The quest for D₅ replacements

TONY O’LENICK*, VALERIO VERGANI
*Corresponding author
1.  Siltech LLC, Dacula, Ga, USA
2.  AKOTT SRL, Milano, Italy

There are a number of applications in which a dry skin feel is important. Cyclomethicone compounds are commonly used in cosmetic products to provide a solvent that feels dry on the skin. The INCI name Cyclomethicone refers to a family of cyclic dimethyl silicones that includes Cyclotetrasiloxane (D₄), Cyclopentasiloxane (D₅), and Cyclohexasiloxane (D₆), a family that has come under increased environmental scrutiny in recent years. Key areas where this family of materials is used include antiperspirants, colour cosmetics and as a base solvent to blend with fragrance oils and perfume oils. Cyclomethicone is a clear, odourless silicone. It leaves a silky-smooth feel when applied to the skin. Cyclomethicone compounds possess a cyclic structure rather than the chain structures of linear dimethyl silicones (dimethicone). Low heat of vaporization and low vapour pressure has led their use as cosmetic vehicles. In other words the feel correctly or incorrectly has been associated with volatility. However, the physical chemistry that results in the dry feel of cyclomethicone is a complex one. Volatility is but one aspect of the complex phenomenon that contributes to a dry feel in a solvent used in cosmetics. Other considerations that impact upon selection of a D₅ replacement include viscosity, surface tension reduction (which affects spreadability), flammability of the solvent, effects of the solvent on skin and cost. Clearly, a D₅ replacement that is flammable, defatting and expensive is unacceptable. Table 1 outlines the assumptions we used in evaluating the suitability of materials as D₅ replacements.

1.  Cosmetic products are used at ambient temperatures, making volatility measurements at high temperature irrelevant.
2.  Flammable materials are highly undesirable in cosmetic formulations.
3.  Dry feel is a consumer perceptible rather than a laboratory metric.

Table 1. Assumptions in evaluating D₅ replacements.

| VOLATILITY |
|------------------|------------------|
| **Table 2. Percent remaining at 20°C.** |
| **Hours** | **D₅** | **D₄** | **0.65 cst** | **1 cst** | **2 cst** |
| 0.0 | 100.0% | 100.0% | 100.0% | 100.0% |
| 1.0 | 99.4% | 97.1% | 40.6% | 86.5% | 99.9% |
| 2.0 | 98.7% | 94.0% | 0.0% | 74.0% | 99.7% |
| 3.0 | 98.1% | 91.0% | 0.0% | 61.6% | 99.5% |
| 4.5 | 96.1% | 82.2% | 0.0% | 23.3% | 98.9% |
| 7.5 | 93.5% | 50.1% | 0.0% | 12.4% | 98.7% |
| 24 | 86.1% | 35.3% | 0.0% | 0.0% | 94.9% |

Volatility is the ability of the compound being tested to evaporate under the temperatures at which the compound is used in formulation. For cosmetic products, this temperature is ambient (~25°C). It has generally been accepted that cyclomethicone compounds provided this feel because they evaporate quickly after helping to carry oils into the top layer of the epidermis. The ability to provide a product that (1) has the dry feel (2), is cyclomethicone free (3), is not capable of making cyclomethicone when exposed to catalyst and (4) is not flammable is a long felt need, un-satisfied need in the cosmetic industry. Volatility a contributor to dry feel, but more importantly, spreadability and low surface tension are major contributors to a dry feel. The assumption that volatility is required for dry feel is due to the fact that historically D₄ has a dry feel and is volatile. D₄ has replaced D₅ in formulations and consequently has been found acceptable in many cosmetic formulations as a D₄ replacement, but is it volatility that is primarily responsible for the dry feel? Personal care products are unique in that they are not applied at elevated temperatures as are many industrial products. It is therefore unreasonable to talk about volatility of a cosmetic solvent at elevated temperatures. The temperature of application is more typically 20°C than 200°C, yet we measure volatility at elevated temperatures. If one looks at a temperature of 20°C the volatility more closely resembles what might occur in topical cosmetic products. Table 2 shows the percentage of material remaining over a 24 hour period at 20°C for several silicone compounds commonly evaluated as replacements for D₅. 0.65 cst fluid (INCI: disiloxane) and 1 cst fluid (INCI: trisiloxane) are volatile if one looks for all of evaporation of all the material in 24 hours. D₄, D₅ and 2 cst fluids are not volatile. However, it is also clear that D₄ >> D₅ >> 2 cst. The problem with 0.65 cst silicone fluid is flammability. The data is presented graphically in Graph 2.
Since the cosmetic industry has accepted D₄ as a replacement for D₃ and it is clearly is much less volatile at temperatures that the consumer is likely to encounter, the dry feel must be caused by other factors.

**STRUCTURES AND PROPERTIES**

**Silicone nomenclature. Linear compounds**
For compounds that have only methyl groups, terminal groups are referred to as M units, internal groups are D units. The structure is given in Figure 1.

- MM: hexamethyldisiloxane - The average value of a is 0.
- MDM: octamethyltrisiloxane - The average value of a is 1
- MD2M: decamethyltetrasiloxane - The average value of a is 2

**Cyclic silicone compounds**
Cyclic compounds are named by the number of Si atoms in the ring.

The structure of D₅ is shown in Figure 2.

**Table 4. Properties of silicones.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Bp(°C)</th>
<th>MP(°C)</th>
<th>CAS</th>
<th>EINECS</th>
<th>Hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₄</td>
<td>175</td>
<td>17.5</td>
<td>556-67-2</td>
<td>209-136-7</td>
<td>Combustible</td>
</tr>
<tr>
<td>D₅</td>
<td>210</td>
<td>-38</td>
<td>69430-24-6</td>
<td>209-136-7</td>
<td>Combustible</td>
</tr>
<tr>
<td>MM</td>
<td>153</td>
<td>12</td>
<td>107-46-0</td>
<td>203-482-7</td>
<td>Flammable</td>
</tr>
<tr>
<td>MDM</td>
<td>194</td>
<td>-80</td>
<td>107-51-1</td>
<td>203-487-4</td>
<td>Combustible</td>
</tr>
<tr>
<td>MD2M</td>
<td>112</td>
<td>-70</td>
<td>141-63-9</td>
<td>205-482-0</td>
<td>Combustible</td>
</tr>
</tbody>
</table>

**Table 5. 0.65 cst Silicone Fluid (MM).**

**Table 6. D4.**

**Table 7. D5.**

**Table 8. 1 cst Silicone Fluid.**

**Table 9. 2 cst Silicone Fluid.**
One of the key properties that make silicone interesting in personal care products is its ability to lower surface tension. Fatty compounds have a surface tension of about 30 dynes/cm². Silicone compounds have a surface tension of about 20 dynes/cm². This is because the fatty compounds have primarily methylene groups (-CH₂-) at the interface, while silicones have methyl groups (-CH₃). Figure 2 shows the many methyl groups present on a silicone polymer. In fact, the compounds shown above all have surface tension values between 22 and 25 dynes/cm².

Silicone compounds that contain alkyl groups are amphiphilic, that is, they possess groups on the same molecule that would be insoluble in each other if mixed in pure form. Despite the fact that alkyl silicones are soluble [clear] in oils, they are surface active. Alkyl silicones when added to oils including triglycerides even at low concentrations, lower surface tension. This lower surface tension together with low viscosity, results in a dry skin feel because of efficient spreading. Graph 1 shows the effect of adding a C₂₂ alkyl silicone to soybean oil. As the concentration of alkyl silicone is increased, the oil forms a gel.

The dry effect achieved on the skin by the efficient reduction of surface tension of a natural oil using low concentrations of alkyl silicone is a patent pending, valuable formulation tool for the formulator. Not only has the approach of replacing D₅ with combination of natural oils and a small amount of alkyl silicone been used to replace D₅, the replacement is more green than D₅ (due to the fact that natural oils are present), not flammable, effective in many formulations, and is cost effective because the majority of the material used is a relatively inexpensive natural oil.

Silicone fluids are most often made by the equilibration of D₄ and MM. The equilibration refers to a catalytic polymerization process that works by a combination of ring-opening and condensation of siloxane bonds. The products of the reaction always include raw materials that are reacted. The excess raw materials can be stripped off in a subsequent step after catalyst is removed. The reaction is has been shown to be an equilibrium that can be established with acid, base or other catalyst (1). The reaction pathways are shown in Table 3. Silicone fluids are stripped of residual D₄ before sale, to low non-zero percent replacements for D₄ or D₅. concentrations. However, the fact that the reaction is reversible means that in formulation it does not matter how well the fluid is stripped, there is always a possibility for D₄ to be formed if acid, base or other catalysts are present. This observation should make the formulator cautious when using low molecular weight silicone polymers as Dimethicone compounds are often made using D₄ as a reactant. They have two methyl groups on each Si, as shown in Figure 4. Methicone compounds are not made using D₅ as a reactant. They are made by hydrosilylation an Methicone compounds conform to the structure in Figure 5 and have only one methyl group on each
repeating siloxane unit. Our patent pending approach to replacing D5 is achieved using a silicone that is a methicone not a dimethicone. The mechanism of action is similar to what was illustrated in Graph 1: the silicone lowers the surface tension of natural oils at low concentrations making the blend have similar properties to D5. Ethyl methicone (Silwax D-02) conforms to the generic structure shown in Figure 6.

Since it is a methicone, not a dimethicone, it is not made using D4. So it cannot re-equilibrate into D4 regardless of the formulation. Additionally, ethyl methicone chosen for low viscosity, spreadability and low surface tension in the organic chosen, have the following properties making them of interest when used in combination with esters or triglycerides as D5 replacements:
- Low surface Tension.
- Low concentration needed in oils to make silicone-like (siliphilic).
- Does not gel oil.
- Not flammable.
- Can be used alone or in properly selected ester.
- Effective at less than 5 percent in many oils.
- Cost effective

Antiperspirant application
Both formulations were found to be similar to the control in terms of cosmetic aesthetics. D5 has also been replaced in several other formulations shown on the right.

REFERENCES AND NOTES