Preparation and Characterization of Surface Modified Mica by Microwave-enhanced Wet Etching

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Abstract: In this study we successfully altered the structural characteristics of the mica surface and were able to control oil-absorption by using the microwave enhanced etching (MEE) technique, which has originally been used in semiconductor industry. When microwave energy is applied to the mica, the surface of the mica is etched in a few minutes. As the result of etching, oil-absorption of the mica was enhanced and surface whiteness was improved by modifying the silicon dioxide layer. Additionally, the high whiteness was maintained even though the etched mica absorbed the sebum or sweat. The surface modification of mica was performed by microwave irradiation after the treatment of hydrofluoric acid. The degree of etching was regulated by acid concentration, irradiation time, the amount of energy and slurry concentration. The surface morphology of the etched mica appears to be the shape of the ‘Moon’. The characteristics of surface area and roughness were examined by Brunauer-Emmett-Teller (BET) surface area analysis, atomic force microscopy (AFM), scanning electron microscopy (SEM), spectrophotometer and goniophotometer.

Keywords: microwave enhanced etching, surface modification, oil-absorption, mica, cosmetics

1. Introduction

To adjust the skin color tone, we combined talc, TiO₂, and Fe₂O₃, the cosmetic raw materials that contain highly refractive pigments. However, the problem with these materials as a high covering powder is that they tend to make the makeup thick, make hair follicles visible to the eye and yet have low skin transparency, and leave an unnatural finish. These inorganic pigments are also in trouble because they originally have low brightness or saturation. When they are wet in water or sebum, the brightness and saturation are reduced...
even further to make the makeup film dark thus spoil the makeup effects.

Meanwhile, the beauty of skin appearance is greatly influenced by skin denseness. If the skin becomes denser, light is more uniformly reflected from the skin, increasing the transparency of the skin. Thus, a transparent, flake-like powder having excellent adhesion to the skin is preferred to the conventional materials that take advantage of the covering action caused by a light scattering effect.

To use the pure transparency of synthetic mica among inorganic pigments as well as the characteristics of the scale-like smooth surface of the synthetic mica, attempts were made to develop new products that have high particle uniformity with high aspect ratio and to produce a cosmetic raw material that has good gloss or transparency to present a dense skin.

However, such transparency or gloss imposes limitations on the use of mica in pact formulations. The scale-like smooth surface of mica tends to present glossiness instead of giving transparency, showing darkness caused by a change in color after the make-up application, thus reducing the make-up lasting properties. Thus, the use of mica in pact formulations has limitation, unlike other formulations. Moreover, mica has a low ability to absorb sebum, and becomes wet easily even in a small amount of sebum that the color thereof becomes dark. This is a common problem in plate-like inorganic pigments.

In an actual make-up film, the secretion of sweat is also a problem. In a high-temperature and high-humidity condition in the rainy or summer season, in which a large amount of sweat is secreted, sebum and sweat interact with each other. When the amount of sebum in a make-up film is excessive, the make-up film is separated and floats on the surface while it is admixed with sebum. In addition, a large amount of sweat was observed to flow and push the flowable makeup film, thus promoting the breakdown of the make-up.

To increase the sebum-absorbing capability of mica, the method of coating mica with a surface-treating substance such as dimethicone or triethoxycarprylsilane, has been used, but it is not easy to solve the problems associated with the inherent glossiness of mica. Thus, mica materials with a relatively low glossiness have been used, but they too have encountered limitations. However, no method has yet been developed for solving the glossiness of mica materials while maintaining the sensory feel thereof.

Transparency and glossiness, the typical characteristics of mica, are not suitable for the base make-up cosmetics. The surface of mica tends to be glossy by a reflection of light. When it is applied to the face, it often absorbs sebum and sweat and tends to appear a dark and dull color. For these reasons, use of the mica has in fact been limited in makeup cosmetics compared with other inorganic components. Furthermore, mica is easily wetted even with a small amount of sebum and sweat because of its low capacity of oil-absorption. As a result, the color of mica becomes dark and dull.

The etching process is used in numerous industrial applications. For example the energy released by the alpha decay is transformed partly into a so-called alpha-recoil track (ART)[1-3]. The track can be enlarged by treating the mica with an appropriate etchant (e.g. HF).

Our study focuses on the application of microwave enhanced etching[4,5], which has been used in semiconductor industry, to alter the surface morphology of synthetic mica and eventually to control the oil-absorption capacity and the optical characteristics of luster and whiteness.

The changes in the microstructure and physical properties of the etched mica obtained are investigated by using Brunauer-Emmett-Teller (BET) surface area analysis, scanning electron microscopy (SEM)[6,7], atomic force microscopy (AFM)[8-10], spectrophotometer, goniophotometer and ASTM D281-95 standard method[11].

2. Materials and Methods

2.1. Sample Preparation

The pretreatment process of fluoro-mica powder is as follows:

   The fluoro-mica with an average size of 12 µm
Table 1. Oil-absorption and Whiteness of Fluoro-mica Before and After Microwave Etching Process

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oil-absorption (cc/g)</th>
<th>Whiteness (L*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-fluoro-mica</td>
<td>0.432 ± 0.023</td>
<td>86.5 ± 0.31</td>
</tr>
<tr>
<td>E-fluoro-mica</td>
<td>0.735 ± 0.038</td>
<td>93.2 ± 0.28</td>
</tr>
</tbody>
</table>

The solution (approximately 0.1 mL) of the dispersed particles was deposited on carbon tape, then oven-dried at 100 °C for 1 h. The preprocessed samples were analyzed in the AFM equipment after temperature equilibration. The solution was diluted until individual or separate particles could be seen in the AFM images. Room temperature and air humidity were kept at around 24 °C and lower than 50 %, respectively. The samples were prepared using the previously described procedure and each sample was imaged at two different positions.

The goniophotometer is based on polarized reflectance at continuous angles, and the changes in polarized phase are used in combination to determine the optical properties of surfaces. The goniophotometer generally measures the intensity and phase around the Brewster angle at which position the reflected intensity of light polarized parallel to the incident plane is zero for a smooth surface. The phase of the polarized light also goes through an 180° change at this angle. Changes in the surface (due to molecular layers, particles or surface roughness) influence the measurable values of the continuous angle. These values determine the optical properties of the surface layer.

3. Results and Discussion

Figure 1 shows the variations in BET surface of mica.
that occurred with the irradiation time of microwave in the etching process. When the mica sample was etched for 180 s under microwave irradiation, the surface area increased up to three times than that of the non-etching mica. However, the SEM image made a little difference between the surface of mica before and after the microwave etching process, as shown in Figure 2.

The increase in the surface area means that the microwave etching process enhances nano-roughness of the mica surface. The surface areas reach the maximum at 180 s and decrease again to less than 3.6 m²/g, which indicates the formation of very smooth surfaces. In addition, the total pore volumes reach the maximum at 180 s, and they gradually decrease. It is reasonable to infer that the nano-roughness induced by the etching process plays an important role in the physical property of mica. E-Fluoro-mica sample refers to the sample obtained by microwave-enhanced etching process for 180 s.

Figure 3 shows the height and friction images of the 1 µm² area obtained in a single particle. It shows AFM images of the highly concentrated holes at two different positions. After scanning a 1 µm² area, an image of the fluoro-mica surface was captured. The holes appeared on the surface when microwave enhanced etching was applied. Some holes that had the shape of the ‘Moon’ (approximately 50 to 150 nm size) were observed in AFM images. The intensities of images in the gray scale of other holes are lower than the bare
surface. The measured depth of the holes is between 7 and 15 nm.

The gloss of fluoro-mica is the shiny appearance perceived on the surface. We quantified the gloss with goniophotometer that measures the multi-directional reflectance for incident angles from 0 to 180°. We measured the reflectance of incidence angles at 15°, 45°, and 75° (Figure 4). The specular reflection is decreased over 20%, and it can be recognized as the soft-focus effect by diffused reflection. The reflection is comprised of a scattered and specular component. The light is dispersed in all directions as it decreased in specular reflection. A scattered component is one that light is reflected through all angles. The surface modification of E-fluoro-mica indicates that there is a soft-focus effect by scattered reflection. The soft-focus effect is the ability of E-fluoro-mica to reduce the visible signs of fine lines. Such an effect is achieved optically by the interaction of visible light with E-fluoro-mica particles.

We measured the oil-absorption in compliance with the American Society for Testing and Materials (ASTM) D281-95 standard method. When the fluoro-mica sample is etched by microwave irradiation, the oil-absorption increases up to over 170% per gram. Also, the luster of fluoro-mica have been examined by Glossmeter. The refractive values decreased on the mica surface after microwave enhanced etching. Oil-absorption was influenced by the surface area, pore volume and mass volume-density. Mass volume-density increased about 150% by microwave enhanced etching (data not shown).

When the fluoro-mica sample is etched by microwave irradiation, the whiteness of oil-absorbed mica was improved (Figure 5). The $L^*$ value of spectrophotometer represents the whiteness of powder. The range of $L^*$ value is 0 to 100. If $L^*$ value is $\Delta L = 1$, the value is recognized as different colors.

4. Conclusion

The alpha-recoil track was enlarged by treating the mica with an appropriate etchant (e.g. HF). We applied microwave enhanced etching technique to alter the surface of inorganic particle and were able to control oil-absorption, luster and whiteness. By using microwave energy and etching inorganic particles on the surface, oil-absorption was increased, and whiteness increased.
was improved on the silicon dioxide layer. The degree of etching was influenced by acid concentration, irradiated time, the amount of energy and slurry concentration until the surface area of mica increased with a 'shape of the Moon'. The width and depth of etched holes were controlled to a fixed quantity with atomic force microscope. The result of the goniophotometer measurement revealed that the specular reflection decreased over 20 %, and the soft-focus effect was identified by diffused reflection. The oil-absorption increased up to over 170 % per gram. We applied microwave enhanced etching to the cosmetic industry for the first time to solve the fundamental problems associated with high luster, low oil absorption, and whiteness. Our application of fluoro-mica not only improved the whiteness but also reduced the gloss significantly.

References