The Novel Inorganic Pigments for Even Skin Tone, Water-resistance and SPF Enhancement

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Abstract

Background: Titanium dioxide (TiO2) is intended to be made to brighten dull skin and give a natural look on the face. However, ordinary TiO2 has a difficulty presenting natural skin tone because of its strong coverage.

For this reason, the surface modified TiO2 has been developed in the previous research. This novel TiO2 gave sheer coverage. However, ordinary TiO2 is hard to apply in the oil in water (O/W) emulsion due to its poor water resistance and results in poor lasting. Thus, the main purpose of this research is to devise developed TiO2, which is expected to have improved UV protection factor, water-resistance, and stability in O/W emulsion by using a new hydrophilic film-former.

Methods: First, the film-former was applied to O/W sunscreens, then UV protective efficacy was evaluated by the ISO 24443 method. Next, the dispersibility of pigments was evaluated by film applicator. The adhesiveness of each formula sample was evaluated by TRIBOGEAR Type: 3.

Results: The selected polymer increased the water-resistance and SPF value but did not affect the formula properties. Also, the TiO2 coated with the polymer has higher dispersibility, adhesiveness and SPF boosting effect.

Conclusion: The newly TiO2 coated with water-resistant polymer is expected to have improved water resistance that is not affected by sweat and moisture. Furthermore, it has more transparency as TiO2 developed in previous research and has a natural brightening effect due to its higher dispersibility. The research also confirms that the developed pigment is a functional material with improved SPF value.

Keywords: Even skin tone, Water-proof, SPF enhancer, surface modified titanium dioxide, sunscreen

Introduction.

Makeup cosmetics are divided into base makeup cosmetic and point makeup cosmetic. More specifically, base makeup cosmetic covers imperfections of the skin such as blemishes, wrinkles, and spots by applying the product to all over the face [1]. Therefore, the purpose of the base makeup cosmetics is to focus on even skin tones and coverage, which is the effect of hiding skin imperfections [2].

Coverage is the effect of masking the background color. In cosmetics, titanium dioxide, one of the white pigments, is mainly used for coverage [3, 4]. Titanium dioxide has a high refractive index and it causes diffuse reflection on the skin [5, 6].

Especially, titanium dioxide is divided into nano-sized and micro sized titanium dioxide according to its particle size, and its properties are different. Nano-sized titanium dioxide, which has under 100 nm size has UV protective effect. However, macro-sized titanium dioxide, which has 200 – 250 nm size has a high coverage effect on the skin. So, micro sized titanium dioxide is applied to cover skin imperfections mainly [7, 8].

Recently, sunscreen products with brightening effects are drawing attention in the cosmetic market. These sunscreen products contain titanium dioxide in the formula, and they are intended to be made to brighten dull skin (even skin tone) and give a natural look on the face compared to a typical face with makeup products. However, ordinary titanium dioxide has difficulty in presenting a natural skin tone because of its strong coverage [9]. Therefore, due to its white cast effect, it is difficult to preserve the natural tone of the skin with the strong coverage of the ordinary titanium dioxide.

For this reason, new titanium dioxide where its surface is coated with $TiCl_4$ solution has been developed in the previous research, and developed titanium dioxide gives sheer Coverage with less white cast. This pigment enhance UV protective effect too. Like this we developed the new functional material with even coverage and SPF enhancement.

However, titanium dioxide pigment has a significant drawback; it is hard to apply in the oil-in-water (O/W) type products due to its poor water resistance and results in poor lasting in daily use. Also, some O/W creams with titanium dioxide have stability issues since they have a high pH value. Therefore, developed titanium dioxide should devise that has stable activity in the aqueous phase.

So in this study, we decided to coat the developed titanium dioxide with polymers that are water-soluble film formers. Before coat, three types of polymers were evaluated that have water resistance effect for their SPF enhancement effect. Among these polymers, PPG-17/IPDI/DMPA copolymer was selected as it has the best SPF enhancement effect. Next, the surface modified titanium dioxide was coated with the PPG-17/IPDI/DMPA copolymer. To confirm the functions of the novel titanium dioxide, it was applied to O/W sunscreens. Finally, UV protective effect, dispersibility and adhesiveness of the sunscreens were evaluated.

Thus, the main purpose of this research is to devise a newly developed titanium dioxide, which is expected to have improved UV protection factor, water resistance, and stability by using a new water-soluble film former.

Materials and Methods.

- Reagents and materials: The UV protection factor was measured by UV-2000s from Labsphere Inc. The friction coefficient of inorganic enhancers was evaluated by Heidon TRIBOGEAR Type: 33 of Shinto Scientific Co. Ltd. Titanium dioxide as a core, was supported by Xentech Inc. The water-soluble was purchased from Curelabs Inc. Other chemical agents were purchased from Sigma Chemical Co.
- Preparation of oil-in-water (O/W) emulsion: Each experimental sample was applied in O/W sunscreens to evaluate their efficacy. The process flow is shown in scheme 1. First, heat the oil phase and aqueous phase until 85℃ and dissolve each ingredient completely. Next, insert aqueous phase into the oil phase slowly with homogenizer (3600rpm, 5min). During emulsifying, add pigments that dispersed with 3-roll mills into the outer phase of the emulsion. Finally, insert the preservative.

- Preparation of surface modified titanium dioxide: before the coat, surface modified titanium dioxide was prepared and used as a core pigment for a novel pigment. This inorganic pigment was developed by the hydrolysis reaction on white pigment such as titanium dioxide that has a high refractive index. The procedure was carried out following methods. In the first step, disperse 250 nm of titanium dioxide (100 g) in distillate water (1000 g, 80 ℃) with stirrer. And adjust pH to 1.5 using HCl solution. Second, dissolve 32 g of TiCl4 in distilled water (100 g). The third step add inorganic solution from step 1 and 30 % of NaOH solution (w/w) into the titanium dioxide suspension. And react for 30 min. This is a hydrolysis reaction, which forms an additional titanium dioxide surface. Then, wash inorganic compounds were with distilled water and dry at 100 ℃ for 12 h. Finally, gain inorganic material after sintering at 750 ℃ for 1 h (Scheme 2.). The surface was then treated with PPG-17/IPDI/DMPA copolymer.

- Effect of making even-skin tone: To confirm the effect of making even skin tone, the even skin tone sunscreens that applied inorganic pigments were tested using image J analysis. the first time, 3% of the pigments was applied to each sunscreen. Next, 30 mg of samples were applied on a polymethylmethacrylate plate (Helio plates HD 6, 4.7 cm X 4.7 cm) and maintained for 30 min for drying. After 30 min, the whiteness of each plate was evaluated using image J analysis.

- UV protective effect: To evaluate the UV protection factor, in vitro SPF test was conducted under ISO24443 method, 28.6 mg of each cosmetic sample was applied on a polymethylmethacrylate plate (Helio plates HD 6, 4.7 cm X 4.7 cm) and stayed for 30 min for drying, UV protection factor was measured by UV-2000s of Labsphere Inc. The UV protection factor was expressed in SPF (Sun Protection Factor).

- Evaluation of adhesiveness: adhesiveness of the materials were evaluated by touch meter (TRIBOGEAR Type: 33) from Shinto Scientific Co. Ltd. This device can measure the friction forces of the materials. So if the material has high adhesion, it will show high friction force.

The measurement method is as follows. First, apply 20 mg of the experimental sample was placed on the sample plate, and then, softly rub the powder unidirectionally (8 times).

- Evaluation of dispersibility: To evaluate the dispersibility of pigments, used a film applicator that has 120um of gap.

Results.

- Confirming a suitable polymer: In this study, three types of water- resist polymers, that are low molecular PPG-17/IPDI/DMPA copolymer (LM-PID), high molecular PPG-17/IPDI/DMPA copolymer (HM-PID), and polyurethane-14 (PU-14) were selected. By evaluating the water resistance of the water soluble film formers, it was confirmed that every polymer had that effect (no data). Also, each polymer was applied to O/W sunscreen by 1%, 2%, and 3%, respectively. As a result, only LM-PID show SPF enhancing effect among the polymers (Figure 1). So LM-PID was chosen as the coating agent. Thus, surface modified titanium dioxide was coated with LM-PID that called SH-PID
- Even skin tone making effect of SH-PID: To evaluate the even skin tone making effect of SH-PID, 3% of the pigment was applied in O/W sunscreen formulation. Also, 3% of ordinary titanium dioxide (CR-50) and surface modified titanium dioxide (SH) were applied in O/W sunscreen as experimental controls. As a result, SH and SH-PID show lower opacity then that of CR-50 (Figure 2). Therefore, the sunscreen with SH-PID could make a more even skin tone than sunscreen with ordinary titanium dioxide.
- UV protective effect of SH-PID: In a previous study, surface modified titanium dioxide show enhancement of UV protective effect. So, to determine whether the PID coating affects UV protective effect, SPF in vitro test was carried out. To evaluate the UV protective effect of the CR-50, SH, and SH-PID, the 2% of the pigment was applied in O/W sunscreen formulation for SPF in vitro test.

SPF in vitro test shows the UV protective effect of each pigment. As a result, sunscreen without the pigment (Blank) shows 9.24 and 5.59 of its SPF and PA values. Next sunscreen with CR-50 shows 14.45 and 7.72 of its SPF and PA values that is a little increase in its UV protective effect compared with the blank. However, sunscreen with the surface modificated titanium dioxide, SH and SH-PID, have a noticeable increase in the UV protective effect. Sunscreen with SH had 32.43 and 18.49 of its SPF and PA values. And sunscreen with SH-PID had 38.79 and 19.45 of its SPF and PA values (Figure 3). Therefore, SH-PID has the effect of SPF and PA enhancement.

- Adhesiveness of SH-PID: For long lasting even skin tone making, the film-forming and water-resistance effect of PID should be maintained even after coating. For this reason, the adhesiveness of SH-PID was evaluated by touch meter. A touch meter was used because it can measure friction, and the high friction means that the SH-PID retains the physical properties of PID, such as film-forming and water-resistance effects.

As a result of the touch meter, SH-PID showed higher friction than SH and CR-50 (Figure 4). This result means SH-PID maintains properties of water-resistance film-former when coated on the titanium dioxide. For these reasons, this novel inorganic pigment could be used for water-resistance even skin tone sunscreens.

- Improved dispersibility: Generally, ordinary titanium dioxide could be dispersed in an oil phase and aqueous phase in a cosmetic formula. However, when dispersed in any phase, its stability is very poor. Moreover, they aggregate over time. For this reason, the improved dispersibility of the pigment will help the formulation with stability and make even skin tone. To confirm dispersibility, used a film applicator that has 120um of gap. If the pigment was dispersed evenly, the sunscreen with the pigment passing through this gap will also look even surface.

Because of surface modified titanium dioxide coated with the polymer (SH-PID) and then applied to the tone-up sunscreen, the dispersibility increased compared to before coating and surface modification (Figure 5). SH-PID had the most even surface in the experiment. Therefore, polymeric coating improved dispersibility of titanium dioxide.

Discussion.

In a previous study, surface modified titanium dioxide (SH) was developed through a hydrolysis reaction. Although the surface modified pigment showed an excellent effect, there were some limitations that low dispersibility in the aqueous phase, poor lasting in O/W formulation and so on. To improve these short comings of SH, the pigment coated with water-resistance polymer in this study.

Before coating, we selected an appropriate film-former, PPG-17/IPDI/DMPA copolymer, which has an effect of water-resistance. Also, it nearly doubled the SPF when a 3% concentration was applied. Therefore, this polymer used as coating agent of the surface modified titanium dioxide. Next, the selected polymer (LM-PID) was coated on the SH pigment. This coated pigment is called SH-PID. To confirm the functions of SH-PID, even skin tone making effect, SPF in vitro test, measurement of adhesiveness and dispersion evaluation was carried out.

First, SH-PID even showed application and sheer coverage on the PMMA plate. These results suggest that the SH-PID can adequately express even skin tone.

Secondly in the SPF in vitro test, these new inorganic compounds served as a sun protect enhancer. When 2.0% of SH and SH-PID was applied to the sunscreens, SPF and PA values were more than twice compared to the in vitro SPF values of ordinary titanium dioxide (CR-50) that has 250 nm of diameter. It is a remarkable result that no other enhancer has shown ever. Moreover, SH-PID had a little higher UV protective effect than SH.

Next, SH-PID was examined whether the properties of the polymer were maintained by confirming the adhesiveness even after coating. As a result, SH-PID maintained physical properties with its high adhesiveness on the surface.

Generally, ordinary titanium dioxide could be dispersed in an oil phase and aqueous phase in a cosmetic formula. However, when dispersed in any phase, its stability is very poor. Additionally, titanium dioxide dispersed in the water phase has a greater effect than titanium dioxide dispersed in the oil phase because of its high pH value. For this reason, ordinary titanium dioxide is hard to apply in O/W formulation. However, developed inorganic pigment (SH-PID) showed great dispersibility in O/W sunscreen. This result means that SH-PID could provide higher stability and even application in the O/W formulation compared with CR-50 and SH.

SH-PID showed great even skin tone making, UV protective effect, adhesiveness and dispersibility. For these reasons, the novel inorganic pigment will present a new direction in the development of cosmetic raw materials in the sunscreen with even skin tone making.

Conclusion.

In this study, newly developed inorganic pigment has water resistance due to the characteristic of coated polymer on the surface of the pigment. Cosmetic products with newly coated titanium dioxide are expected to have improved water resistance that is not affected by sweat and moisture. Furthermore, it has transparency as titanium dioxide developed in previous research and has a natural toning effect due to its higher dispersibility.

The research also confirms that newly developed pigment is a functional material with improved SPF value.

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Conflict of Interest Statement. NONE.

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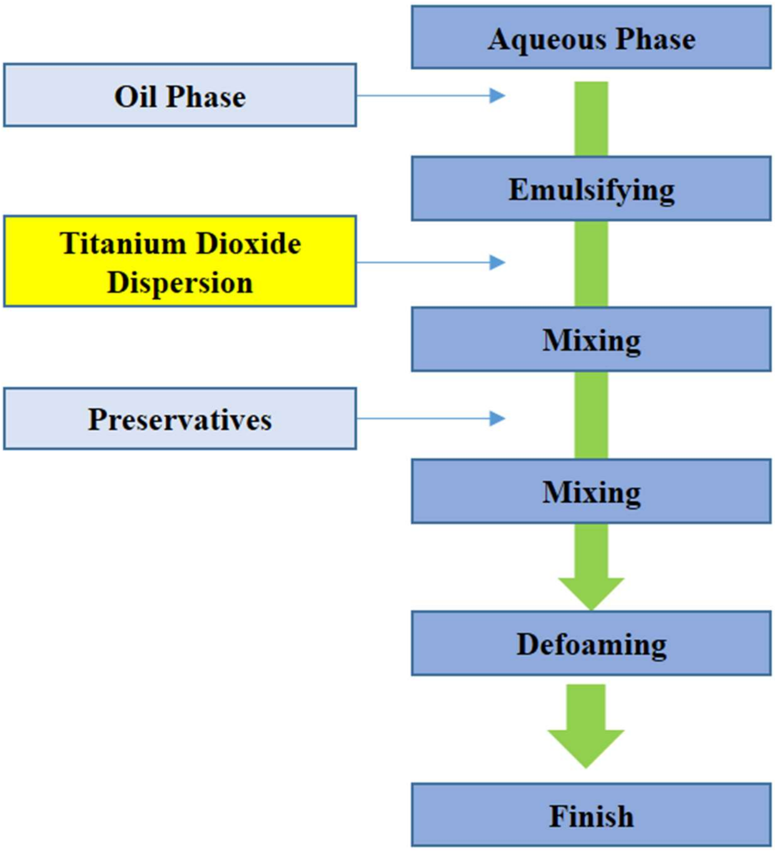
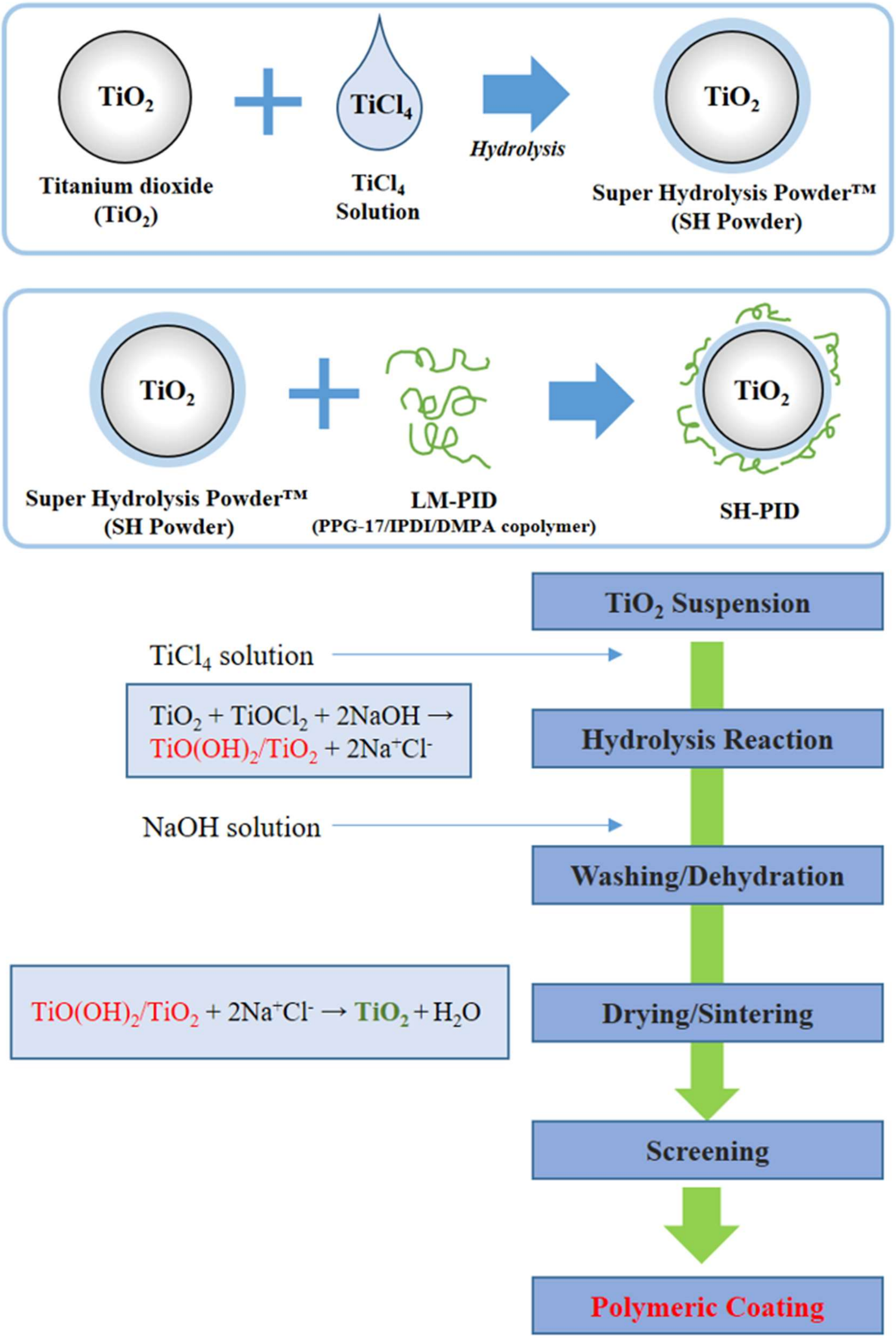


Scheme 1. Preparation of O/W Sunscreen



Scheme 2. Schematic Image of the Surface Modification of Titanium Dioxide (SH) and Polymeric Coating (SH-PID)

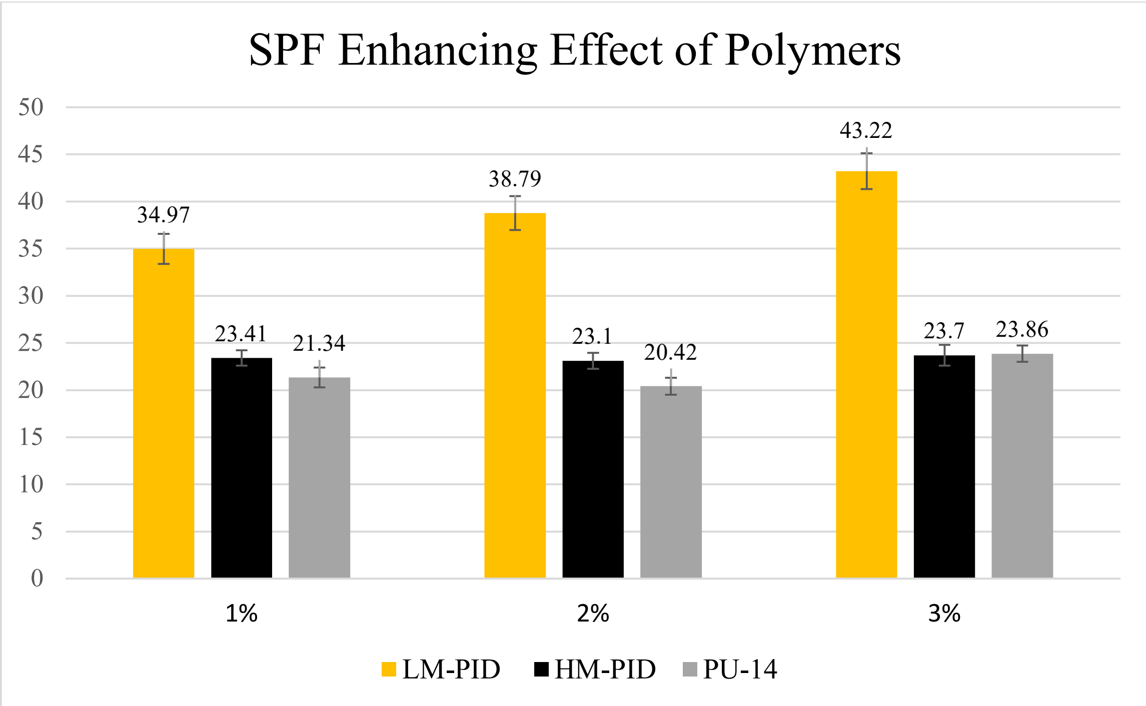


Figure 1. SPF Enhancing Effect of Polymers

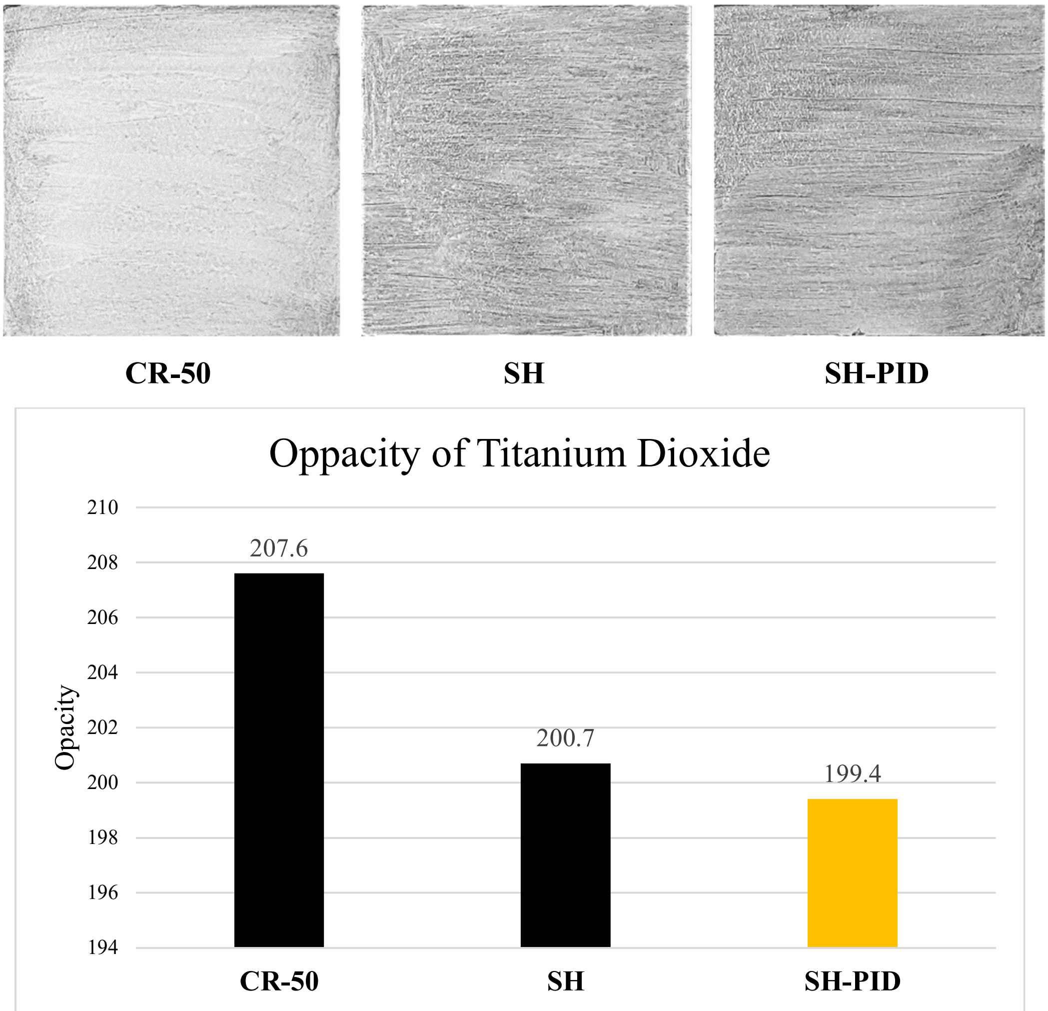


Figure 2. Evaluation of making Even-skin Tone by Image Analysis.

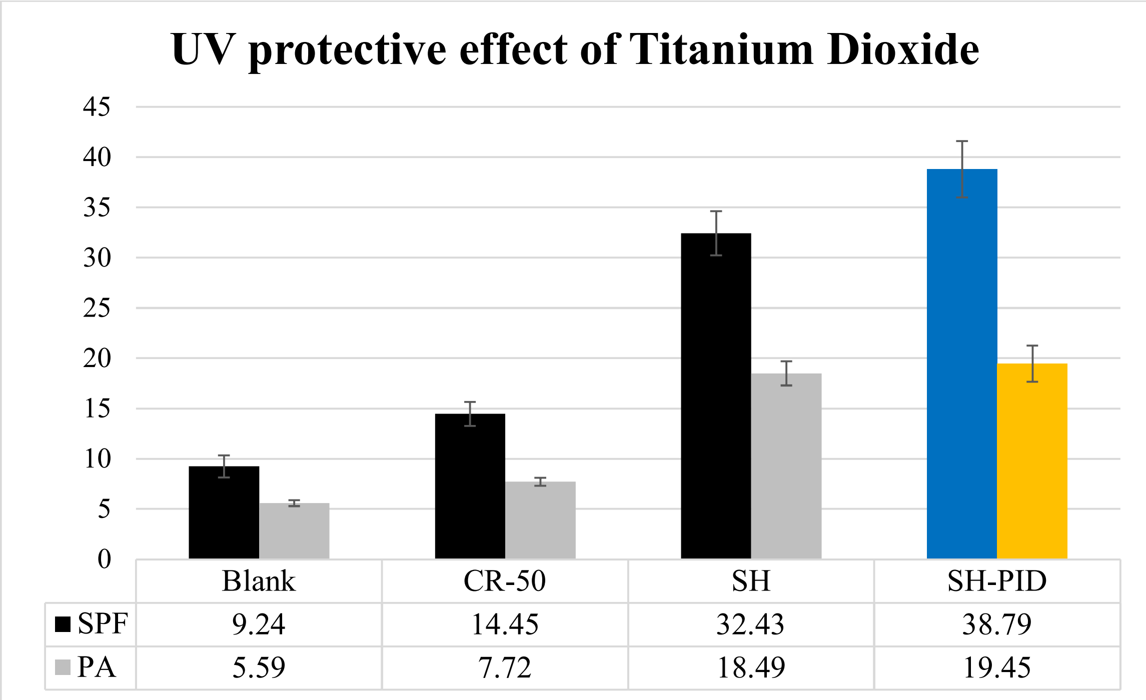


Figure 3. UV protective effect of Titanium Dioxide

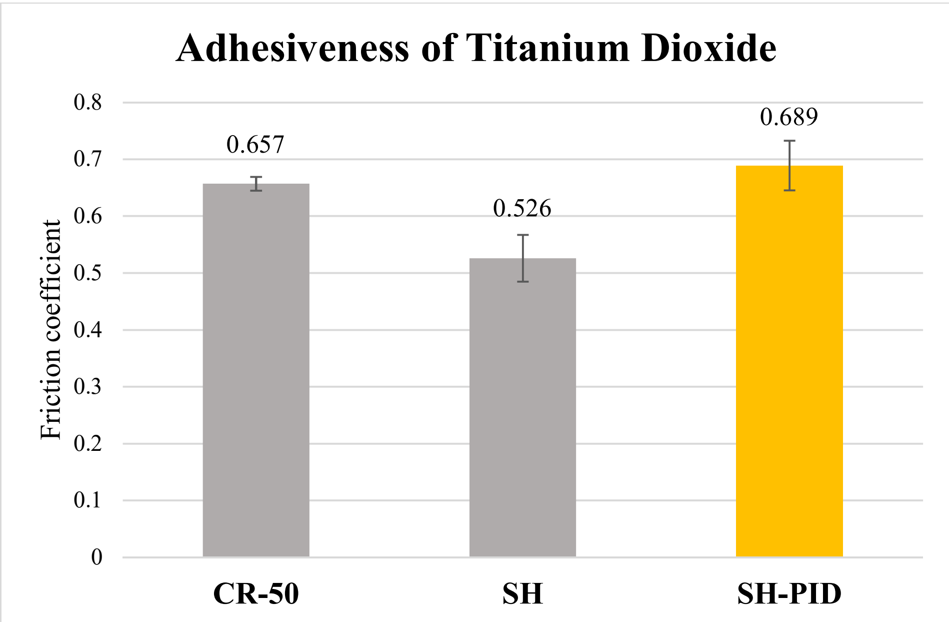


Figure 4. Adhesiveness of Titanium Dioxide

a) Dispersibility of CR-50

b) Dispersibility of SH

c) Dispersibility of SH-PID

Figure 5. Dispersibility of Titanium Dioxide.