Optical properties of hair: Effect of treatments on luster as quantified by image analysis

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Synopsis

Image analysis has been employed to measure the luster of hair simulated by light reflected from a curved hair tress. Hair samples (up to four) were mounted side-by-side in a special sample holder in the form of a cylinder and illuminated by a uniform beam of white light. Digital images of hair tresses were captured with a high-resolution camera and were analyzed by scanning across highlighted and dark areas of the resultant image using image analysis software with developed macros. Plots, similar to goniophotometric scattering curves, were used to calculate luster values according to previously published work by Nickerson, Stamm, and Reich-Robbins. Both the Stamm and Reich-Robbins approaches were found to give similar results, while the Nickerson gloss parameter exhibited less sensitivity to hair modification with cosmetic ingredients. The procedure was employed to assess the luster of natural white, light blonde, light brown, medium brown, and dark brown hair, and revealed an increase in luster indices in proportion to an increase in fiber pigmentation. Cosmetic oils such as phenyl trimethicone, amodimethicone, and castor oil were also found to increase the luster of hair as a result of the change in contrast between specular and diffuse reflection. Styling resins such as butyl ester of PVM/MA copolymer, vinyl caprolactam/PVP/dimethylaminoethyl methacrylate copolymer, and isobutylene/ethylmaleimide/hydroxyethylmaleimide copolymer were shown to increase hair gloss by a similar mechanism, as evidenced by calculated higher values of the Stamm and Reich-Robbins luster parameters. An effect of hair dulling by deposition of micronized ZnO at various concentrations, as well as by synthetic sebum, is also discussed.

INTRODUCTION

The attribute of hair luster has been of significant concern to the consumer and marketers for quite some time, especially recently because of the proliferation of reactive and damaging hair treatments. Luster is commonly defined as the ability of a given material to produce a bright reflection. A quantitative analysis of luster and comparison with theoretical models was carried out as recently as the seventies by Stammet al. (1,2). In the last twenty years there have been a number of studies published in this area that employed improved instrumentation. Stamm et al. (1,2) employed a goniophotometer **and multiple fibers to record the light distribution curves necessary to calculate luster parameters. This work was later expanded by Czepluch et al. (3), who constructed a computerized goniophotometer. Reich and Robbins (4) and Bustard and Smith (5), who also utilized a goniophotometer, employed single fibers to study the effects of sham-**

335

pooing and dyeing on the luster of hair. Maeda et al. (6) have presented luster measurements performed by using a color image processor, which analyzed the pattern of light reflected by a natural-hair wig on a model head. The data were obtained by scanning across highlighted and dark areas of the obtained image, and could be presented in a plot similar to a goniophotometric scattering curve. The authors reported good agreement between calculated luster and the rating of luster obtained by visual inspection of hair tresses. Recently, hair luster was measured using diffuse reflectance spectrophotometry in which the color difference parameter, ΔE , was used as an indicator of luster (7).

The method of subjective shine evaluation is also commonly used and can provide a useful guidance for formulators. The results can be in good agreement with instrumental methods provided the experimental setup assures uniform orientation of hair samples and reproducible (from sample to sample) illumination conditions.

In this paper we discuss the experimental details of luster measurements by employing image analysis for quantifying the light distributions of hair illuminated with white, collimated light. The results for various types of untreated hair, as well as for dark brown hair modified with polymers and oils, are discussed. The interpretation of the data is based on the character (shape) of the light-scattering curves, calculated luster parameters, and visual examination of the digital images of hair.

EXPERIMENTAL

METHODS

The entire luster evaluation apparatus was housed in a wooden box coated with black Formica and having the dimensions of 2 ft in width, $2\frac{1}{2}$ ft in depth, and 3 ft in height. **As shown in Figure 1, hair tresses were mounted on an anodized aluminum cylinder, 31/2** inches in diameter. A collimated halogen light source was placed $7\frac{1}{2}$ inches above the digital camera, providing an incident angle of approximately 30° relative to the optical **axis. Linear polarizers were placed in front of the light source and the camera. This allowed us to view all reflected light (specular and diffuse) when the polarizers were parallel and diffuse reflection when they were perpendicular. The camera, the polarizer, and the mounting cylinder were attached to aluminum posts that were mounted to an anodized optical peg board, which provided the underlying support for the instrument. An Olympus Camedia El0 digital camera with a resolution of 4 megapixels was employed as the image collection device for all studies presented in this report.**

Image analysis was carried out using Sigma Scan Pro 5.0 (SPSS) software, which enabled us to obtain the light intensity (luminance) distributions along a given hair tress. The method was previously described by Maeda et al. (6). Based on this procedure we are able to plot the data in Excel 2000 (Microsoft) in the form of a two-dimensional graph, providing luminance as a function of distance along the hair tress. The data were further analyzed by integrating the area under the luminance curves in order to obtain the values of the luster parameters.

All luster data represent an average of the results obtained on at least three tresses except for Nickerson contrast gloss data, which were not analyzed statistically. On the other hand, the luster parameters for untreated hair represent an average of measurements obtained on 28 tresses.

Figure 1. Scheme of an apparatus to measure the luster of hair.

MATERIALS

Luster analysis was performed on natural white, light blonde, light brown, medium brown, and dark brown hair purchased from IHI & Products, Inc. (Valhalla, NY). Hair samples were pre-cleaned with a 3% ALS solution and thoroughly rinsed prior to experimentation. Hair tresses were obtained by gluing 3 g of fibers to 1.5×1.5 -inch **plexiglass tabs with Duco cement. The length and width of each hair tress were 10 inches and 1.25 inches, respectively.**

Dark brown hair was treated with a variety of polymers and oils. Phenyl trimethicone (Si Tec TM PTM 200, ISP), amodimethicone (DC Q2-8220, Dow Corning), and castor oil (Hanson) were used as ethanolic solutions. Butyl ester of PVM/MA copolymer (Gantrez © ES-425), vinyl caprolactam/PVP/dimethylaminoethyl methacrylate copolymer (Advantage © LC-A), and isobutylene/ethylmaleimide/hydroxyethylmaleimide copolymer (Aquaflex ©FX-64) were all ISP products and were also used in the form of ethanolic solutions. All polymer and oil solutions were applied to hair in the amount of 1 g at a concentration of 2% (w/w) using a disposable pipette.

A product containing ZnO was formulated as a 1.5% aqueous suspension stabilized with **a combination of acrylates/beheneth-25 methacrylate copolymer (Aculyn © 28, ISP) and VP/acrylates/lauryl methacrylate copolymer (Styleze® 2000, ISP).**

A synthetic sebum formula containing the following ingredients was prepared as a 5 % (w/w) solution in hexane: 20% Olea europaea (olive) fruit oil (Lipovol O, Lipo Chemicals); 15% cetyl esters (synthetic spermaceti, Koster Keunen); 15% Cocos nucifera (coconut) oil (Lipovol C-76, Lipo Chemicals); 10% palmitic acid (Aldrich); 10% paraffin (paraffin wax fully refined, Frank B. Ross Company); 10% oleic acid (Emersol 6321, Cognis Corporation); 5 % stearic acid (Emersol 150, Cognis Corporation); 5 % squalene **(shark squalene, Arista Oils); 5% cholesterol (Aldrich); and 5% linoleic acid (Emersol 315, Cognis Corporation).**

RESULTS AND DISCUSSION

MEASUREMENTS OF UNTREATED HAIR

The phenomena accompanying the interaction of light with objects include reflection, scattering, refraction, diffraction, interference, and absorption. The most important for luster is reflection, which can be further categorized as "specular reflection" and "diffuse reflection." Other phenomena, such as scattering, refraction, and absorption, also play a critical role in the interaction of light with hair. Refer to R. Stamm's work for an explanation of these terms (1).

Every measurement set of untreated hair consisted of two images, one recorded with the polarizers parallel (Figure 2) and the other with the polarizers perpendicular (Figure 3) to each other. In the case of parallel polarizers, all reflected radiation is captured in the image, while in the case of perpendicular polarizers, the specular reflection is eliminated **and the observed image is due to diffuse scattering. It should also be added that all images shown in Figures 2, 4, 6, 8, 10, 12, and 14 are exposed in such a way that one can view the details in the highlight area (f8 and 1/13 s or f8 and 1/6 s as aperture and shutter speed settings, respectively). These images do not show as much detail in the dark areas, making this region of the tress more difficult to evaluate by visual examination. In contrast to this, we have also employed exposure values corresponding to the**

Figure 2. Digital image obtained for untreated dark brown hair with polarizers oriented parallel to each other. Exposure values: f8 and 1/13 s.

Figure 3. Digital image obtained for untreated dark brown hair with polarizers oriented perpendicular to each other. Exposure values: f8 and 1/3 s.

average light intensity for the entire image (f8 and 1/3 s). With such an exposure value, the specular reflection falls into slightly overexposed highlights, with no details visible in this area; however, differences in the regions of the tress peripheral to the specular reflection are accentuated.

In order to quantify the luminance along the hair tress, light intensity measurements were performed with image analysis software. This is demonstrated in Figure 4, in which the four red lines, 50 pixels in width, represent the region from which the luminance **readings were obtained for each tress. A plot of luminance as a function of distance along each hair tress is provided in Figure 5 for both the specular (Figure 2) and diffuse (Figure 3) light images. The specular curves in Figure 5 are characterized by the presence of one sharp peak corresponding to the reflected light from the dark brown hair. It is noteworthy that a similar examination of diffuse images provides a curve in which two peaks could be resolved, one for diffuse reflection from the front face (22 mm) of the hair fibers and the other for diffuse reflection from the back face (17 mm) of the fibers.**

The luster parameters were calculated using three different models, one of which is the Nickerson contrast gloss:

$$
N_c = \frac{S - D}{S} \tag{1}
$$

where S represents the area underneath the specular curve and D is the area under the diffuse curve.

Stamm et al. (2) proposed another model, based on equation 1, in which the area under a straight line obtained by connecting the first and last points of the specular reflection curve was used as a measure of diffuse reflection, D_{Stamm} .

Figure 4. Scheme of the image analysis procedure employed to determine light intensity as a function of **tress length.**

Figure 5. Light distribution curve showing light intensity (luminance) as a function of distance along the hair tress. The data were obtained for untreated dark brown hair.

$$
L_{Stamm} = \frac{S - D_{Stamm}}{S}
$$
 (2)

Similar to the data of Stamm et al. (1,2), we found that the use of equation 2 leads to **larger differences in luster values for different hair types and hair treatments. Reich and Robbins (4) determined the diffuse reflection in the same manner as Stamm et al., but they utilized a different relationship to define luster:**

$$
L_{Reich-Robbins} = \frac{S}{D_{Stamm} * W_{1/2}}
$$
(3)

where $W_{1/2}$ represents the width of the specular peak at half of its maximum intensity. **Repeated measurements of various tresses of untreated hair yielded the following values** of luster parameters for exposure settings of f8 and $1/13$ s: $L_{Stamm} = 0.72 \pm 0.02$ and $L_{Reich-Robbins} = 0.67 \pm 0.006$; for f8 and 1/6 s: $L_{Stamm} = 0.72 \pm 0.03$ and $L_{Reich-Robbins} =$ 0.54 ± 0.07 ; and the values $N_C = 0.80 \pm 0.02$, $L_{Stamm} = 0.67 \pm 0.02$, and $L_{Reich-Robbins}$ $= 0.37 \pm 0.02$ for exposure values of f8 and $1/3$ s. These numbers give an assessment of **the precision and reproducibility of the luster parameters determined by the described measurement method.**

In order to validate the measurement method and provide a reference point to the literature data, we have studied the luster for various types of hair (1,2). It can be seen in Figure 6 that hair pigmentation has a significant effect on the optical properties of hair and in particular on its luster. Figure 6 presents images of reflected light from natural white, light blonde, light brown, and dark brown hair. These images were obtained by selecting the exposure values in such a way as to visualize the details of the specular reflection band (f8 and 1/13 s). The light distribution curves are presented in Figure 7, and they are consistent with the visual representation of the images shown in **Figure 6. For example, one can clearly see two specular reflection bands for natural white and light blonde hair (Figure 6), which are evident by two peaks in the light distribution** curves (Figure 7). The peak at 16 mm gets progressively smaller with an increase in the

Figure 6. Images of light reflections from various types of hair. Exposure values: f8 and 1/15 s.

Figure 7. Light intensity (luminance) as a function of distance along the hair tress for various types of hair.

extent of fiber pigmentation, which indicates that it is due to reflection from the back face of the hair fibers. The narrowest light distribution curve was obtained, as expected, for dark brown hair. Hair luster parameters, calculated according to equations 2and 3, are presented in Table I.

The calculations carried out by both formulas indicate lower luster values for fibers containing less melanin pigment, i.e., the highest luster for dark brown hair and the lowest for natural white hair. A similar result was previously reported by Stamm et al. (2). Also, $W_{1/2}$ follows the same trend, consistent with visual perception, pointing to an **increase in the width of reflected light distribution for less pigmented fibers.**

MEASUREMENTS OF OIL-TREATED HAIR

We have performed aseries of measurements on hair treated with silicone oils including phenyl trimethicone and amodimethicone as well as with the hydrocarbon oil and castor oil. The structures of these cosmetic raw materials are shown below (Schemes 1-2). Castor oil consists of triglycerides of fatty acids with the predominant presence of ricinoleic acid residues (97%) (Scheme 3).

Luster Parameters for Various Hair Types (f8; 1/13 s)					
Hair type	$W_{1/2}$ (mm)	L_{Stamm}	$L_{Reich-Robbins}$		
Dark brown	5.28 ± 0.44	0.72 ± 0.020	0.67 ± 0.006		
Medium brown	5.44 ± 0.16	0.72 ± 0.006	0.67 ± 0.005		
Light brown	10.46 ± 0.30	0.70 ± 0.001	0.32 ± 0.008		
Light blonde	14.91 ± 0.23	0.65 ± 0.005	0.19 ± 0.006		
Natural white	22.78 ± 0.24	0.32 ± 0.013	0.06 ± 0.002		

Table I

HO•C17H32'COOH

Scheme 3. Ricinoleic acid.

Phenyl trimethicone is commonly used in leave-in cosmetic formulations as a shining agent. Amodimethicone, on the other hand, is typically employed in rinse-off conditioners as a conditioning agent effective in reducing combing forces. Castor oil usually plays the role of a texture modifier and conditioner in a variety of cosmetic products.

Figure 8 provides the images obtained for dark brown hair treated with phenyl trimethicone, amodimethicone, and castor oil, which were applied at 2% concentration in ethanol. It is apparent that all three materials modify the contrast between specular reflection and other regions of the tress. As a result of treatment with these oils, one can observe a lightening effect in the region of the tress immediately adjacent to the specular reflection and darkening of the area further away from the specular band, located in the regions corresponding to 0-10 mm and 35-50 mm, respectively (compare with Figure 9, which provides the distance scale for the images shown in Figure 8). The lightening effect (or broadening of specular reflection) is most evident in the case of castor oil but **is also clearly visible for phenyl trimethicone-treated hair. A graph of luminance as a function of tress length for phenyl trimethicone is presented in Figure 9. The broadening of the specular band takes the form of a left-hand-side shoulder in the**

Figure 8. Images of hair treated with various oils. Exposure values: fS, 1/6 s.

Figure 9. Light-scattering curves for untreated and phenyl trimethicone-treated hair.

light-scattering peak. Similar widening is not noticeable in the light-scattering curve obtained for untreated hair. All three investigated compounds displayed asimilar effect, although, for the sake of brevity, relevant light-scattering plots are not presented in the paper. The values of luster parameters, calculated according to the previously discussed **equations, are gathered in Table II and suggest increases in hair gloss, as compared to untreated hair, for all three of the oil treatments.**

As pointed out previously, the N_C luster parameters calculated for oil-treated hair are not **substantially different from those obtained for untreated hair. Actually, the numbers corresponding to oil-modified hair are slightly smaller, indicating no shining effect or even a small reduction in luster. It is also obvious that treatment of hair with oil leads** to a reduction in the maximum intensity of the specular reflection. However, the L_{Stamm} and $L_{Reich-Robbins}$ luster parameters, which utilize the quantity D_{Stamm} for diffuse reflection **(calculated as the area under the straight line connecting the ends of the light distribution curve), substantiate significant increases in the calculated luster parameters. The** reason for this is that D_{Stamm} accounts for the darkening effects of the treatments that **provide more contrast between the specular band and the background (iffuse area of the hair tress).**

POLYMER-TREATED HAIR

Polymers are believed to increase the luster of hair when used as film formers in hairsprays, hair gels, or special hair glazes. We have tested a series of polymers (see Schemes 4-6 for structures of these compounds), frequently employed as fixatives, by their deposition on dark brown hair using 2% ethanol solutions. The treatments were applied uniformly to the surface of the hair to assure thin film formation. It should be stressed that the same polymers applied as dispersions or emulsions, or in mixtures with incompatible ingredients, may not form uniform and homogenous films, leading to a reduction in intensity and a broadening of specular reflection. Figure 10 shows the images of untreated and treated fibers obtained by using exposure parameters of f8 and 1/6 s. As in the case of oil treatments, an apparent increase in luster is due to an enhancement in contrast between the specular and diffuse reflection areas as a result of darkening in the region of the tress corresponding to diffuse reflection. This is further illustrated by the light distribution curves obtained for one of the investigated polymers, vinyl caprolactam/PVP/dimethylaminoethyl methacrylate copolymer (Figure 11). The curves corresponding to polymer-modified hair show a shift of the specular reflection as compared to untreated hair and a decrease in diffuse light intensity, i.e., at the regions peripheral to the reflection band. A shift along the distance axis can likely be ascribed to the evening of the fiber surface by a polymer film, thus minimizing the effect of cuticle inclination. On the other hand, a decrease in the intensity of diffuse light leads to an increase in the calculated luster parameters, as shown in Table III.

The results of calculations for polymer-treated hair reveal increases in luster parameters, with $L_{Reich-Robbins}$ and L_{Stamm} providing the largest differences as compared to untreated

Scheme 4. Vinyl caprolactam/PVP/dimethylaminoethyl methacrylate copolymer (VCL/VP/DMAEMA).

Scheme 5. Butyl ester of PVM/MA copolymer (PVM/MA).

Scheme 6. Isobutylene/ethylmaleimide/hydroxyethylmaleimide copolymer (IEHC).

hair. As indicated in the previous section for oil treatments, the Nickerson contrast gloss parameter appears to be rather insensitive to the polymeric treatments of hair, as suggested by only minimal increases in the values of this parameter for modified fibers. In terms of peak intensity, we observed an increase for VCL/VP/DMAEMA-treated hair relative to untreated hair. On the other hand, hair treated with PVM/MA and IEHC resulted in peak intensities similar to or slightly less than that found for untreated dark brown hair.

DULLING OF HAIR

In order to examine the effect of hair dulling by surface deposits, we applied various amounts of a formulation containing 1.5% micronized ZnO. The micronized ZnO particles, ca. 50 nm in diameter, typically provide light absorption and scattering centers

Figure 10. Images of hair treated with vinyl caprolactam/PVP/dimethylaminoethyl methacrylate copolymer, butyl ester of PVM/MA copolymer, and isobutylene/ethylmaleimide/hydroxyethylmaleimide copolymer (IEHC). Exposure values: f8, 1/6 s.

Figure 11. Light distribution curves for untreated hair and hair treated with vinyl caprolactam/PVP/ dimethylaminoethyl methacrylate copolymer.

in sunscreen products, hence resulting in an increase in diffuse reflection. ZnO is, however, frequently employed in formulations because its light-scattering efficacy in the visible range is lower than in the case of other pigments such as titanium dioxide. Thus,

348 JOURNAL OF COSMETIC SCIENCE

Treatment				
	Peak intensity	N_c	$E_{Reich-Robbins}$	L_{Stamm}
Untreated	$168 + 4$	0.80 ± 0.02	0.54 ± 0.07	0.72 ± 0.03
VCL/VP/DMAEMA	177 ± 3	0.83	0.68 ± 0.07	0.76 ± 0.02
PVM/MA	$164 + 4$	0.81	0.73 ± 0.03	0.80 ± 0.01
IEHC	170 ± 10	0.81	0.67 ± 0.13	0.79 ± 0.02

Table III Calculated Luster Parameters for Various Polymeric Treatments of Hair (f8; 1/6 s)

ZnO displays less tendency for whitening skin or hair, resulting in esthetically acceptable products. For demonstration, Figure 12 contains images of hair treated with various quantities of ZnO ranging from 7.5 mg ZnO/1 g of hair to 30 mg ZnO/1 g of hair. As the amount of ZnO on hair increases, the specular reflection curve becomes wider. This **is evident not only in the images in Figure 12, but also in the plot of luminance as a function of tress length in Figure 13. Also shown in Figure 13 are the diffuse reflection curves (obtained with cross-polarizers) that reveal an increase in width and intensity for** higher concentrations of ZnO. It is important to note that all images of the ZnO-treated **hair were obtained using the exposure values f8 and 1/3 s, allowing us to accentuate areas** of the hair tress outside the periphery of the specular reflection band.

The luster parameters, calculated according to the three different methods, are collected **in Table IV. They all reveal numerical decreases with increasing ZnO concentrations, which is consistent with the visual impression of the images presented in Figure 12 and the shape of the light distribution curves shown in Figure 13.**

Finally, we have also examined the dulling effect on hair produced by treatment with artificial sebum. A photographic record of untreated and sebum-treated hair is shown in Figure 14. It demonstrates a significant loss in maximum light intensity as well as a broadening of the specular reflection. Quantitatively, the peak maximum light intensity was reduced from 168 ± 4 for untreated hair to 127.01 ± 3.56 for sebum-modified hair (Figure 15). Peak width increased from 6.71 ± 0.35 to 11.39 ± 0.29 for untreated and

Figure 12. Images of hair treated with various amounts of ZnO. Exposure values: f8 and 1/3 s.

Figure 13. Light distribution curves for hair treated with various amounts of ZnO.

sebum-treated hair, respectively. In contrast to this, luster parameters $L_{Reich-Robbins}$ and L_{Stamm} were found to be equal to 0.34 ± 0.05 and 0.74 ± 0.03 for sebum-treated hair **versus 0.72 + 0.03 and 0.54 + 0.07 for untreated hair, respectively. Thus, the observed dramatic loss of gloss in sebum-treated hair is not reflected in the calculated values of** L_{Stamm}. However, L_{Reich-Robbins} coincides very well with visual observations.

SUMMARY AND CONCLUSIONS

An image analysis system was employed to quantify the optical and luster properties of hair. Untreated and treated hair tresses were mounted on a cylindrical support and illuminated with a collimated polarized halogen light at an incident angle of approximately 30° relative to the horizontal optical axis. A digital camera with a resolution of **4.0 megapixels was employed as the recording device. Data, obtained in three different**

Figure 14. Images of untreated hair and hair treated with synthetic sebum. Amount of treatment was 1 g of 5% solution per 3-gram tress. Exposure values: f8 and 1/6 s.

Figure 15. Light distribution curves for untreated hair and hair treated with synthetic sebum.

exposure modes, were converted into light distribution curves similar to those obtained in goniophotometer experiments (1,3,4). Several equations, empirically verified by various authors, were utilized to calculate the luster parameters. The results were generally consistent with the literature data and visual observations. It was shown that:

- **© Natural white, light blonde, light brown, medium brown, and dark brown hair showed a gradual increase in luster proportional to the amount of melanin pigmen**tation. Light-colored hair clearly displayed two specular reflection bands correspond**ing to the front- and back-face reflections from hair fibers.**
- **© Silicone and hydrocarbon oils, specifically phenyl trimethicone, amodimethicone, and castor oil, increase the luster of hair by enhancing the contrast between specular and diffuse areas. Phenyl trimethicone was found to be the most effective treatment.**
- **© Luster can be increased by the deposition of polymers, such as hairspray or styling resins, forming thin films on the hair surface.**
- **© A controlled reduction in hair luster can be achieved by deposition of various amounts of micronized ZnO, which increases the width and intensity of both specular and diffuse reflection from hair. Additionally, a decrease in luster was demonstrated with the use of a synthetic sebum.**

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