Present in the hair cortex is melanin, which gives hair its natural colour. Modern consumers often use colorants with variable degree of longevity in order to change or enhance their natural hair colour. The permanent hair dyes, also referred to as oxidative dyes, have two components which are mixed just before application. The alkalisising agent, hydrogen peroxide, swells the hair, enabling the dye precursors and a catalysing agent to reach the cortex. These promptly undergo several steps of chain reactions, producing new chromophores which are too large to diffuse out of the hair fibre. Despite that, it is observed that hair treated with red oxidative dye is particularly prone to fading after UV exposure and shampooing. Studies have quantified the precise degree of colour loss using spectrophotometric measurements based on the CIELAB (Commission Internationale de l’Eclairage or ‘International Commission on Illumination’ [eng.]) system. For example, Medice and Joekes found that brown and blond hair dyes, recording ΔL, Δa and Δb values >5, while Fernandez et al measured total hair colour loss of bleached and coloured hair as ΔE=2.97. Zhou et al recorded ΔE>4 for dyed hair tresses soaked in surfactant solutions, also noting time and pH dependant curves.

Thus colour fastness of the hair dyes is not only a key performance characteristic of the dye formulation, but could be also of high importance when formulating targeted wash products. Primary surfactants are most commonly anionic, due to the superior cleansing and foaming performance of these materials. Kiplinger et al studied the effects of surfates (SLS and SLES) on colour changes, concluding that their substitution by milder anionics, or the addition of amphoteric co-surfactants, can reduce the rate of colour fading during shampooing. One common approach to reducing colour loss is the inclusion of polymers in post-colouring treatment products, with the aim of forming protective hydrophobic coating on the hair. Cationic polymers, also referred to as polyquaterniums, are known to confer properties such as slip, sheen and body, while their substantivity to hair is further enhanced by the presence of cationic sites along their backbone. Jaynes et al reported 11% to 44% reduction of colour-fading of hair tresses subjected to

**ABSTRACT**

The colour-fading of hair treated with oxidative dyes is attributed to the effects of ultraviolet light and other environmental factors, but mostly it occurs during shampooing. This effect is caused by the diffusion of chromophores from within the cortex towards the cuticle surface. The colour fading of dyed hair during shampoo washing is determined by a range of factors, most significantly by the chemistry of the chromophores, the porosity of the hair fibres, and the properties of the used surfactants.

Optimising the cleansing efficacy of shampoos in relation to colour protection claims is of interest to formulators. This study investigates the effects of two co-surfactants and a range of conditioning additives, polycationic and silicone-based, on the colour-fading of hair tresses treated with red oxidative hair dye and put through repeated wash-and-dry cycles. The results indicate that the choice of co-surfactant alone, and in combination with the conditioning additives, can significantly influence the colour fading of red oxidative dye treated hair during shampooing. The amphoteric co-surfactant offered statistically significant improved colour retention, compared to the nonionic. Furthermore, the silicone based conditioning additive delivered enhanced colour retention in comparison with the selected cationic polymers.

Table 1: Investigational materials: INCI names, abbreviations and properties.

<table>
<thead>
<tr>
<th>INCI name</th>
<th>Properties</th>
<th>Additional information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cocoaamidopropyl Betain (CAPB)</td>
<td>Amphoteric surfactant</td>
<td>pH dependant charge, mild</td>
</tr>
<tr>
<td>Coco-Glucoside (CG)</td>
<td>Non-ionic surfactant</td>
<td>Considered mild</td>
</tr>
<tr>
<td>Disodium Laureth Sulfosuccinate (DLS)</td>
<td>Anionic surfactant</td>
<td>Considered mild, possible substitute of SLES</td>
</tr>
<tr>
<td>Sodium Trideceth Sulfate, Sodium</td>
<td>Anionic, amphoteric and non-ionic surfactant blend</td>
<td>Commercially available blend claiming optimised colour protection</td>
</tr>
<tr>
<td>Lauroamphoacetate, Coco Monoethanolamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(surfactant blend)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyquaternium-28 (PQ-28)</td>
<td>Copolymer of vinyl/pyrroldione and methacrylamidopropyl trimethylammonium chloride (VP/MAPOC)</td>
<td>Hair substantive polymer due its quaternised groups</td>
</tr>
<tr>
<td>Polyquaternium -55 (PQ-55)</td>
<td>VP/DMAPO/C12-MAPTAC copolymer</td>
<td>Hydrophobically modified copolymer, claims for enhanced substantively and colour protection</td>
</tr>
<tr>
<td>Dimethicone</td>
<td>Silicone polymer</td>
<td>350 cps</td>
</tr>
<tr>
<td>Sodium Laureth Sulfate (SLES)</td>
<td>Anionic surfactant</td>
<td>Used as primary surfactants due to good solubility and cleansing properties</td>
</tr>
</tbody>
</table>
Schlosser silicone polymers, are attracted to the hair with consecutive wash-and-dry cycles. This project investigated the effects of wash-and-dry treatments with leave-on conditioners containing cationic polymers. No relationship between the colour protection and the molecular weight of the polymers was found. The colour protective properties of cationics, based on the formation of hydrophobic protective film on the hair, were also reported by Zhou et al. and Rigoletto et al.

Other, less polar materials such as silicone polymers, are attracted to the hair surface by strong hydrophobic Van de Walls forces, as the cuticle is largely hydrophobic. Schlosser et al. measured silicone deposition from permanent hair dye and related it to the measurements of hair colour fading after consecutive wash-and-dry cycles, evidencing a positive effect of dimethicone on colour retention. Furthermore, when combined application of polyquaterniums and silicones in a shampoo was investigated by Gamez-Garcia et al. applying combined fluorescent techniques, a synergistic depositioning effect was observed.

This project investigated the effects of surfactants and conditioning additives on the colour-fading of hair tresses, treated with red oxidative hair dye and put through consecutive wash-and-dry cycles.

### Materials and methods

**Investigational materials**

Surfactants included in the screening tests: Sodium laureth sulfate (SLES), cocoamidopropyl betain (CAPB), coco-glucoside (CG), disodium laureth sulfoacuate, and a surfactants blend of sodium trideceth sulfate, sodium lauroamphoacetate and coco monoethanolamine.

Investigational materials included in the treatment tests: SLES, cocoamidopropyl betain (CAPB), coco-glucoside (CG), polyquaternium-28, polyquaternium-55 and dimethicone. Further descriptions of the properties of the investigational materials, relevant to this study are given in Table 1.

**Methods**

**Co-surfactant screening tests**

Co-surfactants soak test (adaptation from Zhou et al.): 400 mL solutions of 5% w/w each respective surfactant were prepared and a test hair tress was immersed in each solution and allowed to soak for one hour. The hair tress was then removed from the surfactant solution, rinsed under constant tap water (t = approx 20°C) for two minutes and blow dried for five minutes at t = 50°C.

Co-surfactants + SLES soak test: 400 mL solutions comprising 2.5% w/w of a respective co-surfactant mixed with 5% w/w SLES were prepared. The remaining stages of this test were identical to the co-surfactant soak test.

Treatment wash tests: Treatment solutions were prepared comprising SLES, the selected co-surfactants, and three conditioning additives (Table 2). A dyed hair tress was immersed in a 2.5% solution of each test combination (preheated to 40°C) for four minutes, under controlled mechanical agitation. The remaining stages of the test were the same as the screening test. The cycle was repeated ten times for each hair tress. Three hair tresses were tested per variable.

Colour measurements: Before and after a complete wash-and-dry cycle each treated hair tress was attached securely to a white ceramic tile and spectrophotometric measurements were taken at three points evenly distributed along its length (Spectrophotometer CM-2600D, Konica Minolta, Japan, illuminator = D65 (daylight), viewing angle = 10°).

The average colour change $\Delta E$ for each treatment was calculated, based on pre- and post-treatment measurements of each hair tress:

$$\Delta E = \sqrt{(\Delta L^2 + \Delta a^2 + \Delta b^2)}.$$  

The colour retention value for each formulation combination, containing a co-surfactant and a conditioning additive, was calculated as follows:

$\% = \Delta E \times 100/\Delta E$ (control).  

Statistical analysis: One-way ANOVA test was applied to the mean $\Delta E$ values and % colour retention of the formulations containing different conditioning additives, followed by Tukey Honest Significant

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### Table 2: Treatment solutions.

<table>
<thead>
<tr>
<th>Raw materials: INCI names</th>
<th>Control CAPB % w/w</th>
<th>Control CG % w/w</th>
<th>CAPB+ PQ-22 % w/w</th>
<th>CAPB+ PQ-55 % w/w</th>
<th>CAPB+ Dimethicone % w/w</th>
<th>CG+ PQ-22 % w/w</th>
<th>CG+ PG-55 % w/w</th>
<th>CG+ Dimethicone % w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLES</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>CAPB</td>
<td>2.5</td>
<td>-</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CG</td>
<td>-</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Polysorbate-80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dimethicone</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>PQ – 22</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PQ – 55</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Citric acid (20% w/w soln)</td>
<td>q.s.</td>
<td>q.s.</td>
<td>q.s.</td>
<td>q.s.</td>
<td>q.s.</td>
<td>q.s.</td>
<td>q.s.</td>
<td>q.s.</td>
</tr>
<tr>
<td>Aqua (deionised)</td>
<td>to 100</td>
<td>to 100</td>
<td>to 100</td>
<td>to 100</td>
<td>to 100</td>
<td>to 100</td>
<td>to 100</td>
<td>to 100</td>
</tr>
</tbody>
</table>

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Figure 1: Total colour changes in hair tresses treated via soak test with a range of co-surfactants vs. their respective blends with 5% SLES.
Difference test as appropriate. Two-way ANOVA was used to further review the \( \Delta E \) values between the variables. Probability results of 95\% (\( p < 0.05 \)) were considered statistically significant.

**Results and discussion**

The co-surfactant screening results for colour fading are presented in Figure 1. From the tested co-surfactants, DSL demonstrated the strongest capacity to remove colour, while CAPB and CG induced 50\% less colour fading. The presence of SLES increased the total colour loss for the milder anionic, non-ionic and amphoteric co-surfactants, due its high solubility and free availability in solution. This effect was not noted with the SLES combination with the commercial surfactant blend.

Further to the surfactant screening tests, CAPB and CG were selected for the further investigation, as they demonstrated good potential for colour retention when tested individually, and for mitigating the colour fading induced by the primary surfactant SLES.

The results for the total colour changes (\( \Delta E \)) and the corresponding colour protection values for all test formulation variables and controls are presented in Figures 2 and 3, respectively. The formulations containing CAPB outperformed those containing CG, showing smaller colour difference of hair tresses before and after the wash-and-dry cycle (Fig. 1) and larger colour protection values (Fig. 2). When comparing the conditioning additive effect on the reduction on red colour fading, it has been shown that dimethicone was superior to the cationic polymers, offering better colour protection, irrespective of the co-surfactant effect.

Statistical analysis performed on the results revealed the following:

**One-way ANOVA tests**

Comparison of the \( \Delta E \) values of the test formulations in the CAPB group produced \( p < 0.05 \), therefore showing a significant difference in total colour change between the formulations in the CAPB group;

Comparison of % colour retention of the variables in the CAPB group has also produced \( p < 0.05 \), confirming the conclusion of different colour protection efficacy.

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**Figure 2:** Total colour changes in hair tresses treated with the formulations containing SLES, one of the two co-surfactants (CAPB or CG) and one of the conditioning additives (PQ-55, PQ-28 or dimethicone) vs. control formulations without conditioning additives.

![Figure 2: Total colour changes in hair tresses treated with the formulations containing SLES, one of the two co-surfactants (CAPB or CG) and one of the conditioning additives (PQ-55, PQ-28 or dimethicone) vs. control formulations without conditioning additives.](image-url)
Tukey HSD test
There was statistically significant difference within each pair the CAPB group, with dimethicone/PQ-28 showing the lowest p value of 0.001.

However, there was no statistically significant difference for the ∆E and % colour retention between the variables within the CG group.

Two-way ANOVA tests
Comparison of the ∆E values of conditioning additives and co-surfactant variables produced p < 0.05, indicating statistically significant difference between the efficacy of the CAPB and the CG group of formulations.

The statistical analysis confirmed the co-surfactant effect on colour fading of dyed hair induced by shampooing. Specifically, the amphoteric surfactant (CAPB) demonstrated more effective colour retention capacity when combined with SLES, than that of the selected non-ionic surfactant – CG.

Furthermore, the study demonstrated that the positive effect of CAPB on colour retention is enhanced by the presence of other hair substantive materials such as polycationics and silicone polymers. In particular, dimethicone alone offered superior colour retention compared to polycationics.

PQ-55 also delivered significant colour protection value when combined with CAPB and better than that of PQ-28. This superior efficacy can be explained by the PQ-55 hydrophobicity, thus enhanced substantively to hair (Fig. 4). These effects could be enhanced via further optimisation of the polymer/surfactants ratio.

Conclusion
This investigation demonstrated that certain ingredients can improve the colour retention of red oxidative dye coloured hair during shampooing.

The choice of co-surfactant was shown to have an effect on the reduction of the colour fading induced by SLES. The amphoteric co-surfactant cocoamidopropyl betain, in particular, was proven to offer statistically significant colour protection efficacyn in shampoo formulations.

This effect could be further enhanced by the addition of appropriate conditioning materials. Dimethicone was identified as the most effective conditioning additive in this study, providing superior colour protection in combination with both CAPB or CG, followed by polyquaternium-55 mixed with CAPB.

Further investigations of the optimal concentration ratios of co-surfactants and conditioning additives could lead to improved colour protection of shampoo formulations while maintaining other important product attributes such as foaming, rinsability and minimised build-up of conditioning additives on hair.

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