New SPF Enhancers Using Surface Modification of Inorganic Pigments

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Introduction:

There are various causes of skin aging, but UV exposure is the main cause [1]. Therefore, UV protection is very critical to prevent skin aging [2, 3]. In the cosmetic industry, there are several products that can protect against UV rays. The sunscreen is the typical product that protects skin from UV light. These UV protective materials are called UV filters. Sunscreen contains UV filters that are classified as chemical filters and physical filters [4].

Most of the chemical filters are organic compounds that UV light is absorbed by delocalized bond such as resonance structure. However, these organic compounds have limitation in use since these compounds can cause skin trouble and skin irritation. Moreover, some chemical filters can harm marine ecosystem and are restricted to use in California and Palau. These issues lead to the limitation of use of the chemical filters [5, 6].

On the other hand, physical filters are inorganic compounds that can scatter UV light by forming a physical layer on the skin. However, physical filters are rough and dry when applied and leave a white cast on the skin which makes the unnatural skin look [7-9].

Recently, SPF enhancers are drawing attention because they have a synergetic effect with sunscreen agents. But, most of these SPF enhancers are organic compounds. Thus, SPF enhancers can have the same issues as the chemical UV filters [10-14].

The purpose of this study is to research new inorganic compounds for SPF enhancer using a surface modification of white pigments which have high refractive index.

Materials & Methods:

- **Preparation of Inorganic SPF enhancer**: Inorganic SPF enhancer was developed by the hydrolysis reaction on white pigment such as titanium dioxide which has high refractive index. The hydrolysis procedure was carried out following methods. First step, diperse 250 nm of titanium dioxide (100 g) in distillated water(1000 g, 80 ℃) with stirrer. And adjust pH to 1.5 using HCl soultion. Second, dissolve 32 g of TiCl4 in distilled water (100 g). Third step, add inorganic solution from step 1 and 30 % of NaOH solution (w/w) into titanium dioxide suspension. And react for 30 minutes. This is hydrolysis reaction, which forms additional titanium dioxide surface. Then, wash inorganic compounds with distilled water and dry at100 ℃ for 12 hours. Finally, gain inorganic material after sintering at 750 ℃ for 1 hour (**Figure 1.**).
- **UV Protective Effect**: In order to evaluate the UV protection factor, 28.6 mg of samples were applied on the Helio plates HD 6 (4.7 cm X 4.7 cm) (**Figure 2.**). After 30 minutes, UV protection factor was measured by UV-2000s of Labsphere Inc. The UV protection factor was expressed in SPF (Sun Protection Factor).
- **Friction Coefficient:** Friction coefficient means toughness of inorganic materials. Normally, titanium dioxide has high friction coefficient that causes rough texture with in cosmetics. In this study, touch meter (TRIBOGEAR Type: 33) of Heidon Inc was used to evaluated the improvement of its. First, apply 20 mg of the inorganic powders on the sample plate, and then, softly rub the powder unidirectionally (8 times).
- **White cast test:** White cast of the inorganic compounds was tested by using image J analysis. At the first time, disperse the inorganic materials in vaseline (1: 9 ratio). Next, 30 mg of samples were applied on the polymethyl methacrylate plate (Helio plates HD 6, 4.7 cm X 4.7 cm)and stay for 30 minutes for drying (**Figure 2 (b)**). After 30 minutes, whiteness of each plates was evaluated by image J analysis.

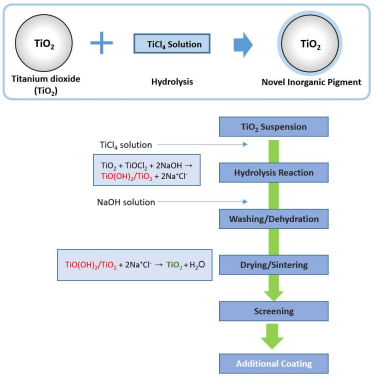

Figure 1. Schematic image of the surface modification of titanium dioxide

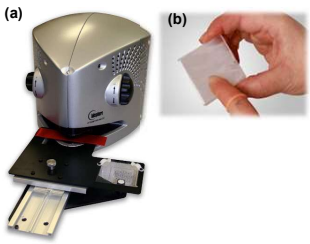

Figure 2. (a) Device for UV Protective Effect (UV-2000S) and **(b)** Image of Applying Sunscreen on the Helio Plate

Results & Discussion:

- **Identifying Surface Modification of Inorganic SPF enhancer:** In this study, FE-SEM and TEM, were used for identifying surface modification of inorganic compounds. Through the both microscopic images, it was confirmed that the surface modification was well formed (**Figure 3**). And we named them SH51, SH 52, SH 53, SH 54 and SH 55, according to the concentration rate of surface modification. Among the inorganic pigments, 20% and 50% (SH 52 and SH 55) surface modificated compounds were selected for further studies.
- **UV protective effect:** SPF in-vitro test shows its UV protective effect of SH 52 & SH 55. sample 1 was applied 2.5% of SH 52, sample 2 was applied 5.0% of SH 52, sample 3 was applied 2.5% of SH 55 and sample 4 was applied 5.0% of SH 55 each other. When applicate 2.5% of the inorganic materials, the increase was not significant, but at 5.0% the SPF value showed about twice (**Figure 4.**)
- **Texture improvement:** Touch meter was used for evaluating texture of the materials. The resistance force can be calculated by friction coefficient. So this value reflects roughness or spreadability of the materials. The friction coefficeint values of SH 52 and SH 55 decrease about 10% and 28% respectively (**Figure 5.**). It means that texture was improved by surface modification. Acctually, titanium di xide (0.25um) has tough and rough feelings, but novel inorganic materials showmuch smoother and higher spreadability.
- **White cast test:** Generally, white cast effect is necessary for color cosmetics for coverage. However, this effect also causes opacity in sunscreens, making unnatural face color. In this study, opacity of the SH 52 and SH 55 was evaluated by image analysis. This figure shows improved opacity compared with macro size titanium dioxide. Even SH 55 looks more transparent than nano size titanium dioxide. So we analyzed this images with image J analysis (**Figure 6.**).

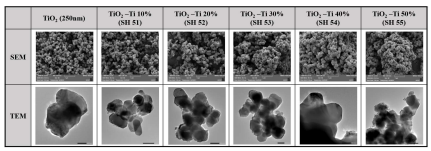

Figure 3. FE-SEM and TEM, were used for identifying surface modification of inorganic compounds. (raw titanium dioxide, 10%, 20%, 30%, 40% and 50% surface modification).

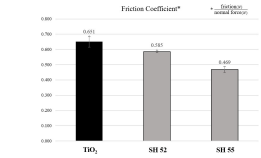

Figure 4. Friction Coefficient of the Inorganic Compounds

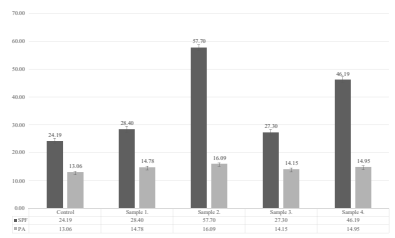

Figure 4. UV Protective Effect of the Surface modificated compounds

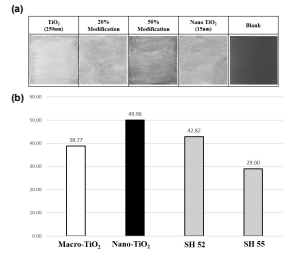

Figure 6. Opacity of Inorganic Pigments Evaluated by Image J analysis. **(a)** Image of PMMA plate **(b)** Data by Image J analysis

Conclusions:

In this study, the inorganic SPF enhancers with a surface modification through hydrolysis reaction have been developed. Under the microscope, we confirmed that the inorganic enhancers have uneven surface which looks like cloud form and created the formed surface. In the in-vitro SPF test, these new inorganic compounds performed as a sun protective enhancer. When 5.0% of SH 52 and SH 55 are applied, SPF value was approximately doubled compared to the in-vitro SPF value of titanium dioxide (250 nm size). It is a remarkable result that no other enhancers have shown ever. Furthermore, these pigments show high spreadability and low opacity compared to titanium dioxide (250 nm size). Even the inorganic SPF enhancers have lower opacity than nano-sized titanium dioxide (15 nm size) which is known to have low white cast. These results imply that these new compounds have overcome the limitation of inorganic compounds. When these new inorganic SPF enhancers are applied in the product, there will be very little cloudiness and less sticky feeling. These advantages are exceptional competitiveness when it is applied in sunscreen products. Also, these new enhancers will present a new direction in the development of cosmetic raw materials.

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