Fashion and Textiles

RESEARCH

Open Access

Effect of surfactant type on the dyeability and color resistance of semi-permanent basic hair dye

Kyeoungsook Yun[1,2] and Cheunsoon Ahn[1,3*]

*Correspondence:
cssong@inu.ac.kr

[1] Department of Cosmetic Science and Management, Graduate School, Incheon National University, (Songdo-Dong) 119 Academy-Ro, Yeonsu-Gu, Incheon, Republic of Korea
[2] Incheon Practical Science High School, (Yeonsu-Dong) 103 Hambakmoe-Ro, Yeonsu-Gu, Incheon, Republic of Korea
[3] Department of Fashion Industry, Incheon National University, (Songdo-Dong) 119 Academy-Ro, Yeonsu-Gu, Incheon, Republic of Korea

Abstract

Basic Brown 16 pigment and three types of surfactants were used to prepare the cationic, nonionic, and anionic basic hair dyes. White hair and bleached hair were dyed using the three basic hair dyes and were shampooed 10 times using acidic, neutral, and alkaline shampoos prepared in the study. White hair and bleached hair dyed with the anionic basic hair dye resulted in a lower L^*, a^*, b^* values and lower K/S values compared to the hair dyed with the cationic and nonionic basic hair dyes and the results were statistically significant at $\alpha = 0.05$. Hair dyed with the anionic basic hair dye showed significantly higher ΔL^*, Δa^*, Δb^*, and ΔE^*_{ab} values after 10 times of shampooing than those dyed with cationic and nonionic basic hair dyes ($\alpha = 0.05$), indicating a lower color resistance for the anionic basic hair dye. Color difference after shampooing was significantly higher when alkaline shampoo was used ($\alpha = 0.05$). Overall, the color difference after shampooing occurred more by the type of dye than by the type of shampoo.

Keywords: Hair, Dyeing, Basic hair dye, Surfactant, Dyeability, Color, Color strength, Color resistance, Semi-permanent hair dye

Introduction

Hair dyeing has become a popular beauty practice among a wide range of age groups as a means to show one's body image and to cover grey hair (Lee & Kim, 2020; Yun, 2019). Hair dye that is generally used today is an oxidative, permanent hair dye which has excellent color resistance (Lee & Kim, 2020). However, the ingredients in the oxidative, permanent hair dye may cause allergic symptoms and can damage the hair (Lee & Kim, 2020). Para-phenylenediamine (PPD)- the major component of oxidative hair dye- stimulates the eyes, causes asthma when inhaled, and may cause skin irritation, contact dermatitis, and renal impairment by skin contact (Seydi et al., 2019). Currently, the hair dye industry is striving to develop hair dye that is safe to the body and convenient to use and does not contain PPD (Lee & Kim, 2020). With this trend, there is a growing interest in the temporary or semi-permanent hair dye which has less color resistance than permanent hair dye but is safer and more convenient (Lee & Kim, 2020).

Springer Open

© The Author(s) 2022. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

Among the types of semi-permanent hair dye the basic hair dye is a hair dye consisting cationic, basic pigments (Massoni, 2004). Basic hair dye is a direct dye which does not need PPD, hydrogen peroxide, nor alkali to color the hair (França et al., 2015; Hehner et al., 2002). While the color of permanent hair dye is produced inside the cortex of hair by the oxidation reaction, basic hair dye applies the basic (cationic) pigment on the hair in its colored form (Tucker, 1971). Basic hair dye do not cause oxidative damage to hair and skin and the dyeing method is simple (França et al., 2015; Hehner et al., 2002).

In June 2016 the Ministry of Food and Drug Safety of Korea announced Notice No. 2016–49 'Partial Revision of Cosmetic Color Types, Standards, and Test Methods' which allowed the usage of 9 basic pigments in hair dye products (Korea Health Industry Development Institute, 2020; Ministry of Food & Drug Safety, 2016). Basic Brown 16 ($C_{19}H_{21}ClN_4O$, CI 12250, CAS No. 26381-41-9) is one among the 9 pigments which began its usage in the hair dye industry in June 2016 (Korea Health Industry Development Institute, 2020; Ministry of Food & Drug Safety, 2016; Scientific Committee on Consumer Safety, 2013). Basic Brown 16 is classified as a monoazo (–N=N–) compound, has a molecular weight of 356.86, and is water soluble (Scientific Committee on Consumer Safety, 2013). The European Commission's Scientific Committee on Consumer Safety (SCCS) defined that Basic Brown 16 is a direct pigment which can be used without oxidizing and can be used up to 2.0% concentration on the head (Scientific Committee on Consumer Safety, 2013).

França et al. (2015) explained that the pH control of basic hair dye is a must for the stability of the color. And a number of research implied that the pH of the dye might have an effect on the color or the dyeability of basic hair dye (França et al., 2015; Hehner et al., 2002; Indrawati et al., 2017). However, compared to the research on permanent hair dye, the research on basic hair dye is very limited so that it is difficult to draw a concrete scenario on the dyeing behavior and the suitable formulation of basic hair dyes. Some examples of available research include França et al. (2015) who suggested that a weak alkali should be added to make the pH of the dye 9.0, and then a weak acid should be added next to bring down the pH to 6.0. Semi-permanent hair dyes prepared by Indrawati et al. (2017) using a natural cationic pigment showed the pH values of 6.50–6.25. The available research suggests that there are some discrepancies on the formulation of the basic hair dye, including the pH level. Considering the growing market segment of the semi-permanent hair dye more empirical research seems necessary for establishing a coherent foundation for the formulation of basic hair dye.

The purpose of this study was to investigate the effect of surfactant type on the color, color strength, and color resistance of the hair dyed with semi-permanent basic hair dye. For this purpose, three types of basic hair dye were prepared by using Basic Brown 16 (Arianor® Mahogany 306002, France) as the pigment and adding cationic, nonionic, or anionic surfactant as the emulsifier. Dyeing was performed on the hair pieces of white hair (WH) and bleached hair (BH), the former which was a commercially bleached white hair and the latter which was bleached in the experiment. White hair was used to simulate the grey-hair-dyeing, and the bleached hair was used to simulate the fashion-dyeing using the basic hair dye. Three types of shampoo with different pH levels were also prepared and used in the shampooing process. To our knowledge this paper presents the first research effort which introduce the empirical data on the basic hair dye specifically related to the effect of surfactant in the dye formulation and the effect of shampoo pH on the color resistance of dyed hair.

Methods

Materials

Asian virgin hair pieces (VH) and white hair pieces (WH) used in the study were purchased from Beauty World (Korea). Hair bleaching agent was purchased from Sewha P&C (Korea), and the agent contained sodium metasilicate as alkaline agent in pack 1, and 6% hydrogen peroxide as oxidant in pack 2. 40 g of Basic Brown 16 (Arianor® Mahogany 306002, France) pigment was kindly provided by Chang Hyup Trading (Korea). Hydroxyethylcellulose (CAS No. 9004-62-0), distilled water, cetearyl alcohol (CAS No. 67762-27-0), glyceryl monostearate SE, Tween 60 (Polysorbate 60, CAS No. 9005-67-8), Arlacel 60 (sorbitan stearate), steartrimonium chloride (CAS No. 112-03-8), ammonium lauryl sulfate (ALS, CAS No. 2235-54-3) were used to prepare the basic hair dye. Distilled water, guar gum (guar hydroxypropyltrimonium chloride, CAS No. 65497-29-2), polymer JR 400 (polyquaternium-10, CAS No. 81859-24-7), ammonium laureth sulfate (ALES, CAS No. 32612-48-9), sodium laureth sulfate (SLES, CAS No. 3088-31-1), dimethicone (CAS No. 9006-65-9), sodium chloride, sodium hydroxide were used to prepare the shampoos. Water used in preparing the basic hair dye was purified by the water purifying system of Human Corporation (Korea).

Experimental

Preparation of hair dye

The three types of hair dye prepared were cationic basic hair dye (CBD), nonionic basic hair dye (NBD), and anionic basic hair dye (ABD). The composition of the three types of basic hair dye is shown in Table 1. For each hair dye, distilled water, hydroxyethylcellulose, cetearyl alcohol, glyceryl monostearate SE, Tween 60, and Arlacel 60 were equally added. In this basic composition, the steartrimonium chloride was added to CBD, and

Table 1 Formulation of three types of basic hair dye

Phase	Function		Materials	CBD		NBD		ABD	
				wt.%	g	wt.%	g	wt.%	g
Water phase	Solvent		D-water	89.00	178.00	85.00	170.00	85.00	170.00
	Thickener		Hydroxyethylcellulose	0.50	1.00	0.50	1.00	0.50	1.00
	Pigment		Basic brown 16	1.50	3.00	1.50	3.00	1.50	3.00
Oil phase	Emulsion stabilizer		Cetearyl alcohol	4.00	8.00	4.00	8.00	4.00	8.00
	Emulsifier (Surfactant)	Nonionic	Glyceryl monostearate SE	1.00	2.00	1.00	2.00	1.00	2.00
			Tween 60	2.00	4.00	2.00	4.00	2.00	4.00
			Arlacel 60	2.00	4.00	2.00	4.00	2.00	4.00
		Cationic	Steartrimonium chloride	4.00	8.00	–	–	–	–
		Anionic	Ammonium lauryl sulfate	–	–	–	–	4.00	8.00
Total				100.00	200.00	100.00	200.00	100.00	200.00

CBD cationic basic hair dye, *NBD* nonionic basic hair dye, *ABD* anionic basic hair dye ammonium lauryl sulfate was added to ABD. For water phase, distilled water, a thickener, and a magnetic bar were added to a beaker. The beaker was heated to 80 °C on a stirrer hot plate and the thickener was completely dissolved using the Mark II (model 2.5) homogenizing mixer (T.K PRIMIX, Japan) at 3000 rpm. In this beaker, Basic Brown 16 was added and completely mixed using the homogenizing mixer (3000 rpm). For oil phase, cetearyl alcohol, glyceryl monostearate SE, Polysorbate 60 and Arlacel 60 were mixed in a beaker, heated up to 80 °C on the stirrer hot plate. NBD was prepared by putting the oil phase in the water phase, mixing it for 5 min, and then cooling in the waterbath. Steartrimonium chloride for CBD and ammonium lauryl sulfate (ALS) for ABD were added to the oil phase following the same procedure as above.

Preparation of shampoo

A 500 g each of acidic shampoo (Ne), neutral shampoo (Ne), and alkaline shampoo (Al) were prepared in the study. The composition of the three types of shampoo is shown in Table 2. For water phase, distilled water, thickener, and magnetic bar were added to a beaker and heated up to 70 °C on the stirrer hot plate to completely dissolve the thickener. For oil phase, ammonium laureth sulfate, sodium laureth sulfate, and dimethicone emulsion were added to a beaker, and the mixture was dissolved by heating up to 70 °C on the stirrer hot plate. The water phase and the oil phase were mixed and stirred using the homogenizing mixer (3000 rpm). 0.1% NaCl was added as a thickener. Differing amount of NaOH was added for the three types of shampoo; 0.2 g for the acidic, 0.25 g for the neutral and 0.35 g for the alkaline shampoo.

Preparation of bleached hair

Hair bleaching agent was prepared by mixing 3 g of the alkaline agent (pack 1) and 3 g of oxidant (pack 2). The mixture was thoroughly spread on one piece of virgin hair for 1 min and 30 s. The treated hair piece was wrapped with an aluminum foil. After 30 min the hair was shampooed using a commercial neutral shampoo and then blow dried. The process was repeated 5 times each to prepare the 18 pieces of BH for the experiment.

Table 2 Formulation of three types of shampoos

Phase	Function	Materials	Ac		Ne		Al	
			wt.%	g	wt.%	g	wt.%	g
Water phase	Solvent	D-water	50.53	252.65	50.52	252.60	50.50	252.50
	Thickener	Guar gum	0.03	0.15	0.03	0.15	0.03	0.15
		Polymer JR 400	0.30	1.50	0.30	1.50	0.30	1.50
Oil phase	Cleanser, Emulsifier	Ammonium laureth sulfate	13.00	65.00	13.00	65.00	13.00	65.00
		Sodium laureth sulfate	25.00	125.00	25.00	125.00	25.00	125.00
	Conditioning	Dimethicone emulsion	1.00	5.00	1.00	5.00	1.00	5.00
Additive	Solvent	D-water	10.00	50.00	10.00	50.00	10.00	50.00
	Viscosity control	Sodium chloride	0.10	0.50	0.10	0.50	0.10	0.50
	pH adjuster	Sodium hydroxide (1%)	0.04	0.2	0.05	0.25	0.07	0.35
Total			100.00	500.00	100.00	500.00	100.00	500.00

Ac acidic shampoo, *Ne* neutral shampoo, *Al* alkaline shampoo

Dyeing white hair (WH) and bleached hair (BH)

White hair (WH) and bleached hair (BH) were dyed using the 3 types of basic hair dyes. 6 pieces were allotted for each type of hair dye. In order to visually identify the hair color before and after dyeing, 9 among 18 pieces were dyed by wrapping the 2 cm length of the upper part with an aluminum foil. The other 9 pieces were dyed entirely. 12 g of each hair dye was evenly coated with a glass rod for 1 min on 3 pieces of hair and left for 20 min. Dyed hair was washed is a 200 mL of distilled water 5 times, each time using a fresh 200 mL water.

Shampooing of dyed hair

Dyed hair was shampooed 10 times using the 3 types of shampoo (Ac, Ne, and Al). 10 mL of distilled water and 1 g of shampoo were added to a beaker (50 mL) and the shampoo was dissolved in a stirrer hot plate. A piece of dyed hair was soaked in the shampoo solution for 1 min. The shampoo solution was squeezed out of the hair by pressing the hair piece between the thumb and the index finger. The remaining shampoo was rinsed out by repeating the soaking and take out process 10 times in a 50 mL of distilled water. The water was squeezed out of the hair by pressing the hair piece between the thumb and the index finger. Three sets of rinsing process were done using each time fresh 50 mL of distilled water.

Analysis

pH measurement of prepared hair dye and shampoo

The pH values of the three types of basic hair dye and the three types of shampoo were measured using a pH meter (Seven Compact pH/Ion meter S220, Mettler Toledo, Switzerland).

Measurement of color and color strength of dyed hair

The color of dyed hair and shampooed hair was measured using the Color i5 (X-rite, USA) spectrophotometer which was coordinated with Color iQC software version 9.2.6. Measurements were made in the reflectance mode of Color i5 employing the standard observer view angle of 10°, D_{65} CIE standard illuminant, aperture size of 6 mm in diameter, SCI mode to include the specular component, and the wavelength range of 360 ~ 750 nm with 10 nm wavelength interval. Such measurement condition included all the lights reflected from the sample including those of regular reflection and the UV wavelength provided by the instrument. The color values obtained from the measurement were L^*, a^*, b^* values and the color difference value ΔE^*_{ab} of the CIE 1976 L*a*b* (CIELAB) color space (ISO/CIE, 2019). The K/S values of the samples were also obtained from the color measurement data provided by the spectrophotometer. The K/S values of WH samples were collected at 470 nm and the K/S values of BH samples were collected at 420 nm each of which were identified as the maximum absorption wavelength of WH and BH. The K/S values were used to evaluate the color strength of hair dyed with the three types of hair dyes.

Color measurements were made on the whole piece of each hair tress. The sample view port of the spectrophotometer was vertically aligned. For the measurement the hair tress was neatly arranged vertically so that the hair strands were all gathered as a bundle and there were minimum strands of stray hair. The hair tress was held on the bound edge and placed vertically covering the aperture so that the aperture of the spectrophotometer was completely blocked by the thick bundle of the hair tress. During the measurement the hair tress was secured in place and pressed by the sample arm device of the spectrophotometer. The pressure of the sample arm made it possible to eliminate the looseness in the surface of the hair bundle and allowed the consistency in surface texture of all measurements.

Data analysis

The test of Analysis of Variance (ANOVA) and the Student t-test were performed using the SPSS Statistical software to evaluate the statistical significance of the differences in the means of L^*, a^*, b^*, ΔE^*_{ab}, and K/S values among the samples. The statistical significance was verified at $\alpha = 0.05$.

Results

Prepared basic hair dyes

Three types of basic hair dye- cationic basic hair dye (CBD in the following), nonionic basic hair dye (NBD), and anionic basic hair dye (ABD)- were prepared using Basic Brown 16 as the pigment and by varying the type and the composition of surfactants used as the emulsifier. Type and amount of basic substances added to the formulation were based on Kim (2015), Massoni (2004), Hehner et al. (2002), and Simončič and Kovač (1998). The concentration of Basic Brown 16 in the three dyes was within the concentration range recommended by the Scientific Committee on Consumer Safety, European Commission (Scientific Committee on Consumer Safety, 2013). The result of the pH measurement of the three types of basic hair dye is presented in Table 3. The pH values of CBD, NBD, and ABD were pH 4.32, 5.61, and 5.33, respectively.

Prepared shampoos

Three different types of shampoo were prepared to test the color resistance of hair dyed with the basic hair dye upon repeated shampooing. The basic composition of the shampoo included the anionic surfactants which were added for the purpose of cleansing and emulsifying. The formulation of the three types of shampoo was based on Kim (2015), Yang (2017), and Hartnett and Kozubal (2016). Result of pH the measurement is shown in Table 4. The pH values of the acidic shampoo (Ac in the following), the neutral shampoo (Ne), and the alkaline shampoo (Al) were pH 5.10, 6.44, and 7.80, respectively.

Hair bleaching

The CIELAB color values of bleached hair (BH in the following) are shown in Table 5. In the CIE 1976 L*a*b* (CIELAB in the following) color space, L^* value represents lightness, a^*

Table 3 Result of pH measurements of the three types of basic hair dyes

Basic hair dye	CBD	NBD	ABD
pH	4.32	5.61	5.33

Table 4 Result of pH measurements of the three types of shampoos

Shampoo	Ac	Ne	Al
pH	5.10	6.44	7.80

Table 5 CIELAB color values of virgin hair (VH) and bleached hair (BH)

Hair	Photographic image	L^*	a^*	b^*	ΔE^*_{ab}
VH		19.35	2.14	1.70	0.00
BH		32.53	8.72	14.65	19.56

Fig. 1 White hair (WH) and bleached hair (BH) after dyeing with Cationic (CBD), Nonionic (NBD), and Anionic (ABD) basic hair dyes

value represents green (-) to red (+) color, and b^* value represents blue (−) to yellow (+) color (ISO/CIE, 2019). The + and − sign denote the direction, and the number denotes the magnitude of the corresponding color (ISO/CIE, 2019). The color difference (ΔE^*_{ab}) was calculated using the CIELAB color difference equation (Eq. 1), where L^*_0, a^*_0, b^*_0 were the color values of the reference and L^*_1, a^*_1, b^*_1 were the color values of the corresponding sample (ISO/CIE, 2019). Here, the reference was VH and the sample was BH.

$$\Delta E^*_{ab} = [(L^*_1 - L^*_0)^2 + (a^*_1 - a^*_0)^2 + (b^*_1 - b^*_0)^2]^{1/2} \quad (1)$$

L^*, a^*, b^* values were all increased after bleaching. The results indicated that the hair became lighter, redder, and yellower after bleaching.

Hair dyeing

White hair (WH in the following) and BH were dyed with the three types of basic hair dye (Fig. 1). Visually, the color of WH dyed with the three types of basic hair dye looked lighter than the color of BH dyed with the same dyes. The color of hair looked different depending on the type of basic hair dye, the difference being more prominent in WH. The hair dyed with NBD looked the darkest and those dyed with ABD looked the lightest in both WH and BH.

The CIELAB color values of the dye hair are shown in Table 6. The color difference (ΔE^{*}_{ab}) was calculated using Eq. 1 where the reference for WH dyed with CBD, NBD, and ABD was the undyed WH, and the reference for BH dyed with CBD, NBD, and ABD, was the undyed BH. ΔE^{*}_{ab} values were calculated manually using the Excel software in order to match the reference data of an undyed sample to the sample data of the identical piece after dyeing.

WH became darker, redder, and yellower after dyeing regardless of the dye type. However, the extent of change in L^*, a^*, b^* values were different across the dye type. WH dyed with ABD showed noticeably higher L^* (35.34), a^* (20.38), b^* (19.49) values than WH dyed with CBD or NBD. BH dyed with all three types of dye became lighter and lost yellowness compared to the undyed sample. However, when a^* value was examined BH dyed with CBD (1.43) and NBD (0.81) lost redness whereas BH dyed with ABD increased in redness (10.28) compared to the undyed sample (8.69). WH showed a much higher ΔE^{*}_{ab} values than BH in all three dye types. For both WH and BH, the highest ΔE^{*}_{ab} value was obtained when the hair was dyed with NBD (58.85, 12.66) followed by those dyed with CBD (57.75, 12.39). The hair dyed with ABD resulted in the lowest ΔE^{*}_{ab} value for both WH (53.88) and BH (8.54).

The Kubelka–Munk (K-M in the following) equation explains the relationship between the absorption and the scattering of an incident light into an opaque substrate using the reflectance of the substrate at infinite thickness (Choudhury, 2015; Yang et al., 2010). The K/S value of the K-M equation is widely accepted in the field of textile dyeing to represent the rate of dye fixation or the color strength of the surface of dyed textile materials based on the reflectance value at the maximum absorption wavelength (λ_{max}) (Samanta, 2022; Zhang, 2014). The linear relationship between the K/S value and the fixation rate of dye on the surface of fabric has been reported in various sources (Ahmed et al., 2006; Zhang, 2014). According to the K-M equation, the relationship between the K/S value and the dye concentration at the surface of a flat, opaque, and colored substrate is as follows.

Table 6 Color values of white hair (WH) and bleached hair (BH) dyed with three types of basic hair dyes

Hair		N	L^*	a^*	b^*	ΔE^{*}_{ab}
WH	Undyed	–	83.95	− 0.75	9.86	–
	CBD	6	29.07	16.30	15.44	57.75
	NBD	6	27.57	15.25	14.91	58.85
	ABD	6	35.34	20.38	19.49	53.88
BH	Undyed	–	29.98	8.69	14.03	–
	CBD	6	22.22	1.43	7.70	12.39
	NBD	6	22.77	0.81	7.29	12.66
	ABD	6	24.02	10.28	8.23	8.54

CBD Cationic basic hair dye, *NBD* nonionic basic hair dye, *ABD* anionic basic hair dye

$$\frac{K}{S} = \frac{(1 - R_{\lambda_{max}})^2}{2R_{\lambda_{max}}} = \alpha C_D \quad (2)$$

where K is the coefficient of absorption, S is the coefficient of scattering, $R_{\lambda_{max}}$ is the reflectance value at maximum absorption wavelength (λ_{max}), C_D is the concentration of dye on the surface, and α is the constant (Samanta, 2022). K/S value is also widely accepted in the field of hair dyeing to explain the color strength or the color resistance of dyed hair (Panwar et al., 2022; Sargsyan et al., 2020; Shin & Lee, 2006). The K/S values was also used in this research as a means to explain the surface color strength (K/S) of hair dyed with 3 types of basic hair dyes. The K/S value at the maximum absorption wavelength (λ_{max}) (470 nm for WH and 420 nm for BH) were collected for each sample from the data provided by the spectrophotometer. The K/S values were used to evaluate the surface color strength of three types of hair dyes and the resistance of color after repeated shampooing. Figure 2 illustrates the K/S values of WH and BH dyed with CBD, NBD, and ABD. For all hair types, dyeing with NBD resulted in the highest K/S values while dyeing with ABD resulted in the lowest. In BH, the difference between the hair dyed with CBD and NBD seemed very small. The K/S values of WH were lower than those of BH regardless of the types of dye.

Test of Analysis of Variance (ANOVA) was conducted on the color values and the K/S values of WH and BH (Table 7). The result indicated that there were significant differences in the variance of all components of color values and K/S values among different dye groups ($\alpha = 0.05$). Duncan's multiple range test conducted as a post hoc test showed that in most cases WH and BH dyed with ABD were different from WH and BH dyed with CBD or NBD. WH dyed with ABD was significantly lighter ($L^* = 35.34$), redder ($a^* = 20.38$), and yellower ($b^* = 19.49$) than WH dyed with CBD or NBD. The color difference ($\Delta E^*_{ab} = 53.88$) and the color strength (K/S = 12.82) of WH dyed with ABD were significantly lower than those of WH dyed with CBD or NBD. BH dyed with ABD showed significantly lightest color ($L^* = 24.02$) among the hairs of three dye groups. BH dyed with ABD was redder ($a^* = 10.28$) and yellower ($b^* = 8.23$) than BH dyed with CBD or NBD. The color difference ($\Delta E^*_{ab} = 8.54$) and the color strength (K/S = 16.95) of BH dyed with ABD were significantly lower than those of BH dyed with CBD or NBD.

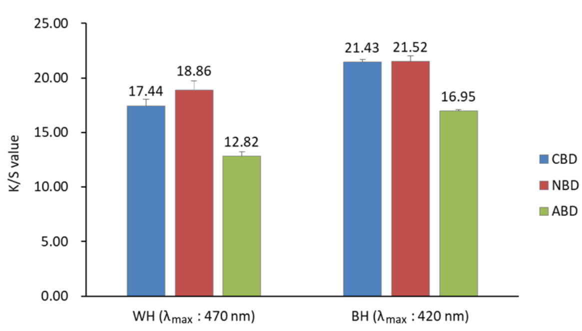

Fig. 2 Color strength (K/S) of white hair (WH) and bleached hair (BH) dyed with the three types of basic hair dyes. *CBD* Cationic basic hair dye, *NBD* Nonionic basic hair dye, *ABD* Anionic basic hair dye

Table 7 Comparison of the color difference and the K/S values of white hair (WH) and bleached hair (BH) by dye type (α = 0.05)

Hair	Color	Hair-Dye	N	Mean	SE	Duncan	F	*p*
WH	*L**	WH-CBD	6	29.07	0.48	a	48.064	.000
		WH-NBD	6	27.57	0.78	a		
		WH-ABD	6	35.34	0.48	b		
	*a**	WH-CBD	6	16.30	0.32	b	92.433	.000
		WH-NBD	6	15.25	0.25	a		
		WH-ABD	6	20.38	0.27	c		
	*b**	WH-CBD	6	15.44	0.36	a	48.619	.000
		WH-NBD	6	14.91	0.43	a		
		WH-ABD	6	19.49	0.27	b		
	ΔE^*_{ab}	WH-CBD	6	57.75	0.47	b	25.017	.000
		WH-NBD	6	58.85	0.66	b		
		WH-ABD	6	53.88	0.40	a		
	K/S	WH-CBD	6	17.44	0.61	b	22.790	.000
		WH-NBD	6	18.86	0.87	b		
		WH-ABD	6	12.82	0.43	a		
BH	*L**	BH-CBD	6	22.22	0.20	a	28.534	.000
		BH-NBD	6	22.77	0.19	b		
		BH-ABD	6	24.02	0.11	c		
	*a**	BH-CBD	6	1.43	0.13	a	254.904	.000
		BH-NBD	6	0.81	0.28	a		
		BH-ABD	6	10.28	0.48	b		
	*b**	BH-CBD	6	7.70	0.17	ab	7.041	.007
		BH-NBD	6	7.29	0.20	a		
		BH-ABD	6	8.23	0.16	b		
	ΔE^*_{ab}	BH-CBD	6	12.39	0.17	b	181.172	.000
		BH-NBD	6	12.66	0.21	b		
		BH-ABD	6	8.54	0.12	a		
	K/S	BH-CBD	6	21.43	0.25	b	57.642	.000
		BH-NBD	6	21.52	0.52	b		
		BH-ABD	6	16.95	0.16	a		

CBD cationic basic hair dye, *NBD* nonionic basic hair dye, *ABD* anionic basic hair dye. The same letter in the Duncan column indicate that the groups were not different at α = 0.05

Shampooing

WH and BH dyed with the three types of basic hair dye were shampooed to examine the color resistance of dyed hair upon repeated shampooing by Ac, Ne, or Al shampoo (Fig. 3). Figures 4 and 5 illustrate the change of ΔE^*_{ab} values of WH and BH which occurred in the course of 10 times of shampooing. ΔE^*_{ab} values were calculated using Eq. 1 where the reference for dyed WH after shampooing was the dyed WH without shampooing, and the reference for dyed BH after shampooing was the dyed BH without shampooing. ΔE^*_{ab} values were larger in WH than BH regardless of the type of dye or the type of shampoo. WH dyed with ABD showed by far the largest ΔE^*_{ab} value among the hair-dye combinations of WH and BH. The differences in ΔE^*_{ab} values due to different type of shampoo with each hair-dye group seemed to be the lowest in BH dyed with CBD.

Fig. 3 White hair (WH) and bleached hair (BH) dyed with Cationic (CBD), Nonionic (NBD), and Anionic (ABD) basic hair dye before and after up to 10 times of shampooing. *Ac* acidic shampoo, *Ne* neutral shampoo, *Al* alkaline shampoo

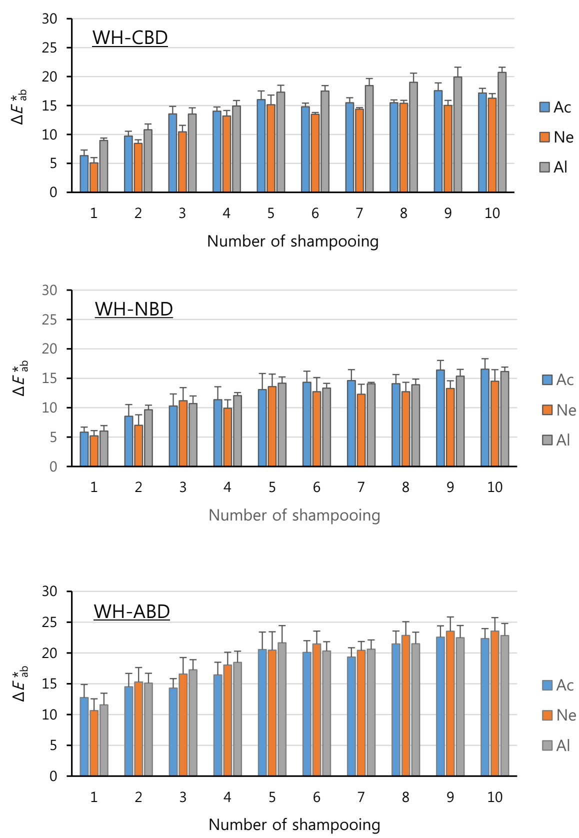

Fig. 4 Color difference (ΔE^{*}_{ab}) of white hair (WH) dyed with three types of basic hair dye after shampooing using Acidic, Neutral, and Alkaline shampoos

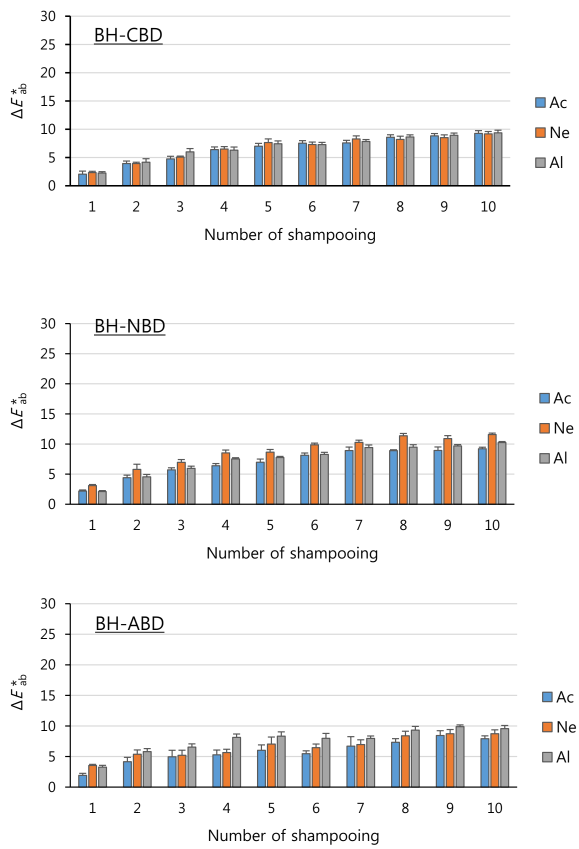

Fig. 5 Color difference (ΔE^{*}_{ab}) of bleached hair (BH) dyed with three types of basic hair dye after shampooing using Acidic, Neutral, and Alkaline shampoos

Color differences (ΔL^*, Δa^*, Δb^*, ΔE^{*}_{ab}) of WH by dye type were compared using the test of ANOVA after 10 times of shampooing with Ac, Ne, or Al shampoos (Table 8). When WH dyed with the three types of dye were shampooed 10 times using Ac, Ne, or Al shampoo, different components of color difference values showed significant differences at $\alpha = 0.05$ among the hair-dye groups. When Ac and Ne shampoos were used, ΔL^*, Δa^*, and ΔE^{*}_{ab} values of WH dyed with CBD, NBD, and ABD were significant differently showing the p values of .021, .010, .026 for those shampooed with Ac, and the p values of .005, .010, .006 for those shampooed with Ne. When Al shampoo was used, ΔL^* and ΔE^{*}_{ab} values of WH dyed with CBD, NBD, and ABD were significantly different with the p values of .027 and .008. The result of Duncan post-hoc test indicated that for both Ac and Ne shampoo groups, WH dyed with ABD became significantly ($\alpha = 0.05$) lighter and lost redness compared to WH dyed with CBD or NBD. For Al shampoo group, WH dyed with ABD became lighter than those dyed with CBD or NBD.

Color differences of BH by dye type were compared using the test of ANOVA after 10 times of shampooing with Ac, Ne, or Al (Table 9). Except for ΔE^{*}_{ab} of BH shampooed by Ac and Al, all components of color difference values showed significant differences at $\alpha = 0.05$ among the hair-dye groups. When Ac shampoo was used, ΔL^*, Δa^*, and Δb^* of BH dyed with CBD, NBD, and ABD were significantly different with

Table 8 Color difference of white hair (WH) by dye type after 10 times of shampooing using three different shampoos (α = 0.05)

Shampoo	Color	Hair-Dye	N	Mean	SE	Duncan	F	p
Ac	ΔL^*	WH-CBD	6	16.75	0.69	a	5.060	.021
		WH-NBD	6	16.28	1.76	a		
		WH-ABD	6	22.37	1.79	b		
	Δa^*	WH-CBD	6	0.21	0.49	b	6.351	.010
		WH-NBD	6	1.10	0.47	b		
		WH-ABD	6	-1.14	0.37	a		
	ΔE^*_{ab}	WH-CBD	6	17.16	0.80	a	4.719	.026
		WH-NBD	6	16.55	1.78	a		
		WH-ABD	6	22.34	1.62	b		
Ne	ΔL^*	WH-CBD	6	14.84	1.05	a	7.809	.005
		WH-NBD	6	14.32	2.03	a		
		WH-ABD	6	24.09	2.52	b		
	Δa^*	WH-CBD	6	0.50	0.58	b	6.357	.010
		WH-NBD	6	0.82	0.52	b		
		WH-ABD	6	-1.90	0.66	a		
	ΔE^*_{ab}	WH-CBD	6	16.26	0.79	b	7.390	.006
		WH-NBD	6	14.50	1.97	b		
		WH-ABD	6	23.55	2.20	a		
Al	ΔL^*	WH-CBD	6	19.11	0.49	a	4.632	.027
		WH-NBD	6	16.59	1.13	a		
		WH-ABD	6	22.17	1.88	b		
	ΔE^*_{ab}	WH-CBD	6	20.72	0.89	b	6.688	.008
		WH-NBD	6	16.15	0.75	a		
		WH-ABD	6	22.82	1.96	b		

[*] ΔL^*, Δa^*, Δb^* values not shown in the table were not significant at α = 0.05. The same letter in the Duncan column indicate that the mean of groups were not different at α = 0.05. *CBD* cationic basic hair dye, *NBD* nonionic basic hair dye, *ABD* anionic basic hair dye, *Ac* acidic shampoo, *Ne* neutral shampoo, *Al* alkaline shampoo

$p < .001$. By using Ne shampoo, the p values of ΔL^*, Δa^*, and Δb^* among BH dyed with CBD, NBD, and ABD showed $p < .001$, and the p value of ΔE^*_{ab} was $p = .001$. When Al shampoo was used, the p value of ΔL^*, Δa^*, and Δb^* of BH dyed with CBD, NBD, and ABD showed $p < .001$. The result of Duncan post hoc test indicated that BH dyed with ABD became significantly (α = 0.05) lighter, lost redness, and increased in yellowness when the hair was shampooed using Ac, Ne, or Al for 10 times.

To examine whether there were significant differences within the hair-dye group by shampoo type, the test of ANOVA was performed on the color difference of WH and BH for each hair-dye group at α = 0.05 (Table 10). For WH, ΔE^*_{ab} values were significantly different by shampoo type only in WH dyed by CBD ($p = .004$), and this difference seemed to be mostly due to the difference in the L^* values, suggested by $p = .005$ of ΔL^*. For WH dyed with ABD, Δb^* ($p = .016$) was significantly different by shampoo type but this did not result in the difference in ΔE^*_{ab} value ($p = .908$). In BH, significant differences were present in Δa^* ($p = .007$) and ΔE^*_{ab} ($p < .001$) of BH dyed with NBD, and in ΔL^* ($p = .003$) of BH dyed with ABD. The rest of the color values of WH and BH were not significant by shampoo type at α = 0.05. The result of Duncan post hoc test indicated that in groups with significant p values more color difference occurred when Al shampoo was used. The mean ΔL^* (WH-CBD: 19.11),

Table 9 Comparison of color difference of bleached hair (BH) by dye type after 10 times of shampooing using three different shampoos (α = 0.05)

Shampoo	Color	Hair-Dye	N	Mean	SE	Duncan	F	*p*
Ac	*L**	BH-CBD	6	3.34	0.23	a	40.245	.000
		BH-NBD	6	2.85	0.32	a		
		BH-ABD	6	6.08	0.27	b		
	*a**	BH-CBD	6	8.53	0.44	b	122.187	.000
		BH-NBD	6	8.55	0.23	b		
		BH-ABD	6	0.32	0.55	a		
	*b**	BH-CBD	6	0.87	0.45	a	23.114	.000
		BH-NBD	6	1.67	0.38	a		
		BH-ABD	6	4.86	0.48	b		
	ΔE^*_{ab}	BH-CBD	6	9.26	0.50	b	3.296	.065
		BH-NBD	6	9.22	0.25	b		
		BH-ABD	6	7.91	0.48	a		
Ne	*L**	BH-CBD	6	2.51	0.43	a	29.439	.000
		BH-NBD	6	2.66	0.50	a		
		BH-ABD	6	6.43	0.26	b		
	*a**	BH-CBD	6	8.98	0.35	b	130.770	.000
		BH-NBD	6	10.43	0.56	c		
		BH-ABD	6	1.57	0.30	a		
	*b**	BH-CBD	6	0.86	0.35	a	27.601	.000
		BH-NBD	6	1.54	0.33	a		
		BH-ABD	6	5.21	0.57	b		
	ΔE^*_{ab}	BH-CBD	6	9.19	0.41	a	11.069	.001
		BH-NBD	6	11.57	0.24	b		
		BH-ABD	6	8.74	0.63	a		
Al	*L**	BH-CBD	6	3.24	0.30	a	68.724	.000
		BH-NBD	6	2.77	0.35	a		
		BH-ABD	6	7.66	0.32	b		
	*a**	BH-CBD	6	1.00	0.41	b	251.659	.000
		BH-NBD	6	9.34	0.16	b		
		BH-ABD	6	0.82	0.28	a		
	*b**	BH-CBD	6	1.36	0.47	a	54.614	.000
		BH-NBD	6	1.54	0.13	a		
		BH-ABD	6	5.98	0.37	b		
	ΔE^*_{ab}	BH-CBD	6	9.37	0.47	a	1.239	.318
		BH-NBD	6	10.24	0.17	a		
		BH-ABD	6	9.57	0.51	a		

* The same letter in the Duncan column indicate that the mean of groups are not different at α = 0.05. *CBD* cationic basic hair dye, *NBD* nonionic basic hair dye, *ABD* anionic basic hair dye, *Ac* acidic shampoo, *Ne* neutral shampoo, *Al* alkaline shampoo

Δb^* (WH-ABD: 2.60), or ΔE^*_{ab} (WH-CBD: 20.72) values were higher in Al than Ac or Ne at α = 0.05. In BH however, the significant difference by shampoo type was accompanied by higher Δa^* (10.43) and ΔE^*_{ab} (11.57) values when Ne shampoo was used for BH dyed with NBD. When BH was dyed with ABD significant difference in ΔL^* was accompanied by higher color difference by Al shampoo (7.66) at α = 0.05. Overall, significant differences occurred in lesser color components by shampoo type compared to the comparison by dye type presented previously. The result implied that the

Table 10 Comparison of color difference of dyed white hair (WH) and bleached hair (BH) by shampoo type (after 10 times of shampooing) (α = 0.05)

Hair-Dye	Color	Shampoo	N	Mean	SE	Duncan	F	*p*
WH-CBD	ΔL^*	Ac	6	16.75	0.69	a	7.513	.005
		Ne	6	14.84	1.05	a		
		Al	6	19.11	0.49	b		
	ΔE^*_{ab}	Ac	6	17.16	0.80	a	8.086	.004
		Ne	6	16.26	0.79	a		
		Al	6	20.72	0.89	b		
WH-NBD	ΔE^*_{ab}	Ac	6	16.55	1.78	a	.466	.636
		Ne	6	14.50	1.97	a		
		Al	6	16.15	0.75	a		
WH-ABD	Δb^*	Ac	6	-2.88	0.44	a	5.571	.016
		Ne	6	-1.96	0.57	a		
		Al	6	2.60	1.06	b		
	ΔE^*_{ab}	Ac	6	22.34	1.62	a	.097	.908
		Ne	6	23.55	2.20	a		
		Al	6	22.82	1.96	a		
BH-CBD	ΔE^*_{ab}	Ac	6	9.26	0.50	a	.040	.961
		Ne	6	9.19	0.41	a		
		Al	6	9.37	0.47	a		
BH-NBD	Δa^*	Ac	6	8.55	0.23	a	6.910	.007
		Ne	6	10.43	0.56	b		
		Al	6	9.34	0.16	a		
	ΔE^*_{ab}	Ac	6	9.22	0.25	a	27.795	.000
		Ne	6	11.57	0.24	c		
		Al	6	10.24	0.17	b		
BH-ABD	ΔL^*	Ac	6	6.08	0.27	a	8.526	.003
		Ne	6	6.43	0.26	a		
		Al	6	7.66	0.32	b		
	ΔE^*_{ab}	Ac	6	7.91	0.48	a	2.315	.133
		Ne	6	8.74	0.63	a		
		Al	6	9.57	0.51	a		

[*] The same letter in the Duncan column indicate that the mean of groups were not different at α = 0.05. ΔL^*, Δa^*, Δb^* values not shown in the table were not significant at α = 0.05. *CBD* cationic basic hair dye, *NBD* nonionic basic hair dye, *ABD* anionic basic hair dye, *Ac* acidic shampoo, *Ne* neutral shampoo, *Al* alkaline shampoo

differences in color of WH and BH after 10 times of shampooing was more due to the type of dye than due to the type of shampoo.

The test of ANOVA was performed on the color strength (K/S) value of WH and BH by dye type after shampooing 10 times using Ac, Ne, or Al shampoos (Table 11). The K/S values of the 10-times-shampooed samples were obtained from the maximum absorbance wavelength (λ_{max}) of the dyed-but-not-shampooed hair, which were 470 nm for WH and 420 nm for BH. The K/S values of all hair-dye groups were significantly different at α = 0.05 regardless of the type of shampoo. NBD showed the highest K/S values especially in WH. The Duncan's post hoc test indicated that in all cases the K/S value of WH or BH dyed with ABD were lower than the K/S values of WH and BH dyed with CBD or NBD at α = 0.05. The Duncan test indicated that CBD and NBD were not statistically different.

Table 11 Comparison of color strength (K/S) of dyed white hair (WH) and bleached hair (BH) by dye type (after 10 times of shampooing) (α = 0.05)

Variable	Shampoo	Hair-Dye	N	Mean	SE	Duncan	F	*p*
Color strength (K/S value)	Ac	WH-CBD	6	4.55	0.57	b	6.194	.011
		WH-NBD	6	5.80	0.96	b		
		WH-ABD	6	2.52	0.27	a		
	Ne	WH-CBD	6	5.33	0.37	b	7.436	.006
		WH-NBD	6	6.64	1.20	b		
		WH-ABD	6	2.52	0.47	a		
	Al	WH-CBD	6	4.39	0.66	ab	4.074	.039
		WH-NBD	6	6.58	1.13	b		
		WH-ABD	6	3.28	0.61	a		
	Ac	BH-CBD	6	15.49	0.33	b	9.617	.002
		BH-NBD	6	15.89	0.35	b		
		BH-ABD	6	13.91	0.33	a		
	Ne	BH-CBD	6	16.22	0.49	b	14.223	.000
		BH-NBD	6	15.82	0.36	b		
		BH-ABD	6	13.55	0.27	a		
	Al	BH-CBD	6	15.99	0.23	b	35.455	.000
		BH-NBD	6	15.69	0.36	b		
		BH-ABD	6	12.85	0.27	a		

[*] The same letter in the Duncan column indicate that the mean of groups were not different at α = 0.05. *CBD* cationic basic hair dye, *NBD* nonionic basic hair dye, *ABD* anionic basic hair dye, *Ac* acidic shampoo, *Ne* neutral shampoo, *Al* alkaline shampoo

Table 12 Comparison of ΔE^{*}_{ab} and K/S values between the groups with different number of shampooing

Hair-Dye-Shampoo	Variable	Shampoo group	N	Mean	SE	t	*p*
WH-CBD-Ac	ΔE^{*}_{ab}	No shampoo	6	0.00	0.00	− 6.471	.001
		Shampoo 1 time	6	6.33	0.98		
		Shampoo 1 time	6	6.33	0.98	− 5.419	.000
		Shampoo 5 times	6	16.02	1.50		
		Shampoo 1 time	6	6.33	0.98	− 8.547	.000
		Shampoo 10 times	6	17.16	0.80		
		Shampoo 5 times	6	16.02	1.50	− .627	.517
		Shampoo 10 times	6	17.16	0.80		
	K/S	No shampoo	6	17.47	0.62	3.663	.004
		Shampoo 1 time	6	11.81	1.41		
		Shampoo 1 time	6	11.81	1.41	4.032	.002
		Shampoo 5 times	6	5.11	0.87		
		Shampoo 1 time	6	11.81	1.41	4.756	.001
		Shampoo 10 times	6	4.55	0.57		
		Shampoo 5 times	6	5.11	0.87	.543	.599
		Shampoo 10 times	6	4.55	0.57		

Example shown on the CBD dyed white hair (WH) shampooed with the Acidic shampoo (Ac) (α = 0.05)

CBD cationic basic hair dye

The t-test was performed on WH dyed with CBD to examine whether there were differences in the ΔE^{*}_{ab} and the K/S values by different number of shampooing (Table 12). By the first shampooing, a significant difference occurred at α = 0.05 in ΔE^{*}_{ab} ($p = .001$)

and the K/S ($p = .004$) values of WH dyed with CBD. And there were significant differences in ΔE^{*}_{ab} and the K/S values between the first shampooing and 5 times shampooing, and also between the first shampooing and the 10 times shampooing. The *p* value of the former groups being $p < .001$ (ΔE^{*}_{ab}) and $p = .002$ (K/S), and the latter group being $p < .001$ (ΔE^{*}_{ab}) and $p = 0.001$ (K/S). However, the difference between the 5 times shampooing and the 10 times shampooing were not significant for both ΔE^{*}_{ab} ($p = .517$) and the K/S ($p = .599$) values. The result indicated that most of the color change occurred with the first shampooing.

Discussion

Hair has a unique pH property due to the types of amino acids forming the keratin of hair and also due to the difference in the chemical characteristics between the whole hair and the surface of hair (Robbins, 2012). The pH of the whole hair, the isoionic point, is 5.8 ± 1 which is primarily due to the higher amount of acidic amino acids than the basic amino acids in the whole hair (Hehner et al., 2002; Robbins, 2012). The pH of the surface of a healthy hair is pH 3.67 which is denoted as the isoelectric point of hair (Hehner et al., 2002; Morel et al., 2008; Robbins, 2012). The isoelectric point of hair is lower than the isoionic point of hair since there is a higher amount of acidic amino acid in the outermost cuticle layer compared to the whole hair (Robbins, 2012). The presence of 18-methyl eicosanoic acid (18-MEA), the fatty acid covalently bonded to hair, and the higher amount of cysteic acid on the surface of hair also contribute to the lower pH at the surface compared to the whole hair (Dias et al., 2014; Morel et al., 2008; Robbins, 2012).

Due to the pH characteristics of hair, the pH of the dye is an important factor for the adsorption of dye to hair and for the reduction of possible damage which may occur by dyeing (Morel et al., 2008). The surface of hair is negatively charged if the hair is in a solution with the pH higher than its isoelectric point (Fernández-Peña & Guzmán, 2020). The negative charge of the hair will attract the positive charge of the basic pigment, enabling the adsorption of pigment to the surface of hair. However, the pH higher than 10 will cause significant swelling and the possible breakage of ionic bond within the hair keratin, causing the weakening of the hair fiber (Bhat et al., 1981; Malinauskyte et al., 2020). All three basic hair dyes prepared in this study had the pH level higher than the isoelectric point of hair. Additionally, the pH levels of all 3 dyes were within the pH level recommended (pH 4 ~ 9) by the Sensient Cosmetic Technologies (provider) for the dye formulated with Basic Brown 16 (Vesque, 2016). The pH values of the three basic hair dyes prepared suggest that the electrostatic interaction will occur between the dye and the hair which will allow for the easy adsorption of pigment to the hair. However, besides the pH of the dyeing medium, it is expected that the presence of charges other than those of the basic pigment would also have an effect on the dyeing behavior of the basic hair dye.

The three basic hair dyes were designed so that the dye would charge in water only by the surfactant that was added intentionally. Any substance that could produce additional charge was excluded from the general recipe of the hair dye. CBD was formulated with the nonionic surfactants and the cationic surfactant, the weight percentages of which were 5.00% and 4.00% respectively relative to the total dye formulation. The cationic surfactant that was used in CBD was Steartrimonium chloride which have positive charge in water due to its positively charged head group (Fernández-Peña & Guzmán, 2020; Scientific Committee on Consumer Products, 2006) (Fig. 6). NBD was formulated with the nonionic surfactants alone by 5.00 wt.% relative to the total dye formulation. The nonionic surfactants that were used in NBD were Glyceryl monostearate SE, Tween 60, and Arlacel 60 which do not ionized in water since they do not have any charge on the head group (COSNET, n.d.; Fernández-Peña & Guzmán, 2020). ABD was formulated with the nonionic surfactants and the anionic surfactant by 5.00 wt. % and 4.00 wt. % respectively relative to the total dye formulation. The anionic surfactant that was used in ABD was Ammonium lauryl sulfate, which have negative charge in water due to its negatively charged head group ("Ammonium lauryl sulfate, 2021; Fernández-Peña & Guzmán, 2020). By the effect of the type of surfactant in the formulation, CBD would provide positive charges and ABD would provide negative charges during the dyeing process. NBD would not provide either positive or negative charges.

Basic hair dyes contain basic pigments which have positive charge in water. The molecular size of the basic pigments is large so that it cannot readily pass through the cuticle layers and into the cortex of hair as do the couplers or dye intermediates of the permanent hair dye (França et al., 2015; Goldwell, n.d.; Massoni, 2004). Owing to the large molecular size and thanks to its positively charged molecules, the main mechanism of dyeing with basic hair dye is its electrostatic attraction with the negatively charged hair, and the following ionic bond with the negative sites on the surface of hair (Alfa Chemistry, 2022; França et al., 2015; Goldwell, n.d.; Hehner et al., 2002; Massoni, 2004).

The interaction of surfactant in the dyeing medium is well studied in the area of textile dyeing. When the dye and the surfactant have the charges opposite to each other, the electrostatic attraction is formed between the dye and the surfactant (Simončič & Kovač, 1998). The attraction leads to the dye-surfactant complex formation which will interfere with the immediate adsorption of the dye to the textiles (Simončič & Kovač, 1998). In textile dyeing, this will prevent the uneven adsorption or differential speed of adsorption of dye to the textile, resulting in the level dyeing (Simončič & Kovač, 1998). If

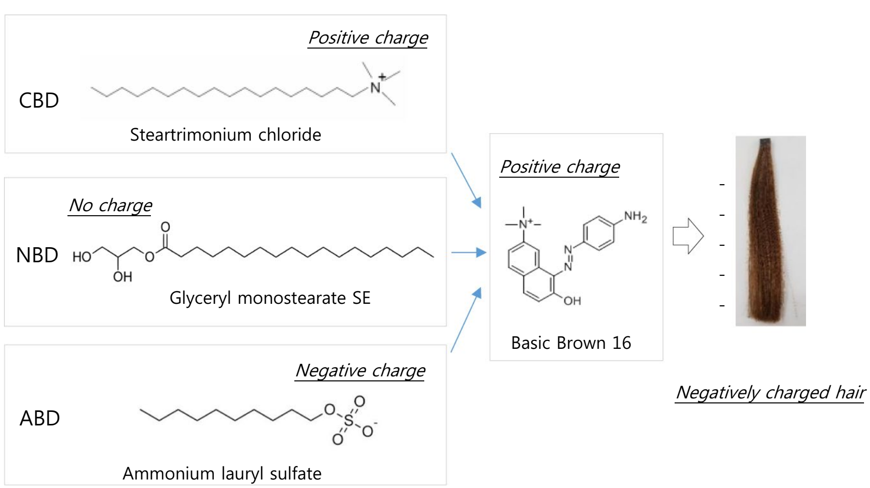

Fig. 6 Schematic diagram illustrating the electric charges of dye (Basic Brown 16), surfactant, and hair in the dyeing medium of Cationic (CBD), Nonionic (NBD), and Anionic (ABD) basic hair dyes

the dye and the surfactant have the same charge, there will be a competition between the dye and the surfactant on the sorption sites of the textile (Simončič & Kovač, 1998). And this will also result in the level dyeing of the textiles (Simončič & Kovač, 1998).

In the present investigation, it is highly likely that the negative charges of the anionic surfactant in ABD interfered with the adsorption of Basic Brown 16 to the hair. It is probable that the electrostatic attraction occurred between the pigment and the surfactant, forming a salt of Basic Brown 16 and Ammonium lauryl sulfate (Yun, 2019). This would lower the concentration of Basic Brown 16 in the dye solution, lowering the number of pigments which can be adsorbed to the hair (Yun, 2019). This must have led to the lower color values, color strength, and color resistance of WH and BH dyed with ABD than those dyed with CBD or NBD.

Considering the dyeing mechanism of basic hair dyes, it is probable that the positive charge of the cationic surfactant competed with the positive charge of the basic dye on the electrostatic attraction between the negatively charged hair (Simončič & Kovač, 1998). And due to this competition the cationic basic hair dye was expected to show an adverse effect on dyeing by taking up the negative sites of hair, resulting in a lower dye adsorption (Simončič & Kovač, 1998; Yun, 2019). However, WH and BH dyed with CBD showed a similar color, and in some cases only slightly lower color strength and color resistance compared to WH and BH dyed with NBD. It might be that the concentration of Basic Brown 16 applied in this study provided fewer number of pigments than the number of negative sites in WH and BH. And due to a large number of negative sites on hair there might have been less competition between the pigment and the cationic surfactant for the binding sites of the hair. This assumption is supported by literatures which explain that the damaged hair, such as bleached hair, has more negative sites than the undamaged hair due to the increased acidic groups (Fernandez-Pena & Guzman, 2020; Robbins, 2012; Morel et al., 2008). Treatment of hair with alkali and oxidizer such as used in bleaching will cause the breakage of disulfide crosslink within the cystine amino acid. As a result, cysteic acid is produced as the degradation product (Robbins, 2012). Alkali or oxidizer can also destroy the covalent bond between cystine or cysteine amino acid and the 18-Methyl eicosanoic acid (Robbins, 2012). WH was a commercially bleached hair which was selected for this study to simulate the grey-hair-dyeing. BH was the hair bleached in our laboratory to simulate the fashion-dyeing. The bleaching treatment would have increased the number of negative charges ($-SO_3^-$) on the surface of hair allowing more adsorption of positive sites from the dye or the surfactant (Robbins, 2012).

Currently, several cosmetic brands in Korea produce and sell hair coloring treatments using basic pigments as raw materials. These products include cationic (+) surfactants such as cetrimonium chloride and cetrimonium methosulfate for the purpose of antistatic, emulsifying, conditioning, and anionic surfactants such as disodium laureth sulfosuccinate for the purpose of foaming, cleansing, or surface activity (COOS, 2020; Kim, 2019, 2022). While these ingredients can do their natural role as surfactants in the hair dye products, they may interfere with the adsorption of basic dye to hair considering the results of the present investigation.

A shampoo is usually composed of chemical substances that act as cleansing agent, conditioning agent, preservative, special caring agent, etc. and water (Cruz et al., 2016).

The anionic surfactant is the primary surfactant that provide cleaning purpose (Cruz et al., 2016). The most common anionic surfactant used in shampoo is sodium laureth sulfate (SLS) and ammonium laureth sulfate (Yang, 2017). In detergency, it is known that a good cleaning effect for greasy dirt occurs if the pH of the detergent is 8.5 ~ 11.0, and for cleaning light oily residue the effective pH range is 5.5 ~ 8.5 (Ullah, 1998–2022). The same condition is applied in the cleansing effect of the shampoos (Barros, 2018). However, shampoo with the pH higher than the isoelectric point of hair can cause the negative charges to develop on the surface of hair, increasing the repulsion between the hairs and causing frizzy hair (Dias et al., 2014). To complicate the situation, the shampoo not only cleanses the hair but it also cleanses the scalp which has the pH value around 5.5, the same as the isoionic point of hair (Dias et al., 2014). Therefore, in order to maintain a healthy scalp and hair, the pH of the shampoo should be kept around 5.5 (Dias et al., 2014).

However, most commercial shampoos commonly have a pH value higher than 5.5. Dias et al. (2014) who investigated the pH values of 123 shampoos of international brands sold in Brazil found that the pH values of all shampoos were in the range of 3.5 ~ 9.0, with 61.78% having the pH values higher than 5.5. Cruz et al. (2016) said that the pH of a shampoo is usually between 5 and 7. Since most of the shampoos have pH higher than the isoionic point of hair, the hair cosmetics industry recommends using a conditioner at the final step of shampooing (Barros, 2018; Dias et al., 2014). Ne and Al shampoos prepared in this study have pH values higher than 5.5. The pH range of the three types of shampoos were designed to reflect the pH range of the commercial shampoos, and the use of conditioner was not included in the experimental design. The present results showed that the effect of shampoo on the hair dyed with basic hair dye was less than the effect of the dye itself. However, it did seem that alkaline shampoo had an adverse effect on the dyed hair, causing more color change after repeated shampooing.

Conclusions

Three types of basic hair dye were prepared in this study using Basic Brown 16 pigment to examine whether the type of surfactant in the formulation of basic hair dye had an effect on the dyeability and the color resistance of the dyed hair. The basic hair dye formulated with anionic surfactant produced significantly different color and lower color strength than those formulated with the cationic surfactant or nonionic surfactant alone. The color resistance of anionic basic hair dye after 10 times of shampooing was significantly lower than that of the cationic basic hair dye or nonionic basic hair dye. The difference between the anionic basic hair dye and the cationic or nonionic basic hair dye were shown in both white hair and bleached hair. The present findings suggested that the cationic or nonionic surfactants were better choice of emulsifying agent than the anionic surfactant in the formulation of basic hair dye containing Basic Brown 16. It appeared that the change in the color, loss of color strength, and loss of color resistance after repeated shampooing was more due to the type of dye than due to the type of shampoo. However, the overall results did indicate that more color change occurred by using the alkaline shampoo than by using the acidic or neutral shampoo. Therefore, it is recommended that the hair dyed with basic hair dye should be shampooed using a shampoo with pH value lower than 7.80, and preferably around the isoionic point of hair.

One of the difficult problems in maintaining the color of dyed hair is that hair grows approximately 1.3 cm per month, and that it does not take more than 10 days to have the natural hair color visible at the root area. This is a troublesome issue especially for the people with grey hair. And because of this phenomenon even the permanent hair dyeing needs to be done at least once a month or preferably sooner to cover the arising grey hair. The repeated practice of permanent hair dyeing inevitably causes damage to the hair and the scalp. The results of this study indicated that the color of hair dyed with the basic hair dye changed by the first shampooing, but further shampooing had little effect on the additional color change. Basic hair dye composed of Basic Brown 16 provided a reasonable color resistance up to 10 shampooing at least by using a cationic or nonionic surfactants in the dye formulation. This means that such basic hair dye can be used to cover the grey hair as often as in 10 days interval. In view of the findings of this study, it is suggested that the basic hair dye formulated with a combination of cationic and nonionic surfactant or nonionic surfactant alone is a good alternative for the permanent hair dye. This research was aimed to provide the empirical data which can aid in the development of safe and convenient semi-permanent hair dye products using the cationic, basic pigments. It is hoped that the result of this research can contribute to the hair dye industry and in the well-being of the hair dyeing population.

Acknowledgements
Not applicable.

Author contributions
The data presented in this manuscript is part of the Doctoral Dissertation of KS. KS designed the research, conducted all the experiments, collected and analyzed the data. CS conducted part of the data analyses and wrote this manuscript. Both authors read and approved the final manuscript.

Authors' information
KY received the Ph.D. degree from the Graduate School of Incheon National University in 2019. The research design, laboratory experiments, and data analysis of this research were conducted while she was a doctoral student in the Department of Cosmetic Science & Management, Graduate School, Incheon National University, Korea. KY is currently, the teacher of Incheon Practical Science High School, Incheon, Korea.
CA is the professor in the Department of Cosmetic Science and Management and also the professor in the Department of Fashion Industry of Incheon National University, Korea. She was the thesis advisor of KY, and together they contributed in the research design and manuscript preparation.

Funding
This work was supported by Incheon National University Research Grant in 2022.

Availability of data and materials
The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Consent for publication
Not applicable.

Competing interests
The authors declare that they have no competing interests.

Received: 25 July 2022 Accepted: 4 December 2022
Published online: 25 January 2023

References

Ahmed, N., Oulton, D. P., & Taylor, J. A. (2006). The use of reflectance measurements in the determination of fixation of reactive dyes to cotton. *Color Research and Application, 31*(2), 117–121. https://doi.org/10.1002/col.20189
Alfa Chemistry. (2022). *Cationic dyes*. https://www.alfa-chemistry.com/products/cationic-dyes-35.htm
Ammonium lauryl sulfate. (2021, May 10). In Wikipedia. https://en.wikipedia.org/wiki/Ammonium_lauryl_sulfate

Barros, C. (2018). *How the pH of shampoos influences its efficiency*. Prospector. Retrieved June 28, 2000, from https://knowledge.ulprospector.com/8746/pcc-how-does-shampoo-ph-affect-its-performance/
Bhat, G. R., Parreira, R. M., Lukenbach, E. R., & Harper, D. L. (1981). Acid-base characteristics of human hair: Absorption of HCl and NaOH, and the effects on physical properties. *Journal of the Society of Cosmetic Chemists, 32*(7), 393–405.
Choudhury, A. K. R. (2015). 4—Instrumental colourant formulation. In A. K. R. Choudhury (Ed.), *Principles of colour and appearance measurement. Volume 2: Visual measurement of colour, colour comparison and management* (pp. 117–173). Woodhead Publishing. https://doi.org/10.1016/C2014-0-01832-1
COOS. (2020). *Magnifying glass of cosmetic substances for professionals*. Appton. https://coos.kr/
COSNET. (n.d.). Glyceryl monostearate SE. Retrieved July 10, 2022, from https://www.cosnet.co.kr/goods_detail.php?goodsIdx=10
Cruz, C. F., Costa, C., Gomes, A. C., Matama, T., & Cavaco-Paulo, A. (2016). Human hair and the impact of cosmetic procedures: A review on cleansing and shape-modulating cosmetics. *Cosmetics, 3*, 26. https://doi.org/10.3390/cosmetics3030026
Dias, M. F. R. G., Almeida, A. M., Cecato, P. M. R., Adriano, A. R., & Pichler, J. (2014). The shampoo pH can affect the hair: Myth or reality? *International Journal of Trichology, 6*(3), 95–99. https://doi.org/10.4103/0974-7753.139078
Fernández-Peña, L., & Guzmán, E. (2020). Physicochemical aspects of the performance of hair-conditioning formulations. *Cosmetics, 7*(2), 26. https://doi.org/10.3390/cosmetics7020026
França, S. A., Dario, M. F., Esteves, V. B., Baby, A. R., & Velasco, M. V. R. (2015). Types of hair dye and their mechanisms of action. *Cosmetics, 2*(2), 110–126. https://doi.org/10.3390/cosmetics2020110
Goldwell. (n.d.). *Direct dyes*. Kao Salon Division. Retrieved July 13, 2022, from https://www.goldwell.com/en-nz/education/hair-science/color-theory/direct-dyes/
Hartnett, D. A., & Kozubal, C. (2016). *Personal care compositions* (US 10391046 B2). U.S. Patent and Trademark Office. https://patents.google.com/patent/US10391046B2/en
Hehner, U., Deutz, H., Braun, P., & Flemming, E. (2002). *Method and composition adjusted to the isoelectric point of hair for conditioning of oxidatively dyed hair* (U.S. Patent 2002/0122783 A1). U.S. Patent and Trademark Office. https://patents.google.com/patent/US20020122783A1/en
Indrawati, T., Syahrin, A., & Irpan. (2017). Preparation of demipermanent and semipermanent hair dyes gels from ethanol extract of *Caesalpinia sappan L*. using carbomer as gelling agent. In T. Mart, D. Triyono, & K. A. Sugeng (Eds.), *AIP Conference Proceedings, Vol. 1862* (030080). https://doi.org/10.1063/1.4991184
ISO/CIE. (2019). *Colorimetry-Part 4: CIE 1976 L*a*b* colour space* (ISO/CIE 11664–4:2019(E)). https://cie.co.at/publications/colorimetry-part-4-cie-1976-lab-colour-space-0
Kim, B. R. (2019, March 6). [Fastidious pouch] The golden days of 'self-hair dyeing'-Hair dyes of Etude, The Face Shop, Michaa, are they safe. *New Daily Economy*. https://biz.newdaily.co.kr/site/data/html/2019/03/06/2019030600072.html
Kim, M. S. (2015). *Beauty care design and practice* [Unpublished lecture note]. Incheon National University.
Kim, T. H. (2022, May 27). ModaModa, reason for popularity-The only 'Natural browning shampoo. *INews24*. https://www.inews24.com/view/1484747
Korea Health Industry Development Institute. (2020). 2020 *Cosmetics industry analysis report*. https://www.khidi.or.kr/board/view?pageNum=1&rowCnt=10&no1=776&linkId=48857409&menuId=MENU00085&maxIndex=00488574099998&minIndex=00002145679998&schType=0&schText=&schStartDate=&schEndDate=&boardStyle=&categoryId=&continent=&country
Lee, R. J., & Kim, J. D. (2020). A study on the awareness and usage status of coloring of human hair. *Journal of the Korean Society of Cosmetics and Cosmetology, 10*(2), 173–186.
Malinauskyte, E., Cornwell, P. A., Reay, L., Shaw, N., & Petkov, J. (2020). Effect of equilibrium pH on the structure and properties of bleach-damaged human hair fibers. *Biopolymers, 111*(11), e23401. https://doi.org/10.1002/bip.23401
Massoni, J. (2004). *Temporary hair dye composition* (US Patent No. 2004/0055094 A1). U.S. Patent and Trademark Office. https://patents.google.com/patent/US20040055094A1/en
Ministry of Food and Drug Safety. (2016). *Partial revision notification of cosmetic color types, standards and test methods* (Notice No. 2016-49). https://www.mfds.go.kr/brd/m_207/view.do?seq=10827&srchFr=&srchTo=&srchWord=%EC%95%BD%EC%A0%84&srchTp=0&itm_seq_1=0&itm_seq_2=0&multi_itm_seq=0&company_cd=&company_nm=&page=2
Morel, O., Christie, R. M., Greaves, A., & Morgan, K. M. (2008). Enhanced model for the diffusivity of a dye molecule into human hair fibre based on molecular modelling techniques. *Coloration Technology, 124*(5), 301–309. https://doi.org/10.1111/j.1478-4408.2008.00157.x
Panwar, V., Dey, B., Sheikh, J. N., & Dutta, T. (2022). Thermostable bacterial laccase for sustainable dyeing using plant phenols. *RSC Advances, 12*, 18168–18180. https://doi.org/10.1039/d2ra02137d
Robbins, C. R. (2012). *Chemical and physical behavior of human hair* (5th ed.). Springer. https://doi.org/10.1007/978-3-642-25611-0
Samanta, P. (2022). Basic principles of colour measurement and colour matching of textiles and apparels. In A. K. Samanta (Ed.), *Colorimetry*. IntechOpen. https://doi.org/10.5772/intechopen.101442
Sargsyan, I., Vill, V., & Hippe, T. (2020). Investigations of vegetable tannins as hair dyes and their interactions with prebleached hair fibres. *International Journal of Cosmetic Science, 42*(4), 320–327. https://doi.org/10.1111/ics.12624
Scientific Committee on Consumer Products. (2006). *Opinion on alkyl (C16, C18, C22) trimethylammonium chloride: For other uses than as a preservative* (SCCP/0917/05). European Commission. https://ec.europa.eu/health/ph_risk/committees/04_sccp/docs/sccp_o_037.pdf
Scientific Committee on Consumer Safety. (2013). *Opinion on Basic Brown 16: Colipa n° C9* (SCCS/1496/12). European Commission. https://ec.europa.eu/health/scientific_committees/consumer_safety/docs/sccs_o_117.pdf
Seydi, E., Fatahi, M., Naserzadeh, P., & Pourahmad, J. (2019). The effects of para-phenylenediamine (PPD) on the skin fibroblast cells. *Xenobiotica, 49*(10), 1143–1148. https://doi.org/10.1080/00498254.2018.1541264
Shin, Y. S., & Lee, S. H. (2006). Natural dyeing of hair using juglone. *Journal of the Korean Society of Clothing and Textiles, 30*(12), 1708–1713.

Simončič, B., & Kovač, F. (1998). A study of dye-surfactant interactions. Part 2. The effect of purity of a commercial cationic azo dye on dye-surfactant complex formation. *Dyes and Pigments, 40*(1), 1–9. https://doi.org/10.1016/S0143-7208(98)00028-X

Tucker, H. H. (1971). The coloring of human hair with semipermanent dyes. *Journal of the Society of Cosmetic Chemists, 22*, 379–398.

Ullah, A. (1998–2022). *The role of pH in cleaning*. Cleanfax. Retrieved June 20, 2022, from https://cleanfax.com/carpet-care/the-role-of-ph-in-cleaning/

Vesque, P. (2016). *ARIANOR basic dyes semi-permanent applications for hair care and hair color* [PowerPoint slides]. DocPlayer. http://docplayer.net/36430868-Arianor-basic-dyes-semi-permanent-applications-for-hair-care-and-hair-color.html

Yang, H., Zhu, S., & Pan, N. (2010). On the Kubelka-Munk single-constant/two-constant theories. *Textile Research Journal, 80*(3), 263–270. https://doi.org/10.1177/0040517508099914

Yang, J. (2017). Hair care cosmetics. In K. Sakamoto, R. Y. Lochhead, H. I. Maibach, & Y. Yamashita (Eds.), *Cosmetic science and technology: Theoretical principles and applications* (pp. 601–615). Elsevier. https://doi.org/10.1016/B978-0-12-802005-0.00036-7

Yun, K. (2019). *Dyeability and dyeing durability of basic hair dye* [Unpublished doctoral dissertation]. Incheon National University.

Zhang, H. (2014). Application of K/S value in determination of fixation rate. *Advanced Materials Research, 1048*, 116–119. https://doi.org/10.4028/www.scientific.net/AMR.1048.116

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Submit your manuscript to a SpringerOpen journal and benefit from:

- ► Convenient online submission
- ► Rigorous peer review
- ► Open access: articles freely available online
- ► High visibility within the field
- ► Retaining the copyright to your article

Submit your next manuscript at ► springeropen.com