NOVEL SILICONE THICKENING TECHNOLOGIES: DELIVERING THE APPROPRIATE RHEOLOGY PROFILE TO OPTIMIZE FORMULATION PERFORMANCE

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Summary

Viscosity is the most well-known expression of rheology and it is frequently used to monitor formulation stability over time and to optimize the sensory and performance attributes of personal care products.

Developments in organosilicone chemistry have led to new ingredients that can affect the rheology of formulations across a wide range of personal care applications. These new materials, alkylmethylsiloxane (AMS) waxes and silicone elastomers, provide a number of performance and sensory attributes. Depending on the product application and required benefits, formulating chemists can select the most appropriate materials from these two product categories.

Studies demonstrate that although the wax increases the consistency of water-in-oil systems, it does not negatively affect sensory performance.

Silicone elastomer technology provides a means of increasing the viscosity of volatile silicones without sacrificing their desirable silicone aesthetics.

The ingredients resulting from this patented technology allow other ingredients such as antiperspirant salts or mineral charges to be suspended in Cyclomethicone while providing a dry, velvety feel that is quite different from the silky feel of conventional silicones.

This paper reviews the impact of new organosilicone materials on rheological behavior as it relates to performance and sensory benefits. An understanding of the unique properties of these materials can help chemists meet new formulation challenges.

Riassunto

La viscosità è l’espressione più conosciuta della reologia e viene utilizzata sia per monitorare la stabilità nel tempo delle formulazioni che per ottimizzare le caratteristiche sensoriali attribuite ai prodotti topici.

Lo sviluppo della chimica degli organo-siliconi quali i polidimetilsilossani, ha ulteriormente arricchito le possibilità date al formulatore di migliorare l’accettabilità dei prodotti topici, aumentandone...
notevolmente la loro gradevolezza.
La tecnologia degli elastomeri siliconici fornisce nuovi mezzi per incrementare, ad esempio, la viscosità dei siliconi volatili senza sacrificare i loro effetti estetico-sensoriali. Così è ora possibile formulare deodoranti o antiperspiranti che donano alla pelle una sensazione setosa, risultano non grassi e non lasciano residui.
Questo articolo offre una panoramica dei nuovi organo-siliconi evidenziando sia le proprietà reologiche che i benefici effetti sensoriali che questa nuova famiglia chimica apporta a tutti i prodotti di uso topico. La piena comprensione di queste caratteristiche innovative aiuterà i chimici a formulare prodotti sempre più innovativi.
INTRODUCTION

Viscosity is the most well known expression of rheology and perhaps the most easy to observe. It is frequently used to monitor formulation stability over time, as well as to define the formulation profile for best delivery as a novel product form or from specialized packaging. Rheology has become increasingly important because an understanding of its parameters has allowed formulators to optimize the sensory and performance attributes of personal care products.

In antiperspirant and deodorant applications, viscosity control plays a significant role in improving application properties and facilitating stability, during both manufacturing and storage. In color cosmetics such as foundations, pigments present a challenge to formulators. They must be stabilized when packaged, and their delivery to the skin must be smooth and homogeneous. The simplest method for stabilizing pigments is to increase the formulation viscosity. However, this approach can lead to difficult spreading and uneven coverage by the pigments. Rheological additives allow pigment stabilization in the package, but a very fluid and smooth application on the skin. The appropriate rheology profile can deliver both benefits.

In general, polydimethylsiloxane (PDMS) materials exhibit Newtonian rheological behavior; that is, they become pseudoplastic with increasing polymer viscosity. The addition of functional groups on the siloxane backbone can modify this rheology profile. Alkyl groups of different chain lengths can be chemically substituted for methyl groups on the siloxane backbone. Varying degrees of substitution can result in wax-like materials with a range of melting points. When added to emulsions for foundation creams or sun care products, these waxes can alter rheology, providing improved product performance and stability.

The viscosity or PDMS can increased in two ways: by increasing the chain length in a linear manner with the addition of Si-O units, or by increasing chain length (and hence, molecular weight) and also employing a cross-linker. The latter approach results in significant rheology changes, allowing formulators to achieve novel formulations with unique sensory characteristics.

\[
\text{CH}_3 \quad \text{CH}_3 \\
(CH_3)_3 - \text{Si} - (\text{SiO})_x (\text{SiO})_y \text{Si} - (\text{CH}_3)_3 \\
\text{CH}_3 \quad (\text{CH}_2)_{30-45}\text{CH}_3
\]

**Fig. 1 Chemical Structure of C30-45 Alkylmethicone**

MATERIALS AND METHODS

The studies described in the paper were conducted using several materials supplied by Dow Corning Corporation. These products are part of the Silky Touch range, Silicone excipients for Pharmaceutical Topical Applications.

**Alkylmethysiloxanes (AMS)**

- INCI Name: C 30-45 Alkylmethicone (Dow Corning® ST-Wax 30)
  Melting Point: 70°C

**Silicone elastomer**

- INCI Name: Cyclomethicone (and) Dimethicone Cross Polymer; Blend of high molecular weight cross-linked silicone elastomer in Volatile Silicone (Dow Corning® ST-Elastomer 10).
  Blend Viscosity: 350,000 mm²/s¹.
The equipment and test methods used for various procedures can be summarized as follows:

**In vitro SPF measurements**
- Difley & Dobson method
- Equipment: Optimetrics 290 SPF analyzer
- Substrate: Transport tape manufactured by 3M

**Rheology measurements**
- Equipment: Carry-med Rheometer CSL at 25°C

**Sensory evaluation**
- Paired comparison
- Complete block experiment with 25 panelists
- Data treatment based on ANOVA non-parametric statistics (Wilcoxon and Kurskal-Wallis tests) and comparison test (general linear procedure: Tukey)

**Moisturisation**
- Corneometer Courage Khasaka

**RESULTS**

Alkylmethysiloxanes: Alkylmethysiloxane (AMS) materials are organo-modified silicones whose methyl groups have been partially replaced by alkyls of longer chain lengths 2,3. By varying the chain length of the silicone backbone and the alkyls, as well as the degree of substitution, it is possible to produce three classes of AMS:
1) Volatile fluids,
2) Nonvolatile fluids and
3) Waxes with a range of melting points (25°C to 70°C)

The most useful AMS waxes are those that combine significant effects on rheology with other functional benefits. For example, the addition of two percent of C30-45 Alkylmethicone, to a water-in-oil emulsion raises the In-Vitro SPF of the formulation. Table I shows how the addition of the high melting point AMS wax affects a prototype sun care formulation.

In color cosmetics formulations, this same wax can have a significant rheological effect on emulsions, particularly in water-in-oil or water-in-silicone emulsions. In this case, two percent is the optimum level required to achieve a bodying effect; The addition of the AMS wax gives a higher initial formulation viscosity, which is perceived as a difference in spreading characteristics and skin feel. The AMS wax provides the structural, matrix-building properties of the highest quality natural and synthetic waxes, combined with the rich, sensory aesthetics of silicone. The siloxane backbone of the material is responsible for its reduced waxy feel, and the high alkyl content imparts compatibility with a range of organic materials and otherwise incompatible ingredients.

The high melting points AMS wax can be used to make stable foundation creams with pigment

<table>
<thead>
<tr>
<th>Water-in-oil Emulsion</th>
<th>Viscosity ( cPs)</th>
<th>Thixotropy ( Pa/s )</th>
<th>In Vitro SPF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>7500</td>
<td>7353</td>
<td>9.9</td>
</tr>
<tr>
<td>2 % ST-Wax 30</td>
<td>22400</td>
<td>10310</td>
<td>17.1</td>
</tr>
</tbody>
</table>
levels up to 15 percent. These creams have excellent spreading and payout. Table II illustrates a formulation of this type.

In addition to the impact on formulation rheology, high melting point wax alkylmethyilsiloxane can also impart moisturizing properties to a formulation. Due to its high content in organic fatty chains, Dow Corning® ST-wax 30 has occlusive properties equivalent to Petrolatum-making it a good candidate for moisturising preparation. After 6 hours, a formulation containing 2% of AMS wax has the same impact on moisturisation, measured with a corneometer than the same formulation containing 10% of petrolatum.

**Table II**

*Foundation-cream formulation with high melting point AMS wax.*

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Phase A</strong></td>
<td></td>
</tr>
<tr>
<td>Cyclomethicone (and )</td>
<td>11.0 %</td>
</tr>
<tr>
<td>Dimethiconol</td>
<td></td>
</tr>
<tr>
<td>Pigment Blend</td>
<td>16.6 %</td>
</tr>
<tr>
<td>C30-40 Alkylmethicone</td>
<td>2.0 %</td>
</tr>
<tr>
<td>Cyclomethicone (and )</td>
<td>10.0 %</td>
</tr>
<tr>
<td>Dimethicone Copolyol</td>
<td></td>
</tr>
<tr>
<td><strong>Phase B</strong></td>
<td></td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>1.0 %</td>
</tr>
<tr>
<td>Polysorbate 20</td>
<td>0.5 %</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>58.9 %</td>
</tr>
</tbody>
</table>

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**Fig. 2 Effect of AMS wax on formulation viscosity**
Novel silicone thickening technologies: delivering the appropriate rheology profile

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Phase A</th>
<th>Phase B</th>
<th>Phase C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petrolatum</td>
<td>10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C30-45 Alkyl Methicone</td>
<td>2%</td>
<td>5%</td>
<td></td>
</tr>
<tr>
<td>Mineral oil</td>
<td>15%</td>
<td>20%</td>
<td>20%</td>
</tr>
<tr>
<td>Laurylmethicone Copolyol</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
</tr>
<tr>
<td>Glycerin</td>
<td>3%</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>Water</td>
<td>To 100%</td>
<td>To 100%</td>
<td>To 100%</td>
</tr>
<tr>
<td>Viscosity</td>
<td>81,000 mm²/s⁻¹</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table III**

Formulations used in the moisturisation study illustrated in figure 3.

**Silicone elastomers**

In this category of materials, rheology change results from increasing the molecular weight of the material, both by adding Si-O units and by cross-linking. The new technology is based on a cross-linked elastomeric silicone made with cyclomethicone in-situ. Figure 3 is a schematic representation of the synthesis of a silicone elastomer.

From a formulating perspective, the most important property of these materials is their ability to thicken cyclomethicone. This effect results in improved stability and viscosity control of products where cyclomethicone is used as a vehicle. In addition, the desirable aesthetics of the cyclomethicone are maintained. Thickening systems of this type have additional benefits over conventional thickening ingredients such as organic thickeners, clay, silica and silicone gums. Compared with organic materials, the effects of the silicone elastomer blends are perceived as drier and less oily, and as having a well-bodied feel. Silicone elastomers eliminate the poor skin feel associated with silica, which can impart drag and a gritty feel. In the case of

![Fig. 3 Synthesis of a silicone elastomer](image)
Silicone gums, high levels are required to achieve the same level of thickening associated with silicone elastomers. At these levels, the silicone gum can make the product heavy and difficult to formulate. Figure 4 compares the effect of shear stress on viscosity in cyclomethicone thickened with silicone elastomer and two other materials.

Silicone elastomers can absorb large volumes of cyclomethicone or low molecular weight silicone without syneresis. The interaction within elastomer chains provides thickening with a yield value. Figure 5 illustrates this thickening effect.

**Figure 4** Viscosity vs. shear stress of cyclomethicone and various thickeners.

**Figure 5** Schematic representation of the thickening effect of a silicone elastomer.
Because of the open nature of the elastomer network, small molecules can escape easily from it. Consequently, the effect of the silicone elastomer on volatility is minimal. For example, in a formulation thickened with silicone elastomer, the initial feel upon application is still that of volatile silicone, which disappears quickly to leave a dry, velvety feel.

Depending on elastomer concentration, these blends display a range of viscous and elastic properties. Figure 6 shows the effect of elastomer concentration on viscosity. In addition to its thickening ability, the silicone elastomer provides a unique sensory profile. Figure 7 summarizes the results of sensory panel testing.

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**Fig. 6** The effect of silicone elastomer concentration on viscosity.

**Fig. 7** Comparison of sensory of 2 w/o creams containing silicone elastomer and silicone gum.---: Significant difference at 95% confidence level
The thickening property of silicone elastomers can be used to formulate thicker water-in-silicone emulsions, as well as anhydrous cyclomethicone gels specifically for antiperspirant and deodorant applications. Figure 8 illustrates the viscosity effect of two concentrations of silicone elastomer on a base antiperspirant gel.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Phase A</th>
<th>Phase B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclomethicone (and) Dimethicone Crosspolymer</td>
<td>15 %</td>
<td></td>
</tr>
<tr>
<td>Cyclomethicone (and) Dimethiconol</td>
<td></td>
<td>15 %</td>
</tr>
<tr>
<td>Cyclomethicone</td>
<td>10 %</td>
<td>10 %</td>
</tr>
<tr>
<td>Laurylmethicone</td>
<td>2 %</td>
<td>2 %</td>
</tr>
<tr>
<td>Copolyol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>1 %</td>
<td>1 %</td>
</tr>
<tr>
<td>Glycerin</td>
<td>3 %</td>
<td>3 %</td>
</tr>
<tr>
<td>Water</td>
<td>To 100 %</td>
<td>To 100 %</td>
</tr>
<tr>
<td>Viscosity</td>
<td>106,000 mm²/s⁻¹</td>
<td>54,000 mm²/s⁻¹</td>
</tr>
</tbody>
</table>

**Fig. 8** Concentration effect of elastomeric gels on antiperspirant gels.
In summary, silicone elastomer blends provide a new approach for thickening cyclomethicone and other silicone fluids. They are more efficient and effective than other thickeners, and they provide unique aesthetics that cannot be achieved with other silicones.

In addition to its impact on formulation rheology, Silicone Elastomer have also the ability to suspend essential oils resulting in new delivery form for aromatherapy products combining sensory and olfactory sensations.

Following is a formulation of such a perfumed gel:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dow Corning ST-Cyclomethicone 5-NF</td>
<td>5.0%</td>
</tr>
<tr>
<td>Essential oil (Lavendula, Parsley) 11</td>
<td>2.0%</td>
</tr>
<tr>
<td>Coloring pigment</td>
<td>0.8%</td>
</tr>
<tr>
<td>Dow Corning® ST-Elastomer 10</td>
<td>92.2%</td>
</tr>
</tbody>
</table>

These gels have been submitted to a panel of employees to evaluate how this new form of fragrance delivery would be perceived. Following are the comments:

- Very silky skin feel
- Easy to spread
- Non Greasy

**CONCLUSION**

The appropriate AMS or silicone elastomer ingredients can help formulators achieve the necessary rheological properties for optimal formulation performance in sun care, skin care, color cosmetic and AP/deo applications. At the same time, these ingredients can maintain or enhance the positive sensory parameters associated with silicones. Additional benefits such as skin moisturisation and new formulation concept for fragrance are 2 others benefits from these rheological additives.
References


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