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# Development of O/W Mineral Only Sunscreen Formulation with High UV Protection

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## Introduction:

The 'Clean Beauty' product line has been expanding as consumers are interested in environmental issues and value consumption when purchasing cosmetics [1]. 'Clean Beauty' cosmetics refer to cosmetics that exclude harmful ingredients to the human body. It is widely applied to the environment and ethical consumption, such as the exclusion of harmful ingredients, opposition to animal testing, exclusion of animal ingredients, the exclusion of plastic ingredients, use of recycling containers, and fair trade.

Organic ultraviolet (UV) filters such as oxybenzone and octinoxate have become controversial due to their potential impact on the environment and their potential human health risks. As such, inorganic UV filters, zinc oxide (ZnO) and titanium dioxide ($TiO_2$), have become paramount in discussions about photoprotection. Among these inorganic UV filters, ZnO has a smaller refractive index than that of $TiO_2$, which reduces the white cast problem and has a better blocking ability in the UVA region (320-400 nm). As a recent global trend, the harmfulness of UVA is perceived to be higher than that of UVB (290-320 nm). Accordingly, there is a tendency to use ZnO with high UVA blocking ability [4]. However, there are insufficient studies on the UV protection effect depending on the formulated ZnO condition and mixing ratio of ZnO with different sizes.

Korean consumers typically prefer sun care products showing a lightweight feel as well as high UV protection index. Therefore, most Korean cosmetics companies are focusing on research on oil-in-water (O/W) sunscreen formulations compared to heavy water-in-oil sunscreen formulations [5, 6]. However, there is a limit to encapsulating high concentration of oil-soluble organic UV filters in the O/W formulations due to the loading capacity and inherent instability of organic UV filters, so it is difficult to develop a stable O/W type sunscreen with a high UV protection index [7].

In this study, we introduce a high UV protective O/W mineral-only sunscreen formulation. As a main inorganic UV filter, we used ZnO nanoparticles coated with triethoxycaprylylsilane. Their UV protection performance was controlled by mixing the ratio of ZnO nanoparticles with different sizes (15 nm, 40 nm, and 150 nm). Their UV protection performance was confirmed from *in vitro* and *in vivo* tests.

## Materials & Methods:

**Preparation of O/W mineral-only sunscreen formulations**

ZnO powders used in this study were Zano 10+ (EverCare, USA), SUNZnO-NAS (SUNJIN BEAUTY SCIENCE, Korea), and SUNZnO-AS (SUNJIN BEAUTY SCIENCE, Korea). ZnO dispersions were SUNCLEAR-Z50(K), SUNCLEAR-Z65C5, and Z65M. $TiO_2$ dispersion was TXD55-AQ. All the dispersions were supplied from SUNJIN BEAUTY SCIENCE (Korea). Polyhydroxystearic acid was purchased from Phoenix Chemical Co. Ltd. (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 benzonate 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, dilauryl citrate were purchased from Evonik Industries (Germany). All other raw materials used in this study were of cosmetic grade.

**Preparation of O/W mineral-only sunscreen formulations**

As shown in Table 1, place phase A into a 200 ml beaker and heat to 60 °C. Next, phase B is slowly added to phase A while stirring phase A at 500 rpm using an Agi Mixer. Then, the mixture is heated again to 80°C. In the powder process, oil and dispersant in phase C, separately weighed and mixed with a stirrer, are dispersed 3 times through a three-step roller. The dispersed powder mixture is heated to 80°C with the addition of an O/W emulsifier. In the dispersion process, phase C is heated to 80°C with the addition of an O/W emulsifier. While stirring the heated the mixture at 3500 rpm using a Homo mixer, slowly add phase C. After adding the oil phase to the water phase, the total mixture is homogenized at 5000 rpm for 5 minutes. And, O/W emulsions described in Table 2 are prepared in the same manner. Here, the ZnO content is equally prepared at 25%.

***In vitro* SPF & PA measurement**

*In vitro* SPF and PA measurements are conducted using solar light SPF-290AS (Solar light, USA).

***In vivo* SPF & PA measurement**

*In vivo* SPF values are measured by clinical experiments in accordance with the ISO-244444 International Cosmetics Autonomous Convention Act. PA values are measured according to ISO-24442.

Table 1. ZnO powder vs, ZnO dispersion

| | Ingredient | Powder | | | Dispersion | | |
|---|---|---|---|---|---|---|---|
| | | ZnO-10 | ZnO-NAS | ZnO-AS | ZnO-10-d | ZnO-NAS-d | ZnO-AS-d |
| 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 Benzoate | 14 | 14 | 14 | - | - | - |
| | Polyhydroxystearic Acid | 0.6 | 0.8 | 0.8 | - | - | - |
| | ZnO-10-d | - | - | - | 47.5 | - | - |
| | ZnO-NAS-d | - | - | - | - | 40 | - |
| | ZnO-AS-d | - | - | - | - | - | 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 |

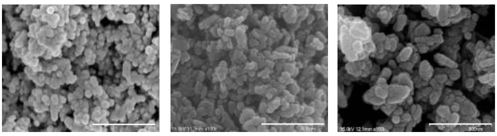
Table 2. Different mixing ratios of ZnO nanoparticles

| | Ingredient | ZnO ratio (ZnO-10-d : ZnO-AS-d) [w%] | | | | |
|---|---|---|---|---|---|---|
| | | 9:1 | 7:3 | 5:5 | 3:7 | 1:9 |
| A | D.I WATER | 38.10 | 38.95 | 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-10-d | 42.88 | 33 | 23.9 | 14.3 | 4.78 |
| | ZnO-AS-d | 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 |

## Results & Discussion:

### SEM observation of ZnO with different sizes

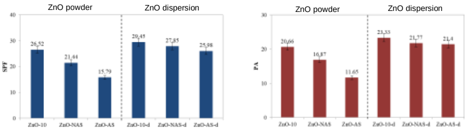
ZnO-10 (D=15 nm) | ZnO-NAS (D=40 nm) | ZnO-AS (D=105 nm)



### Improved UV performance of ZnO dispersion

UV protection effect of ZnO was better in the dispersions than in powders. Furthermore, ZnO-10 with an average size of 15 nm showed the highest UV protection effect among both the tested powders and dispersions.

- *In vitro* test results



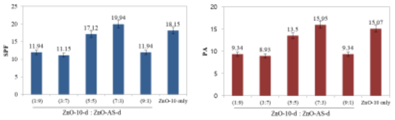

- *In vivo* test results

| | Powder | | | Dispersion | | |
|---|---|---|---|---|---|---|
| Test Result | ZnO-10 | ZnO-NAS | ZnO-AS | ZnO-10-d | ZnO-NAS-d | ZnO-AS-d |
| *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 | | | | | | |

ZnO-10, which shows the smallest size, showed the highest UV protection index in both powder type and dispersion type. In addition, when dispersion and powder were compared, the effectiveness of dispersion was confirmed to be excellent, such as in vitro.

### *In vitro* UV performance vs. Mixing ratio of ZnO dispersions

The 7:3 ratio of ZnO-10-d and ZnO-As-d was the highest SPF and PA value. The PA value was higher than that of using only a single ZnO of a small size.




### High UV performance of mineral-only O/W formulations

- Tested formulations

| | 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 | $TiO_2$ dispersion | - | 7.80 |
| D | ZnO-10-d | 33.00 | 33.00 |
| | ZnO-AS-d | 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 |

The UV protection effect was more effective in $TiO_2$ added formulation, which target UV protection value was confirmed by in vivo test.

- *In vivo* test results

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

White index

ZnO only: 48.11 | Mineral only: 53.26

## Conclusions:

In this study, we have developed an inorganic O/W sunscreen with a high UV protection performance as well as good stability. Specifically, we used ZnO nanoparticle with different average sizes, 15 nm, 40 nm, and 150 nm. The UV protection index increased with the decrease in the size of ZnO nanoparticles. In addition, the UV blocking effect was better when formulated with ZnO dispersion than with ZnO powder. This can be attributed to the fact that in the case of ZnO dispersion, the pre-dispersed ZnO nanoparticles are more uniformly dispersed in the formulation and then spread evenly on the test surfaces. Interestingly, when the ZnO nanoparticles of different sizes were mixed in different ratios, the UV blocking effect was highest at a mixing ratio of 7:3 (ZnO-10-d : ZnO-AS-d). This indicates that UV blocking performance can be controlled by mixing ZnO nanoparticles of different sizes due to the size-dependent UV blocking effect. Finally, we developed mineral-only O/W sunscreen formulations using optimized ZnO mixture and TiO2, which showed UV blocking performance of SPF 50 and PA++++. We expect that our O/W mineral-only sunscreen formulations have great potential as a clean beauty sunscreen in cosmetic markets.

## References:

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