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Protection of oxidative hair color fading from shampoo washing by hydrophobically modified cationic polymers

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Synopsis

The fading of oxidative color in hair as a result of daily shampoo washing activities has become a common problem and a source of frequent complaints by consumers. The fading occurs primarily through hair dye solubility in water. One aspect of the current study investigates the physical and chemical factors that influence hair color fading during the washing process. This is accomplished by testing hair dye dissolution in water from dyed hair samples with variation of surfactant type, pH, and hair type. Furthermore, a new approach to preventing color fading is developed aiming to provide an effective barrier function for hair dye from dissolving into water. The preliminary investigation of a series of polymers with various functional groups indicates that polymers with hydrophobically modified and cationic functionalities are most effective in preventing hair dye dissolution in water. It is also evident that a synergistic effect of the polymer's hydrophobic moieties and cationic charges are important on hair color protection during shampoo washing processes. A primary example of a polymer within this category is a cationic terpolymer of vinylpyrrolidone, dimethylaminopropyl methacrylamide, and methacryloylaminopropyl lauryldimonium chloride (INCI: Polyquaternium-55). The color protection benefit of this polymer is evaluated using newly developed methodologies for evaluating hair color changes, such as hair color fading tests through multiple shampoo washes with mannequin heads and hair tresses, both derived from human hair, colorimetry, and quantitative digital image analysis. In addition, new infrared spectroscopic imaging techniques are used to detect the hair dye deposition behavior inside hair fibers both with and without the color protection treatment. Both visual and instrumental measurement results indicate that Polyquaternium-55 provides a high level of color protection when formulated in a hair color protection regimen with up to 50% color protection. This regimen significantly outperforms commercial products that were tested containing a color protection claim. The proposed mechanism for the anti-fading action of hydrophobically modified polymers includes a cationic charge-reinforced hydrophobic barrier. This model is supported by evaluating the color fastness effect of several different polymer chemistries and by measuring hair surface hydrophobicity changes.

INTRODUCTION

Coloring hair becomes increasingly popular year to year. However, fading of artificial hair color has become a common problem and a source of frequent complaint by consumers. Lush, colorful hair begins to look dull with a loss of vibrancy and intensity, yielding a shade shift deemed non-desirable after a couple of weeks before roots grow out. The loss of dye hair color typically occurs because of color wash-out during the daily shampooing process or can be initiated by environmental circumstances such as exposure to UV radiation which can break down the color molecule. It was found that the washing process is

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the most significant factor in the removal of hair color, while UV exposure has a significant impact only after 90 hours of intense irradiation (1).

Though the hair color fading mechanism associated with the shampoo process is not yet well understood, there are some main factors attributed to fading. One is the dye solubility in water. Most dyes used on hair are water soluble. Shampoo removal rate of dye is related to dye solubility. Dye solubility is related to dye structure and usually binuclear dyes are more soluble. Color fading is especially pronounced with red dye because it is more water soluble and is removed to a greater extent during washes, resulting in shade changes. In addition, the degree of hair damage has a significant contribution to color fading through wash-out. Damaged hair is more porous which allows the dye molecules to leak out easily during the washing process. Therefore, bleached hair fades much faster than non-bleached hair because bleached hair is damaged with loss of F-layer protection and larger pore sizes on cuticle cells. Besides the pores on cuticle cells, the CMC and cortex swell with water, providing additional channels for dye to leach out. The surfactants in shampoo and conditioner products provide wetting function and bring moisture into the hair shaft which facilitates the dye molecules to come out with the water during washing. Although off and on-shade fading occurs during washing process, off shade fading is much more objectionable by the consumer.

Consumers want to maintain the vibrancy of the color until the next oxidative process. This translates to protecting hair color from fading for up to six weeks when color will need to be refreshed as noticeable re-growth will need to be colored. Meeting this consumer need continues to be a significant challenge to the cosmetic industry. Color protection is now considered to be an important area in hair care market (2–4). For the last couple of years, products for hair color protection have grown significantly with over 170 color care products launched to the market globally (5). The majority of these products are in the form of shampoo and conditioners. Some of them use silicones which form a hydrophobic film on the hair surface to protect color and there are several studies which have claimed the color retention effect by using this approach (1,6).

The primary objective of our research was to understand the physicochemical factors affecting shampoo-caused off-shade fading and develop approaches that provide measurable and consumer perceivable protection against color loss during shampoo washing of dyed hair. Our focus was to prevent color stripping of permanent, level 3, oxidative dye treated hair, as this comprises the majority of the professional and mass market formulations. To accomplish this objective, new methodologies for evaluating hair color change were developed and these methods and measurements were linked to consumer perceivable changes in hair color. With these methods, various types of polymers were tested for their effect on reducing hair color fading. An effective hair color protection treatment regimen containing a hydrophobically modified cationic polymer was developed (patent pending).

MATERIALS AND METHODS

POLYMERS AND SURFACTANTS

Polyquaternium-55 (Styleze W-20®) and other polymers tested in the dyed hair soaking tests, unless specified, were supplied by International Specialty Products (ISP). Alky hydroxy ethyl cellulose was supplied by Hercules. Quaternary salt of hydroxy ethyl cellulose was supplied by Rita.

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Alkyl–HEC quaternary salt was supplied by Amerchol. Sodium lauryl either sulfate (SLES, Rhodapex ES-2) was supplied by Rhodia. Centrimonium chloride (CETAC) was supplied by Stepan. Coco trimonium chloride (Arquard C-33 W) was supplied by Akzo Nobel.

HAIR SAMPLES

Bleached hair, grey hair and piedmont hair samples were purchased from International Hair Importers. Each hair tress is 1.5″ wide, 3.5 g in weight, and 6.5″ in length of loose hair. The hair tresses are dyed using commercial hair dye products for subsequent multiple shampoo washing tests and soaking tests.

HAIR DYE AND PREPARATION OF DYED HAIR TRESSES

Hair samples were dyed with commercial two-component, permanent, level 3 oxidative hair dye formulations having shades of intense red, dark brown, and deep red. Each hair tress was treated with a mixture of 7 g of hair dye base and 7 g of developer lotion. The hair tresses were dyed one hour and 10 minutes and covered with aluminum foil at room temperature. After dying, hair tresses were rinsed under running tap water for 2 minutes which was enough to extract the surface residual dye from the hair. The dyed hair tresses were dried in air at room temperature for 24 hours before they were used for color fading and fastness tests. The primary dyes and couplers of the commercial permanent hair dyes used in this study to treat hair tresses and mannequin designated as Gabrielle are listed in Table I.

The ingredients of another commercial two parts, permanent hair dye (ruby red color) used for mannequin designated as Dephne in hair salon test are as follows: aqua/water, trideceth-2 carboxamide MEA, propylene glycol, hexylene glycol, PEG-2 oleamine, polyglyceryl-4 oleyl ether, oleyl alcohol, alcohol denat., ammonium hydroxide, polyglyceryl-2 oleyl ether, oleic acid, sodium diethylaminopropyl cocoaspartamide, 4-amino-2-hydroxytoluene, pentasodium pentetate, parfum/fragrance, ammonium acetate, p-aminophenol, sodium metabisulfite, p-phenylenediamine, erythorbic acid, phenyl methyl pyrazolone, 2-methyl-5-hydroxyethylaminophenol, 6-hydroxyindole, resorcinol, F.I.L. #D9617/1.

The hair dye used for dying hair samples which are used in FTIR image analysis is burgundy color and its ingredient labels are as follows: water, C12-15 Pareth-3, Oleth-10,

Table I
Primary Dyes and Couplers in the Level-3 Oxidative Permanent Commercial Dye Formulations Used in This Study

Color of hair dye	Primary dye	Coupler
Intense red	1-Hydroxyethyl 4,5-diamino pyrazole sulfate	m-Aminophenol
Deep red	1-Hydroxyethyl 4,5-diamino pyrazole sulfate	1-Naphthol
	P-phenylene diamine (PPD)	Resorcinol
	P-aminophenol (PAD)	
Dark brown	P-phenylene diamine (PPD)	1-Naphthol
	N,N, Bisc(2-hydroxy ethyl) PPD sulfate	Resorcinol
	P-aminophenol (PAP)	m-Aminophenol

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Cocamide MEA, dilinoleic acid, linolamidopropyl dimethylamine dimer dilinoleate, Streareth-21, ammonium hydroxide, behentrimonium chloride, Polyquaternium-22, sodium sulfite, sodium metasilicate, 4-amino-2-hydroxytoluene, P-phenylenediamine, P-aminophenol, N,N-Bis(2-hydroxytoluene), P-phenylenediamine sulfate, mica, iron oxides, 1-hydroxyethyl 4,5-diamino pyrazole sulfate, titanium dioxide.

COMMERCIAL COLOR LOCK PRODUCTS

Two commercial color lock products were used as benchmarks. The first was a two step system consisting of a shampoo and conditioner. The ingredient labels are: aqua/water, sodium laureth sulfate, disodium cocoamphodiacetate, glycol distearate, cocamide MIPA, sodium chloride, hexylene glycol, disodium ricinoleamide, MEA-sulfosuccinate, parfum/fragrance, carbomer, disodium EDTA, methylparaben, Polyquaternium-10, DMDM hydantoin, benzophenone-3, ethylhexyl methoxycinnamate, hexyl cinnamal, benzyl salicylate, glycine soja/soybean oil, tocopherol, isopropanolamine, butylphenyl methylpropional, linalool, amyl cinnamal, hydroxycitronellal, limonene; water, cetearyl alcohol, behentrimonium chloride, cetyl esters, amodimethicone, fragrance, methylparaben, trideceth-5, benzophenone-3, ethylhexyl methoxycinnamate, soybean oil, tocopherol, hexyl cinnamal, Trideceth-10, benzyl salicylate, citric acid, chlorhexidine dihydrochloride, butylphenyl methylpropional, linalool, amyl cinnamal hydroxycitronellal.

The second commercial color lock system was a three step system and consisted of a leave in treatment cream, shampoo and conditioner. The ingredient labels for the shampoo and conditioner are: water (aqua), sodium laureth sulfate, cocamidopropyl betaine, disodium cocamphodipropionate, phosphoric acid, phenoxyethanol, PPG 5 Ceteth 10 phosphate, fragrance, sodium chloride, methylparaben, ethylparaben, disodium EDTA, arginine HCl, taurine, Polyquaternium 10, hydroxypropyl hydrolyzed soy protein, wheat amino acids, Oleth 10, lecithin, trehalose, tocopherol, octyl salicylate; water (aqua), cetearyl alcohol, dimethicone, propylene glycol, Ceteth 3 acetate, behentrimonium chloride, hydroxyethyl cellulose, phenoxyethanol, fragrance (parfum), disodium EDTA, sodium citrate, arginine HCl, taurine, ethylhexyl methoxycinnamate, PPG 5 Ceteth 20, wheat amino acids, hydrolyzed soy protein, Oleth 10, disodium cocoamphodipropionate, lecithin, hydroxypropyl trimonium hydrolyzed wheat protein, phosphoric acid, trehalose, tocopherol, ethylhexyl salicylate. The ingredient label for the leave-in the treatment is: water, Quaternium-87, stearyl alcohol, potato starch modified, behetrimonium chloride, amodimethicone, phenoxyethanol, 2-oleamido-1,3-octadecanediol, parfum/fragrance, Polysorbate 20, C11-15 pareth-7, methylparaben, C12-16 parath-9, glycerin, Trideceth-12, glycine, SOJA/soybean oil, tocopherol, taurine, ethylhexyl methoxycinnamate, trisodium HEDTA, citric acid, pentasodium pentetate, limonene, butylphenyl methylpropional, hexyl cinnamal, chlorhexidine dihydrochloride, PPG-5-ceteth-20, linalool, Oleth-10, disodium cocoamphodipropionate, citronellol, lecithin, ethylparaben, phosphoric acid, trehalose, ethyl-hexyl salicylate.

SOAKING TEST OF DYED HAIR

Hair dye dissolution in water was determined by soaking known amount of dyed hair samples (typically 0.4 to 0.8 g) in 100 ml of the aqueous solution which may contain testing

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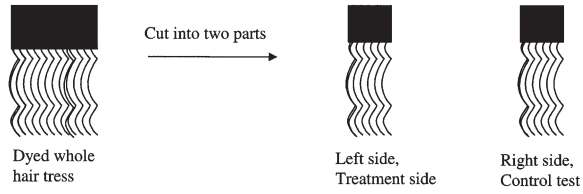
ingredients such as surfactants. Small aliquots of soaking liquors were sampled after fixed time period of soaking and the sample aliquots were read for L, a and b values on Hunter-Lab colorimeter (the values at t = 0 were read before adding hair sample into the soaking liquors). Color changes in soaking liquor were determined as ΔE calculated from L, a, b values of the soaking liquors before and after soaking.

For testing the surfactant effect on hair color fading in a soaking test, color changes are measured on the hair itself. Because some surfactants such as some anionic surfactants change the color of soaking liquors in which hair dye dissolves, the color changes of soaking liquor can not be totally credited to the hair dye dissolution in the soaking liquors. 1% surfactant solutions were made in water. pH was adjusted to the same value around 5.5. Hair dye removal in the presence of surfactants was determined by soaking 0.46 g dyed hair samples in 100 ml of the surfactant solutions. Instead of reading the color change of the soaking liquor during soaking, the soaked hair samples were taken out after a fixed time, dried then read for L, a and b values (the L, a and b values of hair samples before soaking were read before adding into soaking liquors) and ΔE of the soaked hair samples were calculated.

10× SHAMPOO WASHING & TREATMENT PROCEDURES



Washing and treatment procedure

Application of pre-shampoo treatment

- Add 0.35 g, leave in treatment sample if part of regimen.
- Blow dry with cool air from hair blowdryer.

Cycling

- Add 0.75 g testing shampoo or SLES, rub 1 minute and rinse 1 minute under warm, running tap water.
- Add 0.35 g conditioner sample if part of regimen, rub through and rinse 20 second under running water.
- Add 0.35 g, leave in treatment again if part of regimen, blow dry.
- Or combination of the above to test various regimens on fading.

Colorimetric measurements

- Taken after 3×, 5×, 8×, and 10× wash cycles to measure color loss.

SALON TEST PROCEDURE WITH HUMAN HAIR MANNEQUINS

Pre-bleached mannequins with human hair were dyed with commercial permanent hair coloring products. For intense red color, the manneqin was dyed twice in order to increase the intensity of the red color. Dyeing time was 30 minutes and 45 minutes long for the

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first and second cycle respectively. For dark brown and dark red color, a one cycle, 45 minute dyeing process was used. The mannequin head was divided into two half sections. The right side of head was treated and washed with a regimen of formulations containing polyquaternium-55; the left side was washed and treated with a commercial color lock product. Ten wash and treatment cycles were conducted on each mannequin test. At the end of 2×, 5× and 10× wash and treatment cycles, digital pictures were taken of the mannequin head. Pictures consisted of both sides of the head as well as front and back. Hunter L, a, b values were measured on these sections of the head as well.

COLOR ANALYSIS METHODS

Hunter L, a, b reading. Color changes were measured by using HunterLab Ultra Scan colorimeter. Color readings of Hunter L, a, b parameters were obtained with "specular included" and D65 light source settings. Hair color changes after washes were determined by dE. dE was calculated using equations 1 and 2 to evaluate color change:

$$dE = ((L_t - L_o)^2 + (a_t - a_o)^2 + (b_t - b_o)^2)^{1/2} \quad (1)$$

$$dC = ((a_t - a_o)^2 + (b_t - b_o)^2)^{1/2}. \quad (2)$$

where L_o, a_o, b_o; and L_t, a_t, b_t are measured Hunter L, a, b color parameters before and after the wash and treatment cycles, respectively. The larger value of dE reflects a greater change of color. The values of L, a, b readings on each hair tress represent an average of ten measurements, each corresponding to a different site on the hair but within the same area (a 0.39″ diameter circle) before and after washes. The result of each test is repeated at least 3 times. The amount of color protection from a treatment is calculated from equation 3:

$$\%\ \text{Color protection} = \%\ dE = \frac{(dE_{control} - dE_{treatment}) \times 100}{dE_{control}} \quad (3)$$

where $dE_{treatment}$ is the total color changes after washes and protective treatment; $dE_{control}$ is the total color change after washes without protective treatment; and %dE over 15% or a dE values of 1 for red color is generally perceivable by eye.

Taking digital pictures. Digital pictures of hair tresses were obtained by scanning the tresses using EPSON Perfection 4990 photo scanner. Digital pictures of mannequin were taken using a professional camera.

Image analysis of digital pictures. Digital pictures of a mannequin were cropped into equal areas from both the right side and left side of the picture using Adobe Photoshop software, CS 3 edition. The cropping was done either from the front or the side areas of the head. Image analysis of digital pictures was performed using Image Pro software. Luminosity histogram analysis of the cropped pictures was obtained. The histogram consists of a plot of pixels versus color scale of luminosity. The number of pixels indicates the color intensity of the hair sample. The darkness of the hair sample was derived from population of darker pixels which was calculated by integrating the area under the curve left to the middle point of the curve.

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OTHER PHYSICAL ANALYSIS

Water contact angle. Contact angles of hair fibers against water were measured using The Thermo Cahn Dynamic Contact Angle (DCA) Analyzer. The instrument uses Wilhelmy technology to measure surface properties of solid and liquid samples. Single fiber contact angle technique was used where measurements were made with the fiber advancing into water. The contact angle data was an average of over 20 fiber measurements for each hair tress and meets the requirement of Cos θ <0.1 between the last two measurements. The hair diameter values required in contact angle measurement were measured by a laser micrometer instrument where the maximum diameter was employed.

FTIR spectroscopic image analysis of hair fibers. Fourier transform infrared imaging spectroscopy (FT-IRIS) is a novel infrared spectroscopic technique, which couples an FT-IR spectrometer to an optical microscope with an array detector. The collection of data, combined with microscopic visualization of the sample, will essentially allow for "infrared imaging" of the sample. Thus, spatially resolved micron-resolution maps of the molecular components of sample can be obtained.

Sample preparation. Hair bundle was emerged in a tissue freezing media liquid and quickly frozen in liquid nitrogen. The hair bundle was mounted with freezing medium on sample holder with cross section of hair fibers facing out. The freezing hair bundle was sliced into a 4 micron thick of hair cross section using a micro slicing machine (Leica *CM* 1850) and was collected on CaF2 IR window for FT-IR imaging analysis use. The hair dye ingredients used for FTIR image analysis are listed in the above hair dye section.

FTIR imaging. FT-IR images were acquired with Perkin Elmer Spotlight system, which consists of a linear array mercury-cadmium-telluride (MCT) detector along with an automated high precision XY sample stage. A typical IR image could contain over 2000 spectra collected in minutes. Spectral Dimensions Isys 3.0 software was used for analysis and construction of the IR images.

RESULTS AND DISCUSSIONS

FACTORS AFFECTING HAIR COLOR FADING

Effect of hair damage. Hair color loss is related to the quality of the hair. This is studied by soaking three types of dyed hair: bleached, grey and piedmont (natural white hair). Figure 1a shows the total color changes of the soaking liquors versus soaking time after soaking dyed bleached hair, dyed grey hair, and dyed piedmont hair in water. The effect of hair quality on color loss is further studied by conducting a multiple shampoo washing test with dyed bleached hair and dyed grey hair. Figure 1b shows the total color changes of dyed bleached hair and dyed grey hair after 10× shampoo washes by 12% SLES. The data demonstrates that dyed bleached hair lose dye more rapidly, about 40% faster than the dyed grey hair and dyed piedmont. This can be explained by the fact that the bleached hair is more damaged and has pores in increasing numbers and sizes, therefore, the dye molecules leach out from bleached hair much easily.

Effect of surfactants. Effect of surfactant on hair dye dissolution in water was studied by soaking dyed bleached hair tresses in 1% aqueous surfactant solution. Three typical surfactants were selected in this study: anionic surfactant, sodium lauryl ether sulfate (SLES); cationic surfactant, cetrimonium chloride (CETAC) and coco trimonium chloride. Figure 2 shows

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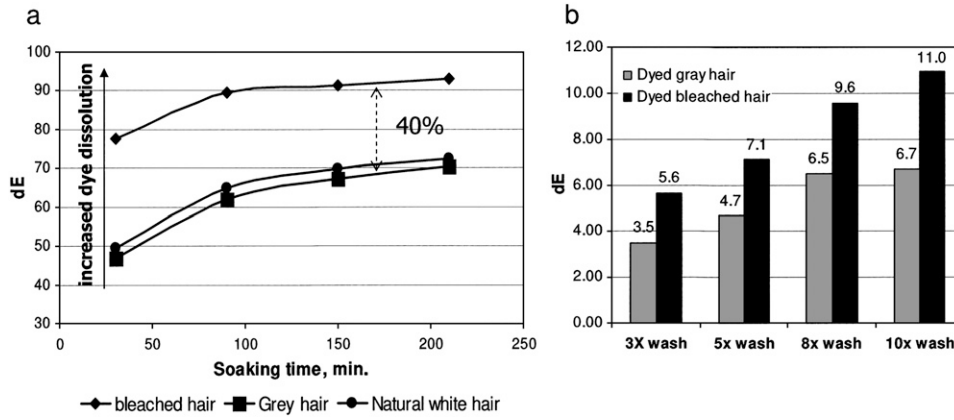

Figure 1. Hair dye dissolution in water: effect of hair damage. (a) Dyed hair soaked in water, intense red color. (b) 10× shampoo washes with 12% SLES.

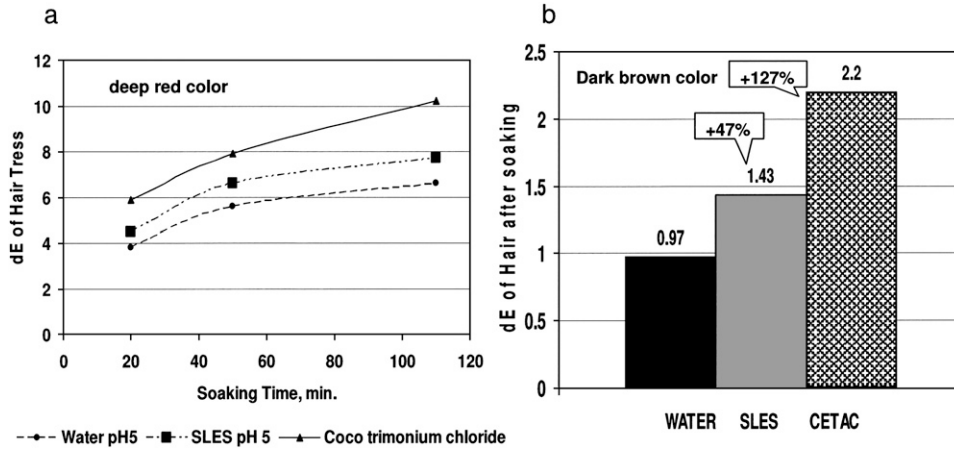

Figure 2. Effect of surfactants on hair dye dissolution in water. (a) Deep red colored bleached hair, pH 5. (b) Dark brown colored bleached hair, 1-hour soaking, pH 7.

the color change of hair dyed with two different colors after soaking in surfactant solutions. The data indicates that surfactants, especially cationic surfactants (CETAC and coco trimonium chloride), increase hair dye dissolution in water. The cationic surfactants evaluated increases hair dye dissolution much more than the anionic surfactant, SLES. Compared with water alone, CETAC increases hair dye dissolution by 127% for dark brown color after 1 hour of soaking, while the anionic surfactant, SLES, increases the hair dye dissolution by only 47% (Figure 2b). Figure 2a shows that another cationic surfactant, coco trimoinium chloride, increases hair dye dissolution significantly more than SLES in deep red colored hair soaked over time at pH 5. This is explained by the fact that the surfactants increase hair dye dissolution by increasing wetting properties on the hair fiber surface, which facilitates moisture going inside the hair shaft and removes the hair dye.

Effect of pH of soaking liquor. The effect of soaking liquor pH on hair dye dissolution was studied by soaking dyed bleached hair tresses in three buffered aqueous solutions. pH 3

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solution was made using citric acid/citrate buffer, pH 6 solution was made using a phosphate buffer, and pH 10 solution was made with a bicarbonate buffer. Figure 3 shows the color change of soaking liquors from soaking dyed bleached hair at three different pHs. The data indicates that hair dye dissolves in water much faster at a higher pH than at a lower pH. The faster dissolution of hair dye in water at a higher pH might be attributed to the known fact that, hair cuticle cells are open or swelled at a high pH. This allows more dye molecules to come out of the hair shaft. At a low pH, hair cuticle is contracted and intact, therefore allows less chance for the dye to come out of the hair. In addition, there is a larger difference between the color loss at pH 3 vs pH 6.5 or 10, especially during the initial soaking period. The pH 6.5 and 10 soaking has a similar hair dye dissolution profile. This can be explained by an increased pH in soaking liquor caused by alkalis inside the dyed hair which are from the hair dyeing process and can come out of the hair then go into the soaking liquor when hair is soaked in water. These alkalis can be neutralized more efficiently in a low pH soaking liquor than in a neutral or a high pH soaking liquor.

ANTI-FADING EFFECT OF HYDROPHOBICALLY MODIFIED CATIONIC POLYMERS

Synergistic effect of hydrophobicity and quaternization. One of the approaches developed in this work for protecting shampooing-induced hair color fading is to minimize hair dye dissolution in water by using a polymer barrier on hair surface. This polymer barrier is designed to prevent moisture from going in and out of hair which will reduce the chance for dye molecules to leach out of the hair shaft. Another approach is to develop a treatment regimen containing the effective polymer to deliver consumer perceivable benefit in leave-in treatments, stylers and shampoos.

A number of polymers have been tested for their anti-fading effect. Test results of selected vinyl pyrrolidone copolymers containing various functional groups such as hydrophobic unit and quaternary groups are reported here. The test polymer was formulated into a leave-in treatment gel formula and tested for their anti-fading effect in a 10× shampoo washing test against the same gel formula but without polymer in it. A leave-in treatment gel formula containing 2% active of Polyquaternium 55 is list in Table II. The chemical structures of the four polymers tested, including an anionic polymer for

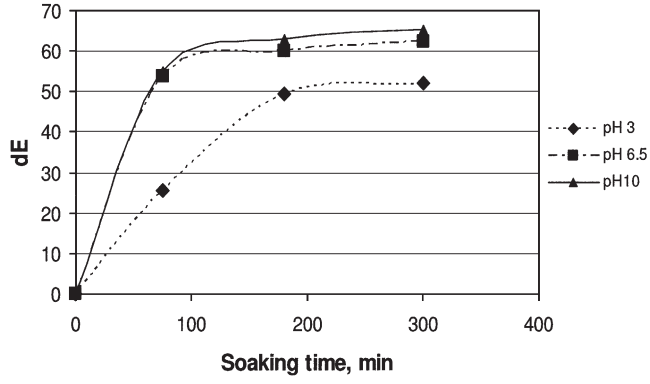

Figure 3. Effect of soaking liquor pH on hair dye dissolution in water, deep red colored hair, pH 5. Dyed bleached dark brown hair.

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Table II
Anti-Fading Leave-In Treatment Gel Containing Polyquaternium-55

Ingredients	%w/w	Supplier
Water	87.00	
Hydroxpropyl guar (Jaquar HP-60)	1.50	Rhodia
Polyquaternim-55 (20% active)	10.00	ISP
Propylene glycol (and) diazoklidinyl urea (and) iodopropynyl butylcarbamate (Liquid Germall® Plus)	0.50	ISP
Glycerin	1.00	1.00

comparison, are shown in Figure 4. Figure 5 shows the anti-fading test results of the four polymers in a leave-in treatment at 2% level using bleached hair tresses. The results demonstrate that Polyquaternium 55 (VP/DMAPA/C12-MAPTAC copolymer) leave-in treatment provides the highest color protection with 38% higher color improvement at the end of 10× washes over the control and the effect is well perceivable by eye as shown in the picture. VP/DMAPA acrylates copolymer which has a similar structure to Polyquaternium 55 (PQ-55) but missing a hydrophobic chain and a quaternary group is less effective than PQ-55, with 17% color protection. Moreover, Polyquaternium-28 (VP/MAPTAC), the quaternized analogue of VP/DMAPA acrylates copolymer without a hydrophobic chain, is not effective on hair color protection. Therefore, the color fading test results of these three polymers demonstrate the synergistic effect of hydrophobicity and quaternary moiety on PQ-55. Consistently, the data in Figure 5 also shows that the hydrophobically modified anionic polymer, VP/acrylates/lauryl methacrylate copolymer provides negligible anti-fading effect due to lack of the cationic unit. Therefore this result supports further a synergistic effect of hydrophobicity and quaternization of PQ-55 on hair color protection.

The anti-fading effect of hydrophobically modified quaternary salt of hydroxyl ethyl cellulose along with other HEC derivatives such as quaternary HEC and alky HEC were tested in a 10× wash color fading test. The results in Figure 6 show that alkyl substituted quaternary HEC provides higher color protection effect than the other two HEC derivatives which have no alky substitution or quaternary unit. These results demonstrate again the synergistic effect of hydrophobic and quaternary moieties of a polymer on hair color protection. The results in Figure 6 also show that PQ-55 is much more effective on hair color protection than the alkyl quaternary HEC tested. The higher color protection benefit provided from PQ-55 might be partly attributed to the additional substantivity effect provided by the DMAPA unit on PQ-55.

Color fastness test results of PQ-55 tested in treatment regimens

Pre-shampoo leave-in treatment with PQ-55. Dyed bleached hair was treated with PQ-55 leave in gel formulation (Table II) then dried before the first shampoo wash. In a control test, the hair tress was treated with the same formula to which 2% PQ-55 was not added. 12% SLES was used as a washing agent for both tresses. The treatment, drying, shampoo washing cycle was repeated for 10 times. Figure 7a shows the total color changes of hair tresses determined as dE values after multiple treatments and wash cycles. The data shows that PQ-55 leave-in gel treatment provides 38% color protection after 10× washes over the control. Figure 7b shows the subjective panel test results of hair tresses after 10× wash and treatment from the test shown in Figure 7a. The 18 panelists agree that the hair tress treated with 2% PQ-55 leave in gel is significantly darker than the hair tress treated

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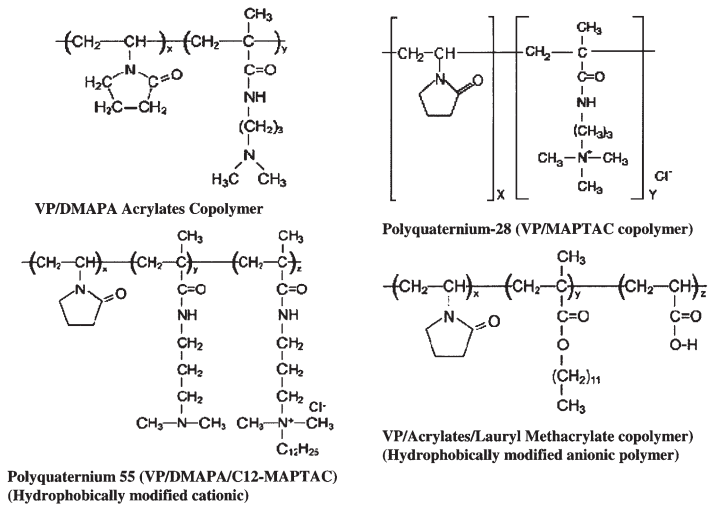

Figure 4. Chemical structures of selected polymers with/without hydrophobic chain and/or quaternization.

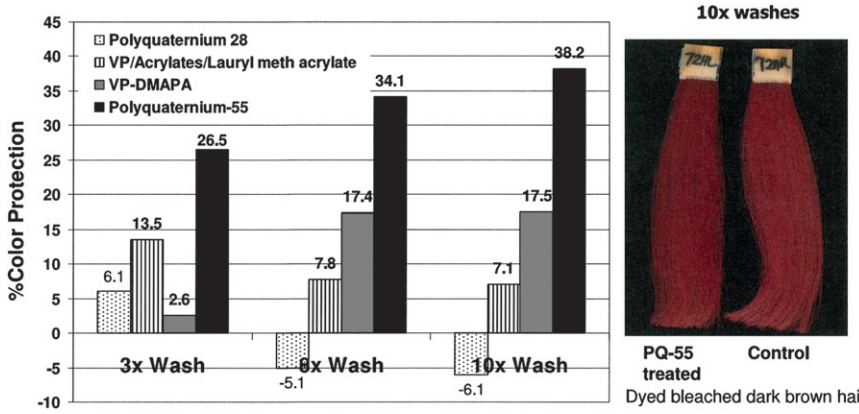

Figure 5. Pictures and color loss of dyed hair samples after 10× SLES washes and leave-in treatment of 2% polymers, intense red colored hair, dyed bleached dark brown hair.

without PQ-55. The color difference of the two tresses determined by the panel test is within the range from slight to moderate under the three light source used. Therefore, the color protection effect of PQ-55 leave-in treatments is perceivable by the naked eye.

Rinse-off treatment with PQ-55 shampoo and conditioner products. The effect of PQ-55 on hair color protection was evaluated in a rinse-off shampoo (Table III) and conditioner formula. The formula for the conditioner is based on a blend of hydroxyethyl cetearamidopropyldimonium chloride and stearamido propyl dimethylamine as conditioning agents in cream base thickened with fatty alcohols and nonionic surfactants.

Figure 8a shows the color fading test results of dyed bleached hair samples washed with a shampoo containing 0.5% PQ-55 against the control, 12% SLES. The result indicates that 0.5% PQ-55 in the shampoo formula provides 21% color retention over the SLES control after 10× washes and the effect is visible by eyes. Figure 8b shows the color fading

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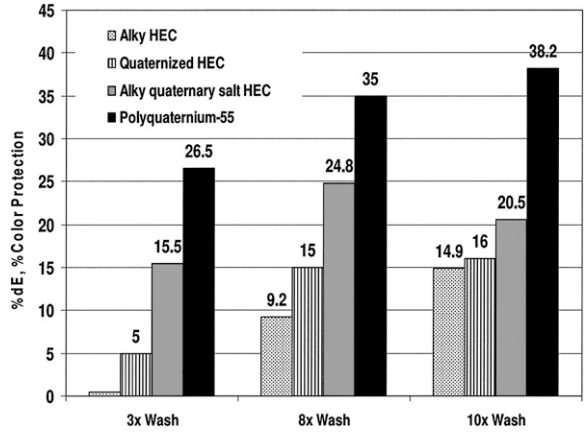

Figure 6. Color loss of dyed hair samples after 10× SLES washes and leave-in treatment of PQ-55 and HEC derivatives, intense red colored hair, dyed bleached hair.

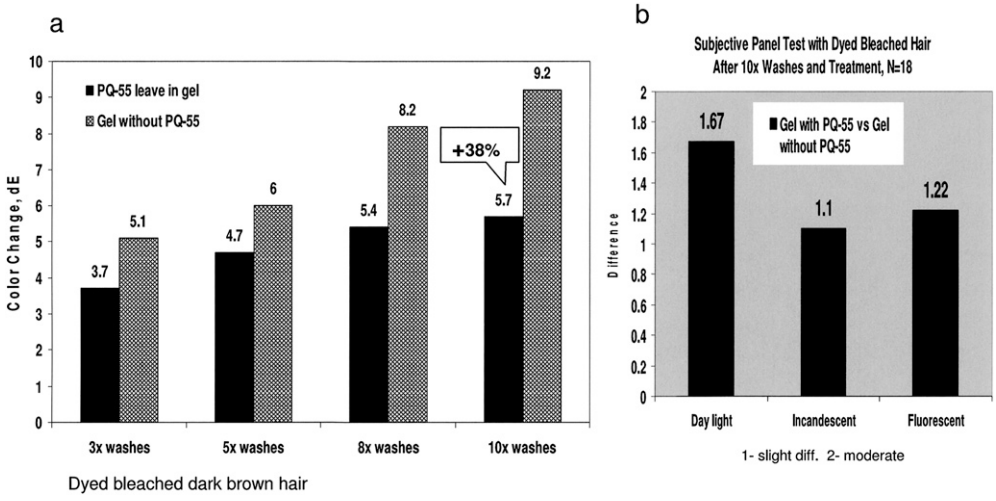

Figure 7. (a) Color loss of dyed bleached hair samples with and without 2% PQ-55 leave-in treatment, intense red colored dye, 12% SLES as washing agent. (b) Subjective panel test results after 10× washes and treatment.

test results of dyed bleached hair treated with the PQ-55 conditioner against the same conditioner but to which PQ-55 was not added, using 12% SLES as a washing agent for both the tested and the control hair tresses. There is limited color protection benefit by using the conditioner formula alone. This is due to the negative effect of cationic surfactant on hair color fading as described in the previous section which balances off the color protection effect of PQ-55.

Combination of PQ-55 leave-in treatment with rinse-off treatment. Figure 9 shows the anti-fading test results and pictures of dyed hair samples after combined treatment of 2% PQ-55 leave-in gel and 0.5% PQ-55 shampoo against the treatment with the same gel formula but without PQ-55 in it and 12% SLES washes. The PQ-55 combined anti-fading system achieves as high as 50% color protection over the control.

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Table III
Polyquaternium-55 2-in-1 Anti-Fading Shampoo

Ingredients	%w/w	Supplier
Water	55.73	
Polyquaternium-55 (20% active)	2.50	ISP
Disodium cocoamphodiacetate (Miranol C2M NP)	15.00	Rhodia
Cocamidopropyl betaine (Miratain CB)	3.52	Rhodia
Ammonium lauryl sulfate (Standapol A)	6.00	Henkel
Sodium lauroyl sarcosinate (Maprosyl 30)	12.0	Stepan
C12-C15 Alkyl lactate (Ceraphyl 41)	0.50	ISP
Glycol stearate (Cerasynt IP)	0.25	ISP
Propylene glycol (and) diazoklidinyl urea (and) iodopropynyl butylcarbamate (Liquid Germall® Plus)	0.30	ISP
Sodium chloride (25% solution)	2.00	
Citric acid (25% solution)	2.20	

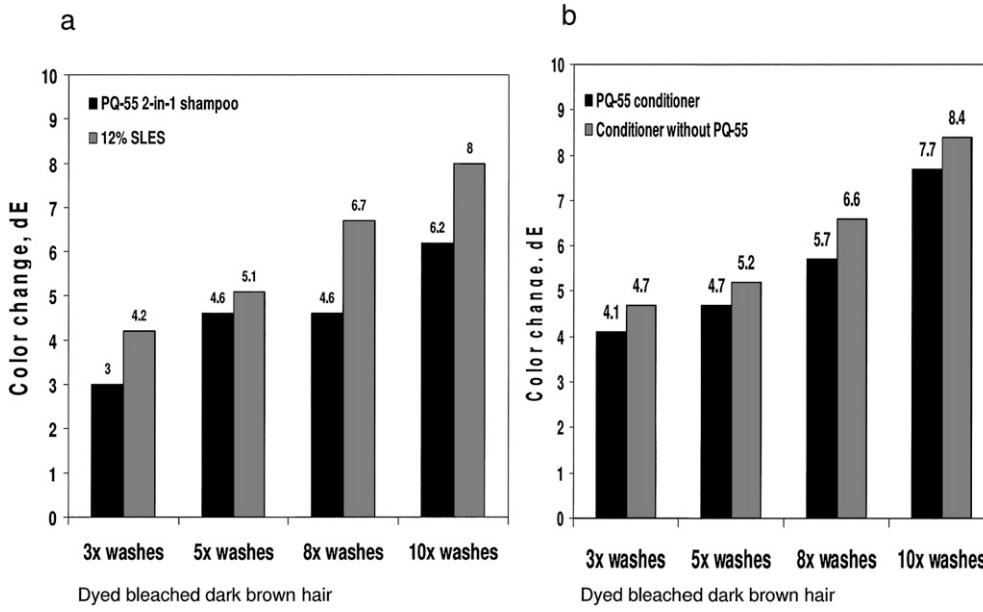

Figure 8. Color loss of dyed bleached hair samples treated with (a) 0.5% PQ-55 2-in-1 shampoo vs 12% SLES and (b) 0.4% PQ-55 conditioner, 12% SLES washes, intense red color dye.

FTIR IMAGE ANALYSIS OF DYED HAIR WITH AND WITHOUT TREATMENT

FTIR spectroscopic image technique was used to study the dye content and distribution inside the dyed hair fibers before and after anti-fading treatment. Array of spatially resolved complete infrared spectra were collected from hair samples. From the spectra, each individual peak representing components of interest such as protein or dye molecules can be imaged. Then, spatial resolution distribution of components can be obtained. Figure 10 shows the FTIR spectrum of hair dye alone and the spectrum of bleached hair fiber before dying. The dye molecule has an absorbance centered at 1106 cm^{-1}. This band is used to evaluate the dye content and distribution within the hair fibers. Figure 11 shows the FTIR spectra and images of dyed hair fibers with the treatment and washes of PQ-55

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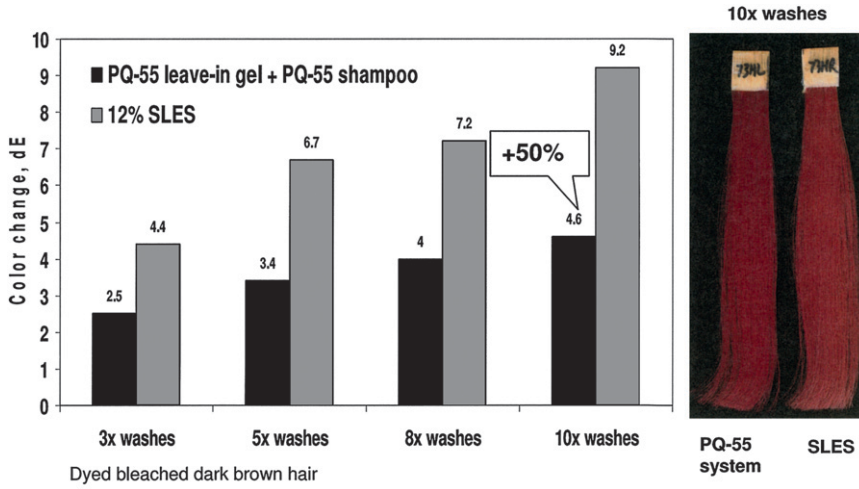

Figure 9. Pictures and color loss of dyed bleached hair samples treated with 2% PQ-55 leave-in gel and 0.5% 2-in-1 shampoo vs 12% SLES, intense red color dye.

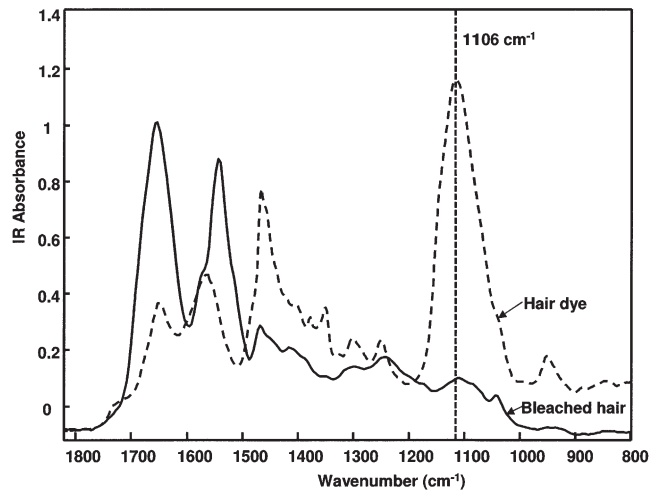

Figure 10. FTIR spectra of dyed and bleached dark brown hair fiber before dyeing.

anti-fading system (leave-in gel treatment, shampoo washing and conditioning) versus no treatment and SLES washes. In Figure 11a, the dye peak signal at 1106 cm^{-1} from the hair fibers treated with PQ-55 system is much stronger than the untreated fibers, indicating that there are more dye molecules retained in the treated hair fibers than in the untreated fibers. This result demonstrates dye molecule retention improvement within the hair fiber of Polyquaternium-55 treated hair. The IR images of hair fibers are created based on the area under the dye band at 1106 cm^{-1}. Therefore, the IR image shows the distribution of dye molecules in the fibers. The color of the images indicates the dye intensity with red color having the highest intensity and the dark blue color having the lowest intensity. The images of hair fibers in Figure 11b suggest that the dye molecules are concentrated more towards the hair fiber surface than to the center of the hair. The

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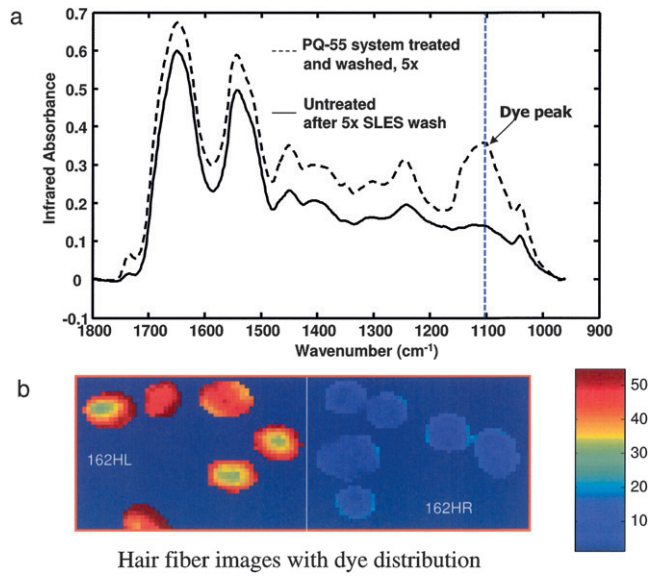

Figure 11. FTIR spectra and images of treated and untreated dyed bleached hair fibers after 5× washes, burgundy color dye. An average spectra of 500 spectra.

images also indicate that the anti-fading system treated fibers have much stronger dye intensity as shown with red or yellow color (higher pixel intensity) than the untreated fibers as shown with blue color (lower pixel intensity).

ANTI-FADING EFFECT OF PQ-55 SYSTEM AGAINST COMMERCIAL COLOR LOCK PRODUCTS

Hair tress tests. A three step PQ-55 anti-fading system consisting of 2% PQ-55 leave in treatment gel, 0.5% PQ-55 shampoo and 0.4% PQ-55 conditioner was evaluated for its color protection effect against a commercial color lock shampoo and conditioner product. The color protection effect of PQ-55 three step anti-fading system versus a commercial benchmark was tested with three types of hair: dyed bleached hair, dyed grey hair and dyed Piedmont hair. Figure 12a shows the color changes of the three different types of dyed hair samples after 10× treatment and washes with PQ-55 three step system and the commercial color lock shampoo and conditioner product, respectively. PQ-55 three step anti-fading system shows superior color protection effect over the commercial color lock shampoo and conditioner system for all three types of hair tested, providing 35%, 38% and 40% higher color protection for dyed bleached hair, dyed grey hair and dyed Piedmont hair, respectively. The results in Figure 12a also indicate that PQ-55 anti-fading system provides similar anti-fading protection on each hair type tested, although they fade to a different extent. Figure 12b shows the pictures of dyed grey hair and dyed Piedmont hair after 10× treatment and washes with PQ-55 anti-fading system and the commercial benchmark. Figure 12c is the subjective panel test results of the dyed Piedmont hair after 10× wash and treatment with PQ-55 anti-fading system vs the commercial benchmark (the hair samples from the test in Figure 12b). The average of eight panelists agrees that the hair tress treated and washed with PQ-55 anti-fading system is darker than the hair tress treated and washed with the commercial benchmark. The

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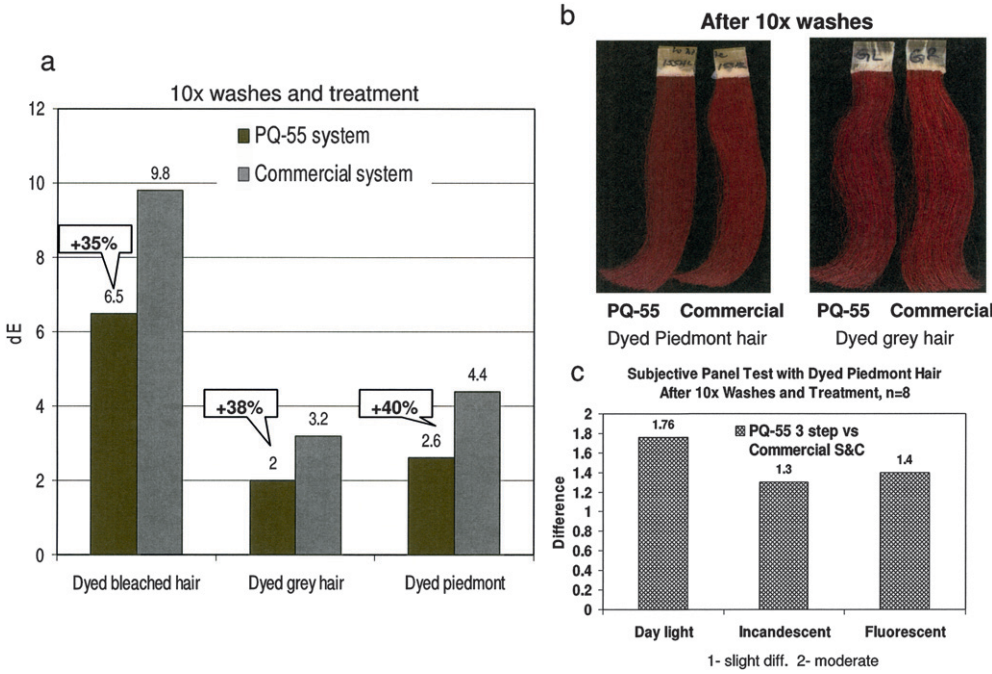

Figure 12. (a) Color loss of dyed hair samples treated with PQ-55 3-step anti-fading system versus commercial benchmark. (b) Pictures of dyed grey hair and dyed Piedmont hair samples after 10× washes and treatment. (c) Subjective panel tests of dyed Piedmont hair after 10× washes.

color difference is within the range from slight to moderate under the three light sources used. Therefore the higher color protection effect of PQ-55 system over the commercial benchmark tested is perceivable by the naked eye.

Salon tests with human hair mannequins. The effectiveness of color protective benefit of PQ-55 in a three step anti-fading system was further evaluated in salon tests on a dyed mannequin head with human hair. This test was conducted with comparison to two commercial color lock products. One was shampoo and conditioner system which claims the color lock effect and the other was a three step commercial color lock system consisting of leave-in treatment, shampoo, and conditioner. The dyed mannequin hair was divided into two halves. The right side of the head was treated with the following regimen: 2% PQ-55 leave-in gel, dried; washed with 0.5% PQ-55 shampoo; treated with 0.4% PQ-55 conditioner, rinsed. The left side of the head was treated with commercial leave-in product (if part of regimen), dried; washed with commercial shampoo, application of commercial conditioner, and then rinsed. The procedure was repeated by 10 times. Color analysis of the mannequin head was conducted in three ways: L, a, b reading of hair on both sides of the head using the Hunter Lab colorimeter; visualization of digital pictures; and image analysis for color intensity and darkness changes as described in the method section.

Figure 13 shows the pictures of mannequin Gabrielle dyed in intense red color after 10 cycles of washed and treatments. It shows clearly that PQ-55 three step anti-fading system is much more effective than the commercial shampoo and conditioner treatment in preventing hair color fading from shampoo stripping.

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Figure 13. Pictures of mannequin Gabrielle dyed in intense red after 10 cycle washes and treatments with PQ-55 anti-fading system (right side) and commercial color lock system (left side). Dyed pre-bleached Asian hair.

Table IV
Color Loss of Mannequin Gabrielle Measured by dE and dC, Intense Red

dE	3× wash	5× wash	10× wash
Right side—PQ-55 system	4.78	7.31	7.43
Left side—commercial system	6.63	9.9	11.18
% dE improvement by PQ-55 system over commercial.	27.9	26.1	33.56
dC	**3× wash**	**5× wash**	**10× wash**
Right side—PQ-55 system	0.87	1.44	1.97
Left side—commercial system	1.53	3.23	4.55
% dC improvement by PQ-55 system over commercial.	43	55.4	56.7

Table IV lists the color changes of mannequin Gabrielle on both sides of the head as measured by L, a, b parameters and calculated as dE & dC values at the end of 3×, 5× and 10× wash cycles. The color protection % (dE%) by PQ-55 anti-fading system is 33.6% higher than the commercial system tested. In addition, dC% by PQ-55 anti-fading system is 56.7% higher than the commercial system. Therefore, PQ-55 anti-fading system provides not only a higher percent color protection but also a significantly reduced level of "off shade" fading. The salon test results are consistent with the results from the same test but using hair tresses for bleached hair (Figure 12).

Figure 14 shows image analysis results of the digital pictures of mannequin Gabrielle after 10× washes and treatments. It indicates that color pixel numbers (color intensity) of PQ-55 treated side of the hair (the right side of mannequin) is 35% higher than the commercial product treated side of the hair (the left side of mannequin), consistent with the %dE values in Table IV. The luminosity curve of the commercial system treated side of the hair also shifts to the right direction in the luminosity scale which is the lighter color direction, relative to the curve of the PQ-55 system treated side of the hair. Both the

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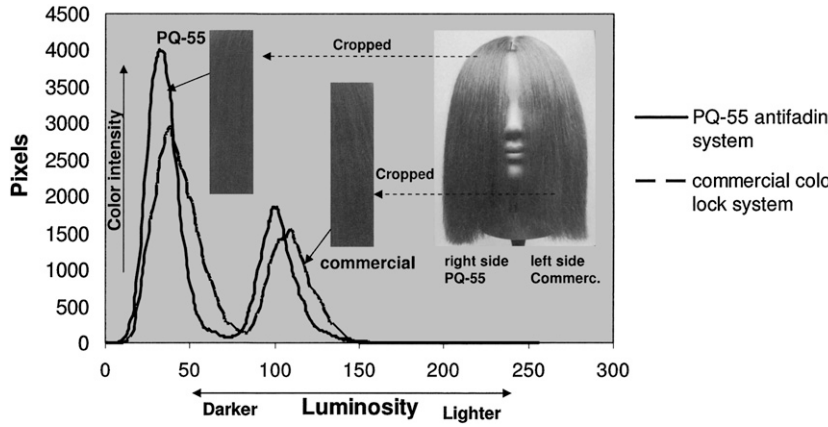

Figure 14. Image analysis of color intensity of mannequin Gabrielle dyed in intense red after 10 cycle washes and treatments with PQ-55 anti-fading system (right side) and commercial color lock system (left side).

higher pixel number and less shift to the left indicates the color protective effects of the PQ-55 system.

Figure 15 shows the pictures of mannequin Dephne dyed with ruby red color before and after 10× wash and treatment cycles with PQ-55 3-step anti-fading system (right side) and a commercial 3-step anti-fading system (left side). The picture of mannequin Dephne demonstrates that the PQ-55 3-step anti-fading system is superior to the commercial 3-step anti-fading system tested in preventing hair color fading from shampoo stripping. Table V lists the color changes of mannequin Daphne on both sides of the head as measured by L, a, b parameters and calculated as dE values at the end of 10× wash cycle. The color protection % (%dE) by PQ-55 anti-fading system is 33.8% higher than the 3-step commercial anti-fading system.

Figure 16 is the image analysis results of the digital pictures of mannequin Daphne after 10× washes and treatments. The color darkness (area under the curve with $L < 116$, darker pixels) of PQ-55 treated side of the hair (right side of mannequin) is 13,321, while that of the commercial 3-step system treated side of the hair (left side of mannequin) is 9,758. This reflects a 35.6% higher color protection from the treatment with the PQ-55 system than the commercial 3-step system, consistent with the %dE improvement listed in Table V. The luminosity curve of the commercial system treated side of hair also shifts to the right side, the lighter direction, relative to that of the PQ-55 system treated side.

SURFACE PROPERTY CHANGES AFTER POLYMER TREATMENT AND PROPOSED COLOR PROTECTION MECHANISM OF PQ-55

It has been reported that cationic polymers and conditioners tends to bind to the cuticle edges and around the pores (7,8). The cuticle edges and pore perimeters are more damaged therefore more charged than other portion of hair, which attract more cationic charged polymers or conditioners.

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Figure 15. Pictures of mannequin Daphne dyed in red after 10 cycle washes and treatments with PQ-55 anti-fading system (right side) and commercial color lock system (left side). Dyed pre-bleached Asian hair.

Table V
Total Color Loss of Mannequin Gabrielle Measured by dE, Ruby Red Color

	PQ-55 3-step anti-fading system	Commercial 3-step anti-fading system
dE	7.09	10.7
%dE improvement by PQ-55 system over commercial system	33.8%	

It is believed that hydrophobically modified cationic polymers such as PQ-55 are able to form a hydrophobic and substantive barrier on hair surface especially on cuticle edges and around the pores, which effectively reduces washing out of hair dye. In order to prove the effect of wash resistant and hydrophobic barrier provided by PQ-55 treatment, water contact angles of dyed hair fibers were measured after 10× SLES washes and with and without treatment of 2% PQ-55 leave in gel. The difference in water contact angles of treated and untreated hair surface is an indication of hair fiber surface hydrophobicity changes. Figure 17a is the result of water contact angle measurement of hair fibers after 10× SLES washes and with or without 10× treatment with 2% PQ-55 leave-in gel. It should be noticed that the treated and untreated hair tresses were the two split halves of a same hair tress before treatment and washes; therefore the treated and untreated hair tresses have the same average contact angle before treatment and washes. The results in Figure 17a indicate that the average water contact angles of hair fiber surface from the treatment with PQ-55 leave-in gel is 60.4° after 10× SLES washes, while the contact angle of hair fibers treated with the gel without PQ-55 after the same washes is 50.4°. These results demonstrate that the hair surface after treatment with 2% PQ-55 leave-in gel is more hydrophobic than the control. The corresponding color protection effect of PQ-55 leave-in treatment is 38% (Figure 5), which is attributed to the increased hydrophobicity and barrier function of the hair surface. Figure 17b is the water contact angles of hair fibers after 10× treatment and wash with PQ-55 3 step anti-fading system

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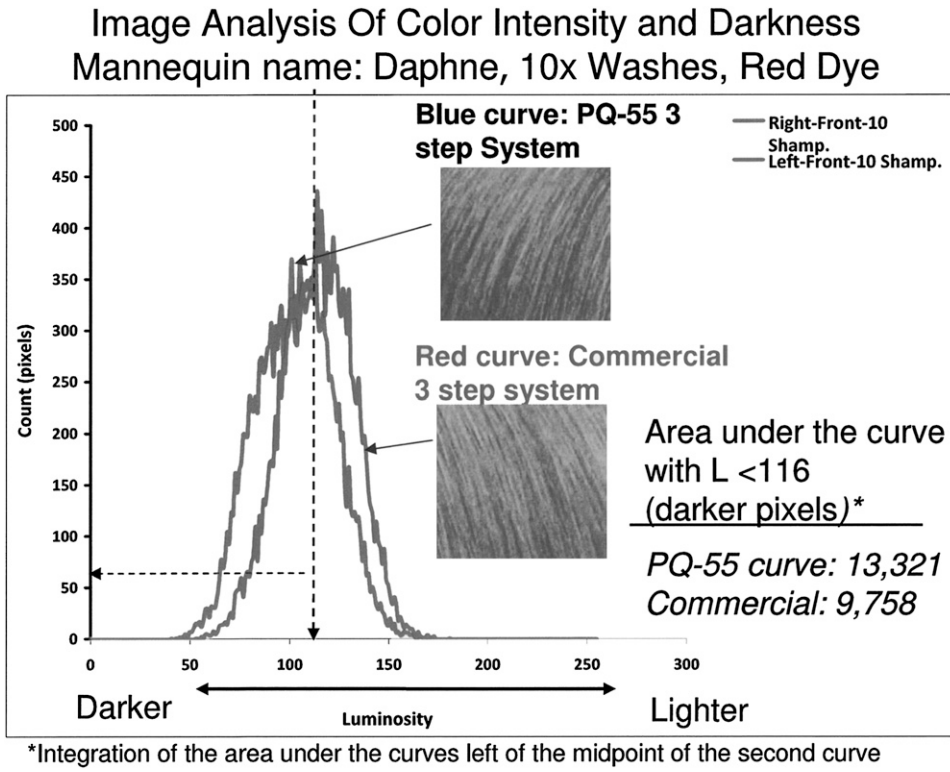

Figure 16. Image analysis of darkness of mannequin Daphne dyed in ruby red after 10 cycle washes and treatments with PQ-55 anti-fading system (right side) and commercial color lock system (left side).

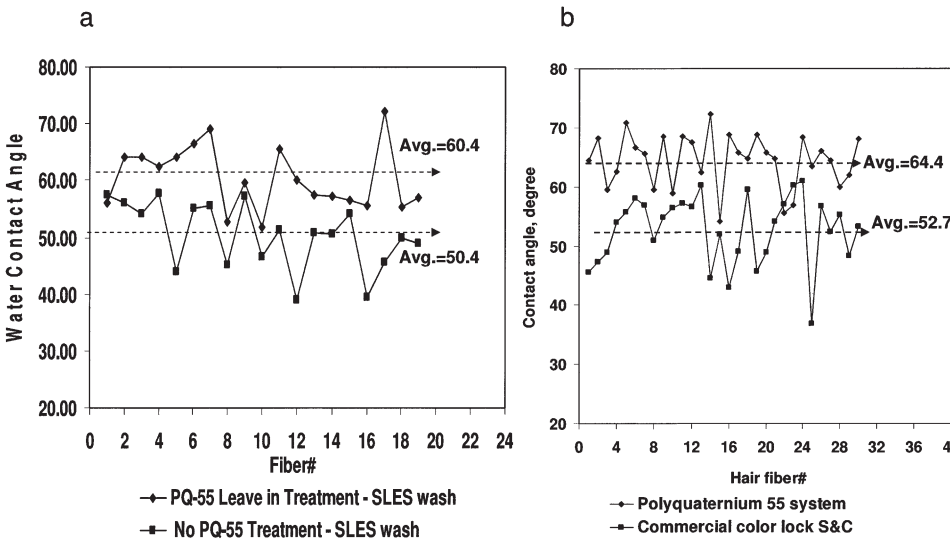

Figure 17. Water contact angles of hair fibers. (a) 2% PG-55 leave-in gel treatments vs gel without PQ-55, both after 10× SLES washes. (b) PQ-55 3 step anti-fading system vs commercial color lock shampoo and conditioner system. 10× washes and treatment, dyed bleached dark brown hair, intense red color.

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(leave-in gel, shampoo and conditioner) and after 10× treatment and wash with a commercial color lock shampoo and conditioner system (from the bleached hair tresses tested in Figure 12). Again, the average water contact angle of PQ-55 anti-fading system treated hair fibers is about 12 degrees higher than that of the commercial color-lock system treated hair fibers, indicating the increased hydrophobic character of the hair surface after treatment with the PQ-55 system. Correspondingly, the treatment and washes by PQ-55 3 step anti-fading system provides 35% higher color protection than the commercial benchmark treatment as shown in Figure 12.

The mechanism for absorption to keratinous substrates is a hydrophobic-driven and charge-driven process (9). The combination of hydrophobic substitution and cationic nature of PQ-55 allows the polymer to maintain good substantivity via its cationic units to color treated hair while provides a hydrophobic barrier to "lock-in" hair dye and prevent it from washing out during daily shampoo washing. The polymer also contains DMAPA unit which has a pseudo-cationic nature, providing additional substantive function to hair. Figure 18 illustrates the proposed mechanism for color protection by Polyquaternium-55. First, it adsorbs to the pores on cuticle surfaces. Some pores have more polymer deposition than the other. The polymer adsorbs around the pores, which leads to the complete sealing of the pores or a reduction in the size of these openings. Also, the polymer binds to the cuticle edges, which provides a protective layer on the cuticle ends. By blocking the two main open channels on hair surface by which dye molecules come out of hair, the polymer effectively protects hair dye being removed during wash. This mechanism can serve as a model for designing other polymer systems that will provide the color protection benefit.

CONCLUSIONS

Effective polymer classes for hair color protection were identified. Among them, Polyquaternium-55 (PQ-55) demonstrated protection of oxidative color from shampoo stripping, exceeding the commercial benchmarks tested. The unique structure and functionality of Polyquaternium-55 has shown utility in helping to fulfill the current

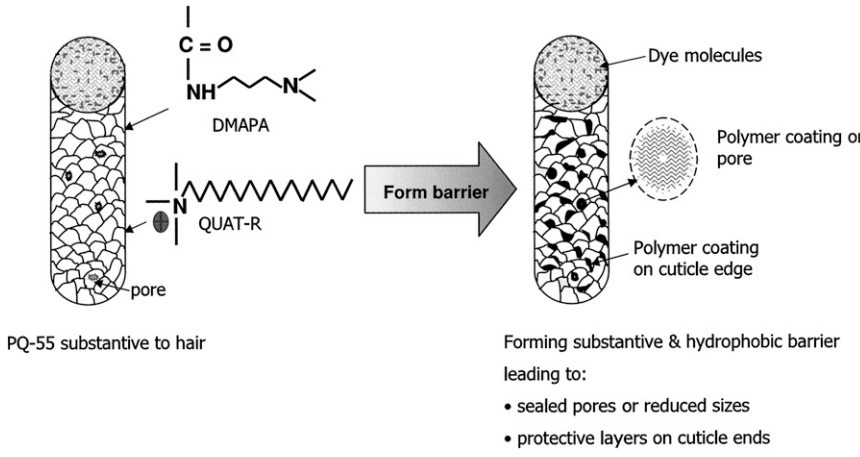

Figure 18. Proposed color protection mechanism for Polyquaternium-55.

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market need of oxidative hair color fastness from shampooing beyond its other hair care benefits such as conditioning and styling. The protective mechanism has been understood to be the combination of hydrophobic substitution and cationic nature of the polymer which forms a hydrophobic and substantive barrier film on hair. The effectiveness of the protective benefit of PQ-55 are substantiated from hair tress and mannequin heads made with human hair and have been quantified with well known measurement techniques such as Hunter L,a,b and digital image analysis. The data from these techniques confirm what is perceivable by the naked eye. In addition, measurements such as contact angle demonstrated the presence of the hydrophobic barrier formed by Polyquaternium-55 on the hair surface and FTIR image analysis confirmed the dye molecule retention improvement within the hair fiber of Polyquaternium-55 treated hair. Multiple washing tests with various treatment regimens with formulas containing PQ-55 indicate that optimal effects are realized by applying a combination of leave-in and shampoo products. The understanding of the structure–functionality relationship of PQ-55 opens the ways to the development of new anti-fading systems to meet the new market need of oxidative hair color fastness from shampooing.

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