Environmental Benefit of Applying Polyglycerol Emulsifiers in Sun-protective Formulation

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Introduction:

Sun-protected products are facing increasing challenges today by the regulation restrictions and the consumer demand for higher performance. That is why SPF boosters are worthy of investigating and being applied to sun-protective formulations.

From the perspective of environmental protection, it is very important to reduce the risk of releasing UV-filters into the environment. During water activities, the sun-protective products are sometimes easy to wash off by the water and lead to the decrease of sun-protective ability. In order to maintain the protection ability, users need to reapply the products frequently, this action eventually rises the risk of releasing greater amount of UV-filter into the environment. By increasing the water resistance ability of sun-protective products, we can effectively avoid this kind of situations happening, and significantly reduce the possibility of polluting the environment.

Polyglycerol-based emulsifiers are surfactants formed by esterification of polyglycerol and fatty acid. The HLB of polyglycerol-based emulsifiers are affected by the polymerization degree of polyglycerol, chain length of fatty acid, and esterification degree. In the previous study, polyglycerol-10 ester had been exhibited good UV-filter solubility and applied in high SPF formulation[1], and improved water-resistant ability by paired with polymer additive[2].

This paper demonstrates the environmental benefits of using polyglycerol ester emulsifiers in sun-protective formulations. The SPF boosting and water-resistant ability of various type of polyglycerol emulsifiers are compared with the traditional PEG-based emulsifier. To further understand the mechanisms of SPF booting and the water resistance ability of polyglycerol ester as emulsifier and co-emulsifier, the results of the polarized micrograph, optical micrograph, and moisture-increment measurement are discussed. Based on the results, the polyglycerol-based emulsifiers, and co-emulsifiers are proven to be the great options for eco-friendly sun-protection formulations.

Materials & Methods:

1. Prepare the Formulations

Table 1. The formulations for tested in this study

	INCI Name	F-1	F-2	F-3	F-4	F-5	F-6	F-7	F-8
Phase A	Butyl methoxydibenzoylmethane	2	2	2	2	2	2	2	2
	Ethylhexyl methoxycinnamate	4	4	4	4	4	4	4	4
	Titanium dioxide	6	6	6	6	6	6	6	
	C12 -15 alkyl benzoate	5	5	5	5	5	5	5	5
	Isononyl isononanoate	5	5	5	5	5	5	5	5
	Caprilic/Capric triglyceride	5	5	5	5	5	5	5	5
	Polysorbate 85	4.2	-	-	-	-	-	-	-
	Polyglyceryl-10 laurate	-	4.2	-	-	4.2	4.2	4.2	4.2
	Polyglyceryl-4 laurate	-	-	4.2	-	-	-	-	-
	Polyglyceryl-4 caprate	-	-	-	4.2	-	-	-	-
	Cetearyl alcohol	2.8	2.8	2.8	2.8	-	-	-	2.8
	Polyglyceryl-2 isostearate	-	-	-	-	2.8	-	-	-
	Polyglyceryl-2 diisostearate	-	-	-	-	-	2.8	-	-
	Polyglyceryl-2 triisostearate	-	-	-	-	-	-	2.8	-
Phase B	Water	62.2	62.2	62.2	62.2	62.2	62.2	62.2	68.2
	Glycerin	3	3	3	3	3	3	3	3
	Xanthan gum	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Preservative	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

2. In vitro SPF measurement

SPF value measurement was conducted by applying the formulation on standard PMMA plate (Schonberg), placing the PMMA plate in a dark area for 15 min, then measuring by UV-2600i spectrometer (Shimadzu). All the SPF measurement procedure, parameters and calculation were according ISO 24443:2012.

3. Water resistance retention

The water resistance ability was evaluated by water resistance retention (%WRR), which was calculated by :

$$WRR(\%) = \frac{SPF_{iw} - 1}{SPF_{is} - 1} \times 100\ \%$$

The SPF_{iw} is SPF after water immersion test and the SPF_{is} is SPF before water immersion test.

- Water immersion test : formulation-coated PMMA plates were immersed in 3L water and stirred under 500rpm for 15 minutes. After removing residual water drops on the PMMA plate, SPF_{iw} can be measured.

Conclusions:

This study has verified the SPF boosting ability of various polyglycerol-based emulsifiers compared with traditional PEG-based emulsifier. The mechanism of SPF boosting by the formation of lamellar liquid crystal has been proved via polarized micrographs and the time-dependent SPF-lamellar liquid crystal relationship. Regarding the water resistance retention study, the formulation containing polyglyceryl-10 laurate paired with polyglyceryl-2 triisostearate improves the water resistance retention significantly due to the formation of W/O/W multi-emulsion. The various polyglycerol-based emulsifiers and co-emulsifiers show significant SPF boosting and great water resistance ability in the sun protection formulation, the UV-filter performance of SPF 30 has been boosted to SPF 50+ and water resistance retention is increased from 13.6% to 75.8%. The lower dosage of UV-filters and higher water resistance ability both can reduce the risk of UV-filters entering the environment, in addition, reduce the impact on ecology, especially marine organisms. Based on the results of this paper, the polyglycerol-based emulsifiers and co-emulsifiers have proven suitable and recommended for use in high-performance environmentally friendly sun protection formulations.

Results & Discussion:

1. Emulsifier and co-emulsifier effects

Table 2. The SPF and water resistance retention for different type of emulsifier and co-emulsifier

	F-1	F-2	F-3	F-4	F-5	F-6	F-7
Emulsifier	Polysorbate 85	Polyglyceryl-10 laurate	Polyglyceryl-4 laurate	Polyglyceryl-4 caprate	Polyglyceryl-10 laurate	Polyglyceryl-10 laurate	Polyglyceryl-10 laurate
Co-Emulsifier	Cetearyl alcohol	Cetearyl alcohol	Cetearyl alcohol	Cetearyl alcohol	Polyglyceryl-2 isostearate	Polyglyceryl-2 diisostearate	Polyglyceryl-2 triisostearate
SPF	30.4	47	46.1	49	46.9	45	59.8
WWR	13.6	38.4	34	30.2	13.1	13.9	75.8

2. The Mechanism of SPF Boosting

- Polarized light microscopy observation

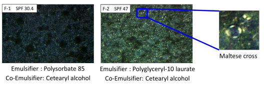

Fig 1. Polarized light microscopy observation

The polarized light micrograph of formulation F-2, Maltese cross could be observed clearly which often appeared in the polarized light micrograph of lamellar liquid crystal emulsions.

- Time-dependent SPF-lamellar liquid crystal relationship

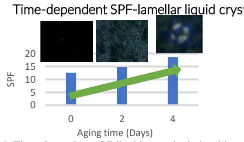

Fig 2. Time-dependent SPF-liquid crystal relationship

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- Mechanism of SPF Boosting

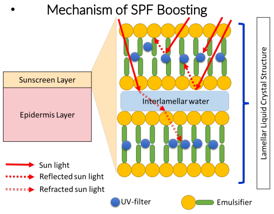

Fig 3. SPF enhanced by interlamellar water

The refraction phenomena as presenting by light passing through a boundary between two different media.
The lamellar-structure and interlamellar water provide the condition to enhance the light refraction, and increase optical path length to act as SPF booster.

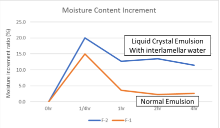

Fig 4. Moisture-increment enhanced by interlamellar water

The formulations (F-2 and F-1) with higher moisture-increment (F-2) is tend to form more liquid crystal structure, afterwards lead to SPF boosting effect.

$$\text{Moisture increment}(\%) = \frac{M_f - M_b}{M_b} \times 100\%$$

The M_f and M_b are moistures of formulation on applied region and blank region respectively

3. The Mechanism of WWR

- The Co-emulsifier Effect of WRR

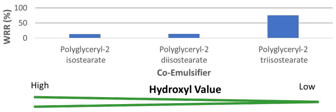

Fig 5. The polarity of Co-emulsifier Effect on WRR

The co-emulsifiers with lower hydroxyl value (non-polar) provide the higher water resistance retention.

- Optical Microscopy Observed of Micelle

The W/O/W multi-emulsion provide the higher WRR than normal O/W emulsion.

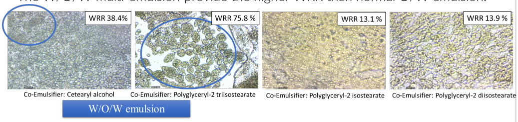

Fig 6. Optical Microscopy Observed of W/O/W emulsion and O/W emulsion

- Mechanism of WRR enhanced in W/O/W emulsion

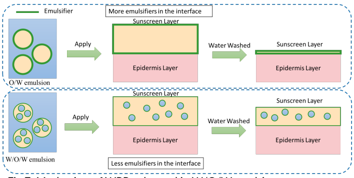

Fig 7. Mechanism of WRR enhanced in W/O/W emulsion

The W/O/W emulsion need to share the emulsifier to the interface of water-in-oil micelle, therefore the less emulsifier on the surface of oil during the washing process.

References:

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2. *YU JIA; LI XIUZHI. (2013) Emulsion composition used for water resistant liquid crystal cosmetics and application thereof. YUMEIJING GROUP CO LTD*