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## ***“Development and application of spontaneous cleansing technology to remove makeup gently for skin only by applying and rinsing with water”***

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### **1. Introduction**

Ideally, makeup should be thoroughly removed at the end of the day and go to sleep with perfectly cleansed skin. Makeup removers are essential for removing UV care products and cosmetic residues that cannot be effectively removed by facial cleansers. The practice of “double cleansing” using separate cleansers for makeup removal and facial cleansing has become a common skincare method among makeup users, contributing to the expansion of the cleansing product market. This market growth has also been influenced by advancements in cosmetic formulation technologies, evolving beauty trends, increased female workforce participation, and changes in lifestyle environments. In recent years, the normalization of makeup use regardless of gender has further accelerated this trend. Contemporary makeup styles range from minimalistic applications emphasizing powder foundations and lipsticks to more intensive routines involving long-wearing liquid foundations and waterproof mascaras. Among these, long-wearing liquid foundations and waterproof mascaras are particularly challenging to remove using water because they are composed of hydrophobic powders and oil phases containing film-forming agents and solid fats.

There are two primary methods of makeup removal. One involves soaking a cotton pad with a cleansing agent and wiping off the makeup. However, this approach often requires multiple pads and vigorous rubbing to effectively remove long-wearing makeup, which can lead to excessive resource use and skin irritation[1,2]. The other method entails applying a cleansing agent directly by hand, massaging it into the skin to blend with makeup, and then rinsing it off with water [3,4,5]. While this method is more resource efficient, it still requires thorough manual massage to achieve complete removal; areas not sufficiently massaged may retain residual makeup. Therefore, developing a new spontaneous cleansing technology that can completely remove makeup by simply applying a cleansing agent (oil-based makeup remover) and rinsing with water without massage has been required.

## 2. Materials and Methods

### 2.1. Confirmation of makeup spontaneous cleansing ability using various surfactant oil solutions

Various nonionic surfactants were dissolved at 20 wt% in an oil agent (triglycerides, viscosity: 110 mPa·s) to prepare surfactant oil solutions, which were used as a cleansing agent. Liquid foundation was applied to the polyurethane model substrate, and after drying, a drop of the cleansing agent was then applied using a dropper, followed by two different treatment conditions; (1) with physical force, by rubbing the surface 10 times using a finger applying approximately 100g of pressure, and (2) without physical force, by allowing the sample to stand for 1 min. After treatment, the substrate was rinsed with tap water and dried. The cleansing efficacy was evaluated by measuring the color difference before and after cleansing using a spectrophotometer (CM-600d, Konica Minolta), and the cleansing ability rate was calculated accordingly.

#### **Nonionic surfactant used** (HLB quotes catalog values)

- Alkyl Ethoxylate ( $C_{12}EO_3$ ) (Kao Corporation, Emulgen 103, HLB: 8.1)
- Alkyl Ethoxylate ( $C_{12}EO_6$ ) (Kao Corporation, Emulgen 106, HLB: 10.5)
- Alkyl Ethoxylate ( $C_{16}EO_3$ ) (Japan Emulsion Co., Ltd., EMALEX 103, HLB: 7.1)
- Polyethyleneglycol Dilaurates ( $EO_4$ ) (Japan Emulsion Co., Ltd., EMALEX 200di-L, HLB: 5)
- Polyoxyethylene Glyceryl Triisostearates ( $EO_{20}$ ) (Miyoshi Oil & Fats Co., Ltd., M Fine Oil ISG-20T, HLB: 10.9)

### 2.2. Analysis of the spontaneous cleansing mechanism of makeup

#### 2.2.1 Observation of the cleansing process

A liquid foundation was first applied to the model substrate and allowed to dry. Then, a drop of cleansing agent was applied using a dropper and left to stand, followed by rinsing with water. The behavior during the standing period and during rinsing was observed using a digital microscope (VHX-5000, KEYENCE). In addition, a model mixture consisting of a 10 wt% surfactant triglyceride solution and 1 wt% foundation powder was applied to the model substrate and immersed in water. The behavior of oil droplets under immersion was similarly using the digital microscope.

#### 2.2.2 Measurement of Oil Droplet Contact Angle ( $\theta$ )

A drop of cleansing agent (8 wt% surfactant triglyceride solution) was placed on a model substrate and the contact angle of the oil droplet in ion-exchanged water was measured over time using the inverted pendant drop method with a contact angle meter (DM-501Hi, Kyowa Interface Science Co., Ltd.).

#### 2.2.3 Measurement of dynamic oil-water interface tension ( $\gamma_{ow}$ )

The dynamic oil-water interfacial tension ( $\gamma_{ow}$ ) between the cleansing agent and water was measured by the drop volume method using a dynamic interfacial tension meter (DVT50, KRUSS).

#### 2.2.4 Confirmation of hydration by FT-IR peak shift at the time of water contact

100  $\mu$ L of water was contacted with 1  $\mu$ L of  $C_{12}EO_3$ , 90wt% triglyceride solution, and the ATR-IR spectrum was measured over time. (Spectrum3, Perkin Elmer)

## 2.3. Verification of the effect on the face

### 2.3.1 Evaluation of makeup removal on the face

A commercially available liquid foundation was applied to the entire face and left for 2 hours. Subsequently, a commercially available oil-based makeup remover or a developed product incorporating spontaneous cleansing technology was gently spread over the entire face without massage. After 30 seconds, the face was rinsed with water and lightly patted dry with a towel. Facial images were taken with a facial photographic device (VISIA-CR, Canfield Scientific) and a digital microscope. The residues on the face were transferred using a coating agent and analyzed by a digital microscope and SEM-EDX. (SEM: Miniscope TM3030, Hitachi High-Tech, EDX: Quantax, Bruker AXS, JSM-7600F, JEOL)

### 2.3.2 Measurement of skin moisture before and after use

The face was washed using a commercially available cleanser and gently wiped it dry with a paper towel. After acclimatization for 15 minutes in a room maintained at 20 °C and 40% humidity, the water content of the cheeks was measured with a cornometer. This value was recorded as the baseline skin hydration level before cleansing with the makeup remover. After that, the developed product was then lightly spread over the face, rinsed off with water until no slimy residue remained, and the skin was gently blotted dry with a paper towel. After another 15 min. acclimatization under the same environmental conditions,, the water content of the cheek area was measured with a cornometer, and the amount of water after cleansing with makeup remover was determined. The rate of change in skin moisture content due to the use of makeup remover developed products was calculated by [moisture content after cleansing] / [moisture content before cleansing].

Measurement date: 2023/6/13~21

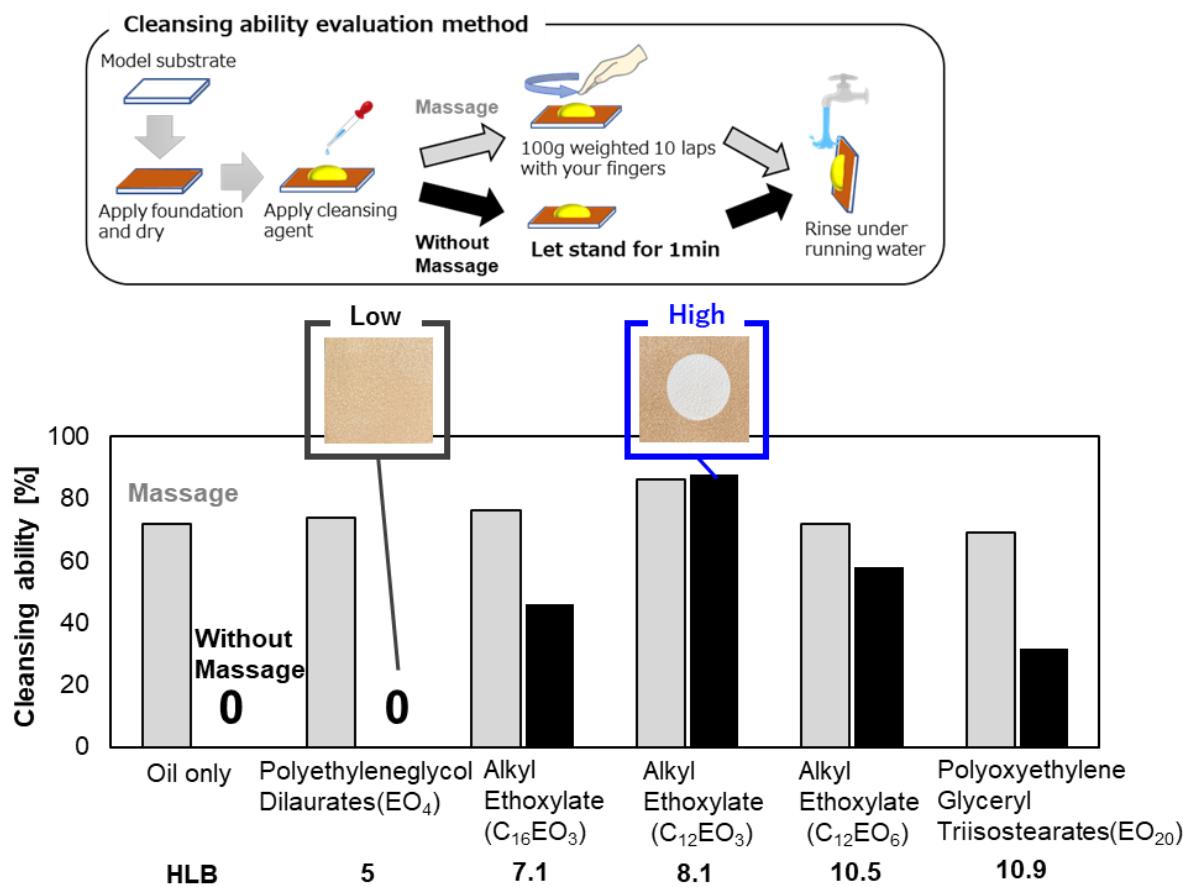
Subjects: Healthy skin males=9

## 3. Results

### 3.1 Evaluation of Spontaneous Makeup Cleansing Performance Using Various Surfactant Oil Solutions

The results are shown in Figure 1. Under conditions with applied physical force, all tested surfactant oil solutions exhibited high cleansing performance, regardless of the surfactant type, indicating that the solubility of the makeup in the oil phase plays a dominant role.

In contrast, under conditions without physical force, the cleansing performance varied significantly depending on the surfactant type. Most formulations showed a marked decrease in cleansing ability compared to the physical force condition. However, the formulation containing an alkyl ethoxylate with a moderate HLB value ( $C_{12}EO_3$ , HLB 8.1) exhibited remarkably high spontaneous cleansing performance.



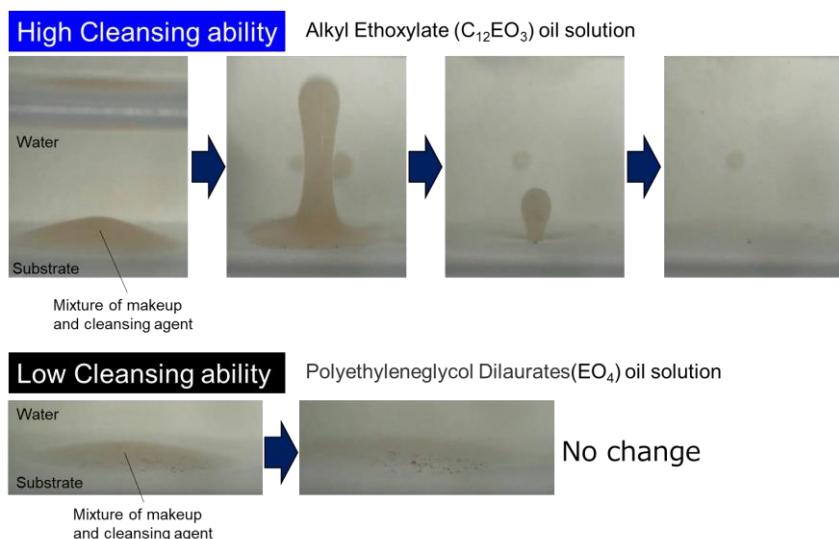
**Figure 1.** Cleansing ability of an oil solution including various nonionic surfactants with different HLB values.

### 3.2 Mechanism of Spontaneous Cleansing of Makeup

#### 3.2.1 Visual observation of the cleansing process

Although FT-IR analysis confirmed that the oily components of the makeup were miscible with the cleansing agent upon application, no visible changes were observed, and the makeup appeared to remain on the substrate. However, upon rinsing the substrate with water, the removal of makeup was clearly observed for the first time.

To better understand the behavior during rinsing, the interaction between water and a mixture of cleansing agent and makeup on a solid substrate was observed from the side. In the case of effective cleansing agents, the removal of makeup occurred via a rolling-up like motion, in which both the cleansing agent and makeup detached together from the surface (Figure 2). In contrast, when using a low cleansing ability oil solution of polyethylene glycol dilaurate (EO<sub>4</sub>), both the cleansing agent and makeup remained adhered to the substrate even after water was added.



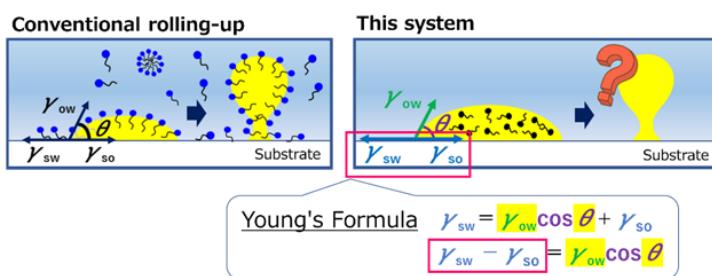
**Figure 2.** Observation results of the rinsing process.

### 3.2.2 Analysis of the rolling-up phenomenon based on interfacial tension changes

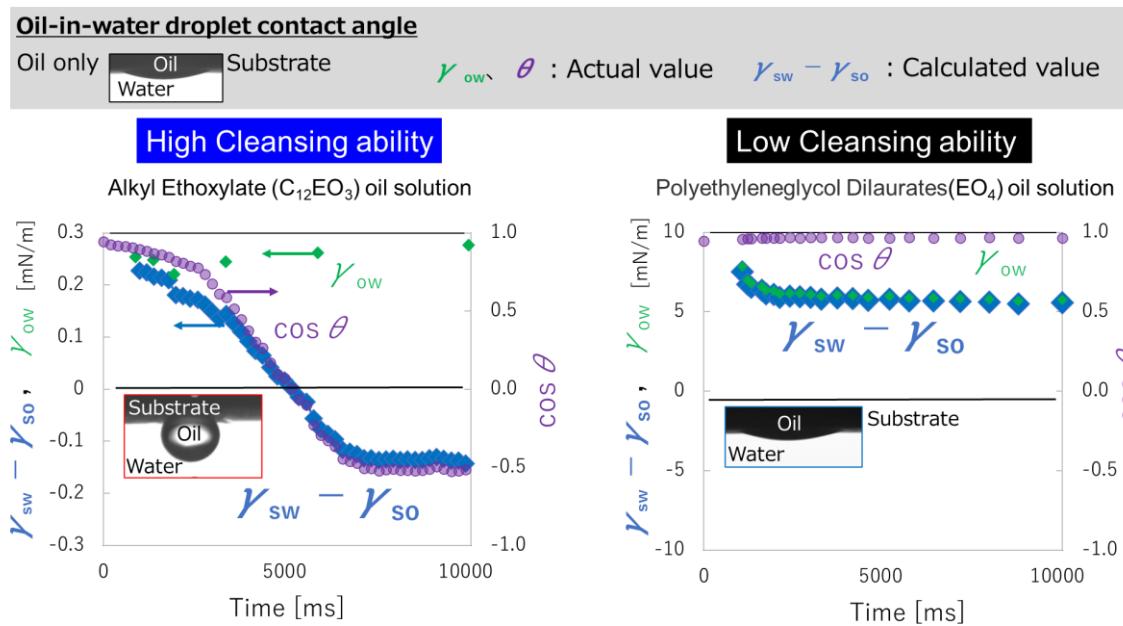
The rolling-up phenomenon arises from changes in the balance of interfacial forces acting along the three-phase contact line of an oil droplet in water. Typically, rolling-up occurs when a surfactant in the aqueous phase reduces the solid–water interfacial tension ( $\gamma_{sw}$ ), thereby altering this balance (Figure 3).

However, in the present system, the surfactant exists solely in the oil phase. Therefore, to evaluate this dynamic process, time dependent contact angles ( $\theta$ ) were obtained from video analysis, and combined with separately measured dynamic oil–water interfacial tensions ( $\gamma_{ow}$ ). Using Young's equation,  $\gamma_{ow} \cos\theta$  was calculated to estimate the temporal variation of the horizontal force balance along the three-phase contact line, expressed as  $\gamma_{sw} - \gamma_{ow}$ .

The results are shown in Figure 4. In the  $C_{12}EO_3$  oil solution,  $\gamma_{sw} - \gamma_{ow}$  decreased substantially over time and eventually became negative. According to thermodynamic principles, interfacial tensions do not increase spontaneously, suggesting that the observed decrease was due to a reduction in  $\gamma_{sw}$ . This implies that the reduction in  $\gamma_{sw}$  shifted the force balance along the three-phase contact line inward, promoting the rolling-up motion. In contrast, the dilauric acid polyethylene glycol ( $EO_4$ ) oil solution showed only minor changes in  $\gamma_{sw} - \gamma_{ow}$ , indicating that  $\gamma_{sw}$  did not significantly decrease.



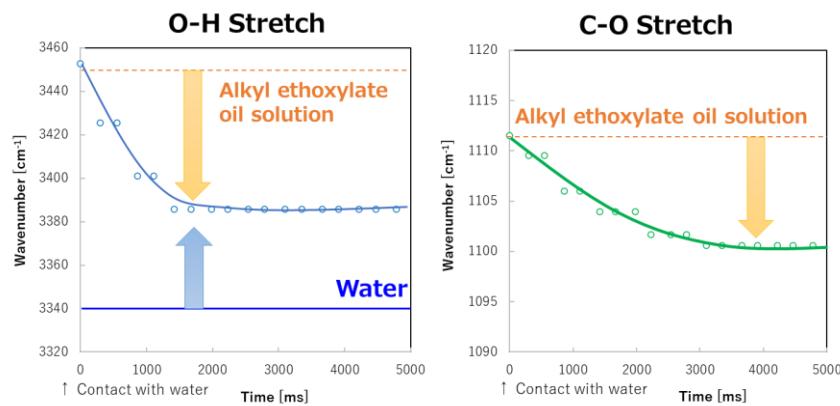
**Figure 3.** Analysis method of the rolling up phenomenon.



**Figure 4.** Calculation of interfacial tension change over time.

### 3.2.3 FT-IR spectral changes of the $C_{12}EO_3$ oil solution upon contact with water

The results are presented in Figure 5. Upon contact with water, the O-H stretching and C–O stretching bands of  $C_{12}EO_3$  in the oil phase immediately shifted to lower wavenumbers. From the aqueous side, the O-H stretching band shifted to higher wavenumbers. These spectral shifts suggest that  $C_{12}EO_3$  became hydrated upon contact with water.



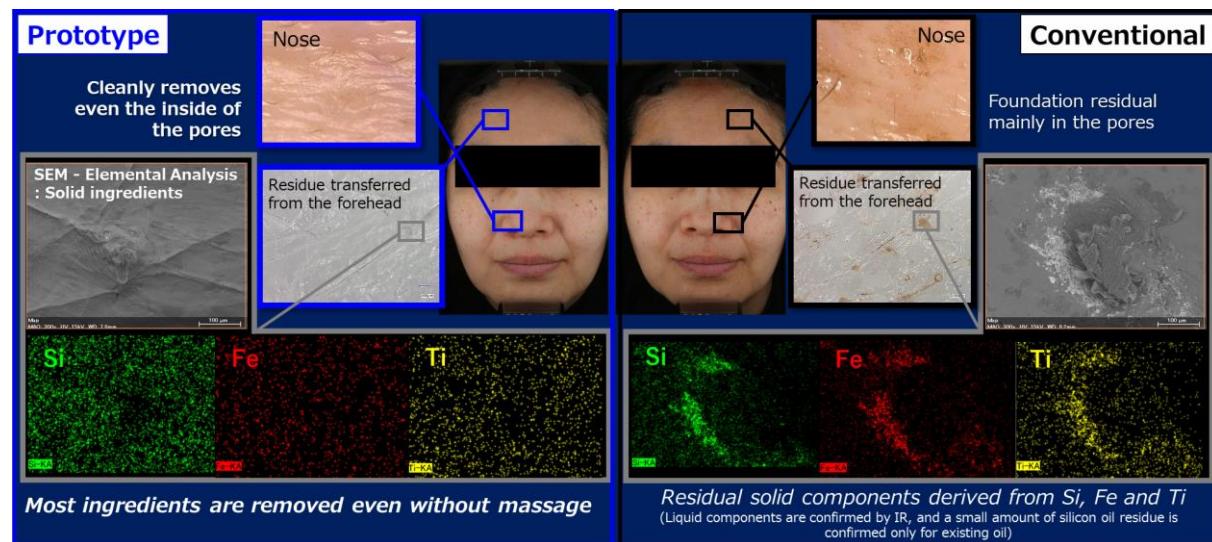
**Figure 5.** FT-IR spectral changes of  $C_{12}EO_3$  oil solution upon contact with water.

## 3.3 In Vivo Evaluation Using Human Facial Skin

### 3.3.1 Evaluation of makeup removal on the face skin

The results of visual observation and residue analysis after applying a makeup remover to foundation coated skin without massage and using only gentle spreading are shown in Figure 6. When a commercially available oil-based makeup remover was used, visible foundation residues remained, particularly around the pores, despite gentle spreading.

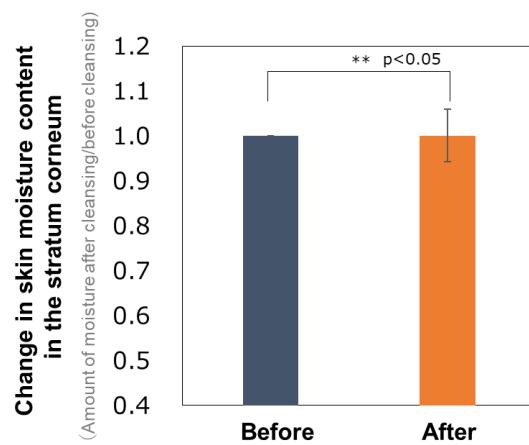
Residues transferred from the forehead were analyzed using SEM-EDX and infrared spectroscopy. The analysis revealed the presence of solid particles derived from silicon (Si), iron (Fe), and titanium (Ti), as well as traces of silicone oil. In contrast, when the prototype product incorporating the spontaneous cleansing technology was used, the vast majority of foundation components were removed, even without massage. This indicates that the developed product was able to remove makeup from pores under real use conditions.



**Figure 6.** The skin and residue after removing makeup without massage

### 3.3.2 Change in skin moisture content in the stratum corneum after use Before and After Use

The skin moisture content before and after using the prototype product with spontaneous cleansing technology is shown in Figure 7. No significant change in moisture level was observed, suggesting that the product cleanses the skin effectively without causing dryness or adverse effects.



**Figure 7.** Change in water content in the stratum corneum after use.

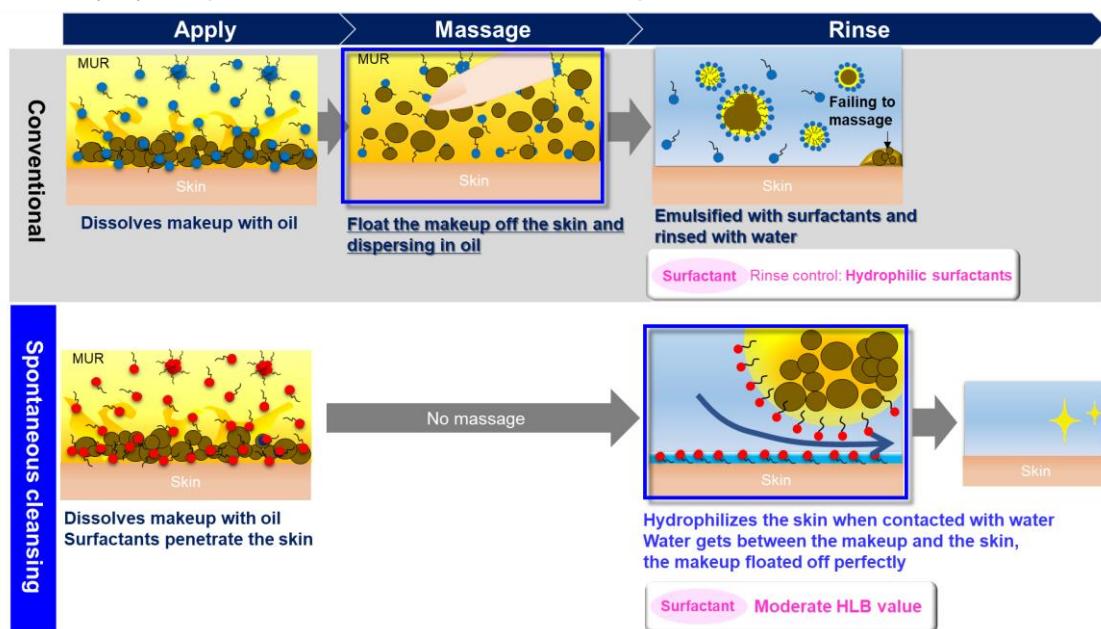
## 4. Discussion

### 4.1 Mechanism of Spontaneous Makeup Removal by Simply Applying and Rinsing Without Massage

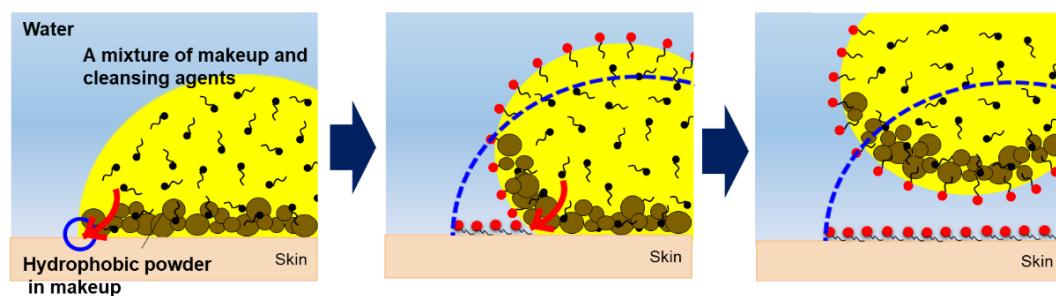
Conventional rinse-off makeup removers typically work by massaging the skin to loosen the makeup, followed by emulsification through nonionic surfactants during rinsing with water. In contrast, the present system enables makeup removal without massage, and visual observation revealed that makeup detachment occurred only upon rinsing with water (Figure 8).

Interfacial tension analysis suggested that when water contacts the cleansing agent on the substrate, the hydrophilic groups of the nonionic surfactant become hydrated, activating interfacial behavior. This causes the surfactant present only in the oil phase to act directly at the solid–water interface, lowering the solid–water interfacial tension ( $\gamma_{sw}$ ) and thereby enhancing wetting. As a result, water infiltrates between the makeup and the substrate, lifting the makeup cleanly from the surface (Figure 9).

Unlike traditional rolling-up mechanisms, which require a high concentration of surfactants in the aqueous phase, this mechanism allows efficient rolling-up by dissolving surfactants in the oil phase. This facilitates the targeted action of surfactants at the three-phase contact line. Thus, this is considered a novel and highly efficient rolling-up mechanism made possible specifically by the presence of surfactants in the oil phase.



**Figure 8.** Difference in cleansing process between conventional and spontaneous cleansing makeup remover.



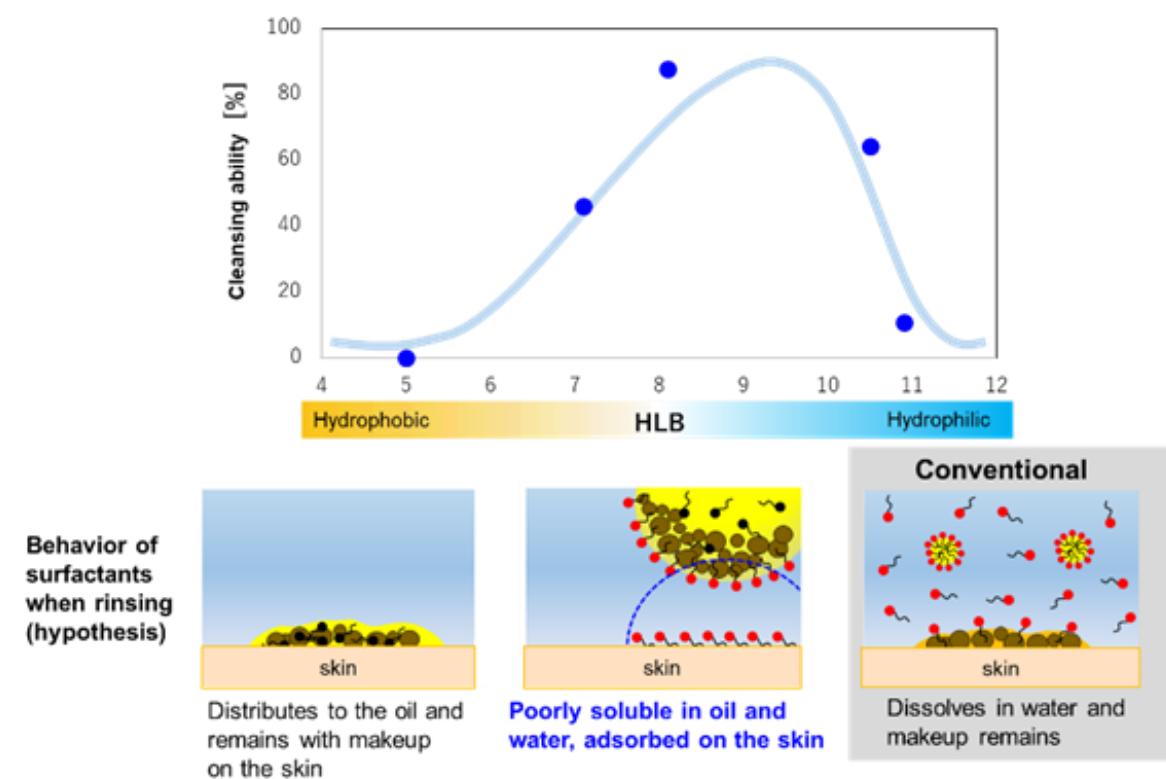
**Figure 9.** New cleansing mechanisms of makeup caused by surfactants dissolved in oil.

#### 4.2 Relationship Between HLB values of surfactants and spontaneous cleansing ability

The relationship between the hydrophilic-lipophilic balance (HLB) of surfactants and their spontaneous cleansing ability is shown in Figure 10. A clear correlation was observed: the highest cleansing ability was exhibited by an alkyl ethoxylate ( $C_{12}EO_3$ ) with a moderate HLB value of 8.1, which is lower than the typical HLB (~10) of nonionic surfactants used for emulsification during rinsing in conventional products.

From the previous results, this can be interpreted as follows: surfactants with low HLB values have high oil solubility and tend to remain dissolved in the oil or makeup phase, resulting in insufficient adsorption at the three-phase contact line. On the other hand, surfactants with high HLB values are highly water-soluble and tend to diffuse into the aqueous phase without adsorbing at the interface.

Surfactants with moderate, optimal HLB values neither highly soluble in water nor in oil remain at the solid surface and are capable of lowering  $\gamma_{sw}$ , thus effectively promoting makeup removal. These findings suggest that spontaneous cleansing is not a property of a specific surfactant structure, but rather a result of balanced interfacial characteristics in relation to water, oil, and substrate. Therefore, this mechanism could potentially be applied to a wide variety of surfactants, including naturally derived and “free-from” ingredients, making it suitable for eco-friendly and skin-friendly formulations.



**Figure 10.** Spontaneous cleansing ability of an oil solution including various nonionic surfactants with different HLB values.

#### **4.3 Value we can provide to consumers**

In evaluations using real human facial skin, it was observed that conventional oil-based makeup removers despite their reputation for high cleansing ability left noticeable foundation residues, particularly in pores, when rinsed without massage. In contrast, the prototype product developed with spontaneous cleansing technology successfully removed makeup even from recessed pore areas without rubbing.

Additionally, no reduction in skin moisture was observed before and after use, suggesting that the product is non-irritating and does not compromise skin hydration. Furthermore, consumer feedback indicated that the product not only removes makeup completely without rubbing but also simplifies the cleansing routine, reduces effort, and eliminates stress associated with makeup removal.

This technology where makeup can be removed simply by applying and rinsing without massage offers benefits beyond avoiding physical abrasion. It enables efficient removal from intricate areas such as pores, reduces the psychological burden of cleansing, and minimizes product usage. Since the product requires only a small amount of liquid and eliminates the need for cotton pads, it also contributes to resource efficiency.

#### **5. Conclusion**

Traditional makeup removal methods have relied on either rubbing with cotton pads or massaging with the hands to lift makeup from the skin. In this study, we successfully developed a novel cleansing technology that enables effective makeup removal without massage simply by applying an oil-based solution of a nonionic surfactant with an appropriate hydrophilic–lipophilic balance (HLB), followed by rinsing with water.

This cleansing mechanism is based on the observation that, upon contact with water, the surfactant present in the oil phase efficiently reduces the solid–water interfacial tension ( $\gamma_{sw}$ ). As a result, even strongly adhering makeup can be detached and lifted by the rinsing water alone. Notably, this rolling-up phenomenon is not driven by surfactants in the aqueous phase, but rather by those dissolved in the oil phase, which render the solid surface more hydrophilic. This represents a novel and intriguing mechanism of spontaneous cleansing.

The developed technology eliminates the need for cotton pads, requires only a minimal amount of liquid to cover the face, and enables thorough removal of makeup including from recessed areas such as pores without the need for physical contact or friction. This approach is expected to significantly reduce both the psychological burden of makeup removal and the environmental impact associated with conventional cleansing methods.

#### **References.**

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