

## **Influence of cellulose polymers on the semipermanent dyestuff process for yak hair: An analytical investigation**

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*Accepted for publication November 28, 2007.*

### **Synopsis**

The aim of this study was to investigate the effect of some cellulose polymers mixed in a semipermanent dyestuff on the dye uptake of yak hair fiber and color fading after repeated washing cycles. Two different classes of commercial polymers were tested: non-ionic and cationic. Formulations based on a mixture of HC and basic dyes, with different molecular sizes, were employed as representative dyestuffs. UV-Vis spectroscopy and colorimetric measurements were used to analyze the extracted dyes from the yak hair cuticle and cortex. The results obtained indicate that the presence of cationic polymers in the dye bath improves both the quality of the dyeing process and the anti-fading effect during the first washing cycles.

### **INTRODUCTION**

In the past few decades, polymers have become increasingly important components of cosmetics as primary ingredients or additives in shampoos, conditioning and styling products, and hairspray. Generally, they have been used in hair cosmetics as conditioning agents to improve combing, manageability, and body or as components to increase emulsion stability (1). As the main function of the polymers is to be adsorbed reversibly onto the hair surface (2), three types of bond can occur within the hair: primary valence bonds (ionic and covalent bond), polar interactions (primarily hydrogen bonds), and dispersion forces (Van der Waals attractions) (1). Although the interaction of polymers on keratinous surfaces has been described in detail in the literature (1,3–5), very few data are available regarding their influence on the mechanism involving molecule adsorption and desorption on the hair fibers, as, for example, in the hair dyestuff process (6,7). The latter essentially consists of two steps (8): the transport of dye from a dyebath into the fiber and then the subsequent uniform distribution of dye molecules over the available dye-binding sites. Moreover, the transport itself is assumed to be divided into three steps with regard to the transfer of the dye from the bulk of the solution to the fiber surface,

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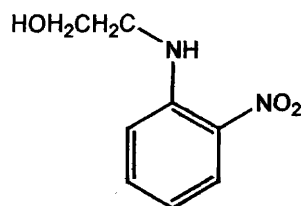
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the sorption of the dye on the surface, and finally the penetration of the dye into the surface (9). Dependent upon the operative conditions chosen, one or another of these steps can assume a prevalent role in determining the outcome of the dyeing process and the quality of the final product. Different parameters can be used for controlling the dyeing conditions (pH, temperature, solvent, etc), the relative contribution of each step can be enhanced or diminished, and thus the course of the overall process can be regulated. In this paper we investigate the effect of two different kinds of cellulose polymers (i.e., cationic and non-ionic), directly incorporated into semipermanent hair dyestuff, on the hair dyeing process. The dyes chosen were a mixture of HC (characterized by a low size) and basic dyes, the relevant formulas of which are reported in Table I (10–12).

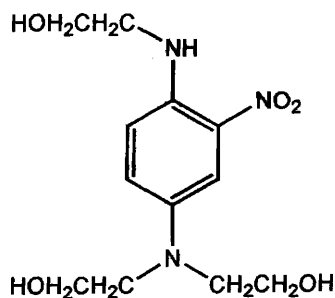
The cellulose polymers studied are two quaternary nitrogen-containing cellulose ether polymers: Polyquaternium 10 (30M) and Polyquaternium 67 (SL-60), which differ in the number of cationic charges (one or two positive charges for glucose units, respectively) and the degree of hydrophobic substitution (i.e., the presence of dimethyldodecyl ammonium groups). These polymers give predominantly ionic interactions with hair (2) and can be strongly adsorbed and/or diffused into the hair dependently via their ionic

Table I  
Dye Formulas

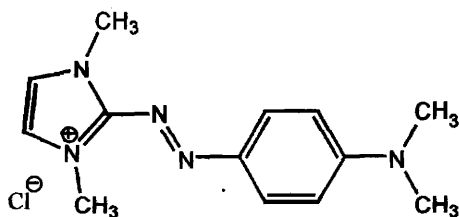
HC Yellow 2



HC Blue 2



Basic Red 51



charge and molecular weight (1,5). Alternatively, we have studied two different non-ionic polymers: hydroxyethylcellulose (250) and cetil hydroxyethylcellulose (PLUS). The primary binding of these molecules to hair is, mainly, by polar and Van der Waals interactions, and generally they are not highly substantive to hair (1). While 30M and 250 have been well known and used in the cosmetic market over these last thirty years, SL-60 and PLUS are relatively new products. The formulas of the studied polymers are reported in Table II. As a control we have used yak hair colored with a base dyebath in which no polymers were present.

## EXPERIMENTAL

### MATERIALS

The semipermanent direct dyes reported in Table I were a generous gift of James Robinson Ltd. (England) and of Ciba (Italy), and were used without further purification. Polyquaternium 10 and Polyquaternium 67 were purchased from Dow Chemical Company; hydroxyethylcellulose and cetil hydroxyethylcellulose were purchased from the Aqualon Company, Wilmington, DE. The surfactant mixture composed of Laureth-8, cocotrimonium chloride, butoxyethanol, PEG-7 glyceryl cocoate, and Quaternium-80 was purchased from LCW, and bi-distillate water (UPP) was purchased from Fluka and Carlo Erba. All these reagents were used as received.

A buffer solution at pH 6.0 was prepared from distilled water with the addition of 2-amino-2-methyl-propanol (3.5% w/w). A regular cleaning shampoo containing sodium laureth sulfate, sodium chloride, sodium lauryl sulfate, and lauryl glucoside was used during the washing procedure.

Yak hair samples, obtained from So. Cap (Naples), were used throughout this work as test fibers. The average diameter was determined microscopically using 20 specimens, and a value of  $70 \pm 1 \mu\text{m}$ , 95% confidence limit, was obtained. All tresses used were 4–5 cm in length and each tress was 0.15 mg in weight.

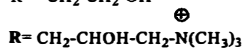
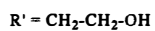
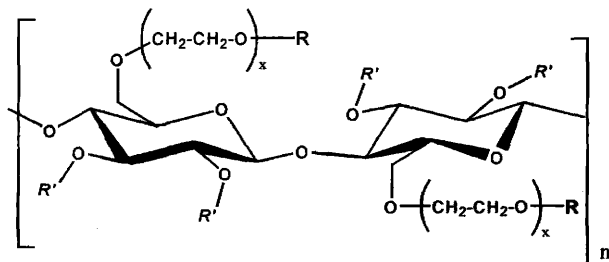
### DYEING EXPERIMENTS

*Preparation of dyeing solution.* A base dyebath composition (control) was prepared by mixing 0.5% of HC Blue 2, 0.5% of Basic Red 51, and 0.5% of HC Yellow 2 with 10% solvariane mixture and 88.5% distilled water. In a first step, Solvariane and 20% of the total water amount were mixed and kept under stirring at room temperature for 15 min until a homogeneous solution was obtained. Successively, all the dyes were added and the mixture was kept under stirring at  $60 \pm 1^\circ\text{C}$  for 2 hr until complete dissolution of the dyes. After 2 hr, the rest of the water was added and the solution was kept under stirring at room temperature for more than 3 hr. Finally, the pH of the resulting dyebath was corrected to 6.0 with the addition of 2-amino-2-methyl-propanol.

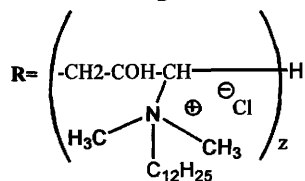
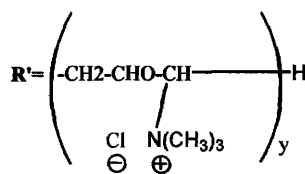
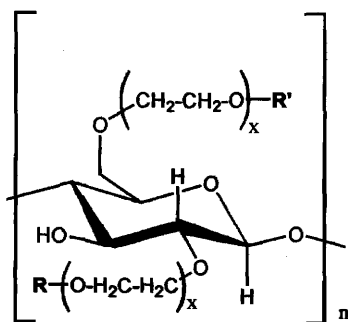
For the preparation of the dyebath containing polymer, 0.1% of the chosen polymer was added to the base bath composition. The polymer was first dissolved in distilled water previously warmed to  $50^\circ \pm 1^\circ\text{C}$  and kept under stirring for 2 hr. The mixed dye solution, obtained as described previously, was then added, and the resulting solution

Table II  
Cellulose Polymer Formulas

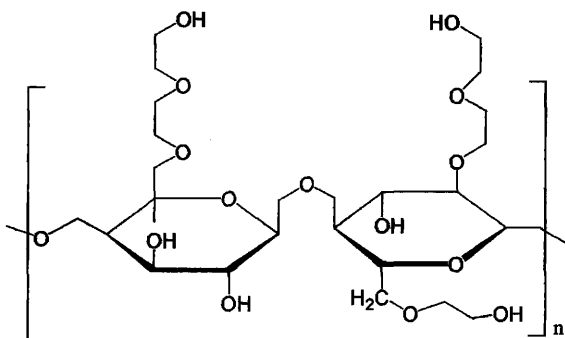
30M



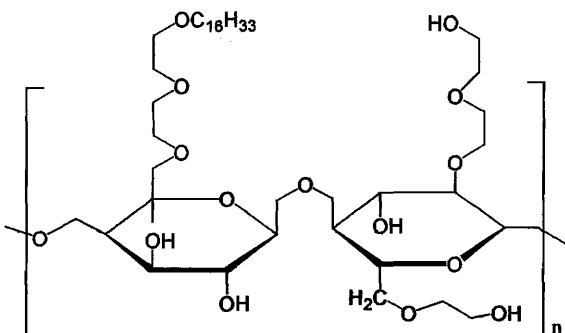
SL-60



250



PLUS



was kept under stirring for a further 10 min. Finally, the pH of the resulting dyebath was corrected to 6.0 with the addition of 2-amino-2-methyl-propanol.

*Dyeing procedure.* Dyeing was performed at room temperature ( $25^{\circ} \pm 1^{\circ}\text{C}$ ) by dipping a total amount of 0.9 g of the yak hair sample (ca. 8–9 cm in length divided into six hair tresses of 0.15 mg each) into a beaker containing 50.0 g of the chosen dyebath solution and then removing the hair tresses after a fixed time of 30 min. All the dyeing experiments were performed without stirring in order to avoid felting of the yak hair. The colored tresses were then rinsed with water.

*Washing.* The dyed hair tresses were washed with a regular cleaning shampoo at  $40^{\circ} \pm 1^{\circ}\text{C}$  from 30 to 45 s, and rinsed off. Finally, the washed tresses were dried with a hairdryer. The described procedure represented a single washing cycle. To obtain the data for this work, different washing cycles were performed. Color change was measured in tresses treated with semipermanent hair dyes after three, six, and nine washing cycles. The sample after the first washing cycle was used as control as it simulated a typical hairdresser dyeing procedure (dyestuff and first shampoo).

*Extraction procedure.* A 50% (v/v) aqueous ethanol solution was used as an extracting medium, at room temperature, using an immersion time for the tresses of 30 s. Under these conditions, the extraction involves only the dyes present on the cuticle of the fiber (outer layer). A further extraction was carried out at room temperature with a similar solution by means of an ultrasound bath (US) for 3–5 hr. In this case, the extraction of the dye adsorbed into the cortex of the hair (inner layer) was also obtained. These procedures were employed for determining the dye amount on the fiber (inner and outer layers) after the dyeing process and the different washing cycles.

*UV-Vis and Color Measurement.* The absorbance of the extracted dyes (after the dyeing process and the third, sixth, and ninth washing treatments, respectively) was monitored using a Cary 1E Varian UV-Vis spectrophotometer. The different dye concentrations or moles were calculated using calibration curves obtained for each single dye in a 50% (v/v) aqueous ethanol solution: a linear relationship according to Beer's Law was found between absorbance and concentration for each dye studied. The total absorbance of the extracted solution containing HC Blue 2, Basic Red 51, and HC Yellow 2 (assuming that there is no interaction between the dyes in the mixtures) could be obtained by simple addition of the absorbance of the individual component at a given wavelength using the formula (12,13):

$$A = \sum_1 A_{\lambda} = \sum_1 \epsilon_i C_i$$

Knowing the value of the molar extinction coefficient  $\epsilon_i$  of the single dye at a selected  $\lambda$ , the concentration of each component can be calculated by making measurements at a number of wavelengths equal to the amount of components present in the mixture, using the system:

$$\begin{cases} A_1 = \epsilon_1 * b * c_1 \\ A_2 = \epsilon_2 * b * c_2 + \epsilon_1 * b * c_1 \\ A_3 = \epsilon_3 * b * c_3 + \epsilon_2 * b * c_2 + \epsilon_1 * b * c_1 \end{cases}$$

In our case the absorbance was measured at  $\lambda_1 = 624.47 \text{ nm}$ ,  $\lambda_2 = 542.61 \text{ nm}$ , and  $\lambda_3 = 390.71 \text{ nm}$  for HC Blue 2, Basic Red 51, and HC Yellow 2, respectively; these wavelengths were chosen comparing the spectra obtained for the single dye.

Colorimetric analysis on yak hair was conducted using a Lambda 35 UV-Vis-Nir Perkin Elmer instrument integrated with a Labsphere RSA-PE-20 reflectance and transmittance integrative sphere and a software color method (CIELAB scale  $L^*$ ,  $a^*$ ,  $b^*$ , using CIED65/10° illuminant/observer condition). Yak hairs were assembled in the apposite Teflon support in such a way that the fibers were aligned and maximum overall smoothness was ensured. Three measurements of the same sample were registered, each time changing the fiber disposition to ensure that any change in the reflectance of the samples was not simply due to a non-uniformity of the yak hair sample preparation assembly; the data reported represent the average of these measurements (14). From the  $L$ ,  $a$ , and  $b$  values measured, the  $\Delta L$  and  $\Delta C$  were calculated and were reported as lightness and color charge, respectively. The  $a$  value represents the green-to-red shift, the  $b$  value the blue-to-yellow shift. The total color difference ( $\Delta E$ ),  $\Delta L$ , and  $\Delta C$  definitions are given below (15):

$$\begin{aligned}\Delta C &= [(a_t - a_o)^2 - (b_t - b_o)^2]^{1/2} \\ \Delta E &= [(L_t - L_o)^2 + (a_t - a_o)^2 + (b_t - b_o)^2]^{1/2} \\ \Delta L &= L_t - L_o\end{aligned}$$

The  $a_t$ ,  $b_t$ ,  $L_t$  data describe the final value obtained after the dyeing process or the different washing cycles;  $a_o$ ,  $b_o$ ,  $L_o$  describe the non-colored yak hair, or alternatively, the initial dyed values (first washing cycle included).

## RESULTS AND DISCUSSION

### HAIR DYE UPTAKE

The sorption of the dye mixture on yak hair was determined using an extraction procedure for the solution containing 0.1% concentration of a different polymer. For comparison, the data obtained in the same experimental condition using a base dye solution (control) are reported. Each amount is the average value of three replicate adsorption experiments. Figure 1 shows the amount of the adsorbed dye mixture (expressed as  $\mu$ moles of uptake versus gram of hair) still present on the hair (inner and outer layer) after the dyestuff process.

It can be seen that in the presence of a cationic polymer there is an increment of about 30% of the dye amount in the hair fiber; whereas no variation in the dye mixture was observed when a non-ionic polymer was employed (compared with the control). Cationic polymers are well known in the literature for their high degree of substantivity to hair (1). The driving force for this appreciable uptake could be ascribed to electrostatic interaction between the positively charged groups (cationic) of the polymers and the negative sites of the hair surface present at any pH above its isoelectric point (pH *ca.* 3.7). Moreover, cationic polymers have been shown to form both association complexes and/or hydrophobic interactions with dye (6). On the other hand, when neutral polymers are used, as the nature of the main binding with the hair fiber is of the polar and Van der Waals kind, they can be easily removed by shampoo, a good hydrogen-bond breaking agent, with the consequent loss of anti-fading power (1). To monitor the effect of the different polymers on the dyes composing the mixture, an analysis of the extracted dyes relative to the outer and inner layers of the fiber was made. In Figure 2 are reported histograms relative to the amount of HC Blue 2, Basic Red 51, and HC Yellow 2 uptake

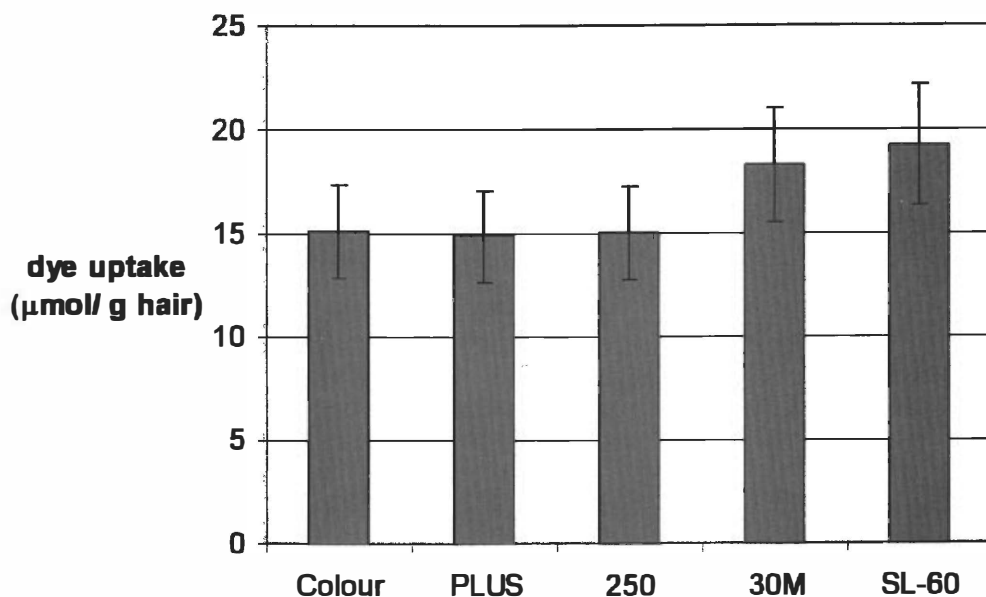


Figure 1. Total dye uptake after the dyestuff process.

(expressed as  $\mu$ moles versus gram of hair) for the different samples in the outer and inner layers. The presence of the non-ionic PLUS polymer in the dyestuff composition gives an increase in the uptake of all the dyes in the outer layer of the fiber; the other polymers show a behavior similar to that of the control sample. This observation can be due to a fast-forming film of PLUS polymer on the hair surface owing to its higher hydrophobicity with respect to the other polymer used. In contrast, when ionic polymers (30M and SL-60) were used in the dyestuff, an improvement (*ca.* 30%) in the dye amounts in the inner layer is observable. This suggests a penetration of these polymers into the hair.

The color measurements were carried out using the samples treated with SL-60 and PLUS polymers, chosen as representative of the two different polymeric classes. In Table III are reported the color parameters:  $L$ ,  $a$ ,  $b$ , obtained after dyeing (control, Plus, SL-60) and without the dyeing procedure (yak), respectively.

The dyestuff treatment always produces a decrease in the  $L$  parameters of the fiber, as observable in comparing the data reported in the first column of Table III. When the polymers are present in the dyebath, this effect seems to be weakened. With regard to the color brightness effect, of the total color difference ( $\Delta E$ ), the chromaticity differences ( $\Delta C$ ), and the lightness differences ( $\Delta L$ ), only the last one seems to be affected by the presence of polymer (see data reported in Table IV).

The color change in the  $a/b$  plane seems not to be influenced by the kind of polymer used, as shown in the  $\Delta C$  data. Therefore, the presence of polymers in the dyebath seems to concern only the lightness parameters and not the color itself, as confirmed by the absence of differences perceptible to the human eye.

#### HAIR DYE WASH-OUT

The effect of the dye mixture wash-out was studied by carrying out extraction tests on tresses after different washing cycles (third, sixth, and ninth, respectively). The percent

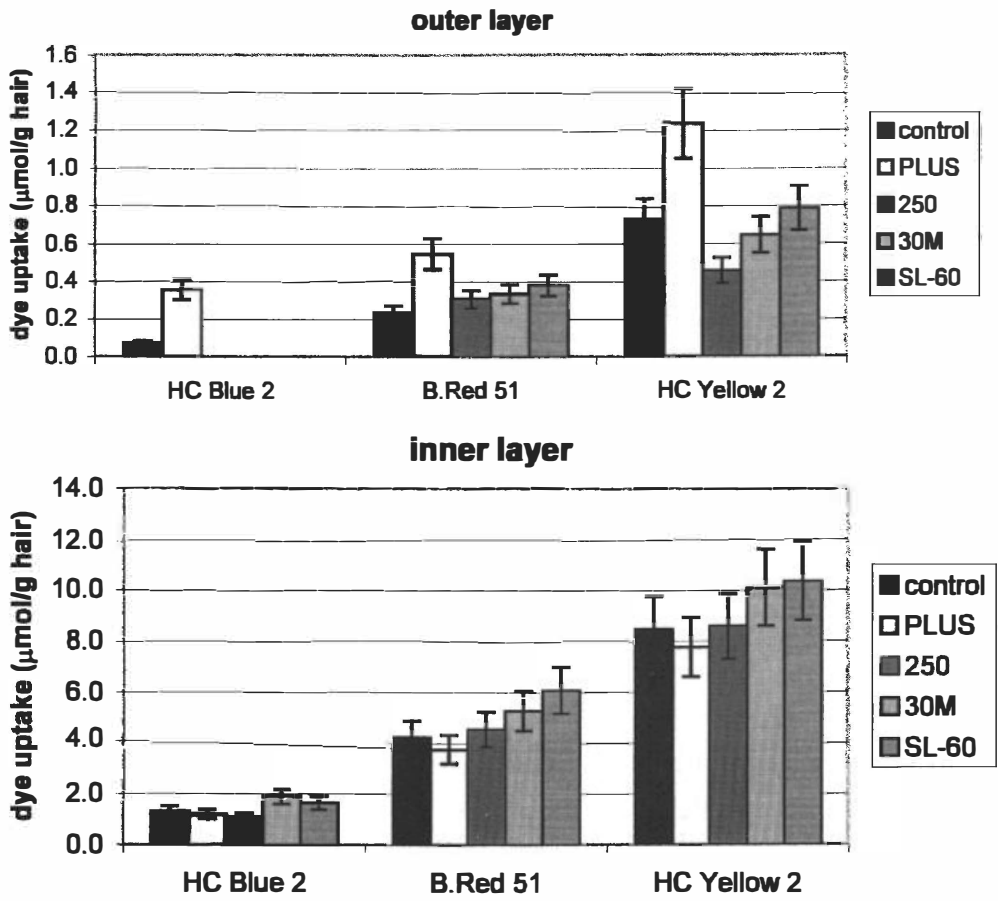


Figure 2. Variation of the μmoles uptake of the different dyes in the function of dyestuff composition. The dye uptake is expressed as μmoles/g hair. The outer layer consists of the hair cuticle; the inner layer consists of the hair cortex.

Table III  
CIELAB, *L*, *a*, *b* Parameters after Dyeing Process

	<i>L</i>	<i>a</i>	<i>b</i>
Control	45.2 ± 1.1	22.9 ± 1.4	12.6 ± 0.3
PLUS	48.5 ± 3.8	21.3 ± 3.1	8.9 ± 2.0
SL-60	46.4 ± 2.2	21.4 ± 3.0	10.3 ± 0.8
Yak	69.3 ± 1.3	0.6 ± 0.1	8.7 ± 0.9

The data represent the means of three different measurements. The estimated standard deviation (S.D.) is reported.

Yak sample represents the value of the yak tress before dyeing.

dye uptake on the hair was then calculated, considering 100% the value obtained after the dyestuff process comprising the first washing cycle. In Figure 3 are reported the data obtained with different dyebaths, compared with the control sample: the PLUS and SL-60 polymers can slow down the fading process during the first washing (third cycle) so that the appearance of freshly dyed hair lasts longer. Beyond the sixth or ninth



Table IV  
Color Difference Values of the Dyed Hair Analyzed

	$\Delta E^1$	$\pm S.D.$	$\Delta C^2$	$\pm S.D.$	$\Delta L^3$	$\pm S.D.$
Control	32.7	$\pm 1.0$	21.9	$\pm 1.3$	-23.5	$\pm 0.1$
PLUS	29.0	$\pm 4.9$	20.7	$\pm 3.1$	-20.2	$\pm 3.6$
SL-60	30.6	$\pm 3.3$	20.8	$\pm 3.0$	-22.3	$\pm 1.8$

The data represent the means of three different measurements. The estimated standard deviation (S.D.) is reported.

<sup>1</sup>  $\Delta E = [(L_{dyed} - L_o)^2 + (a_{dyed} - a_o)^2 + (b_{dyed} - b_o)^2]^{1/2}$

<sup>2</sup>  $\Delta C = [(a_{dyed} - a_o)^2 - (b_{dyed} - b_o)^2]^{1/2}$

<sup>3</sup>  $\Delta L = L_{dyed} - L_o$

$L_o, a_o, b_o$  = non-dyed yak hair.

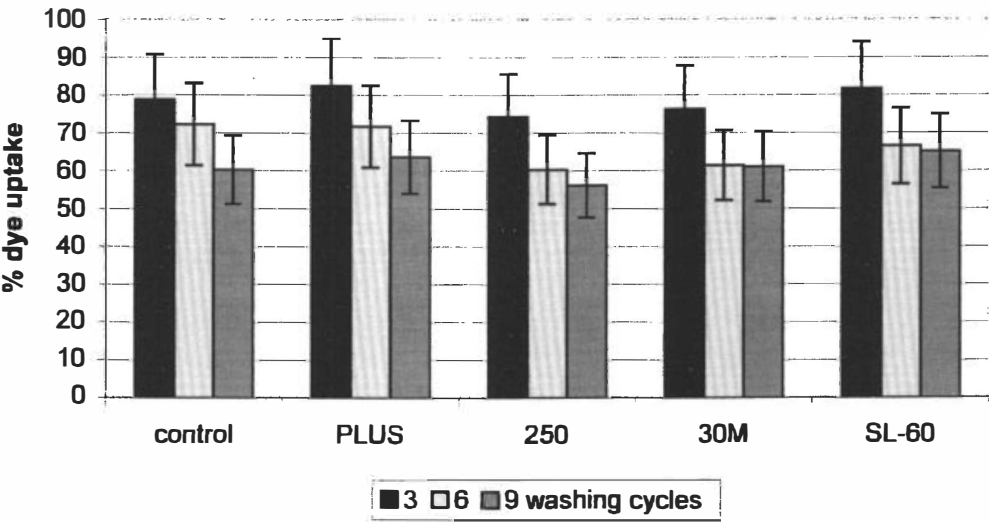


Figure 3. Percent dye uptake with increased washing cycles for the different samples.

washing cycles, when non-ionic polymers (PLUS and 250) were used, a progressive decrease in the dye percent present on the hair occurs, similar to that observed on the control sample. In contrast, when cationic polymers (30M or SL-60) were used, a steady state of dye release was achieved after the sixth cycle.

Moreover, following the dye uptake amount, a slow decrease occurs for the control, PLUS, and 250 samples with increasing washing cycles, while, with the 30M or SL-60 samples, a fast decrease (rapid change in the slope) occurs between the fifth or sixth washing cycles (Figure 4 reports, as an example, SL-60 and control data). This observation seems to suggest that, due to the high substantivity of the ionic polymers on hair, the anti-fading effect is present until a fast washing out of these polymers does not occur, while the non-ionic polymers follow a progressive release during the washing cycles.

Again, comparison of the  $\Delta E$ ,  $\Delta L$ , and  $\Delta C$  data obtained from PLUS, SL-60, and control samples after the ninth washing cycle (see Table V) with the data of Table IV reveals no color change in the  $a/b$  plane and, once again, the main contribution of the polymer presence after the shampoo treatments is due to the lightness variation. The color

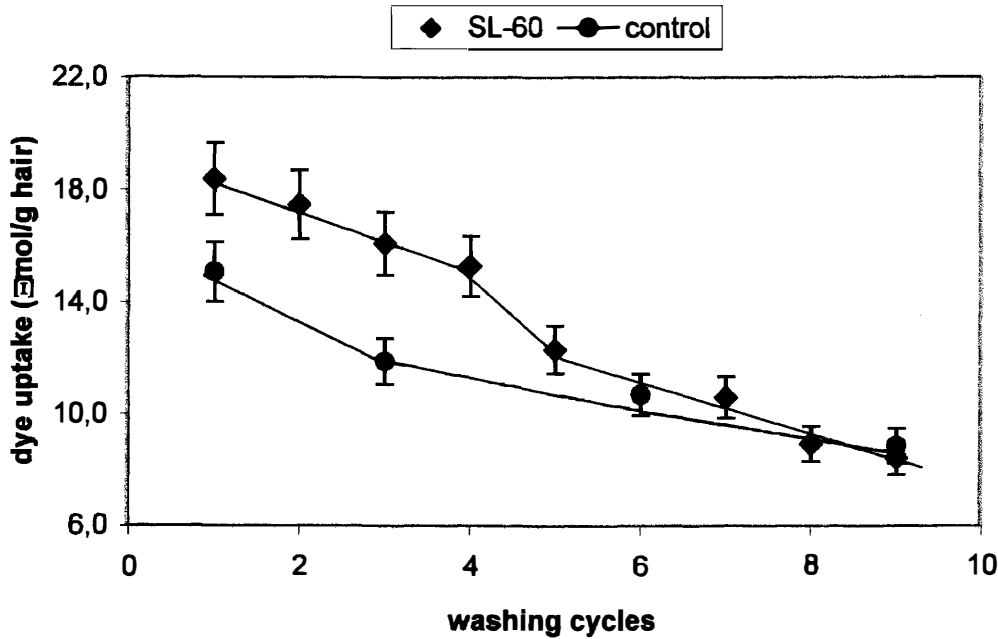


Figure 4. Effect of washing cycles on dye uptake.

Table V  
Average Value of the Color Difference Parameters Obtained after the Ninth Washing Cycle

	$\Delta E^1$	$\pm S.D.$	$\Delta C^2$	$\pm S.D.$	$\Delta L^3$	$\pm S.D.$
Control	32.9	$\pm 2.2$	23.8	$\pm 1.8$	-21.3	$\pm 1.7$
PLUS	26.6	$\pm 3.4$	19.6	$\pm 2.1$	-17.6	$\pm 3.4$
SL-60	25.7	$\pm 3.9$	19.8	$\pm 2.8$	-16.3	$\pm 2.8$

The data represent the means of three different measurements. The estimated standard deviation (S.D.) is reported.

$$^1 \Delta E = \{(L_{wash} - L_{dyed})^2 + (a_{wash} - a_{dyed})^2 + (b_{wash} - b_{dyed})^2\}^{1/2}$$

$$^2 \Delta C = \{(a_{wash} - a_{dyed})^2 + (b_{wash} - b_{dyed})^2\}^{1/2}$$

$$^3 \Delta L = L_{wash} - L_{dyed}$$

$L_{dyed}$   $a_{dyed}$   $b_{dyed}$  = data obtained with dyed yak hair.

$L_{wash}$   $a_{wash}$   $b_{wash}$  = data obtained after the ninth washing cycle.

Table VI  
Color Longevity

	Color longevity	S.D.
Control	96.9	$\pm 2.4$
PLUS	86.4	$\pm 1.2$
SL-60	86.6	$\pm 2.4$

The data represent the means of three different measurements. The estimated standard deviation (S.D.) is reported.

longevity effect, calculated as  $\Delta E_{wash}/\Delta E_{dyed} \times 100$ , is reported in Table VI; after nine washing cycles, the color longevity effect results are smaller for the samples treated with the dyebath containing polymers if compared with the control sample. These data prove

that the desired wash-out of a semipermanent hair dye, after several washing cycles, should not be hindered by the polymer presence.

## CONCLUSION

A systematic investigation has been made concerning the effects governing dye uptake and color loss from yak fiber with HC Blue 2, Basic Red 51, and HC Yellow 2 dyes in the presence of cationic and non-ionic polymers. It has been shown that the presence of cationic polymers in the dye bath improves the quality of the dyeing process and reduces dye fading during the first washing cycles. However, the desired wash-out for a semipermanent hair dye, after several washing cycles, is not hindered by the presence of polymers.

## ACKNOWLEDGMENTS

The authors thank the Spinner Consortium, financed by the Social European Fund, the Ministry of Work and of Social Policies, and the Region of Emilia Romagna, Italy.

## REFERENCES

- (1) C. R. Robbins, "Polymers and Polymer Chemistry in Hair Products," in *Chemical and Physical Behavior of Human Hair*, 4<sup>th</sup> ed. (Springer-Verlag, New York, 2002), pp. 345–385 and literature therein.
- (2) A. Pfau, P. Hossel, S. Vogt, R. Sander, and W. Schrepp, The interaction of cationic polymers with human hair, *Macromol. Symp.*, 126, 241–252 (1997).
- (3) E. D. Goddard, J. A. Faucher, R. J. Scott, and M. E. Turney, Adsorption of polymer JR on keratinous surfaces—Part II, *J. Soc. Cosmet. Chem.*, 26, 539–550 (1975).
- (4) R. B. Hannan, E. D. Goddard, and J. A. Faucher, Desorption of a cationic polymer from human hair: Surfactant and salt effects, *Textile Res. J.*, 57–58 (January 1978).
- (5) J. A. Faucher and E. D. Goddard, Influence of surfactants on the sorption of a cationic polymer by keratinous substrates, *J. Colloid. Interface Sci.*, 55, 313–319 (1976).
- (6) T. V. Drovetskaya, R. L. Kreeger, J. L. Amos, C. B. Davis, and S. Zhou, Effects of low-level hydrophobic substitution on conditioning properties of cationic cellulosic polymers in shampoo systems, *J. Cosmet. Sci.*, 55 (Supplement), S195–S205.
- (7) A. Schlosser, Silicones used in permanent and semi-permanent hair dyes to reduce the fading and color change process of dyed hair occurred by wash-out or UV radiation, *J. Cosmet. Sci.*, 55 (Supplement), S123–S131 (2004).
- (8) I. D. Ratee and M. N. Breuer, "Kinetics of Dyeing," in *The Physical Chemistry of Dye Adsorption*, (Academic Press, London, 1974), pp. 48–49.
- (9) R. McGregor and R. H. Peters, Some observations on the relation between dyeing properties and fibre structure, *JSDC*, 82, 267–276 (1968).
- (10) J. S. Anderson, *The chemistry of hair colorants*, *JSDC*, 116, 193–196 (2000).
- (11) C. Zviak, "Tinture per Capelli: non ossidanti," in *Scienza della Cura dei Capelli* (Emiliano Panconesi, Masson, Milan, 1987), pp. 249–255.
- (12) B. Ballarin, S. Galli, and M. Morigi, Study of dyeing properties of semipermanent dyestuffs for hair, *Int. J. Cosmet. Sci.*, 29, 49–57 (2007).
- (13) S. K. Han, Y. K. Kamath, and H. D. Weigmann, Diffusion of semipermanent dyestuff in human hair, *Proceedings of the 7<sup>th</sup> International Wool Textile Research Conference, Tokyo*, 5, 269 (1985).
- (14) J. T. Guthrie, A. Kazlaucinas, L. Rongong, and S. Rush, The characterization of treated and dyed hair, *Dyes and Pigments*, 29, 23–44 (1995).
- (15) P. Maillan, UV protection of artificially coloured hair using a leave-on formulation, *Int. J. Cosmet. Sci.*, 24, 117–122 (2002).