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나노 ZnO 입자가 코팅된 판상 분체의 합성과 사용감 증진 효과에 대한 연구

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The Study of Plate Powder Coated Nano Sized ZnO Synthesis and Effect of Sensory Texture Improvement

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요 약: 20~30 nm 크기를 갖는 나노 사이즈 ZnO 입자는 염료, 러버 첨가제, 가스 센서, 바리스터, 감광제와 광촉매로서 여러 산업분야에서 사용되고 있다. 반면에 화장품 산업에서는 나노 미터 크기의 ZnO 입자는 UV 차단물질과 자연스러운 메이크업 효과를 증진시키는 소재로서 사용되고 있다. 그러나 순수 ZnO 입자는 화장품에 적용했을 때 사용감 악화로 인해 그 사용량이 제한되고 있는 실정이다. 따라서 본 논문에서는 사용감은 판상 분체의 특성을 갖으면서 ZnO 본연의 특성을 유지하는 분체를 합성하기 위해 화장품 산업에서 널리 사용되고 있는 세리사이트, 보론나이트라이드, 비스무스옥시클로라이드와 같은 판상분체에 나노 사이즈 ZnO가 코팅된 고기능성 무기복합분체를 하였다. 본 논문에서는 열수침전법에 의해 무기복합분체를 합성하였다. Zn원으로서 $ZnCl_2$가 사용되었고 침전제로는 hexamethylenetetramine (HMT)과 urea를 사용하였다. 실험변수로서 출발물질의 농도, 침전제의 종류, 핵생성제의 농도, 반응온도와 반응시간을 변화시켜 실험하였다. 합성된 무기복합분체의 형태, 결정상 변화, 열특성, UV-차단효과를 관찰하기 위해 각각 FE-SEM, XRD, FT-IR, TGA-DTA, *In vitro* SPF 테스터 기기를 이용하여 확인하였다. 합성된 무기복합분체를 메이크업 제품에 적용시켜 사용감 테스트하였다. 본 실험 결과 판상분체의 종류에 상관없이 일정한 합성조건 범위에서 나노크기 ZnO 입자가 균일하게 코팅되었다. 코팅된 판상분체를 프레스트 파우더제품에 적용시켜 사용자 테스트한 결과 판상분체 특유의 광택은 현저히 감소되는 반면 자연스러운 화장 연출, 사용감 개선 및 부착력 향상 효과를 얻을 수 있었다.

Abstract: Nano sized ZnO particle as 20~30 nm applies for material, pigments, rubber additives, gas sensors, varistors, fluorescent substance as well as new material such as photo-catalyst, sensitizer, fluorescent material. ZnO with a particle size in the range 20~30 nm has provided to be an excellent UV blocking material in the cosmetics industry, which can be used in sunscreen product to enhance the sun protection factor and natural makeup effect. But pure ZnO particles application limits for getting worse wearing feeling. We make high-functional inorganic-composite that coated with nano-ZnO on the plate-type particle such as sericite, boron nitride and bismuthoxychloride. In this experiment, we synthesized composite powder using hydrothermal precipitation method. The starting material was $ZnCl_2$. Precipitation materials were used hexamethylenetetramine (HMT) and urea. We make an experiment with changing as synthesis factors that are concentrations of starting material, precipitation materials, nuclear formation material, reaction time, and reaction temperature. We analyzed composite powder's shape, crystallization and UV-blocking ability with FE-SEM, XRD, FT-IR, TGA-DTA, *In vitro* SPF test. The user test was conducted by product's formulator. In the results of this study, nanometer sized ZnO was coated regardless of the type of plate-powder at fixed condition range. When the coated plate-powders were applied in pressed powder product, the glaze of powder itself decreased, but natural make-up effect, spreadability, and adhesionability were increased.

Keywords: *zinc oxide, UV blocking, cosmetics, hexamethylenetetramine, coating*

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1. Introduction

Typical UV-blocking materials were used by organic and inorganic materials. Generally, organic UV-absorbers show effective UV-B (290~320 nm) absorption property, but doesn't show with modest UV-A (320~400 nm) absorbing ability. Also, they posed a safety problem when used at high concentrations. Inorganic UV blockers act mechanism with blocking vibration, diffraction, reflection and so on. The fine powders of cerium oxide, titanium oxide and zinc oxide have ideal characteristics for use as a broad-spectrum inorganic UV radiation blocking material in personal-care products. In many inorganic UV blocking materials, titanium oxide fine particles have been used and it has the best blocking ability of inorganic UV blocking materials[1,2]. The titanium oxide fine particles not only blocked UVA and UVB but also had drug-proof property and the safety of human health and skin. Their high refractive indices, however, can make the skin look unnaturally white, and their high photocatalytic activity facilitates the generation of reactive oxygen species, which can oxidize and degrade other ingredients in the formulation. On the other hands, zinc oxide possessing a lower refractive index was relatively transparent to visible light and appears natural on the skin without imparting an excessively pale white look, but has excellent UV radiation absorption properties. Zinc oxide has little impurities, anti-bacteria, and deodorization as well as good blocking ability in broad spectrum. Zinc oxide is a good material to overcome titanium oxide's transparency problem and to be safe for human's skin, and that was effective inorganic sunscreens, which are popularly used in the cosmetic industry nowadays[3-6]. Also, zinc oxide has been used in a wide variety of technological applications including sensor devices, electro-luminescent devices, semiconductor devices, piezoelectric materials, and optical waveguides, as a catalyst.

Inorganic UV-blockers had defaults such as deteriorating adhesion properties, having rough on the skin, having high reflection index and high covering-ability. We used coating base with many characteristics such as ultra-fine and plate type particle materials that used in the cosmetic industry. These materials were mica, boron nitride and bismuthoxychloride. We used hydrothermal precipitation method because it synthesized ultra-fine particles that metal salts and precipitation materials were mixed with liquid stats and then, we gained metal oxide materials by heating procedure. This method could control the morphology, size and distribution of synthesized composites with many kinds of variables, such as the concentration of zinc chloride, precipitation, sorts of precipitation materials, reaction time, reaction temperature, and nuclear generation agent [7-17]. We analyzed composite powder's shape, crystallization and UV-blocking ability with FE-SEM, XRD, FT-IR, TGA-DTA, and *in vitro* SPF test.

2. Experimental

2.1. The Pretreatment Procedure of Coating Base Powder

The pretreatment carried out mica, boron nitride (the following BN) and bismuthoxychloride (the following BOC) with dilute hydroxy chloride for 2 h. And then, after drying at 100℃ for 24 h, we used pretreated-base-powders. The pretreatment worked the decomposition of organic materials and impurities in coating base materials. And it was easy to coat procedure with attaching the hydroxy group.

2.2. The Synthesis of Zinc Oxide with Hydrothermal Precipitation Method

We used starting zinc chloride ($ZnCl_2$) as salt. We used two kinds of precipitation materials for testing effect of precipitation kinds. First precipitation material used HMT, so to speak, hexamethylenetetramine ($C_6H_{12}N_4$). Second precipitation material used urea (NH_2CONH_2).

A chemical reaction formula as first precipitation material HMT. A chemical reaction formula as second precipitation material urea.

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4\ NH_3$$
$$NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2$$
$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$
$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

We used a waterbath for controlling a constant temperature and stirrer for homogeneous mixing. We mixed starting salt material and precipitation material with

aqueous states for 1hr. After then, mixed solution was stirred with keeping with 80℃ for 1 h. Adding ammonium hydroxide (NH_4OH) as nuclear generation material, we varied the reaction time. The reacted material was filtered and washing with warm distilled water and then, was filtered again. After upper process, dried at 100℃ for 24 h. We varied the starting salt material concentrations from 0.05 M to 0.2 M. For evaluating the effect of precipitation concentration, we varied HMT concentration from 0.05 M to 0.2 M and varied urea concentration from 1 M to 5 M. Table 1 showed the experimental condition and variables.

3. Results and Discussion

3.1. The FE-SEM Analysis of the ZnO Coated-particles

The size of synthesized particles had from 20 nm to 30 nm and the shapes of synthesized particles were rod type, sphere type, and board type. Figure 1 showed that the higher $ZnCl_2$ concentration, the larger particles quantity of coated materials. When $ZnCl_2$ concentration was 0.1 M, the particles of coated materials were sphere type and homogeneous state, but under 0.1 M, the particles of coated materials didn't coat ZnO because of early terminating nuclei generation and growth reaction. Over 0.15 M, the particles of coated materials were from rod type to board type because of overgrowing the nuclear generation and increasing the particle for priority growth direction. Figure 2 showed the particles synthesized at different HMT concentration. When HMT concentration was 0.05 M (Figure 2(a)), the particle shape was the middle shape between rod type and sphere type because hydrolysis reaction of HMT happened slowly and pH of materials increased so slowly. Figure 2(b) shows when HMT concentration was 0.1 M, the particle shape was sphere type and the coating area was increased. But, Figure 2(c) shows when HMT concentration was 0.2 M, the particle shape was changed from sphere type to rod type because nuclei were excessively generated and ZnO grew rod type. Figure 3 showed the particles synthesized at dif-

Table 1. Synthesis Conditions of Mica, Boron Nitride, Bismuthoxychloride-ZnO Composite

Sample No.	Materials				Reaction Time (h)	Reaction Temp. (℃)
	Starting Mat.	Precipitation Matrials		Nuclear Mat.		
	$ZnCl_2$ Con. (mol/L)	HMT Con. (mol/L)	Urea Con. (mol/L)	NH_4OH (mL)		
SZ 1 SZ 2 SZ 3 SZ 4	0.05 0.1 0.15 0.2	0.1		5	12	80
SZ 5 SZ 6 SZ 7	0.1	0.1		5	3 7 12	80
SZ 8 SZ 9 SZ 10	0.1	0.05 0.1 0.2		5	12	80
SZ 11 SZ 12 SZ 13	0.1		1 3 5	5	12	80
SZ 14 SZ 15 SZ 16	0.1		1 3 5	5	12	90
SZ 17 SZ 18 SZ 19	0.1	0.1		3 5 7	12	80
SZ 20 SZ 21 SZ 22	0.1	0.1		5	12	70 80 90
BZ, BOZ 1 BZ, BOZ 2	0.1 0.2	0.1		5	12	80

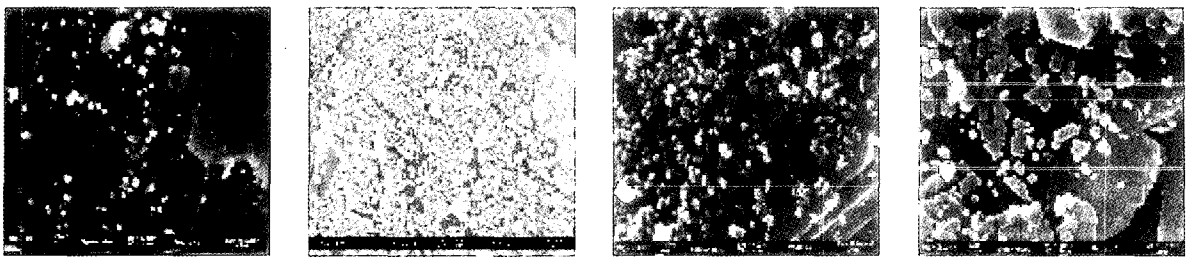

Figure 1. SEM photographs of synthesized composite from $ZnCl_2$ concentration (a) SZ1, (b) SZ2, (c) SZ3, (d) SZ4.

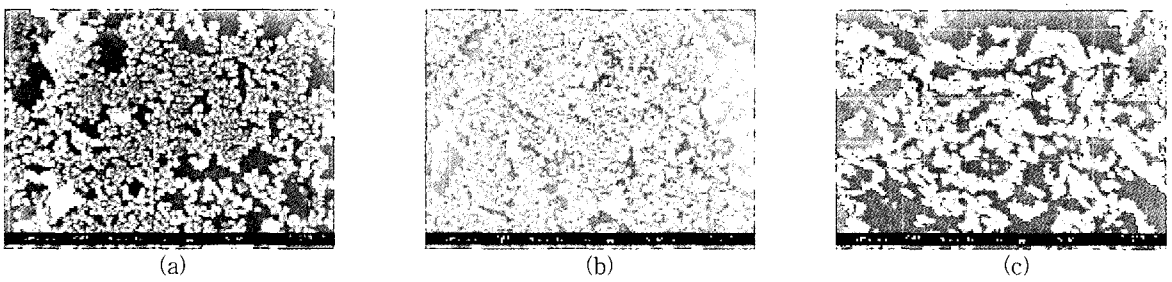

Figure 2. SEM photographs of synthesized composite from HMT concentration (a) SZ8, (b) SZ9, (c) SZ10.

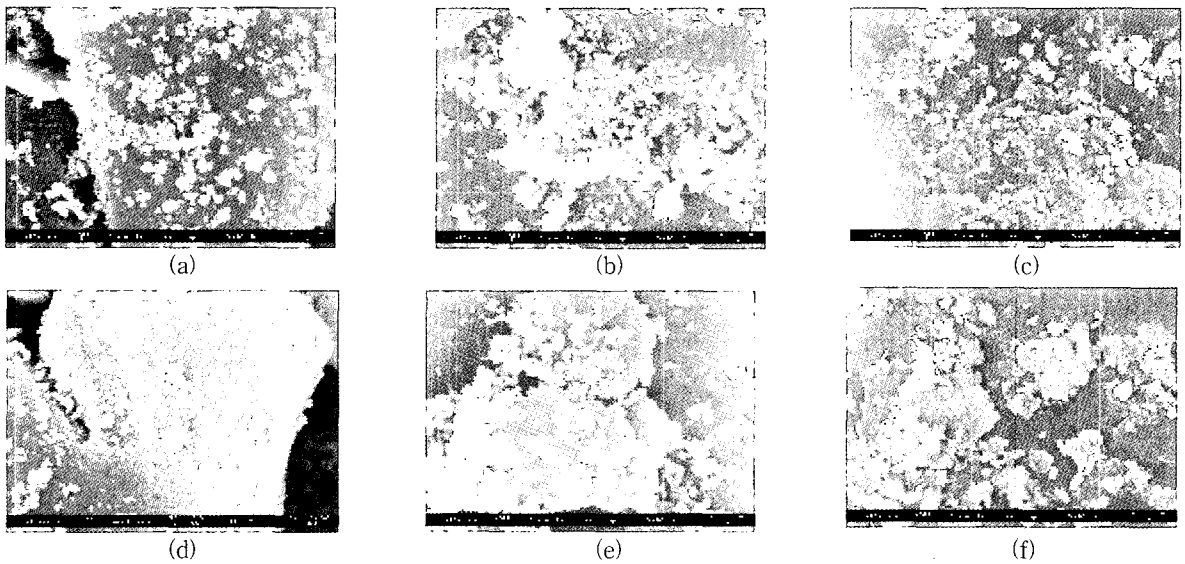

Figure 3. SEM photographs of synthesized composite from urea concentration (a) SZ11, (b) SZ12, (c) SZ13, (d) SZ14, (e) SZ15, (f) SZ16.

ferent urea concentration. Figure 3(a), (b), (c) were synthesized at reaction temperature 80℃ and Figure 3(d), (e), (f) were synthesized at reaction temperature 90℃. When Urea concentration was so low, the hydrolysis rate of urea was slow and reaction nuclei didn't make coated-particles (Figure 3(a)). When Urea concentration was so high, the hydrolysis rate of urea was fast and reaction nuclei made board-type particles (Figure 3(c)). The higher reaction temperature worked, the smaller coated-areas became. But, HMT as precipitation was better than urea because HMT was the faster hydrolysis rate than urea and generated many reaction nuclei. Figure 4 and 5 show the coated-particles of BN and BOC with coating base powder at

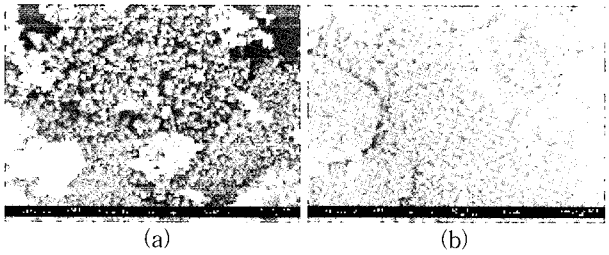

Figure 4. SEM photographs of synthesized composite from BN-ZnO (a) BZ1, (b) BZ2.

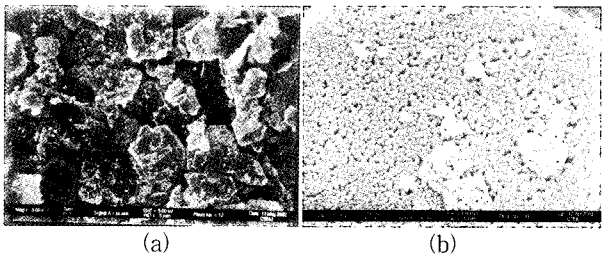

Figure 5. SEM photographs of synthesized composite from GLO-ZnO (a) BOZ1, (b) BOZ2.

best coating conditions.

3.2. The Analysis of FT-IR

After coating ZnO on mica, dry at 100℃ and then, sintered at 300℃, 500℃, and 700℃. Figure 6 showed the result of FT-IR at different calcined temperature. Figure 6 shows Al-O bond at 1070 cm^{-1}. 1100 cm^{-1} was piled up 1070 cm^{-1}, and it was larger than other peaks. After sintering at 500~700℃, 3600 cm^{-1} peak proved zinc hydroxy salt radical that was evidence of reaction material as OH^- radical. But, this peak didn't appear at 700℃, because the decomposition of OH and salt in zinc hydroxy salt occurred to reduce the mass at 600℃ in TGA-DTA curves. After sintering, ZnO peak generated 480 cm^{-1}.

3.3. The Analysis of XRD Patterns

Figure 7 shows the XRD patterns of BZ2 specimen in BN-ZnO composites that were made by changing sintering temperatures. This result matched JCPDS value and we knew that the particle structure of this specimen was hexagonal type. Coated-ZnO particles looked like sphere type with FE-SEM in spite of being anisotropy, because many nuclei with critical size grew into about 0.5 nm to 5 nm with first growth. And then first-growth particles formed second-particles of sphere

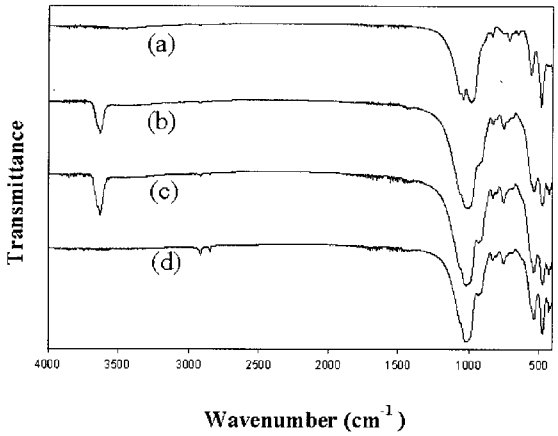

Figure 6. FT-IR spectra of SZ 4 from (a) pure mica, (b) 300℃, (c) 500℃, and (d) 700℃.

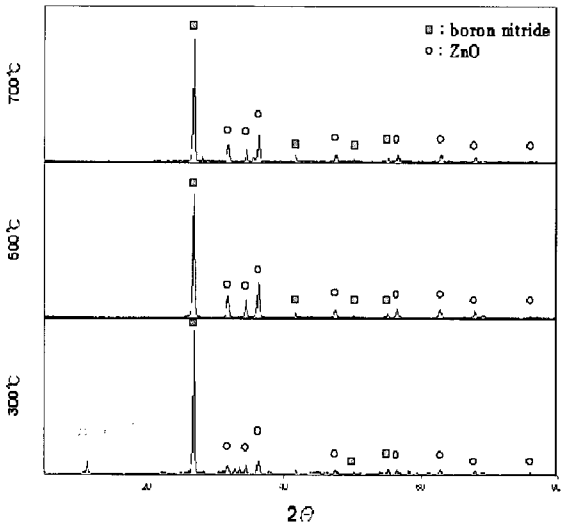

Figure 7. XRD patterns of BZ2 from various sintering temperature at 300℃, 500℃, and 700℃.

type by equal aggregation. The XRD patterns of SZ4 and BOZ2 was similar to the results of BZ2.

3.4. The Analysis of TGA-DTA

Figure 8 shows the TGA-DTA peak of BZ2. The major mass reduction at 180℃ was occurred by the decomposition of water and organic materials. The mass reduction at 450℃ and 650℃ were occurred by the decomposition of OH^- and Cl^- radicals in hydroxy-salt.

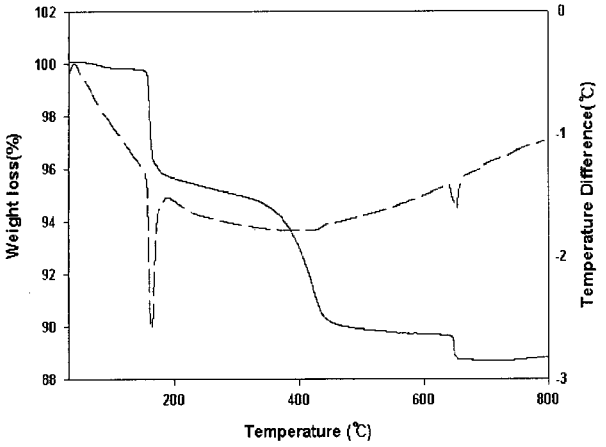

Figure 8. TGA-DTA curve of synthesized composite from BZ 2.

3.5. The Analysis of *In-vitro* SPF Test and User Test

Table 2 showed the results of *in vitro* SPF and UVA blocking ability. The results were important to compare relatively uncoated specimens (sample A, B, C) and ZnO coated plate type materials (sample D, E, F). The result of *in-vitro* SPF test were not useful to determine an absolute value but useful to compare with others. The results of *in-vitro* SPF were increased over 10 by coating or non-coating. In specially, BOC had relatively high SPF data because it had relatively higher reflexive index and covering ability than mica and BN. Table 3 showed formulation of pressed power. Table 4 confirmed that the application sense of uncoated materials was deteriorated, but adherence sense was enhanced. ZnO fine particles had good adherence sense and good absorbance of smegma. Using the press type cosmetics, it enhanced cosmetic lasting effects. The spread effects of EX-4 and S/T samples were not different but EX-5 as substituting for same amount of pure ZnO remarkably deteriorated sensory feeling and spreadabilty. Because coating procedure could make two powders as ZnO and plate powders with one powder and, it could make highly covering ability, malleability and extensibility. In addition, it could give natural and transparent feeling, and could remarkably reduce shinning feeling. From upper effects, this procedure overcame the default of cosmetic formulas limitation such as about 10.00% as well as had good product characteristics.

4. Conclusions

In this study, hydrothermal precipitation method was used to synthesis functional inorganic composite powder having narrow ZnO coated plate particle distribution. The optimal coating condition was determined by variation of concentrations of starting material, precipitation materials, nuclear formation material, reaction time and reaction temperature.

(1) We used HMT and urea as precipitation agent. This study showed that HMT possessed superior characteristics of precipitation agent than urea. Because the hydrolysis rate of HMT was more fast than that of urea, the reaction could be happened as uniform and simultaneous.

(2) When the reaction temperature was increased, the rate of hydrolysis grow up, then the amount of coated ZnO was increasing and the shape of coated ZnO maintained sphere type. But, when the reaction temperature be more than 90℃, the rate of hydrolysis so high, then the shape of coated ZnO was needle type.

(3) The coated ZnO particle maintained the original shape after calcinations of 700℃. From XRD data, hexagonal ZnO was synthesized at 300℃, and pure ZnO was synthesized at 700℃.

(4) According to *in-vitro* UV blocking test, the functional composite powder sample was higher than

Table 2. The Results of *in vitro* SPF and UVA Blocking Ability

Sample No.	UVB blocking ability	UVA blocking ability	
	In vitro SPF	Critical Wavelength (nm)	UVA/B ratio
Sample A (Pure mica)	1.28±0.02	385.2	0.590±0.025
Sample B (Pure BN)	2.62±0.07	379.3	0.555±0.005
Sample C (Pure BOC)	7.60±0.71	386.9	0.726±0.009
Sample D (ZnO coated mica)	12.90±1.70	389.6	0.872±0.006
Sample E (ZnO coated BN)	13.90±0.09	390.2	0.936±0.007
Sample F (ZnO coated BOC)	19.60±0.70	387.7	0.946±0.005

Table 3. Formulations for Pressed Powder Foundation with Various ZnO Coated Plate Powder

	S/T	EX-1	EX-2	EX-3	EX-4	EX-5
Talc/Methicone/Dimethicone	Q.S. to 100					
Talc/Perfluoromethyl Isopropyl Ether	5.00	5.00	5.00	5.00	5.00	5.00
Aluminum Starch Octenyl Succinate	4.00	4.00	4.00	4.00	4.00	4.00
PTFE	3.50	3.50	3.50	3.50	3.50	3.50
Mica/TiO_2/Mineral oil/Methicone	5.00	5.00	5.00	5.00	5.00	5.00
ZnO	-	-	-	-	-	0.50
Mica	15.00	-	15.00	15.00	-	15.00
BN	15.00	15.00	-	15.00	-	15.00
BOC	15.00	15.00	15.00	-	-	15.00
Coated Mica	-	15.00	-	-	15.00	-
Coated BN	-	-	15.00	-	15.00	-
Coated BOC	-	-	-	15.00	15.00	-
IOY	0.48	0.48	0.48	0.48	0.48	0.48
IOR	0.24	0.24	0.24	0.24	0.24	0.24
IOB	0.03	0.03	0.03	0.03	0.03	0.03
Binder	5.70	5.70	5.70	5.70	5.70	5.70

Table 4. The Results of User Test

	S/T	EX-1	EX-2	EX-3	EX-4	EX-5
Sensory Feeling	5	4	3	4	4	2
Adhesion Feeling	3	4	4	4	5	3
Spreadabilty	5	4	4	4	3	2
Shinning	5	4	3	4	2	5
Coverage	5	3	3	4	2	4

<5: Exellent 4: Good 3: General 2: Bad 1: Worst>

non-coated powder beyond decuple. Because UVA/B ratio above 0.8, we could confirm that this sample possessed the blocking ability of broad spectrum. When the coated plate-powders were applied in pressed powder product, the glaze of powder itself decreased, but natural make-up effect, spreadability, and adhesionability were increased.

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