Powder Treatments using Atmospheric Pressure Glow Plasma
< Silica Coating of TiO₂ Fine Powder >

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1. Introduction

Some kinds of pigments that are used for cosmetics give rise to a skin irritation problem when they contact the skin directly. TiO₂ is an UV reflective white pigment powder for cosmetics. But naked TiO₂ is a kind of photosensitive catalyst, so the powder easily attacks a human skin surface and oxidizes oil in the sweat as a squalene. Oxidized squalene molecules will produce many kinds of peroxo-organic compounds that may cause an allergy or cancer. So we need to avoid such effects caused by the catalytic ability of TiO₂ particles.

Some previous studies reported the possibility of powder handling with atmospheric pressure glow discharge [1-5]. Then, at the first stage in this experiment, we will try to develop some SiO₂ coating on the TiO₂ powder pigments by means of atmospheric pressure glow discharge using TEOS adsorbing and plasma oxidation to prevent the oxidation of squalene oil in the UV irradiation.

On the other hand the SiO₂-coated TiO₂ powders will not have only a very high refractive index for the UV region but also high transparency for visible and IR regions. For such reasons, silica-treated powders will have too white a tint to use for the cosmetics and cannot prevent IR penetration through the powder, which is also a cause of human skin irritation. We can expect that some metal ion doping can achieve wide band light absorption in TiO₂. At the second stage, we will try to obtain a thin deposition layer of iron between the TiO₂ surface and the silica layer to eliminate the photo-catalytic ability and to suppress the wide band light transparency of bulk TiO₂.

Finally, we measure the catalytic effect and light absorption of the new material iron doped silica-coated TiO₂.

2. Experimental

The mean diameter of TiO₂ particles is two hundred nm; they contain 80% of anatase and 20% of rutile (Toho Titanium Corporation, HT-170R). For iron doping, we used tris (2, 4-pentanedionato) iron (IAA). In this study, we employed the Adsorb and Dry method to achieve the coated surface [5]. The schematics of the discharge reactor is shown in Figure 1. The discharge conditions are as follows: discharge frequency, 13.56 MHz; power, 1.5 - 2.5 kW; O₂/He gas flow rate, 100 ml min⁻¹/10 l min⁻¹. Treating rate is about 2 g min⁻¹ for the powder.

To examine the photo catalyst ability of the powders, we irradiated the squalene oil (2, 6, 10, 15, 19, 23-hexamethyl-2, 6, 10, 14, 18, 22-tetracosahexaene) that contained the powder samples by UV in a Pyrex glass bottle. After 1 hour UV-irradiation by Xe lamp, the gas products were measured by GC-MS (Shimazu QP5050).

Process 1) Silica coating on TiO₂

At first we tried to make sure of the possibility of the Adsorb and Dry method with TEOS to coat SiO₂ on the bulk TiO₂. In this treatment, adsorbed TEOS is partly reacted with naturally adsorbed water on the TiO₂ surfaces to deposit SiO₂. The percentages
Process 2) Iron ion doping

TiO₂ powders were pre-treated with IAA-ethanol mixture to adsorb organic metal molecules on the surfaces of the particles. The amount of IAA in ethanol are calculated using same equation (1) as in TEOS adsorption. After the evaporation of the ethanol, the IAA adsorbed powders are treated to have iron ion doped TiO₂ using atmospheric pressure glow plasma in He-O₂ system to eliminate the organic part from the adsorbed IAA molecules.


After process 2, the iron-doped TiO₂ powders were pre-treated with TEOS (tetraethoxyxilane) - ethanol mixture aero - sol to adsorb TEOS on the surfaces of the particles. After the ethanol evaporation, the powders are oxidized in atmospheric pressure glow plasma. Using the plasma treatment, SiO₂ was deposited on the iron-doped TiO₂ surface as an inorganic fine layer. The thickness of SiO₂ deposited can be controlled by the concentration of TEOS in the solvent ethanol during the adsorbing process.

3. Results and discussion

Process 1

From the XPS analysis, we found Si2p and Ti2p spectra for TiO₂ that adsorbed TEOS (b), and for TiO₂ that adsorbed TEOS and then was oxidized in the He-O₂ plasma (c), as shown in figure 2. After plasma oxidation (c), Si atomic concentration is increased because the naked TiO₂ surfaces are completely covered by an inorganic SiO₂ thin layer.

In figure 3, sharp peaks of O₂⁺ were obtained in the spectra of (a), (b) and (c). In the spectrum of (a) only one peak (529.9 eV) assigned to TiO₂ existed. On the other hand, in the spectrum of (b) the peak

![Graph showing atomic concentration ratios of Si/Ti on the treated TiO₂ powder surfaces.](image-url)
(532.5 eV) assigned to SiO₂ newly appeared while the peak assigned to TiO₂ decreased. Therefore, we concluded that the surface of (b) was coated with SiO₂ but the coating was not enough. The surface of TiO₂ is still partly covered by half-dissociated TEOS molecules that are reacted with adsorbed water on the surface of TiO₂. In the spectrum of (c), the peak assigned to TiO₂ has almost disappeared and the shape of the peak looked like that of pure SiO₂. So, we could confirm that the surface of (c) was almost completely coated with an inorganic SiO₂ layer without any organic contamination.

A TEM photo of silica-coated TiO₂ particles is shown in photo 1. In the photo, homogeneous SiO₂ thin layer (1-2 nm in thickness) is found on the particles. So we attained a very homogeneous SiO₂ layer with the TEOS Adsorb and Dry method.

**Process 2)**

Figure 4 shows the XPS Fe2p spectra of IAA-treated TiO₂ particles oxidized in the O₂/He plasma. In the figure, we can find Fe2p1/2 and Fe2p3/2 peaks assigned as Fe ion, but the binding energies of Fe²⁺ and Fe³⁺ ions are very close to each other. So it is difficult to define which ion is on the TiO₂. The amount of deposited Fe ion can be controlled by the concentration of IAA in the solvent ethanol at the adsorbing process. Figure 5 shows the UV-VIS reflection spectra of naked TiO₂, IAA 1% adsorbed TiO₂; adsorbed, then plasma -treated TiO₂; and pure IAA powder. Naked TiO₂ show a high and flat reflectivity from near IR region to UV region. Light incident to the surface partly penetrates into the bulk and is absorbed in the solid, then it reflects to the surface boundary, so the reflection spectra contain the absorption characteristics. IAA-adsorbed TiO₂ shows small peaks attributed to adsorbed IAA on the TiO₂ but such a peak is lost in the plasma-irradiated IAA itself. It seemed that plasma-treated IAA on the TiO₂ were completely oxidized to inorganic Fe ion.
Figure 5 show the GEMS spectra of TiO$_2$; IAA adsorbed TiO$_2$; adsorbed, then plasma-treated TiO$_2$; and pure IAA, powder.

Figure 6 show the GCMS spectra of gas products in squalene which contained the powders after being irradiated by an Xe lamp for one hour.

Untreated TiO$_2$ produces many kinds of organic oxides such as ethanol, acetone and long chain oxidant compounds that should be harmful materials for human skin. Also, the oil emits a foul odor. The product concentrations decreased with increasing of the concentration of the doped iron. However even for 2.5% iron-doped TiO$_2$, we still have a small amount of alcohol in the spectrum. But using silica-coated iron-doped TiO$_2$ which is produced in process 3), we have almost no signal assigned as an organic oxide in the GC-MS spectra of the UV irradiated squalene, except for a very small amount of ethanol signal. Normally the anatase-type TiO$_2$ crystals have small rectangular open spaces, such a few angstroms in size, in the structure. It seemed that the iron ions are partly inserted into the open spaces of the TiO$_2$ lattice. However, the crystal lattice of iron-doped TiO$_2$ is the same as that of untreated one measured by XRD. So we could not infer whether the iron ion is in solid solution in TiO$_2$.

The treated powder shows fine and flesh colour with pearl-like glowing, that should be caused from a multi-reflection effect from the thin layer boundaries of silica-iron-TiO$_2$. Especially, the powder can cover the skin furrows and prevent easy drop-off of the powder from the skin surface by sweat, because of the high reflection for the incident light in the skin furrow and the strong absorbing ability of the nano powder to absorb the skin oil.

4. Conclusion
We attained Fe ion doped TiO$_2$ particles by means of atmospheric pressure glow discharge using IAA, TEOS adsorbing and plasma oxidation method. The particles were coated by a silica protection layer to avoid the UV catalytic ability of TiO$_2$. The plasma-treated TiO$_2$ powders will provide many functional contributions for the future cosmetics.

4. Reference