J. Cosmet. Sci., **58**, 283–294 (July/August 2007)

Formation of nanostructure on hair surface: Its characteristic optical properties and application to hair care products

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Synopsis

Uneven structures on hair fiber surface, such as lift up of cuticle or build up of hair spray ingredients, generally cause a diffuse reflection which results in a dull and unhealthy appearance. However, in the case of finer structure than wavelength of visible light, the optical properties change significantly. An application of the phenomenon to hair care products is reported in this paper.

Formation of the fine structure on hair surface was achieved by only a shampoo and rinse-off conditioner system including amino-silicone. Chroma enhancement of hair and light introduction into hair fibers were observed simultaneously with formation of the fine structure on the hair surface. The light introduction phenomenon is understood in terms of "Effective Medium Approximation" (EMA). The simulation study based on EMA indicates that a very low refractive index surface is expected to be realized, which well explains the optical experimental results. When the shampoo and conditioner system developed to form the structure on fiber surface was applied to dyed hair, enhancement and long-lasting of vivid appearance was confirmed in spite of dye elution.

INTRODUCTION

Hair optical factors have been analyzed to understand beautiful and healthy appearance of hair. Especially, shine, color and texture based on optical properties of hair fiber have been focused (1,2). Cuticle has relatively higher refractive index (n = 1.55, 3) as an organic material which may lead to both relatively intense surface reflection. For healthy shine, cuticle smoothness is one of the most important factors to reduce diffuse reflection on hair surface. Furthermore, in the case of lighter hair including less amount of melanin granule, reflection light with colors of fiber from inside also becomes more emphasized. Therefore, the optical transparency of hair fiber is added in important factors in order to obtain beautiful appearance.

In general, it is known that chemical treatments, excessive dryer heat, or residue by incomplete shampooing induce a formation of pores in hair fiber or roughness on hair surface. If their sizes are larger than light wavelength, they behave as diffuse reflection sources which result in dull or colorless dry appearance. Combination of solvents and organic acids under a low pH condition were reported as a hair treatment system to reduce such diffuse reflection sources. Penetration of the acids is accelerated in the system to swell hair fiber protein resulting in reduction of inner pores (4,5). Additionally, re-adhesion effect of cuticle lift-up part and removal effect of scam are also reported to regain the original optical natures of hair (6).

In this paper, a novel approach to develop hair optical properties is attempted by modification of hair surface. If an asperity of hair surface is finer than light wavelength, the structure doesn't work as a light drying, the color was measured as 6 parts on hair tress to calculate the mean value. This series of operation was repeated for 30 cycles. Deference from the original color of untreated tress (cycle = 0) was evaluated as a color change of each cycle.

EVALUATION OF DYED HUMAN HEAD

Color change of dyed hair was evaluated by half head comparing method of the control and the test systems. Originally brown color hair American women were evenly dyed using commercial red oxidation dye. Colors of 20 parts for both sides were measured as the original color value before the treatment. Shampoo and conditioner treatment, and color measurement after each treatment was performed cyclically for 12 times. The treatment process was performed by a beautician.

OBSERVATION OF HAIR FIBER SURFACE

Atomic Force Microscopy (Nano Scope □/Multi Mode AFM, Digital Instrument Inc., Tapping Mode measurement) was used for measurement of fine structure size on hair fiber surface. Element distribution on the structure was evaluated using Field Emission Type Scanning Electron Microscopy attached with Energy Dispersive Spectroscopy (FE-SEM-EDS/JSM5200, JEOL, 1KeV) with no courting on surface.

REFLECTION MEASUREMENT ON HAIR FIBER SURFACE

Reflection intensity dependence on light wavelength was measured using Goniophotometer (GP-200, Murakami Color Research Laboratory). Light source (halogen lamp parallel light) was isolated into 3 kinds of monochromatic light using narrow-band interference filter (center wavelength = 410 nm, = 550 nm, 690 nm / FWHM = 10 nm, Edmund Optics Inc.). Aligned 10 pieces of hair fiber on a stage were irradiated at 45 degree of incident angle from root side to tip side of hair fiber. Reflection was detected at 45 ± 15 degree. In ±15 degree of detecting range, maximum peak value was evaluated as surface specular reflection.

RESULTS

CHROMA CHANGE AND SURFACE OBSERVATION OF HAIR TRESS

Chroma changes in the treatment cycles of the control and the test systems were showed in Figure 1. Continuous chroma enhancement and subsequent saturation were observed in the treatment cycles of the test system. Visually-apparent color enhancement was also confirmed simultaneously. In contrast, slight chroma enhancing at first several cycles and getting back to the original level after further cycles were observed in the control system treatment, and no change of color was also visually confirmed. AFM observations of hair fiber surface sampled at each cycle showed a relation between fine structure formation on the surface and chroma enhancement (Figure 2). In the case of the control system, asperity appearance in the first several cycles and its flatting out after further treatments were observed. This process is considered as a result of adsorption saturation of fatty alcohol, the major ingredient of conditioners, on hair fiber surface, because no change on surfaces was observed with only the control shampoo. However, continuous growing of the asperity was observed by the test system treatments. Element analyses on the hair surface after 20 cycles of the test system treatment showed a web like pattern of silicon with the similar scale in size of the structure (Figure 3). The result indicates an inhibition of fatty alcohol saturation on hair surface by amino-silicone. Deposition pattern control of amino-silicone is thus supported to be important point of the phenomenon.

LIGHT REFLECTION ON THE HAIR FIBER SURFACE TREATED BY THE TEST SYSTEM

Intensities of surface specular reflection in the test system treatment cycles are shown in

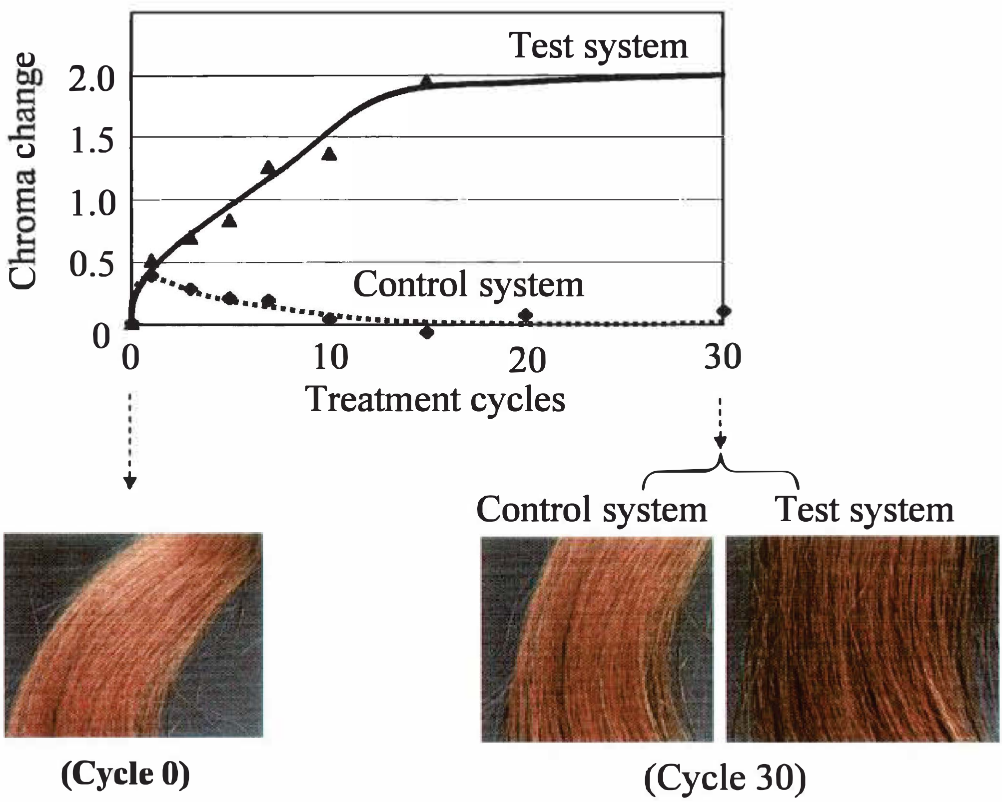

Figure 1. Chroma change in the shampoo and conditioner treatment cycles.

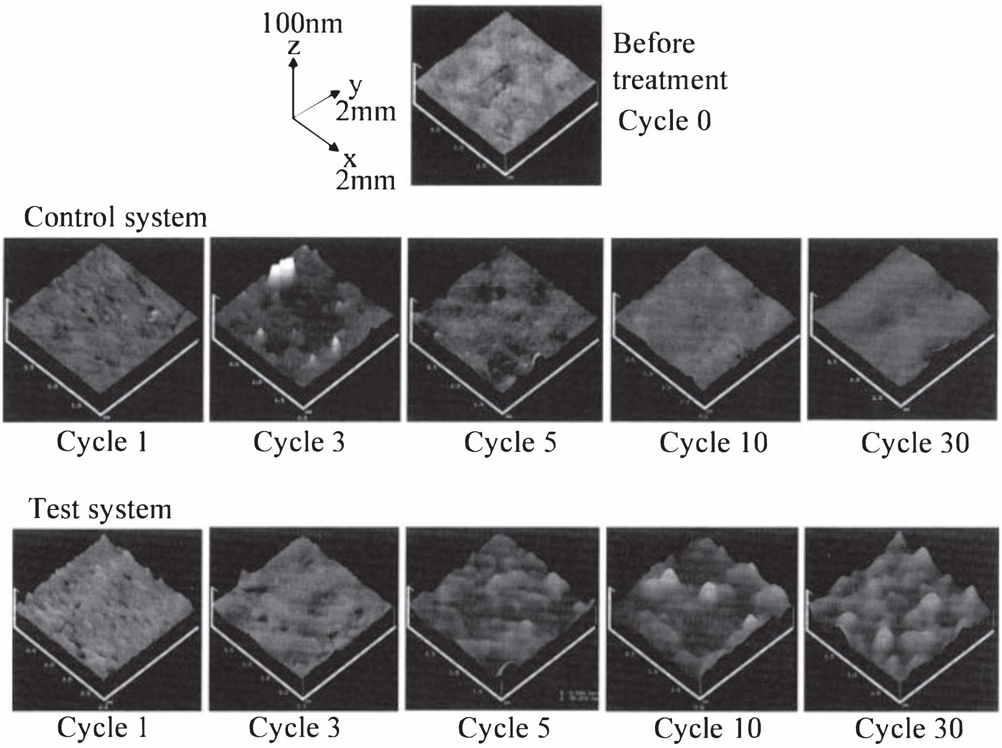

Figure 2. AFM observation of hair surface in the shampoo and conditioner treatment cycles.

Figure 4. The intensity was calculated as a relative value based on the intensity of cycle 0, and three wavelengths of light, 690, 550 and 410 nm were evaluated as incident light. Decreasing of surface reflection intensity for all wavelengths were observed with increasing the treatment cycles. No enhancement of half bandwidth of the reflection peak

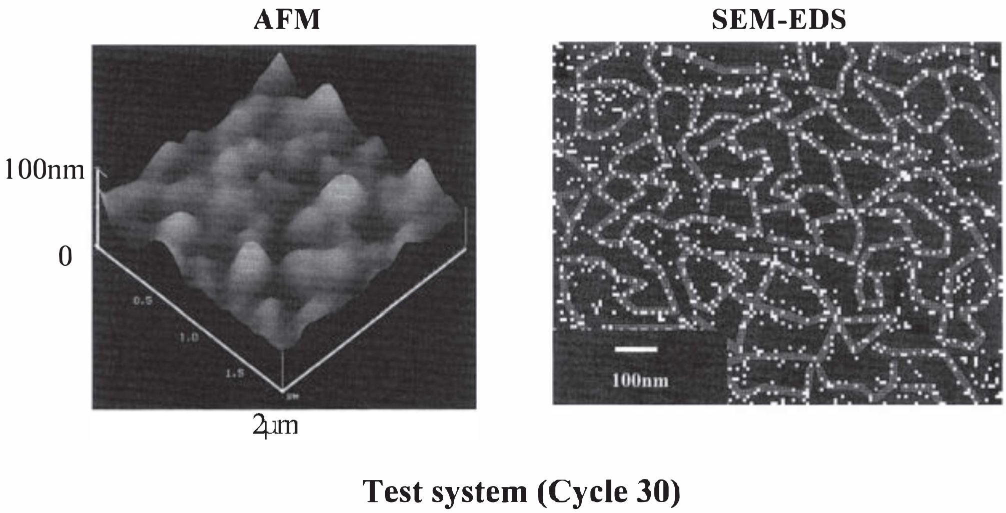

Figure 3. Silicon distribution (white dots) on fine structure formed by test shampoo and conditioner treatments.

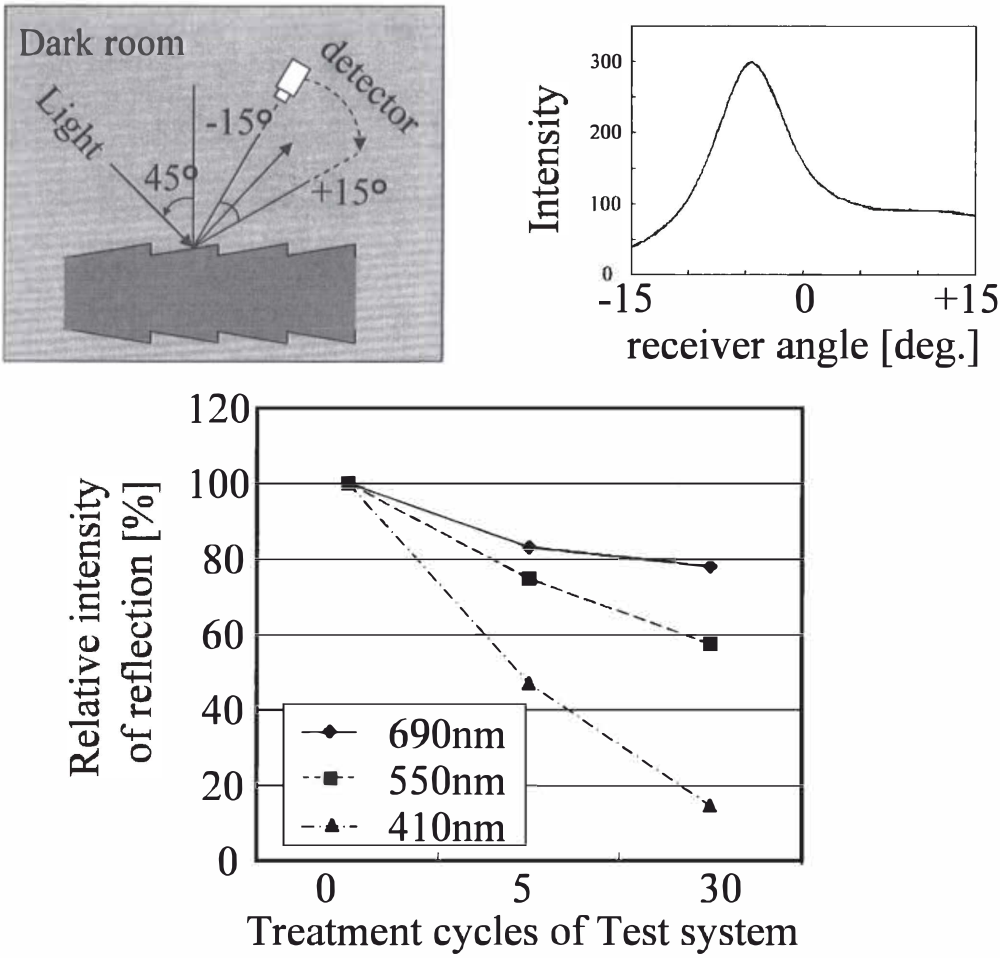

Figure 4. Intensity change of surface specular reflection on the hair fiber surface by test system treatments.

was also observed, namely, no enhancement of random reflection caused by increase of surface roughness was occurred. These phenomena are explained as enhancement of light introduction into the hair fiber with fine asperity on their surface. The amount of light introduction strongly depends on light wavelength, the more red, the light tend to be reflected more.

CHROMA CHANGE MEASUREMENT OF DYED HEAD

Chroma change of red dyed panelist's head after half head tests with the control and the test system is shown in Figure 5. The control system showed a simple chroma decrease, suggesting dye elution is simply occurred with the control system resulting in remarkable color fading. In contrast, the test system showed chroma enhancement in spite of occurrence of the dye elution. Further treatment induced chroma decrease, but the chroma was kept significantly higher level than the control system. Visual color was also identified by naked eyes more intense than the control system (Figure 6). The result of the Test system is explained as the balance of light introduction effect and dye elution.

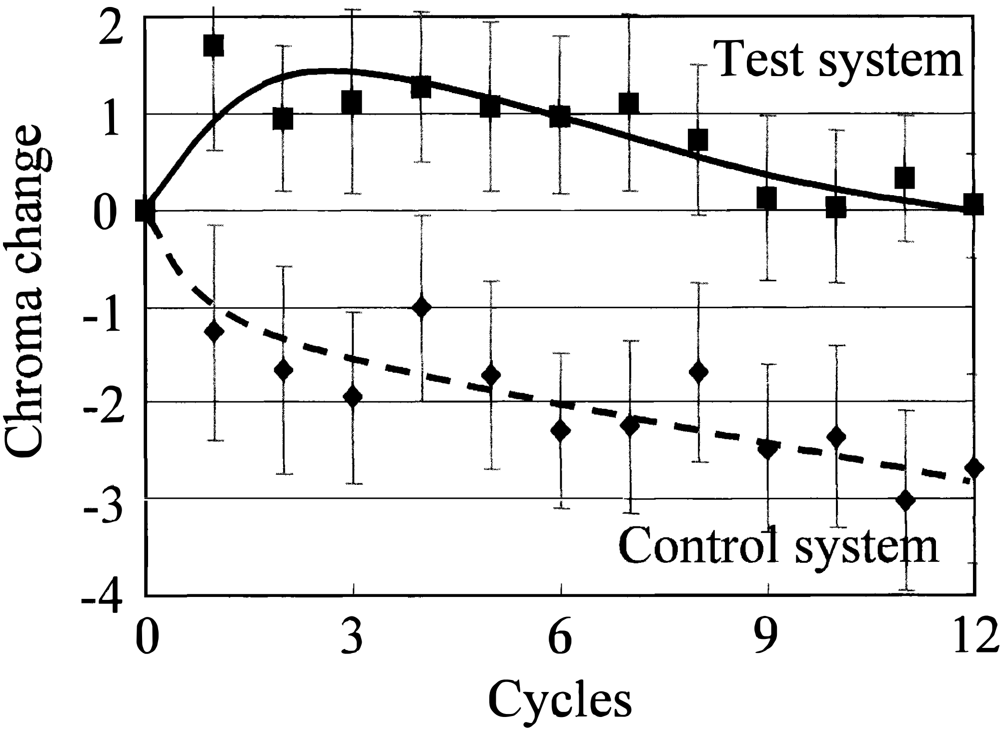

Figure 5. Chroma change of red dyed human head in the shampoo and conditioner treatment cycles.

DISCUSSION

Experimental results showed that the fine asperity on hair fiber surface is related to light introduction and chroma enhancing phenomena. In general, asperities on surface induce diffuse reflection of light. However, if asperities are finer enough than incident light wavelength, diffuse reflection diminishes and light introduction into inside materials develops, and of the most popular example is uneven structure on the surface of moth's eyes. The surface has an asperity of 200nm in height and 300nm in lateral space which allows night view and wide eyesight (Moth-eye structure, 7–9) The structures have been applied to industry such as optical devices, anti-reflection film and so on (10–14). Light introduction phenomena induced by fine structures can be explained by the effective medium approximation (EMA, 15–17). EMA is an approximation theory to approximate a refractive index of the surface with a finer structure than an incident light wavelength by a mean value based on volume fractions of air and substrate of the structure (Monolayer model/EMA, Figure 7). For example, if a fine structure is composed of paraffin (n_1 = 1.43) and air (n_0 = 1.00) and the volume ratio is 1:1, the mean refractive index of the layer is approximated to be 1.22. There is no such a low refractive index material with flat surface in cosmetically available materials, so it can be said that a super fine structure realizes super-low refractive index surface. Lower refractive index surface leads to more light introduction from Snell's law. Furthermore, advanced models by EMA treat a structure with a volume fraction gradient along depth direction like a saw-edged structure to be a longer with a gradual change in the density, i.e. the refractive index density (Multilayer model/EMA, Figure 7). Sizes to characterize the fine structure obtained by

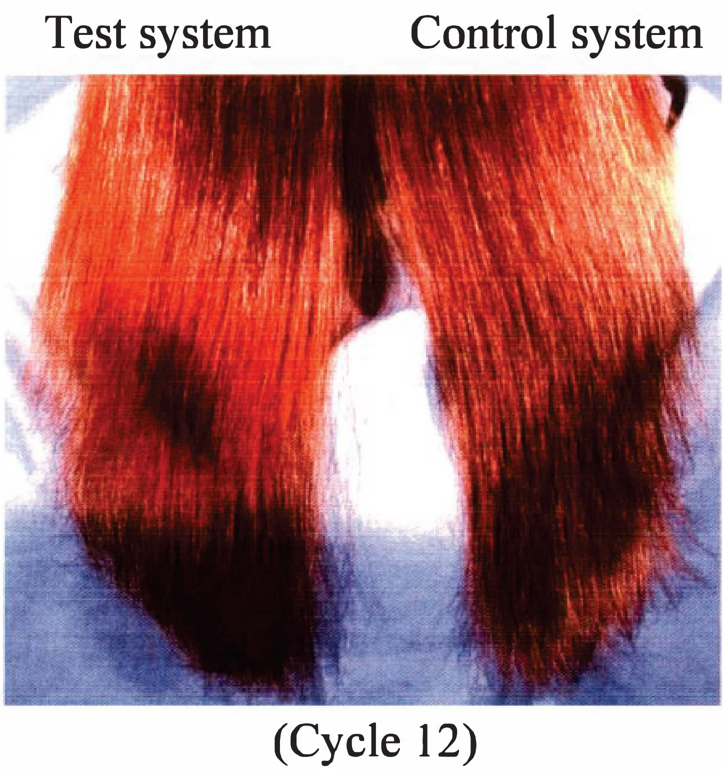

Figure 6. Anti-fading effect of test system for dyed hair.

the test system were estimated at vertically 50nm in peak height or 25nm in roughness, (Figure 8) and laterally 170 nm in correlation length between random by chosen two points (Figure 9). The volume ratio of air and the substrate in the structure was estimated to be about 1:1. These estimations indicate a possibility of the super low refractive index as 1.2 for the surface on hair fiber.

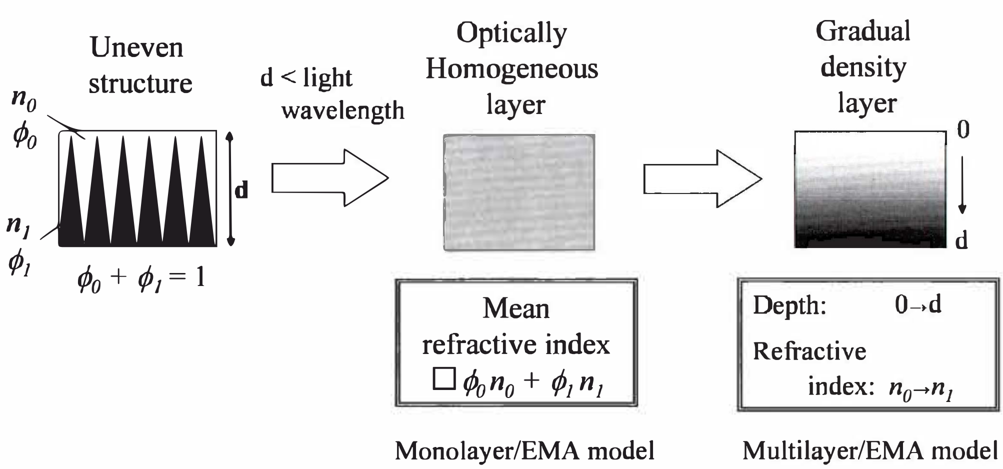

Figure 7. Effective medium approximation. *n:* refractive index, ϕ*:* volume fraction (subscript 0: air, 1: substrate).

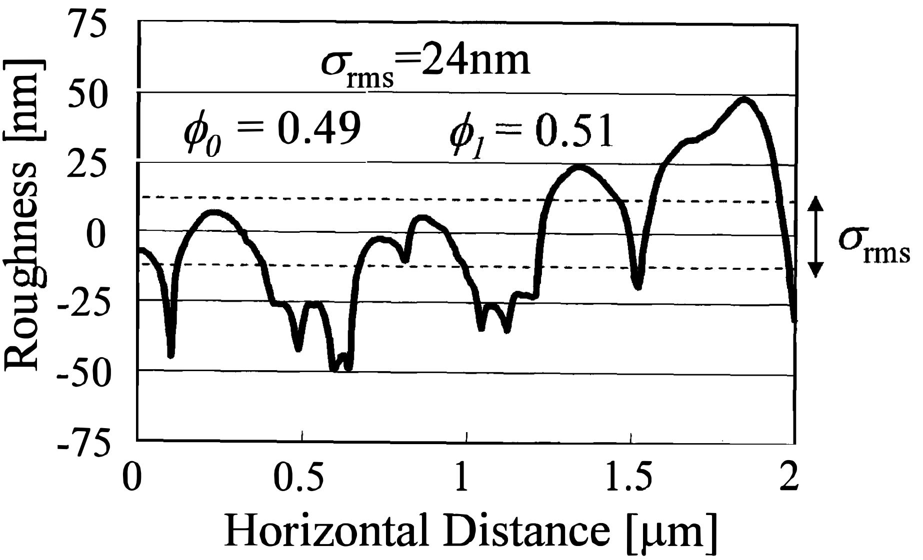

Figure 8. Vertical size and volume fraction estimations of the fine structure (σ_{rms}: root mean square roughness, ϕ_0 and ϕ_1: volume fraction of air and substrate in σ_{rms}).

To explain the light introduction phenomenon for the test system, simulation study on light reflection (Matrix method, 14) was conducted. In the case of homogeneous top surface of a typical organic material (n_1 = 1.45) on hair cuticle (n_2 = 1.55), remarkable light introduction doesn't occur even though the thickness is less than light wavelength (d ≤ 100 nm, Monolayer in Figure 10). However, the change of refractive index to the order of 1.2 is expected to occur more light introduction (d ≤ 100 nm, Monolayer/EMA, Figure 10). Satisfiable consistency was obtained between the experimental result (Figure 4) and the simulation result (d = 50 nm, EMA in Figure 10). The light introduction

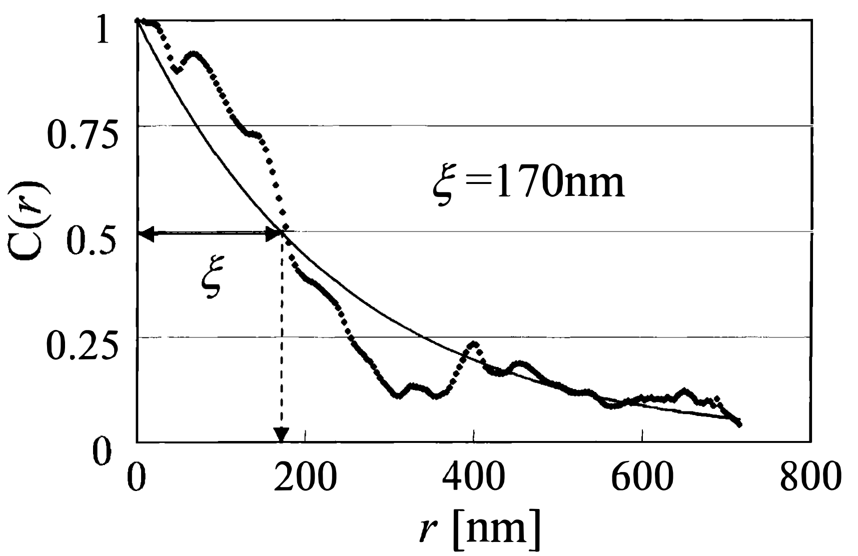

Figure 9. Lateral size estimation of the fine structure (ξ: correlation length, C(*r*): correlation function, *r*: horizontal distance between random two points).

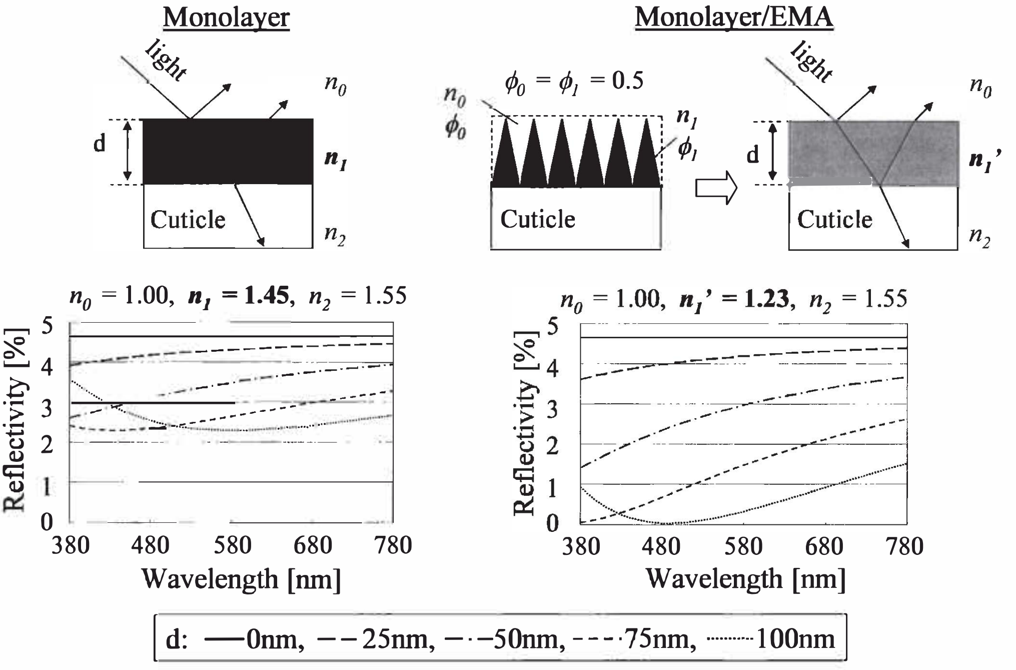

Figure 10. Simulation study on surface reflection, monolayer model, d ≤ 100 nm.

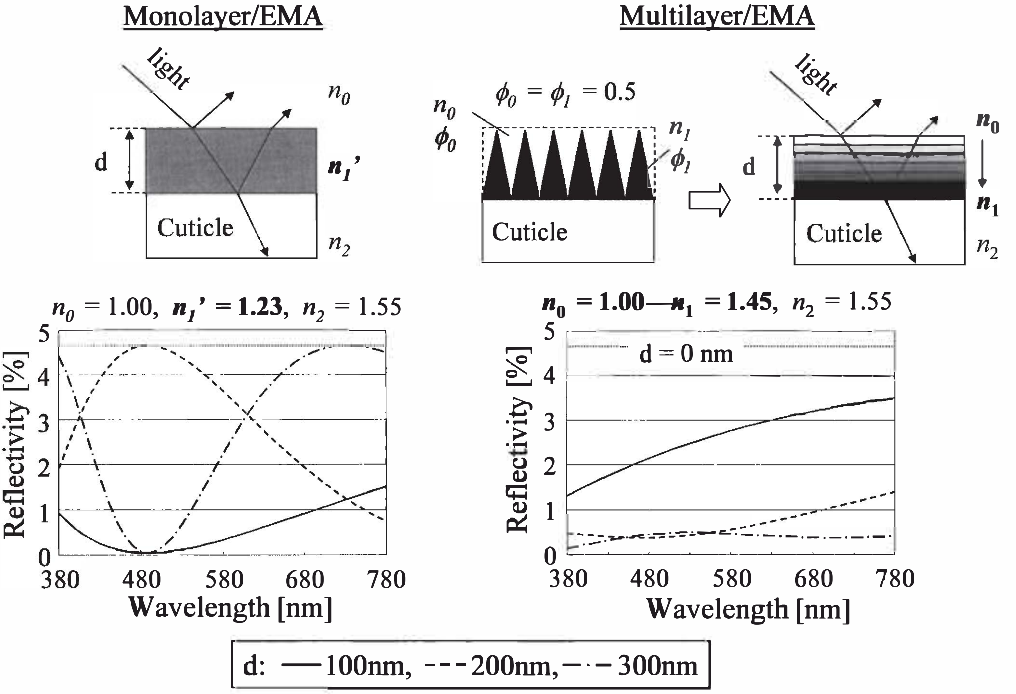

Figure 11. Simulation study on surface reflection, monolayer and multilayer EMA model, 100 ≤ d ≤ 300 nm.

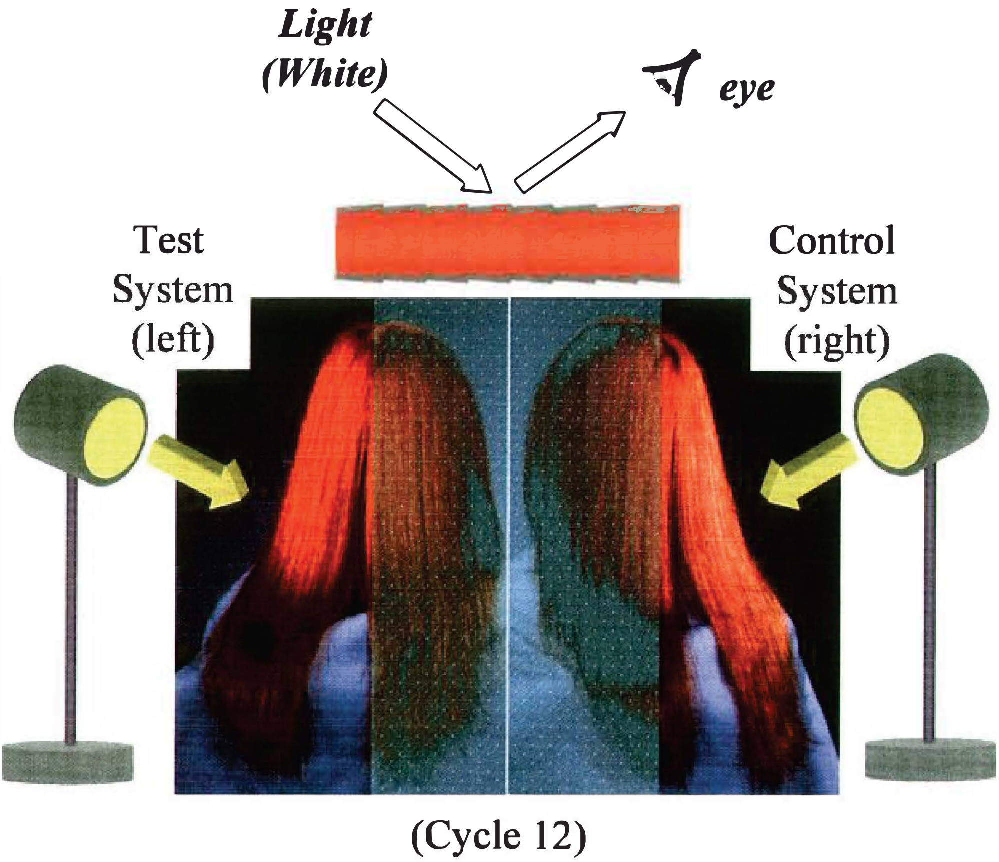

Figure 12. Observation of surface supecular reflection on red dyed hair.

phenomenon by the test system can be thus explained by formation of super-low refractive index hair surface with about 50nm asperity composed of fatty alcohol and air.

In the range of the structure size from 100 to 300 nm, simulation study shows that influence of light interference phenomenon inhibits the light introduction even though the super low refractive index layer (Monolayer/EMA in Figure 11). This result goes against the light introduction phenomena as typically observed in Moth-eye structure (200 nm in height and 300 nm in space uneven surface). In such a size range, the gradual density layers model (approximated as multilayer using EMA in Figure 11) is to be applied. The surface shape obtained by the test system shows gentle curvatures. The gradual density model predicts a possibility of further effective light introduction if the structure has more heights with enough high special densities. (But still has finer sizes than an incident light wavelength.)

Another characteristic of the obtained structure is light introduction dependence on light wavelength. Both of experimental and simulation results show effective light introduction of shorter wavelength. Those results also imply a fine structure on surface can bias a wavelength of surface reflection toward reddish shift. Observation of surface specular reflection shows whitish diffuse reflection on human head when treated by the control system, but reddish reflection was observed by the test system (Figure 12). Therefore, in the case of red dyed hair, vivid red color can be observed from any angle (the test system in Figure 13).

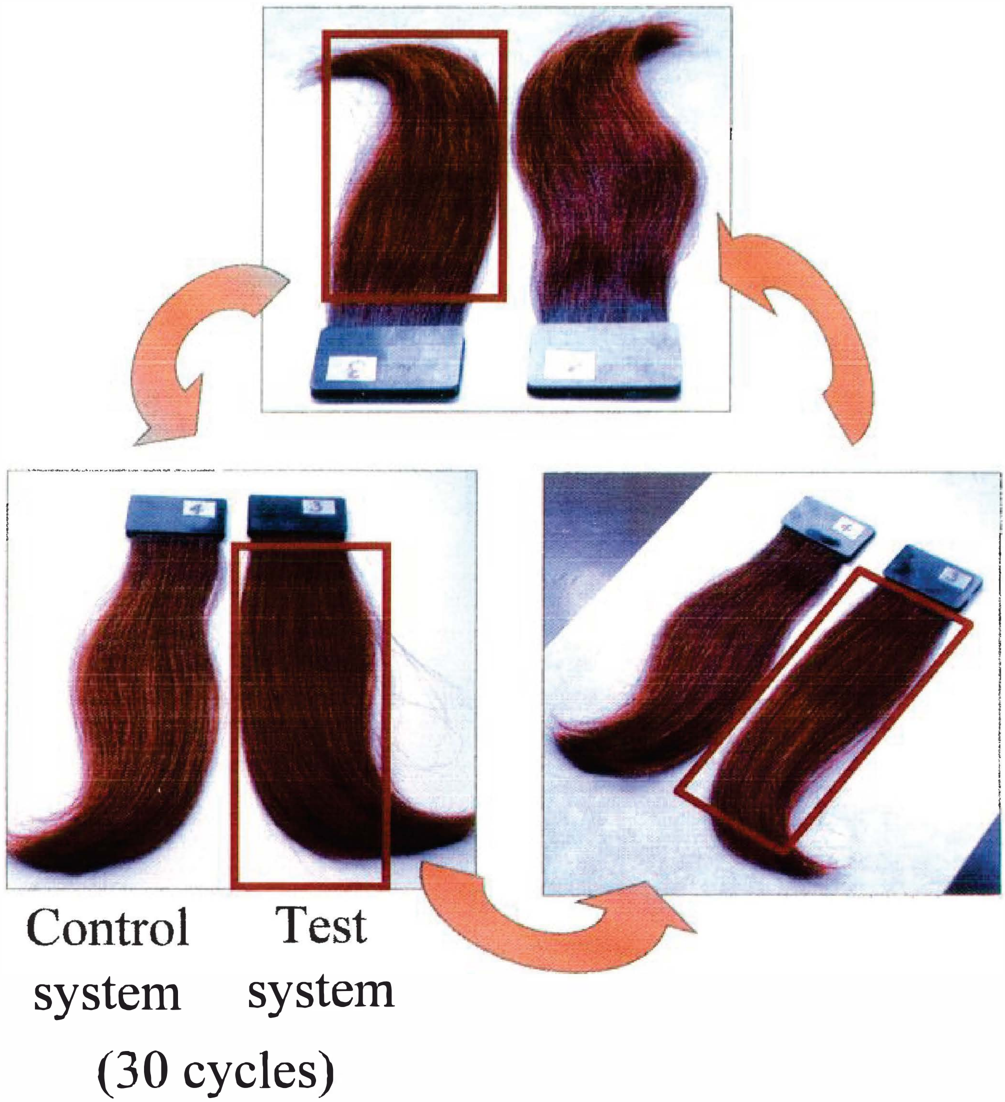

Figure 13. Vivid appearance of red dyed hair from any angle.

CONCLUSION

For a goal to make hair appearance more beautiful and healthy, control of hair optical property was examined by hair surface modification.

1. Finer uneven structures than light wavelength were succeeded to be formed on hair surface by a shampoo and conditioner system. Formation of the structure, composed of fatty alcohol, was controlled by amino-silicone.
2. Both colors of natural hair and dyed hair were confirmed to be more vivid by formation of the fine structure on hair fiber surface. Furthermore, a long lasting effect of the vividness was also confirmed for dyed hair.
3. Optical studies and simulation studies showed light introduction phenomena by

formation of the finer structure. The phenomenon is explained by the Effective Medium Approximation as super-low refractive index surface. It is considered that light introduction enhances colors of the inside of hair fiber.

4. Obtained structure sizes were about 50 nm in height and 170 nm in lateral space. In such a size range of structure, a light with shorter wavelength was more introduced than with longer one. Surface reflection was shifted to reddish, realizing an angle independent vivid appearance of red dyed hair by the effects of light introduction and reddish surface reflection.

ACKNOWLEDGMENTS

The authors are grateful to Mr. Dave Muenz, Ms. Bryer Heather, Ms. Weaver Conni, Ms. Christine Hall and Ms. Linda Baird, Kao Brands Company, for technical assistance and helpful discussion. The authors also thank to Dr. Naohisa Kure, Mr. Hiroyuki Saijou and Mr. Satoshi Onitsuka, Kao Corporation, for helpful discussion and guidance.

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