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Ceramics International 40 (2014) 3433–3438

CERAMICS INTERNATIONAL

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Preparation and powder properties of zinc phosphates with additives

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Received 8 August 2013; received in revised form 11 September 2013; accepted 20 September 2013
Available online 25 September 2013

Abstract

In this work, zinc phosphates were prepared from zinc nitrate and phosphoric acid 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. The obtained materials had a Zn/P ratio of about 1.5, which corresponds to zinc orthophosphate $Zn_3(PO_4)_2$. Spherical particles were formed in a sample prepared using sodium lactate and glycerin, and in a sample prepared using urea, sodium lactate, and glycerin. 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 showed a high reflectance within the range of ultraviolet and visible light at 100 °C. The slipping resistance and roughness of the powder decreased as a result of the addition of sodium lactate.

Keywords: White pigment; Zinc phosphates; Water retention compounds; Photocatalytic activity; Particle shape

1. 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 for preparing ceramic materials, catalysts, adsorbents, fluorescent materials, dielectric substances, biomaterials, metal surface treatments, fertilizers, detergents, food additives, fuel cells, pigments, and so on [4–8]. 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 [9,10], we prepared a titanium phosphate pigment with no catalytic activity. The moisture retention of the materials used in cosmetics is also important for preventing dry skin. Urea is generally added to improve the moisture retention for cosmetic products [10]. Further, sodium lactate and glycerin make it easy for water to remain in the materials, and these are therefore generally used in cosmetic products [11]. These compounds improved the moisture retention of titanium phosphates. Titanium phosphates are expected as a novel white pigment. As well as titanium dioxide, zinc oxide is used as a white pigment and has the photocatalytic activity. In the same way with titanium phosphate, zinc phosphate has a possibility to use as a novel white pigment.

For this work, as a novel white pigment, zinc phosphate, was prepared from zinc nitrate and phosphoric acid using the

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http://dx.doi.org/10.1016/j.ceramint.2013.09.088

water retentive additives of urea, sodium lactate, and glycerin. 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.

2. Experimental

0.1 mol/l of a zinc nitrate solution was mixed with 0.1 mol/l of a phosphoric acid solution in a molar ratio of Zn/P = 3/2 at room temperature for more than 1 h. Urea, sodium lactate, and glycerin were added to a 0.5 mol/l phosphoric acid solution before mixing [10]. The mixing conditions are shown in Table 1. The precipitates were then filtered off, washed with water, and dried at room temperature over 3 days. These samples are denoted as "sample A–H" in this paper. 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 titanium 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 and 200 °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 and 200 °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 [12,13]. 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 an 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 (load of sample; about 50 mg), 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. The dispersions of the MIU and MMD values were 0.03 and 0.002 in 3 times measurements, respectively.

3. Results and discussion

3.1. Chemical composition and powder properties of zinc phosphates

Table 1 shows the Zn/P ratios of the samples prepared under various conditions. All samples had about a 1.5 Zn/P ratio, which corresponds to a composition of $Zn_3(PO_4)_2$. The additives had no

Table 1
Zn/P ratios of precipitates prepared under various conditions.

Sample	Urea/ mol l^{-1}	Sodium lactate/ mol l^{-1}	Glycerin/ mol l^{-1}	Zn/P ratio in precipitates
A	0	0	0	1.51
B	0.5	0	0	1.47
C	0	0.5	0	1.45
D	0	0	0.5	1.48
E	0.5	0	0.5	1.51
F	0.5	0.5	0	1.45
G	0	0.5	0.5	1.50
H	0.5	0.5	0.5	1.43

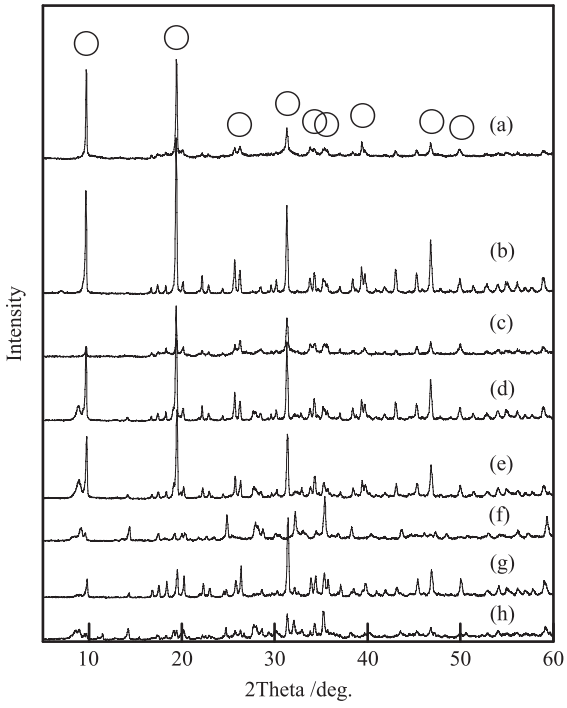

Fig. 1. XRD patterns of samples prepared using various additives: (a) no additives, (b) urea, (c) sodium lactate, (d) glycerin, (e) urea and glycerin, (f) urea and sodium lactate, (g) sodium lactate and glycerin, and (h) urea, sodium lactate, and glycerin, ○; $Zn_3(PO_4)_2 \cdot 4H_2O$.

influence on the Zn/P ratio of the phosphate materials. Fig. 1 shows the XRD patterns of the samples prepared using various additives (without heating). The XRD pattern of a sample prepared with sodium lactate and glycerin corresponded with standard pattern of $Zn_3(PO_4)_2 \cdot 4H_2O$ (Fig. 1(g))[14]. The other samples indicated the specified strong peaks. These were caused from the crystal growth of specific face. Additives had influence on the crystal growth of zinc phosphate. However, the peaks due to raw materials were not observed. The reaction between zinc nitrate and phosphoric acid sufficiently took place. XRD patterns of thermal products at 100 °C had little difference with those of samples without heating. Thermal products at 200 °C had wide peaks in XRD patterns. The crystallite size of sample prepared with sodium lactate and glycerin without heating was 46 nm by Scherrer equation. This crystallite size changed to 46 nm and 20 nm by heating at 100 °C and 200 °C, respectively. These crystallites were much smaller than particle size from below-mentioned SEM images and a centrifugal precipitation particle-size distribution. The phosphate particles contained the small crystallites.

In terms of particle shape, spherical particles are suitable for cosmetic applications. Fig. 2 shows some SEM images of the samples prepared with various additives. A sample prepared without additives had various particle shapes (Fig. 2(a)). The amount of plate particles increased through the addition of urea

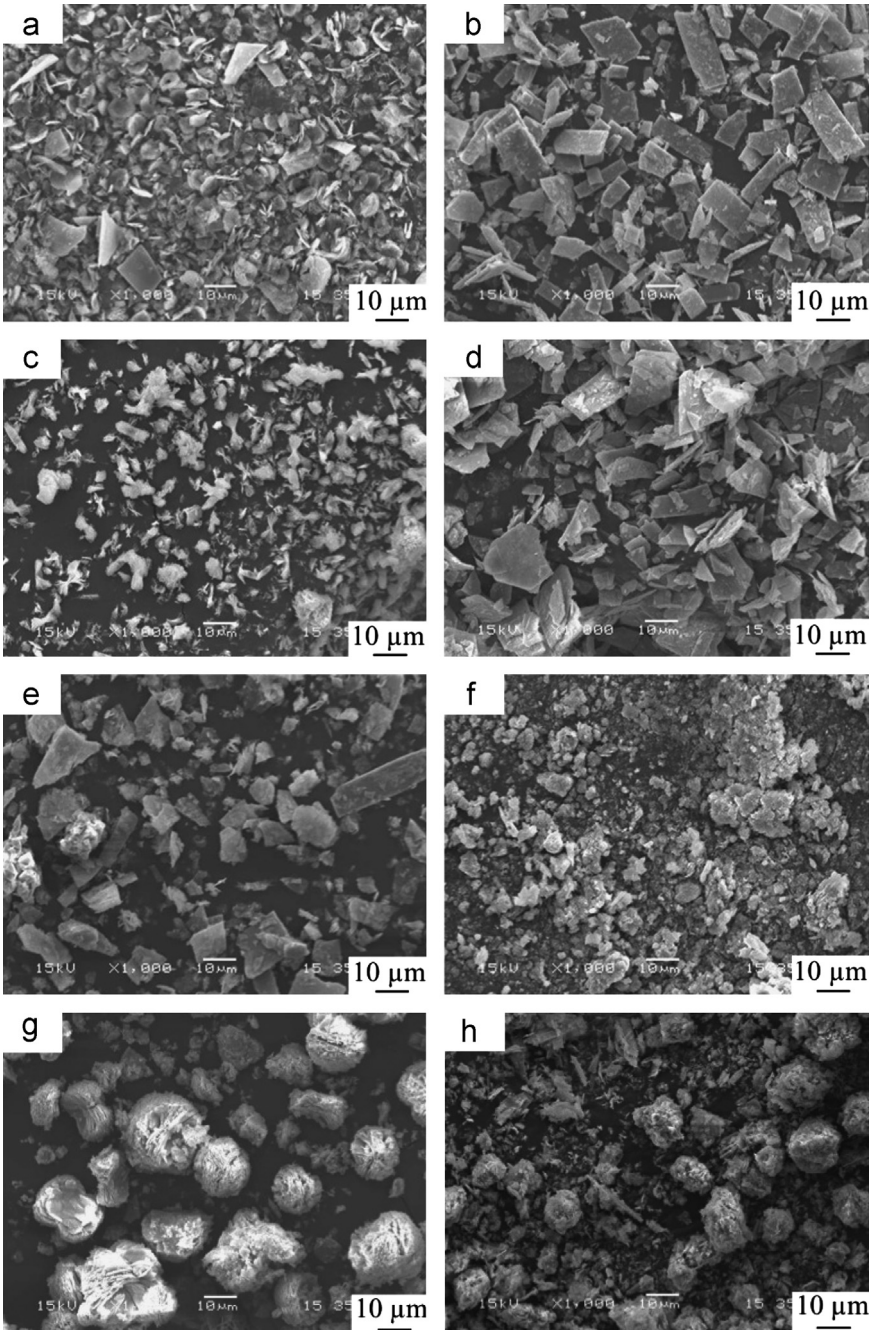

Fig. 2. SEM images of samples prepared using various additives: (a) no additives, (b) urea, (c) sodium lactate, (d) glycerin, (e) urea and glycerin, (f) urea and sodium lactate, (g) sodium lactate and glycerin, and (h) urea, sodium lactate, and glycerin.

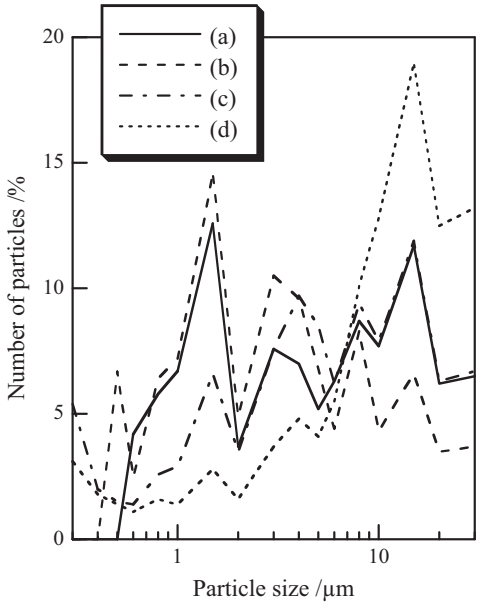

Fig. 3. Particle size distribution of samples prepared using various additives: (a) no additives, (b) sodium lactate, (c) urea and sodium lactate, and (d) urea, sodium lactate, and glycerin.

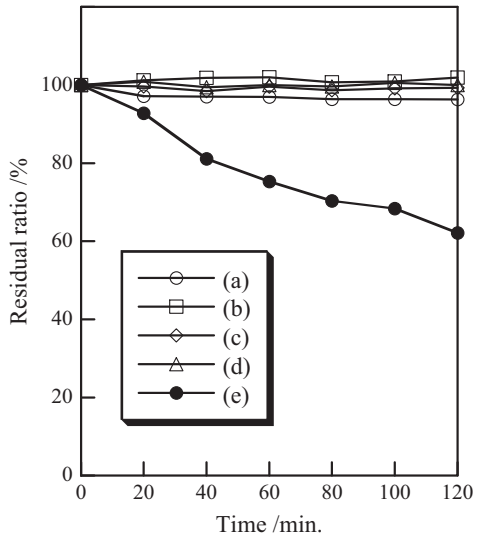

Fig. 4. Photocatalytic activity of samples prepared using various additives: (a) blank, (b) sample A, (c) sample C, (d) sample H, and (e) ZnO.

and glycerin (Fig. 2(b) and (d)). Spherical particles were formed in a sample prepared using sodium lactate and glycerin, and in a sample prepared with urea, sodium lactate, and glycerin (Fig. 2(g) and (h)). Sodium lactate was effective additive to obtain spherical particles of zinc phosphate. On the other hand, urea and glycerin produced plate particles. Because sample prepared with urea, sodium lactate, and glycerin had spherical particles, the effect by sodium lactate was stronger than that by urea and glycerin.

Fig. 3 shows the particle size distribution of the samples prepared using various additives. The samples prepared without additives and with sodium lactate contained a large amount of particles with 1.5 μm in particle size (Fig. 3(a) and (b)). Sodium lactate had small influence on particle size. On the other hand, by the addition of urea and glycerin, particle size of zinc phosphates increased (Fig. 3(c) and (d)).

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.

3.2. Cosmetic properties of zinc phosphates

Fig. 4 shows the respective photocatalytic activities of the samples prepared under various conditions. Because zinc oxide

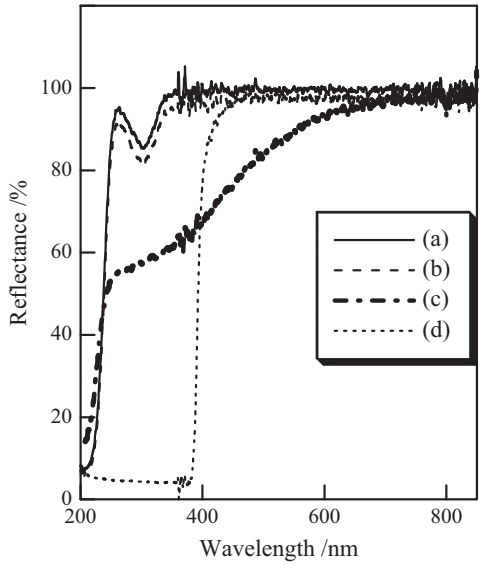

Fig. 5. UV–vis reflectance of sample H heated at several temperatures with zinc oxide: (a) RT, (b) 100 °C, (c) 200 °C, and (d) ZnO.

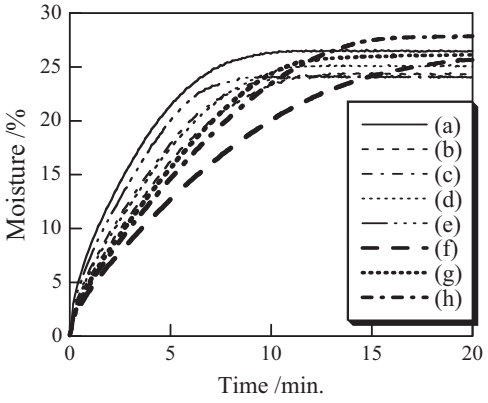

Fig. 6. Water retention of samples prepared using various additives: (a) no additives, (b) urea, (c) sodium lactate, (d) glycerin, (e) urea and glycerin, (f) urea and sodium lactate, (g) sodium lactate and glycerin, and (h) urea, sodium lactate, and glycerin.

Table 2
Smoothness of samples prepared under various conditions.

Sample	Urea/mol l^{-1}	Sodium lactate/mol l^{-1}	Glycerin/mol l^{-1}	Temp./°C	MIU	MMD
A	0	0	0	R.T.	0.589	0.016
B	0.5	0	0	R.T.	0.649	0.012
C	0	0.5	0	R.T.	0.377	0.006
D	0	0	0.5	R.T.	0.656	0.005
E	0.5	0	0.5	R.T.	0.558	0.008
F	0.5	0.5	0	R.T.	1.466	0.014
G	0	0.5	0.5	R.T.	1.015	0.008
H	0.5	0.5	0.5	R.T.	1.567	0.012
A	0	0	0	100	1.378	0.013
A	0	0	0	200	1.992	0.023
H	0.5	0.5	0.5	100	1.151	0.008
H	0.5	0.5	0.5	200	0.514	0.005

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 sebum on the skin, had little photocatalytic activity in spite of the types of additives used (Fig. 4(b)–(d)).

Fig. 5 shows the UV–vis reflectance spectra of the zinc phosphates prepared with urea, sodium lactate, and glycerin. The zinc phosphates had a higher reflectance under ultraviolet light than zinc oxide. Samples without heating, and samples heated at 100 °C, showed a high reflectance within the range of visible light (Fig. 5(a) and (b)). The samples heated at 200 °C showed a lower reflectance owing to the incomplete combustion of additives (Fig. 5(c)). Heat treatment at 200 °C was unsuitable for obtaining zinc phosphate white pigments prepared with additives. The wide peaks were observed in XRD patterns of samples heated at 200 °C. Samples heated at 200 °C had plenty of large particles. These results were also related with the incomplete combustion of additives.

Moisture helps to prevent the itchiness and damage to the skin. It is important that the pigments for used in cosmetics retain the moisture on the skin [13]. 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 without additives indicated 21.4% of weight loss, on the other hand, sample prepared with urea and sodium lactate indicated 12.7% of weight loss. The samples prepared with additives had a higher water retention than a sample prepared without additives. The addition of urea and sodium lactate (Fig. 6(f)) greatly improves the moisture retention of zinc phosphates. These were related with the additives included in samples. From the results of UV–vis reflectance spectra, the additives in this work were included in 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 [15]. 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. The MIU and MMD values decreased as a result of the addition of sodium lactate (sample C). Heat treatment is simple method to remove the adsorbed water in inorganic materials. After heating, the MIU value of sample A increased. This result was related with that the heated sample A had large particles. However, the MIU value of sample H decreased by heating. The influence of the additives and heat treatment on the powder smoothness of the zinc phosphates is not clear.

4. Conclusion

Zinc phosphates were obtained from zinc nitrate and phosphoric acid solution, with the addition of urea, sodium lactate, and glycerin. The obtained materials had a Zn/P ratio of about 1.5. This ratio corresponds with zinc orthophosphate $Zn_3(PO_4)_2$. Spherical particles were formed in a sample prepared with sodium lactate and glycerin, and in a sample prepared with urea, sodium lactate, and glycerin. The obtained zinc phosphates exhibit less photocatalytic activity, thereby protecting the sebum on the skin. The zinc phosphates showed a higher reflectance of ultraviolet light than zinc oxide did. Samples without heating and those heated at 100°C showed a high reflectance within the range of visible light. Samples prepared with additives had a higher amount of water retention than the sample prepared without an additive. Finally, the slipping resistance and roughness of the powder particles decreased as a result of the addition of sodium lactate.

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