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SYNTHESIS OF NOVEL COSMETIC WHITE PIGMENT BY CONDENSED PHOSPHORIC ACID TREATMENT OF ZINC OXIDE

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Zinc oxide is used as a white pigment in cosmetics, but has the disadvantage of having photocatalytic activity. A certain amount of sebum on the skin is decomposed by ultraviolet rays in sunlight due to the photocatalytic activity of this cosmetic, causing damage to the skin. In this study, a new white pigment for cosmetics was prepared by shaking a mixture of zinc oxide and various condensed phosphate solutions or condensed phosphoric acid to react the surface of zinc oxide to phosphate. The chemical composition, particle size distribution, photocatalytic activity, hue, and smoothness of the resulting powder materials were examined. The condensed phosphoric acid treatment caused some of the zinc oxide to react with the zinc phosphate. The reaction was relatively advanced in the samples prepared in a protonated solution. Most of the sample powders were of a size suitable for white pigments for cosmetics. The condensed phosphoric acid treatment suppressed the photocatalytic activity of the zinc oxide. The obtained samples had sufficiently high reflectance in the visible light range. Judging from the particle size and the photocatalytic activity, the sample prepared with polyphosphoric acid is most suitable as a white pigment for cosmetics.

INTRODUCTION

Zinc oxide is used as a white pigment for cosmetic applications, and it is well known that this oxide has photocatalytic activity [1, 2]. Therefore, a certain amount of sebum on the skin is decomposed by the ultraviolet rays contained in sunlight through the use of cosmetics. Several technological treatments have been considered and used to control the load on the skin caused by this photocatalytic activity. For example, composite particles with silicon dioxide have been used as one such technology [3]. However, these particle materials have the disadvantage of being too hard for use on the human face. Therefore, a milder material is needed for use as a white pigment for the face. In addition, pigments with particle sizes that are too small are adsorbed by the skin, so it is necessary to use white pigments with sizes that are not adsorbed [4].

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

The size distribution of phosphate particles is important when used as a pigment in cosmetics. Homogeneous spherical particles are expected to spread well on the skin [8]. However, particles that are too small are unsuitable because the pigment may penetrate into the skin's pores. In general, pigments with a size of 0.1 to 1 µm are preferred. However, the standard size of white pigment particles used in cosmetics cannot be precisely determined because skin pores vary in size due to age, gender, climate, and other factors [9]. If the particles are too large, they may break when applied to 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 without photocatalytic activity were prepared as novel pigments. However, the particle size of the zinc phosphate was more than 1 µm. These particles were too large, so a new process was needed to produce smaller particles as a white pigment.

Zinc phosphate particles without photocatalytic activity were too large, while zinc oxide particles with a smaller particle size had photocatalytic activity. In a previous study, zinc oxide was shaken in phosphoric acid at 30, 40, and 50 °C to obtain zinc oxide particles coated with zinc phosphate [13]. The target particles have a core-shell structure with a core of zinc oxide and a shell of zinc phosphate without photocatalytic activity. However, the resulting zinc phosphate-coated zinc oxide contained particles larger than 10 µm. This was considered to be due to the formation of more zinc phosphate on the surface of the zinc oxide due to the high reactivity of the phosphoric acid treatment. The aim of this study was to obtain submicrometre-sized white pigments with suppressed photocatalytic activity by using various condensed phosphoric acids, which are less reactive than phosphoric acid.

It is known that phosphates can be converted to various condensed phosphates by heating or other means. These condensed phosphates have different reactivity from non-condensed orthophosphates, and it is expected that new materials can be obtained by using these condensed phosphates. In a previous study, novel white pigments for cosmetics were prepared by a condensed phosphate treatment of titanium dioxide [14]. The results showed that condensed phosphates are suitable for mild phosphoric acid coatings.

In this study, new white pigments were prepared from zinc oxide and various condensed phosphate solutions or condensed phosphoric acid. The chemical composition, particle size distribution, photocatalytic activity, hue, and smoothness of the obtained samples were investigated for cosmetic applications.

EXPERIMENTAL

Sodium pyrophosphate, $Na_4P_2O_7$, was synthesised by heating disodium hydrogen phosphate (Na_2HPO_4) at 400 ºC for 5 h [14]. Sodium triphosphate ($Na_5P_3O_{10}$) was synthesised by heating a mixture of disodium hydrogen phosphate (Na_2HPO_4) and sodium dihydrogen phosphate (NaH_2PO_4) at a Na_2HPO_4/NaH_2PO_4 ratio of 2/1 at 400 ºC for 5 h. Sodium polyphosphate, $NaPO_3$, was synthesised by heating sodium dihydrogen phosphate, NaH_2PO_4 at 700 ºC for 2 h, followed by rapid cooling. This salt, sodium polyphosphate, is known to be an inorganic phosphate polymer with a polymerisation number of about 110 [15].

Various sodium condensed phosphate solutions (phosphorus; 0.05 $mol \cdot L^{-1}$) were prepared with sodium pyrophosphate ($Na_4P_2O_7$), triphosphate ($Na_5P_3O_{10}$), and polyphosphate ($NaPO_3$) synthesised as described above. Pyrophosphoric acid ($H_4P_2O_7$), triphosphoric acid ($H_5P_3O_{10}$), and poly-phosphoric acid (HPO_3) (phosphorus; 0.05 $mol \cdot L^{-1}$) were prepared with a cation exchange resin (DOWEX TM 50WX8, 100-200 mesh) and each condensed phosphate solution.

Zinc oxide was added to 50 mL of the above condensed phosphate solution or condensed phosphoric acid at a P/Zn molar ratio of 1/2 in a glass tube. These mixtures were shaken in hot water (50 ºC) at a shaking rate of 100 times/min for 1 h [13, 14]. The powder samples were decanted, washed with water, and dried at 50 ºC over 3 days. All the chemicals were commercially pure (FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) and used without further purification.

The crystalline phase compositions of these materials were analysed using X-ray diffraction (XRD). The XRD patterns were recorded on an X-ray diffractometer (MiniFlex; Rigaku Corp., Akishima, Japan) using monochromatic CuKα rays. The infrared (IR) spectra were measured on a HORIBA FT-IR 720 (Horiba Ltd., Kyoto, Japan) using the KBr disk method. To estimate the ratios of the 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 the 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 analyser (SA-CP3L, Shimadzu Corp., Kyoto, Japan).

The cosmetic properties were evaluated by the photocatalytic activity, hue, and smoothness. The photocatalytic activity of samples was estimated with the degradation of methylene blue upon irradiation with a 365 nm light source [16,17]. A sample weighing 0.01 g was placed in 4 mL of methylene blue solution (1.0×10^{-5} $mol \cdot L^{-1}$), and then this solution was irradiated. The decrease in the absorption at about 660 nm was estimated for 120 min.

The colour of the phosphate pigments was estimated by the ultraviolet–visible (UV–Vis) reflectance spectra using a spectrometer (UV2100; Shimadzu Corp., Kyoto, Japan) (reference compound; $BaSO_4$). The whiteness was also estimated in L*a*b* colour space using a TES135 plus colour analyser (TES Electrical Electronic Corp., Taipei, Taiwan) (an average of 5 times).

The smoothness of the sample powder was evaluated by static friction resistance on artificial leather using a Portable Friction Meter 94i-II (SHINTO Scientific Co., Ltd., Tokyo, Japan). The sample powder was applied on the artificial leather and the sensor was run on it.

RESULTS AND DISCUSSION

Chemical composition and powder properties

Figure 1 shows the XRD patterns of the samples prepared with various condensed phosphate solutions. All the samples showed the XRD peak patterns attributed to zinc oxide. Regardless of the type of condensed phosphate or H/Na type, no new peaks were observed due to the condensed phosphate treatment. Figure 2 shows the IR spectra of the samples prepared with various condensed phosphate solutions. In all the samples, an absorption peak due to zinc oxide at 400 − 600 cm^{-1} and peaks due to phosphate at about 920 and 1130 cm^{-1} were identified. This confirmed that all the samples had a zinc oxide portion and a phosphate portion. The MP-AES analysis was performed to evaluate the proportion of the phosphate in the samples. Table 1 shows the P/Zn ratio of the samples prepared with various condensed phosphate solutions. The samples treated with the H-type solutions indicated a higher P/Zn ratio than those with the Na-type solutions. This may be attributed to the lower pH value of the H-type solution, which makes it more reactive.

Table 1. P/Zn ratio, L* value and static friction resistance (S.F.R.) of the samples prepared with various condensed phosphate solutions.

Phosphate	Na/H	pH	P/Zn	L* value	S.F.R./-
ZnO	-	-	0	96.10	0.664
Pyro-	Na	10.85	0.075	99.54	0.469
Pyro-	H	1.38	0.121	98.11	0.441
Tri-	Na	10.22	0.062	97.20	0.336
Tri-	H	1.87	0.134	98.38	0.545
Poly-	Na	6.68	0.062	98.77	0.397
Poly-	H	1.86	0.131	99.73	0.538

Figure 3 shows the particle size distribution of the samples prepared with various condensed phosphate solutions. White pigments for cosmetics are generally considered to be desirable in the size range of 0.1 to 1 μm. The samples prepared in this study had a high percentage of particles less than 1 μm and were suitable for this application size. In particular, the sample prepared with polyphosphoric acid had the lowest percentage of particles larger than 1 μm (Figure 3f).

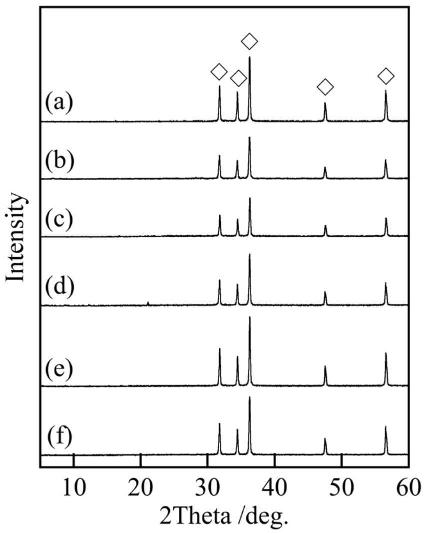

Figure 1. XRD patterns of the samples prepared with various condensed phosphate solutions, (a) $Na_4P_2O_7$, (b) $H_4P_2O_7$, (c) $Na_5P_3O_{10}$, (d) $H_5P_3O_{10}$, (e) $NaPO_3$, and (f) HPO_3, ◊ ZnO.

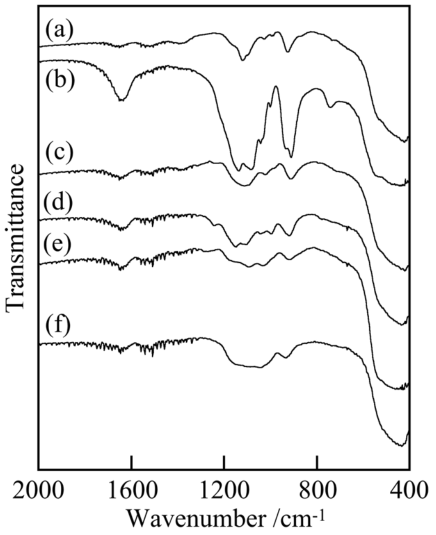

Figure 2. IR spectra of the samples prepared with various condensed phosphate solutions, (a) $Na_4P_2O_7$, (b) $H_4P_2O_7$, (c) $Na_5P_3O_{10}$, (d) $H_5P_3O_{10}$, (e) $NaPO_3$ and (f) HPO_3.

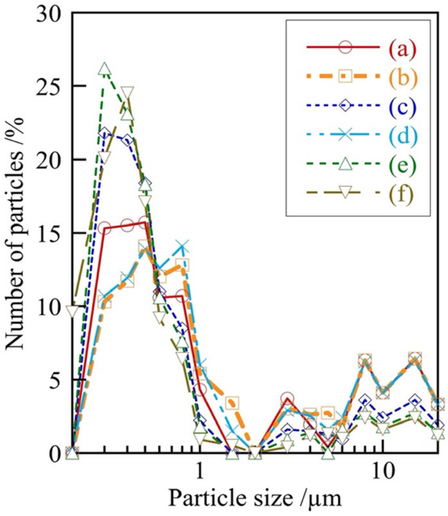

Figure 3. Particle size distribution of the samples prepared with various condensed phosphate solutions, (a) $Na_4P_2O_7$, (b) $H_4P_2O_7$, (c) $Na_5P_3O_{10}$, (d) $H_5P_3O_{10}$, (e) $NaPO_3$ and (f) HPO_3.

Cosmetic properties

Figure 4 shows the photocatalytic activity of the samples prepared with various condensed phosphate solutions. Methylene blue was decomposed with the original zinc oxide using UV radiation (Figure 4b). On the other hand, the samples treated with the H-type solutions showed a high residual ratio of methylene blue (Figure 4d, f, h), indicating that their photocatalytic activities were low. In particular, the photocatalytic activities of the samples prepared with triphosphoric acid and polyphosphoric acid were low. The phosphoric acid treatment formed zinc phosphate on the particle surface, which has no photocatalytic activity [11, 12], which may have reduced the overall photocatalytic activity of the sample powder. The samples treated with the Na-type solution showed relatively high photocatalytic activity (Figure 4c, e, g). This was due to the low reactivity of the Na-type solution, which resulted in less zinc phosphate formation. In particular, the sample prepared with the sodium polyphosphate solution showed photocatalytic activity comparable to that of zinc oxide.

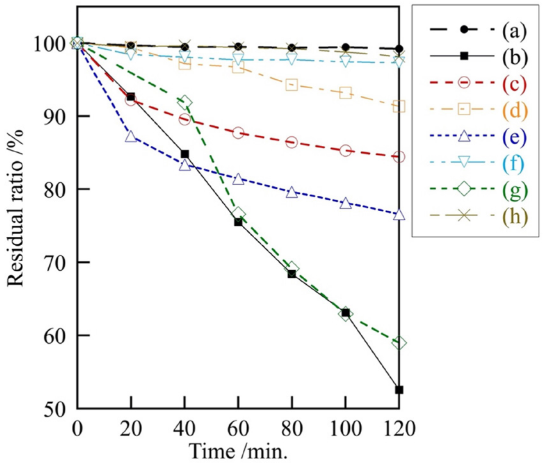

Figure 4. Photocatalytic activity of the samples prepared with various condensed phosphate solutions, (a) blank, (b) original ZnO, (c) $Na_4P_2O_7$, (d) $H_4P_2O_7$, (e) $Na_5P_3O_{10}$, (f) $H_5P_3O_{10}$, (g) $NaPO_3$ and (h) HPO_3.

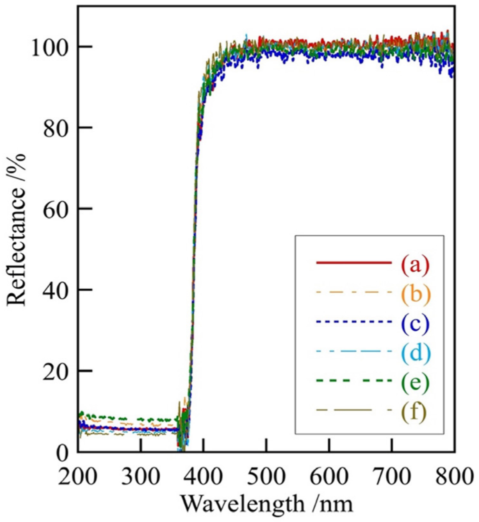

Figure 5. UV-Vis reflectance spectra of the samples prepared with various condensed phosphate solutions, (a) $Na_4P_2O_7$, (b) $H_4P_2O_7$, (c) $Na_5P_3O_{10}$, (d) $H_5P_3O_{10}$, (e) $NaPO_3$ and (f) HPO_3.

Figure 5 shows the UV-visible reflectance spectra of the samples treated with various condensed phosphate solutions. All the samples showed high reflectance in the visible light region. Since zinc phosphate shows high reflectance in the UV region, it was expected to show some reflectance in that region. However, all of the samples prepared in this study showed weak reflectance. This may be due to the fact that the ratio of zinc phosphate was too small.

The colour of sample powder was also estimated by L*a*b* colour space. The L* values of the samples prepared with various condensed phosphate solutions are shown in Table 1. Note that the a* and b* values are not shown because they are all close to 0. All the samples showed higher L* values than zinc oxide, indicating that the obtained samples are suitable as white pigments. These L* results corresponded to the UV-Vis reflectance spectra of the samples.

As mentioned above, pigments with high smoothness spread better on the skin. Therefore, the smoothness of the powders is also important in cosmetics [18]. Table 1 shows the static friction resistance values of the samples prepared with various condensed phosphate solutions. Low static frictional resistance means high smoothness. All the samples prepared in this study showed higher smoothness than the original zinc oxide, indicating that they are suitable as white pigments for cosmetics.

CONCLUSIONS

Zinc oxide was shaken in various condensed phosphate solutions or condensed phosphoric acid. In this process, some of the zinc oxide reacted with the zinc phosphate. In particular, the samples prepared in the H-type solutions reacted more to zinc phosphate than the sample prepared in the Na-type solution. The samples prepared in this study contained a high proportion of particles less than 1 µm, which are suitable for white pigments in cosmetics. The sample prepared using polyphosphoric acid had the lowest ratio of particles larger than 1 µm. Furthermore, the photocatalytic activity of the sample prepared using triphosphoric acid or polyphosphoric acid was extremely suppressed. The obtained samples had sufficiently high reflectance in the visible light region. The samples prepared in this study exhibited higher whiteness (L*) than the original zinc oxide. All the samples had higher smoothness than the zinc oxide. The results of the particle size distribution and photocatalytic activity indicate that the sample prepared with polyphosphoric acid is the most suitable white pigment for cosmetic use.

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REFERENCES

1. Lu P., Huang S., Chen Y., Chiueh L., Shih D. Y., (2015): Analysis of titanium dioxide and zinc oxide nanoparticles in cosmetics. *Journal of Food and Drug Analysis, 23*, 587-594. Doi:10.1016/j.jfda.2015.02.009
2. Lee K. M., Lai C. W., Ngai K. S., Juan J. C. (2016): Recent developments of zinc oxide based photocatalyst in water treatment technology: A review, *Water Research, 88*, 428-448. Doi:10.1016/j.watres.2015.09.045
3. Totu E. E., Cristache C. M., Perieanu V. S., Burlibasa M., Petre D. C., Burlibasa L. (2021): Are Nano TiO_2 Inclusions Improving Biocompatibility of Photocurable Polydimethylsiloxane for Maxillofacial Prosthesis Manufacturing?, *Applied Science, 11*, 3777. Doi:10.3390/app11093777
4. Leite-Silva V. R., Lamer M. L., Sanchez W. Y., Liu D. C., Sanchez W. H., Morrow I., Martin D., Silva H. D. T., Prow T. W., Grice J. E., Roberts M. S. (2013): The effect of formation on the penetration of coated and uncoated zinc oxide nanoparticles into the viable epidermis of human skin in vivo. *European Journal Pharmaceutical and Biopharmaceutics, 84*(2), 297-308. Doi:10.1016/j.ejpb.2013.01.020
5. Wang F., Yuan Z., Liu B., Chen S., Zhang Z. (2016): Catalytic oxidation of biomass derived 5-hydroxymethylfurfural (HMF) over Ru^{III} -incorporated zirconium phosphate catalyst. *Journal of Industrial and Engineering Chemistry, 38*, 181-185. Doi:10.1016/j.jiec.2016.05.001
6. Zhou X., Bai H., Ma H., Li H., Yuan W., Du H., Zhang P., Xin H. (2015): Synthesis of zinc phosphate and zinc ammonium phosphate nanostructures with different morphologies through pH control. *Materials Characterization, 108*, 22-28. Doi:10.1016/j.matchar.2015.08.012
7. Lu J., Yu H., Chen C. (2018): Biological properties of calcium phosphate biomaterials for bone repair: a review. *RSC Advances, 8*, 2015-2033. Doi:10.1039/c7ra11278e
8. Lee Y., Schade N. B., Sun L., Fan J. A., Bae D. R., Mariscal M. M., Lee G., Capasso F., Sacanna S., Manoharan V. N., Yi G. (2013): Ultrasmooth, Highly Spherical Monocrystalline Gold Particles for Precision Plasmonics. *ACS Nano, 7*(12), 11064-11070. Doi:10.1021/nn404765w
9. Jand S. I., Lee M., Jung Y., Jeong M. K., Ryu J. H., Kim B. J., Suh B., Kim E. (2021): Skin characteristics following repeated exposure to simulated outdoor and indoor summer temperatures in South Korea and Southeast Asia. *International Journal of Cosmetic Science, 43*(3), 352-358. Doi:10.1111/ics.12702
10. Yingngam B., Kacha W., Rungseevijitprapa W., Sudta P., Prasitpuriprecha C., Brantner A. (2019): Response surface optimization of spray-dried citronella oil microcapsules with reduced volatility and irritation for cosmetic textile uses. *Powder Technology, 355*, 372-385. Doi:10.1016/j.powtec.2019.07.065
11. Onoda H., Haruki M., Toyama T. (2014): Preparation and powder properties of zinc phosphates with additives. *Ceramics International, 40*(2), 3433-3438. Doi:10.1016/j.ceramint.2013.09.088
12. Onoda H., Haruki M., Toyama T. (2014): Influence of pH, concentration of sodium lactate as an additive and ultrasonic treatment on synthesis of zinc phosphate white pigments. *International Journal of Cosmetic Science, 36*(4), 321-326. Doi:10.1111/ics.12129
13. Onoda H., Higashide D. (2019): Low temperature phosphoric acid treatment of zinc oxide for novel white pigments. *Ceramics-Silikáty, 63*(3), 291-296. Doi:10.13168/cs.2019.0023
14. Onoda H., Matsukura A. (2017): Surface Modification of Titanium Dioxide for Novel White Pigment with Condensed Phosphoric Acid Treatment. *European Chemical Bulletin, 6*(4), 140-144. Doi:10.17628/ecb.2017.6.140-144
15. Miyajima T., Maki H., Kodaka H., Ishiguro S., Nariai H., Motooka I. (1996): 27Al NMR study on the complexation of long-chain polyphosphate anions. *Phosphorus Research Bulletin, 6*, 281-284. Doi:10.3363/prb1992.6.0_281
16. Atchudan R., Edison T. N. J. I., Perumal S., Karthikeyan D., Lee Y. R. (2016): Facile synthesis of zinc oxide nanoparticles decorated graphene oxide composite via simple solvothermal route and their photocatalytic activity on methylene blue degradation. *Journal of Photochemistry and Photobiology B., 162*, 500-510. Doi:10.1016/j.jphotobiol.2016.07.019
17. Cha B. J., Woo T. G., Park E. J., Kim I. H., An J. E., Seo H. O., Kim Y. D. (2017): Photo-catalytic activity of hydrophilic-modified TiO_2 for the decomposition of methylene blue and phenol. *Current Applied Physics, 17*(11), 1557-1563. Doi:10.1016/j.cap.2017.07.002
18. Niskanen I., Hibino K., Raty J. (2016): Immersion liquid techniques in solid particle characterization: A review. *Talanta, 149*, 225-236. Doi: 10.1016/j.talanta.2015.11.051