Pickering Emulsifiers Balancing Excellent Sensory and Emulsion Stability

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Emulsifiers are substances that work at interface between two incompatible components such as oil and water, and to create a stable emulsified state of these components. They are widely used in various cosmetics such as emulsions, creams, and sunscreens. Generally, surfactants that dissolve in water or oil are mainly used as emulsifiers, but when applied to the skin as a cosmetic, they may cause adverse effects such as negative sensory sanitation of slimy feel, characteristic odor, and makeup-comes-off due to sweat. Furthermore, surfactants do not necessarily impart stable emulsions to all types of oils, requiring the combination of several appropriate surfactants for different oil types.

This paper introduces a new emulsifier, "SOLIEMAR®" (under development), which solves these surfactant issues.

What is Pickering Emulsification?

Pickering emulsification, a well-known method for solving the above mentioned issues in emulsification without the use of surfactants, uses solid particles insoluble in water and oil as emulsifiers[1]. In pickering emulsification, unlike surfactants, the solid particles used as emulsifiers are characterized by the high adsorption energy to the oil-water interface. Consequently, the resulting emulsion exhibits remarkable emulsification stability as it is physically stabilized by the solid particles **(Figure 1)**.

However, when applied to cosmetics, picking emulsification may be adversely affected by other cosmetic ingredients, leading to poor emulsification and stability. In addition, since the solid particles used in Pickering emulsification (Pickering emulsifier) are often very fine nano-sized, there are issues such as unpleasant sensory due to solid particles such as creakiness and poor handling during formulation.

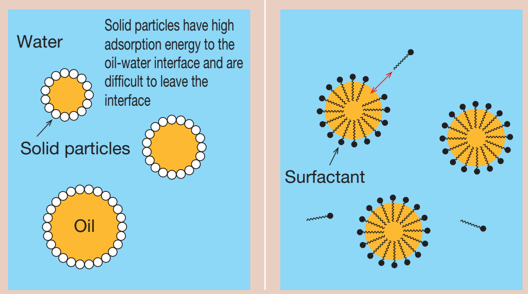
Types of Emulsifiers	Pickering emulsifier	Surfactant
Adsorption energy to interface	Large	Small
Emulsion stability	High	Low
Schematic diagram		

Fig. 1 Comparison of Pickering emulsifiers and surfactants

Pickering Emulsifier "SOLIEMER®" Achieving both Excellent Sensory and Emulsion Stability

By applying our expertise in interface control technology, we have developed the Pickering emulsifier "SOLIEMER®" that solves the issues associated with conventional Pickering emulsification. "SOLIEMER®" is a submicron-sized amphiphilic silica. Typically, obtaining a stable emulsion with solid particles of this size is difficult. However, through precise control of silica's size, shape, surface structure, and hydrophobicity, along with finding the optimal emulsification method in cosmetic formulations, we have successfully achieved stable emulsions.

Additionally, the emulsion expected to lead separation of the oil and water phase due to coalescence through creaming or Ostwald ripening. Thus, in a system such as the O/W emulsion of "SOLIEMER®" prepared this time, stability is generally considered to be low, but since "SOLIEMER®" forms a Pickering emulsion in which solid particles are oriented at the oil-water interface, it is considered to have high emulsification stability.

On the other hand, conventional Pickering emulsifiers require a high viscosity continuous phase in order to obtain stable emulsions, and the emulsification stability in accelerated tests was sometimes insufficient for some formulations. Moreover, nonionic surfactants, which are commonly used in cosmetic emulsions, have a very fine emulsion particles, providing high emulsion stability, but the sensory experience is expected to be the same as conventional formulation. But emulsions with large particle size obtained by using "SOLIEMER®" are expected to deliver the novel sensory experience that is difficult to achieve with nonionic surfactants.

Therefore, among the emulsions prepared in this study, sensory evaluation was conducted on emulsions prepared with "SOLIEMER®" and a nonionic surfactant, both having excellent emulsifications and emulsion stability, by five researchers who agreed to participate in the test **(Figure 6)**. In the sensory evaluation, the O/W emulsion with "SOLIEMER®" was evaluated regarding the feel during and after application, using his O/W emulsion using a nonionic surfactant as a standard (3 points). As a result, it was found that although the O/W emulsion of "SOLIEMER®" is a Pickering emulsion, its creakiness is equivalent to that of a nonionic surfactant, and it is also superior in its non-sliminess and freshness.

This is thought to be due to the fact that "SOLIEMER®" itself has a smooth texture, and since no surfactant is used, a non-slimy formulation can be made, maximizing the freshness that is a feature of emulsions with the larger particle size.

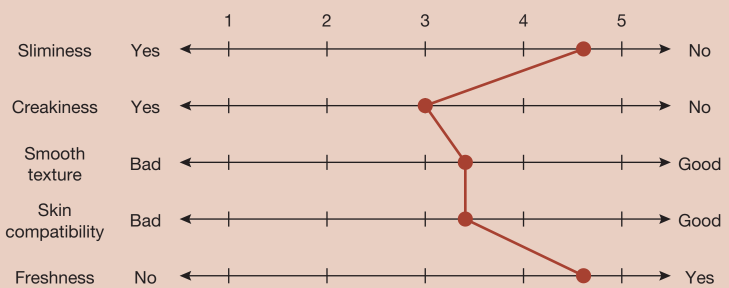


Fig. 6 Sensory evaluation of SOLIEMER® O/W emulsions based on nonionic surfactants

Future Plans

"SOLIEMER®" allows the preparation of O/W emulsions completely without surfactants, which suppresses the surfactant-derived sliminess and gives a fresh feeling of use. It is also expected to provide water resistance by preventing the re-emulsifying of oil on the skin due to sweat after applying the cosmetic product. Therefore, "SOLIEMER®" can be applied not only to lotions and emulsions, but also to sunscreen products and makeup products that require water resistance, which are normally prepared with water-in-oil (W/O). It is expected that it can be used as an emulsifier in various O/W emulsions.

References (This is a machine translation of Japanese references)

1) W. Ramsden, *Proc. R. Soc. London*, 72, 156-164(1903)
2) T. Okamoto, et al., *J. Soc. Cosmet. Chem. Jpn.*, 39(4), 290-297(2005)
3) K. Hamano, Y. Nakamura, Fine Chemicals, 52(12), 37-44(2023)

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obtained using "SOLIEMER®" is characterized by extremely large particle diameters. While large particle sizes in emulsions generally result in a fresh feel, they also tend to cause emulsion coalescence and reduce emulsion stability[2]). Nevertheless, since "SOLIEMER®" is a Pickering emulsifier, we were able to resolve this conflicting issue and successfully achieve a balance between excellent sensory and emulsion stability.

Preparation of Oil-in-Water (O/W) Emulsions Using "SOLIEMER®"

"SOLIEMER®" has hydrophobic trimethylsilyl groups and hydrophilic silanol groups on the particle surface, exhibiting amphiphilic properties. But it is difficult to disperse uniformly in water or oil and tends to agglomerate. Therefore, when simply adding and stirring "SOLIEMER®" to emulsify, much of it will aggregate.

To solve this problem, we considered that it would be effective to pre-disperse "SOLIEMER®" uniformly and then efficiently orient it toward the oil-water interface for emulsification. We discovered that the affinity of "SOLIEMER®" to the aqueous phase can be controlled by basic substances and lower alcohols, and established a new emulsion preparation method with high emulsification efficiency[3]).

First, disperse "SOLIEMER®" in water or oil to prepare the emulsion. Each emulsion formulation is shown in **Table 1**, and images of the prepared emulsions are illustrated in **Figure 2**.

In the formulation a in **Table 1**, "SOLIEMER®" was added to mineral oil, and while stirring at 8,000 rpm with a homo mixer, water and a 1% aqueous solution of Hydroxyethylcellulose (hereinafter referred to as HEC) were slowly added and stirred, then defoamed and left to stand to obtain an O/W emulsion.

Table 1 Emulsification formulation using SOLIEMER®

Ingredients	Formulation a	Formulation b
Water	0.0	20.0
SOLIEMER®	3.0	3.0
Mineral oil	20.0	20.0
Water	27.0	7.0
HEC* 1 % aq.	50.0	50.0
Total	100.0	100.0

*HEC: Hydroxyethylcellulose

Formulation a The method to disperse SOLIEMER® in oil for emulsification
Formulation b The method to disperse SOLIEMER® in water for emulsification

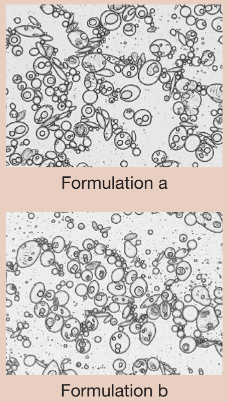


Fig. 2 Emulsion images of formulations a and b

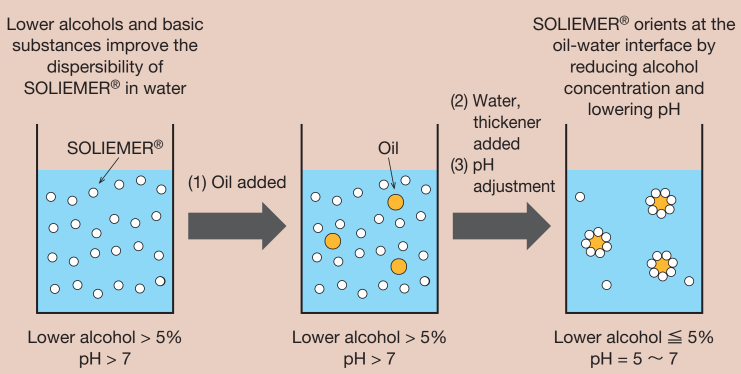


Fig. 3 The Discovered Emulsification Preparation Method for SOLIEMER®

Table 2 Emulsification formulation using SOLIEMER®

Ingredients	Formulation c (Fig.3)
Water	15.0
Isopentyldiol	5.0
Potassium Hydroxide 10% aq.	0.05
SOLIEMER®	3.0
Mineral oil	20.0
Water	6.9
HEC 1 % aq.	50.0
Citric acid 10% aq.	0.05
Total	100.0

Formulation c Emulsification method in Figure 3

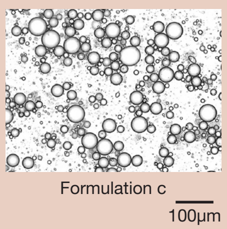


Fig. 4 Emulsion image of formulation c

In Formulation b, the order of blending ingredients was changed, and "SOLIEMER®" was added to water, and O/W emulsion was obtained by adding mineral oil, water, and HEC 1% aqueous solution in this order while stirring at 8,000 rpm using a homo mixer. As shown in the microscopic images of each O/W emulsion, aggregates of "SOLIEMER®" were observed as expected. Despite the vigorous stirring at 8,000 rpm with a homo mixer, "SOLIEMER®" did not disperse uniformly in either water or oil, leading to the formation of aggregates in the formulation. This indicates "SOLIEMER®" was not oriented efficiently at the oil-water interface, and there were concerns about a decrease in emulsification efficiency and adverse effects on the sensory experience of cosmetics.

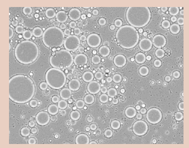
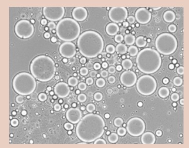
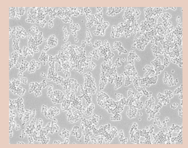
On the other hand, **Figure 3** shows our discovered emulsion preparation method of "SOLIEMER®". We focused on the zeta potential of silica in aqueous solution and the hydrophobicization of the aqueous phase by alcohol, and found that Pickering emulsions can be efficiently formed by using a basic substance and a lower alcohol. In Formulation c, we selected potassium hydroxide and isopentyldiol, commonly used in the cosmetics industry as a basic substance and lower alcohol, respectively, and HEC was selected as a thickener to stabilize the emulsion.

Emulsification was conducted based on the formulation in **Table 2**. First, "SOLIEMER®" was added to the aqueous phase containing potassium hydroxide and isopentyldiol. While stirring at 4,000 rpm with a homo mixer, oil, water, a 1% HEC aqueous solution, and a 10% citric acid aqueous solution as a pH adjuster were gradually added. The mixture was degassed and left to stand to obtain O/W emulsion. The results are shown in **Figure 4**. The obtained emulsion was confirmed to form a spherical O/W emulsion with no agglomerates of "SOLIEMER®". This result suggests that controlling the affinity of "SOLIEMER®" to the aqueous phase enabled efficient orientation at the oil-water interface.

In addition, emulsions prepared with formulas a and b had a lot of bubbles generated in the degassing process, but the emulsion prepared with formulation c had a very small amount of bubbles generated. This difference can be attributed to the high affinity of "SOLIEMER®" to the aqueous phase during the dispersion process in formulation c. "SOLIEMER®" did not orient at the gas-liquid interface due to its high affinity to the aqueous phase in its dispersion process. It was only after the addition of oil, water, and pH adjuster that the affinity to the aqueous phase was reduced, allowing "SOLIEMER®" to develop emulsification ability and orient at the oil-water interface. Based on these observations, our developed emulsification preparation method can achieve efficient Pickering emulsification by controlling the dispersibility of "SOLIEMER®" with basic substances and lower alcohols.

Performance Evaluation of Oil-in-Water (O/W) Emulsions using "SOLIEMER®"

Figure 5 shows the results of comparing the performance of O/W emulsions using "SOLIEMER®" with that of other emulsifiers. It was confirmed that "SOLIEMER®" has good emulsification properties, and the emulsion was maintained without oil separation even after an accelerated test at 50°C for 30 days. This result was the same for a variety of oils, from non-polar to polar and silicone oils, regardless of oil type. Generally, it is known that the particle size of an emulsion has a large effect on emulsion stability, and when the particle size of an emulsion is large or the particle size distribution is wide, the emulsions are

	SOLIEMER®	Conventional Pickering emulsifier	Nonionic surfactant
Emulsifying	+ Good	− Bad	++ Excellent
Stability (50°C/30 days)	++ Excellent	− Bad	++ Excellent
Microscope observation image			

100μm

Fig. 5 Performance comparison of emulsifiers