T-shaped Siloxane Microemulsion for Improved Hair Conditioning and Protection

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KEY WORDS: silicone quat, heat protection, color retention, clear shampoos, conditioner rinses

ABSTRACT: Described here is a T-shaped cationic siloxane incorporated in a microemulsion to provide a high silicone character material with balanced solubility and high hair substantivity. Wet and dry combability and hair feel were evaluated by panelists, while combing force measurements and differential scanning calorimetry measured conditioning and heat protection, respectively. Color washfastness also was tested using a spectrophotometer.

High molecular weight silicones are known for outstanding hair conditioning and protecting properties. A pronounced silicone character gives rise to a smooth and soft feel in hair, in addition to manageability and combability. Yet while conditioning efficacy usually increases with the molecular weight of the silicone, high molecular weight silicones are difficult to use due to their hydrophobic and viscous character. In shampoos, they can cause turbidity and/or separation, and in conditioners, their homogeneous distribution is difficult to achieve.1 Furthermore, buildup on hair over time can become an issue.

One approach to overcome these limitations is to incorporate organic modifications onto the silicone backbone. Especially suited for this task are cationic groups that can improve processability, solubility, deposition and substantivity. Damaged hair in particular forms anionic centers on the protein surface—where cationic conditioning agents show improved attraction and substantivity via Coulomb interactions. But even for organomodified silicones, increased molecular weight results in difficult formulation, as they too are high molecular weight silicones and thus highly viscous and difficult to handle. However, when delivered as an emulsion, small droplets of the high molecular weight silicone are pre-formed, which can be easily mixed into cosmetic formulations.

Especially beneficial to the formulator are thermodynamically stable microemulsions of very fine silicone droplets.

Especially beneficial to the formulator are thermodynamically stable microemulsions of very fine silicone droplets, i.e., smaller than the wavelength of visible light, which are therefore also transparent. This approach using fine droplets was employed to develop a microemulsion based on high molecular weight silicone quaternium-22. Its abilities to condition and protect hair were then compared with a silicone quaternium-16 product, as discussed here.

Microemulsion Development

The silicone microemulsion described contains a unique high molecular weight T-shaped cationic siloxane as depicted in Figure 1. This structure aims to provide effective conditioning, substantivity and protection, and is distinct from conventional linear silicone structures.2 The substantivity of this silicone quaternium-22 to hair, especially in damaged areas, was first confirmed by confocal laser scanning microscopy using a small amount of fluorescein-labeled silicone quat (see Figure 2). For this purpose, a fluorescein-labeled derivative of silicone quaternium-22 was prepared without significantly changing its molecular structure or surface interaction.

The microemulsion was then processed by emulsifying the high molecular weight silicone quaternium-22 with the polyglycerin emulsifier polyglyceryl-3 caprate, in combination with a small amount of cocamidopropyl betaine. The product therefore contains no polymer or preservatives. The active silicone content in the microemulsion is approximately 30%. In contrast to other aminomodified silicones, this silicone

* ABIL ME 45 (INCI: Silicone Quaternium-22 (and) Polyglyceryl-3 Caprate (and) Dipropylene Glycol (and) Cocamidopropyl Betaine) is a product of Evonik Industries AG.
quaternium-22 also does not contain reactive primary or secondary amino groups, therefore showing no yellowing effects in final formulations under storage or with perfumes. Furthermore, it is not based on secondary amines as raw materials, which are possible sources for nitrosamine formation.

Materials and Methods

Once substantivity was confirmed, various tests were conducted to assess the performance benefits of the microemulsion. Wet and dry combability and hair feel after shampooing and conditioning were evaluated by panelists. Combing force measurements were taken to assess conditioning benefits, and differential scanning calorimetry (DSC) was used to determine the efficacy of the microemulsion in protecting hair fibers against heat damage. Finally, the ability of the microemulsion to improve color washfastness was tested using a spectrophotometer. These tests are described here.

Conditioning Tests

Two hair treatments were used to assess the efficacy of the silicone quaternium-22 microemulsion: a standard shampoo (see Formula 1) and a conditioning rinse (see Formula 2). The test shampoo was based on a combination of sodium laureth sulfate and cocamidopropyl betaine, incorporating polyquaternium-10 (PQ-10) as a standard cationic polymer. Due to its pronounced substantivity and coacervation properties, PQ-10 acts as a cationic deposition polymer in shampoo formulations. In this function, it supports the activity of silicone-based conditioning agents and significantly increases the amount deposited onto the substrate. For comparison, a competitive silicone quat emulsion, INCI: Silicone Quaternium-16 (and) Undeceth-11 (and) Butyloctanol (and) Undeceth-5, known for its intensive conditioning, also was tested, as were formulations of PQ-10 alone and a control, i.e., formulations without PQ-10 and the silicone.

The test conditioner rinse was based on cetyl alcohol and ceteareth-25 and...
used cetrimonium chloride (CTAC) as the standard organic conditioning agent. Silicone derivatives commonly are used in combination with organic quats due to known synergistic effects. The microemulsion was incorporated into these base formulations using a standardized procedure.

**Panel assessment:** The conditioning performances of the test shampoo and conditioner were first rated in a sensory hair swatch test by an expert panel (n = 5) using a scale of 1–5, with “1” representing poor performance and “5” characterizing excellent performance. The sensory evaluation was carried out using bundled, bleached Caucasian hair*. The shampoo formulations were applied twice to the pre-washed hair swatches in a standardized way by a trained expert. After 30 sec of massage application of 0.25 g shampoo/1 g of hair, and 60 sec of rest, the tresses were rinsed with water (38°C) for 60 sec. On the other hand, 0.25 g of conditioner formulation/1 g of hair were applied just once to the pre-washed hair swatches using massage for 60 sec, then allowed to rest for 60 sec. The tresses were rinsed with water (38°C) for 3 min. Directly after the treatment, the wet evaluations of the hair swatches were performed by the panel. The evaluations of the dry properties were conducted after drying the hair under defined climatic conditions overnight; 23°C, 50% relative humidity. The sensory assessments of the test and control shampoos for detangling, wet comb and wet feel are shown in Figure 3a, with the corresponding results for dry hair comb and feel shown in Figure 3b. Figures 4a and 4b show the detangling, wet comb and wet feel results, and the dry comb and dry feel results, respectively, for the conditioner.

**Combining force:** In addition to sensory assessments, combing force measurements were taken before and after application of Formulas 1 and 2 using a tensile tester*. Tests were conducted on virgin brown Caucasian hair swatches pre-damaged by a permanent wave treatment. The formulations were applied to the hair swatches as described above in the panel assessment. Measurements for the shampoo and conditioning rinse are shown in Figures 5 and 6, respectively; results are based on four hair swatches each.

### Conditioning Results: Shampoo

Due to its pronounced substantivity and coacervation properties, PQ-10 acted as a cationic deposition polymer in the shampoo formulations (see Formula 1), supporting the activity of silicone-based conditioning agents and significantly increasing the amount deposited onto the substrate. Figure 3a illustrates the improvement in wet sensory characteristics for the combination of PQ-10 and the silicone quaternium-22 microemulsion. The silicone quaternium-22 microemulsion provided excellent conditioning properties such as superior combability and hair smoothness following its use. Also, in the dry hair test (see Figure 3b), the silicone quaternium-22 microemulsion achieved noticeably better conditioning.

These sensory findings were confirmed by wet combing force measurements. The shampoo composition applied was identical to the one shown in Formula 1 but as shown in Figure 5, the silicone quaternium-22 microemulsion significantly reduced

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* The hair used in this evaluation was from Kerling International Haarfabrik GmbH.

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### Formula 1. Test shampoo formulation

<table>
<thead>
<tr>
<th>% w/w</th>
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<tbody>
<tr>
<td>A. Polyquaternium-10 (PQ-10, UCare Polymer JR-400, Dow Chemicals)</td>
<td>0.2</td>
</tr>
<tr>
<td>B. Water (aqua)</td>
<td>qs to 100.0</td>
</tr>
<tr>
<td>C. Silicone Quaternium-22 (and) Polyglyceryl-3 Caprate (and) Dipropylene Glycol (and) Cocamidopropyl Betaine (ABIL ME 45, Evonik Industries AG)</td>
<td>1.7</td>
</tr>
<tr>
<td>D. Sodium Laureth Sulfate (Texapon NSO, BASF/Cognis)</td>
<td>32.0</td>
</tr>
<tr>
<td>E. Sodium Chloride</td>
<td>0.5</td>
</tr>
<tr>
<td>F. Cocamidopropyl Betaine (TEGO Betaine F 50, Evonik Industries AG)</td>
<td>8.0</td>
</tr>
<tr>
<td>G. PEG-18 Glyceryl Oleate/Cocoate (ANTIL 171, Evonik Industries AG)</td>
<td>2.5</td>
</tr>
<tr>
<td>H. Citric Acid</td>
<td>qs to pH 5.5</td>
</tr>
</tbody>
</table>

**Procedure:** Dissolve A into B and C into D. Add AB, E and F to CD. Adjust the pH with G to 5.5.

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### Formula 2. Test conditioning rinse formulation

<table>
<thead>
<tr>
<th>% w/w</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Silicone Quaternium-22 (and) Polyglyceryl-3 Caprate (and) Dipropylene Glycol (and) Cocamidopropyl Betaine (ABIL ME 45, Evonik Industries AG)</td>
<td>1.0</td>
</tr>
<tr>
<td>~ 0.3% active silicone quat</td>
<td></td>
</tr>
<tr>
<td>Cetrimonium Chloride (VARISOFT 300, Evonik Industries AG)</td>
<td>3.0</td>
</tr>
<tr>
<td>Ceteareth-25 (TEGO Acid C, Evonik Industries AG)</td>
<td>0.5</td>
</tr>
<tr>
<td>Cetyl Alcohol (TEGO Alkanol 16, Evonik Industries AG)</td>
<td>5.0</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>qs to pH 4.0</td>
</tr>
<tr>
<td>Water (aqua)</td>
<td>qs to 100.0</td>
</tr>
</tbody>
</table>

**Procedure:** Add all ingredients in water and heat to 75°C with adequate mixing. Homogenize at 75°C and cool while stirring. Adjust the pH with citric acid to 4.0.
Figure 3. Shampoo assessments: a) in wet conditions and b) in dry conditions

Figure 4. Conditioner assessments: a) in wet conditions and b) in dry conditions
combing forces after the shampoo application. Similar results from shampoo formulations also were obtained with deposition polymers like guar quat; tests on, e.g., Asian hair showed comparable performance (data not shown).

**Conditioning Results:**

**Conditioner**

Figures 4a and 4b show that the conditioning properties of the test conditioner with CTAC were significantly improved by the addition of the silicone quaternium-22 microemulsion, even at the low level of 0.3% active matter silicone. These sensory results were confirmed by technical combing force measurements. **Figure 6** illustrates the significant reduction of wet combing forces after combining the silicone quaternium-22 microemulsion with CTAC; see **Formula 2**, with only 0.5% active matter silicone. Also, results from the longer rinse times indicate the microemulsion formulation partly rinses off with just water. Accordingly, no build-up effects were found for the silicone quaternium-22 microemulsion, and shampooing removed the product from the hair. Similar conditioning results in rinse applications were observed with organic quats like behentrimonium chloride.

**Heat Protection**

Whether consumers use flat irons or curling irons to shape their hair, these treatments at around 180–220°C thermally damage hair’s keratinous structure. Specialty silicones can be used to protect hair from heat, which is explained by their film-forming properties and low thermal conductivity. These properties result in reduced heat flow from the source to the hair fiber, and subsequent reduced water loss from the hair. The denaturation temperature of hair as determined by DSC is therefore a significant parameter in assessing the degree of damage to keratin structures.

Virgin hair has a high phase transition (denaturation) temperature. The more damaged the hair is, e.g., by heat treatment, the lower the phase transition temperature. Thus, the efficacy of the silicone quaternium-22 microemulsion to protect hair from thermal damage was tested on virgin brown Caucasian hair using DSC.

**Method:** Flat hair tresses of a 0.5 cm width were pre-washed with a sodium laureth sulfate (SLES) solution and treated with the conditioning rinse (see description of panel assessment). Conditioner incorporating 3.3% silicone quaternium-22 microemulsion was compared with a standard conditioner for heat-protecting efficacy (see **Formula 2**). After rinsing with water and drying at room temperature and 50% relative humidity, the tresses were treated three or nine times, for 10 sec each, with a flat iron at approximately 190°C. Subsequently, the areas treated with the flat iron were prepared for DSC analysis. Non-thermally damaged hair tresses were used as reference.
Four hair tresses were used for each measurement.

Results: Figure 7 shows that the strongest decrease in denaturation temperature by thermal damage was induced in the CTAC-only treated tresses. By incorporating the silicone quaternium-22 microemulsion, the required temperature to denature hair became higher, indicating the hair was less damaged by the thermal treatment. A 70–80% improvement in heat protection was achieved, which could be ascribed to improved deposition of silicone quaternium-22 from the microemulsion.

Color Protection

Method: The color washfastness efficacy of the silicone quaternium-22 microemulsion was tested in a shampoo (see Formula 1). Hair swatches of bleached Caucasian hair were colored with a commercially available demi-
20 times according to a standard procedure and tested with a spectrophotometer. Color variations are expressed as DE values, calculated based on changes in brightness ($L^*$), and the red-green ($a^*$) and blue-yellow ($b^*$) shift. Lower differences in the color values before and after the shampoo treatments indicate better washfastness properties of the tested formulation.

**Results:** Figure 8 shows the color washfastness efficacy of the silicone quaternium-22 microemulsion by comparing the shampoo incorporating 3.3% of the ingredient (see **Formula 1**) against the same formulation without the microemulsion. After five wash cycles using the control formulation, significant change in hair color was observed; in general, a ΔE value greater than two is detectable by the human eye.

After 20 cycles, the color-protecting effect of the silicone quaternium-22 microemulsion was pronounced (see **Figure 9**). Swatch A is the hair swatch directly after dyeing, swatch B was treated 20 times with the control shampoo, and swatch C was treated 20 times with the shampoo containing the test microemulsion. The results show a clear improvement in the washfastness properties of shampoo formulations containing the silicone quaternium-22 microemulsion. The authors are currently investigating how these results can be explained.

By incorporating the silicone quaternium-22 microemulsion, hair was less damaged by thermal treatment.

**Application**

The described silicone quaternium-22 microemulsion is a low viscosity liquid, < 200 mPa·s, and is therefore easy to handle and process. It is soluble in water, cold processable and can be added to shampoo formulations by simple stirring during any production step. Fine, homogeneous distribution of the silicone quat enables clear shampoo formulations, thereby reducing the risk of buildup effects on hair fibers. In conditioning rinse formulations, it can be added to the water phase or to the final formulation to homogeneously distribute the silicone quaternium-22.

**Conclusions**

The described silicone quaternium-22 microemulsion is a multiple-benefit silicone conditioning agent. It was shown here to efficiently maintain and regenerate the soft look and feel of hair by providing highly efficient and intensive conditioning. The PEG-free microemulsion has a unique silicone structure that provides a high silicone character of balanced solubility with high substantivity to hair. Further, due to its low viscosity, processing is simple and the material can be added at any time during the process for even crystal clear formulations. Combine these benefits with its heat-protecting and improved color retention benefits, and the microemulsion is especially suited for hair care treatments targeting damaged, colored, bleached or straightened hair.

**References**

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