Performance-Driven: New Silicone Copolymers

Experimenting with Dimethicone Copolyols for personal care products.

By David T. Floyd & Holger I. Leidreiter

It is hard to recall when silicones were not considered key ingredients for personal care products. In general, silicones are utilized in many new formulations on the market, allowing for flexibility and creativity by the formulator. Silicones can aid in the differentiation of products by influencing desirable aesthetic or functional characteristics.

While silicones have had a long-use history, \textsuperscript{1-4} Dimethicone Copolyols, recognized as safe, \textsuperscript{5} have not seen as wide an application profile as had been envisioned by the manufacturers of these raw materials. Although a number of marketed formulations have used Dimethicone Copolyols and their use has been widely proposed and discussed, \textsuperscript{6-12} formulators have often turned to linear fluids to achieve perceivable effects in formulations.

Experimental

While Dimethicone Copolyols are interesting polymers, from a structural point-of-view, they often fail to perform as expected in surfactant systems. Dimethicone Copolyols as a group can be soluble in ethanol, stearyl alcohol, and water; as a result, they can have applica-

Panelist preferences:

Determining foam quality and rinseability of formulations tested, Goldschmidt.
New Silicone Copolymers

tions in non-durable skin-care formulations where they could provide the necessary silicone properties, and then wash off. They can serve as lubricants in non-durable skin creams and lotions, as wetting agents in aerosol shaving lather, and as emollients in liquid conditioning soaps. Because of their solubility, many Dimethicone Copolyols could be useful in shampoo formulations requiring clarity.

When using levels ranging from 0.1 to 1.0 weight percent, Dimethicone Copolyols are sufficient in providing lubricating and wetting characteristics to skin lotions. Using levels from 1.0 to 5.0 percent improves (decreases) wetting time and adds lubrication and foam stability properties to shaving products. In hair styling mousse, levels ranging from 0.1 to 1.0 percent make products spread easily and reduce resin tack. Addition of a silicone glycol can lower the surface tension of a water-based mousse to 28 dynes/cm, the critical surface tension needed to wet virgin hair. These silicones have also found use in ethnic hair-care products, where they add non-greasy lubricating and softening qualities, act as humectants, and help reduce tackiness.

In skin preparations, Dimethicone Copolyols can enhance water-repellency and improve retention of humidity, due to strong interaction between the polyethylene glycol units and water. This is done without an adverse influence on the natural skin transpiration.

Like pure dimethicones, Dimethicone Copolyols are tasteless, oxidation-resistant, and have a low odor. These properties and their unique behavior as surfactants make Dimethicone Copolyols a very versatile and valuable group of personal-care chemicals. Dimethicone Copolyols are recognized as safe-for-use in cosmetics and, in fact, studies show their inclusion in anionic surfactant-based products can reduce both eye- and skin-irritation.

The essential feature of dimethicone copolymer surfactants, compared to purely organic surfactants, is the much higher surface activity provided to the dimethicone moiety. For this reason, dimethicone copolymer surfactants are more effective surface tension depressants and provide superior wetting and lubricating properties than hydrocarbon-based organic surfactants.

The outstanding surface activity of dimethicone copolymers is realized both in aqueous and organic solutions. Depending on overall polydimethylsiloxane/polyoxyalkylene ratio and on the polyethylene glycol/polypropylene glycol ratio in the polyether chains, the solubility behavior of dimethicone copolymers in water, alcohol, and other organic solvents can be varied over a wide range. Starting with a certain polydimethylsiloxane moiety, watersoluble copolymers, which are insoluble in mineral oil, are obtained by linking them to polyethers, predominantly composed of polyethylene glycol. On the other hand, copolymers, which contain polyethers consisting mainly of polypropylene glycol, are easily soluble in oils but less soluble in water. The base structure of Dimethicone Copolyol is shown in Figure 1.

It was quickly observed that while copolyols have very good surfactant qualities with corresponding cosmetic qualities, the laboratory’s observable effects are often overlooked by consumers. What seemed to be lacking was a good expression of the silicone nature of the molecule. Experiments were made to lengthen the siloxane backbone, but led to problems with viscosity and general incorporation into a cosmetic vehicle. The typical backbone length used in Dimethicone Copolyols, when related directly to linear silicones, show good surface effects on skin and hair. It was speculated that traditional pendant structures used to place the polyethers on the backbone may be masking the silicone nature of the polymer.

The siloxane to siloxane bonds in the backbone of silicone are quite flexible and allow for rotation. (See Figure 2.) The polyethers, since they are chains of repeating monomers, can also wrap around the siloxane backbone. Both of these motions could serve to mask the silicone nature of a polymer.

Goldschmidt has had previous successes with an α,ω silicone quaternary (Quaternium–80). This quaternary, in addition to a strong anti-static effect, also has a strong silicone nature. The α,ω structure is an end organo-modification to a siloxane chain. (See Figure 3.)
New Silicone Copolymers

A chain length similar to that of the silicone quaternary was selected after several trials varying the siloxane backbone. A polyether was selected with a moderate EO/PO length with a ratio of polyethylene glycol to polypropylene glycol of 40:60. The polyether used was based on several experiments that looked at surfactant surface tension reductions in sodium lauryl sulfate, thus giving the resultant polymer a good water dispersability that could be clearly solubilized in water with a minimum amount of the surfactant. (See Figure 4.) To evaluate the effects of the polymer on both hair and skin, in-vitro testing was conducted.

The copolyol was examined for its foam effects. A simple sodium lauryl sulfate/sodium laureth sulfate base was examined for the effects on flash foam, foam height, foam longevity, and foam density (weight). The foam was also evaluated for visual appearance. In all cases, the inclusion of the copolyol showed improvements in the foam generated. Figure 5 shows the effect on foam generated through a foam valve when the copolyol is included in the surfactant base.

Skin-Care

A simple hand-wash was developed. (See Table 1.) Twenty panelists were asked to alternate hand washing between the test and control bases. Panelists were not made aware of which formula was the test base.

Panelists were asked to comment on foam quality and rinseability of products tested. They assessed the feel of the products during use, and after rinsing and drying the hands. Panelist preferences are noted in Table 2.

### Table 1 Formulations Tested

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Control</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>50.9</td>
<td>50.4</td>
</tr>
<tr>
<td>Tetrasodium EDTA</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Ammonium Laureth Sulfate</td>
<td>25.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Ammonium Lauryl Sulfate</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Cocamidopropyl Betaine</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>PEG-18 Glyceryl Oleate/Cocoate</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Experimental Copolyol</td>
<td>—</td>
<td>0.5</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>Q.S.</td>
<td>Q.S.</td>
</tr>
<tr>
<td>% Total</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

### Table 2 Hand-Wash Preferences

<table>
<thead>
<tr>
<th>Control</th>
<th>Test</th>
<th>None</th>
</tr>
</thead>
<tbody>
<tr>
<td>Better Foam</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>Smooth/Silky/Soft</td>
<td>4</td>
<td>13</td>
</tr>
<tr>
<td>Clean Rinse</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Conditioning</td>
<td>3</td>
<td>13</td>
</tr>
</tbody>
</table>
Hair-Care

Hair evaluations were conducted first on tresses and then on a shampoo panel to correlate observations. For these studies, a simple shampoo base was developed. (See Table 3.)

The formulations were diluted to one part in 20 in de-ionized water. Tresses in triplicate were immersed in the solutions for 15 minutes under slight agitation. The tresses were removed, rinsed, and hung for a wet evaluation. Following the wet evaluation, the tresses were oven-dried at 40°C in an air circulation oven for three hours and re-evaluated. A total of 20 individuals evaluated the tresses. The results are presented in Table 4.

Two shampoo bases were given to 20 panelists. The panel was split with half receiving the control formulations, and the other half receiving the test formulations. The panel was reversed to correct for bias and the products re-evaluated. All panelists shampooed with each formula three times. Each panelist was instructed to daily shampoo their hair as they normally would and at the end of the shampooing, record their results. After trying both formulations, panelists were asked to select preferences for the formulations evaluated. Panelist responses were recorded and the results were tabulated. (See Table 5.)

It is interesting to note the test panelists observed the same results directionally as did the tress evaluators.

### Moisturization

Both the hand wash and shampoo panel offered comments concerning skin (hand) moisturizing and softening/smoothing. The copolymer was further evaluated for the effects of moisturization and softening/softening.

The moisturization study was conducted by the Institut Dr. Schrader in Germany using a modification of recognized techniques.22,23
A moisturizing effect of a cosmetic formulation is normally investigated by a long-term application study using a corneometer technique. This method determines the content of moisture in the skin. Because a skin cleansing formulation cannot be applied over a long period of time without causing further skin problems, the direct measurement of a long-term moisture effect is not possible for a skin-wash. A tool for indirect determination of a moisturizing effect is the measurement of the barrier function of the skin. The Transepidermal Water Loss (TEWL) is monitored by standard equipment (Tewameter TM 210) as the rate of water evaporation from the skin in [g/m² h].

In this test, the copolyol was investigated at a level of 4 percent in a formulation with 14 percent Sodium Laureth Sulfate (SLES). For comparison, a 14 percent SLES solution was applied. The high level of 4 percent of the copolymer was selected to achieve highly significant results.

The TEWL was measured before application, after four applications (two days), and after a total of five days application time. Each application was an enforced washing process for two minutes. The rate of water evaporation increases from measurement to measurement. This enforced damage of the skin barrier is reduced by the presence of the copolymer in the surfactant solution. (See Figure 6.) The length of the bar is the difference in TEWL between application and starting value. Control value of the untreated skin area showed a slight increase. This was due to environmental and climatic effects. Both test areas with and without the copolymer show an increase in TEWL. Taking into consideration the control area, the area with the copolymer is about 25 percent better than the pure SLES solution.

A direct moisturizing effect, of course, cannot be derived from this test procedure, but a reduced impact on the skin barrier function, shown by the application of the copolymer, should result in an increased amount of moisture remaining in the skin. This would support a moisturizing claim for skin-care applications.

**Skin Smoothing**

One of the major properties of a cosmetic formulation, beside its moisturizing effect, undoubtedly lies in the formulation’s ability to have a positive effect on the surface structure of the skin. Skin-feel is related to the condition of skin, including the overall smoothing effect. Modern optical, topometric methods provide a powerful tool to measure skin roughness. The copolymer was tested by the Fast Optical In-vivo Topometry of human Skin (FOITS) procedure. This method allows the researcher to scan the skin surface without contact in a high-resolution mode within a second. No replicas are needed. The skin observed has an area of 875 mm²; the resolution is 43 µm in horizontal direction and 4 µm in vertical direction.

In this test, the copolymer was investigated in a standard shower gel/liquid skin-wash formulation. It is known that pure surfactant solutions increase skin roughness significantly. PEG-7 Glyceryl Cocoate was used as a marker for improvement of skin-feel. Figure 7 shows the results obtained using the FOITS procedure. Again a relatively high-level of the test product (4 percent) was used to achieve a significant differentiation of the measurement. Test area for this application was the inner-side of the forearm. The image was taken before three applications of the shower gel. Four hours after the third application, a second image was made. Figure 7 shows the difference of roughness between both images. Two parameters, Ra and Rz, were evaluated. Ra indicates the fine structure of the skin profile; Rz represents the more coarse structure. The control value denotes those effects caused by climatic and other environmental impacts on the test subject. In this case, the skin smoothness of the untreated skin decreased during application. PEG-7 Glyceryl Cocoate (as an additive to a SLES-based skin-wash) provided improved skin smoothness compared with untreated skin. The formulation with the α,ω silicone polymer provided a result two to three times better than the PEG-7 Glyceryl Cocoate. Thus, the α,ω Dimethicone Copolyol investigated showed a good skin smoothing potential.
New Silicone Copolymers

Summary
A new Dimethicone Copolyol has been synthesized using an \( \alpha,\omega \) structure. From the results obtained in testing this polymer, it was concluded that the \( \alpha,\omega \) structure is not a compromise between the organic modification and the polysiloxane backbone, but a synergistic expression of the contribution of both chemistries. The new polymer developed should play a role in personal-care products, offering smoothness and moisturizing to skin; and glossing, moisturizing, combing, and conditioning for hair-care products. The \( \alpha,\omega \) modification offers new potential for polysiloxane polymers in personal-care products.

References

Figure 7 FOITS data

Relative changes of skin roughness parameters \( R_z \) and \( R_a \) before and after application in the untreated area (control) and two test formulations.

Figure 8

Skin Smoothness

relative difference to start value %

Untreated area
Standard (PEG-7 Glyceryl Cocoate)
Copolymer

Roughness parameters (according to DIN 4768)

-2
-1
0
1
2
3
4
5

Relative difference to start value %

-\( R_z \)
-\( R_a \)