New Formulation Possibilities Offered by Silicone Copolyols

Make stable, water-in-silicone and w/o/w emulsion products having a wide range of possible flow characteristics

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Using silicones in personal-care products can improve the aesthetic performance of formulations. For example, silicones (in particular, cyclomethicone and dimethicone) were essential to the development of dry antiperspirants, conditioning shampoos, and “oil-free” skin-care products. The aesthetic benefits come from the unique chemical and physical properties that silicones possess and conventional, hydrocarbon-based materials do not. However, these same unique chemical and physical properties can mean that special formulation techniques are needed to assure the compatibility and stability of silicones in personal-care formulations.

Siloxane copolymer emulsifiers: One approach to formulating with silicones in personal-care products has been to use emulsifiers specifically designed for this purpose. In these cases, emulsifiers have been developed based on siloxane copolymers. Polyethylene-oxide-based hydrophilic groups are added to polydimethylsiloxane hydrophobic polymers (dimethicone copolyols). Water-in-cyclomethicone emulsion formulations using this technology are commonly found in antiperspirant, skin-care and color-cosmetic formulations.

The insights gained from the creation of water-in-silicone (w/s) emulsifiers have been used to design new water-in-oil (w/o) emulsifiers with broader utility. The new emulsifiers allow w/o formulations to incorporate a greater range of oils or emollients in the external phase. This was accomplished by adding hydrocarbon chains (for greater oil solubility) to silicone polyether polymers (for example, laurylmethicone copolyol).

The advantages of the silicones over conventional hydrocarbon chemistry were used to create siloxane polymer w/o emulsifiers that provide more benefits than conventional w/o emulsifiers. For instance, w/o emulsions using siloxane polymer emulsifiers can be prepared by cold-processing techniques. Improved aesthetics resulted from the elimination of high-melt-point waxes (previously added for stability). These emulsifiers are finding uses in leading skin-care and color-cosmetic formulations where the advantages (such as improved pigment spreading) of w/o systems are sought.

To keep pace with the new applications and uses of siloxane-based emulsifiers (hereafter referred to as silicone copolyols), we studied how these materials stabilize w/o and w/s emulsions to gain a better understanding of the surface chemical mechanism. The highlights of this study, presented here, are used to suggest new formulating possibilities, such as multiple-phase emulsions.

Interface Behavior

Silicone copolyols exhibit high surface activity and other diverse advantages compared to conventional emulsifiers. The reasons for these characteristics are found in the structural properties associated with the ternary molecular configuration of the polymer emulsifier molecule.

The general structure of a silicone copolyol emulsifier is shown here:

\[
\text{Alkyl side chain} \quad 1 \quad \text{Me}_3\text{SiO(Me}_2\text{SiO)}(\text{MeSiO}),(\text{MeSiO}),\text{SiMe}, \quad 1 \quad \text{polyether side chain}
\]
Formula 1. Day cream

A. Laurylmethicone copolyol 2.00% w/w
Avocado oil 5.00
Tocopheryl acetate 2.00
Mineral oil 10.00
Sunflower oil 3.00
Capric/caprylic triglyceride 5.00

B. Electrolyte
Glycerin 4.00
Water, demin 68.00

Procedure: Heat A and B separately to 75°C. Add B to A at 75°C, stirring intensively in a heated vessel, blade stirrer; circulation speed = 3.115 m/s. Cool to 25°C, stirring intensively at the same speed.

Formula 2. Antiperspirant cream

A. Dimethicone copolyol (and) cyclomethicone 10.00%
Cyclomethicone 15.00

B. Glycerin 4.00
Aluminum chlorohydrate 20.00
Water, demin 51.00

Procedure: Heat A and B separately to 75°C. Add B to A at 75°C, stirring intensively in a heated vessel, blade stirrer; circulation speed = 3.115 m/s. Cool to 25°C, stirring intensively at the same speed.

The siloxane molecular weight \((x+y+z)\), alkyl/polyether ratio \((y/z)\), and the molecular weights of the alkyl and polyether side chains are the molecular variables that can be adjusted for optimized emulsifier performance.

Silicone copolys function similarly to traditional organic emulsifiers. A silicone copolyol molecule is anchored at the water/oil phase boundary -- in the water phase by its hydrophilic polyether fraction and in the oil phase by the lipophilic alkyl group. In contrast to hydrocarbon-based emulsifiers, however, the silicone copolys possess a highly flexible siloxane backbone between the two anchor groups. Because of this flexible behavior, the siloxane backbone can adapt to interface geometries very easily, without creating steric hindrances.

Even silicone emulsifiers with high molecular weights can remain fluid, unlike hydrocarbon emulsifiers with higher molecular weights. This inherent property creates very stable visco-elastic films at the water/oil interface. Thus, silicone emulsifiers are very efficient; lower concentrations of silicone emulsifiers are needed than hydrocarbon ones to obtain emulsions with excellent stability.

**Adsorption at the o/w interface:** To get a reasonably accurate assessment of an emulsifier's performance, you first have to test its adsorption capability at the oil/water interface. Studies reported in the literature show that diagrams of interfacial tension plotted against log concentration provide a good basis for determining the adsorption efficiency. In these studies, when the interfacial tension is reduced by 20 mN/m, the oil/water interface is already saturated at emulsifier concentrations from 84 to 99.9%. For this reason, you should measure the negative logarithm of the emulsifier concentration necessary to reduce the interfacial tension by 20 mN/m.

\[
- \log C_{(\alpha y = 20)} = p C_{20}
\]
tional properties silicone copolyol emulsifiers add to w/o systems is the possibility to modify their viscosity by changing either the oil polarity or the phase-volume ratio.

This is done based on the general viscosity equation for emulsions, namely:

$$\ln \frac{\eta}{\eta_o} = A / HLB_e \cdot C_e \cdot \varphi \cdot B$$

where $\eta$ = viscosity of the emulsion
$\eta_o$ = viscosity of the continuous oil phase
$C_e$ = emulsifier concentration
$HLB_e$ = HLB value of the emulsifier system used
$\varphi$ = concentration of the water phase

**Phase-volume adjustment of an emulsion:** We use Formula 3 to discuss the possibilities presented by adjusting the phase-volume ratio, as well as the problems that may occur, are discussed using this example. The flow behavior and stability behavior of this substance were tested in the oil phase range of 15 to 35%.

A cone-plate rheometer (Carrimed CSL 500) took rheological measurements on each emulsion in this phase-volume range 24 hours after manufacture, at 25°C. The yield point of each emulsion was determined by shear stress controlled yield tests; the storage module ($G'$) and the loss module ($G''$) \( G'/G'' \) as well as the relationship $G'/G''$ was determined by oscillation tests.

The analysis of the yield point ($t_y$) reveals a direct correlation with the amount of oil phase employed ($\varphi_o$). This relationship can be expressed by the equation below (Figure 3):

$$t_y = A \cdot \exp (\varphi_o \cdot B)$$

$t_y$ = yield point
$\varphi_o$ = concentration of the oil phase
$A,B$ = system-specific material constants

This mathematical relationship retains its validity even when you replace $\varphi_o$ with the modules $G'$ or $G''$ or with other rheorheological parameters (Figures 4 and 5).

The data obtained for a 15% oil-phase fraction are too low, however, and are not congruent with the mathematical relationship described above. The reasons for this discrepancy can be found in the sample’s stability behavior. After only a few days’ storage at room temperature, distinct water separation is observed; obviously, coalescence has taken place, resulting in increased droplet size. Quite naturally, the values for the module of elasticity, $G'$, have decreased as a result.

If you look at the storage stability of the emulsion made with Formula 3 at various storage temperatures (Table VI), you see that, in this case as well, there is a clear-cut relationship between the chosen phase-volume ratio and emulsion stability.

**Oil Phase Concentration and Stability**

It is also interesting to note that there is a direct relation-
Table VI. Stability of Formula 3 relative to the oil phase concentration

<table>
<thead>
<tr>
<th>Storage conditions</th>
<th>Oil phase conc. [% w/w]</th>
<th>15.00</th>
<th>17.50</th>
<th>20.00</th>
<th>22.50</th>
<th>25.00</th>
<th>27.50</th>
<th>30.00</th>
<th>32.50</th>
<th>35.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>5°C, 2 weeks</td>
<td>trace water</td>
<td>OK</td>
<td></td>
<td>OK</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25°C, 6mo</td>
<td>10% water</td>
<td>OK</td>
<td></td>
<td>OK</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40°C, 2 weeks</td>
<td>3% water</td>
<td>trace water</td>
<td>OK</td>
<td></td>
<td>OK</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40°C, 4 weeks</td>
<td>17% water</td>
<td>2% water</td>
<td>1% water</td>
<td>OK</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50°C, 1 week</td>
<td>7% water</td>
<td>5% water</td>
<td>1% water</td>
<td>trace water</td>
<td>OK</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table VII. Stability of Formula 2 relative to the oil phase (cyclomethicone) concentration

<table>
<thead>
<tr>
<th>Storage conditions</th>
<th>Oil phase conc. [%w/w]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.00</td>
</tr>
<tr>
<td>5°C, 4 weeks</td>
<td>OK</td>
</tr>
<tr>
<td>25°C, 6mo</td>
<td>OK</td>
</tr>
<tr>
<td>40°C, 1 week</td>
<td>OK</td>
</tr>
<tr>
<td>40°C, 6mo</td>
<td>4/W(20%)OK</td>
</tr>
<tr>
<td>50°C, 1 week</td>
<td>OK</td>
</tr>
</tbody>
</table>

In this case as well, the stability line -- determined after 1 week of storage at 40°C -- intersects the critical flow range at tan δ = 1 (Figure 8.) Therefore, one can assume that stable pump deodorant formulations of extremely low viscosity, for example, can be developed with this method.

It is not all that easy to achieve a correct adjustment of viscosity for extremely thin, stable systems. The viscosity of the emulsion also changes in accordance with the following equation:

$$ \eta = A \cdot \exp(\varphi_{oil} B) $$

where

- $\eta$ = emulsion viscosity
- $\varphi_{oil} = $ concentration of cyclomethicone
- $A, B$ = material constants

Polyol-in-Silicone Emulsions

Added in small amounts, polyols have quite a positive effect on w/o emulsions based on conventional emulsifiers of low molecular weight. Larger amounts of polyols, by contrast, have a disruptive effect. Frequently, decomposition phenomena are already observable during the manufacture of polyol-in-oil emulsions based on hydrocarbon emulsifiers. Emulsions of this kind exhibit storage stability of only a few days at best.

A totally different situation occurs when silicone emulsifiers are used. Here, very stable emulsions with any desired flowability can be achieved by varying the phase-volume ratio.

These emulsions, like all emulsions based on silicone copolymers, can be manufactured without a great mixing effort. However, as with any emulsion system, changing the mixing intensity can cause substantial shifts in the phase-volume ratio.
Table IV. Impact of MgCl₂ concentration on interfacial tension

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>0.70%</th>
<th>1.40%</th>
<th>2.40%</th>
<th>5.00%</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>1.04</td>
<td>0.82</td>
<td>0.95</td>
<td>1.11</td>
</tr>
<tr>
<td>50</td>
<td>0.75</td>
<td>0.66</td>
<td>0.81</td>
<td>0.75</td>
</tr>
<tr>
<td>45</td>
<td>0.74</td>
<td>0.48</td>
<td>0.52</td>
<td>0.50</td>
</tr>
<tr>
<td>40</td>
<td>0.62</td>
<td>0.45</td>
<td>0.52</td>
<td>0.44</td>
</tr>
<tr>
<td>35</td>
<td>0.60</td>
<td>0.37</td>
<td>0.51</td>
<td>0.44</td>
</tr>
<tr>
<td>30</td>
<td>0.65</td>
<td>0.37</td>
<td>0.41</td>
<td>0.55</td>
</tr>
<tr>
<td>25</td>
<td>0.66</td>
<td>0.37</td>
<td>0.32</td>
<td>0.55</td>
</tr>
<tr>
<td>20</td>
<td>0.55</td>
<td>0.37</td>
<td>0.29</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Table V. Impact of various electrolytes at 0.70% concentration on interfacial tension

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>MgSO₄</th>
<th>NaCl</th>
<th>KCl</th>
<th>MgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>0.63</td>
<td>0.63</td>
<td>1.08</td>
<td>1.04</td>
</tr>
<tr>
<td>50</td>
<td>0.40</td>
<td>0.49</td>
<td>0.88</td>
<td>0.75</td>
</tr>
<tr>
<td>45</td>
<td>0.32</td>
<td>0.45</td>
<td>0.62</td>
<td>0.74</td>
</tr>
<tr>
<td>40</td>
<td>0.31</td>
<td>0.41</td>
<td>0.63</td>
<td>0.62</td>
</tr>
<tr>
<td>35</td>
<td>0.31</td>
<td>0.38</td>
<td>0.58</td>
<td>0.60</td>
</tr>
<tr>
<td>30</td>
<td>0.33</td>
<td>0.36</td>
<td>0.51</td>
<td>0.65</td>
</tr>
<tr>
<td>25</td>
<td>0.33</td>
<td>0.36</td>
<td>0.50</td>
<td>0.66</td>
</tr>
<tr>
<td>20</td>
<td>0.33</td>
<td>0.34</td>
<td>0.49</td>
<td>0.55</td>
</tr>
</tbody>
</table>

If you compare the efficiency of the interface adsorption exhibited by laurylmethicone copolyol (MW ~ 25,000) with that of commonly used w/o emulsifiers, such as sorbitan oleate (MW ~ 400) or polyglycerin-3 diisostearate (MW ~ 700), on the mineral oil/water model, you see that laurylmethicone copolyol is distinctly superior to the other emulsifiers (Figure 1, Table I).

If you then compare the adsorption efficiency of laurylmethicone copolyol and polyglycerin-3 diisostearate on a real interface consisting of an oil and a water phase (with 1% NaCl) -- as in Formula 1 -- you obtain the same interface adsorption efficiency (Figure 2). On the basis of this behavior, therefore, you can see that silicone copolyls are highly effective even at low concentrations.

Interfacial viscosity: By carrying out coalescence tests with droplets at the oil/water interface, according to the method described by Gillespie et al., we determined that silicone copolyls create interfacial films of high viscosity as well as high adsorption efficiency.

As with conventional emulsifiers, adding electrolytes to the water phase affects interfacial viscosity when silicone copolyls are used. For personal-care products, chlorides or sulfates of sodium, potassium or magnesium are preferred for their physiological compatibility.

The effect of these salts depends greatly on the concentration and polarity of the particular oil phase used. Both below and above the optimal dosage, their effect may vary greatly, as has been shown by interfacial tension studies using NaCl, KCl, MgCl₂, MgSO₄ and Na₂SO₄ in Formula 1 (Tables II through V). The trials discussed here show clearly that the impact of inorganic electrolytes depends on the type and amount of electrolyte used.

It is not surprising, therefore, that large amounts of aluminum chlorohydrate can be worked into w/s emulsions with certain types of silicone copolyls, as in Formula 2.

Viscosity Adjustment of w/o Emulsions

The viscosity of w/o emulsions can be regulated by other techniques. The most common method uses waxes to thicken the continuous, oil phase. It is very easy to use too much wax, however, which lessens the emulsion’s spreadability and can make it feel less pleasant on the skin.

A more elegant technique for regulating viscosity is adjusting the phase-volume ratio. One of the most excep-
Multiple Emulsions

The most common technique for manufacturing multiple emulsions is the two-pot method, in which a water phase plus an appropriate emulsifier is converted into a multiple w/o/w emulsion via the addition of w/o emulsion.

A second method converts an emulsified mixture (with an oil phase and a water phase) into a multiple w/o/w emulsion using a single-pot process. Once the emulsifiers are dissolved in the oil phase, this is combined with the water phase while stirring. For a formulator to use this process, the oil phase must be viscous and/or have a high interfacial viscosity. Also needed is a small emulsifier fraction, soluble only in the oil phase, that has w/o emulsifying properties.

**Using silicone copolyol emulsifiers:** Interface studies conducted with silicone copolyls at mineral oil/water and silicone oil/water interfaces reveal a highly pronounced interfacial viscosity that permits the formation of in-situ w/o/w emulsions.

The high interfacial viscosity not only stabilizes the interface, it also affects interfacial vibration behavior. Increasing interfacial viscosity changes the wave number (2/[1/m]) at the interface. The silicone copolyol concentration can be varied to give an interfacial viscosity that, under certain mixing conditions, creates a Rayleigh-Taylor instability. This Rayleigh-Taylor instability can be identified by the projection of fingerlike structures from the heavier into the lighter phase at a certain defined vibration at the interface. At the tips of these fingerlike structures, droplets break off. The extent to which these droplets are stable in the lighter phase depends primarily on the presence of sufficient amounts of an emulsifier system in this oil phase. If the water droplets in the oil phase possess adequate stability, in-situ multiple emulsions are produced.

![Figure 9. Microphotograph of typical w/o/w multiple emulsion using silicone copolyol emulsifiers](image)

**Formula 5**

A. Sorbitan stearate 6.75%
Laurylmethicone copolyol 0.75
Mineral oil 25.00
B. Water, demin 67.30
C. Phenoxethanol (and) methylparaben (and) butylparaben (and) ethylparaben (and) propylparaben (Phenonip)(Nipa) 0.20

Procedure: Heat A and B to 80°C. Add A to B and homogenize 1 min. Cool to 25°C stirring. Add C at 25°C.

The results obtained via interface analysis were tested on Formula 5, which is based on a conventional emulsifier system that can create stable o/w gel networks. To adjust the interfacial viscosity, a laurylmethicone copolyol was employed.

Microscopic analysis has shown that all the emulsions listed here are 100% w/o/w. The microphotograph (Figure 9) is characteristic for all w/o/w emulsions produced using silicone copolyls.

**Stability:** Surprisingly, these multiple w/o/w emulsions show excellent long-term stability from -18°C to 45°C. The lack of stability at 50°C can be corrected completely by the addition of hydrocolloids -- such as xanthan gum and, in particular, carbomer -- without compromising the 100% multiple w/o/w character.

Moreover, additives in the water phase -- such as propylene glycol, which often has a destabilizing effect on w/o/w emulsions--do not exhibit any negative impact on emulsion stability and the yield of multiple droplets in the systems being discussed here. Here again, a 100% w/o/w yield is obtained.

**Summary**

Silicone copolyls differ from traditional emulsifiers by having a flexible ternary polymer structure. Employing silicone copolyls allows formation of stable polyol-in-oil, polyol-in-silicone and even multiple emulsions. Moreover, larger amounts of water-soluble active substances can be used in water-in-oil emulsions without lessening storage stability. This opens up possibilities for the development of antiperspirants based on w/o or w/s emulsions. By varying the phase-volume ratio between the oil and the water phases, moreover, emulsion viscosity and emulsion rheology may be adjusted to almost any desired values.

**References**

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