PREPARATION OF THE PLANARIZED SIO_2 PARTICLES TO MAKE IDEAL SIO_2/TIO_2 COMPOSITE PARTICLES FOR COSMETIC PRODUCTS

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ABSTRACT

The planarized SiO_2 particles were prepared by two-step reduction method of making much smaller particles, micron-sized ones, to improve spreadability, adherence, and smoothness. Various pigments known as flaky extender usually have terrace layers on their surfaces, but SiO_2 particles in this study exhibit a smooth surface structure. These single SiO_2 particles were used as core particles to prepare the composite particles coated with ultra fine TiO_2 particles by a homogeneous precipitation method. The thickness and the morphology of the deposited TiO_2 layers could be modified by adjusting the reactant concentrations, the reaction time and the temperature. The characteristics of SiO_2/TiO_2 composite in the field of color cosmetics are to give an UV-cut effect and to enhance the chroma of human skin color, one of optical properties.

1. INTRODUCTION

Synthetic SiO_2 particles whose mean volumetric diameters are 3~5, particle shapes are spherical and morphological characteristics are porous structure are widely used as color cosmetic materials, to reduce the friction forces and achieve good spread-ability, to absorb sebum while being applied on skin, and to increase the fluidity of mixtures for easy handling during conveying, feeding, and discharging.

But the spherical particles are likely to make an uneven make-up film onto the skin due to their high fluidity when the consumer's finger forces are biased, and to make poor smoothness and poor skin-adhesion due to their smaller contact surface area. To overcome the disadvantage of the spherical particles, the methods of making the flaky SiO_2 particles were suggested[1,2], but the industrial manufacturing is difficult and their properties are quite similar to the existing ones.

In this report, study has been done on the manufacture of SiO_2 coarse particles and the multi-step size-reduction process for SiO_2 particles with better smoothness and skin-adhesion, and higher fluidity than flaky ones.

Meanwhile, it is normal to mix several kinds of powders to achieve good smoothness and skin-adhesion, and to have good skin color expression as it is most important for color cosmetics. Also, many new powder materials have been developed with multi-functions, decreasing the number of powders to be mixed and maintaining the even qualities. For example, powders such as talc, mica and sericite have good smoothness but low degree of adhesion to skin. Meanwhile titanium dioxide and zinc oxide, in spite of rough feeling on skin, show excellent adhesion characteristics. Thus general technology is to compound ultra-fine particles with adhesive properties to smooth particles for optimization of both particles[3].

Our study has been conducted to do the surface coating treatment of ultra-fine titanium dioxide by the homogenous precipitation method with fine Silica particles which have 2.0~2.2 specific gravity, flat surface, and porous structure of low bulk density, different from the exiting composite powders of which the surfaces of titanium dioxides are treated with the existing clay mineral composite pigments of 2.5~2.8 specific gravity. This gives heavy feeling on skin due to higher specific gravity, and to control the surface treatment degree and the particle size in order to modify their optical properties[4, 5] making a light reflect more at the long wavelengths of above 600nm which are the central wavelengths of skin color to express strong skin color tone[6].

As mentioned above, the purpose of our study was to develop new morphological and optical properties of powder particles using the existing common cosmetics materials, and to review the manufacturing results of single silica particles planarized by grinding, and to review those of silica composite particles coated with ultra fine titanium by the homogenous precipitation method.

2. EXPERIMENTS

Aqueous sulfuric acid solution is added to aqueous sodium silicate solution in a four-neck reactor while stirring at room temperature, to reach pH range of 7.0~8.0, then stoodstill sufficiently, washed and filtered to get silica gel slurries. The slurries were sprayed in water, filtered and dried to make coarse silica bead particles whose particle sizes were 0.5~1.0 mm. The beads were grounded, first, to the mean particle sizes of 50~100 µm by the impact mill(Impact Mill, Retsch Gmbh, German) and, secondly, to those of 5.0~10.0 µm by air jet mill (Super Sonic Jet Mill, Nippon Pneumatic MFG Co.) to obtain the planarized SiO_2 particles for making composite particles.

The planarized ones were dispersed in distilled water in a reactor, and 0.2~0.3 mol/l of urea, 0.3~0.4 mol/l of sulfuric acid and 0.007~0.015 mol/l of titanyl sulfate were added respectively while stirring. And the mixture was heated to the temperature of 60~90°C and precipitated to coat the surface of flaky silica particles with titanium hydroxide as ultra fine ones. Then, after washing and drying, the composite particles were baked at the temperature of 700~900°C and the heating rate of 5°C/min during 2~4 hours in air.

The shape of single SiO_2 particles, composite particles, and ultra fine TiO_2 particles on the surface of composites were observed with SEM (JEOL, JSM-840A). The changes of particle size distribution at the two step size reduction process of making the planarized fine particles from coarse silica beads and the shapes of silica fine particle composite were measured by laser particle size analyzer (Mastersizer X, Malvern). And to compare the UV-cut effect of titanium dioxide fine particles coated on composite ones, the UV absorbencies of 1 wt% composite powder and methanol dispersion were measured by UV spectrometer (UV-160A, Shimadadzu).

Then, to review the properties and the manufacturing conditions of powders, which are useful for cosmetics, the optical properties of skin coats and powder layers were observed as follows. To evaluate the film evenness of the composite particles on skin, 0.02 g of the composite particles were applied on the 30 cm^2 area of skin from the center to the outer, drawing concentric circles. The lightness (L*) were measured at the distances of 0 cm, 0.5 cm, 1.0 cm, 1.5 cm, 2.0 cm from the center to the right and to the left, respectively with spectrophotometer (SpectroGuard II Color System, Pacific Scientific Co.). And to evaluate the optical properties of the composite particles applied on skin, each samples were dispersed into 10wt% polyvinylpyrrolidone and isopropyl alcohol solution and were applied them on skin-colored glass plate by 100mm film applicator, and the reflectance at the range of visible light wavelengths by spectrophotometer (Cary5E, Varian) were measured.

3. RESULTS AND DISCUSSION

3.1 Changes of the size distribution and changes of the shape by size reduction

To make the planarized SiO_2 fine particles, coarse particles of 0.5~1.0 mm particle size distribution were, first, made when silica gel slurries were sprayed into water tank through 2.0 mm diameter of nozzles at the pressure of 4.0 kg/cm^2, and then suitable particle distribution of powders like that of Figure 1 was obtained by two-step grinding process. Figure 1 shows the measured result of the particle distribution of talc for cosmetics and the changes of the particle size distribution by grinding process. The impact mill played a great role to get equi-dimensional grinding and 50~100 μm mean particle size could be obtained with the sieve size of 0.5 mm at 2,000~4,000 rpm. And when the particle distributions like Figure 1. (a) was obtained, 5mm mean particle size of the planarized silica fine particles were obtained by second grind of air jet mill at pressure of 7 kg/cm^2 during 120 min.

As mentioned above, coarse particles were, first, ground into multi-surface shapes by the external impact as volumetric grind, and made into the planarized fine particles by the air jet system as interparticle impact. Generally, flaky particles have the surface structure of multi-layers of terraces, but silica particles made in our study are thought to have better skin adhesion and smoothness due to their planar surface condition different from flaky ones.

3.2 Preparation of composite particles

Sulfuric acids were needed to dissolve titanyl sulfate at the process of ultra fine titanium dioxide surface treatment by the homogenous precipitation, but the growth of particles was difficult at high concentration due to the hydrolysis of titanyl sulfate. The growth rate of particles was increased when urea was not added, and the growth was not done as intended with much higher concentration of urea. Also the surfaces of silica particles were coated, in shorter time, with the precipitated reactants and the particle sizes were increased by the increment of precipitation temperature, while the coating rate was increased and the particle sizes were decreased by the decrement of precipitation temperature. As result, the coated particles were crystallized into titanium dioxide by the firing, the crystallization of titanium dioxide was affirmed by X-lay diffraction pattern at the firing temperature of 700°C, 800°C, 900°C, and the converting quantity to rutile from anatase was increased at higher firing temperature. Moreover, by the firing treatment, the combining forces of titanium dioxide with silica particle surfaces became stronger and the compact surface coated films were formed.

Therefore, by the firing temperature and time, the react temperature and time, and the reactant temperature, it is possible to control the coat condition, the particle size, the accumulation number of titanium dioxide fine particles precipitated on the surface of planary silica fine particles, and it is affirmed by the SEM measurement in Figure 3. Figure 3 shows the results obtained by controlling the reactant temperature and time with 0.2 mol/l of urea, 0.35 mol/l of sulfuric acid and 0.01 mol/l of titanyl sulfate. Also it resulted that the particle sizes of titanium dioxide fine particles could be modified to 0.01~0.03, the monolayers of fine particles like Figure 3. (b), (c) could be obtained from the islandsome like Figure 3. (a) by controlling the firing temperature and the accumulation number of coated fine particles, and the thin films of coated titanium dioxide could be obtained. It is necessary to increase the accumulation number of the precipitated particles per unit time at the first reacting stage and to slowly precipitate them for the growth of films to obtain ultra fine titanium dioxides like Figure 3. (b), (c).

3.3 The spread status on skin by the shapes of the composite particles

The purpose of use of SiO_2/TiO_2 composite particles made by fusing or coating TiO_2 pigments into spherical silica particles for cosmetics powders is to have an even spread-ability on skin utilizing the fluidity of the original silica. And the shapes of the composite particles and the mixing ratio in products should be limited for the types of products, because the shapes of the composite particles affect the qualities of color cosmetics such as fluidity, skin-adhesion, smoothness, hiding powder, and stability. But the planar composite particles in our study show better spread-ability and skin-adhesion than the spherical ones in view of morphological characteristics, making it possible to have a variety of product formulas and to release the limitation of quantity. To confirm the above characteristics by comparing the film evenness, we measured the color of each parts of skin before and after spreading and compared the lightness (L*) whose values show higher when spread with higher thickness due to the hiding power of composite powders containing TiO_2 and lower when spread thinly. Figure 4 shows the measured results of various samples. In case of the spherical shape of composite powders, overall spread became uneven by the spreading power biased toward outer sides from central parts of skin due to their high fluidity, showing that the outer sides, the higher lightness as in Figure 4. While, in case of the planar composite particles, it is possible to control the adhesion power and the fluidity to get an even spread because of their smooth spreading, showing that the lightness of spread surfaces are quite similar to those of naked skin as in Figure 4.

3.4 The optical properties of make-up film on the skin

Mica powders coated with luster pigments of TiO_2 show the optical properties of pearls by the light intervention, but composite particles with the monolayers of fine particles of TiO_2 show the soft-focus effects. As mentioned above, fine particles of silica made in our study as core particles whose shapes are similar to the flaky ones reduce the diffused reflection to have good light transparency, resulting that the optical properties are changed by the appearances of TiO_2 coated on powder pigments. Therefore, new optical properties different from those of the exiting spherical silica fine particles coated with TiO_2 were found.

In our study, to observe the optical properties of powder layers on skin, we measured the reflectance at the visionary infrared spectrum of the spread powders, the composite ones and the exiting spherical composite ones, on glass plates, which are single silica ones made in this experiments. The spreading quantities are weighed 50 mg/cm^2 similar to the actual spreading quantities of twin-cake on skin, showing the results in Figure 5. Observing the reflection distributions in Figure 5, the measured result of skin on glass plate [Figure 5. (a)], that of spherical composite powders on [Figure 5. (b)], that of the composite ones made in our study [Figure 5. (c)], and that of flaky silica fine particles which are core composite ones on [Figure 5. (d)] are all rather same, but (c) and (d) of Figure 5 are much more quiet alike. And it concluded that the spherical composite particles show comparatively high reflection at the short wavelengths to reduce the chroma of skin color. While composite particles coated with TiO_2 in our experiments show comparatively high reflection at the above 600nm wavelengths which are the central ranges of skin color to improve the chroma of skin color. Also, it concluded that the UV-cut effects of the composite particles made in our study were superior to the spherical ones as in Figure 6, because the spread layers of the planary composite particles became more compact and the hiding unit areas of TiO_2 surfaces were much larger while those of the spherical ones were viceversa.

Therefore, the composite particles made in our study have UV-cut effects and could be used as powder pigments for color cosmetics to express clear and healthy skin color.

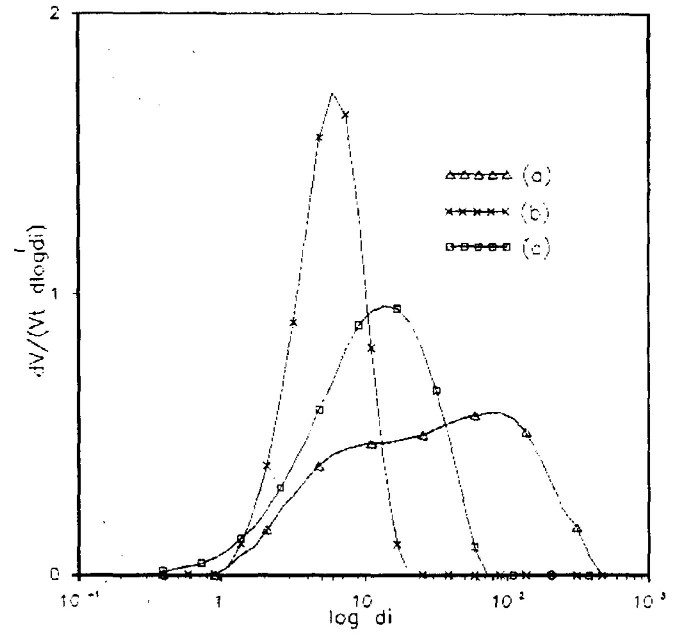
4. CONCLUSION

In our study to modify the week-points of the spherical silica fine composite particles which are usually used as cosmetics powders, the planar silica fine particles of 5 mm mean particle size which have high layer dispersion were made by grinding the coarse silica particles, first, with impact mill and, secondly, with air jet mill. And with the manufactured silica fine particles as core particles for making composite ones by the precipitated reaction of TiO_2 ultra fine ones, the composite particles were made to have the characteristics of single silica particles which show better fluidity, smoothness, and skin adhesion. And when the composite particles made in our study were used as color cosmetics materials, the UV-cut effects and the optical properties of silica surfaces coated by TiO_2 ultra fine particles as the reflection characteristics at visionary infrared ranges were used to express the skin color more effectively.

In conclusion, we modified the morphology of composite silica used as color cosmetics to give new powder characteristics and modified the morphology of inorganic oxidant composites for color cosmetics materials to have new properties and to find the possibilities of developing new materials. Also, from our study it is thought to be possible to make new cosmetics powder materials in view of the particle properties of morphology, optics, and surface through the development of new composite particles compounded with the existing single particles, as we deliberately made the special structure of particle space by coating with TiO_2 ultra fine particles to make the composite particles which have new optical properties.

EXPLANATION OF FIGURE

Figure 1. Size distributions of silica particles prepared by two-step reduction method.



(a) primary (impact mill, sieve size 0.5 mm, 3000 rpm),
(b) secondary (air jet mill, pressure 7 kg/cm2, 120 min),
(c) Talc

Figure 2. SEM photograph of planarized SiO2 particles.

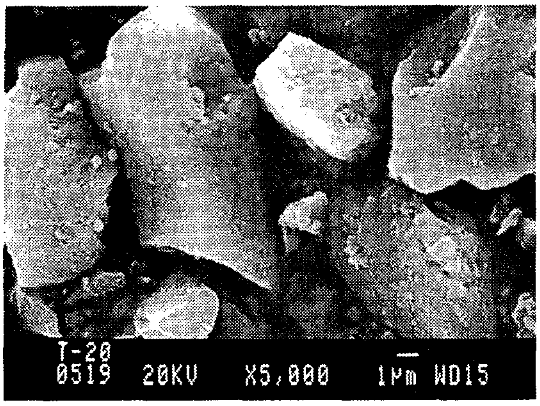
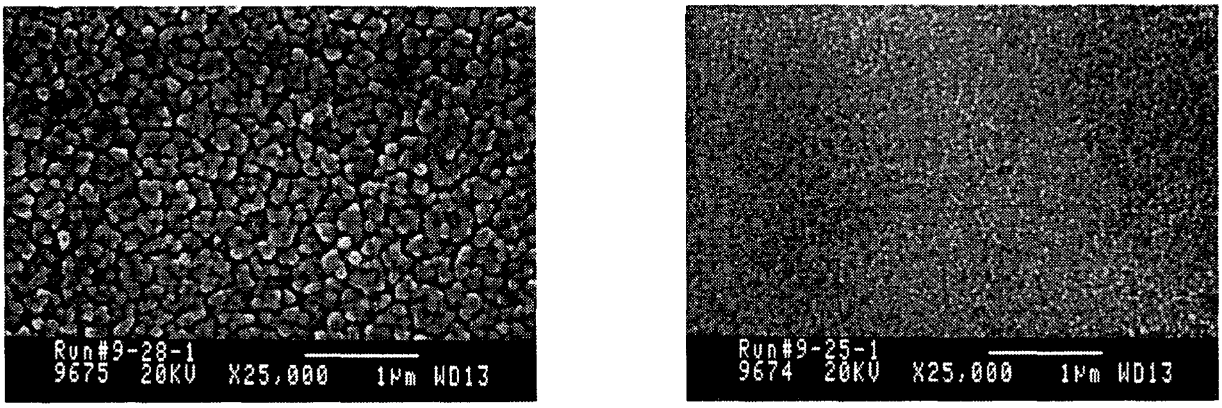
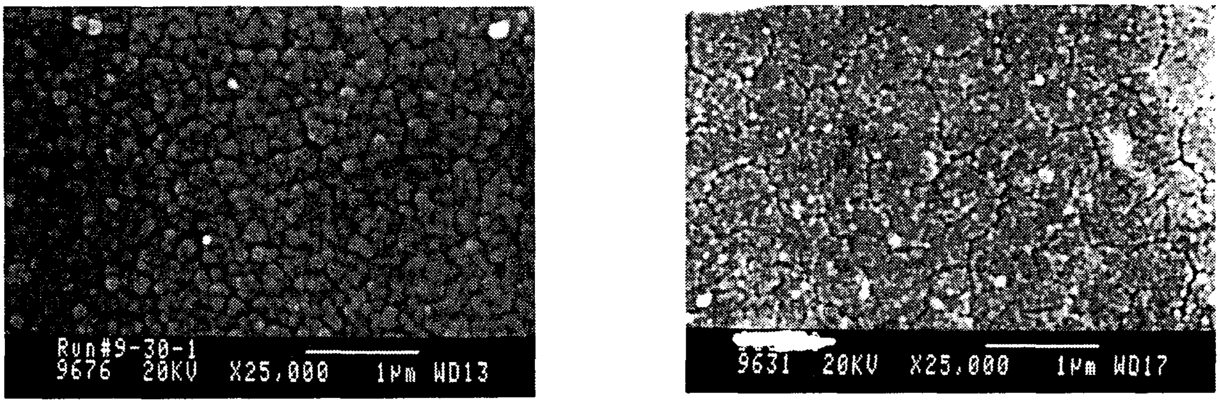


Figure 3. SEM photograph of the surface of SiO2 / TiO2 composite particles prepared by a homogeneous precipitation method. coating condition: [TiOSO4] 0.01 mol/l, [H2SO4] 0.35 mol/l, [(NH2) 2CO] 0.2 mol/l



(a) reaction temperature 90°C, 3 hours,

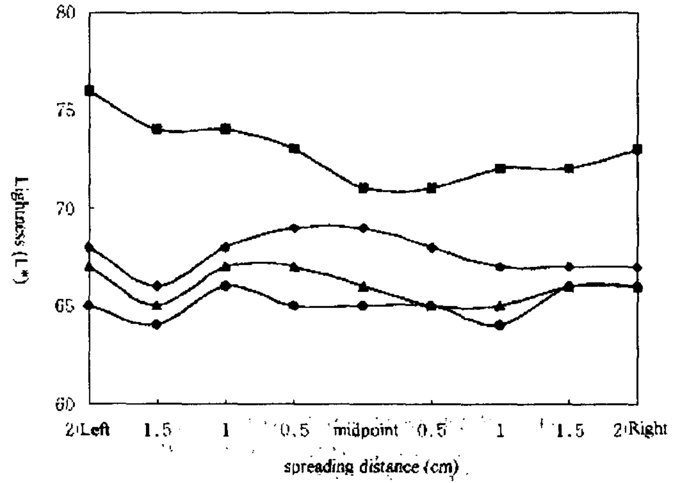
(b) reaction temperature 70°C, 6 hours,



(c) reaction temperature 80°C, 6 hours,

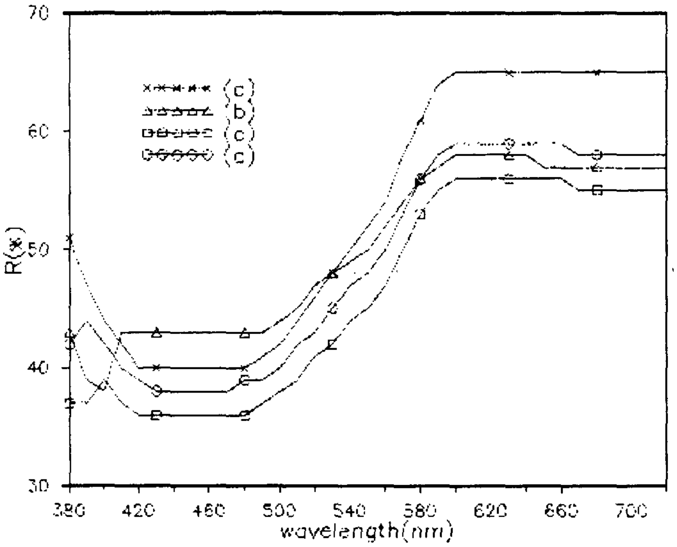
(d) calcination at 800°C, 2 hours, from (c)

Figure 4. Lightness (L*) variations on the skin surface with different Si02 / Ti02 composites.



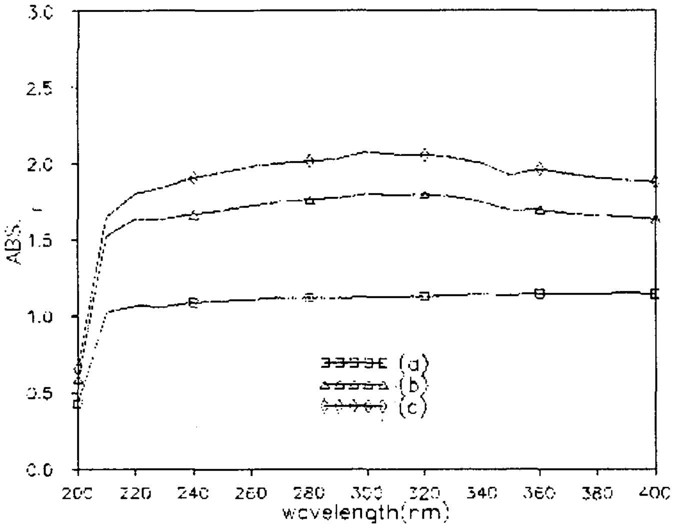
Naked skin surface ("●"); planarized composite particles containing 20wt% Ti02 ("▲"), 28 wt% Ti02 ("◆"); spherical composite particles containing 50 wt% Ti02 ("■")

Figure 5. Reflectance of skin-colored glass plate with Si02 / Ti02 composite particles and single Si02 particles.



(a) skin-colored glass plate,
(b) with spherical composite particles containing 50 wt% Ti02,
(c) with planarized single Si02 particles,
(d) with planarized composite particles containing 20wt% Ti02

Figure 6. UV absorption spectra different types of SiO2/TiO2 composites.



(a) spherical composite particles containing 50 wt% TiO2,
(b) planarized composite particles containing 20 wt% TiO2,
(c) planarized composite particles containing 28 wt% TiO2

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