Modern hair treatments have to fulfill not only technical requirements but also high emotional demands. While data on combing work, tensile strength or fatigue testing are common to support technical claims, the market success of a product is essentially determined by fulfilling those emotional characteristics which are claimed in the advertisement.

In hair care, these emotional aspects are determined mainly by feel and appearance. Both parameters are not easily measured by direct, objective methods. They have to be scored by sensory assessment or derived from a combination of various technical investigations.

In this study the appearance of hair tresses has been evaluated by colour measurements, fibre tensile strength and a keratin degradation parameter. The type of damage selected was irradiation by UV/Vis light simulating the sun.

**Methods**

The UV-absorber investigated in this study was a siloxane copolymer grafted with methoxycinnamic acid ester and cationic alkylamidopropyl dimethyl ammonium groups (ABIL UV Quat 50, Fig. 1). In earlier studies [Protection of Hair Fiber Appearance and Strength against UV-Damage, H.I. Leidreiter, U. Kortemeier, U. Maczkiewitz, M. Pascaly, Proc of 23rd. IFSCC Congress (2004).] the molecular weight, the degree of cationic substitution as well as type and number of UV-absorbing chromophors have been optimised by the same methods as described in this investigation.

This new compound was compared with other commercially available cationic UV-screens and a nonionic, silicone based material. All these products were selected from the group of ingredients offered for hair protection against UV-irradiation. The silicone based material was Polysilicone-15 (PS-15, Diethylbenzylidene Malonate Dimethicone) and the other cationic UV-absorbers were Dimethylpabamidopropyl Laurdimonium Tosylate (DMPLT), Polyquaternium-59 (PQ-59) and Polyamide-2 (PA-2).

The absorption spectra of all investigated material are shown in Figure 2. The data was obtained with concentrations 50 mg/l in ethanol. Strong UVB absorption is observed with DMPLT. This material is a monomeric quat without any polymeric backbone; therefore it is the material with the highest density of chromophors. Among the polymeric test products, ABIL UV Quat 50 shows the strongest and widest absorption in UVA and UVB range.

**Figure 2:** UV-traces of test products of competition. Abbreviations see text.

<table>
<thead>
<tr>
<th>Table 1: Test formulation shampoo.</th>
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<tbody>
<tr>
<td>Test material</td>
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<tr>
<td>Texapon NSO</td>
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<tr>
<td>TEGO Betain F 50</td>
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<tr>
<td>Citric Acid</td>
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<td>Water</td>
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Hair treatments

Two types of cosmetic treatments have been applied as model systems. One was a standard shampoo (Table 1) with Sodium Laureth Sulfate (SLES) and Cocamidopropyl Betaine (CAPB) as surfactant system and the other formulation was a rinse conditioner (Table 2) based on fatty alcohol and Cetrimonium Chloride. The test compounds have been incorporated into these base formulations.

The evaluation was conducted using European hair. The fibres or tresses used in this investigation have been pretreated by a bleaching process. This pretreatment realistically simulates the condition of the target end consumer’s hair. For colour fading tests, hair tresses were dyed using commercially available coloration kits, purchased from retailers. Two types, permanent and demipermanent dyes were applied (Table 3). The products were selected to provide a red shade, because these colours are reputed to fade more than other shades.

UV irradiation

For UV/Vis irradiation a sun simulator (Hoenle sun simulator SOL2, Dr. Hoenle AG, Graefeling, Germany) was used, providing a light spectrum (D65) which simulates within 4h the dose rate of 1 day sunlight at 50° northern latitude. In most tests, the irradiation time period between single test treatments and measurements did correspond to twice the natural daily dose. All measurements were calibrated by pair-wise comparison of the values before and after irradiation.

Three parameters have been evaluated by means of technical measurement: hair colour, hair fibre tensile strength and fibre keratin integrity.

Tensile strength

For the quantification of the effect of sun irradiation on the tensile strength of single hair fibres European virgin brown hair, pre-damaged by bleaching (10% H2O2, 30’, 22°C) and the test compounds have been incorporated into these base formulations.

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Andover, UK). The value of Delta-Load is the difference before and after the treatment procedure. After measurement of the start value the hair fibres had to be relaxed by soaking in water for 2 hours.

**Keratin integrity**
The fibre keratin integrity has been investigated by differential scanning calorimetry [F.J. Wortmann, C. Springob, G. Sendelbach, J. Cosmet. Sci. 53, 219-228 (2002)]. This method delivers information about the degree of damage to the keratin structure of the hair fibre. In the test setup, flat tresses (European human hair, single bleached) of 0.5 cm width have been used. The tresses underwent 4 treatment cycles, including a shampoo (0.5 g/tress for 30 sec., 1 min residence, 1 min rinsing) followed by a conditioner (0.5 g/tress, 2 min residence, 2 min rinsing). In the shampoo tests, the application was repeated once in each cycle without applying any conditioner. In the conditioner tests, the control shampoo as well as the test conditioner formulations were applied only once per cycle. After drying at room temperature the tresses were irradiated for 4.25 h (does rate of approx. one day sunlight). To maintain homogeneous irradiation the hair tresses were spread to single fibres. Finally the hair tips were cut to the required amount for the DSC determination. Each application was conducted threefold.

**Colour measurement**
Colour has been measured using a CIE-L* a*b Colorimeter [spectrophotometer micro colour, Dr. Lange, Düsseldorf, Germany]. The colour variations are expressed as integral difference ‘delta-E’, where changes of brightness (L*), red-green (a*) and blue-yellow (b*) shift are considered. Best differentiation was obtained when measuring the change directly before and after irradiation, without any intermediate treatment. Shampoo as well as rinse conditioner application lead to fading of a hair dye. The interpretation of colour measurements obtained from superposition measurements obtained from superposition of both, UV irradiation and treatment with formulations would not be accurate. In the operation procedure flat glued tresses of single bleached European human hair, 4 g weight, 16 cm length and 2 cm width, were used. The dye was applied according to all steps given in the operating guidelines delivered by the package. Eleven tresses were treated with each single colouration kit. After a drying time of minimum 24 hours, the tresses were treated by the test formulations, shampoo and (in case) conditioner. The tresses were dried again. The colour value has been determined by L2 single measurement of the CIE-L* a*b*-colour values. Seven hours irradiation time was chosen to apply a dose rate of approx. two days sunlight. Following, the colour values were taken again and the integral colour change “delta-E” was calculated using the following formula:

\[ \Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \]

**Results**

**Tensile strength**
The UV-fraction of sunlight irradiation can cause a reduction of the tensile strength of hair fibres. The test conditions in this study for unprotected hair fibres resulted in a reduction of the force measured at 15% extension by about 5 mN per fibre. This is a change of about 3% relative to the starting value. Some of the UV filters provided protection when used in a conditioner formulation. The best effect observed was up to 40% less reduction of the tensile strength change when using ABIL UV Quat 50. PA-2 provided the same efficacy. The other two products evaluated in this test did not score protection values which were significantly lower than the control.

![Figure 5: Colour fading of hair tresses with permanent dye. UV-absorbing ingredients in conditioner application, 1.0% actives level. ABIL UV Quat 50 provides about 40% reduced colour fading.](image)

**Table 3: Ingredients of colourations used for colour fading test.**

<table>
<thead>
<tr>
<th>Ingredient</th>
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<tr>
<td>Permanent (level 3): Poly Brilliance, number 868 “grenadine” Schwarzkopf &amp; Henkel.</td>
<td>Aqua, cetearyl alcohol, ammonium hydroxide, coconut alcohol, isostearic acid, sodium laureth sulfate, sodium lauryl glucose carboxylate, lauryl glucoside, potassium hydroxide, myristic acid, sodium sulfide, ceteareth-12, ceteareth-20, ascorbic acid, sodium silicate, etidronic acid, parfum, linalool, citrus, sorbic acid toluene-2,5-diamine sulfate, resorcinol, 4-amino-m-cresol, m-aminophenol, 1-naphtol, 1,3-bis-(2,4-diaminophenoxo) propane HCL, 2-methyl resorcinol, 4-amino-2-hydroxytoluene, hydroxyethyl-2-nitro-p-toluidine, 2-amino-3-hydroxypropyridine, 4-chlororesorcinol, 2-amino-6-chloro-4-nitrophenol, 2,7-naphthalenedicarboxylic, 6-methoxy-2-methylamino-3-aminopyridine hcl, 1-hydroxyethyl 4,5-diamo pyrazole sulfate, 3-amino-2,4-dichlorophenol HCL, tetraaminopyrimidine sulfate, 2,2-methylenebis 4-aminophenol, phenyl methyl pyrazolone, 5-amino-6-chloro-o-cresol, 2,6-dihydroxy-3,4-dimethylypyridine, 2-amino-4-hydroxyethylaminoisole sulfate, 4-amino-2-nitrophenylamine-2-carboxylic acid, 1,5-naphtalenediol, 2,4-diamino phenoxetylhenol HCl.</td>
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</table>
different from the control formulation, which was CTAC. Figure 3 shows the data in comparison.

**Keratin integrity**

The DSC data exhibited high reproducibility and small standard deviation. Non-irradiated hair shows a DSC signal at about 154°C, while the treatment without protection lead to a reduction of the decomposition temperature to about 142°C. The standard deviation in the data of this evaluation is below ±0.5°C. The best protection of the keratinous structure according to DSC measurement was provided by ABILUV Quat 50. The best protection effect was observed with conditioner application and yielded 28%. In shampoo application, ABIL UV Quat 50 provided about 10% protection.

**Colour protection**

The colour change generated by the equivalent of approximately two days sunlight was about 2 to 3 units of delta-E for the permanent dye and about 3 to 4 units for the demi-permanent dye. It was possible to show that the use of a UV-absorbing material in a rinse-off formulation leads to an improved preservation of the colour. This was observed in both application types, shampoo and conditioner.

The use of ABIL UV Quat 50 in both shampoo as well as rinse provided the best protection effect for the permanent colouration. Non of the other materials provided better performance. The colour fading was reduced by of 50% in the shampoo and about 40% in the conditioner application (see Fig. 4 and 5). Besides ABIL UV Quat 50 also Polyamide-2 performed well in the shampoo application while Polyquaternium-59 provided a good performance in the conditioner formulation.

The protection effect for the demi-permanent colouration was less clearly differentiated among the test material. In conditioner applications, ABIL UV Quat 50 reduced the fading by about 50%. In this comparison a maximum effect of 65% protection was obtained with PS-15. In shampoo applications, the protection of the demi-permanent dye was generally smaller with about 20%. Here a maximum effect of 25% was observed by both ABIL UV Quat 50 and PA-2 (see Fig. 6 and 7).

**Conclusion**

The fastness of hair dyes against sunlight fading is improved by using UV-absorbers. The damage of hair by sunlight including UV is also expressed by a loss in tensile strength. This degradation effect as well as the UV-impact on the integrity of the hair fibre keratine can be reduced too. The investigated UV filters can be incorporated in shampoo or rinse formulations for frequent application which sufficient success, when the ingredients are substantive. This necessary substantivity to the hair fibre surface is provided by cationic groups. Siloxane derivatives, with their specific surface activity, also have sufficient substantivity.

The new siloxane copolymer ABIL UV Quat 50 with a high content of UV absorbing methoxycinnamic acid groups and a small ratio of cationic functions combines both characteristics, silicone and cationic. This ingredient provides overall best protection in both types of rinse-off formulations, shampoo and conditioner.