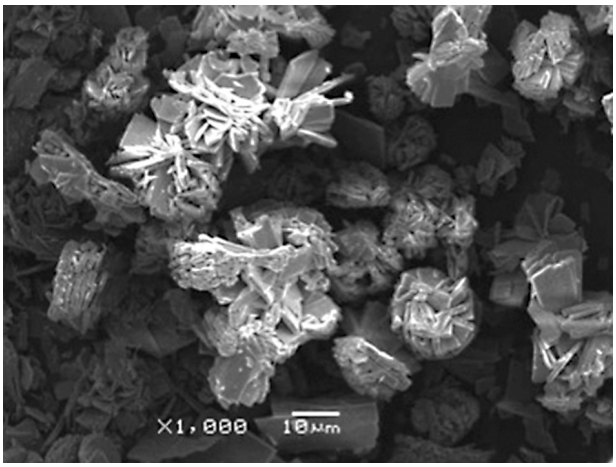
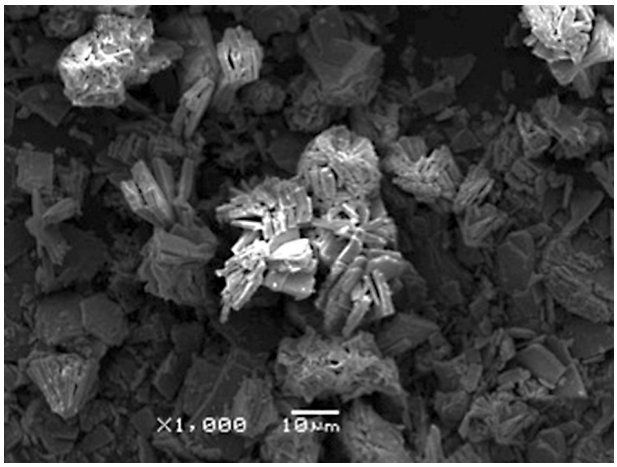


d)



e)



f)

Figure 2. SEM images of samples prepared under various Zn/P ratios with and without sodium lactate: a) Zn/P = 2/1, without, b) 2/1, with, c) 3/2, without, d) 3/2, with, e) 1/1, without, f) 1/1, with.

these samples had the strong peaks in XRD patterns, the plane parts on particles were related with the crystalline growth of zinc phosphate tetrahydrate. Figure 3 shows the particle size distribution of the samples prepared under various conditions. Sample prepared at Zn/P = 2/1 without sodium lactate indicated high ratio of particles at 8 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 particle size distribution. Since these results in particle size distributions were corresponding with 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

Figure 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 (Figure 4h). On the other hand, zinc phosphate, which is a mild material that can protect the sebum on the skin, had little photocatalytic activity (Figures 4b-g). Figure 5 shows the UV-Vis reflectance spectra of the zinc phosphates prepared under various conditions. All samples showed a high reflectance within the range of visible light. Samples heated at 100°C also had a high reflectance (not shown). Samples without heating and heated at 100°C were white powder in spite of the Zn/P ratio in preparation and the addition of sodium lactate.

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]. Figure 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 minutes, sample prepared at Zn/P = 3/2 without sodium lactate indicated 22.9 % of weight loss (Figure 6c), on the other

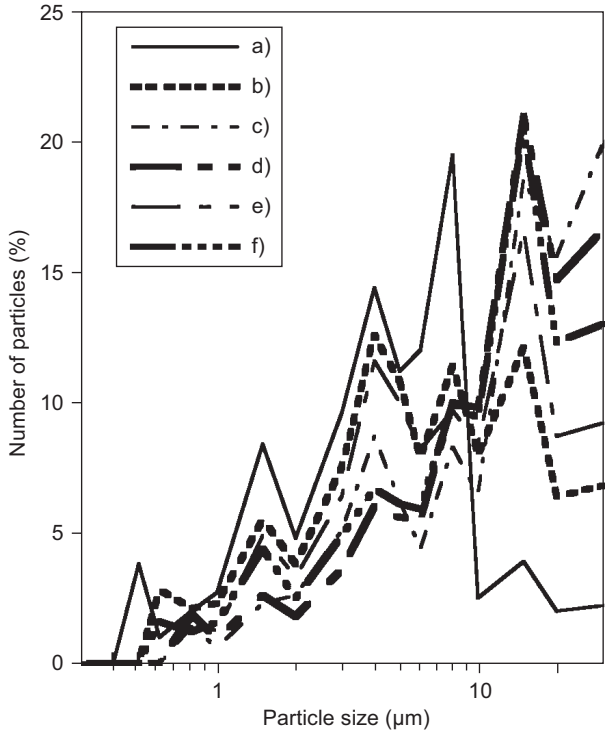


Figure 3. Particle size distribution of samples prepared under various Zn/P ratios with and without sodium lactate: a) Zn/P = = 2/1, without, b) 2/1, with, c) 3/2, without, d) 3/2, with, e) 1/1, without, f) 1/1, with.

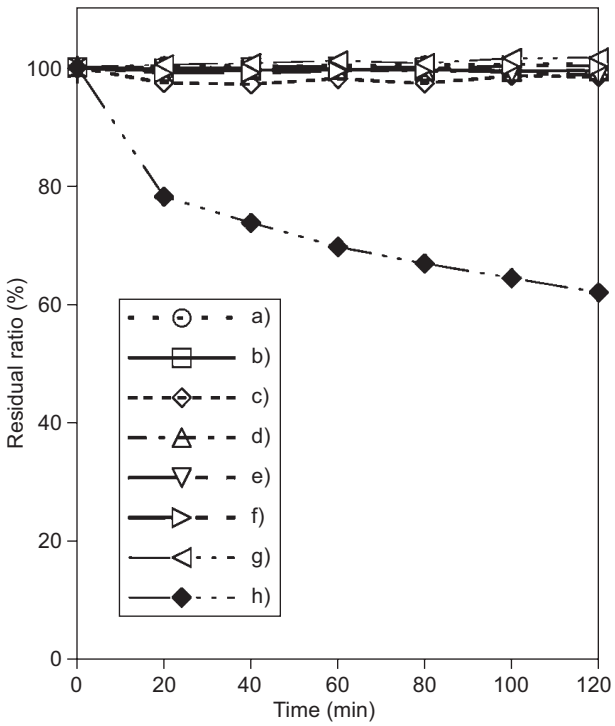


Figure 4. Photocatalytic activity of samples prepared under various Zn/P ratios with and without sodium lactate: a) blank, b) Zn/P = 2/1, without, c) 2/1, with, d) 3/2, without, e) 3/2, with, f) 1/1, without, g) 1/1, with, and h) ZnO.

hand, sample prepared at Zn/P = 2/1 with sodium lactate indicated 17.1 % of weight loss (Figure 6b). The samples prepared at Zn/P = 2/1 with sodium lactate had a higher water retention than other samples. The water retention of samples prepared at Zn/P = 2/1 and 3/2 improved by the addition of sodium lactate, on the other hand, that of samples at Zn/P = 1/1 had little change.

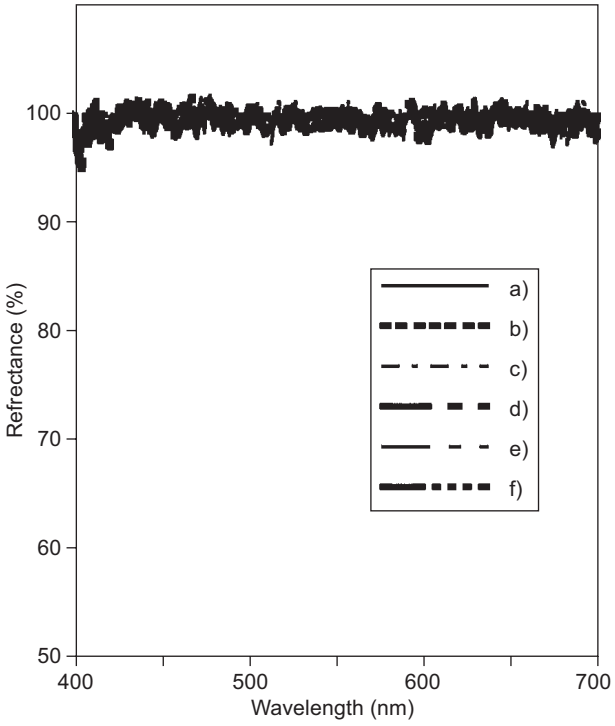


Figure 5. UV-Vis reflectance of samples prepared under various Zn/P ratios with and without sodium lactate: a) Zn/P = = 2/1, without, b) 2/1, with, c) 3/2, without, d) 3/2, with, e) 1/1, without, f) 1/1, with.

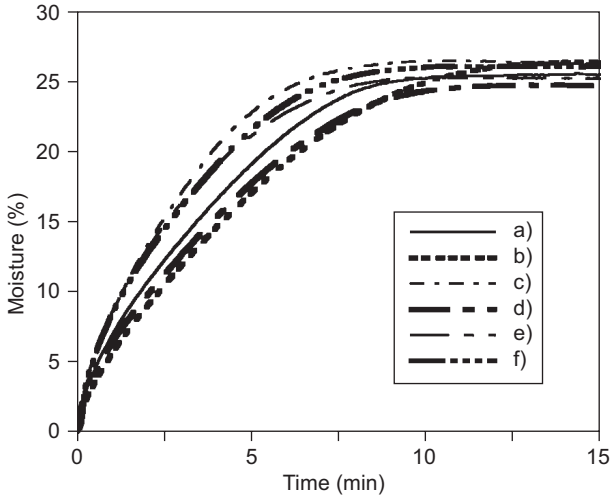


Figure 6. Water retention of samples prepared under various Zn/P ratios with and without sodium lactate: a) Zn/P = 2/1, without, b) 2/1, with, c) 3/2, without, d) 3/2, with, e) 1/1, without, f) 1/1, with.

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 2 shows the smoothness of the samples prepared under various conditions. Generally, for a cosmetic application, the suitable MIU and MMD values are smaller than 0.6 and smaller than 0.04, respectively. All samples had small MIU and MMD values. The MIU values decreased as a result of the addition of sodium lactate.

Table 2. Smoothness of samples prepared under various Zn/P ratios with and without sodium lactate.

sample	Zn/P ratio in preparation	sodium lactate (mol l^{-1})	MIU	MMD
A	2/1	0.0	0.440	0.007
B	2/1	0.5	0.320	0.006
C	3/2	0.0	0.350	0.005
D	3/2	0.5	0.293	0.006
E	1/1	0.0	0.565	0.012
F	1/1	0.5	0.310	0.005

CONCLUSION

Zinc phosphates were obtained from zinc chloride and phosphoric acid solution at various Zn/P ratios, with and without the addition of sodium lactate. All samples 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 and the addition of sodium lactate. The plane parts on particles were observed in SEM images, related with the crystalline growth of zinc phosphate tetrahydrate. The obtained zinc phosphates exhibit less photocatalytic activity, thereby protecting the sebum on the skin. Samples without heating and those heated at 100°C showed a high reflectance within the range of visible light. Finally, the slipping resistance of the powder particles decreased as a result of the addition of sodium lactate.

Acknowledgement

The authors are grateful to Dr. Takeshi Toyama, Nihon University, Japan, for smoothness measurements.

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