

Development of Aqueous Metal Oxide Dispersion having Water-resistance Property by Forming Self-assembled Structure and its Application to Sun-care Products

NAKANO, Junya^{1*}; NAKAMURA, Shohei¹; MISONO, Takeshi¹; NAGATANI, Noboru¹; SUZUKI, Toshiyuki¹

¹ R&D Center, Nikko Chemicals Co., Ltd., Tokyo, Japan

* NAKANO, Junya; 3-24-3 Hasune, Itabashi-ku, Tokyo, 174-0046, Japan, +81-3-3966-7755, nakajuny@nikkolgroup.com

Abstract

O/W sun-care products have a problem of enhancing both water-resistance and UV shield capability. To solve this problem, we developed an aqueous dispersion that contains hydrophobic-treated metal oxide that has water-resistance property upon drying by utilizing diethylhexyl sodium sulfosuccinate (AOT) as dispersing agent. In this work, we clarify the mechanisms for water-dispersibility of hydrophobic-treated metal oxide and the water-resistance of cosmetic film, and then apply the developed aqueous dispersion to sun-care products.

The mechanism for water-dispersibility was evaluated by zeta potential at hydrophobic-treated surface substrate/anionic surfactant solution interface. The change in zeta potential at triethoxycaprylsilane (TC)-treated surface substrate/AOT solution interface was larger than that of other anionic surfactants. The mechanism for water-resistance was evaluated by Small-Angle X-ray Scattering (SAXS) measurement of anionic surfactant's structure formation on hydrophobic-treated surface substrate. In the SAXS measurement of AOT, formation of self-assembled structure was observed. As an application, the water-resistance of cosmetic film made of O/W sun-care product formulated using the 'developed' aqueous dispersion was studied. It was found that the O/W sun-care product that used the 'developed' dispersion had superior water-resistance compared to the O/W sun-care product that used the 'comparison' dispersion.

Keywords: water-resistance, self-assembled structure, aqueous dispersion.

1. Introduction.

Since International Organization for Standardization published ISO16217:2020 [1] (Water immersion procedure for determining water resistance) and ISO18861:2020 [2] (Percentage of water resistance), water-resistance of sun-care products is valued globally. In a conventional design of O/W sun-care products, hydrophobic-treated metal oxides, TiO₂ and ZnO, are formulated to inner oil phase as oil dispersions. However, if there is a need to increase the content of formulated metal oxides in inner oil phase for the purpose of enhancing UV shield capability, formulation design is difficult due to the instability and the poor texture of the formulation. In another conventional design of O/W sun-care products, metal oxides can also be formulated to the outer water phase as aqueous dispersions, but that did not provide water-resistance to sun-care products. To disperse metal oxides into water efficiently, hydrophilic treatment of metal oxides and/or formulation of highly hydrophilic nonionic surfactant are selected. However, the added these hydrophilicities are factors for decreasing the water-resistance of cosmetic film. Thus O/W sun-care products have a problem of enhancing both water-resistance and UV shield capability. To solve this problem, we have designed and developed aqueous dispersion of hydrophobic-treated TiO₂ that has water-resistance property

upon drying by utilizing diethylhexyl sodium sulfosuccinate (AOT) as dispersing agent [3]. However, the function of AOT for dispersing hydrophobic-treated TiO₂ into water stably and the formation of water-resistant cosmetic film are not clear. In this work, we clarify the mechanisms for water-dispersibility of hydrophobic-treated TiO₂ and expression of water-resistance of cosmetic film upon drying by AOT. In the analysis of the water-dispersibility of hydrophobic-treated TiO₂, the absorption behavior of several anionic surfactants towards triethoxycaprylylsilane (TC)-treated surface and AOT's absorption behavior towards hydrophobic-treated surface are investigated. In the analysis of the expression of water-resistance of cosmetic film, the anionic surfactant's structure formation on TC-treated surface is also examined. As an application to sun-care products, water-resistance evaluation of O/W sun-care products formulated the using the 'developed' aqueous dispersion is conducted. Furthermore, the O/W and W/O sun-care product's UV shield capabilities by controlling the phase (inner/outer) of formulated metal oxides are confirmed.

2. Materials and Methods.

2.0. Materials

2.0.1. Preparation of TC-treated Glass Substrate

After washing slide glass with 1wt% sodium lauryl sulfate (SLS) in deionized water, the slide glass was further washed with ultrasonic cleaning for 10 min in deionized water. The slide glass was then treated with piranha solution (25wt% NH₃ aqueous solution: 30wt% H₂O₂ aqueous solution: deionized water = 1: 1: 5) for 30 min at 60°C. The oxidized slide glass was impregnated with 10wt% surface treatment agent triethoxycaprylylsilane (TC) ethanol solution for 60 min at room temperature and then the slide glass was heated for 60 min at 90°C by oven. Washing with ethanol and drying the slide glass afforded TC-treated glass substrate.

2.0.2. General Procedure for Preparation of Metal Oxide Dispersions

The formulations of metal oxide dispersions are presented in Table I. The metal oxides (TiO₂) were added to dispersing agent in dispersing media, and the mixture was grinded by disper mixer at 1500 rpm for 30 min to give the desired metal oxide dispersions.

Table I. Formulations of Metal Oxide Dispersions

	Aqueous TiO ₂ disp. (development) (%)	Aqueous TiO ₂ disp. (comparison) (%)	Aqueous TiO ₂ disp. (30) (%)	Ester TiO ₂ disp. (%)	Silicone TiO ₂ disp. (%)
TC-treated TiO ₂	50.0	-	30.0	30.0	30.0
Silica-treated TiO ₂	-	50.0	-	-	-
Deionized water	45.0	50.0	67.0	-	-
Ester	-	-	-	67.0	-
Silicone	-	-	-	-	60.0
AOT	5.0	-	3.0	-	-
Polyhydroxy stearic acid	-	-	-	3.0	-
PEG-10 dimethicone	-	-	-	-	10.0
Total	100.0	100.0	100.0	100.0	100.0

2.1. Analysis of Mechanism for Water-dispersibility of Hydrophobic-treated TiO₂

2.1.1. Evaluation of Anionic Surfactant's Zeta Potential on TC-treated Surface

0.01wt% anionic surfactant (AOT, SLS and potassium laurate (PL)) electrolyte solutions and 1 mM KCl aqueous solution were prepared. Zeta potentials at the TC-treated glass substrate/anionic surfactant electrolyte solution interface were measured using streaming potential measurements performed with the clamping cell in the zeta potential analyzer (SurPASS 3, Anton Paar) for solid surface analysis. Zeta potential measurements were initially performed using 1 mM KCl from 0 to 450 seconds (electrolyte solution flow). Then it was changed to 0.01w% anionic surfactant from 450 to 1000 seconds (anionic surfactant solution flow). Based on the change in the zeta potential, water-dispersibility by anionic surfactant was assessed.

2.1.2. Visual Wettability Test of Hydrophobic-treated TiO₂ with AOT

6.25wt% AOT aqueous solution was gradually added to hydrophobic-treated (TC, hydrogendimethicone- and isostearic acid-treated) pigment TiO₂ powders on glass plates while stirring. When the same amount of the AOT aqueous solution was added to each hydrophobic-treated pigment TiO₂, visual observation of wettability of the TiO₂ was conducted. Depending on the wetness of the TiO₂, AOT's absorption behavior towards hydrophobic-treated surface was evaluated.

2.2. Analysis of Mechanism for Expression of Water-resistance of Cosmetic Film

2.2.1. Evaluation of Anionic Surfactant's Structure Formation on TC-treated Surface

TC-treated glass substrates were impregnated with each 1wt% anionic surfactant aqueous solution (AOT, SLS or PL), and then dried at room temperature. The self-assembled structures of each surfactant on glass substrates were characterized by Grazing-Incidence Small-Angle X-ray Scattering (GISAXS), using an Anton Paar SAXSpoint 5.0, which gives a Q range between 0.6 nm⁻¹ and 7 nm⁻¹. Scattered X-rays (Cu K α , 0.154 nm) were detected by EIGER2-R-1M (DECTRIS). The 1D profiles were generated from the 2D scattering patterns using the Anton Paar SAXS analysis software.

2.3. Application of the 'Developed' Aqueous Dispersion to Sun-care Products

2.3.1. Water-resistance Evaluation of O/W Sun-care Products Formulated using the Developed Aqueous Dispersion

O/W sun-care formulations containing the 'developed' and 'comparison' metal oxides from Table I were prepared (Table II). Two tests were done to evaluate water-resistance. In the first test, the O/W sun-care products were applied to artificial leathers by applicator with 500 μ m gap. Afterwards, the artificial leathers were dried for 30 min at 40°C to give cosmetic films. 5 μ l of deionized water was dropped onto the cosmetic films and the water-resistance of the cosmetic film was estimated by visual observation. In the second test, the O/W sun-care products were applied to quartz glasses by applicator with 25 μ m gap. Afterwards, the quartz glasses were dried for 30 min at 40°C to give cosmetic films. Approx. 0.35 ml of deionized water was sprayed to the cosmetic films from a distance of 40 cm. UV absorbance of cosmetic film before and after spraying deionized water was measured using UV-visible spectrophotometer (V-750, JASCO). Based on the change in UV absorbance, the water-resistance of cosmetic film was evaluated.

2.3.2. Study of O/W Sun-care Product's UV Shield Capability by Controlling Phase (inner/outer) of Formulated Metal Oxides

UV shield capability of two O/W sun-care product formulations containing TiO₂ were compared. The first one labeled 'Practical example (O (TiO₂)/W (TiO₂))' contains TiO₂ in both inner oil phase (Ester TiO₂) and outer water phase (Aqueous TiO₂ dispersion (30)). The second one is O/W sun-care product formulation which contains TiO₂ in inner oil phase only. The product is

labeled as 'Conventional example: (O (TiO₂)/W)' and was also prepared with Ester TiO₂ dispersion in inner oil phase (Table II). The total amount of TiO₂ is the same in both conditions. The O/W sun-care products were applied to quartz glasses by applicator with 20 µm gap. Then the quartz glasses were dried for 30 min at 40°C to give cosmetic films. UV absorbance of cosmetic film was measured using UV-visible spectrophotometer (V-750, JASCO). Based on the UV absorbance, UV shield capability of the cosmetic film was studied.

2.3.3. Study of W/O Sun-care Product's UV Shield Capability by Controlling Phase (inner/outer) of Formulated Metal Oxides

UV shield capability of two W/O sun-care product formulations containing TiO₂ were compared. The first one is a W/O sun-care product formulation which contains TiO₂ in inner water phase (Aqueous TiO₂ dispersion (30)) and outer oil phase (Silicone TiO₂ dispersion), labeled as 'Practical example: (W (TiO₂)/O (TiO₂))'. The second one is a W/O sun-care product formulation which contains TiO₂ in outer oil phase only (Silicone TiO₂ dispersion), and is labeled as 'Conventional example: (W/O (TiO₂))' (Table II). The total amount of TiO₂ is the same in both conditions. UV shield capability of cosmetic film was studied in the same method as 2.3.2..

Table II. O/W and W/O Sun-care Formulations

	O/W formulation 2.3.1.		O/W formulation 2.3.2.		W/O formulation 2.3.3.	
Material	with development (%)	with comparison (%)	Practical example (%)	Conventional example (%)	Practical example (%)	Conventional example (%)
Emulsifier	3.0	3.0	3.0	3.0	2.5	2.5
Fatty alcohol	2.0	2.0	2.0	2.0	-	-
Ester	13.0	13.0	13.5	3.0	5.0	5.0
Silicone	-	-	-	-	27.5	20.0
Ester TiO ₂ dispersion	-	-	15.0	30.0	-	-
Silicone TiO ₂ dispersion	-	-	-	-	15.0	30.0
Water	54.5	54.5	51.0	61.5	29.6	37.1
Polyol	7.0	7.0	-	-	5.0	5.0
Preservative	0.5	0.5	0.5	0.5	0.4	0.4
Aqueous TiO ₂ dispersion (development)	20.0	-	-	-	-	-
Aqueous TiO ₂ dispersion (comparison)	-	20.0	-	-	-	-
Aqueous TiO ₂ dispersion (30)	-	-	15.0	-	15.0	-
Total	100.0	100.0	100.0	100.0	100.0	100.0

3. Results.

3.1. Analysis of Mechanism for Water-dispersibility of Hydrophobic-treated TiO₂

3.1.1. Evaluation of Anionic Surfactant's Zeta Potential on TC-treated Surface

The change in zeta potential at TC-treated surface substrate/0.01wt% AOT electrolyte solution interface (blue line) was larger than that of SLS and PL (yellow and green line) (Figure 1 (left)). These results suggest better water-dispersibility of TC-treated TiO₂ by charge repulsion of AOT. These Zeta potentials correspond the result of simple wettability test of TC-treated TiO₂ with anionic surfactants (AOT, SLS and PL) in aqueous solution (Figure 1 (right)). The TC-treated TiO₂ is fully dispersed in the AOT solution. However, the SLS and PL solution did not fully disperse the hydrophobic TiO₂, as seen by the separation of layers.

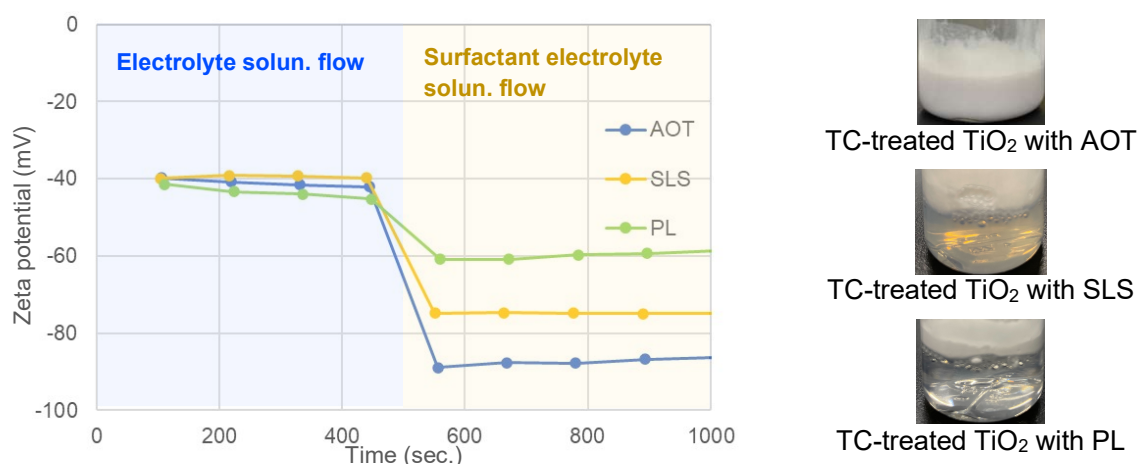


Figure 1. Zeta Potentials at TC-treated Surface Substrate/Anionic Surfactant Electrolyte Solution Interface (left) and Simple Wettability Test of TC-treated TiO₂ with Anionic Surfactant (right)

3.1.2. Visual Wettability Test of Hydrophobic-treated TiO₂ with AOT

As the results of wettability test (Figure 2), wettability of TC-treated pigment TiO₂ with AOT was higher than that of hydrogendimethicone- and isostearic acid-treated pigment TiO₂. This result indicates AOT has an affinity for TC-treated surface.

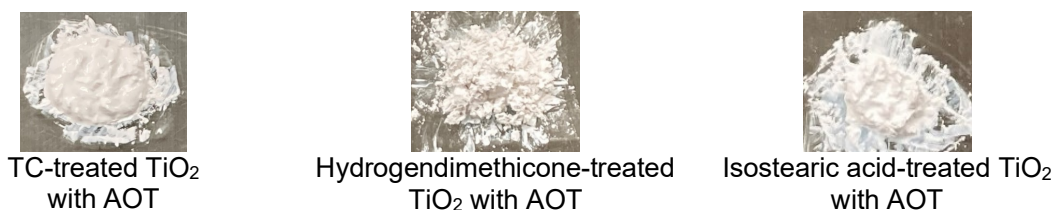


Figure 2. Wettability Test of Hydrophobic-treated Pigment TiO₂ with AOT Aqueous Solution

3.2. Analysis of Mechanism for Expression of Water-resistance of Cosmetic Film

3.2.1. Evaluation of Anionic Surfactant's Structure Formation on TC-treated Surface

The GISAXS 1D profiles of anionic surfactants are shown in Figure 3. For AOT applied glass substrate, two peaks with the ratio of 1: $\sqrt{3}$ were observed. Thus, it was suggested that the observed hexagonal structure on the substrate was the reverse hexagonal structure from the AOT/water two phase diagram [4,5]. On the other hand, the three peaks with the ratio of 1: 2: 3 due to lamellar structure were observed for the substrates applied SLS and PL. Specially, the two kind of lamellar structure observed by PL applied substrate was confirmed the dependence on the material by the result of powder SAXS measurement for only PL. Thereby, it was confirmed that AOT formed reverse hexagonal structure on the TC-treated glass substrate.

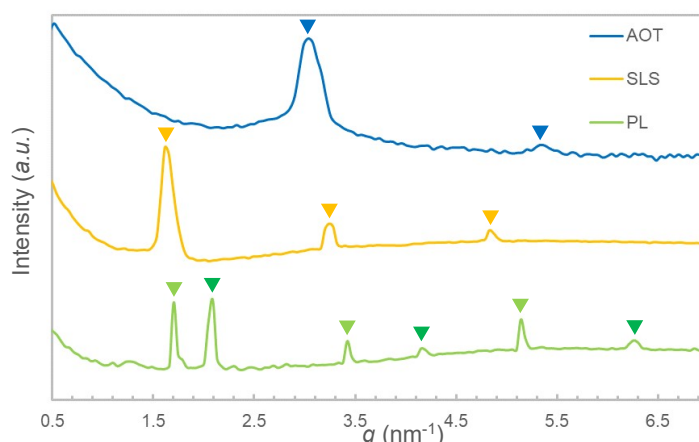


Figure 3. GISAXS 1D Scattering Profiles of Anionic Surfactants on TC-treated Glass

3.3. Application of the ‘Developed’ Aqueous Dispersion to Sun-care Products

3.3.1. Water-resistance Evaluation of O/W Sun-care Products Formulating Developed Aqueous Dispersion

In visual observation, cosmetic film made of formulation with ‘developed’ aqueous dispersion showed better water-resistance than that of formulation with ‘comparison’ (Figure 4 (left)). In another test using UV absorbance, the cosmetic film made of formulation with ‘developed’ aqueous dispersion had small variation of UV absorbance before and after spraying deionized water (blue solid and broken line in Figure 4 (right)). On the other hand, UV absorbance of cosmetic film made of formulation with ‘comparison’ aqueous dispersion dropped after spraying deionized water (gray solid and broken line in Figure 4 (right)). Thus water-resistance of cosmetic film made of O/W sun-care formulation with ‘developed’ aqueous dispersion was confirmed by visual observation and UV absorbance.

Droplet on cosmetic film of O/W formulation with development



Droplet on cosmetic film of O/W formulation with comparison

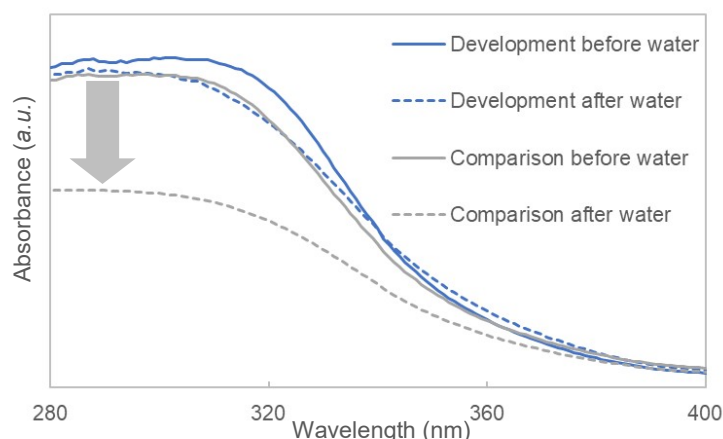


Figure 4. Water-resistance Evaluation of Cosmetic Film Made of O/W Sun-care Formulation by visual observation (left) and UV Absorbance Before and After Exposure to Water (right)

3.3.2. Study of O/W Sun-care Product’s UV Shield Capability by Controlling Phase (inner/outer) of Formulated Metal Oxides

UV absorbance of cosmetic film made of Practical example: O (TiO₂)/W (TiO₂) (blue line) was clearly higher than that of Conventional example: O (TiO₂)/W (gray line) (Figure 5), and this means that the Practical example has superior UV shield capability.

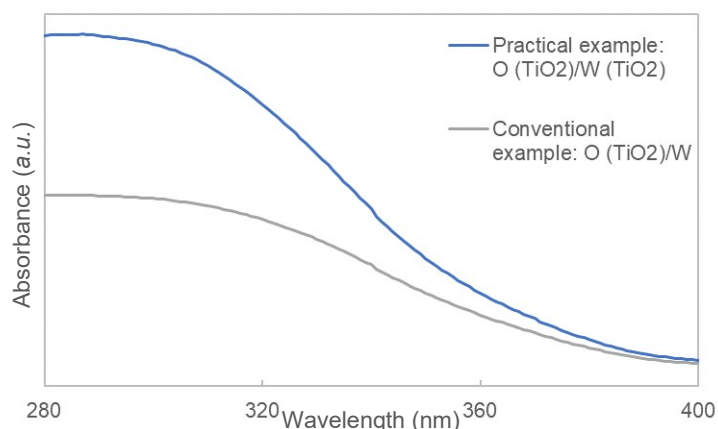


Figure 5. UV Absorbance of Cosmetic Film Made of O/W Sun-care Formulation Controlling Phase (inner/outer) of Formulated Metal Oxides

3.3.3. Study of W/O Sun-care Product's UV Shield Capability by Controlling Phase (inner/outer) of Formulated Metal Oxides

UV absorbance of cosmetic film made of Practical example: W (TiO₂)/O (TiO₂) (blue line) was higher than that of Conventional example: W/O (TiO₂) (gray line) (Figure 6), and this means that Practical example: W (TiO₂)/O (TiO₂) has superior UV shield capability.

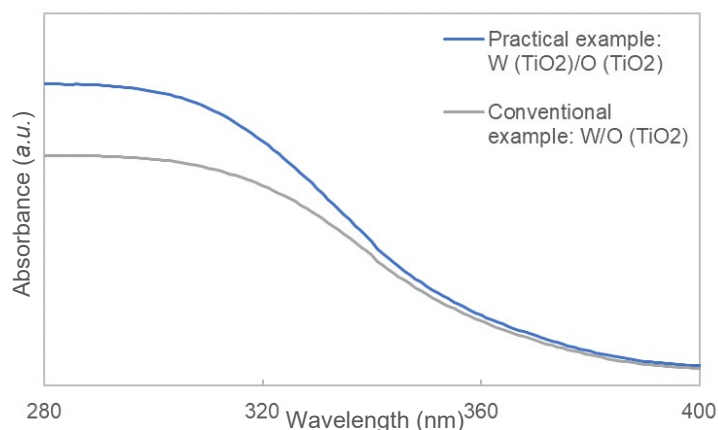
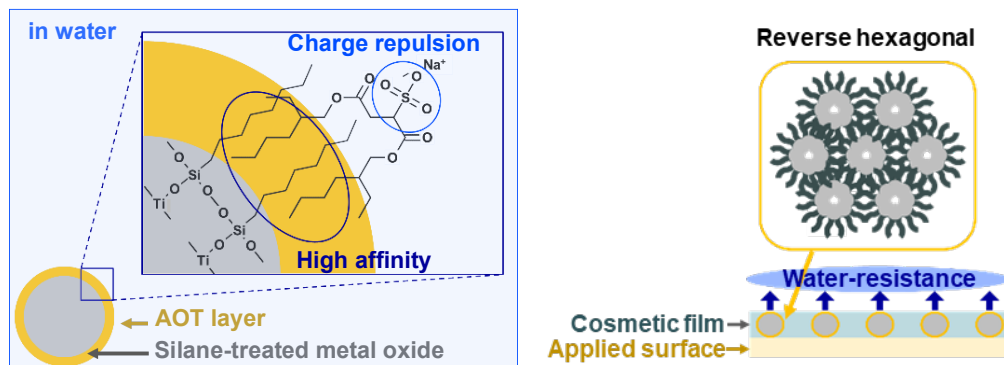


Figure 6. UV Absorbance of Cosmetic Film Made of W/O Sun-care Formulation Controlling Phase (inner/outer) of Formulated Metal Oxides

4. Discussion.

In analysis of the mechanism for water-dispersibility of hydrophobic-treated TiO₂, according to the result of zeta potential of TC-treated surface substrate/anionic surfactant electrolyte solution interface, it was suggested that TC-treated TiO₂ was dispersed in water stably by charge repulsion of AOT. In addition, in the result of the wettability test of hydrophobic-treated TiO₂ with AOT, favorable affinity between TC-treated surface of the TiO₂ and alkyl chains of AOT was also suggested (Scheme 1 (left)). In analysis of the mechanism for expression of water-resistance of cosmetic film, evaluation of anionic surfactant's structure formation on TC-treated surface by GISAXS and binary phase diagram of AOT/water system, formation of self-assembled reverse hexagonal of AOT was confirmed. When 'developed' aqueous dispersion was applied onto surfaces and was subsequently dried, it refuses redispersion when exposed

to water. Prevention of metal oxides redispersion in water by hydrophobicity of the reverse hexagonal contributed to expression of water-resistance of the cosmetic film (Scheme 1 (right)).



Scheme 1. Mechanism for Water-dispersibility (left) and Water-resistance (right)

In the study of O/W sun-care product's UV shield capability, the O/W sun-care product formulated with metal oxides in both inner phase and outer phase (Practical example) demonstrated superior UV shield capability than that of conventional O/W sun-care product that was formulated with metal oxides in inner phase only (Conventional example). This suggests that uniform distribution of metal oxides in cosmetic film is more effective for UV shielding (Table III (above)). In study of W/O sun-care product's UV shield capability, the W/O sun-care product formulated with metal oxides in both inner phase and outer phase (Practical example) demonstrated superior UV shield capability than that of conventional W/O sun-care product formulated with metal oxides in outer phase only (Conventional example). This suggests that in W/O sun-care formulation, uniform distribution of metal oxides in cosmetic film is also more effective for UV shielding (Table III (bottom)).

Table III. Position of Formulated Metal Oxides in Design of O/W Sun-care Products (above) and W/O Sun-care Products (bottom)

O/W Formulation	Oil phase	Water phase	Water	Oil	Metal oxide
Practical example	TiO_2	TiO_2			
Conventional example	TiO_2				

W/O Formulation	Water phase	Oil phase	Water	Oil	Metal oxide
Practical example	TiO_2	TiO_2			
Conventional example		TiO_2			

O/W sun-care products formulated with the 'developed' aqueous dispersion are expected to have the following advantages.

1. High content of metal oxides in the formulation will be more possible because metal oxides are formulated into outer water phase as broad continuous phase. In addition, compared to formulating metal oxide oil dispersion into inner oil phase, better texture is prospected because of reducing of oil content in inner oil phase.
2. Enhancement of water-resistance and UV shield capability is to be anticipated due to the formulation of hydrophobic-treated metal oxides into both inner and outer phase.

5. Conclusion.

In summary, unique aqueous TiO₂ dispersion having water-resistance property upon drying was developed by dispersing TC-treated TiO₂ into water stably with AOT as dispersing agent. The O/W sun-care product formulated with the 'developed' aqueous TiO₂ dispersion demonstrated water-resistance when turned into a cosmetic film. In the mechanism for water-dispersibility of hydrophobic-treated TiO₂, it was suggested that this is due to charge repulsion of AOT and favorable affinity between TC-treated surface and AOT. In the mechanism for water-resistance of cosmetic film, it was suggested that formation of self-assembled hydrophobic reverse hexagonal of AOT contributed to the water-resistance. By utilizing this technology, development of O/W and W/O sun-care products that has superior water-resistance and UV shield capability will be expected.

Conflict of Interest Statement.

NONE.

References.

1. ISO 16217:2020 Cosmetics — Sun protection test methods — Water immersion procedure for determining water resistance.
2. ISO 18861:2020 Cosmetics — Sun protection test methods — Percentage of water resistance.
3. J Nakano, S Nakamura, T Misono, N Nagatani, T Suzuki (2023) *1st Annual Congress of SCCJ*.
4. J Rogers, P. A. Winsor (1967) Optically Positive, Isotropic and Negative Lamellar Liquid Crystalline Solutions. *Nature* 216:477.
5. H Kunieda, K Sinoda (1978) Solution Behavior of Ionic Surfactants Containing Two Long-chain Alkyl Groups. *J. Jpn. Oil Chem. Soc. (YUKAGAKU)* 27 (7):417–424.