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Development of a Sunscreen Stick Formulation which is Water Resistant but Easily Washable

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Abstract: The aim of this study is to develop a sunscreen stick formulation technology with excellent water resistance and washability. Consumers' needs for sunscreen products are diversifying. Water resistance and ease of washing are both important factors in sunscreen products. However, it is difficult to develop a sunscreen formulation that satisfies these two factors at the same time, because these two elements are in conflict. Fatty acid has a hydrophobic property against the water with low or neutral pH, but when it contacts with soapy water which has high pH, saponification occurs and the fatty acids become surfactants and can be dispersed in the water. Using the reaction characteristics of fatty acids, we can make sunscreen that is highly resistant to water or sweat, but is only selectively removed from soapy water. We found that the sunscreen stick containing fatty acids had better water resistance and washability than the sunscreen sticks without fatty acid. The sunscreen stick containing fatty acids showed a tendency to improve water resistance by scattering ultraviolet rays of long wavelength area by forming insoluble precipitation with divalent ions in tap water after immersion. In addition, an increase in the fatty acid content tended to also increase the ease of cleaning the sunscreen stick. Solid fatty acid was advantageous in improving water resistance than liquid fatty acid, but there was no difference between solid fatty acids and liquid fatty acid in washability. When it comes to stability, the sunscreen stick using liquid fatty acids maintained a high hardness and melting point, and showed no sweating. Based on this study, it is possible to develop an easy washable sunscreen stick formulation technology that has excellent water resistance but is selectively removed only in soapy water.

Keywords: sunscreen stick, sunscreen, water resistance, easy washable, fatty acid

1. Introduction

As interest in the harmfulness of ultraviolet rays has increased, users of sunscreen have recently been increasing. Consequently, consumers' demands for functions other than the UV blocking effect are also diversifying. The water resistance of the sunscreen product is one of the important elements of the sunscreen product, because sunscreens with poor water resistance may be erased by sweat or water. At the same time, the ease of washing of sunscreen products is also an important factor. If sunscreen is not completely removed on the skin, it may not only feel uncomfortable but also cause skin trouble.

However, it is not easy to achieve both the water resistance and the ease of washing of a sunscreen product at the same time, because the two factors are conflicting. The water resistance and ease of washing of the sunscreen product are determined by the emulsifier in the formulation. O/W emulsifier reduces the water resistance of sunscreen products. Since the general UV filters are hydrophobic, they are not erased easily by water when they form a film on the skin. However, if O/W emulsifier is dispersed together in the film, the O/W emulsifier re-emulsifies the film when it contacts with water. Then, the film is washed out with the O/W emulsifier and water. When it comes to cleaning process, the O/W emulsifier dispersed in the UV blocking film helps the surfactant of the cleaning agent to

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wash by the same principle. Conversely, when the film has a W/O type emulsifier or no emulsifier, it has excellent water resistance but poor cleaning properties.

To overcome this technical limitation, Osawa and colleagues have developed a titanium oxide powder that can be selectively removed only in soapy water by coating titanium dioxide powder with a pH-sensitive polymer to make it hydrophobic at low pH and hydrophilic at high pH[1,2]. A different study of coating N-acyl amino acid on inorganic sunscreens was published for the same purpose[3]. As another attempt, there is a patent that uses vinyl acetate polymer to be easily removed only by warm water[4]. In addition, another patent showed that the W/O type sunscreen formulation with fatty acids has excellent water resistance in low pH water, but is well washed in high pH water[5]. Theoretically, a method using a saponification reaction of fatty acids is most preferred. This is because fatty acids in UV blocking film remains hydrophobic when the pH is low. Therefore, the film has water resistance when it is in contact with neutral water such as a tap water. However, the fatty acid evenly dispersed in the UV-blocking film is reactive to water having a high pH like soapy water, and turn to O/W surfactant, which can help improve the washability. However, this technology has a disadvantage that it is difficult to stabilize the high content of the fatty acid in the W/O formulation, making it difficult to apply to the general emulsion type sunscreen product.

Recently, the sunscreen stick which can be easily applied has been popular in the market. In general sunscreen sticks do not contain emulsifiers with excellent water resistance, however they are not easy to remove from the skin. Therefore, the aim of this study is to develop an ideal sunscreen stick formulation that is selectively washed only in soapy water with excellent water resistance by using saponification of fatty acids. In this study, water resistance and ease of washing of sunscreen sticks with various content and types of fatty acids were evaluated. In addition, basic physical properties such as hardness, melting point, and sweating for a sunscreen stick containing a high content of fatty acids were evaluated. As a result, it was found that the sunscreen stick containing fatty acids was superior in water resistance and washability than the general sunscreen sticks without fatty acids. In addition, their stabilities could be enhanced by using a liquid fatty acid. This research can be used for the development of easy washable sunscreen stick products that are excellent in water resistance and can be washed well only in soapy water.

2. Materials and Method

2.1. Materials

The reagents and materials used in this study are as follows. A mixture of stearic acid and palmic acid (palmac 55-16, Acid Chem, Malaysia), myristic acid (palmac 98-14, Acid Chem, Malaysia), palmitic acid (palmitic acid, Emery, Malaysia), stearic acid (Lunac S 98, KAO, Japan), isostearic acid (Kokyu Alcohol Kogyo, Japan), behenic acid (TOA KASEI, Japan), hexyl laurate (KAK HL, Kokyu Alcohol Kogyo, Japan), polyethylene (performalene 400, NPT, USA), a mixture of synthetic wax and ethylene/ propylene copolymer (LIPWAX PZ80-20, Japan Natural Products, Japan), bis-ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb-S, BASF, Germany), diethylamino hydroxybenzoyl hexyl benzoate (Uvinul A Plus, BASF, Germany), triethylhexanoin (TIO, BASF, Germany), ethylhexyl methoxycinnamate (Uvinul MC80, BASF, Germany), ethylhexyl salicylate (ESCALOL 587, Ashland, USA.), octocrylene (ESCALOL-597, Ashland, USA.), polymethylsilsesquioxane (SESQ-101, N&M TECH, Korea), tromethamine (Tris Amino Utra PC, Angus Chemical, USA.).

2.2. Preparation of Sunscreen Sticks

Sunscreen sticks were prepared as follows. The raw materials of the sunscreen sticks were heated to 90 ℃ until they were completely melted. After the dispersion, they were prepared by filling in cylindrical stick-type cosmetic containers with a diameter of 2.5 cm at 80 ℃ and cooling to room temperature.

2.3. *In-vitro* Water Resistance Evaluation

In-vitro water resistance evaluation was conducted as follows. The sample was applied to a PMMA plate (HD6, HelioScreen Labs, France) at a thickness of 1.3 mg/cm^2, dried for 15 min, and then measured for initial transmittance through a spectrophotometer (Epoch, Biotek, USA). The transmittance of at least three different locations was measured from 290 nm to 400 nm in 1 nm increments. After measuring the transmittance, the PMMA plate was immersed in tap water at 30 °C for 30 min. The friction strength with water was set to three conditions: high, medium, and low. The strength of friction was adjusted by varying the method of fixing the PMMA plate and the speed of the disperser. In the high friction condition, a completely fixed PMMA plate was vortexed with an intensity of 3,000 rpm. In the medium friction condition, the PMMA plate was hanged so that it could move freely, and the vortex was made at a strength of 3,000 rpm. In the low friction condition, a completely fixed PMMA plate was stirred at 350 rpm. Then allowing the PMMA plate to dry sufficiently for 30 min and measure the transmittance after immersion using a spectrophotometer. The measured transmittance is converted into an *in-vitro* SPF value by the following equation, and the ratio of the SPF value before and after immersion is calculated.

$$\text{SPF} = \sum_{290}^{400} E_\lambda S_\lambda / \sum_{290}^{400} E_\lambda S_\lambda T_\lambda \qquad (1)$$

Where E_λ: Erythemal action spectrum, S_λ: Spectral irradiance (W/m^2/nm), T_λ: Transmittance.

2.4. *In-vitro* Ease of Washing Evaluation

In-vitro cleansing evaluation was performed as follows. After applying the sample to the PMMA plate at a thickness of 1.3 mg/cm^2 and drying it for 15 min, the initial transmittance was measured using a spectrophotometer in the same way as the water resistance evaluation. Soapy water was prepared by mixing the foam cleanser and purified water in a ratio of 2 : 8. After washing the PMMA plate with 0.2 g of soapy water for 20 s using an electric cleanser, rinse with running water. The PMMA plate is dried for 30 min and the transmittance of the plate is measured again. The wash rate was calculated by the following equation. The value of the transmittance, higher than the standard (PMMA plate with nothing applied) was replaced with value of the standard and it was assumed that the wash rate was 100%.

$$\text{Wash Rate (\%)} = \sum_{290}^{400} \frac{T_\lambda^{after} - T_\lambda^{before}}{T_\lambda^{control} - T_\lambda^{before}} \times 100 \qquad (2)$$

Where $T_\lambda^{control}$: Control PMMA plate transmittance at a given wavelength, T_λ^{before} : Transmittance before washing at a given wavelength, T_λ^{after} : Transmittance after washing at a given wavelength.

2.5. Measurement of Hardness

The hardness of the sunscreen stick was evaluated as follows. Each sample was made into a stick of a cylindrical shape with a diameter of 2.5 cm. The maximum value was measured when cutting a sunscreen stick at a rate of 2 cm/min at a depth of 1.5 cm using an applicator (#30) for measuring the cutting stress on a Fudoh Rheo meter (RTC 3005D, Rheotech, Japan).

2.6. Differential Scanning Calorimetry (DSC) Analysis

The melting point and phase change characteristics of the sunscreen stick were investigated using DSC (DSC4000, PerkinElmer, USA). The sample temperature was increased from 30 °C to 95 °C at 10 °C per min for DSC experiment.

2.7. Statistics

All experiments were conducted in triplicate. The results were expressed as mean ± SD, and significance was verified through *t*-test.

3. Result and Discussion

3.1. Water Resistance and Washability of Sunscreen Stick with Fatty Acid

3.1.1. Contents of Fatty Acid

Sunscreen sticks were prepared with various contents of fatty acids. Water resistance and washability of sunscreen sticks were evaluated. Sunscreen stick with fatty acids were prepared as in Table 1. Palmitic acid and stearic acid were in a 1 : 1 ratio. Figure 1 shows the results of dispersion test. The alkali solution was prepared with a 10% solution of tromethamine, having a pH higher than 10. Samples of 2 - 3 g were added to 30 g of neutral water or alkali solution for dispersion test. As a result, EZ_0, which did not contain fatty acids, was not dispersed in both the neutral and alkaline solution. EZ_1-40 containing fatty acids were not dispersed in neutral pH water, but dispersed only in alkaline solutions. This is because the fatty acid does not react with a neutral pH water, retaining hydrophobic properties. However, it reacts with an alkali solution, turning to surfactant. Even if a sunscreen stick contains only 1% of the fatty acid, the solution appeared cloudy. From 3% or more, dispersion began to be working well. When the fatty acid content was 15% or more, they were completely dispersed.

In order to compare the water resistance effect according to the content of fatty acids, an *in-vitro* water resistance evaluation was performed. Recently, various attempts have been made to develop an *in-vitro* water resistance test method[6-8]. In this study, the method of measuring the *in-vitro* water resistance ratio was designed by modifying the water resistance SPF experiment method by the Korean Ministry of Food and Drug Safety. *In-vitro* SPF was calculated after measurement of absorbance with a spectrophotometer[9]. This method was verified by comparison with the commercially developed *in-vitro* SPF machine (SPF-290S, Optometrics Corporation, USA) with eight dif-

Table 1. Sunscreen Stick Formulation with Various Contents of Fatty Acids

	EZ_X
Stearic acid, palmitic acid	X
Hexyl laurate	to 100
Polyethylene	15.0
Synthetic wax	2.4
Ethylene/propylene copolymer	0.6
Bis-ethylhexyloxyphenol methoxyphenyl triazine	2.0
Diethylamino hydroxybenzoyl hexyl benzoate	2.0
Triethylhexanoin	8.0
Ethylhexyl methoxycinnamate	7.0
Ethylhexyl salicylate	4.0
Octocrylene	7.0
Polymethylsilsesquioxane	10.0

X = 0, 1, 3, 5, 10, 15, 20, 25, 30, 35, 40

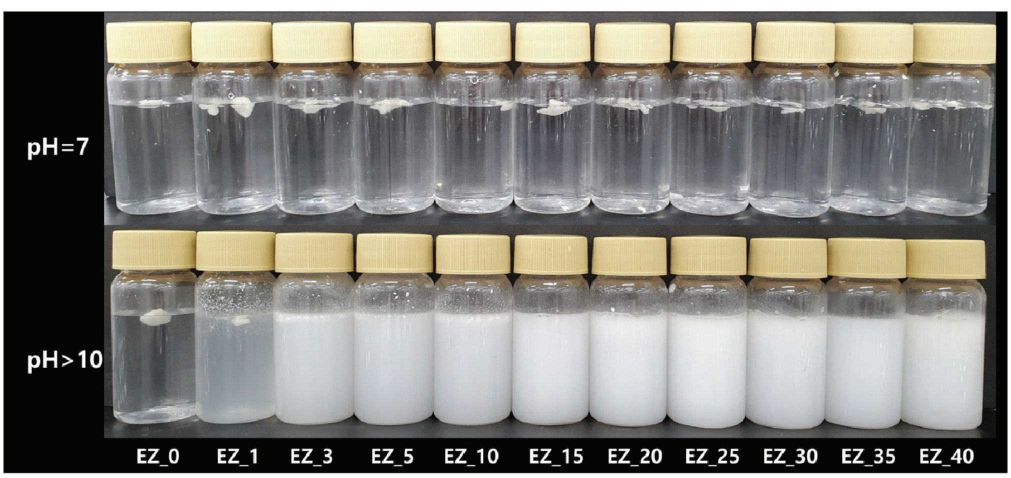

Figure 1. Dispersion test of sunscreen sticks with various contents of fatty acids.

ferent samples (Figure 2). As the result of *in-vitro* water resistance were very sensitive to the friction with water, the intensity of friction by water was set to high, medium, and low, and the average value was used. The water resistance of the sunscreen stick containing the fatty acid was higher than that of the sunscreen stick without the fatty acid (Table 2). Since sunscreen sticks with more than 25% of fatty acid had too much solid component, it was difficult to apply them evenly to the PMMA plate. Therefore, accurate experimental results could not be obtained when the fatty acid content exceeded 25%. However, it was obvious that the *in-vitro* water resistant rate increased as the fatty acid content increased. Sunscreen sticks with 10% to 20% of fatty acid had great water resistant rate. Sunscreen sticks containing 20% of fatty acids had the water resistance ratio which even exceeded 100%. Absorbance before and after immersion of EZ_0 and EZ_15 with medium water friction were compared. Absorbance of EZ_0 without fatty acids decreased overall in the whole range of UV light area, whereas absorbance of EZ_15 containing 15% of fatty acids increased the absorbance in longer wavelength area after immersion (Figure 3). In addition, it was observed that PMMA plate of the sunscreen stick with higher fatty acid was opaquer after immersion. This is because fatty acids react with divalent ions in the tap water to form an insoluble precipitate, and the insoluble precipitate scatters the long wavelength of light. Shiseido group reported a sunscreen formulation technology that increases SPF after immersion in hard water due to the same effect of fatty acid[10,11]. This technology also explains the effect of SPF boosting by the insoluble precipitation of fatty acid and divalent ions in the water.

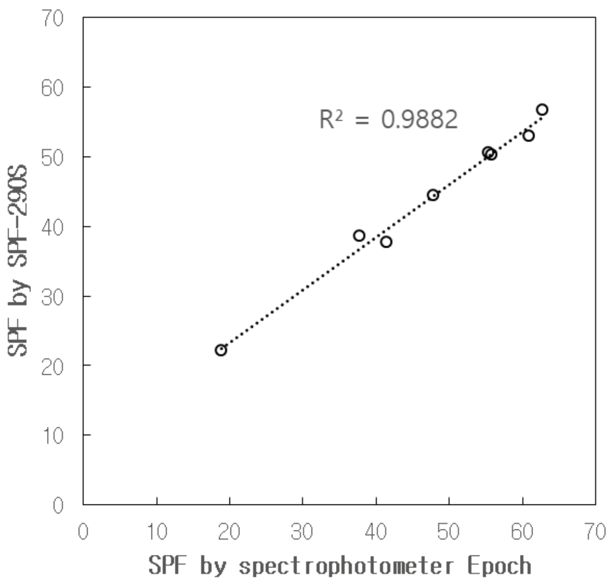

Figure 2. Comparison of *in-vitro* SPF values measured from SPF-290S and spectrophotometer Epoch.

In order to compare the effect of the ease of washing according to the fatty acid content, an *in-vitro* ease of wash-

Table 2. Water Resistant Rate and Wash Rate of Sunscreen Sticks with Various Contents of Fatty Acids. Each value represents the mean ± SD ($^*p < 0.05$)

	In-vitro SPF before immersion	*In-vitro* SPF after immersion	Water resistant rate (%)	Wash rate (%)
EZ_0	73.32 ± 13.97	27.55 ± 30.52	39.45 ± 47.94	64.56 ± 4.49
EZ_1	72.25 ± 10.20	32.89 ± 26.21	47.54 ± 37.38	70.50 ± 2.77
EZ_3	81.54 ± 17.69	40.44 ± 32.13	47.96 ± 39.91	71.76 ± 10.21
EZ_5	90.89 ± 26.56	83.02 ± 74.07	87.90 ± 86.96	*80.08 ± 4.07
EZ_10	84.93 ± 25.25	72.15 ± 52.99	91.33 ± 81.42	*78.24 ± 4.64
EZ_15	73.88 ± 21.19	69.37 ± 32.60	91.93 ± 20.58	*83.62 ± 1.90
EZ_20	94.53 ± 51.76	175.59 ± 117.69	180.48 ± 83.43	*79.81 ± 4.34
EZ_25	*45.40 ± 5.66	29.96 ± 11.93	68.60 ± 35.47	*89.34 ± 0.29
EZ_30	52.60 ± 17.74	212.93 ± 256.87	415.29 ± 430.26	*85.88 ± 1.54
EZ_35	*23.59 ± 14.65	290.30 ± 236.69	2027.87 ± 2254.09	*83.41 ± 2.90
EZ_40	*15.74 ± 16.75	*104.05 ± 21.00	1389.49 ± 1269.71	*81.21 ± 4.65

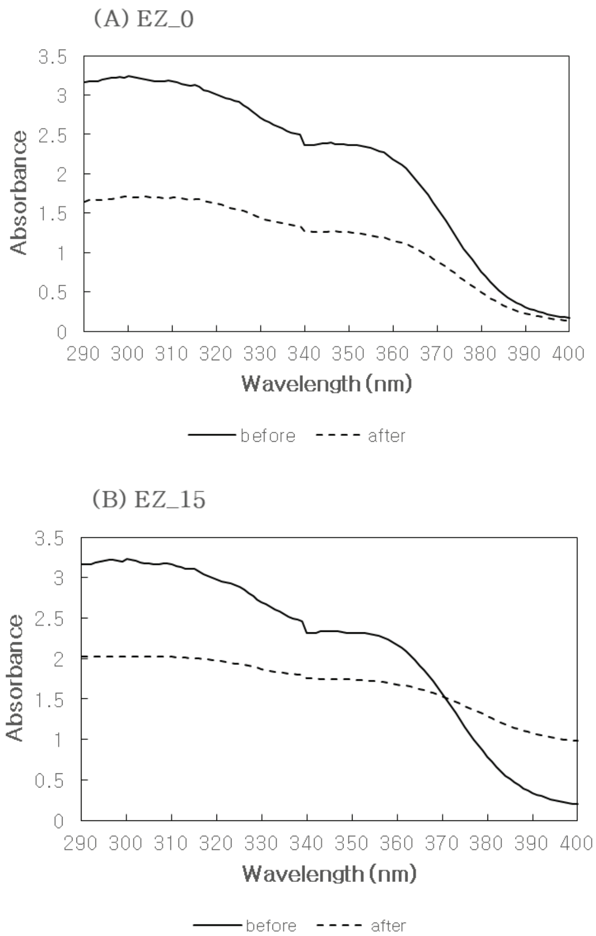

Figure 3. Change of absorbance of sunscreen sticks EZ_0 and EZ_15 before and after immersion with medium water friction.

ing was performed (Figure 4). As expected, the washability of the sunscreen stick containing fatty acids was higher than that of the sunscreen stick without fatty acids. The fatty acid evenly dispersed in the UV blocking film positively affected the cleaning process by the saponification with soapy water which has high pH. The washability tended to increase until the fatty acid content was 25% and then decreasd. This is because the solid content of the formulation was too high when the fatty acid content exceeded 25%.

It was found that the proper fatty acid content was about 15 - 25% to maximize the washability for minimum quality of sunscreen stick. When the fatty acid was above 25%, the spreadability of sunscreen sticks were significantly reduced. Therefore, even if it contained the same amount of sunscreen, the initial SPF was lower because of the poor spreadability, making uneven UV protecting film on surface.

3.1.2. Types of Fatty Acid

As shown in Table 3, water resistance and washability properties were assessed according to the types of fatty acids. Myristic acid, palmitic acid, stearic acid, behenic acid which have linear hydrocarbon chains were used. Isostearic acid having a branched hydrocarbon chain was

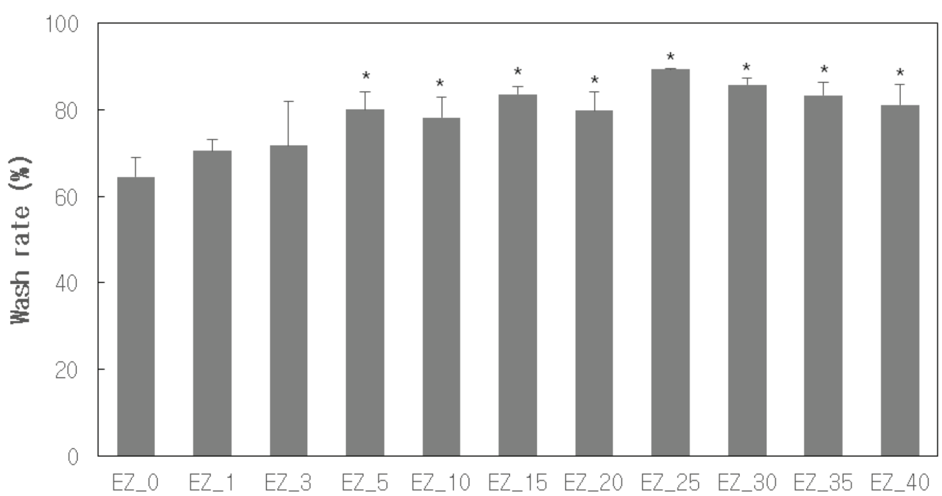

Figure 4. Wash rate of sunscreen sticks with various content of fatty acids. Each value represents the mean ± SD ($^{*}p < 0.05$).

Table 3. Sunscreen Stick Formulation with Various Contents of Fatty Acids

	EZ_ L15	EZ_ P15	EZ_ S15	EZ_ IS15	EZ_ B15
Myristic acid	15.00				
Palmitic acid		15.00			
Stearic acid			15.00		
Isostearic acid				15.00	
Behenic acid					15.00
Hexyl laurate	27.00	27.00	27.00	27.00	27.00
Polyethylene	15.00	15.00	15.00	15.00	15.00
Synthetic wax	2.40	2.40	2.40	2.40	2.40
Ethylene/propylene copolymer	0.60	0.60	0.60	0.60	0.60
Bis-ethylhexyloxyphenol methoxyphenyl Triazine	2.00	2.00	2.00	2.00	2.00
Diethylamino hydroxybenzoyl hexyl benzoate	2.00	2.00	2.00	2.00	2.00
Triethylhexanoin	8.00	8.00	8.00	8.00	8.00
Ethylhexyl methoxycinnamate	7.00	7.00	7.00	7.00	7.00
Ethylhexyl salicylate	4.00	4.00	4.00	4.00	4.00
Octocrylene	7.00	7.00	7.00	7.00	7.00
Polymethylsilsesquioxane	10.00	10.00	10.00	10.00	10.00

also used. Fatty acids with linear hydrocarbon chains are solid at room temperature, but isostearic acid with a branched hydrocarbon chain is liquid at room temperature. The content of fatty acids was fixed at 15% and only the types of fatty acids were changed to evaluate dispersion tendency, water resistance, and ease of washing.

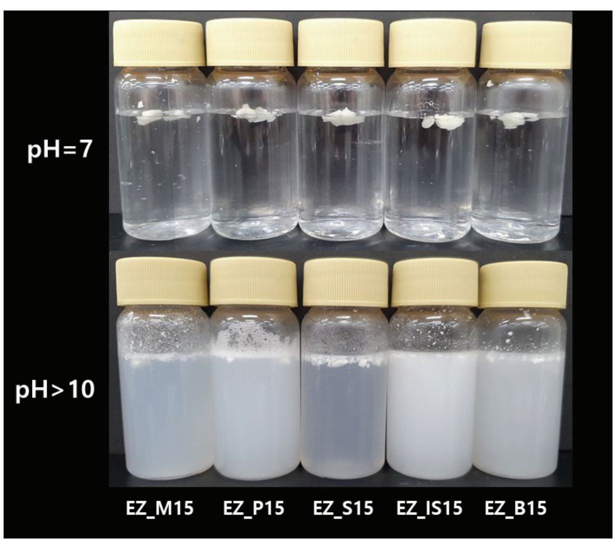

Figure 5. Dispersion test of sunscreen stick with various types of fatty acids.

Figure 5 shows the results of a dispersion test according to the type of fatty acids. It was not dispersed in neutral water as expected, however it dispersed in an alkali solution. Dispersion was the best for isostearic acid, which is liquid at room temperature, and stearic acid was the worst. It is because isostearic acid is in a liquid phase, the saponification reaction is more likely to occur. It was interesting that the dispersion ability of stearic acid with hydrocarbon chain length of 18 was lower than both that of palmitic acid which has shorter hydrocarbon chain and that of behenic acid which has longer hydrocarbon chain. It could be explained by melting point and emulsifying ability of the fatty acids. Lower melting point of fatty acid could be advantageous in terms of reaction rate. On the other hand, the ability to emulsify depends on the length of the carbon chain. Since palmitic acid has lower melting point than that of stearic acid, it would would be an advantageous dispersion because of the reaction rate. On the other hand, behenic acid may be more advantageous to emulsify the long chain wax than stearic acid because of the longer hy-

Table 4. Water Resistant Rate and Wash Rate of Sunscreen Sticks with Various Types of Fatty Acids. Each value represents the mean ± SD ($^{*}p < 0.05$)

	In-vitro SPF before immersion	*In-vitro* SPF after immersion	Water resistant rate (%)	Wash rate (%)
EZ_M15	105.22 ± 19.29	176.55 ± 132.95	159.79 ± 104.03	*80.09 ± 3.28
EZ_P15	103.82 ± 18.04	105.49 ± 52.27	99.49 ± 40.52	*77.75 ± 1.56
EZ_S15	64.29 ± 9.36	78.38 ± 76.07	126.61 ± 132.78	*82.04 ± 2.53
EZ_IS15	102.19 ± 23.22	58.51 ± 48.93	53.33 ± 45.62	*82.80 ± 3.64
EZ_B15	59.31 ± 9.85	40.36 ± 24.43	68.44 ± 39.83	*80.65 ± 4.43

drocarbon chain.

In-vitro water resistance was evaluated and the results are shown in Table 4. Sunscreen sticks containing myristic acid, palmitic acid, and isostearic acid had similar *in-vitro* SPF, while those of sunscreen stick including behenic acid and stearic acid had low *in-vitro* SPF before immersion. Sunscreen stick containing behenic acid showed the lowest *in-vitro* SPF before immersion. This is because there is too much solid content in the sun stick, so it has poor spreadability. The *in-vitro* water resistance ratios of sunscreen stick with any types of fatty acids were higher than that of EZ_0 which did not contain fatty acids. Fatty acids which are solid at room temperature tend to have a higher water resistance rate. This is because the insoluble precipitates of the solid fatty acids scattered the light more effectively than that of the liquid fatty acids. Actually, the EZ_IS15 plate was more transparent than the plate containing solid fatty acids after immersion.

There were similar washability regardless of the length and shape of the fatty acids in Table 4. This result was different from the expected because there was a difference in dispersion ability depending on the hydrocarbon length and shape. We suggest two explanations. Firstly, it can be explained by the difference in the sample form. The saponification reaction takes place on the surface. Therefore, even if the reaction tendency is different according to the types of fatty acids, the difference may not be significant in the form of a very thin film on the surface which is very optimal condition for reaction. Secondly, the surfactant in the soapy water is the actual main cleansing agent in the washing process. Thus, even if there are difference in dispersion ability among the fatty acids, its effect on cleaning process was very limited. Even though fatty acid did not work as a main cleaning agent, fatty acid makes crack on the UV blocking film when it goes under the reaction of saponification by contacting soapy water. Therefore, the surfactant in the soapy water can remove the film easily because of the crack created by saponification of fatty acid.

3.2. Physical Properties of Sunscreen Stick with Fatty Acid

3.2.1. Hardness of Sunscreen Sticks

The hardness of solid stick type cosmetics is an important factor because it is directly related to stability and texture. If the hardness is too low, it is likely to break easily during use. On the contrary, if it is too high, it may be uncomfortable because of its poor spreadability. Therefore, it is important that the solid stick type cosmetics have a proper range of hardness.

Figure 6 shows the change in hardness of sunscreen

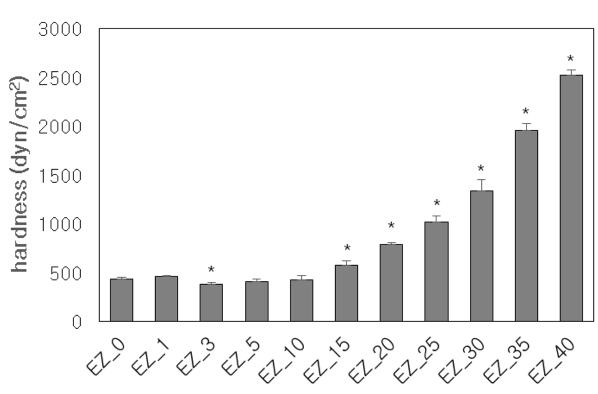

Figure 6. Hardness of sunscreen sticks with various contents of fatty acids. Each value represents the mean ± SD ($^{*}p < 0.05$).

sticks according to the content of fatty acids. Hardness was not affected until the fatty acid content was less than 10% of fatty acid. Rather, some samples showed slightly lower hardness than EZ_0, as fatty acids participated in crystalline formation and caused changes in crystal structure. In other words, the fatty acid acts as an impurity, so the hardness decrease even though it has more solid component in the formulation. However, when the fatty acid content was more than 15%, the hardness increased as the fatty acid content increased. This is because when the fatty acid content is more than 15%, the fatty acid became a major component forming the entire structure.

Figure 7 shows the change in hardness depending on the type of fatty acid. The hardness increased as the length of the hydrocarbon chain of the fatty acid increased. However, sunscreen stick with isostearic acid, and liquid fatty acid, has the highest hardness. It is about 13% higher than that of stearic acid which has the same number of carbon, and 3% higher than that of behenic acid which has the four more carbons. This is because solid fatty acids affect the existing wax crystal structure as described above, while liquid isostearic acid does not affect the existing wax crystal structure. Isostearic acid seems to be stabilized in the liquid phase without participating in wax crystal formation while forming an oil wax gel.

3.2.2. Melting Point of Sunscreen Sticks

One of the most important factors in solid stick cosmetics is the melting point. This is because if the melting point is not high enough or if phase changes occur at low temperatures, the product may deform under various storage conditions. Therefore, in order to stably maintain the quality of the solid stick type cosmetics, it must have a sufficiently high melting point. Since the melting points of solid fatty acids are not high enough, fatty acids have not been used in solid stick type cosmetics as a structuring agent. Instead of fatty acid, polyethylene or ceresin having a higher melting point have been mainly used.

The melting point of fatty acid increases as the carbon chain length increases. Pure fatty acids have a fixed melting point, but in a mixture like a cosmetic formulation, a phase change temperature become lower and broader than the own melting point. Therefore, evaluating the phase change temperature is useful for predicting stability of solid type cosmetics.

The phase change temperature was evaluated using DSC according to the type of fatty acid (Figure 8). The sample temperature was increased from 30 ℃ to 95 ℃ at a rate of 10 ℃ per min for DSC operation. As a result, phase changes occur in the sunscreen sticks with solid fatty acids below 60 ℃. If the phase change occurs at such a relatively low temperature, long term stability of the sunscreen stick may not be good. However, isostearic acid and liquid fatty acid, showed no apparent phase change below 60 ℃ and showed a typical endothermic tendency of the general sunscreen stick. Since isostearic acid does not affect the crystal structure, it does not make any difference in phase transition tendency, existing in a liquid phase in the oil

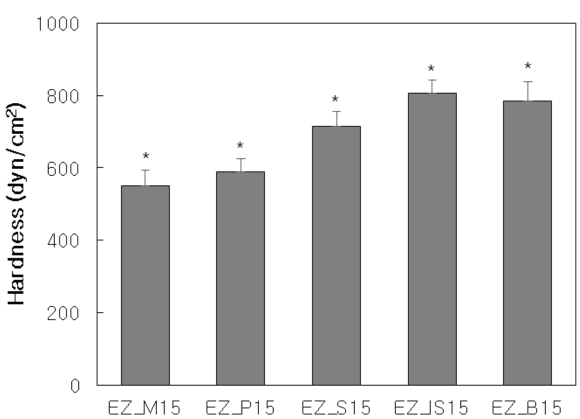

Figure 7. Hardness of sunscreen sticks with various types of fatty acids. Each value represents the mean ± SD ($^{*}p < 0.05$).

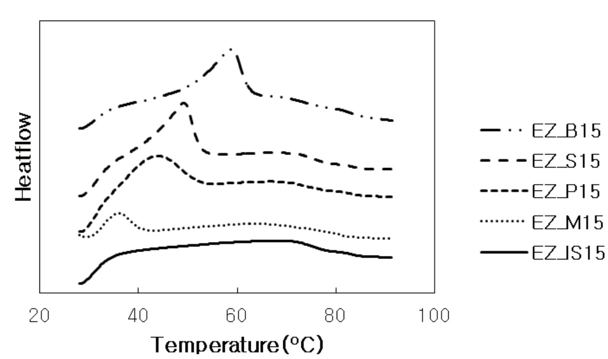

Figure 8. DSC results of sunscreen stick with various fatty acids.

wax gel system. Therefore, it is more advantageous for the stability of the formulation.

3.2.3. Sweating of Sunscreen Stick

Finally, the sweating phenomenon of the solid stick formulation containing fatty acids was evaluated. While the temperature of the oil wax gel increases, some oil wax gel secrete oil on the surface as if sweating. The sweating of the solid formulation is caused by a change in the lattice structure of the oil wax gel as temperature change[12,13]. Highly stabilized solid stick type cosmetics should not have sweating phenomena. The sweating phenomenon was evaluated according to the types of fatty acids and it was evaluated by observing the surface of the sunscreen stick at 50 °C every 20 min. Sweating phenomena occurred in all the sunscreen sticks with solid fatty acids. Sunscreen sticks with myristic acid and palimitic acid shows sweating phenomena in the first 20 min while the sunscreen stick with behenic acid showed very fine sweating. However, we observed the sunscreen stick with isostearic acid and it showed no sweating phenomena because the liquid fatty acid did not affect the wax crystal structure unlike solid fatty acids.

In conclusion, it is advantageous to use liquid fatty acids to develop a stable sunscreen stick formulation with a high content of fatty acids. Liquid fatty acids do not participate in crystallization of wax, which is advantageous for hardness, melting points, and sweating.

4. Conclusion

Fatty acid was applied to a sunscreen stick formulation to impart excellent water resistance and ease of washing. Fatty acids are basically hydrophobic, but they can turn to anionic surfactants by saponification with alkali solution as soapy water. By using this reactive property of fatty acid, we developed a sunscreen stick that is excellent in water resistance and selectively removed only in soapy water. In particular, solid fatty acids have a positive effect on water resistance because they combine with divalent ions in water to produce insoluble substances giving a scattering effect. In terms of ease of washing, the fatty acid evenly dispersed in the film and selectively react with high pH soapy water, turning it into anionic surfactant to help remove sunscreen film from the surface. Physical properties of sunscreen stick with high content of fatty acid were also studied, and we found that the use of liquid fatty acids was advantageous in hardness, melting point, and sweating phenomena. Finally, this study is expected to support developing an ideal sunscreen stick product that has both water excellent resistance and washability.

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