Characteristics of natural derived surface treated pigments for the achievement of SDGs

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Abstract

Recently, the development of cosmetic products focused on eco-friendly concept for the achievement of SDGs has been accelerating. In this study, we revealed the characteristics of natural derived surface treated pigments by evaluations of mechanical, tactile feelings and friction properties. These results indicated that natural derived surface treatment could replace the conventional petrochemical surface treatment. Furthermore, surface treated pigment by amphiphilic chemical compounds, such as sodium dilauramidoglutamide lysine (SDL) treatment and mannosyl erythritol lipid (MEL) treatment, showed self-emulsification and pickering emulsification abilities. These knowledges would be very useful for cosmetic formulators who would like to prepare the new natural cosmetic formulations without using conventional petrochemicals.

Key word: surface treated pigment, natural ingredients, tactile feeling,

Introduction

Due to the high functional properties, surface treated pigments have been formulated into a lot of make-up cosmetics and sunscreen cosmetics. Various types of cosmetic pigments coated with various kinds of surface treatment agents, have been developed for improving water-resistance, dispersibility, tactile feelings, and so on. However, each type of surface treated pigments shows completely different characteristics depending on the chemical structures of each surface treatment agents. Therefore, it has been very important for cosmetic engineer, especially cosmetic formulators, to understand the behavior of each type of surface treated pigments in their formulations. Conventionally, because of the advantage of performance and costs, petrochemicals, such as silicone and alkyl silane, have been widely used as surface treatment agents. However, the public awareness concerning about global environment issues are recently enhancing. In 2015, sustainable development goals (SDGs) were adopted by United Nation and now almost all countries, companies and people in the world are working hard to accomplish SDGs. In the cosmetic field, the development of raw materials accordant with the concept of SDGs, especially biomass ingredients without using petrochemicals and the research and developments of biodegradable ingredients are greatly accelerating. Under this circumstance, several surface treated pigments using natural origin agents also have been developed. In this work, to reveal the characteristics of each type of surface treated pigments, especially focused on natural surface treatments, we evaluated their mechanical properties, tactile feeling, and frictional properties.

Materials

Each surface treated pigment: sodium dilauramidoglutamide lysine (SDL), mannosyl erythritol lipid (MEL), magnesium stearate (MS), lauroyl lysine (LL), polyglyceryl-2 tetraisostearate (P2T), isopropyl titanium triisostearate (TT) alkyl silane (AS) and methylhydrogen polysiloxane (SI) were obtained from DAITOKASEI KOGYO CO., LTD. Surface treatment was conducted by 5wt% (LL), 2wt% (P2T, TT, AS and SI), 1wt% (SDL, MEL and MS) of treatment agent against the whole amount of the pigment.

Methods

Measurement of physical properties of surface treated TiO_2.

The measurement of the contact angle was conducted as follows: after making a tablet of powder with the hydraulic press at 10 MPa, a water or 1,3-butylene glycol (1,3-BG) drop was dropped on the tablet. Then the contact angle was measured with a contact angle measurement system (LSE-B100; Nick Corp., Japan). Particle size distributions were determined with a laser diffraction/scattering particle size distribution apparatus (Microtrac MT3300EX II; Nikkiso Co., Ltd., Japan). Measurements of angle of repose have been performed as follows: The funnel (diameter of discharge nozzle: 20 mm) was fixed vertically at 40 mm height over the petri dish (diameter: 50 mm). After that, the powder was applied at 30 g/min by using quantitative feeding apparatus (Constant feeder type F3, Toyo seiki seisaku-sho, Ltd., Japan) to form cone-shaped accumulation of powders. The bulk specific gravity measurements after tapping were performed on the measuring instrument, TPM-1P/TPM-3P (Tsutsui scientific instruments Co., Ltd., Japan). Specific surface area of powders was determined with surface area & pore size analyzer (NOVA touch, Quantachrome INSTRUMENTS, Anton paar GmbH, Austria). Oil absorption of each powder was measured by an ordinary apparatus (S410D, FRONTEX Co., Ltd., Japan) in accordance with JIS K 6217-4. After the sample powders were poured into a double-blades mixer, 9-12 Alkane oil was titrated into the mixing chamber at a constant rate while measuring the torque continuously.

Oil dispersibility evaluation of surface treated pigments.

After the 40 g of sample powders were poured into 60 g of cosmetic oil, the mixture was stirred for 10 mins by 1,000 rpm. Then the viscosities of obtained oil pastes were measured by viscometer TVB-10M (Toki Sangyo Co., Ltd.). Dispersibility evaluations were conducted using each surface treated TiO_2 and four kinds of cosmetic oils: 9-12 Alkane, caprylic/capric triglyceride, squalene and dimethicone. We also prepared w/o emulsions using surface treated red iron oxide and three kinds of cosmetic oils: 9-12 alkane, caprylic/capric triglyceride and dimethicone. After making w/o emulsion, we evaluate the oil dispersibility and localization of sample powders by digital microscope. we prepared o/w emulsions as follow: at first, prepare a solution with 1 g of surfactant (POLYGLYCERYL-3 DIISOSTEARATE) and 20 g of cosmetic oil. Then add 5 g of each surface treated red iron oxide into the solution and shake well by hand. After that, add 20 g of water and finally shake well again to obtain w/o emulsions.

Evaluations in the Lipstick formula prepared by simple process

We evaluated high pigmented lipsticks using each kind of surface treated powders prepared by simple process. In general manufacturing procedure of lipsticks, pre-dispersion process using three roll mill is included to avoid producing ununiform colored product. However, in this study, to make clear the difference of dispersibility of each kind of surface treatment, we prepared and evaluated lipsticks without pre-dispersion process. Lipsticks were prepared according to the formulation shown in **Table 1**. Prepared phase A and heat it up at 80°C. After that add phase B into phase A with stirring at 1,000rpm. Pour the mixture into suitable containers at 70-80°C.

Table 1. lipstick formula prepared by simple process

<Phase>	<Ingredient>	<%>
A	VELVET WAX	5.00
A	SYNTHETIC WAX	5.00
A	DIISOSTEARYL MALATE	20.35
A	CAPRYLIC/CAPRIC TRIGLYCERIDE	10.00
A	POLYGLYCERYL-2 TRIISOSTEARATE	12.50
A	OCTYL DODECANOL	10.00
A	PENTAERYTHRITYL TETRAISOSTEARATE	5.00
A	PRESERVATIVE	0.10
A	TOCOPHEROL	0.05
B	(Treated) Yellow iron oxides	8.89
B	(Treated) Red iron oxides	19.55
B	(Treated) Black iron oxides	3.56
	TOTAL :	100.00

Sensory evaluations.

Sensory evaluations of powder foundation were performed by 4 formulator of 25 to 35 years old. The evaluations were performed in a quiet room at 25 ± 1 °C. The powders were e valuated in a random order to eliminate order effects. When the subjects touched the powders, they picked them up with the thumb and forefinger of their dominant hand for 3 seconds. After that, they rubbed their fingers together for 25 seconds. After evaluation, the subjects scored 1-10 point to each 11 tactile sensations regarding the tactile dimensions as follows: warm, cold, soft, hard, moist, dry, smooth, sticky, rough, slippery, and creak feels [1]. Preparations of powder foundation have been performed as follows; firstly, the powder components shown in **Table 2** were blended uniformly in a mixer. And then, the oil component was added to the powder components and mixed again. After further mixing, the mixture was passed through a screen to obtain homogeneous samples.

Table 2. formulation of powder foundation

<Ingredient>	<%>
Treated TALC	35.67
Treated SERICITE	35.67
Treated Titan dioxides	8.70
Treated Yellow iron oxides	1.74
Treated Red iron oxides	0.52
Treated Black iron oxides	0.26
Diphenyl Dimethicone/Vinyl Diphenyl Dimethicone/Silsesquioxane Crosspolymer	4.35
Presavative	0.09
Dimethylpolysiloxane	13.00
Total:	100.00

Friction evaluations of powder foundation.

Frictional evaluations were performed according to previous papers [2-4]. The friction force was evaluated using a sinusoidal motion friction evaluation system in which the contact probe slid on objects under sinusoidal motion (**Figure 1**).

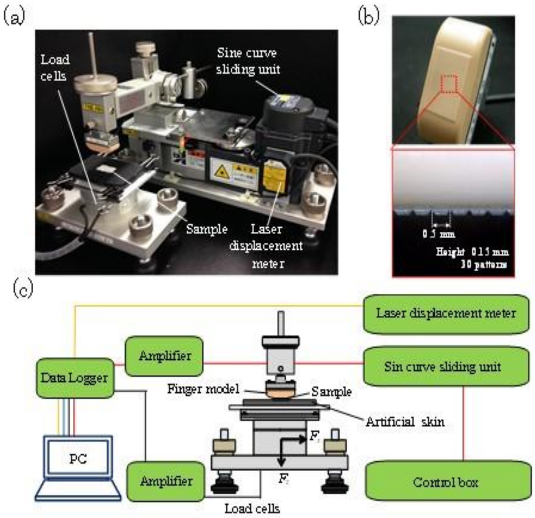


Figure 1. Images of (a) Sine movement sliding system (b) Human finger model (c) Conceptual diagram.

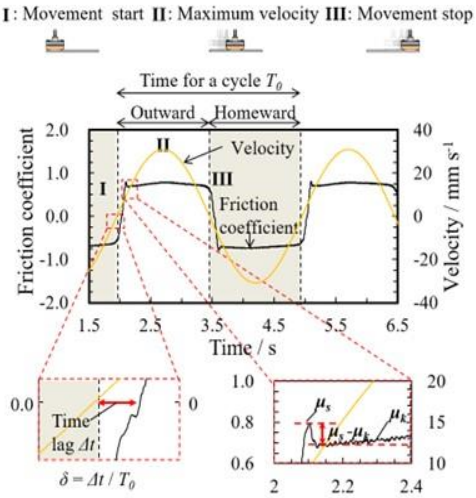


Figure 2. Typical friction profile and definition of parameters. The parameters μ_s and μ_k are static friction coefficient and kinetic friction coefficient, respectively.

The powder was sieved with a sieve opening of 0.5 mm.
Friction evaluations were carried out when 20 mg of the powder was applied to the artificial skin. Data for one round trip from the point where the contact probe changed direction for the first time were selected for quantitative analysis. The velocity V during sinusoidal motion is described by the following equation:

$$V = A\omega \cos \omega T$$

where A, ω, and T are the moving width, angular velocity, and time, respectively. The experimental conditions were as follows: $\omega = 2.1$ rad s^{-1} (maximum velocity = 30 mm s^{-1}), vertical load = 0.98 N, A = 14.5 mm, number of rotations = 11. To confirm the repeatability, evaluations were conducted three times. Data for one round trip from the point where the contact probe changed direction for the first time were selected for quantitative analysis. The friction data were analyzed on the basis of the following four parameters: (1) static friction coefficient (μ_s); (2) kinetic friction coefficient (μ_k); (3) normalized delay time δ ($\delta = \Delta t / T_0$ where Δt, T_0 are time lag between the velocity and the friction force and time for a cycle, respectively); (4) $\mu_s - \mu_k$ (the difference between static and kinetic friction coefficients) (**Figure 2**).

Result & Discussion

Mechanical properties of each surface treated pigments

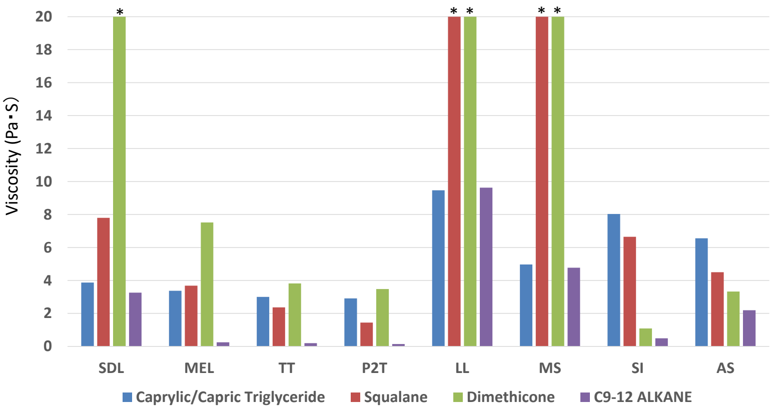
Table 3 shows mechanical properties of each kind of surface treated TiO_2. AS and SI treated TiO_2 exhibited high contact angles against both water and 1,3-BG. The values were AS (water: 158, 1,3-BG: 144) and SI (water: 152, 1,3-BG: 140), respectively. This result indicated that surface free energy of TiO_2 was largely decreased by these treatments. On the other hand, SDL and MEL treated TiO_2 showed moderate contact angles. The Values were SDL (water: 120, 1,3-BG: 33) and MEL (water: 122, 1,3-BG: 35), respectively. In general, powders showing lower surface free energy exhibit higher contact angle values. For this reason, it is assumed that the order of surface free energy of each treated TiO_2 is as follow: AS, SI＜TT, P2T＜MS, LL＜SDL, MEL. Especially, SDL and MEL treated TiO_2 could be easily dispersed in 1,3-BG. As we reported 2016 [2], this property would be useful for making water base cosmetics having water-resistance property. **Table 3** is also including the results of oil absorption values for 9-12 alkane oil and maximum torque during oil absorption measurement of each kind of surface treated TiO_2. TT, P2T and AS treated TiO_2 showed lower oil absorption and lower torque values compared with SI and MS and LL treated TiO2. In general, pigments indicating lower oil absorption are formulated into oil base cosmetics, because of higher dispersibility and wettability. Therefore, these results indicated that TT, P2T and AS treated TiO_2 are suitable for preparing oil base cosmetics. Because TT and P2T showed very similar physical properties including bulk specific gravity and specific surface area, P2T treatment could be a candidate of natural alternative of TT treatment.

Table 3. Mechanical properties of each kind of surface treated TiO2.

	Contact angle_water (°)	Contact angle_1,3 BG(°)	Particle size*(μm)	Angle of repose(°)	Bulk specific gravity(g/mL)	Specific surface area (m2/g)	Oil absorption (9-12alkane)(mL/100g) /MAX torque (Nm)
SDL	120	33	0.386	38.0	1.08	8.4	24.1/48.1
MEL	122	35	0.341	39.0	1.00	8.2	23.0/11.5
TT	153	65	0.338	39.0	1.18	6.2	18.3/8.3
P2T	153	60	0.183	36.0	1.00	5.0	14.5/6.1
LL	145	48	0.334	33.0	0.95	8.9	31.0/33.3
MS	143	60	0.318	38.0	1.03	7.7	24.8/23.5
AS	158	144	0.298	38.5	1.43	8.4	15.7/7.8
SI	152	140	1.553	49.5	1.05	6.3	25.4/51.0
NT	-	-	0.313	45.0	0.93	10.7	40.2/37.8

Oil dispersibility TEST of surface treated pigments.

TT and P2T treatment showed similar behavior on the oil absorption measurement using 9-12 alkane oil. However, we use a lot of cosmetic oils in the formulations. Then, we evaluated oil dispersibility of each kind of surface treated TiO_2 by measuring the viscosity of oil paste using following four kinds of cosmetic oils: caprylic/capric triglyceride, squalene, dimethicone and 9-12 Alkane. Conventionally, due to the high oil dispersibility, TT treated pigments have been formulate into a lot of oil base cosmetics. As shown in **Figure 2**, with P2T treated TiO_2, we could prepare oil pastes showing almost the same low viscosity as TT treated TiO_2 for all kinds of cosmetic oils suggesting that even in the cosmetic formulations, P2T treated pigment could be substituted for TT treated pigment. The viscosity of oil pastes with MS and LL treated TiO_2 were greatly increased, whereas oil pastes with MEL and SDL treated TiO_2 exhibited moderate viscosity. It is highly probable that these results stem from the difference of surface free energy of each kind of surface treated pigments. In general, powder exhibiting closer surface free energy value to the medium oil shows higher oil dispersibility and wettability. As mentioned in **table 3**, surface free energy of TT and P2T treated pigments exhibited higher than that of SI and AS treated pigment. Therefore, with using relatively higher surface free energy cosmetic oils, such as caprylic/capric triglyceride and squalene, TT and P2T treated TiO_2 showed higher dispersibility than SI and AS treated TiO_2. Since surface treatment agent of MS and LL are solid compound at room



*: unmeasurable, too viscosity.

Figure 2. oil dispersibility test of each kind of surface treated red iron oxide.

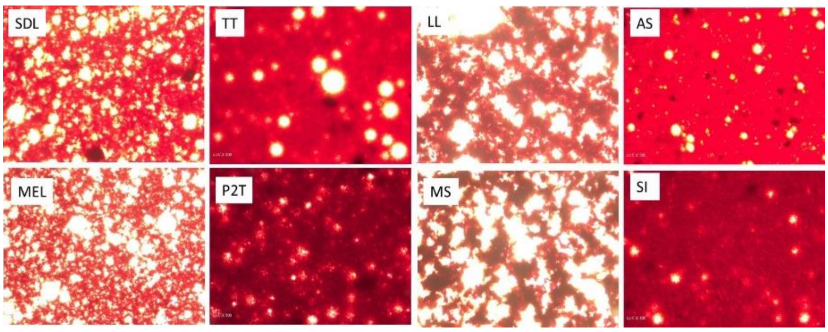


Figure 3A. digital microscopic images of w/o emulsions using each kind of surface treated iron oxide and 9-12 alkane oil.

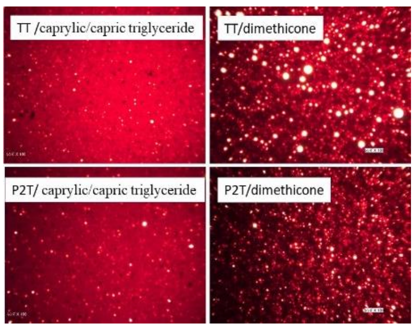


Figure 3B. digital microscopic images of w/o emulsions using TT and P2T treated iron oxide and caprylic/capric triglyceride and Dimethicone oil, respectively.

temperature, surface free energy of MS and LL treated powders tend to become much higher than that of other treatments. For this reason, strong thickening of oil pastes with MS and LL treated TiO_2 were induced by the increase of the gaps of surface free energy between treated pigment and medium oil. Although it is presumed that surface free energy of SDL and MEL treated TiO_2 are also high, strong thickening was not observed. This result suggested that due to the amphiphilic structures of surface treatment agent, SDL and MEL treated pigment could behave not only as hydrophobic powder but also as surfactant which could reduce the interfacial energy between particles and medium oil. **Figure 3A** shows digital microscopic images of w/o emulsions using each kind of surface treated red iron oxide and 9-12 alkane. TT, AS, SI and P2T treated powders showed good dispersibility, while huge agglomerations were observed in the w/o emulsions using MS and LL treated powders. Especially, P2T treated pigment also showed almost the same dispersibility as TT treated pigment in caprylic/capric triglyceride and dimethicone (**Figure 3B**). Although SDL and MEL treated pigments showed good dispersibility in the w/o emulsions, these treated pigments were located around emulsified water drops. These characteristics would be also affected by the amphiphilic structures of SDL and MEL treatment agents.

Evaluations in the Lipstick formula

Figure 4 shows dispersibility of each kind of surface treated pigments in the lipstick formulations. In case of using P2T treated pigments, uniform colored lipstick was obtained, whereas black lines were observed in lipsticks with AS, SI, TT and LL treatment. This result indicated that high oil wettability and dispersibility of P2T treated pigments enable formulators to prepare products with less agitation intensity than usual. This property could contribute to the manufacturing cost saving and reduction in environmental load.

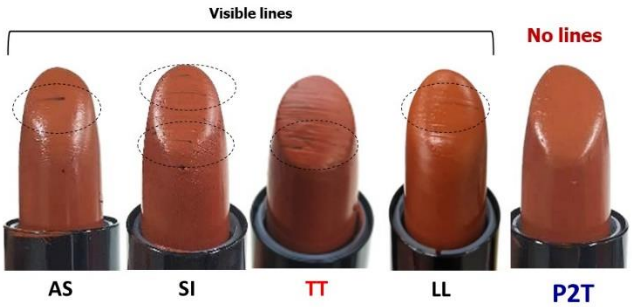


Figure 4. lipsticks using each kind of surface treated pigments prepared by simple process.

Sensory evaluations.

The improvement of tactile feeling is also important function of surface treatment of cosmetic powders. The tactile differences depending on the surface treatment in powder foundation are much easier to recognize, compared with liquid foundation whose tactile feelings is greatly affected by medium oil. In particular, because of moist and creamy feelings, AS treated pigments have been formulated into a lot of cosmetics. As shown in **Figure 5**, powder foundation with MS treated pigments showed very similar tactile feeing to powder foundation using AS treated pigments. And also, powder foundation with LL treated pigments showed very similar tactile feeing to powder foundation using SI treated pigments. These results indicated that especially for the powder foundation, MS and LL treatment could be natural alternative of AS and SI treatment, respectively.

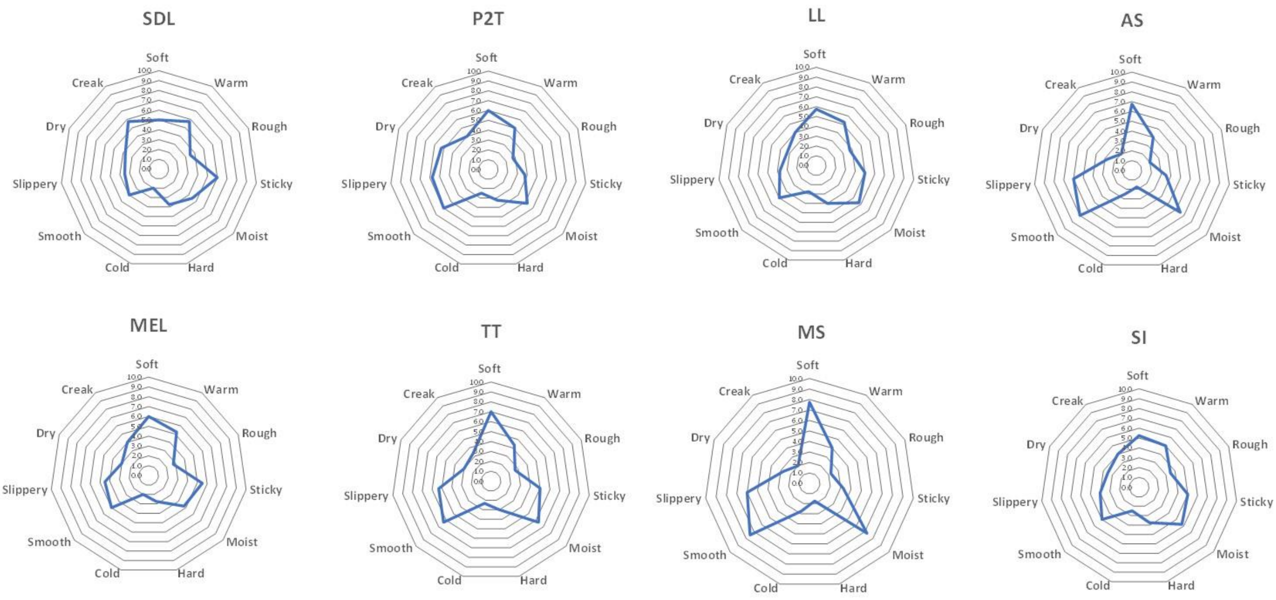


Figure 5. Tactile evaluation charts of powder foundation using each kind of surface treated pigments.

Friction evaluations of powder foundation.

In 2016, We have already reported the slight frictional difference depending on the kinds of surface treatment on the TiO_2 pigment using friction evaluation meter [3]. In this study, we could not detect the significant relationships between tactile feeling and frictional properties of powder foundations using each kind of surface treated powders (**Figure 6**). This result would be induced by spherical beads and platelet powders containing in powder foundations. Since in general, these powders could greatly reduce the friction coefficient of powder foundations, the influence of surface treatment on frictional properties of powder foundation becomes unclear. Although the significant difference caused by surface treatments has not been detected in the friction evaluation, the tactile evaluations among each kind of surface treatment were clearly different. From these results, it is assumed that tactile differences of types of surface treatments in powder foundation were affected not only by frictional properties but also by compatibility with the skin, moisture effect of surface treatment. Further study will be needed to reveal the influence of surface treatments on tactile feeling of powder foundations.

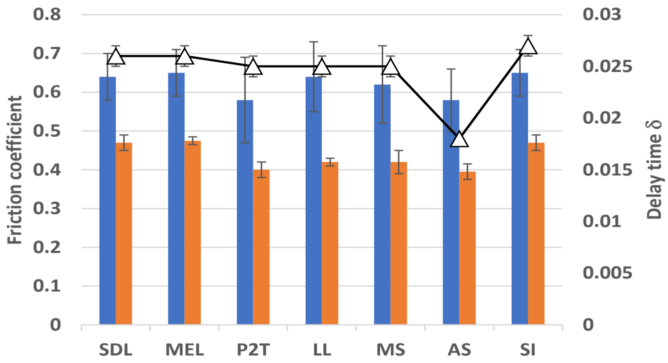


Figure 6. Friction evaluation of powder foundation using each kind of surface treated pigments.

Conclusion

TT and PT whose chemical structures are including long-chain branched fatty acid esters show high dispersibility and wettability in all kinds of cosmetic oils. This result indicates that TT and P2T treated pigments would be suitable for oil-based cosmetics, such as W/O liquid foundations, concealers and lipsticks. From the viewpoint of tactile feeling of powder foundation, MS and LL treatment could be natural alternative of AS and SI treatment, respectively. SDL treatment shows similar characteristics to MEL treatment, such as relatively low hydrophobicity, self-emulsification and pickering emulsification ability. Due to the high utility of SDL and MEL treatment, multi types of cosmetics, such as pressed powder foundation, W/O, O/W liquid foundation, lipsticks, and so on, could be prepared with these treatments. These results reveal that characteristics of each type of surface treated pigments will be greatly affected by chemical structure of each surface treatment agents. From these results, we succeed in classifying these surface treated pigments by their functions and tactile feeling (**table 4)**. These knowledges would be very helpful for developments of eco-friendly cosmetic product without using conventional petrochemicals.

Table 4. Friction evaluation of powder foundation using each kind of surface treated pigments.

	INCI name	Origin	Character	Recommended usage
P2T	Polyglyceryl-2 Tetraisostearate	Palm and rape seed oil	Hydrophobicity High dispersibility in oil Natural alternative of isopropyl titanium triisostearate treatment	Oil foundation W/O liquid foundation Lipsticks
MS	Magnesium Stearate	Palm oil and mineral	Hydrophobicity Improvement of tactile feeling (Moist and creamy) Natural alternative of alkyl silane treatment	Powder foundation Loose powder
LL	Lauroyl Lysine	Palm oil and・carbohydrate solution	Hydrophobicity Improvement of tactile feeling (smooth) Natural alternative of methylhydrogen polysiloxane treatment	Powder foundation Loose powder
SDL	Sodium Lauroyl Glutamate Lysine Magnesium Chloride	Palm oil	Hydrophobicity Self- emulsification Pickering emulsification	Powder foundation Oil foundation W/O liquid foundation O/W liquid foundation
MEL	Glycolipids	Olive oil	Hydrophobicity Self- emulsification Pickering emulsification	Powder foundation Oil foundation W/O liquid foundation O/W liquid foundation

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