

Deposition of 18-MEA onto alkaline-color-treated weathered hair to form a persistent hydrophobicity

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Synopsis

A technology for the deposition of a persistent hydrophobicity to alkaline-color-treated weathered hair surfaces using 18-MEA (18-methyleicosanoic acid) is presented. Two approaches were examined in order to make 18-MEA bind tightly to the alkaline-color-treated weathered hair surface. One was to apply 18-MEA as an acid form and the other was to apply 18-MEA as a salt or complex. It was found that the combination of 18-MEA with specific cationic surfactants [stearyoxypropyldimethylamine (SPDA) and docosyldimethylamine (DSDA)] makes the alkaline-color-treated weathered hair surface hydrophobic and that its hydrophobicity is maintained even after shampooing. Characterization of adsorbed layers of 18-MEA/SPDA on a mica surface, as a possible hydrophilic surface model, was performed using atomic force microscopy (AFM) and angle-resolved X-ray photoelectron spectroscopy (AR-XPS). The results revealed that 18-MEA/SPDA formed a layer with high wear resistance, with an alkyl chain, the hydrophobic moiety, oriented at an angle of around 25° to the air interface.

INTRODUCTION

18-MEA has been subjected to study for years in hair research science since the discovery of its presence on keratinous fibers (1–3). 18-MEA is thought to be covalently bound, probably via a thioester or ester linkage, to the outer surface of the cuticle (4–7) and is located specifically in the cuticle, not in the cortex (6). It is also known that 18-MEA makes the surface hydrophobic and acts as a boundary lubricant to decrease friction resistance (8–11). The precise role of 18-MEA remains unclear, but the large segmental volume of the anteiso-moiety is expected to provide molecular mobility and exhibit liquid-like behavior compared with a straight-chain fatty acid (12,13).

Since 18-MEA is covalently bound to the cuticle surface via thioester linkages, it can be easily removed under alkaline conditions, such as hair coloring or permanent waving, after which the hair surface becomes hydrophilic and friction increases (14,15). The absence of 18-MEA is considered one of the reasons for an increase in friction on the surface of the cuticle, and it may have an influence on the sensory perception of hair, such as inducing a dried-out feeling and being hard to finger/comb (10).

Cationic surfactants, polymers, or silicone derivatives are commonly used in hair care products for improving damaged hair surfaces by, for example, moisturizing, reducing friction, and making hair easier to finger/comb. Silicones in particular are used. The improving effects of these chemicals, however, are not permanent.

Although it is expected that a damaged hair surface should be repaired if the 18-MEA layer can be repaired, restoration of 18-MEA on the damaged hair surface has not been reported so far. The objective of this study is to develop a method to bind 18-MEA onto a damaged hair surface to provide persistent hydrophobicity and low friction to the damaged hair surface. It is well known that it is impossible to regenerate covalently bound 18-MEA on the damaged hair surface. Therefore, two approaches were examined in this study in order to make 18-MEA bind tightly to the alkaline-color-treated weathered hair surface. One was to apply 18-MEA as an acid form and the other was to apply 18-MEA as a salt or complex.

EXPERIMENTAL

MATERIALS

Hair samples. Hair fibers were kindly provided by a Japanese female aged 30. The fibers were cut at a distance of approximately 20 cm from the root end on the back of the head. The hair had never been treated with any chemical agents, such as bleaching, coloring, or permanent waving.

Preparation of alkaline-color-treated weathered hair. The hair was exposed to alkaline coloring four times, coupled with model weathering 360 times, where model weathering was done 90 times, between every interval of alkaline coloring. This resulted in a process of alkaline coloring combined with daily weathering that simulated a one-year period, assuming the hair was alkaline colored every three months. The model weathering treatment consisted of a series of daily hair care procedures: shampooing, conditioning, drying with a hot drier, and brushing. Hair fibers were treated with an alkaline-colored lotion (Table I) for 20 minutes at room temperature at a liquor:hair ratio of 1:1. The solution was then rinsed for one minute under running water. A plain shampoo [0.5 ml; 15 wt% of sodium polyoxyethylene lauryl ether sulfate (2.5 E.O.) with 2 wt% N,N-bis(2-hydroxyethyl)-dodecanamide solution, adjusted to pH 7 with phosphoric acid] was applied to the wet hair tress (5 g) and was massaged by hand for 30 seconds. The hair tress was then rinsed for 30 seconds under running water. A plain conditioner (0.5 ml; formulation No. 6 listed in Table II) was applied to the wet hair tress and distributed manually for 30 seconds, then left on for one minute. The hair tress was rinsed for 30 seconds under running water. The hair tress was towel dried and dried using a hot dryer for three minutes with brushing 20 times.

Chemicals. 18-MEA and stearyloxypropyldimethylamine (SPDA) were obtained by chemical synthesis (16,17). Other chemicals were commercially available.

Table I
Formulation of Alkaline-Color Lotion

35% Hydrogen peroxide	10
28% Ammonia water	2.7
Ammonium bicarbonate	5.6
Cethyl trimethylammonium chloride	2.0
EDTA/2Na	0.5
Water	Balance

pH 9.0

Table II
Formulation of Conditioners

	1	2	3	4	5	6 (control)
Stearoxypropyldimethylamine	2	—	—	—	—	2
Dimethylaminopropylstearamide	—	2	—	—	—	—
Stearyltrimethylammonium chloride	—	—	2	—	—	—
Docosyldimethylamine	—	—	—	2	—	—
Stearoxyhydroxypropyldimethelamine	—	—	—	—	2	—
Benzyl alcohol	0.5	0.5	0.5	0.5	0.5	0.5
Stearyl alcohol	3	3	3	3	3	3
18-MEA	1	1	1	0.3	0.3	0.6
Lactic Acid	0.3	0.3	—	—	—	0.3
Water				Balance		

METHODS

Measurement of surface properties of the hair. The wetting forces of the hair were measured by the Wilhelmy method using a K100MK2 tensiometer (Kruss). Single hair fibers were scanned over 3 mm at a velocity of 2 mm/min for the advancing mode. Dynamic contact angles were calculated from

$$F = \pi d \gamma \cos \theta$$

where F is the wetting force, π is the circular constant, d is the diameter of hair, γ is the surface tension of water, and θ is the contact angle of the fiber surface. The hair fiber diameter was measured on the transverse section of each fiber with a rotating fiber diameter measurement system equipped with a laser (Kato Tech Co.) at 20°C and a relative humidity of 65%. The wetting force measurements were also performed at 20°C, 65% relative humidity (RH).

Friction forces on the cuticle surface of the hair were measured using the KEF-SE friction tester (Kato Tech. Co., Ltd). The hair strands were mounted on a glass plate in such a way that all strands of the hair were separated and parallel to each other at 5-mm intervals. The test was conducted at a temperature of 20°C and a relative humidity of 65%.

Quantitative analysis of 18-MEA. Semi-quantitative analysis of 18-MEA adsorbed on the outermost surface of the hair fiber was measured by the TOF-SIMS IV instrument (ION-TOF GmbH, Germany) using 25-keV Au+ primary ions (average current, 0.3 pA; pulse width, 100.0 ns; repetition rate, 10 kHz) at high-spatial-resolution mode. The analysis

area of $50 \times 50 \mu\text{m}$ was randomly rastered by primary ions and was charge-compensated by low-energy electron flooding.

The amount of 18-MEA adsorbed to the hair fiber was measured using liquid chromatography/mass spectrometry (LC-MS, Agilent Technologies, Palo Alto, CA). Hair fibers were immersed in chloroform/methanol (1:1 by volume) for 1 h at room temperature. The extracts were dried using a nitrogen stream. The residues were then dissolved in chloroform/methanol (1:9 by volume). In the system, a 1100 binary pump was connected to two mobile phases [M1, methanol/water (8:2 by volume) containing 100 mM ammonium acetate and 50 mM acetic acid; and M2, methanol containing 100 mM ammonium acetate and 50 mM acetic acid] that were eluted at a flow rate of 0.2 ml/min. The mobile phases were programmed consecutively, as follows: a linear gradient of M1 100–0% (M2 0–100%) between 0 and 20 min, an isocratic elution of M1 0% (M2 100%) for 10 min, and an isocratic elution of M1 100% (M2 0%) from 30.1 to 40 min for column equilibrium (a total run time of 40 min). The injection volume was 5 μl . The column (L-column ODS 2.1-mm inner diameter \times 150 mm; Chemicals Evaluation and Research Institute, Tokyo, Japan) temperature was maintained at 40°C. ESI measurements in the mass spectrometer were performed with the following settings: polarity, negative; heater temperature of nitrogen gas, 350°C; flow of heated dry nitrogen gas, 11.01/min; nebulizer gas pressure, 30 psi; capillary voltage, –4000 V; fragmenter voltage, 200 V. The selected ion monitoring (SIM) measurement in negative ion ESI was performed using the unit mass resolution mode. To detect deprotonated ions for 18-MEA, $m/z = 325.2$ was monitored.

Measurement of surface properties of mica

(A) Atomic force microscopy

AFM images of the adsorbed layers on the mica surfaces were obtained using a Nanoscope IIIa Multi Mode AFM (Veeco Instruments, Santa Barbara, CA) with E-scanner. Tapping mode imaging was used to obtain the topography images of the adsorbed membrane layers. To ensure that imaging the membrane caused no damage, the tapping force was set at the lowest possible level. The nominal spring constants of cantilevers are reported by the manufacturer to be 20–100 N/m, respectively. All images presented in this work were obtained reproducibly over at least three spots on the sample surfaces. The images were acquired with a scan rate of either 0.5 or 1.0 Hz and were flattened with a first-order polynomial before analysis.

The mechanical properties of the adsorbed membrane were analyzed by the AFM scratching method. Scratching the adsorbed membrane was performed in contact mode with constant force, and a micro-fabricated tip made of silicon nitrate and a cantilever having a spring constant of 0.38 N/m were used. First, an image (typically $5 \mu\text{m} \times 5 \mu\text{m}$) of the adsorbed membrane was acquired; then a smaller area (typically $1 \mu\text{m} \times 1 \mu\text{m}$) was scanned while loading the hard tip onto the surface. Following this, the scanning was repeated over the larger area. This method is hereafter called “scratching.” Thus, if the adsorbed layer was strongly bound to the surface, it was harder to remove.

(B) Angle-resolved X-ray photoelectron spectroscopy (ARXPS)

ARXPS is a nondestructive method to obtain elemental and chemical-state information as a function of depth. ARXPS data was obtained using a Quantera SXM spectrometer (ULVAC PHI, Kanagawa) with a monochromatized Al K alpha X-ray source at 15 kV and 25 W. Survey spectra were recorded at a takeoff angle of 45° with pass energy of 280 eV by a cylindrical-mirror analyzer. Angle-resolved spectra were recorded at five takeoff

angles, 70, 45, 25, 15, and 10 degrees, in a high-energy resolution mode with pass energy of 112 eV.

RESULTS

CHARACTERIZATION OF ALKALINE-COLOR-TREATED WEATHERED HAIR

Surface properties of alkaline-color-treated weathered hair are shown in Figure 1. Since 18-MEA is covalently bound to the cuticle surface via a thioester linkage, it can be removed with alkaline treatments such as perming, coloring, and bleaching. It is well known that the reduction of 18-MEA affects surface properties of hair such as hydrophobicity and friction. Figure 1(A) shows the relative ion yield of 18-MEA versus the total ion yield on the outermost surface of hair measured by TOF-SIMS. In the case of alkaline-color-treated weathered hair, most of the 18-MEA has been removed. Figure 1(B) shows the hydrophobic property of normal hair and alkaline-color-treated weathered hair. A higher value means that the surface is more hydrophobic, and a lower value means that the surface is more hydrophilic. The contact angle of normal hair was around 90°, which means that it was hydrophobic because of the presence of 18-MEA. On the other hand, that of alkaline-color-treated weathered hair was around 65°, which means that it was more hydrophilic because of the absence of 18-MEA and the oxidation of sulfur groups to sulfate. Figure 1(C) shows the dynamic friction coefficients of normal hair and alkaline-color-treated weathered hair. It shows that surface friction increased when 18-MEA was removed. Since it was confirmed that the results obtained here correspond to previous knowledge, alkaline-color-treated weathered hair was used in the subsequent experiments.

The objective for this study was to attach 18-MEA onto alkaline-color-treated weathered hair and to provide persistent hydrophobicity and low friction on an alkaline-color-treated weathered hair surface. In the following sections, contact angles after one instance of shampooing were measured in order to make sure that the damaged hair surface maintained its hydrophobicity even after shampooing.

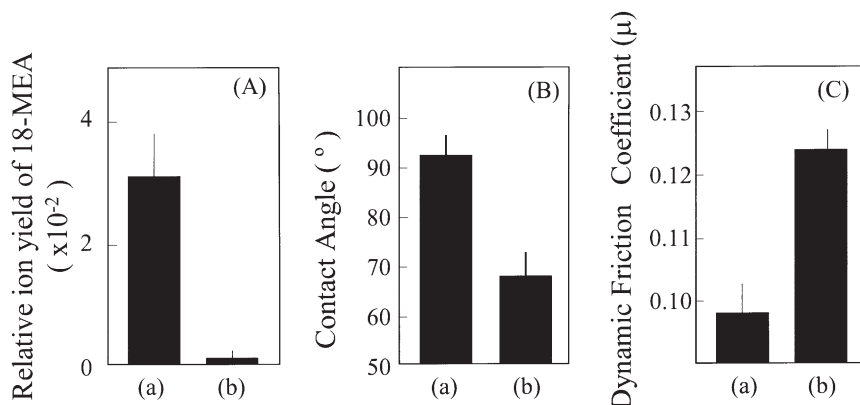


Figure 1. Surface properties of alkaline-color-treated weathered hair. Relative ion yield of 18-MEA versus the total ion yield (A), contact angle (B), and dynamic friction coefficient (C) are presented. The bars represent means for $n=5$; the whiskers represent the standard deviations. (a) Normal hair. (b) Alkaline-color-treated weathered hair.

APPLICATION OF 18-MEA AS AN ACID FORM

Contact angles of alkaline-color-treated weathered hair treated with 18-MEA as acid type are shown in Figure 2. When the alkaline-color-treated weathered hair was treated with 1 wt% of 18-MEA in chloroform, the contact angle became 90° , corresponding to that of normal hair (Figure 2c). That means the surface of the alkaline-color-treated weathered hair recovers hydrophobicity just after 18-MEA application. The contact angle decreased after shampooing (Figure 2d), however, meaning the surface reverts to being hydrophilic. This is because 18-MEA applied as an acid form does not have shampoo resistance.

APPLICATION OF 18-MEA AS A SALT OR COMPLEX

Contact angles of alkaline-color-treated weathered hair treated with 18-MEA salts or polymer complexes and subsequently shampooed are shown in Figure 3. The contact angles of all samples were almost the same as that of alkaline-color-treated weathered hair. These results indicate that these 18-MEA salts or complexes could not provide persistent hydrophobicity to an alkaline-color-treated weathered hair surface.

Contact angles of alkaline-color-treated weathered hair treated with 18-MEA and long-chain tertiary amine or quaternary cationic surfactant complexes in conditioners, after one-time shampooing with a plain shampoo [15 wt% of sodium polyoxyethylene lauryl

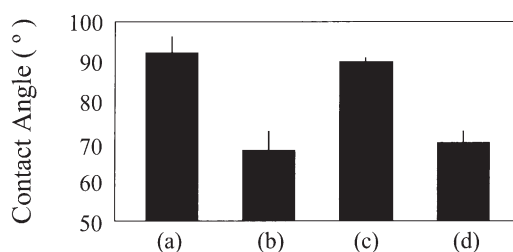


Figure 2. Contact angle of alkaline-color-treated weathered hair treated with 18-MEA as an acid form. The bars represent means for $n=5$; the whiskers represent the standard deviations. (a) Normal hair. (b) Alkaline-color-treated weathered hair. (c) Alkaline-color-treated weathered hair treated with 18-MEA as an acid form (1 wt% of 18-MEA in chloroform was applied). (d) Alkaline-color-treated weathered hair treated simply with 18-MEA as an acid form and shampooed.

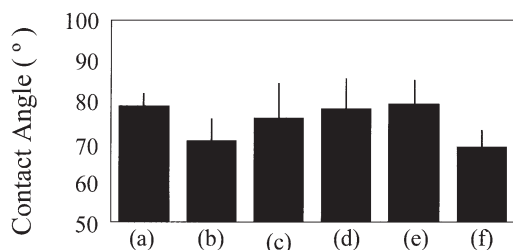


Figure 3. Contact angle of alkaline-color-treated weathered hair treated with 18-MEA salts or complexes after shampooing. The bars represent means for $n=5$; the whiskers represent the standard deviations. 1 wt% of 18-MEA salt or complex in water was applied. (a) Sodium salt. (b) Potassium salt. (c) Ammonium salt. (d) Monoethanol amine salt. (e) Cationic hydroxyethyl cellulose complex (polyquaternium-10). (f) Guar hydroxypropyltrimonium complex.

ether sulfate (2.5 E.O.) with 2 wt% N,N-bis (2-hydroxyethyl)-dodecanamide solution adjusted to pH 7 with phosphoric acid], are shown in Figure 4. The chemical structures of these surfactants are shown in Figure 5, and the conditioner formulations are listed in Table II. When alkaline-color-treated weathered hair was treated with the 18-MEA/SPDA complex (conditioner 1), the contact angle became nearly 90°, approaching that of normal hair. To further investigate the differences in the dynamic contact angles, analysis of variance (ANOVA) was conducted. It demonstrated that there were significant differences in the contact angle between the hair treated with the 18-MEA/SPDA complex (conditioner 1) and alkaline-color-treated weathered hair, and that there were not significant differences in the contact angle between the hair treated with 18-MEA/SPDA complex (conditioner 1) and normal hair. This means that the surface of alkaline-color-treated weathered hair treated with the 18-MEA/SPDA complex (conditioner 1) could maintain its hydrophobicity even after one instance of shampooing with a plain shampoo [15 wt% of sodium polyoxyethylene lauryl ether sulfate (2.5 E.O.) with 2 wt% N,N-bis(2-hydroxyethyl)-dodecanamide solution adjusted to pH7 with phosphoric acid], while the hair treated with other complexes could not.

Figures 6 shows the dynamic friction coefficient of alkaline-color-treated weathered hair treated with 18-MEA/SPDA, 18-MEA/DAPS, and 18-MEA/STAC complexes. The dynamic friction coefficient of alkaline-color-treated weathered hair treated with the 18-MEA/SPDA was the nearest to that of normal hair, and it was much lower than that of hair treated with the other complexes. To further investigate the differences in the dynamic friction coefficient, analysis of variance (ANOVA) was conducted. The results of ANOVA showed that there was a significant difference in the dynamic friction coefficient between the hair treated with the 18-MEA/SPDA complex (conditioner 1) and alkaline-color-treated weathered hair, and that there were no significant differences in the dynamic friction coefficient between the hair treated with the 18-MEA/SPDA complex (conditioner 1) and normal hair. That means that the surface of alkaline-color-treated weathered

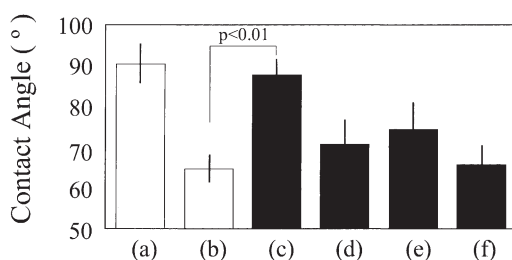


Figure 4. Contact angle of alkaline-color-treated weathered hair treated with 18-MEA complexes after shampooing. The bars represent means for $n=7$; the whiskers represent the standard deviations. The p -value was obtained from ANOVA analysis. (a) Normal hair. (b) Alkaline-color-treated weather hair. (c) 18-MEA/SPDA (conditioner 1). (d) 18-MEA/DAPS (conditioner 2). (e) 18-MEA/STAC (conditioner 3). (f) Control (conditioner 6).

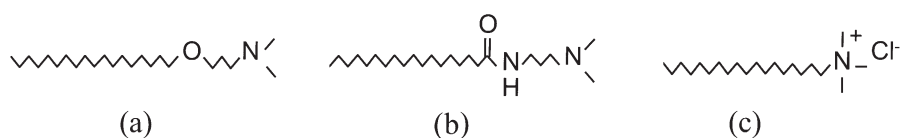


Figure 5. Chemical structures of surfactants. (a) Stearoxypropyldimethylamine (SPDA). (b) Dimethylaminopropylstearamide (DAPS). (c) Stearyltrimethylammonium chloride (STAC).

hair treated with the 18-MEA/SPDA complex (conditioner 1) could maintain its low friction even after one instance of shampooing with a plain shampoo [15 wt% of sodium polyoxyethylene lauryl ether sulfate (2.5 E.O.) with 2 wt% N,N-bis(2-hydroxyethyl)-dodecanamide solution adjusted to pH7 with phosphoric acid], while the hair treated with other complexes could not.

Figure 7 shows the amount of 18-MEA sorption in alkaline-color-treated weathered hair treated with 18-MEA/SPDA, 18-MEA/DAPS, and 18-MEA/STAC complexes measured by LC-MS. Figure 8 shows the relative ion yield of 18-MEA versus the total ion yield of alkaline-color-treated weathered hair treated with 18-MEA/SPDA, 18-MEA/DAPS, and 18-MEA/STAC complexes measured by TOF-SIMS. As we expect from the contact angle and surface friction results, the amount of 18-MEA absorbed on the surface of alkaline-color-treated weathered hair treated with the 18-MEA/SPDA complex was much higher than that of hair treated with the other complexes.

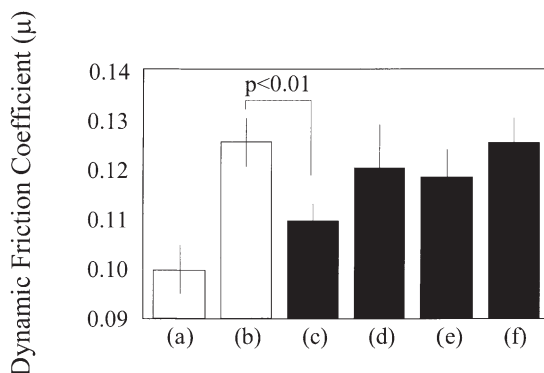


Figure 6. Dynamic friction coefficient of alkaline-color-treated weathered hair treated with 18-MEA complexes after shampooing. The bars represent means for $n=5$; the whiskers represent the standard deviations. The p -value was obtained from ANOVA analysis. (a) Normal hair. (b) Alkaline-color-treated weathered hair. (c) 18-MEA/SPDA (conditioner 1). (d) 18-MEA/DAPS (conditioner 2). (e) 18-MEA/STAC (conditioner 3). (f) Control (conditioner 6).

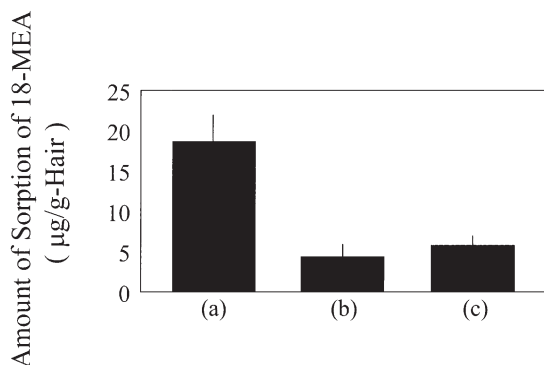


Figure 7. Amount of 18-MEA sorption of alkaline-color-treated weathered hair treated with 18-MEA complexes after shampooing, measured by LC-MS. The bars represent means for $n=3$; the whiskers represent the standard deviations. (a) 18-MEA/SPDA (conditioner 1). (b) 18-MEA/DAPS (conditioner 2). (c) 18-MEA/STAC (conditioner 3).

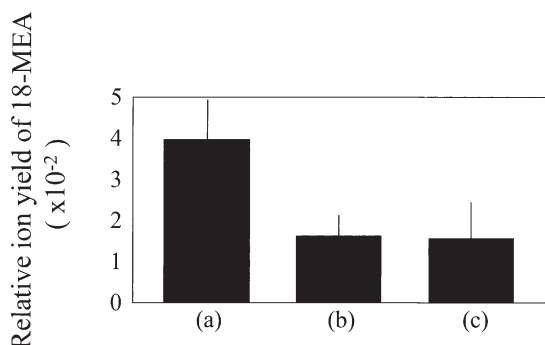


Figure 8. Relative ion yield of 18-MEA versus the total ion yield of alkaline-color-treated weathered hair treated with 18-MEA complexes and shampooed, measured by TOF-SIMS. The bars represent means for $n=3$; the whiskers represent the standard deviations. (a) 18-MEA/SPDA (conditioner 1). (b) 18-MEA/DAPS (conditioner 2). (c) 18-MEA/STAC (conditioner 3).

DISCUSSION

There are many different types of chemicals used for improving the damaged surface of hair, such as cationic surfactants, polymers, and silicones. The aim of the present study was to develop a method to deposit 18-MEA onto alkaline-color-treated weathered hair in order to provide persistent hydrophobicity and low friction. By combining 18-MEA with stearoxypropyldimethylamine (SPDA), we were able to establish a technology that provides persistent hydrophobicity to alkaline-color-treated weathered hair surfaces.

The question remains as to why the combination of 18-MEA and SPDA provides persistent hydrophobicity to alkaline-color-treated weathered hair surfaces, and additional surface studies are needed to determine the answer. Atomic force microscopy (AFM) is a very powerful technique commonly used in nanotechnology. Here, a sharp tip interacts with surfaces to generate high-resolution images or to obtain local physical information such as indentation and adhesion. It is very difficult to examine the exact situation of an 18-MEA/SPDA layer adsorbed onto the alkaline-color-treated weathered hair surface, however, since the surface of hair is too rough for the AFM investigation. In order to investigate the thickness and physical properties of the layer formed by 18-MEA/SPDA, an atomically flat surface is needed for the AFM observation. A mica surface and the alkaline-color-treated weathered hair surface are both hydrophilic, although the components of these substance are different: mica consists of a hydrous potassium aluminum silicate mineral and the alkaline color-treated weathered hair surface consists of a mixture of modified proteins. In this study, mica was used for AFM investigation as a hydrophilic model surface instead of hair, although it might be open to question that these surfaces would behave differently due to the different compositions of these surfaces. We believe, however, that the attachment and orientation of the 18-MEA/SPDA could be similar in human hair.

Figure 9 shows AFM height images of the adsorbed layers on the mica surfaces treated with 18-MEA/SPDA (a), 18-MEA/DAPS (b), or 18-MEA/STAC (c) conditioner solutions. These areas were reimaged after $1000 \text{ nm} \times 1000 \text{ nm}$ scratching tests by rastering a tip with constant force, and the adsorbed membrane was analyzed by the AFM scratching method, as shown in Figure 10. If the layer is hard to remove, it means that the adsorbed layer is strongly bound to the surface. In the image of adsorbed film treated by

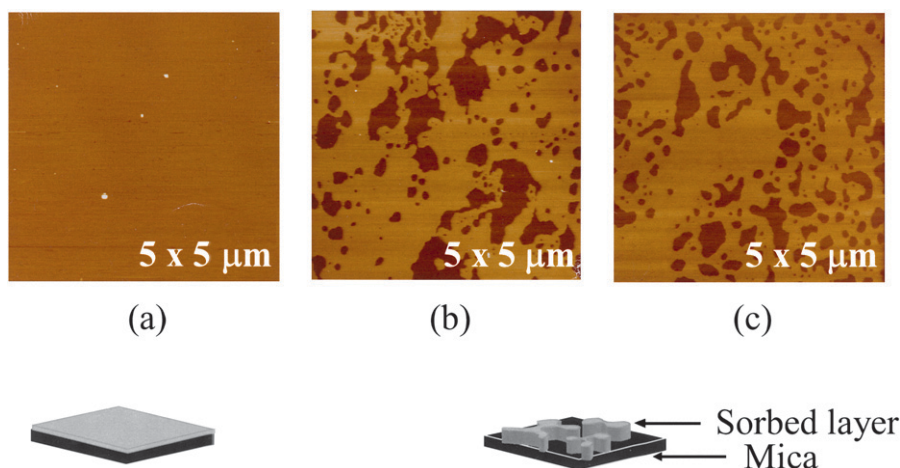


Figure 9. AFM height images of adsorbed layer on mica surface. Dark areas are mica without sorption; bright areas are sorbed layer from conditioner. (a) 18-MEA/SPDA. (b) 18-MEA/DAPS. (c) 18-MEA/STAC.

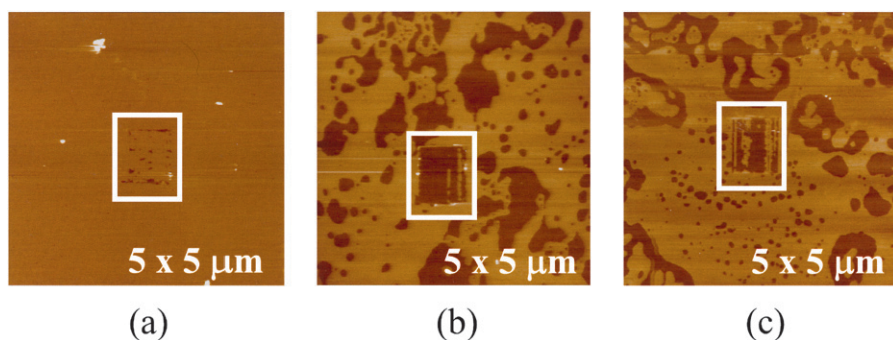


Figure 10. AFM height images of adsorbed layer on mica surface. Dark areas are mica without sorbed compound; bright areas are sorbed chemicals from conditioner. The white squares indicate where 1000 nm \times 1000 nm scratching tests were done by rastering the tip with constant force. (a) 18-MEA/SPDA. (b) 18-MEA/DAPS. (c) 18-MEA/STAC.

18-MEA/DAPS (b) or 18-MEA/STAC (c), a square groove was observed. On the other hand, treatment by 18-MEA/SPDA (a) showed no such groove. These results indicate that the 18-MEA/SPDA conditioner adsorbed homogeneously on the mica surface and had a high wear resistance. Regarding the thickness of the layer, it was estimated that the layer of 18-MEA/SPDA was about 1-nm thick.

Molecular orientations of the adsorbed layers investigated by ARXPS are shown in Figure 11. The peak area ratio of COO (carboxyl) from 18-MEA/C (carbon) from conditioner ingredients, such as surfactant, stearyl alcohol and so on, increased with the measurement depth. The peak area ratio of N (nitrogen)/C (carbon) from SPDA increased as a function of the measurement depth in a similar manner. These results suggest that the hydrophilic moiety of the molecules, the carboxyl group of 18-MEA and the amide group of SPDA, attach to the mica surface and orient the alkyl chain (the hydrophobic moiety) to the air interface. Taking into account our results obtained here, the thickness of 18-MEA/SPDA

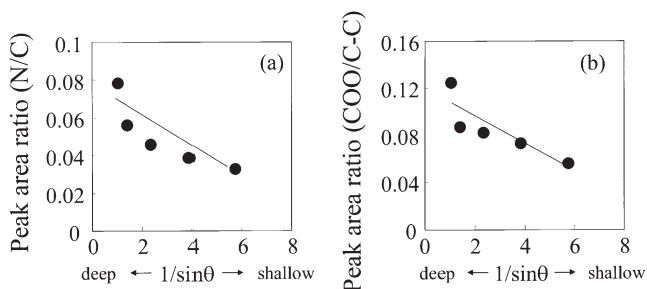


Figure 11. Molecular orientation analysis of 18-MEA/SPDA membrane by angle-resolved X-ray photoelectron spectroscopy (ARXPS). θ represents photoelectron take-off angle. (a) Angle dependence of nitrogen/carbon concentration derived from SPDA. (b) Angle dependence of COO/C-C concentration derived from 18-MEA.

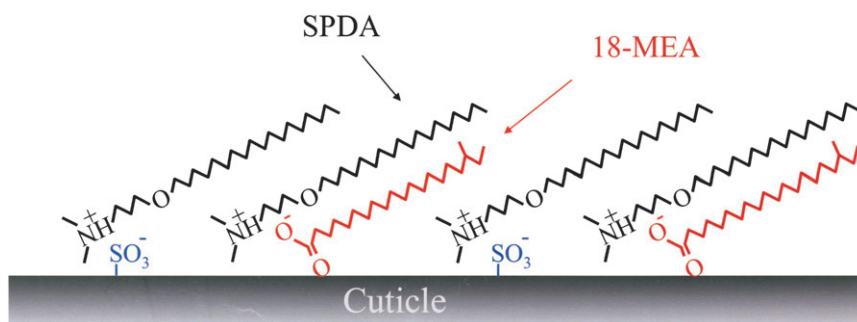

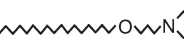

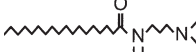


Figure 12. Schematic diagram of the cuticle surface of alkaline-color-treated weathered hair treated with 18-MEA/SPDA. 18-MEA/SPDA forms a layer with high wear resistance, orienting the alkyl chain (hydrophobic moiety) at an angle of around 25° to the air interface.

is about 1 nm, and since the alkyl chain length of 18-MEA is 2.39 nm, the 18-MEA/SPDA layer orients at an angle of around 25° to the air interface. Thus, the following model (Figure 12) is suggested, based on the results obtained from the present investigation: 18-MEA/SPDA forms a layer 1 nm in thickness, with both 18-MEA and SPDA bound tightly to the surface by the carbonyl and amide groups, orienting the hydrophobic part to the air interface at an angle of around 25° .

Another question was whether SPDA is special for providing persistent hydrophobicity to alkaline-color-treated weathered hair surfaces. Additional studies, on the dynamic contact angles and the amount of 18-MEA sorption measurements, were conducted to elucidate the issue with the complexes of 18-MEA and a variety of long-chain tertiary amines. Table III shows the dynamic contact angles and the amount of 18-MEA sorption of alkaline-color-treated weathered hair treated with 18-MEA/long-chain tertiary amines. The chemical structures of these tertiary amines and the logP value, which is calculated by the ClogP method, are also listed in Table III. The combination of 18-MEA with SPDA or DSDA made the alkaline-color-treated weathered hair surfaces hydrophobic, and their hydrophobicity was maintained even after one instance of shampooing with a plain shampoo [15 wt% of sodium polyoxyethylene lauryl ether sulfate (2.5 E.O.) with 2 wt% N,N-bis(2-hydroxyethyl)-dodecanamide solution adjusted to pH7 with phosphoric acid], while the combination of 18-MEA with SHDA and DAPS could not.

Table III
Effects of a Long-Chain Tertiary Amine Structure in 18-MEA/Tertiary Amine Complexes
for a Persistent Hydrophobicity

Chemical structure				
	Docosyldimethyl- amine (DSDA)	Stearoxypropyl- dimethylamine (SPDA)	Stearoxyhydroxypropyl- dimethylamine (SHDA)	Dimethylaminopropyl- stearamide (DAPS)
logP	11.127	9.496	8.393	8.255
Dynamic contact angles*	87.2 ± 2.5°	87.6 ± 3.7°	71.1 ± 4.1°	70.6 ± 5.6°
Amount of 18-MEA sorption**	18.9 ± 0.6	18.7 ± 6.0	2.7 ± 0.1	4.0 ± 2.3

*Dynamic contact angels of alkaline-color-treated weathered hair treated with 18-MEA/tertiary amine complexes after shampooing were measured (n=7).
**Measured by LC/MS (µg/g-hair) (n=3).

The amount of 18-MEA absorbed on the surface of alkaline-color-treated weathered hair treated with 18-MEA/DSDA or 18-MEA/SPDA complexes was much higher than that of hair treated with the other complexes (18-MEA/SHDA or 18-MEA/DAPS). The logP values of DSDA, SPDA, SHDA, and DAPS are 11.127, 9.496, 8.393 and 8.255, respectively. DSDA and SPDA are more hydrophobic tertiary amines than SHDA and DAPS. The combination of 18-MEA with the relatively hydrophobic tertiary amines (DSDA and SPDA) could make the alkaline-color-treated weathered hair surfaces hydrophobic, and their hydrophobicity was maintained even after one instance of shampooing with a plain shampoo [15 wt% of sodium polyoxyethylene lauryl ether sulfate (2.5 E.O.) with 2 wt% N,N-bis(2-hydroxyethyl)-dodecanamide solution adjusted to pH 7 with phosphoric acid]. It seems that the results relate to how the alkyl chain of 18-MEA and the alkyl chain of the tertiary amines align with each other in the complexes in molecular order, that is, the alkyl chain of the hydrophobic tertiary amines, DSDA and SPDA, could make packed alignments with the alkyl chain of 18-MEA, while the alkyl chain of the hydrophilic tertiary amines, SHDA and DAPS, could not make packed alignments with the alkyl chain of 18-MEA because the hydrophilic moiety of the hydrophilic tertiary amines, the hydroxypropyl group in SHDA and the amide group in DAPS, would hinder closer packing between the alkyl chain of the tertiary amines and the alkyl chain of 18-MEA.

Regarding the 18-MEA lipid layer on the untreated healthy hair, two models have been proposed, although there is still some contradiction regarding the thickness of the 18-MEA layer. The first model is the one in which 18-MEA orients to the air interface straight, based on the length of a 20-carbon chain of 18-MEA (18). The second model is the one where 18-MEA is folded back in the direction of the surface (19), based on the result that the thickness of the surface lipid layer is 0.9 nm, as obtained by Ward *et al.* using XPS (20). Here, we would like to compare the surface model of hair treated with 18-MEA/SPDA and the natural 18-MEA layer on untreated healthy hair. The surface models of hair treated with 18-MEA/SPDA and the 18-MEA layer on untreated healthy hair seem to have some characteristics in common, including being about 1 nm in thickness, having the hydrophilic area of molecules binding tightly to the surface, and orienting the

hydrophobic part to the air interface. Therefore, it seems reasonable that 18-MEA/SPDA could provide persistent hydrophobicity to the alkaline-color-treated weathered hair surface.

CONCLUSIONS

The main conclusions are as follows:

1. The application of a combination of 18-MEA with relatively hydrophobic tertiary amines (DSDA or SPDA) made damaged hair surfaces hydrophobic, and the hydrophobicity was maintained ever after one instance of shampooing with a plain shampoo [15 wt% of sodium polyoxyethylene lauryl ether sulfate (2.5 E.O.) with 2 wt% N,N-bis(2-hydroxyethyl)-dodecanamide solution adjusted to pH 7 with phosphoric acid].
2. AFM and ARXPS analysis revealed that 18-MEA/SPDA attaches to a mica surface and forms a layer with high wear resistance, with the alkyl chain (hydrophobic moiety) oriented at an angle of around 25° to the air interface. We believe this attachment and orientation could be similar in human hair.
3. The mechanism of sustainable hydrophobicity of the hair surfaces generated by 18-MEA/SPDA has some characteristics in common with the natural 18-MEA layer formed on untreated healthy hair, including being about 1 nm in thickness, having the hydrophilic area of molecules binding tightly to the surface, and orienting its hydrophobic part to the air interface.

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