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To dye for! – A natural colouration booster

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Changing hair colour has been frequently practiced by both women and men since ancient times. Today, we can differentiate between products on the basis of colour durability after application in terms of semi-/demi-permanent and permanent dyes.¹

Semi-permanent hair dyes provide temporary colouration, and do not require the use of peroxide or a developer. The pigments sit on the surface of the cuticula, and these products are not strong enough to lighten hair colour. The colouration is short-lived and will last up between five and 12 washes.

Demi-permanent dyes do not contain any ammonia but do have enough peroxide to enter into hair cuticles where the pigments are deposited in the first cortex layers. Colouration lasts between 12 to 24 washes, and the products are not as harsh to hair as permanent colourations. Permanent hair dyes are the most efficient; the colouring results from a mixture of substances and involves complex reactions between precursors in the presence of an oxidising agent. The pigments are trapped inside the cortex.²

In order to enhance the colouration performance of hair dyes, propylene glycol (an effective humectant), monoethanolamine (an alkaline agent, currently the subject of concern because of nitrosamine formation - trisaminomethane (a base with buffering properties) or amino acids (pyrrolidone

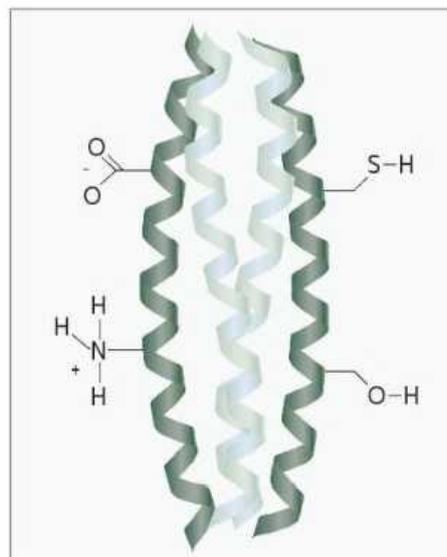


Figure 1: Possible keratin association sites

carboxylic acid – with colour retention properties,³ for example, are used as colour boosters. Other components which contribute to the retention of water can also be helpful as they can assist in the trapping of water-soluble molecules, such as pigments, in hair fibres.

The accumulation of copper - or any other metal ion - in hair can have an enormous impact on the colouration effects of dyes. On

ABSTRACT

Rahn's Radicare®-Eco is an antioxidant based on rosmarinic acid from lemon balm, young shoots of barley grass and α-glucosyl hesperidin, which are all sourced via a climate-neutral production and supply chain. Following application of 1% Radicare-Eco to three commercially available semi-/demi-permanent hair dyes, there were significant improvements to dye performance, giving an additional edge when it came to the resultant colouration. In addition, it was able to enhance the resistance to sun-induced bleaching of hair colouration.

one hand, the ions interact with the oxidants in dyes and are able to decompose hydrogen peroxide (Fenton reaction), leading to the generation of very reactive hydroxyl radicals at the direct protein or lipid sites.⁴ This causes damage to hair and affects the colouration process.⁵ On the other hand, they combine with free thiol or even disulphide groups, hindering the deposition of the pigments.

In relation to hair damage/integrity, our hair is very complex; it mainly consists of keratin fibres, which have a negative surface charge thanks to the presence of carboxylated glutamine and aspartic acid and sulphonic acid groups (Figure 1).

Furthermore, thanks to the outermost 18-MEA lipid layer, hair is highly hydrophobic.⁶ If daily hair treatment results in the removal of this layer, exposure to UV irradiation or chemical stress means that hair fibre becomes hydrophilic and is thus susceptible to interaction with any ions. Water absorption causes hair shafts to swell, increasing pressure, which leads to loss of amino acids and weakened hair over time. The binding of metal ions within hair may induce photo-oxidative protein damage, which in turn facilitates even more metal ion binding.

Material and methods

The powerful and natural ingredients of Radicare-Eco (INCI: water, glucosyl hesperidin, melissa officinalis leaf extract, sodium benzoate, hordeum distichon (barley) extract, citric acid) namely, a well-known medicinal plant - lemon balm (*Melissa officinalis*) - tender young shoots of barley grass (*Hordeum*

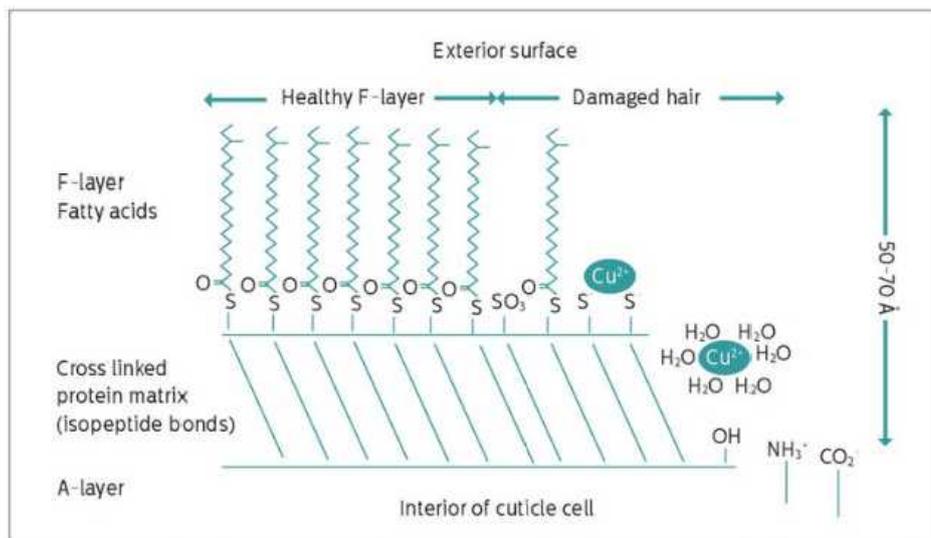


Figure 2: Representation of hair surfaces with an intact and damaged F-layer and possible Cu(II) coordination sites

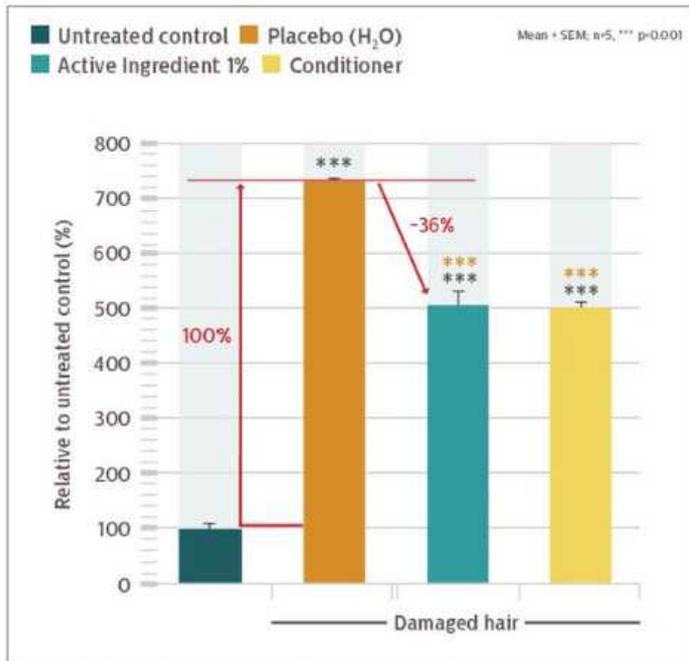


Figure 3: The active ingredient improves the integrity of damaged hair. The extent of protection is comparable with that provided by a conventional conditioner. The statistical values in black are the results of comparison with the untreated control and those in light blue are the results of comparison with placebo

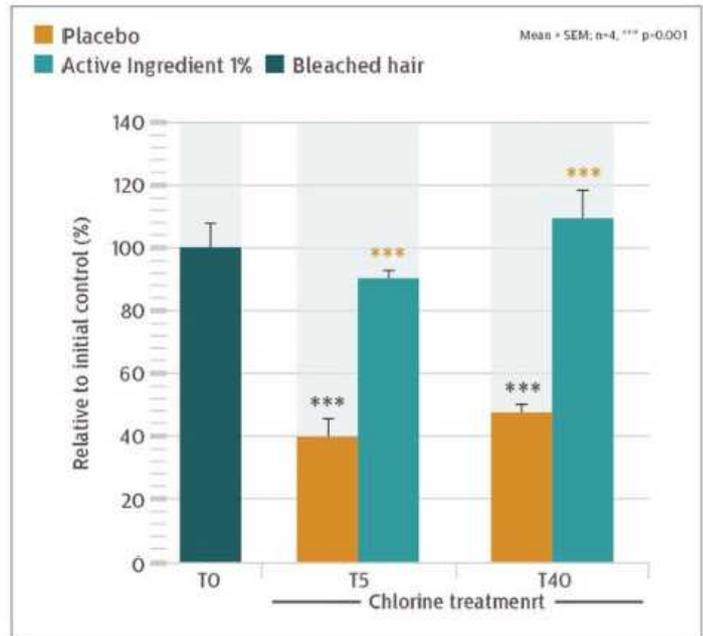


Figure 4: The active ingredient preserves the shine of bleached and chlorine-stressed hair. The bar graphs represent the results of measurement of the gloss of Caucasian bleached hair tufts after active ingredient treatment and exposure to water containing chlorine. The statistical values in black are the results of comparison with the untreated control and those in light blue are the results of comparison with placebo

distichon) and bio-technologically produced α -glucosyl hesperidin were tested to see how they improve hair integrity and hair shine.

To study hair integrity, double-bleached hair shafts (Kerling) were used. The hair was treated with a 1% solution containing the active ingredient. Untreated, virgin brown hair was used as a control. Water was used as a negative placebo control. A conventional silicon-based conditioner was used as positive control (INCI: water, glycerin, behentrimonium chloride, PPG-7, aminopropyl dimethicone, cetyl alcohol).

The hair was cut into lengths of 1cm and samples of 10mg hair were incubated with a 1% solution of the active ingredient in H₂O for 20 minutes. The hair was then washed with distilled water and incubated in a 40mM solution of CuSO₄ for ten minutes. The hair was then washed twice in distilled water and inserted into a Magnetech MS-300 ESR spectrometer. Five repetitions - five different hair samples - for each hair treatment were analysed.

To test hair shine, virgin brown Caucasian hair tufts were bleached for 45 minutes, washed and dried. Subsequently, they were immersed either in a 1% solution of active ingredient or in water for 20 minutes. The samples were dried and immersed in 5% aqueous chlorine solution for five minutes or 40 minutes. The hair shafts were dried, and gloss was measured using a glossmeter made by Courage and Khazaka.

For study of hair colouration, the lower sections of virgin light blond Caucasian hair tufts - Kerling; 15cm length/1.5cm width, ten per condition - were bleached for 45 minutes using Basler Professional Blond Claire powder bleach with 12% cream peroxide.

Whole tufts were dyed according to the manufacturers' instructions with three different conventional, commercially-available semi- (product A and B) and demi- (product C) permanent hair dyes with and without the 1% active ingredient for ten minutes. Tufts were washed, dried and spectrometric measurements (CIE-LAB-system; Minolta Spectrophotometer CM-600d) were performed at 22°C and 50% humidity.

To test sun-induced bleaching, the hair tresses used in the hair colouration experiment (only product A) were placed in a sun simulator (Suntest CPS, Heraeus) for 31 and 62 hours. These times were equivalent to between one and two weeks of sun exposure in southern France. The values were subsequently measured with a colorimeter by Courage and Khazaka.

Results

Hair integrity

Used for the basis of analysis were the Cu (II)-amino acid complexes (Cu[aa]_n) formed in human hair. Cysteine is mainly present in these complexes. During chemical/physical stress (oxidation reactions), the F-layer (18-MEA) of the hair can be destroyed and/or the disulphide bonds of the keratin fibres in the cuticle can be disrupted and the resulting -SH groups are oxidised, making them available for complex formation with bivalent ions.

Cu (II) is a transition metal ion that is known to readily form complexes with several amino acids. Since this ion is paramagnetic (one unpaired electron in the d-orbital), it is suitable for analysis using electron spin resonance (ESR) spectroscopy. The amount of complexed copper and the type of bonds can be determined directly from the spectral manifold.

The treatment for 20 minutes with a 1% solution of active ingredient resulted in a high level of protection (36%) of the cysteine groups of oxidatively damaged hair (Figure 3). As a comparison, values for conditioner-treated hair were recorded. The extent of protection provided by the conditioner and active ingredient was similar. However, the mode of action seems to be different.

The data for penetration of copper in the form of a water-coordinated ion showed that the active ingredient does not have the hydrophobic nature of the conventional conditioner. The active ingredient directly protected the cysteine in hair without the formation of the film layer that occurs in the case of conditioner-treated hair.

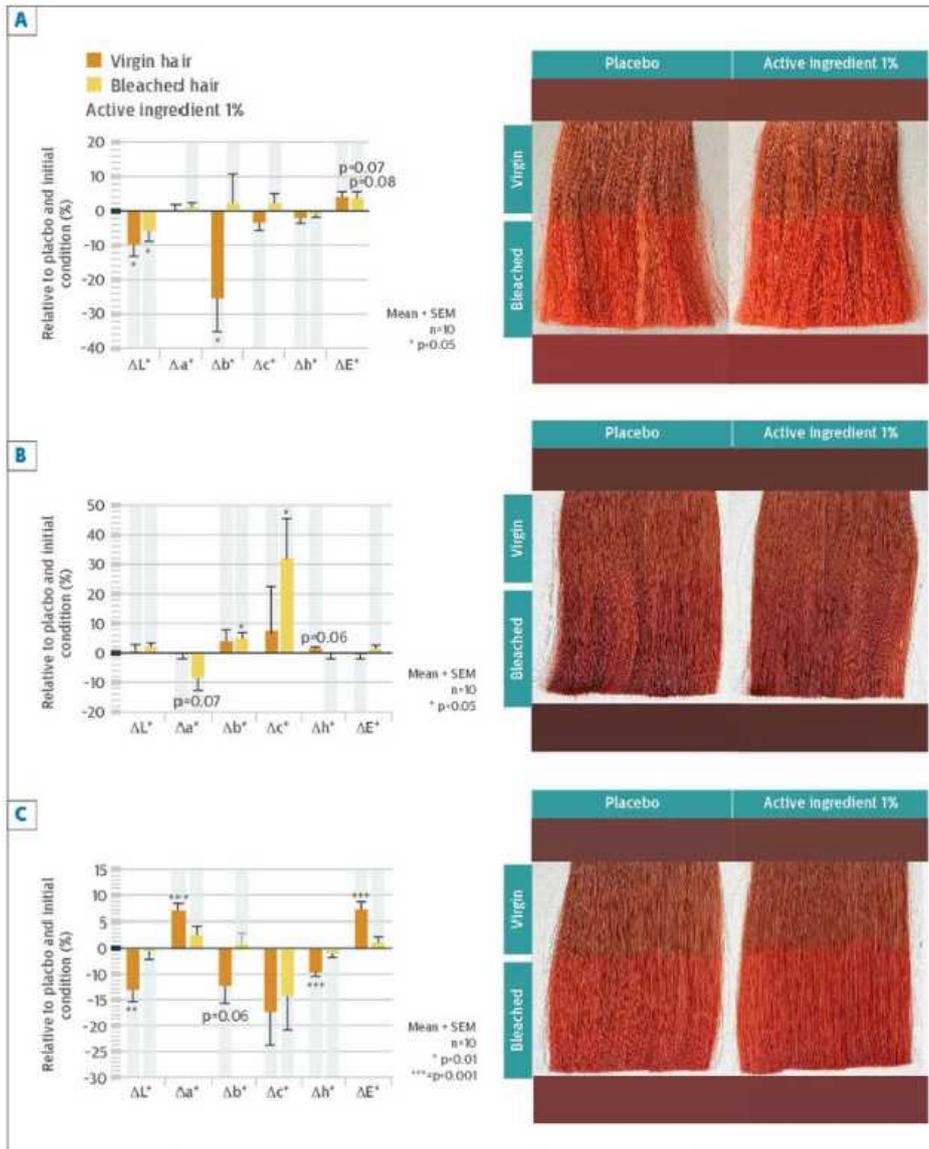
Hair shine

Treatment for 20 minutes with a 1% solution of active ingredient (leave-on) resulted in significant protection of gloss on exposure to chlorine (Figure 4). The results of measurement of gloss revealed no changes in the case of active ingredient-treated samples after five or 40 minutes in water with chlorine, while the gloss of placebo-treated samples was significantly reduced by 60% and 52% respectively. The experiment shows that the gloss of hair is quickly damaged when water with chlorine comes in contact with it.

Hair colouration

The active ingredient exhibited a significant colour-boosting effect at a concentration of 1% when applied directly during the dyeing processes. The degree of colour boost was dependent on the hair dye and the extent to which hair was pre-damaged.

In the case of product A (semi-permanent



Figures 5a-5c: Spectroscopic measurement shows the active ingredient has significant colour-boosting properties. Figure 5a shows values for product A, Figure 5b for product B and Figure 5c for product C. The panels on the right show digital photographs of colourised hair tresses with and without 1% active ingredient with the corresponding RGB colours

colouration), the result produced by the hair dye plus active ingredient was darker and less yellow on undamaged hair than that produced by active ingredient-free dye. On pre-damaged (bleached) hair, the result produced by the dye plus active ingredient was darker (Figure 5a).

In the case of product B (semi-permanent colouration), no significant difference between the results for dye plus active ingredient and active ingredient-free dye was documented on undamaged hair. On pre-damaged (bleached) hair, the result of the use of dye plus active ingredient was slightly more yellow and more colour-intensive than the result for active ingredient-free dye (Figure 5b).

In the case of product C (demi-permanent colouration), the result produced by the dye plus active ingredient was darker and more reddish than that produced by active ingredient-free dye on undamaged hair. Furthermore, the hue shifted more from yellow to red and the overall colour change was more

marked. No significant difference between the results produced by dye plus active ingredient and active ingredient-free dye was detected on pre-damaged (bleached) hair (Figure 5c).

Sun-induced bleaching

The experimental data obtained for the dyed (Product A) tresses following sun bleaching showed that samples treated only once with 1% active ingredient during the colouration stage were darker. This was the case for both virgin (not shown) and bleached hair tresses (Figure 6a).

Furthermore, this trend was detectable for both exposure times, 31 hours and 62 hours – which corresponds approximately one to two weeks on the beach. The red-green and blue-yellow units are shown in Figure 6a as corresponding pairs for samples treated with and without 1% active ingredient.

Here it is apparent that the results of active ingredient treatment were always redder than in the case of samples treated with placebo. It should be noted that a green colouration of

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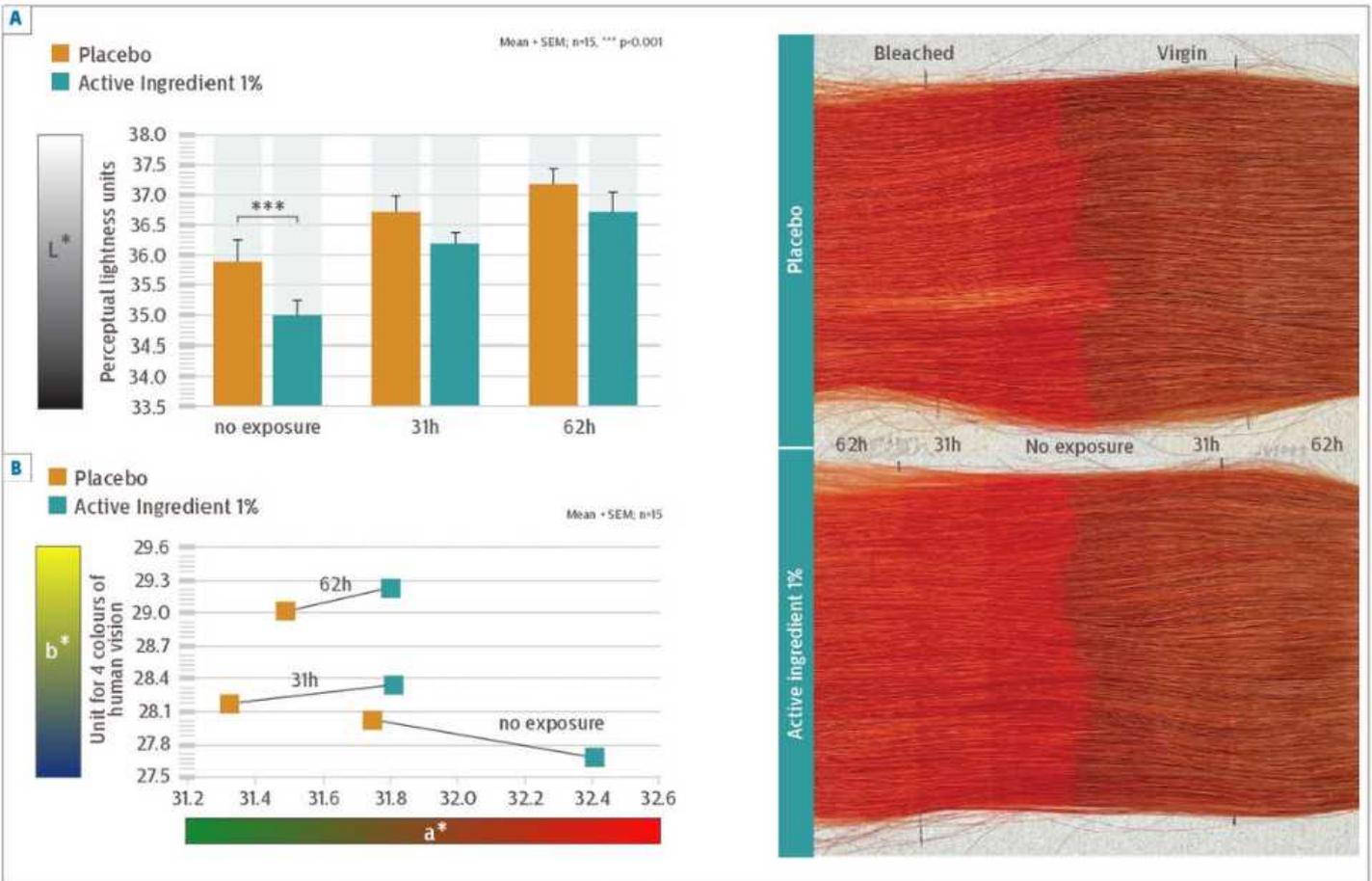
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Figures 6a and 6b: The active ingredient has UV-protecting properties. Figure 6a shows the lightness-black/white values in terms of appearance of hair tresses (bleached and dyed with product A) after different sunlight exposure times. Figure 6b shows the comparable pairs of red-green (a*, x-axis), and blue-yellow (b*, y-axis) values respectively. Images of the hair tresses with and without previous bleaching prior to colouration are shown in the right panel. Note the better combability of the treated hair treated with the active agent (anti-flyaway)

hair is perceived by the human eye as a dull colour tone. The hair tresses are depicted in Figure 6b.

A transition in bleaching effect over the two periods of 31 and 62 hours was apparent only in the case of the bleached hair treated with 1% active ingredient, while for the placebo-treated samples this was not the case, indicating the protective efficacy of the active ingredient. Calculation of the ΔE^* colour difference values revealed significant differences between active ingredient-treated samples and placebo-treated samples (Table 1). In particular, the differences for bleached hair after exposure for 62 hours were large enough to be perceptible by the human eye.

Conclusion

In the case of Radicare-Eco and its powerful ingredients, we considered the effects on hair dyeing not only in terms of colorimeter results but from the perspective of consumers and scientific analysis. This means we have been

able to demonstrate natural and market-oriented effects that provide the basis for achieving better colour results. The mode of action behind the colour-boosting efficacy seems to be associated with improved hair integrity.

The active substances were able to hinder the binding of copper ions - representative of any other ions in water - to keratin association sites, such as free thiol groups for example. This effect enables better attachment of the pigments and boosts colouration. Furthermore, the anti-oxidative capacity of Radicare-Eco seems to be beneficial not only during the (semi- and demi-) colouration process but also in the case of sun-induced bleaching.

A single application of the active ingredient was enough to protect hair colouration against bleaching for a significant period. Moreover, there was not only an improvement to colour intensity but to also colour brilliance thanks to increased gloss. **PC**

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TABLE 1: ΔE^* VALUES FOR VIRGIN AND BLEACHED HAIR AFTER 31 HOURS AND 62 HOURS OF SUN EXPOSURE

E* colour difference values	31 hours of sun exposure			62 hours of sun exposure		
	Virgin hair	Bleached hair	p-value (t test)	Virgin hair	Bleached hair	p-value (t test)
Placebo	1.6	1.3	0.003	2.8	1.9	0.0006
Active ingredient 1%	2.2	2.0	0.005	3.7	2.9	0.0004