Development of O/W Mineral Only sunscreen Formulation with high UV Protection

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Abstract

The Hawaiian government banned the distribution and sale of sunscreen containing organic compounds oxybenzone and octinoxate, because organic sunscreens were reported to cause "destruction" of coral reefs. Therefore, inorganic sunscreens are receiving attention in the cosmetics industry. Accordingly, we aimed to develop a new O/W sun care formulation that is suitable for the transparent and clean beauty trend while demonstrating a high (UV) protection effect. The three types of ZnO (ZnO-10, NAS, and AS) used in the study were coated with triethoxycaprylylsilane, and their particle sizes were determined as 15, 40, and 105 nm, respectively, using scanning electron microscopy. The UV protection effect of the new O/W formulation was evaluated. The *in vitro* and *in vivo* measurements reveal that ZnO-10 with the smallest particle size demonstrates the highest UV protection efficacy. Additionally, the effect of different composition ratios on increasing the UV blocking efficiency is confirmed by mixing each ZnO-containing dispersion with different particle size powders. The oil dispersion is simultaneously used and compared with each powder. When the ratio of ZnO–oil dispersion is ZnOdis-15: ZnOdis-105 = 7:3 with different particle sizes, the highest UV protection efficiency is obtained. This study confirms the UV protection efficacy, degree of white cast, and stability of each particle size by applying ZnO powder and ZnO oil dispersion to the O/W prescription. Therefore, the diverse needs of consumers who prefer clean beauty can be satisfied, and new sunscreen products incorporating clean beauty can be developed.

Keywords: O/W sunscreen, Inorganic UV filter, Clean beauty, High UV protection effect, Mineral-only sun care

Introduction

The clean beauty product line has been expanding, because consumers are interested in environmental issues and consumption value when purchasing cosmetics [1]. Clean beauty cosmetics refer to those that exclude ingredients that are harmful to the human body. This term is widely applied with reference to the environment and ethical consumption and comprises factors such as excluding harmful ingredients, opposing animal testing, excluding animal ingredients, excluding plastic ingredients, using recyclable containers, and fair trade [2]. Moreover, the Hawaiian government recently banned the distribution and sale of sunscreen containing organic compounds oxybenzone and octinoxate, because the results of a study indicated that organic sunscreen causes "bleaching" of coral reefs. Therefore, inorganic sunscreens are gradually receiving increased attention in the cosmetics industry [3, 4].

Among inorganic sunscreen agents, zinc oxide (ZnO) has a smaller refractive index than that of titanium dioxide. This reduces the problem of white cast and displays a better blocking ability in the UVA region (320–400 nm) than that of titanium dioxide. Globally, the harmful effect of UVA (320–400 nm) is perceived to be higher than that of UVB (290–320 nm) [4]. Thus, ZnO with high UVA blocking ability is increasingly being used. However, studies on the effectiveness according to the particle size of ZnO and the UV protection effect based on the size ratio are insufficient.

Korean consumers typically prefer sun care products demonstrating good applicability, high UV protection index, and low irritation. Therefore, most Korean cosmetics companies are investigating O/W formulations that are more comfortable to use than heavy W/O formulations [5, 6]. However, most organic sunscreens are oil-soluble, and they are difficult to develop owing to the limitations of low stability and low UV protection effect of the developed O/W formulations. Particularly, a sun care prescription with a high UV protection index requires extensive investigation [7].

In this study, we verify an optimal configuration with the best UV protection effect depending on the size and ratio of ZnO particles. The same configuration is used to develop a transparent inorganic mineral-only clean beauty sun care prescription with a high UV protection effect.

Materials and methods

2.1. Materials

Polyhydroxystearic acid was purchased from Phoenix Chemical, Inc. (USA). Hydroxyethyl acrylate/sodium acryloyldimethyl taurate copolymer and polyacrylate crosspolymer-6 were purchased from SEPPIC (France). Ammonium acryloyldimethyltaurate/VP copolymer was purchased from Clariant (Switzerland). C12-15 alkyl benzoate was purchased from SABO S.p.A. (Italy). Cetearyl olivate and sorbitan olivate were purchased from Shaanxi Hallstar Company (USA). Beheneth-2 was purchased from BASF (Germany). Sorbitan laurate, polyglyceryl-4 laurate, and dilauryl citrate were purchased from Evonik Industries (Germany). All other raw materials used in this study were of cosmetic grade.

2.2. Equipment

A homo mixer (Primix, Korea) and an agi mixer (PL-SS11D, Korea) were used as emulsifying devices. Scanning electron microscope (SEM) analysis (JEOL Ltd, Japan) was used to observe the particle size and surface structure of ZnO. Solar light analyzer SPF-290AS (Solar Light, USA) was used for *in vitro* sun protection factor (SPF) and protection grade of UVA (PA) measurements, and Model 601 Multiport® SPF Testing 6 Output Solar Simulator (Solar Light, USA) was used for *in vivo* measurements.

2.3 Preparation of O/W emulsion

An O/W emulsion optimized for clean beauty was prepared without using polyethylene glycol and polypropylene glycol. The water phase A is accurately measured in a 200 ml beaker and heated to 60 ℃. (Table 1)

Subsequently, while phase A is stirred at 500 rpm using the agi mixer, the measured B phase is gradually added. The stirred mixture is then heated to 80 ℃. In the powder process, the oil and dispersant (1.5 times the amount of oil) are measured separately in phase C, pre-mixed by stirring, and dispersed thrice through a three-roller. The dispersed powder is heated to 80 ℃ by adding an O/W emulsifier. Moreover, the effective dissolution of the emulsifier is checked while hand-mixing. In the dispersion process, the temperature in a 100 ml beaker is measured up to 80 ℃, and the contents are hand-mixed to check whether the emulsifier is dissolved well. While stirring the heated contents in the homo mixer at 35000 rpm, the oil phase is slowly added and emulsified. The stirring speed is then increased to 5000 rpm and maintained for approximately 5 min to prepare an O/W emulsion. After emulsifying, vacuum desiccation is performed. The results in Table 2 are obtained using the same procedure as the dispersion process mentioned above. In addition, the ZnO content was equally prepared at 25%.

Table 1. Applied O/W sun care formulation using different sizes of ZnO particles for powders and dispersions [wt%]

Ingredient		Powder			Dispersion		
		ZnO-10	NAS	AS	Zno-10dis	NAS-dis	AS-dis
A	D.I WATER	Up to 100	Up to 100	Up to 100	Up to 100	Up to 100	Up to 100
	1,3-BG	10	10	10	10	10	10
B	Hydroxyethyl acrylate/Sodium acryloyldimethyl taurate copolymer	0.36	0.36	0.36	0.36	0.36	0.36
	Polyacrylate crosspolymer-6	0.18	0.18	0.18	0.18	0.18	0.18
	Ammonium Acryloyldimethyltaurate/VP Copolymer	0.24	0.24	0.24	0.24	0.24	0.24
C	ZnO-10	25	-	-	-	-	-
	ZnO-NAS	-	25	-	-	-	-
	ZnO-AS	-	-	25	-	-	-
	C12-15 Alkyl Benzonate	14	14	14	-	-	-
	Polyhydroxystearic Acid	0.6	0.6	0.6	-	-	-
	Zno-10dis	-	-	-	47.5	-	-
	NAS-dis	-	-	-	-	40	-
	AS-dis	-	-	-	-	-	38
	Cetearyl Olivate, Sorbitan Olivate	0.7	0.7	0.7	0.7	0.7	0.7
	Beheneth-2	3	3	3	3	3	3
	Sorbitan Laurate, Polyglyceryl-4 Laurate, Dilauryl Citrate	-	-	-	-	1	1

Table 2 Applied OW sun care formulation for ratios of two different sizes of ZnO dispersions

		ZnO ratio (ZnO-dis : AS-dis) [wt%]				
	Ingredient	9:1	7:3	5:5	3:7	1:9
A	D.I WATER	38.10	39.95	41.50	43.40	45.15
	1,3-BG	10	10	10	10	10
B	Hydroxyethyl acrylate/Sodium acryloyldimethyl taurate copolymer	0.35	0.35	0.35	0.35	0.35
	Polyacrylate crosspolymer-6	0.2	0.2	0.2	0.2	0.2
	Ammonium Acryloyldimethyltaurate/VP Copolymer	0.25	0.25	0.25	0.25	0.25
C	Zno-10dis	42.58	33	23.9	14.3	4.75
	AS-dis	3.83	11.55	19.1	26.8	34.6
	Cetearyl Olivate, Sorbitan Olivate	0.7	0.7	0.7	0.7	0.7
	Beheneth-2	3	3	3	3	3
	Sorbitan Laurate, Polyglyceryl-4 Laurate, Dilauryl Citrate	1	1	1	1	1

2.4 Stability of the O/W emulsion

An O/W sun cream formula (Table 6) was prepared to observe the phase stability of the O/W emulsion under three acceleration conditions (room temperature, 4 ℃, and 40 ℃) [8]. Parameters such as the separation phenomenon were ascertained visually according to the change over time (1 month), and the phase stability of the O/W emulsion was observed [9].

2.5 UV Performance SPF and PA

2.5.1 *In vitro* SPF and PA determination

Solar light SPF-290AS (Solar light, USA) was used for *in vitro* SPF and PA measurements. A specimen with a thickness of 0.75 mg/cm^2 was applied on a poly methyl methacrylate (PMMA; USA) plate and dried for 15 min. After 4 MED pre-light irradiation, the UV protection index was measured using SPF-290AS. The average values of the measured readings at nine different positions of the PMMA plate were considered the final SPF and PA [10].

2.5.2 *In vivo* SPF and PA determination

The *in vivo* SPF measurement was performed by clinical experiments in accordance with the ISO-244444 International Cosmetics Autonomous Convention Act. PA was measured according to ISO-24442. For SPF measurement, using surgical gloves, the sample formula was applied to a thickness of 2 mg/cm^2 on the back of the subject. At this point, the sample area had to be at least 24 cm^2, and it was allowed to dry for at least 15 min. The UV rays were irradiated by increasing the constant ratio up to 23% [6]. The method for measuring PA was similar to that of SPF. However, UV rays had to be irradiated by increasing the constant ratio to less than 25%. SPF and PA are calculated as shown in (1) and (2) and expressed as integers by rounding the arithmetic mean value.

$$SPF = \frac{\mathrm{MEDp}}{\mathrm{MEDu}} \qquad \begin{aligned} &\mathrm{MEDu} = \text{Read Port Light Volume} \times 60\ \mathrm{s} \times 0.001 \\ &\mathrm{MEDp} = \text{Read Port Light Volume} \times \text{UV times} \times 0.001 \end{aligned} \qquad (1)$$

$$\mathrm{PA} = \frac{\mathrm{MPPDp}}{\mathrm{MPPDu}} \qquad \begin{aligned} &\mathrm{MPPDu} = \text{Read Port Light Volume} \times 240\ \mathrm{s} \times 0.001 \\ &\mathrm{MPPDp} = \text{Read Port Light Volume} \times \text{UV times} \times 0.001 \end{aligned} \qquad (2)$$

Results and discussion

3.1 SEM analysis

Fig. 1 shows the SEM images of the surface-treated ZnO particles. The ZnO surface is equally coated with triethoxyacrylicsilane. The average diameters of ZnO-10, NAS, and AS are 15, 40, and 105 nm, respectively; all three exhibit the same round spherical particles.

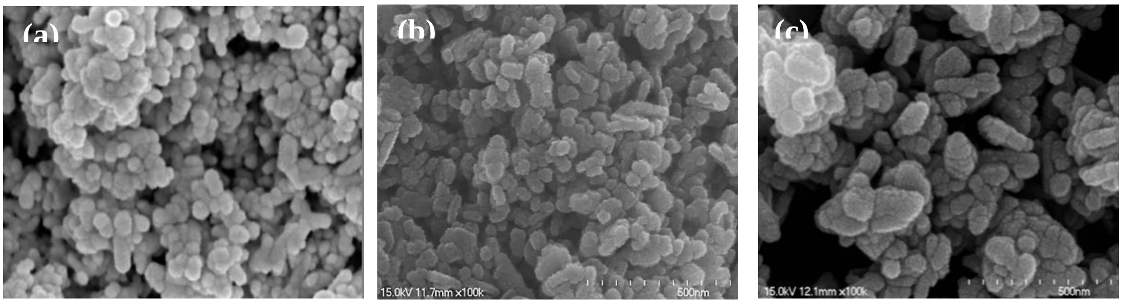


Fig. 1 Scanning electron microscopy images of zinc oxide (ZnO) particles in this study. (a) ZnO-10 (b) NAS, and (c) AS. The scale bar is equal to 500 nm.

3.2 Comparison of UV protection effectiveness using different sizes and ratios of ZnO

3.2.1 UV protection effect according to different sizes of ZnO

The *in vitro* results of the O/W emulsion prepared by emulsifying the ZnO powder and dispersion for each size are compared with the compositions listed in Table 1. The *in vitro* test was conducted using the SPF self-regulation measurement method of the Korean Cosmetics Association as a general standard method. As shown in Fig. 2, ZnO-10 with an average size of 15 nm is confirmed to exhibit SPF 26.52 and PA 20.66, which indicates the highest UV protection effect among the tested powders. Next, NAS and AS demonstrate high UV protection efficacy. In addition, the UV protection effect is better in the dispersions than in powders. It is confirmed that the excellent UV protection effect is because of good dispersibility and that the high UV protection index is because of the small size.

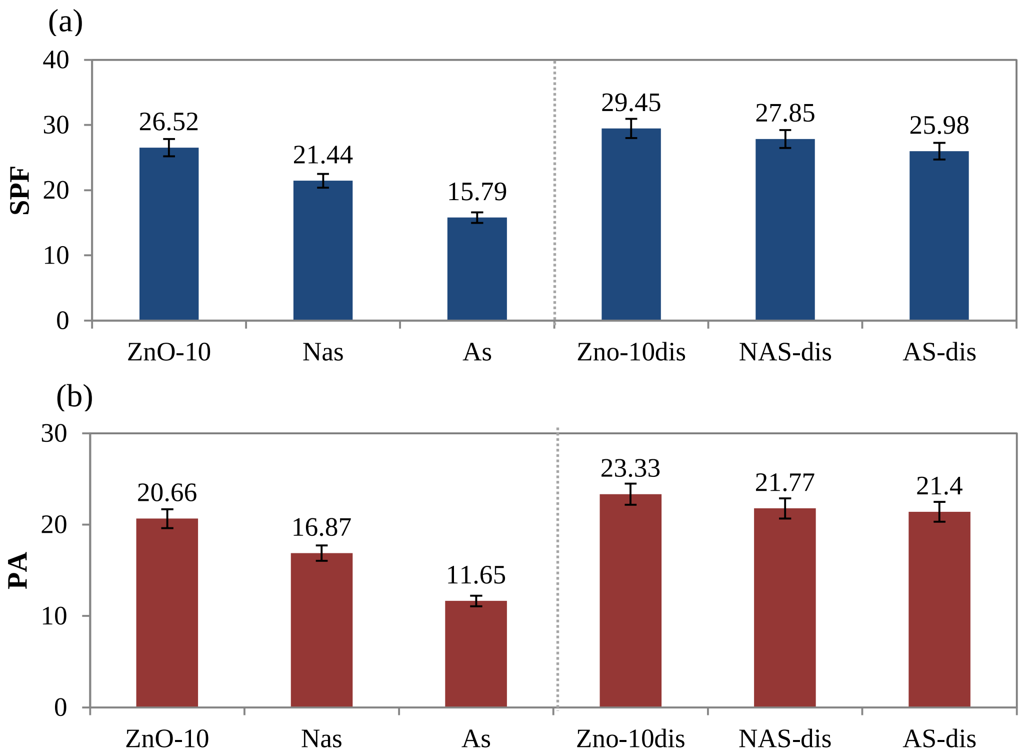
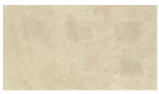


Fig. 2 (a) *In vitro* SPF (Sun protection factor) and (b) *in vitro* PA (Protection factor) of O/W emulsions for each size of ZnO powders and dispersions. *($p<0.05\%$, $p>95\%$)*

3.2.2 *In vivo* results of UV protection effect according to size

The UV protection effect was measured in a clinical trial in accordance with the International Cosmetics Autonomous Covenant Bill. The UV intensity of each probe of the Multi-port Solar Simulator was adjusted to six stages, and UV rays were irradiated. Each subject consisted of 10 participants per group. Table 4 shows the average SPF and PA and representative UV irradiation results for 10 participants [10]. Clinical evaluation of the SPF index and PA grade according to size indicate the same tendency as that observed *in vitro*. When comparing the UV protection effect according to size, ZnO-10 (average size of 15 nm), which exhibits the smallest size, produces the highest UV protection index both in powders and dispersions. In addition, on comparing the dispersion and powder, the effectiveness of the dispersion is confirmed to be excellent, as observed *in vitro*.

Table 4. SPF and PA values of the *in vivo* test for 10 volunteers considering each size of the ZnO powder and dispersion

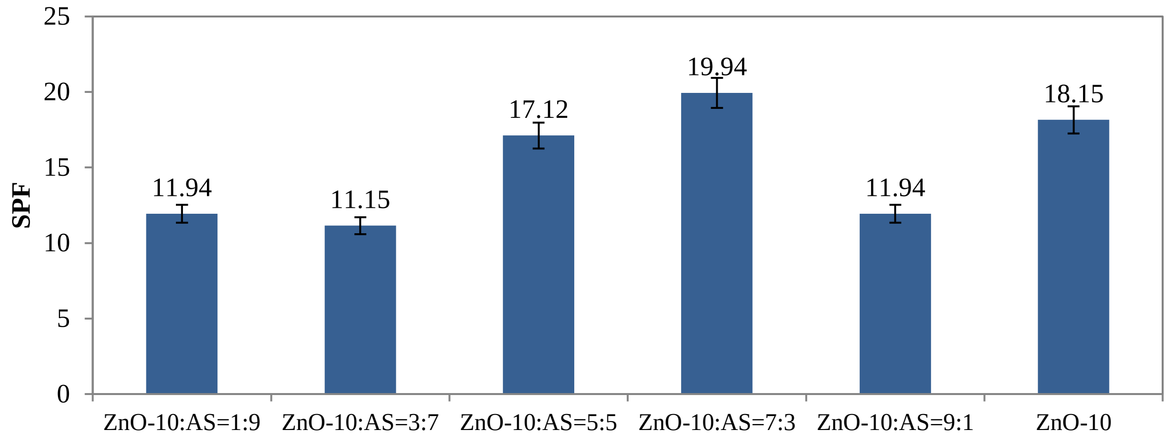
	Powder			Dispersion		
Test Result	ZnO-10	NAS	AS	ZnO-10dis	NAS-dis	AS-dis
in vivo SPF	32.40	32.40	30.00	42.86	39.69	36.69
Determine						
in vivo PA	9.16	10.50	9.16	13.91	13.91	12.10
Determine						

3.2.3 Comparison of UV protection effect for different size of Zinc oxide *in vitro*

The formulation in Table 2 was prepared by mixing a small-size ZnO-10dis and a large-size AS-dis using a dispersion by ratio. Based on the *in vitro* confirmation, the 7:3 ratio of ZnO-10dis and AS-dis demonstrates the highest values at SPF 19.94 and PA 15.95. (Fig. 3) This shows that the PA value of the mixed sample is higher than that of only

ZnO of a small size, and it confirms that the optimal UV protection effect is obtained when ZnO of a small size and a large size are mixed at a certain ratio.

(a)



(b)

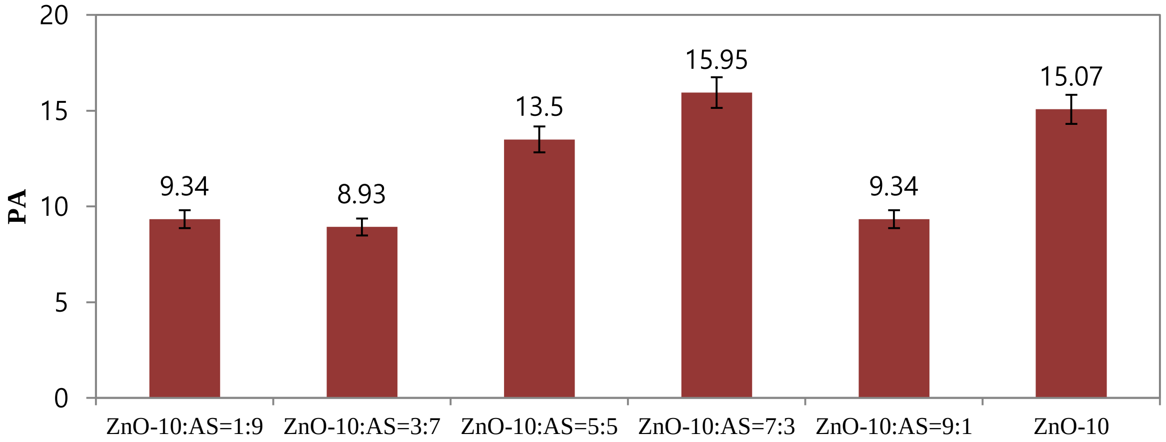


Fig 3. Effects of the ratios of ZnO sizes on *in vitro* (a) SPF and (b) PA. *($p<0.05\%$, $p>95\%$)*

3.3 Development of O/W mineral-only formulation with SPF 50 and PA 16

Recently, in the Korean cosmetics market, consumers have been favoring sun care products that exhibit high UV protection index effectiveness. Therefore, in this study, TiO_2, an inorganic sunscreen, was applied to develop sun care products with SPF 50 and PA 16 based on the abovementioned results. In addition, when sunscreen was applied to areas with both trauma and internal injury, the UV protection effect was more effective (Data not shown). Consequently, a TiO_2-water dispersion was applied when the prescription was developed in this study (Table 6). As a result of *in vivo* (Table 7) the results of SPF 50 and PA 18.38 are obtained, and the target UV protection value is confirmed. The phase stability for the prescription was performed for 8 weeks for each visual plate under three acceleration conditions (room temperature, 4 ℃, and 40 ℃) (Table 8). Subsequently, the separation phenomenon was not visually confirmed, and a stable form was presented. According to the transparency measurement, the ZnO-only formulation exhibits a high white index (WI) value of about 5 in WI = 48.11, and the formulation to which TiO_2 was applied has WI = 53.26 (Fig. 4).

Table 6. O/W mineral-only sun care formulation for high UV protection (SPF 50 and PA 16) [wt%]

	Ingredient	ZnO Only	Mineral Only
A	D.I WATER	Up to 100	Up to 100
	1,3-BG	10.00	10.00
B	Hydroxyethyl acrylate/Sodium acryloyldimethyl taurate copolymer	0.35	0.35
	Polyacrylate crosspolymer-6	0.20	0.20
	Ammonium Acryloyldimethyltaurate/VP Copolymer	0.25	0.25
C	TiO_2dis-water	-	7.00
D	Zno-10dis	33.00	33.00
	AS-dis	11.55	11.55
	Cetearyl Olivate, Sorbitan Olivate	0.70	0.70
	Beheneth-2	3.00	3.00
	Sorbitan Laurate, Polyglyceryl-4 Laurate, Dilauryl Citrate	1.00	1.00

Table 7. *In vivo* results of O/W emulsion

Test Result	ZnO only	Mineral only
in vivo SPF	36.75	50.00
Determine		
in vivo PA	18.38	18.38

Determine		

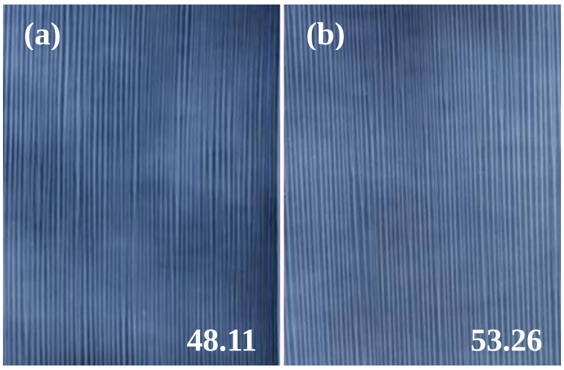


Fig 4. White index of O/W emulsion. White index values and images of (a) ZnO-only and (b) mineral-only formulations.

Conclusions

An inorganic O/W sunscreen with a high UV protection effect was developed in this study, satisfying clean beauty and mixing at an optimal ratio for each particle size. Measuring the UV protection effect by applying different sizes of ZnO to the O/W emulsion shows that the UV protection index increases as the size decreases, and the UV protection effect of dispersions is better than that of powders. The dispersions exhibit good efficacy, because the sunscreen is evenly and uniformly dispersed in the formulation. In addition, when different ratios of small and large-sized ZnO are applied, the UV protection effect is the highest in the ratio of 7:3, which indicates a higher fraction of small-sized particles. The smaller the particle size, the higher the blocking effect in the short wavelength region of UV rays, and the greater the effect on the SPF; the larger the particle size, the higher the blocking effect in the long wavelength region, and the greater the effect on the PA. Moreover, we confirm that the UV protection effect is attained more uniformly on the skin while using the mixed formulation than while using single-size ZnO, thus resulting in a higher UV protection index (Fig. 5).

In summary, this study confirms the best configuration for UV ray protection according to the size and ratio of ZnO particles, and a transparent inorganic mineral-only clean beauty sun care formulation is developed with a high UV ray protection effect.

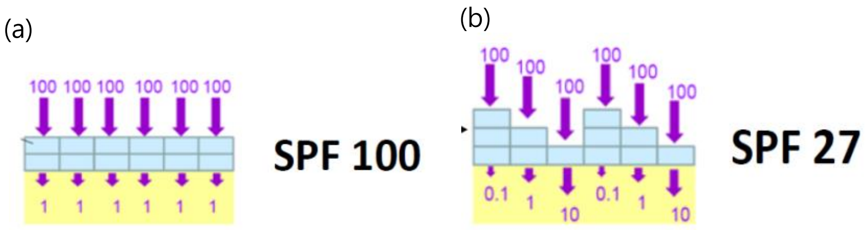


Fig. 5 The reason for a good UV protection index upon even application. (a) Even spread and (b) uneven spread.

Acknowledgments.

NONE.

Conflict of Interest Statement.

NONE.

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