

## Fading of artificial hair color and its prevention by photofilters

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### Synopsis

Fading of artificial hair color has been investigated by simulating actual usage conditions through exposure to artificial radiation in a weatherometer, with  $0.35 \text{ mW}/(\text{m}^2 \text{ nm})$  at 340 nm, for 16 to 48 hours, and by periodical washing. Hair color was produced by using commercial two-part, permanent hair dyes with light auburn, medium auburn, and dark auburn shades. Formulations based on red couplers, such as 4-amino-2-hydroxytoluene and 1-naphtol, as well as primary intermediates, such as 1-hydroxyethyl-4,5-diamino pyrazole sulfate, were employed. Results indicate that the extent of fading, as measured by the total color change parameter,  $dE$ , is greatest for colored hair subjected to both irradiation and shampooing, and significantly smaller for hair undergoing only irradiation or washing. Color loss has been also found to be dependent upon the hair type employed, with colored natural white and bleached hair undergoing much greater change than colored brown hair. It has been also shown that hair color based on pyrazole intermediates displayed the deepest fading as a result of shampooing ( $dE \sim 4\text{--}6$  after ten shampoos) and irradiation/shampooing ( $dE \sim 14\text{--}16$  after 32 hours of light exposure and four shampoos).

The contribution of UV light (UVB + UVA) to the artificial hair-color loss was found experimentally to be dependent upon the irradiation dose and varied from 63% at 16 hours of irradiation time to 27% at 48 hours of light exposure. The theoretical extent of photoprotection by a formulation was assessed by calculating the percentage of UV light it attenuates in the wavelength range from 290 nm to 400 nm. The results indicate that UVB photofilters, such as octyl methoxy cinnamate, absorb less than 25% of the total UV irradiation at concentrations as high as 30 mg/(g hair). UVA absorbers were found to be more effective, with benzophenone-3 and benzophenone-4 absorbing about 40% of UV at the same concentration. Corresponding experimental data were in reasonable agreement with the theoretical predictions.

The data are also presented for color protection with treatments containing two photo-absorbers: benzophenone-3–ZnO; benzophenone-4–ZnO; octyl methoxy cinnamate–ZnO; and dimethylpabamidopropyl laurdimonium tosylate-benzophenone-3.

### INTRODUCTION

Hair photodamage was shown to consist of a number of concurrent processes that result in chemical and physical changes in fiber properties (Figure 1). Lipid oxidation, disulfide bond cleavage, tryptophan degradation, and cysteic acid formation lead to an increase in fiber porosity, loss of mechanical strength, and an increase in surface roughness (1–3). The most perceptible is the change in fiber coloration as a result of photoreactions of the natural pigments, either eu- or pheomelanin (4,6), as well as photodecomposition of

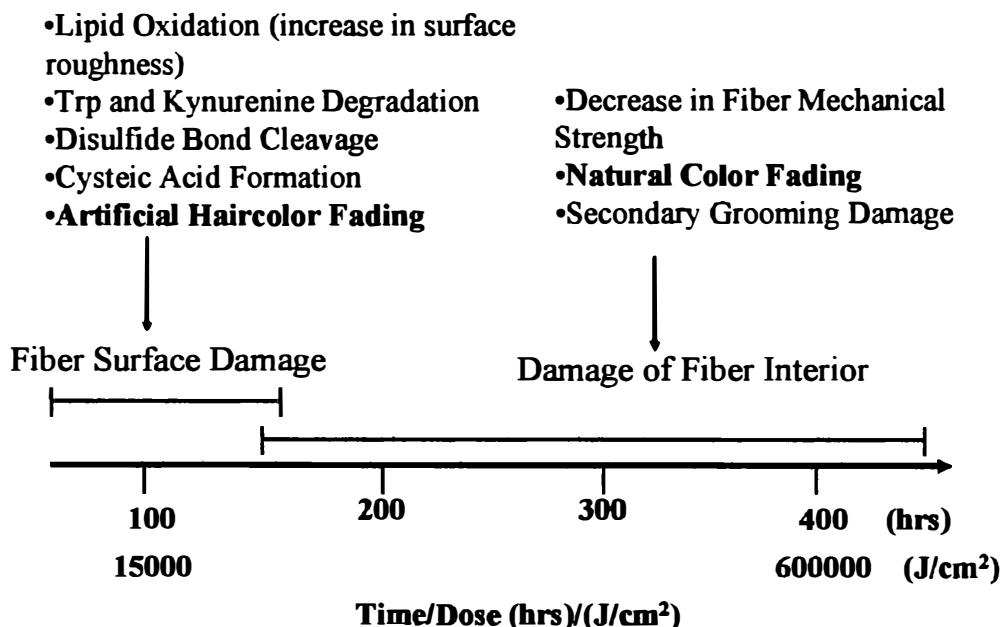


Figure 1. Hair structural photodamage and color fading as a function of irradiation dose.

artificial hair dyes (6–9). As far as the latter is concerned, we refer to permanent oxidative hair color, which is expected to last indefinitely and resist washing and weathering. Other types of hair color, such as semipermanent and temporary treatments, are characterized by limited durability. Semi-permanent hair color can be removed by eight to ten shampoos, while temporary coloration is typically washed off in a single shampoo. The time scales of photoreactions of melanins and synthetic oxidative hair dyes are different. Both eu- and pheomelanins require exposure times on the order of at least two hundred hours to produce a perceptible shift in color shade, especially for highly pigmented fibers. In addition, natural pigmentation is resistant to washings and does not fade even after multiple applications of these processes. In contrast to this, artificial oxidative hair color fades at a much faster rate, with dark auburn shades typically undergoing perceptible lightening within 8–10 hours of irradiation and one shampoo application.

It is also worth mentioning that it has been found that artificial coloration has a photoprotective effect on hair keratin (10,11).

It is generally agreed that artificial hair color instability, caused by weathering and habitual grooming practices, has several underlying components, such as (a) removal of a dye from hair during shampooing, (b) photodecomposition of hair color chromophores as a result of irradiation, and (c) thermal decomposition of the dye in the dark. In addition to this, the hair-coloring dyes exhibit different sensitivities to the UVB (280 nm–320 nm), UVA (320 nm–400 nm), visible (370 nm–780 nm), and IR (750 nm–2800 nm) portions of solar radiation (Figure 2). It has been demonstrated in the literature that visible and UVA light are mostly responsible for the photofading of artificial hair color (6).

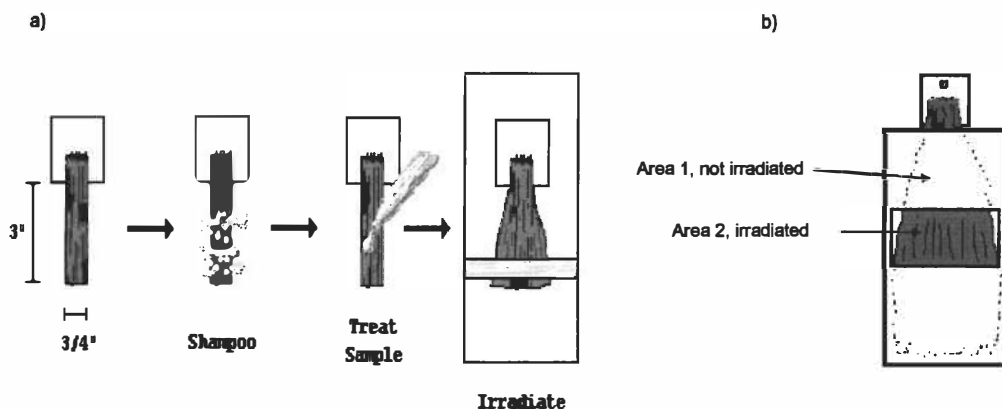


Figure 2. Experimental procedures of hair weathering: (a) Irradiation of the whole tress with color measurements taken at the tress center. (b) Irradiation through window with measurements taken in the areas indicated in the scheme.

Prevention of the fading of natural and artificial hair color has been the subject of research in many cosmetic laboratories. Several papers and patents related to this area have been published in recent years (6–9), and a number of commercial products were introduced into the marketplace, which claimed efficacy in color loss prevention. There has also been a lot of activity related to the development of new photo-absorbers of the UVB and UVA type, and an introduction of antioxidants and/or free radical scavengers into hair care products.

In this work, we have reassessed the contributions of various portions of radiation to the process of photofading by using special filters, which can effectively block UVB and UVB/UVA light. The results indicate that considerable color protection can be achieved by employing UVA filters or combinations of UVB and UVA photo-absorbers. We have also carried out experiments to demonstrate the color protection effects by employing selected absorbers in the concentration range of 0.5–6.0% in leave-in products. The observed effects were correlated with the results of theoretical calculations of photoprotection for individual absorbers and their mixtures. Finally, we have explored the use of blends of organic and inorganic photo-absorbers, e.g., benzophenone–ZnO. In addition, we have studied the effect of mixtures or salts of photo-absorbers and polymers, e.g., the system benzophenone–4–PVP/DMAPMA copolymer.

## EXPERIMENTAL

### INSTRUMENTATION

Hair tresses were weathered by exposure to artificial radiation in an Atlas weatherometer. This instrument uses a xenon lamp with type “S” high-borate borosilicate filters, which simulates solar radiation on the surface of the earth. The irradiation was similar to that of average April sunlight in Florida, with an intensity of  $0.35 \text{ mW/m}^2\text{-nm}$  at 340 nm, controlled by means of an irradiation control sensor. Such light intensity corresponds to the total irradiation of  $149.4 \text{ J/(hr cm}^2\text{)}$  for the wavelength range of 400–800 nm. A typical test involved 21 tresses and a total exposure time that varied from 8 to 32 hours,

i.e., 1195 to 4780 J/cm<sup>2</sup>. Irradiation was carried out at a relative humidity of 35% and at temperatures in the range of 45° to 50°C.

Hair samples, treated with a hair color, and subsequently with a product containing a photofilter, were placed in a sample holder and exposed to radiation in the weatherometer through a 5 × 2.5-cm exposure window for eight hours (Figure 2). Part of the tress, which was not exposed to light, served as a control area in subsequent measurements. Separate control tresses, which were not treated with a photoprotection formula, were also employed.

Color measurements were performed by using a HunterLab Ultrascan Model D25P-9. Color readings were obtained with “specular included” and D65 light-source settings. Hunter L-a-b parameters were used for quantifying color changes. The change in the color of the samples was determined using equations 1a and 1b from measurements taken before and after irradiation:

$$dE = \sqrt{((L_0 - L_t)^2 + (a_0 - a_t)^2 + (b_0 - b_t)^2)} \quad (1a)$$

$$dC = \sqrt{[(a_0 - a_t)^2 + (b_0 - b_t)^2]} \quad (1b)$$

where L, a, and b are the measured Hunter color parameters for time 0 or after irradiation time *t*. Larger values of *dE* reflect greater variation in color. It is noteworthy that color differences with *dE* greater than 1 are generally perceptible in panel tests. It should also be mentioned that in experiments performed according to Figure 2b, *dE* due to irradiation and washing is measured in area 2 of the tress, *dE* due to washing alone is measured in area 1, and *dE* due to irradiation is equal to *dE*(area 2) – *dE*(area 1). The results presented in this paper represent an average of readings on five tresses, with the value for each tress being an average of ten measurements, each corresponding to a different site on the hair (within a specific treated or untreated area). The standard deviation of *dE* measurements was ± (10–20) %.

The absorbance of dyes deposited in hair was determined from the reflection curves obtained using an Ultrascan colorimeter. The reflection curves provide the fraction of light reflected from the sample at 1-nm intervals from 380 nm to 750 nm. The reflection values (REF) were converted to absorbance by using Equation 2:

$$OD = -\log_{10}(\text{REF}) \quad (2)$$

where OD is the absorbance at a given wavelength, and REF is the fraction of light reflected from the sample (with values falling in the range from 0 to 1). The examples of the reflectance spectra of hair dyed to dark auburn color are shown in Figures 3a and 3b.

The spectrum of untreated white hair demonstrates significant reflectance of light in the visible range, with green and red light reflected predominantly, which results in a slight yellow tinge to the hair. Dyeing reduces the intensity of reflected light in general, with the reflection of red light characterized by the highest intensity. Thus, the hair appears dark red in coloration. After the irradiation, as a result of photodecomposition of dye chromophores, the sample reflects more light and appears lighter in coloration.

#### HAIR

Piedmont Caucasian or yak hair from International Hair Importers was used. Dark

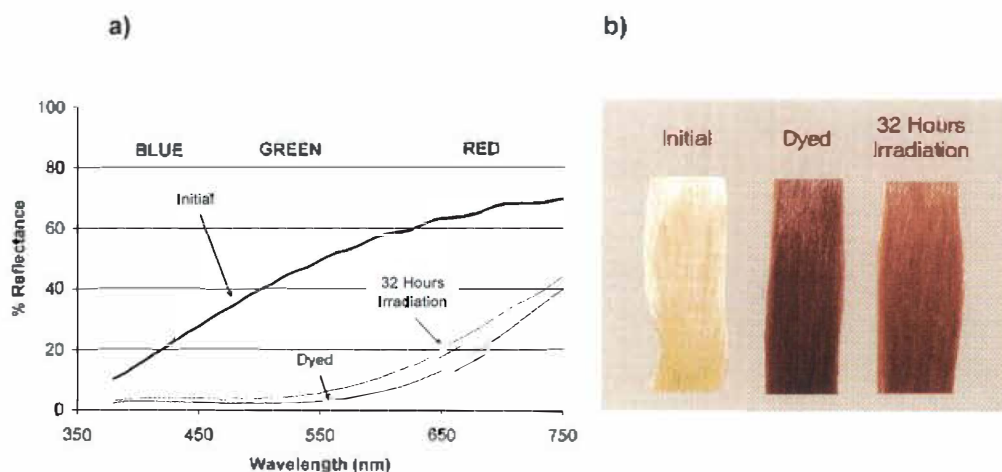


Figure 3. (a) The reflectance spectra of hair (I), shown in (b).

brown Caucasian and bleached hair were purchased from DeMeo Brothers (New York). Tresses were either 3 inches long by 1 inch wide, with the weight of the hair at 1.2 g, or 6 inches long by 1 inch wide, with weight of 2.0 g.

#### TREATMENTS

Hair samples were dyed with commercial two-part, permanent hair dyes having shades of light auburn, medium auburn, and dark auburn based on the following compositions:

*Dark auburn coloring lotion (I):* water, propylene glycol, ethoxyglycol, lauramide DEA, soytrimonium chloride, isopropyl alcohol, oleic acid, ammonium hydroxide, olerth-10, fragrance, oleth-2, panthenol, hydrolyzed soy protein, hydrolyzed wheat starch, hydrolyzed wheat protein, behentrimonium chloride, citric acid, hydroxyethylcetyltrimonium phosphate, dicetyltrimonium chloride, erythorbic acid, sodium sulfite, EDTA, p-aminophenol, p-phenylenediamine, 4-amino-2-hydroxytoluene, resorcinol, N,N-bis(hydroxyethyl)-p-phenylenediamine sulfate, 1-naphthol.

*Dark auburn developing lotion:* water, hydrogen peroxide, acrylates copolymer, steareth-21, oleth-2, oleth-5, PEG-50 tallow amide, acrylates/steareth-20 methacrylate copolymer, simethicone, oleyl alcohol, etidronic acid, disodium EDTA.

*Medium auburn coloring lotion (II):* oleic acid, lauramide DEA, ammonium hydroxide, cetyl alcohol, fragrance, laureth-23, erythorbic acid, stearyl alcohol, sodium sulfite, EDTA, sodium metasilicate, p-aminophenol, 4-amino-2-hydroxytoluene, resorcinol, mica, titanium dioxide, p-phenylenediamine, 1-naphthol, iron oxides, 2-methyl-resorcinol, m-aminophenol.

*Medium auburn developing lotion:* water, nonoxynol-4, nonoxynol-9, hydrogen peroxide, disodium EDTA, propylene glycol, trimethylsilylamodimethicone, isolaureth-6, octoxynol-40, phosphoric acid.

*Light auburn coloring lotion (III):* water, decyl polyglucose, dilinoleic acid, linoleamidopropyl dimethylamine dimer dilinoleate, behentrimonium chloride, steareth-21, ammonium hydroxide, cetearyl alcohol, polyquaternium-22, amodimethicone, algae extract,

EDTA, erythorbic acid, fragrance, nonoxynol-10, sodium metasilicate, sodium sulfite, sorbitol, tallowtrimonium chloride, 1-naphthol, 2-methylresorcinol, 4-amino-2-hydroxytoluene, iron oxides, m-aminophenol, mica, p-aminophenol, p-phenylenediamine, resorcinol, titanium dioxide.

*Light auburn developer:* water, nonoxynol-9, nonoxynol-4, hydrogen peroxide, EDTA, phosphoric acid.

*Pyrazole-containing intense red lotion (IV):* water, C<sub>12-13</sub> pareth-3, oleth-10, cocamide MEA, dilinoleic acid, linoleamidopropyl dimethylamine dimer dilinoleate, steareth-21, ammonium hydroxide, behentrimonium chloride, polyquaternium-22, algae extract, sorbitol, fragrance, erythorbic acid, EDTA, sodium sulfite, sodium metasilicate, sodium sulfate, 1-hydroxyethyl-4,5-diamino pyrazole sulfate, m-aminophenol, mica, iron oxides, titanium dioxide.

*Intense red developer:* water, hydrogen peroxide, cetearyl alcohol, laureth-23, steareth-21, polyquaternium-37, propylene glycol dicaprylate/dicaprate, styrene/PVP copolymer, PPG-trideceth-6, etidronic acid.

*Pyrazolone-containing dark auburn (V):* water, hexylene glycol, propylene glycol, soytrimonium chloride, isopropyl alcohol, ethoxydiglycol, ethanolamine, oleth-5, oleic acid, ammonium hydroxide, oleth-2, fragrance, C<sub>11-15</sub> pareth-9, cocamidopropyl betaine, C<sub>12-15</sub> pareth-3, erythorbic acid, citric acid, EDTA, sodium sulfite, 2-methylresorcinol, 4-amino-2-hydroxytoluene, m-aminophenol, p-phenylenediamine, p-aminophenol, phenyl methyl pyrazolone, resorcinol, N,N-bis(2-hydroxyethyl)-p-phenylenediamine sulfate.

*Dark auburn developer:* water, hydrogen peroxide, acrylates copolymer, steareth-21, oleth-2, oleth-5, PEG-50 hydrogenated palmamide, acrylates/steareth-20 methacrylate copolymer, oleyl alcohol, etidronic acid, disodium EDTA, simethicone.

Dye colorant and developer solutions were combined, and the tresses saturated with the mixture were then allowed to react for 25 minutes at 40°C. Samples were then rinsed thoroughly under room-temperature tap water and shampooed twice with 3% ammonium lauryl sulfate (ALS). The conditioners enclosed with the hair-dye products were not used. Tresses were kept under ambient conditions overnight, and then shampooed again. After drying, the initial color was read using a HunterLab Ultrascan. The change in the color of the samples was determined, using equation 1, from measurements taken before and after irradiation.

Shampooing consisted of adding approximately 1.5 ml of a 3% ammonium lauryl sulfate (ALS) solution per gram of hair to wet tresses and massaging for one minute, then rinsing under room-temperature tap water for one minute. For treatment with leave-in formulations, the formulation was added to wet hair after shampooing and the tresses were massaged and combed to ensure even distribution. When necessary, the hair was dried using a hair dryer, operating with the room-temperature setting. At no time were the tresses dried with heat.

To assess the effectiveness of individual sunscreens in their ability to prevent color fading, the following treatments were employed:

*Benzophenone-4.* 1–7% w/w aqueous solutions were employed. The pH was adjusted to 4 with 1M NaOH. Typically, 2-g hair tresses were treated with 1 g of solution. For 5–7%

treatment solutions, the hair displayed a noticeable deposit of the photofilter on the surface.

*Benzophenone-4-ZnO combinations.*

- (a) Control: 0.5 g PEG-20 stearate, 0.75 g glyceryl stearate (and) laureth-23 were added to 20 g of deionized water. The dispersion was heated to 50°–60°C with stirring until the emulsifiers melted or dissolved. The solution was cooled to room temperature, 0.25 g of preservative (propylene glycol and diazolidinyl urea and propylparaben) was added, and the formulation mass was brought to 25 g with deionized water.
- (b) 2% ZnO: 0.5 g PEG-20 stearate, 0.75 g glyceryl stearate (and) laureth-23, and 0.50 g ZnO were added to 20 g of deionized water. The dispersion was heated to 50°–60°C with stirring until the emulsifiers melted or dissolved. The solution was cooled to room temperature, 0.25 g of preservative (propylene glycol and diazolidinyl urea and propylparaben) was added, and the formulation was brought to 25 g with deionized water. The formulation needed to be shaken before use due to the settling of the ZnO.
- (c) 2% Benzophenone-4: 0.5 g PEG-20 stearate, 0.75 g glyceryl stearate (and) laureth-23, 0.50 g benzophenone-4, and 1.60 g 1M NaOH were added to 20 g of deionized water. The dispersion was heated to 50°–60°C with stirring for 15 min, and then the solution was cooled to room temperature, 0.25 g of preservative (propylene glycol and diazolidinyl urea and propylparaben) was added, and the formulation was brought to 25 g with deionized water.
- (d) 1% Benzophenone-4-1% ZnO: 0.5 g PEG-20 stearate, 0.75 g glyceryl stearate (and) laureth-23, 0.25 g benzophenone-4, 0.8 g 1M NaOH, and 0.25 g ZnO were added to 20 g of deionized water (pH was about 7). The dispersion was heated to 50°–60°C with stirring until the emulsifiers melted or dissolved. The solution was cooled to room temperature, 0.25 g of preservative (propylene glycol and diazolidinyl urea and propylparaben) was added, and the formulation was brought to 25 g with deionized water. The formulation needed to be shaken before use due to the settling of the ZnO.
- (e) Benzophenone-3: 1–5% w/w EtOH solutions were employed with 2-g hair tresses treated with 1 g of solution.
- (f) Benzophenone-3-ZnO: 0.75 g isocetyl alcohol, 0.50 g cetearyl alcohol and cetareth-20, 0.75 g benzophenone-3 (Escalol 560), and 0.75 g ZnO were stirred in 20.50 g EtOH. After dissolution of the surfactants, 2.50 g of cyclomethicone was added. Products based on benzophenone-3 (Escalol 560, ISP), ZnO, and control systems were prepared according to the same recipe.
- (g) Benzophenone-4-octyl methoxy cinnamate (OMC)-ZnO: 3% UV absorber (OMC, benzophenone-4, ZnO, or 1.5% OMC or 1.5% benzophenone-4 with 1.5% ZnO), 1% butylated PVP (Ganex P-904 LC, ISP), 2% cetearyl alcohol (Emulgade 1000 NI, Cognis), and 0.5% preservative (Liquid Germall Plus, ISP). The preservative was a mixture of propylene glycol, diazolidinyl urea, and iodopropynyl butylcarbamate. OMC (Escalol 557) and benzophenone-4 (Escalol 577) were ISP products. Micronized ZnO was from Presperse.
- (h) Dimethylpabamidopropyl laurdimonium tosylate-benzophenone-3: dimethylpabamidopropyl laurdimonium tosylate (Escalol HP-610), 1%; isocetyl alcohol (Cera-phyl ICA, ISP), 0.4%; benzophenone-3, 1%; propylene glycol, 0.4%; dimethiconol

and cyclopentasiloxane (Si-Tec™ GF 3092), 10%; phenyl trimethicone (Si-Tec™ PTM 20), 3%; amodimethicone (Si-Tec™ AM 652), 0.1%; cyclopentasiloxane (Si-Tec™ CM 040), 29%; tocopheryl acetate, 0.1%; SD-40 Alcohol, 55%.

## RESULTS AND DISCUSSION

### COLOR FADING BY SHAMPOOING VS IRRADIATION AND SHAMPOOING

It is commonly observed that shampooing and solar exposure of dyed hair leads to a noticeable color loss, even for hair treated with permanent hair dyes. This effect is dependent upon the hair color shade and, consequently, the composition of the dyeing system employed in a hair-color formulation (12). The most pronounced fading effects are typically observed for red shades such as light auburn, medium auburn, and dark auburn. Traditional compositions of such hair dyes are based on 4-amino-2-hydroxytoluene, 1-naphthol, or 2-methyl-1-naphthol as red shade couplers (12,13). More vivid red colors can be obtained by using pyrazole derivatives such as 1-hydroxyethyl-4,5-diamino pyrazole sulfate, which act as primary intermediates (12). Other novel intermediates, such as phenyl methyl pyrazolone and 6-hydroxyindole, can serve as couplers (14,15).

In order to compare the color changes from shampooing and exposure to sunlight, we analyzed the samples of three types of hair, which included natural white, dark brown, and bleached hair, all dyed with a dark auburn shade of a commercially available hair color based on non-pyrazole technology (I). One set of samples was shampooed ten times without exposure to sunlight, in which case the hair samples were allowed to dry between each shampooing. Another set of samples was exposed to 32 hours of irradiation and shampooed after every eight hours of exposure. Figure 4 shows the total color change in terms of  $dE$  values for hair after the completion of treatments. It is evident that the color variation depends on the type of hair. Washing alone produced the same extent of color change, with  $dE$  values of 1.7–1.8 in bleached and white hair. There was less color variation in shampooed dark brown hair subjected to shampooing alone. In contrast to this, dyed white hair underwent very significant color fading ( $dE = 8.1$ ) as a result of light exposure and shampooing. Most likely, this can be ascribed to the limited photostability of the hair-color chromophores and the lack of the photoprotective effect of a natural pigment such as melanin. Additionally, white hair (Piedmont hair) is lightened as a result of irradiation, which might be a contributing factor to the observed large photofading effect. Photo-irradiation/shampooing of bleached hair resulted in a smaller color loss. It is possible that such a result is the consequence of two reactions occurring in bleached hair. First is the fading of the artificial hair color and second is the darkening of background hair as a result of the recondensation of residual melanin products that remain in hair after bleaching. Such a phenomenon was observed and reported for photo-irradiated bleached hair (16). In contrast to this, highly pigmented brown hair showed only small color variation, with a  $dE$  value of about 1, after 32 hours of irradiation and four shampooings.

Further details of color changes are given in Figures 5a and 5b, which show the absorbance spectra of natural white and bleached hair before and after dyeing. The figures also

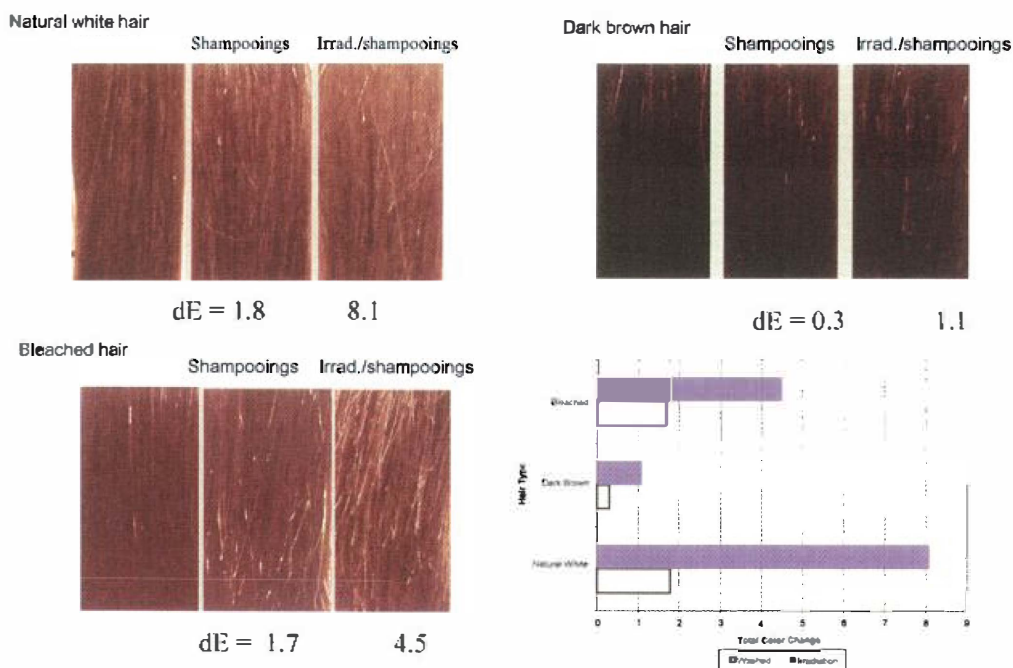


Figure 4. Color loss for samples dyed dark red after ten shampoos or 32 hours of irradiation, with washing after every eight hours of exposure (irradiation).

include the absorbance curves of hair subjected to ten shampoos and to 32 hours of irradiation/shampooing combination treatments. Dyed natural white and bleached hair exhibits maximum absorbance of approximately 1.5–1.6 near 500 nm, which declines above 550 nm. Bleached hair is characterized by greater absorbance above 600 nm, leading to the darker appearance of the samples treated with a hair color. Based on the absorbance spectra it is evident that only a small percentage of the dye is removed as a result of shampooing alone, for both types of hair. Combination treatments (irradiation/shampooing) lead to a greater loss of color for the natural white and bleached hair. In contrast to this, as demonstrated by results not shown here, dyed dark brown hair had a maximum absorbance of approximately 1.6, with a smaller decrease in absorbance above 600 nm. The absorbance of the dark brown samples at 700 nm was  $\sim 1$ , with little change after shampooing or irradiation.

Figure 6a shows images of natural white (Piedmont) hair dyed with a medium auburn dye (11, non-pyrazole) and exposed to 16 and 32 hours of irradiation. One set of samples was shampooed after every eight hours of irradiation, while the other was irradiated with no shampooing. All tresses had sections that were not exposed to light, and their color loss is thought to be related to elevated temperature and humidity during irradiation. As in the experiment described in the preceding paragraph, dyed hair samples exposed to both irradiation and shampooing lost noticeably more color than samples that were only irradiated or shampooed (Figure 6b). The average total color changes for areas of the samples shampooed but not exposed to irradiation were 1.1 and 1.5 after 16 and 32 hours of irradiation, which corresponds to two and four shampoos, respectively. For areas exposed to irradiation but not shampooed the total color changes were 3.3 and 7.5

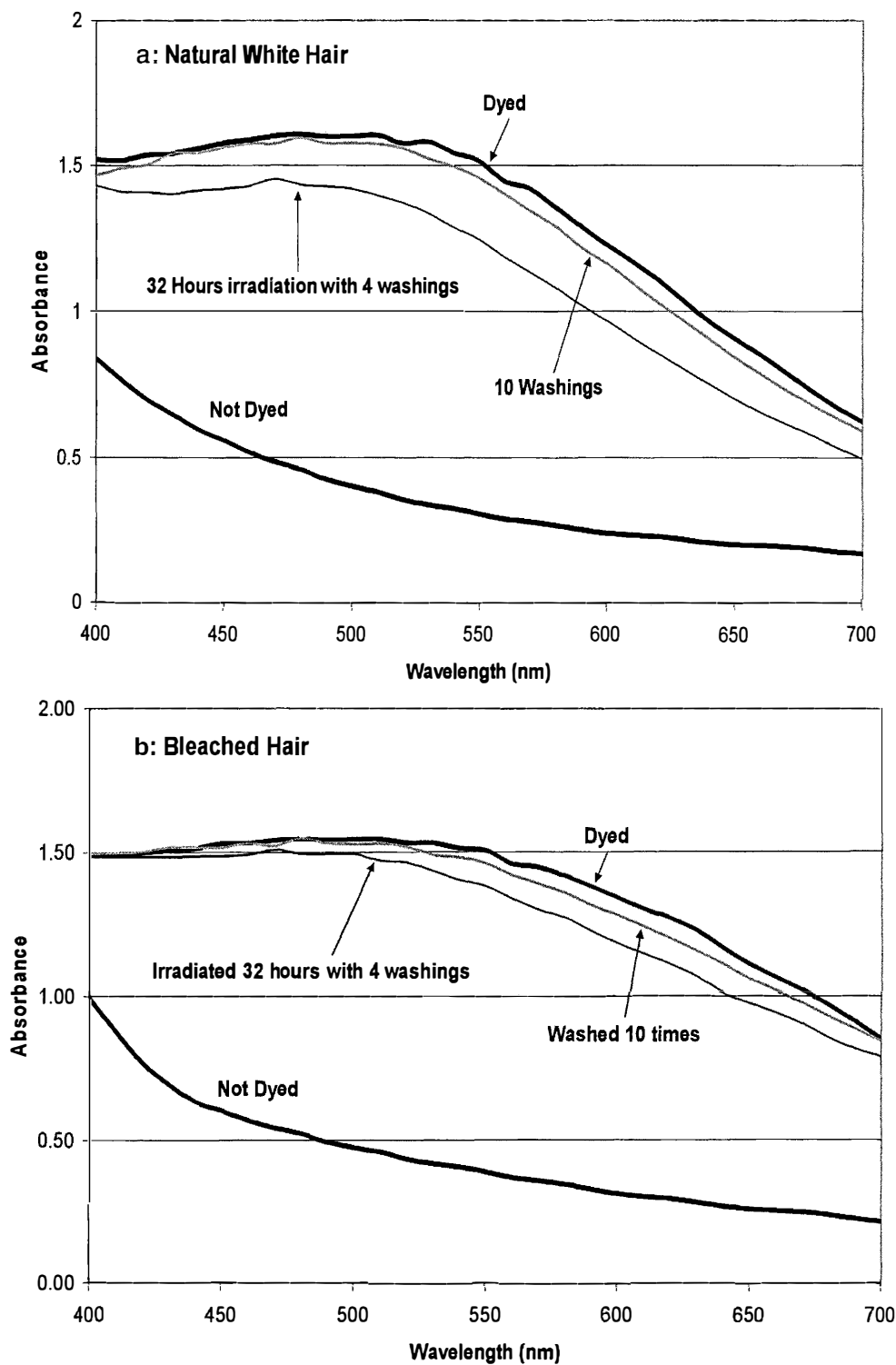


Figure 5. Absorbance spectra of natural white (a) and bleached (b) hair before and after dyeing, and after ten washings or 32 hours of irradiation, with washing every eight hours.

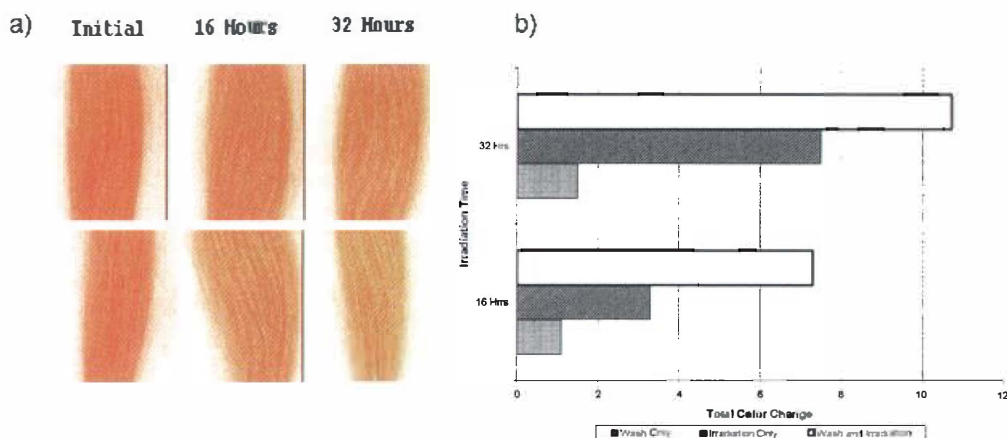


**Figure 6.** (a) Loss of hair color for white hair dyed with a medium auburn dye and exposed to irradiation for 16 and 32 hours. The top-row sample was only exposed to irradiation, while the bottom-row sample was shampooed after every eight hours of irradiation. (b) Color change parameter ( $dE$ ) for hair shown in (a). The figure also shows the  $dE$  values for shampooed-only hair (samples placed in the weatherometer, which was covered and not exposed to radiation) and hair shampooed after every eight hours.

after 16 and 32 hours, while for areas of the samples that were irradiated and shampooed the total color changes were 7.3 and 10.7 after 16 and 32 hours of irradiation. In an additional experiment, employing another batch of Piedmont hair dyed with a medium auburn shade of hair color,  $dE$  and  $dC$  for shampooed but not irradiated areas were  $3.6 \pm 0.7$  and  $1.2 \pm 0.4$ , respectively, after 32 hours of weathering (four shampoos). For irradiated and shampooed areas, the changes were  $10.5 \pm 2.7$  and  $2.7 \pm 0.4$  for  $dE$  and  $dC$ , respectively. Thus, the combination of irradiation and shampooing leads to the greatest loss of color ( $dE$ ), with some change in color shade ( $dC$ ). While shampooing alone produces a relatively small color loss, additional irradiation greatly enhances this effect. Such a result may not be surprising, since exposure to irradiation is known to damage the hair fiber and increase its porosity, making the loss of larger dye molecules by shampooing easier (17,18).

Finally, color fading experiments were performed on white hair treated with pyrazole- and pyrazolone-containing intense red and dark auburn shades of hair color (IV and V). Intense red (IV) and dark auburn (V) formulations produce hair color characterized by tristimulus parameters  $L = 31.2 \pm 0.6/a = 30.0 \pm 0.2/b = 9.5 \pm 0.1$  and  $L = 24.0 \pm 1.4/a = 7.7 \pm 0.03/b = 7.0 \pm 0.4$ , respectively. After ten shampoos,  $dE$  was  $4.7 \pm 1.3$  and  $5.6 \pm 1.0$  for (IV) and (V) treated hair, respectively. Both values are significantly higher than those of the corresponding color changes measured for non-pyrazole dyed natural white hair (Figure 4). Similarly, after 32 hours of irradiation/shampooing  $dE$  was  $15.0 \pm 2.4$  and  $16.5 \pm 1.3$  for (IV) and (V), respectively, which shows greater color loss for pyrazole-based permanent hair dyes. In addition to this, the fading of hair coloration can be measured in terms of  $dC$ , which measures a change in color shade. Thus, after ten shampoos,  $dC$  was  $1.4 \pm 0.5$  and  $2.1 \pm 0.7$  for hair treated with (IV) and (V), respectively. As a result of irradiation, the change in color shade becomes much larger, especially for product (IV). The observed  $dC$  values were  $10.7 \pm 0.6$  and  $3.8 \pm 0.5$ , for (IV) and (V), respectively, after 32 hours of irradiation/shampooing.

The observed difference in shampoo fading of hair treated with product (IV), containing 1-hydroxyethyl-4,5-diamino pyrazole sulfate, and hair treated with products (I) or (II) can be probably explained by the higher water solubility of the dye products formed in hair as a result of the use of (IV). One should also point out that the mechanism of reactions involving pyrazolone coupler and its role in the formation of red color was not fully elucidated (12). It was suggested that the material does not participate in the final color formation. An additional complication in the interpretation of the data is the use of ethanolamine and ammonia as alkalizing agents in formula (V), which may affect the dye penetration into the hair.

#### COLOR FADING BY UVB AND UVA

It is a common practice to include UV absorbers in hair-care formulations designed for treatment of dyed hair. While visible light can also cause fading, visible-light absorbers are colored, which precludes their use in commercial products. The relative color-fading efficacy of various segments of solar radiation (UVA [320–400 nm], UVB [280–350 nm], visible [370–780 nm], and IR [750–2800 nm]) was investigated by Hoting and Zimmerman for red-colored hair (6). They found that the photo-fading efficiency per 1 W/m<sup>2</sup> of light intensity (calculated as  $dE/(\text{light intensity [W/m}^2\text{)])$  is the greatest for UVB (0.38 m<sup>2</sup>/W) and the smallest for IR (0.0019 m<sup>2</sup>/W), with a relative efficiency varying in the following order: UVB > UVA > Vis > IR. However, considering the relative intensity of various portions of radiation, which were chosen to approximate the intensities of natural summer sunlight in central Europe, the actual photo-fading effect expressed as  $dE$  equaled 8.5, 3.8, 0.95, and 0.84 for hair subjected to visible, UVA, UVB, and IR light irradiation, respectively. Thus the contribution of UVB and UVA to the total photo-fading effect is about 34%.

In order to determine if filtering off UV radiation from natural light would result in noticeable color protection, we irradiated hair with simulated solar light passing through special filters such as a Schott glass-type GG 420 UV filter, which effectively blocks UV light (~0% transmission below 390 nm), and the quartz filter, which is nearly transparent to light with a wavelength above 290 nm. White hair treated with a commercial medium auburn dye (II) was employed in these experiments. Figure 7 shows the total color change of hair,  $dE$ , after 16, 32, and 48 hours of irradiation. Hair samples covered with the UV filter showed ~30–60% less color loss and were noticeably darker and redder than the samples covered with the quartz plates. The amount of protection offered by the UV filter is calculated from the formula

$$\% \text{Protection} = \frac{100 \times (dE_C - dE_P)}{dE_C} \quad (3)$$

where  $dE_C$  and  $dE_P$  are the total color changes after the irradiation of unprotected (quartz filter) and UV filter-protected hair, respectively. Results presented in Figure 7 refer to hair samples that were irradiated without shampooing. It should be noted that the amount of protection varied in the range of 27% to 63%, depending upon the time of exposure. Longer irradiation times led to smaller photoprotection values. This result could be expected as a consequence of the existence of a limiting value of residual concentration of chromophores in a hair color, which are gradually depleted during photo-exposure (at sufficiently long exposures the coloration should completely fade

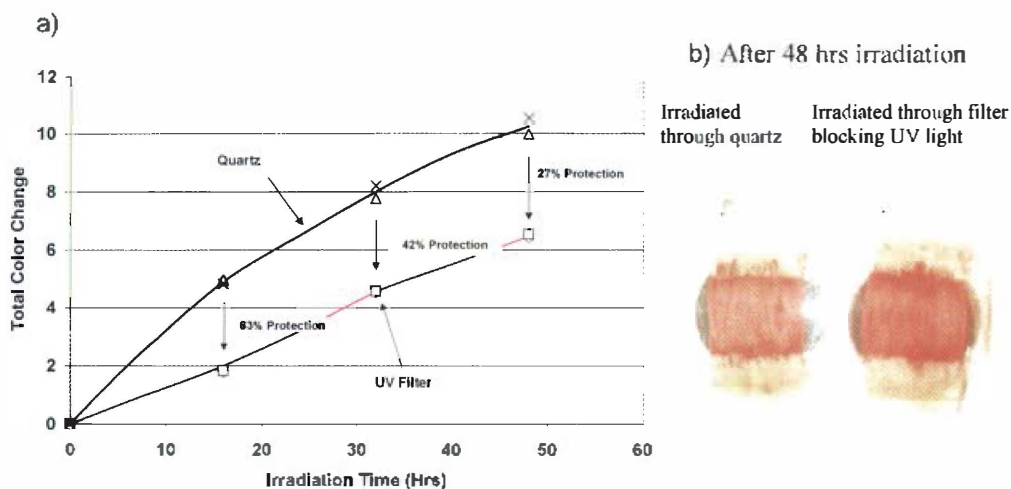


Figure 7. Total color loss for white hair, dyed with medium auburn dye (a) and irradiated through a quartz filter and a filter completely absorbing UV light (b).

away, and % protection would be reduced to zero). In summary, the present data confirm the previous suggestion that blocking UV light can significantly limit artificial hair-color fading.

#### THEORETICAL AND EXPERIMENTAL ANALYSIS OF PHOTOPROTECTION BY UVA AND UVB PHOTOFILTERS

The theoretical extent of photoprotection by a formulation, containing photo-absorbers and evenly distributed on hair, can be assessed by calculating the percentage of UV light it absorbs. It can be shown that the attenuation of light, at a given wavelength, by a multi-component photofilter system is given by the following relationship, which is a modification of Beer's equation:

$$\frac{\sum_i I_i(\lambda)}{I_s(\lambda)} = \sum_i 10^{-\left[ \varepsilon_i(\lambda) \frac{10m_i c_i}{A \rho M_{wi}} \right]} \quad (4)$$

where  $I_i(\lambda)$  is the absorbance of photofilter  $i$  at wavelength  $\lambda$ ,  $I_s(\lambda)$  is the intensity of solar radiation,  $\varepsilon_i(\lambda)$  is the molar extinction coefficient of photofilter  $i$  at wavelength  $\lambda$ ,  $m_i$  is the amount of formulation deposited on hair (g/g hair),  $c_i$  is the concentration of a photofilter in a formulation (% w/w),  $A$  is the specific surface area of hair assumed to be  $800 \text{ cm}^2/\text{g}$ ,  $\rho$  is the density of a dry formulation (assumed to be approximately  $1 \text{ g/cm}^3$ ), and  $M_{wi}$  is the molecular weight of an  $i$ -th photofilter.

Equation 4 can be used to calculate the fraction of light absorbed at each wavelength by a given quantity of absorber on the hair. The total percentage of absorbed UV radiation can be determined by integrating (numerically) equation 4 over the wavelength range 290–400 nm. For calculations, values for the solar irradiation on the surface of the earth between 290 nm and 400 nm were taken from the literature (19). Figure 8 shows the percentage of attenuated UVB and UVA light (290–400 nm) as a function of the

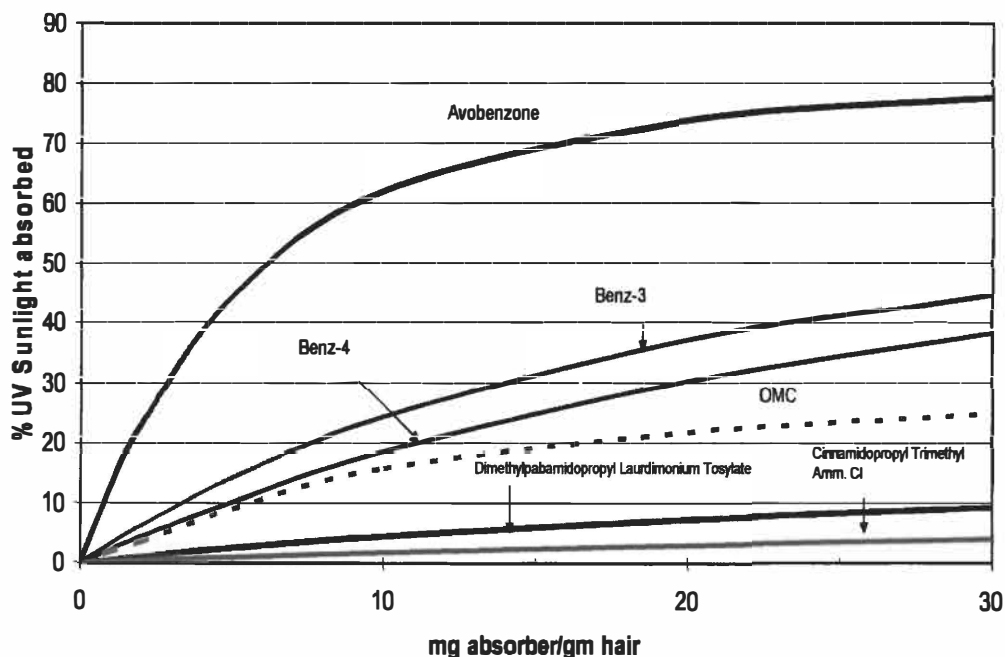


Figure 8. Calculated proportion of attenuated UVB and UVA light (290–400 nm) as a function of the amount of photo-absorber deposited on the surface of hair.

amount of UV photo-absorbers deposited on the hair. The data show that UVB absorbers such as dimethylpabamidopropyl laurdimonium tosylate, cinnamidopropyl ammonium chloride, and octyl methoxy cinnamate absorb less than 25% of the total UV radiation. This is because UVB (290–320 nm) constitutes only about 9% of the total solar radiation in the UV range. As might be expected, the compounds with a greater UVA absorbance (benzophenone-3, benzophenone-4, and butyl methoxydibenzoylmethane) absorb a greater percentage of the radiation between 290 nm and 400 nm. It has to be stressed that the theoretical assessment of the performance of various photofilters presented in Figure 8 assumes that they are characterized by perfect photostability. Such an assumption is justified in the case of materials such as benzophenone-3 and benzophenone-4. For butyl methoxydibenzoylmethane, which is very unstable under irradiation, the results of the calculation probably overestimate the capacity of this compound to absorb UV light under practical usage conditions.

In a series of experiments, tresses of natural white hair dyed with a medium auburn dye were treated with leave-in aqueous or ethanol solutions of benzophenone-3 and benzophenone-4, respectively. Figure 9 presents a gradual decrease in  $\Delta E$  as a function of the concentration of benzophenone-3 after 16 hours of irradiation and two shampoos. Figure 10 is a plot of percent color protection (calculated according to equation 3 from the experimental data) for both benzophenone-3 and benzophenone-4 as a function of the calculated extent of UV attenuation (calculated from spectroscopic data by using equation 4) by a given treatment. Extrapolation of the linear least-square fit to the data points suggests 72% color protection for 100% UV attenuation. This is in reasonable agreement with the 63% protection observed in an experiment in which glass filters were employed to completely eliminate UV radiation (Figure 7), but it has to be kept in mind

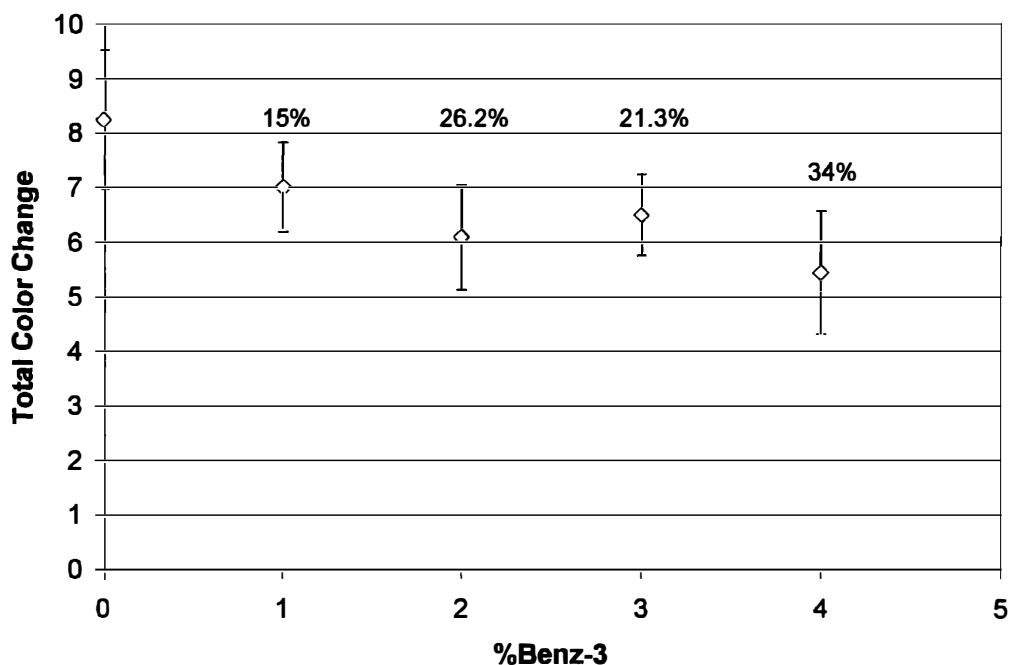


**Figure 9.** Color changes in dyed hair treated with formulations containing benzophenone-3 at various concentrations. Percent protection is indicated for each data point shown in the figure. Data were obtained for white hair tinted with a medium auburn hair dye and treated with a 0.5 formulation per 1 g of hair. Irradiation time was 16 hours (two shampoos).

that the experiment employing organic photofilters included two shampoos in addition to irradiation.

It should also be pointed out that hair-color protection products containing high concentrations of photofilters (above 5% w/w) may lead to excessive modification of hair tactile properties. Such formulations cannot be designated as everyday treatments but only as special-use, color-protection leave-in lotions or fixatives for use during the time of highest-intensity solar exposure.

#### HAIR COLOR PROTECTION BY A COMBINATION OF PHOTOFILTERS

We have also investigated multicomponent photoprotection systems containing two photo-absorbers, such as benzophenone-3 or benzophenone-4 and zinc oxide. It was anticipated that a combination of an organic photofilter and an inorganic photofilter/scattering agent might result in a synergistic effect similar to that reported for sunscreen formulations designed for skin protection (20–22). In one experiment, white yak hair was dyed with a light auburn dye, treated with a leave-on formulation containing a total of 3% UV absorber (benzophenone-3 and ZnO), and subjected to two eight-hour irradiation/shampooing cycles. The greatest color protection was observed for the mixture of 1.5% benzophenone-3–1.5% ZnO, and it was greater than the protection offered by an equal concentration of either ZnO or Benzophenone-3 alone (Figure 11a). The use of

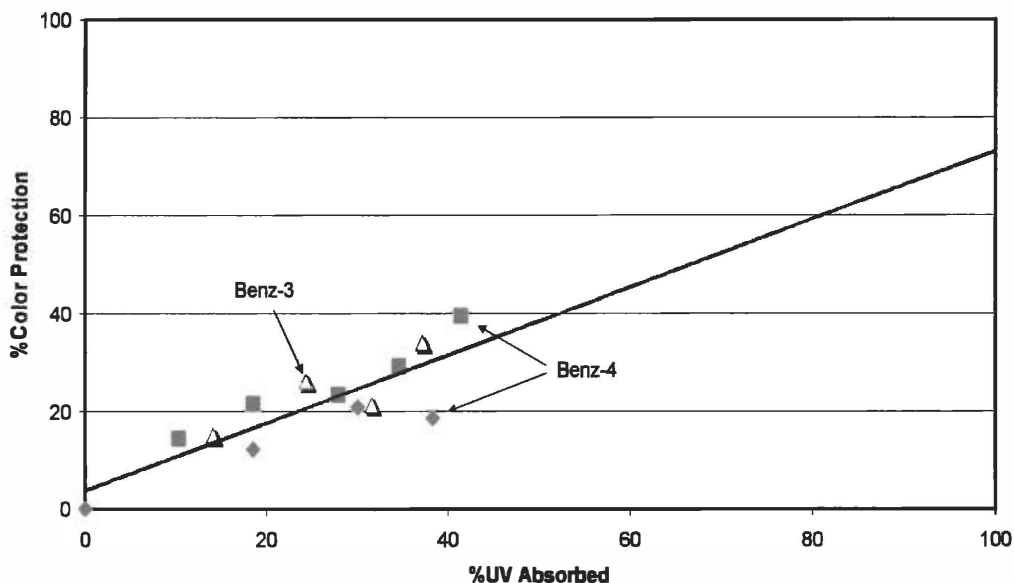


Figure 10. The relationship between color protection and the calculated percentage of UV light absorbed by formulations containing benzophenone-3 and benzophenone-4.

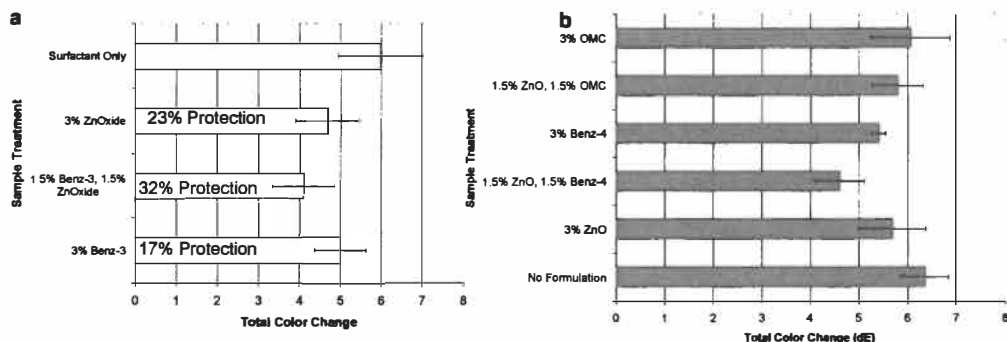


Figure 11. Hair color protection by (a) benzophenone and ZnO (micronized) and (b) benzophenone-4, octyl methoxy cinnamate (OMC), and ZnO (micronized). The treatment amount was 0.5 g of formulation per 1 g hair. Irradiation time was 16 hours (two shampoos). Yak hair was dyed with auburn hair color.

the product results in a small luster loss, which can be minimized by using micronized ZnO (23).

Similar results were obtained for the system benzophenone-4-ZnO (Figure 11b), with the greatest effect produced by a 1:1 w/w blend of the photo-absorbers. Figure 11b also includes the data obtained for hair treated with octyl methoxy cinnamate (OMC) and the mixture OMC-ZnO. As mentioned in a preceding paragraph, UVB absorbers attenuate only a small fraction of total UV and prevent color loss only to a small extent. This is supported by the data shown in Figure 11b, with 3% and 7.9% photoprotection by 3% OMC and 1.5% OMC-1.5% ZnO, respectively.

We have also conducted experiments to ascertain the effect of formulations containing other UVB-UVA photofilter systems, such as that composed of 1% dimethylpabaime-dopropyl laurdimonium tosylate (1%) and benzophenone-3 (1%) (see formulation in the Experimental section). Natural white hair was dyed with a red dye; one group of samples was irradiated under artificial sunlight and shampooed every eight hours, and the second was treated with 0.17 g of formulation per gram of hair, using an oil-based formulation, and irradiated and shampooed similarly to other samples. A reduced treatment amount was employed in order to simulate the practical usage conditions and to minimize the unfavorable tactile modification of the hair. After 24 hours of total irradiation, samples treated with the oil formulation had an average color loss of  $4.59 \pm 0.54$  while samples not treated with the formulation had an average color loss of  $4.82 \pm 0.83$ , amounting to 4.5% color protection. After 48 hours of irradiation, the average color losses were  $7.22 \pm 0.25$  and  $8.24 \pm 0.47$  for the treated and untreated samples, respectively, which corresponds to 12% color protection.

Finally, color fading could be reduced by including cationic polymers or silicones, in combination with photo-absorbers, in the photoprotection products (24,25). Such raw materials are typically included in the commercial formulations of conditioners, fixatives, or shampoos. The mechanism of color-loss prevention could be explained by a "sealing effect" of absorbed layers of polymer or silicone slowing down the diffusing out of hair dyes during shampooing. The use of film-forming polymers and/or oils could also improve the uniformity of distribution of photo-absorbers, resulting in a greater attenuation of incident light. In one experiment, natural white hair, dyed with medium auburn hair color, was treated with 2% benzophenone-4 and 2% benzophenone-4 in the form of a salt of PVP/DMAPA copolymer. After 16 hours of irradiation and two shampooings, the  $dE$  was  $7.9 \pm 1.0$ ,  $7.1 \pm 0.8$ , and  $6.4 \pm 0.8$  for untreated, benzophenone-4 treated, and benzophenone-4-polymer-treated hair, respectively. Thus, the observed photoprotection effect of 19% for benzophenone-4-PVP/DMAPA was greater than that (10%) measured for benzophenone-4 alone. In another experiment, natural white hair dyed with medium auburn hair color was treated with 2% benzophenone-4-PVP/DMAPA copolymer; 2% benzophenone-4-PVP/DMAPA copolymer-2% amodimethicone; and 2% benzophenone-4-PVP/DMAPA copolymer-2% trimethylsiloxyamodimethicone, which, after 16 hours of irradiation and two shampooings, gave a  $dE$  of  $5.5 \pm 0.6$  (14% protection),  $4.8 \pm 0.9$  (25% protection), and  $5.6 \pm 1.1$  (12.5% protection), respectively, versus a  $dE$  of  $6.4 \pm 0.6$  (0% protection) for the untreated control. Such result suggests that cross-linkable, aminofunctional silicone can lower color loss when used in combination with a photo-absorber.

## CONCLUSIONS

The main conclusions from this study can be summarized as follows:

- Fading of artificial, permanent hair color is greatest for hair subjected to both irradiation and shampooing, and significantly smaller for hair undergoing only irradiation or washing. Color loss has been found to be dependent upon the hair type employed, with hair melanin displaying significant protection of artificial hair dyes. Artificial hair color based on pyrazole intermediates showed the deepest fading as a

result of shampooing and irradiation/shampooing, probably because of the high water solubility of the coloring products and intermediates.

- Photofading of artificial hair color is caused by UV and visible light and can be reduced by 27% to 63%, depending on the irradiation dose, by a complete elimination of UV radiation by the use of an inorganic glass filter. According to theoretical calculations, the attenuation of UV light (290–400 nm) by organic photofilters depends on the amount deposited on the hair and varies from 10% to 25% for UVB filters and 40% to 60% for UVA filters at the deposition amount of 30 mg/(g hair).
- The use of organic photofilters such as benzophenone-3 and benzophenone-4 affords color protection ranging from 15% to 40% for the deposited amounts of photofilters from 5 mg/(g hair) to 25 mg/(g hair).

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