A Study of Hair Dye using Henna and Haematoxylon Campechianum Dye

Hanchieh Wang^{*1} and Chonyu Chen^{*2}

^{*1} Department of Cosmetic Applications & Management, Yuh-Ing Junior College Of Health Care & Management, No. 15, Lane 420, Dachang 2nd Road, Sanmin District, Kaohsiung City 807, Taiwan

^{*2} Department of Fashion Design, Shu-Te University, NO. 59, Hengshan Rd., Yanchao District, Kaohsiung City 82445, Taiwan

Abstract: This study added *Haematoxylon campechianum* dye, propylene glycol, and menthol in henna, and carried out 8 times of shampoo dyeing. The experimental results showed that the L^* values of the dyed hair pieces, containing 5% and 7% *Haematoxylon campechianum*, were 32.1 and 30.2, respectively. The addition of 7% *Haematoxylon campechianum* dye extract in the hair dye to coat on 3 groups of hair pieces showed that, there is no significant difference ($P>0.05$) between the ΔE mean value 16.68 ± 0.30 of the 3 groups of hair pieces after 8 shampoos, and the ΔE mean value 16.29 ± 0.43 of the 7th shampoo. This result indicates that the degree of hair color fading tends to be smooth after the 7th shampoo. The L^* mean value 33.36 of the 8th shampoo is significantly different from the 56.33 of bleached hair color, indicating that after 8 shampoos, hair color lightness can still fade. The hue a^*b^* mean values decrease from 12.95 and 11.59 after the 1st shampoo to 3.34 and 7.79 after the 8th shampoo, respectively, and the hair color obviously changes from red to brown. This hair dye increases the tensile strength of the bleached hair by 53.69%. The experiments proved that henna mixed with *Haematoxylon campechianum* dye, propylene glycol, and menthol can withstand more than 8 times of shampooing, and it can effectively cover white hair and strengthen hair.

(Received 6 May, 2011 ; Accepted 6 August, 2011)

1. Introduction

Semi-permanent hair dyes can be divided three types, which are acidic, basic, and disperse dyes. Normally the molecular size of acidic dyes is large and unlikely to penetrate the cortical layer of hair. The dyeing fastness of acidic hair dye is better than that of other semi-permanent hair dyes, which normally can withstand 6-8 shampoos. However, the anionic nature of the acidic dye may cause damage to hair quality [1]. In Japan, besides using disperse dyes and basic dyes, acidic dyes, alkaline agents, and multivalent phenol are commonly used in hair dyes [2].

There are few current studies related to the penetration mechanism of natural dye, thus, this study intends to discuss the penetration enhancers for percutaneous absorption of drugs. Propylene glycol is used as a solvent in preparation to help active ingredients permeate and soften cutins, which has been proven effective for promoting the penetration of many kinds of drugs. Moreover, previous studies have also proven that 2% Azone or 5% oleic acid can enhance penetration [3, 4, 5]. Menthol is a keto penetration enhancer of Terpenes, which promotes the penetration of meloxicam,

indomethacin, and tamoxifen drugs, whether used solely or jointly, in the percutaneous absorption system [6, 7, 8]. Menthol excels at promoting the penetration of multiple fat soluble and water soluble cardiovascular drugs [9]. Furthermore, 2% menthol and 2% propylene glycol can increase the percutaneous rate of fast-acting slimming plasters by 1.49 times. It has been reported that the major active mechanism destroys the lipid barrier of cells, and enlarges the distribution of drugs as a water soluble base in the horny layer [10, 11]. According to the results of Fourier Transform Infrared Spectroscopy (FT-IR), menthol increases the penetration modes of tamoxifen, but not the distribution of tamoxifen in the horny layer [8].

Hair is a very tensile fiber, and can endure a force to 12 kg/mm^2 ($12\times10^7 \text{ Pa}$). Its maximum load is larger than that of aluminum. Improper hair perming and dyeing may affect the elasticity of hair [12]. In addition to being used as skin and hair dyes, henna can be used as medicine for skin tinea [13]. According to investigation, henna can strengthen bleached wool when $\text{pH}<6$ [14]. Eucalyptus, oleic acid, and propylene glycol dyeing accelerants, at concentrations of 1%, were added in henna to dye hair ; the results showed that propylene glycol has the best dyeing effect [15].

Haematoxylon campechianum is of Fabaceae, also known as black wood. The extract from its wood and bark create an excellent deep color stain, which is mostly used in cell and clothes dyeing. Its primary structure is shown in Fig. 1. *Haematoxylon campechianum* also performs well in anti-friction and light fastness after stock dyeing [16].

At present, the technique of using henna for hair dyeing is mature; however, the resulted hue is dull. Therefore, this study added *Haematoxylon campechianum* dye extract, propylene glycol, and menthol to henna in order to evaluate hair dyeing fastness.

2. Experimental materials and method

2.1 Dye extraction

The heartwood of *Haematoxylon campechianum* (250 g), imported from South America to Taiwan, was immersed in 6 L of pure water (Mili-Q) for 2 hours, and boiled until the water volume reduced to 1/3~1/4 of the original; 3 L of pure water was then added to continue boiling; the above steps were repeated twice; filter paper (Advantec No. 1 and Advantec 5C) were used for filtration, and a vacuum pressure reduction concentrator (EYELA N-1000s) was used for drying; and the solution was then diluted to 10% *Haematoxylon campechianum* dye extract for future use.

2.2 Prepare hair pieces

Real hair pieces (about 26 cm wide, 40 cm long, and 0.4-0.8 cm thick) were bleached with L'OREAL Platifiz Precision, and mixed uniformly with 9% hydrogen peroxide in a 1 : 2 ratio three times, where each bleaching lasted 30 min; the hair pieces were then rinsed with tap water, blow-dried, and numbered for future use.

2.3 Preparation of Haematoxylon campechianum dye hair dye

Henna powder, 10% *Haematoxylon campechianum* dye, and pure water were added to formulas A and B to 100 g in ratio, respectively, and then 2 g propylene glycol and 2 g menthol were added to homogenize at 3000r.p.m for 3 min; a dyeing brush was used to coat the mixture on the hair, from top to bottom; the hair pieces sat at

Fig. 1 Structural formula of Hematoxylin.

Table 1 Formula table of henna powder with *Haematoxylon campechianum* dye.

	Control group	Formula A	Formula B
Henna powder	15 g	15 g	15 g
10% <i>Haematoxylon campechianum</i> dye	-	50 g	70 g
Pure water	85 g	35 g	15 g
Propylene glycol	-	2 g	2 g
Menthol	-	2g	2g

room temperature for 1 h, and then rinsed in water and blow dried. The CIE L^* value represents the color lightness change, thus, hair dyeing can be identified by the L^* value.

A part of the natural dye adhered to the hair surface between the 1st and the 4th shampoo [17], and the dyeing situation cannot be identified. Therefore, this study used those with low L^* values after the 8th shampoo as the formula concentration for subsequent research. Henna powder (Abid & Company (Pvt) Ltd.) with pure water (15 : 85) was the control group. In order to determine the effect of dyeing white hair, a small portion of hair containing 70% white hair was used for the experiment (Table 1).

2.4 Water washing method

The dyed hair was placed in a 500 mL conical flask, which underwent a shake bath (FIRSTEK Shaking bath B630D) at a constant temperature for 7 min, with an oscillation frequency of 200 rpm. The water washing conditions are as shown in Table 2. When the hair dye was rinsed, 400 mL tap water was added and oscillated for 3 min. The hair was washed twice under the same water washing conditions. The rinsed hair was removed, soaked in 1% hair conditioner for 1 min, rinsed with tap water, and placed in a moisture-proof box for future use.

2.5 CIE $L^*a^*b^*$ value

A color difference meter (X-Rite Sphere Spectrophotometer SP60) was used to measure five points of dyed hair pieces B-1, B-2, and B-3 in order to determine the mean value and standard deviation, and then, analyze CIE $L^*a^*b^*$ and color difference ΔE value. The ΔE value increased as the number of shampoos increased, thus, a larger color difference means a larger difference between colors and higher fading rate. In

Table 2 Water washing conditions.

T (°C)	pH	Shampoo (g)	Water (ml)	Stainless ball ^a	Flask (ml)	Time (min)
40±2	7.5	5	400	10	500	7

^aThe diameter of stainless ball is 0.635 cm.

addition, the dyeing effect was determined according to the degree of variation in L^* value and the hue a^*b^* value. The color difference ΔE value in this study is obtained from the following equation.

$$\Delta E = [(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2]^{1/2} \quad (1)$$

2.6 Hair strength analysis

Tensile experiments were conducted to observe variations in the hair strength after dyeing. A thickness gauge (TELOCK SM-1201) was used to measure the diameter of three hair samples selected from each group of hair pieces. A tensile strength tester (MICRO-COMPUTER TENSILE STRENGTH TESTER GT-7010D1-PC) was then used to test the tensile force, record the mean value of destruction work, and determine the standard deviation and the fiber breaking strength of each sectional area [kg(load)/mm(sectional area)]. Finally, the fiber breaking strength was compared to determine whether the hair quality is affected.

3. Results and discussion

3.1 CIE $L^*a^*b^*$ analysis

The concentration of *Haematoxylon campechianum* dye was diluted with pure water to 1%, according to the experimental process, and scanned by spectrophotometer (HITACHI U-1800). As shown in the UV/VIS spectrogram, the main wavelength absorption peak of *Haematoxylon campechianum* dye was 434 nm. The L^* value of henna dye of the control group after 8 shampoos was 55.27, which is an insignificant difference as compared with 54.37 after dyeing. This result indicates that the dyeing effect of the henna dye is poor. The experimental results showed that the L^* values of the two groups of hair pieces of formulae A and B, after 8 shampoos, were 32.1 and 30.2, respectively. Compared with the bleached hair color ($L^* = 59.6$), the L^* value of

formula B with 7% *Haematoxylon campechianum* dye is better. Therefore, in the following experiment, formula B was used for hair pieces B-1, B-2, and B-3 as the experimental group. The results was compared with the L^* value of the control group, and found that when henna is added with *Haematoxylon campechianum* dye, after 8 shampoos, the L^* value of the dyed hair (30.2) was lower than that without *Haematoxylon campechianum* dye. This result proved that henna with *Haematoxylon campechianum* dye can deepen dyed hair color.

In order to learn the number of washing and dyeing fastness for the experimental groups after dyeing, the ΔE and L^* mean values were used for analysis. According to Table 3, the ΔE values of the three groups of hair pieces, after 8 shampoos, are 16.26, 16.86, and 16.91, indicating that the color differences of the ΔE values of the three groups of hair pieces are within 98%. Thus, this experiment was proved to have good accuracy. The ΔE mean values of the 8th shampoo and the 6th shampoo of the experimental group were compared, and the results showed a significant difference ($P < 0.05$). However, there is no significant difference ($P > 0.05$) between the color difference ΔE mean values of the 8th shampoo and the 7th shampoo. Therefore, this difference means that the hair piece color continues to fade after the 6th shampoo ; however, after the 7th shampoo, the hair fading slows down and presents a stable hue. In other words, the fading of the dyed hair piece becomes stable to some extent after the 7th shampoo, with no obvious fading. The L^* mean value of the three groups of hair pieces after the 8th shampoo was 33.36, which is obviously different from the 56.33 of the bleached hair. Therefore, the three groups of dyed hair pieces have good dyeing fastness, and allow several shampoos.

Most natural hair dyes in Taiwan's market use dry henna powder as the main formula, added with water, coffee, and black tea to produce thick liquid dyes. Studies of product formula have not concerned improving the

Table 3 CIE $L^*a^*b^*$ values N=3 (Mean $\pm$ S. D.).

Washes		Dyed Hair	1	2	3	4	5	6	7	8
CIE	L*	54.37	55.36	55.89	55.39	55.87	55.48	55.34	55.25	55.27
	a*	10.69	9.81	9.63	9.66	10.92	9.14	9.34	8.96	9.29
Control group (Henna)	b*	29.33	28.56	28.44	27.76	30.98	27.98	27.71	27.40	27.22
	ΔE		1.53	2.06	2.14	2.24	2.34	2.32	2.75	2.69
Experimental group	L*	27.04 $\pm$ 0.16	29.78 $\pm$ 0.40	28.18 $\pm$ 0.12	29.96 $\pm$ 0.05	29.88 $\pm$ 0.79	30.18 $\pm$ 0.62	31.65 $\pm$ 0.21	32.17 $\pm$ 0.84	33.36 $\pm$ 0.67
	a*	17.53 $\pm$ 0.36	12.95 $\pm$ 0.79	9.70 $\pm$ 0.90	7.76 $\pm$ 0.60	5.71 $\pm$ 0.30	4.52 $\pm$ 0.14	4.32 $\pm$ 0.50	3.717 $\pm$ 0.46	3.34 $\pm$ 0.32
	b*	14.30 $\pm$ 0.25	11.59 $\pm$ 0.83	6.47 $\pm$ 0.29	6.12 $\pm$ 0.24	7.05 $\pm$ 1.71	6.67 $\pm$ 0.82	7.50 $\pm$ 1.11	7.48 $\pm$ 0.63	7.79 $\pm$ 0.44
	ΔE		5.80 $\pm$ 0.27	10.97 $\pm$ 0.42	13.05 $\pm$ 0.52	14.71 $\pm$ 0.30	15.43 $\pm$ 0.33	15.82 $\pm$ 0.25	16.29 $\pm$ 0.43	16.68 $\pm$ 0.30

washability of products or different hue changes. Therefore, the results of this study suggested that henna dye only adheres to the hair cuticle, and it cannot permeate into hair cortex. However, when *Haematoxylon campechianum* dye, propylene glycol, and menthol are added in the red effect on hair is strengthened, and the hair color is deepened after 8 shampoos.

3.2 Color shade and wash fastness of dyed hair

Table 4 shows that the hue of henna after 8 shampoos is golden yellow, and there is no significant difference as compared with that after dyeing. This difference is shown in control group and experimental group in Table 4 (B-1, B-2, and B-3), where the colors of dyed hair on the left are deeper than that of bleached hair on the right. The red gradually fades as the number of shampoo increases, whereas, the a^*b^* value after henna dyeing, and the a^*b^* value after 8 shampoos, have no significant variation.

Table 5 shows that white hair is dyed with a semi-permanent hair dye containing *Haematoxylon campechianum* dye. After 8 shampoos, according to the preliminary check, this semi-permanent hair dye formula can effectively cover white hair, and has an excellent dyeing effect.

According to the above results, when henna is mixed with *Haematoxylon campechianum* dye, the hair dye allows more than 8 shampoos ; however, the color will change from red to brown. Such an obvious change in hue may be resulted from the reaction between *Haematoxylon*

campechianum dye and the metal ions in tap water. In the experiment, the dyed hair was placed in pure water (Mili-Q) for the shampoo test, and the result showed that the color of the hair piece did not change, thus, the color of the hair piece might be affected by water quality.

3.3 Hair strength analysis

Hair strength is determined by hair cortex ; improper perming, dyeing, and ultraviolet radiation may cause damages to the hair [18, 19]. Therefore, this study attempted to discuss whether the formula of the experimental group would decrease hair strength.

According to Table 3, the color difference ΔE value linearity ($y = 0.351x + 14.483$ $R^2 = 0.9935$) of hair piece B-1, after 4~8 shampoos, was better than both B-2 ($y = 0.48x + 14.708$ $R^2 = 0.9087$) and 3-3 ($y = 0.606x + 13.86$ $R^2 = 0.9668$). Therefore, bleached hair quality was compared with the B-1 experimental group for hair strength analysis. The result showed that the tensile energy value (kg-mm) of bleached hair was 0.67 ± 0.1 , and the hair strength was lower than the 1.49 ± 0.09 (kg-mm) of the B-1 experimental group. In other words, henna mixed with *Haematoxylon campechianum* dye extract can strengthen bleached hair by 53.69%.

4. Conclusions

In conclusion, *Haematoxylon campechianum* dye can be used in semi-permanent hair dyes, and it can cover white hair. The penetration enhancer for drugs could enhance the dyeing effect of natural dye. Future studies can discuss the dye ability under different dyeing accelerant concentrations.

References

1. Nil, *Manufacturing Chemist.*, Jan, 34 (1997).
2. J. Kawase and T. Yoshihara, *Fragrance Journal*, **22**, 18 (1994).
3. H. Y. Thong, H. Zhai and H. I. Maibach, *Skin pharmacology and physiology.*, **20**, 272 (2007).
4. B. Mollgaard and A. Hoelgaard, *Int J Pharm.*, **15**, 185 (1983) .
5. H. Herai, T. Gratieri, J. A. Thomazine, M. V. L. B. Bentley and R. F. V. Lopez, *Int J Pharm.*, **329**, 88 (2007) .
6. Q. Huan and M. J. Cheng, *Heilongjiang Medical J.*, **20**, 584 (2007).
7. K. K. Levison, K. Takayama, K. Isowa, K. Okabe and T. Nagai, *J. Pharm. Sci.*, **83**, 1367 (1994).
8. K. Zhao and J. Singh, *J control Rel.*, **55**, 253 (1998) .

Table 4 Comparison table for hue of dyed hair.

	Bleached and dyed hair	1st shampoo wash	2nd shampoo wash	3rd shampoo wash	4th shampoo wash	5th shampoo wash	6th shampoo wash	7th shampoo wash	8th shampoo wash
Henna
B - 1
B - 2
B - 3

Table 5 White hair dyeing test.

Virgin hair	Dye hair	2nd shampoo wash	4th shampoo wash	6th shampoo wash	8th shampoo wash

9. D. Kobayashi, T. Matsuzawa, K. Sugibayashi, Y. Morimoto, M. Kobayashi, and M. Kimura, *Biol Pharm Bull.*, **16**, 254 (1993) .
10. L. P. Yu and X.Q.Xie, *Heilongjiang Medical Journal.*, **21**, 4 (2008).
11. K. A . Walters and J. Hadgraft, "*Pharmaceutical skin penetration enhancement*", Marcel Dekker, New York (1993).
12. C. Zviak, "*The Science of hair care*", Informa Healthcare , New York (1986).
13. S. Wales, *International Journal of Cosmetic Science.*, **24**, 5, 302 (2002) .
14. L. Gao, Y. J. Wang and Z. X. Yang, *Journal of Qingdao University (Engineering & Technology Edition).*, **19**, (2004).
15. S. y. Lin, "*The Promotion of Chemical Enhancers on Hair Coloring with Henna Dyes*", Master thesis, SHU-TE University, Taiwan, (2008).
16. P. Y. Wang, "*Color Characteristics of Cotton, Flax and Ramie Fabrics Dyed with Vegetable dyes*", Master thesis, National Chung Hsing University, Taiwan, (1999).
17. H. C. Wang and C. Y. Chen, *Sen'i gakkaiishi.*, **65**, 276 (2009).
18. C. R. Robbins and R. J. Crawford, *Journal of the society of cosmetic chemists.*, **42**, 59 (1991).
19. A. C. Santos Nogueira, and I. Joekes, *Journal of Photochemistry and Photobiology B : Biology.*, **74** (2-3) , 109 (2004).