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Science for Formulators

This is the third* of a series of articles in a new approach to providing science to formulators. The concept is to provide the underlying science and to present it with formulation tips that make the information useful. Happy reading!

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Why use silicones in Personal Care products Part 3 - Oil soluble silicones polymers

KEYWORDS: Silicone, dimethicone, formulation, hair care.

Abstract This is the third of three articles on the use of different types of silicone polymers in personal care formulations. The question "Why Use Silicones in Personal Care Products?" is an important question all formulators need to consider. The fact that silicone polymers have been made commercially available that are soluble in other silicone polymers, soluble in water and soluble in oil makes these polymers of use in almost all formulations. The fact that different members of the family of compounds can perform differently in each phase makes proper selection and optimization a requirement. Properly formulated personal care formulations are like fine gourmet meals in which proper choice for the silicone polymers is to function as the spice of the meal, not the meat or potatoes. These versatile polymers need to be used at low concentrations to provide formulations that cannot achieve the overall effect without them. The first article in the series dealt with silicone polymers that contained no functional groups to alter the solubility. Our second article dealt with water soluble silicone surfactants that provide functional properties in aqueous phases. This article will deal with silicone polymers that contain oil soluble groups.

INTRODUCTION

Silicone Polymers are chosen for formulation to fulfill a basic need that cannot be achieved using other chemistries. Silicone polymers have a handful of salient properties that make them value able in formulation. They are outlined in the Silicone Attributes box.

The formulator must first decide which of these properties is required in a given formulation then evaluate the proper type of silicone.

We suggest minimally disruptive formulation technique to evaluate several silicone polymers in formulation. This powerful approach makes changes to formulations in which the silicone is present in low concentrations with other silicone polymers to evaluate each in an established chassis, allowing for fine tuning of the silicone polymer for the effect desired by the formulator.

Alkyl dimethicone polymers are amphiphilic materials that contain an oil soluble group and a water soluble group that would each be insoluble in the other if not on the same silicone polymer.

Silicone Attributes

A properly closed silicone polymer can provide the following attributes to formulations;

1. Lowering surface tension to around 25 dynes/cm
2. Providing unique skin feel, cushion and playtime
3. Providing unique solubilities (are soluble in silicone, oil, water and fluoro compounds)
4. Can provide emulsification with unique aesthetics (especially invert emulsions)
5. Provide film/formation
6. Provide water resistance
7. Provide foaming for non-traditional formulations

Product	"a" D units	"b" D ^o Units	"m" Alkyl
Alkyl 2-1	0	4	25
Alkyl 2-2	32	8	17
Alkyl 2-3	12	12	17
Alkyl 2-4	20	10	25

Table 1. Representative Alkyl Dimethicone Polymers.

Alkyl dimethicone polymers date back to the 1950's (4), but the optimization of their use in personal care products is far more recent (5).

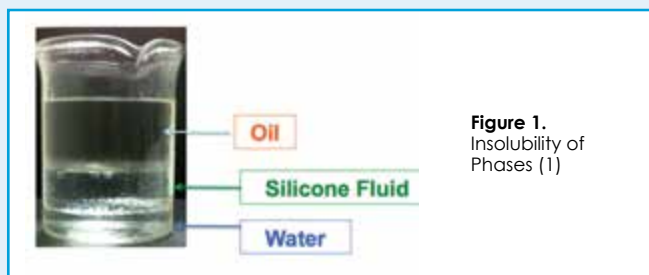


Figure 1. Insolubility of Phases (1)

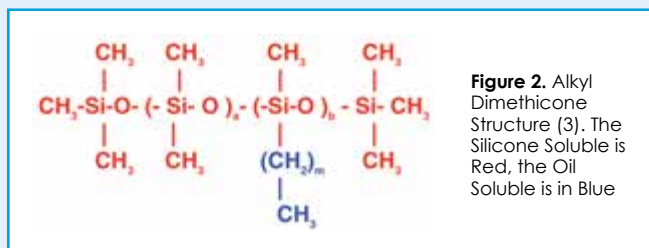


Figure 2. Alkyl Dimethicone Structure (3). The Silicone Soluble is Red, the Oil Soluble is in Blue

Melt Point

As the number of carbon atoms in the alkyl group increases the melt point increases as shown in Table 3. Alkyl dimethicone compounds having less than 18 carbon atoms in the alkyl chain are liquid at ambient temperatures. Those with more than 18 carbon atoms in their alkyl chain are solids. The higher the number of carbon atoms, the higher the melting point.

Formulation Implications

Liquid alkyl dimethicone are used in as additives for polar oils (esters primarily) provide a unique alteration in the aesthetics. Polar oils spread better and have a dryer feel as a consequence of a thinner lower surface tension coating on the skin or hair.

- Play time
- Skin feel
- Alter skin properties

What distinguishes these polymers from dimethicone polymers is the fact that these materials have an oil loving group in them. It must be clearly understood that water, oil, silicone and furor compounds that have only one group present on them will not be soluble in the others. Figure 1 shows that each of oil, water and silicone are insoluble and separate into three distinct effects.

Product	Water	Mineral Oil	Mineral Spirits	Propylene Glycol	D5	Silicone Fluid 350 cps	IPA	Aromatic Hisol 15
Alkyl 2-1	I/I	S/S	D/D	I/I	I/D	I/D	I/I	S/D
Alkyl 2-2	I/I	S/S	S/S	I/I	S/S	D/D	I/I	S/S
Alkyl 2-3	I/I	S/S	S/S	I/I	I/D	I/D	I/I	S/S
Alkyl 2-4	I/I	S/S	D/D	I/I	I/I	I/I	I/I	S/S

Table 2. Typical Solubility at 1% and 10% by weight Polymers in Table 1.
Legend: I = Insoluble; D = Dispersible; S = Soluble

The structure of alkyl dimethicone polymers is shown in Table 2. The alkyl group shown in blue is a C16 or cetyl group. The reaction that enabled such a compound is the hydrosilylation reaction, in which a silanic hydrogen containing polymer is reacted with an alpha olefin. The presence of the oil soluble alkyl group can be controlled by controlling the ratio of "a" and "b". The higher the "b" value relative to the "a" value the more oil loving (oleophilic) the polymer.

Increasing the "m" value enables one not only to increase the oleophilic nature, but also the melt point of the polymer.

Product	State RT	% Sil	% Alk	MP
Cetyl dimethicone	liquid	50.2	49.8	-
Behenyl dimethicone	Solid	68.0	32.0	46
Behenyl dimethicone	Soft solid	45.0	55.0	37
C26 dimethicone	Solid	41.0	59.0	47
C26 dimethicone	Solid	69.0	31.0	43
C26 dimethicone	Solid	81.0	19.0	37
C32 dimethicone	Hard solid	64.0	36.0	60

Table 3. Melt Point of Alkyl Dimethicone Compounds (6).

Cushion and Playtime (7)

The terms cushion and playtime are commonly used to describe the feel of ingredients and formulations on the skin. If one places a compound or formulation on the index finger and rubs it on the forearm, both cushion and playtime can be evaluated.

Cushion refers to the amount of compound that persists between the finger and forearm. That is the greater the "distance" between the finger and the forearm the greater the cushion. Honey has a great cushion. When tested in this manner there is a feeling of a great deal of material between finger and forearm. Water has little of no cushion. There is little "distance" between finger and forearm.

Playtime refers to the length of time cushion persists. If the cushion is felt for a long period of time, the playtime is said to be long. If the cushion collapses rapidly the playtime is said to be short.

In most compounds the cushion and playtime are directly related. Honey has both a high cushion and high playtime. There are however materials that have a good cushion but rapidly collapse having a low playtime. Most important in this class are multi-domain alkyl silicone compounds having both liquid and solid portions in the same molecule. There are many applications in which in a high level of cushion, and a short playtime are desired. These include lipsticks, sun products and many lotions.

Formulator tip

In the past cushion and playtime were thought of properties that were found in an oil phase that were inseparable. Honey for example has a long playtime and a lot of cushion. Isopropyl myristate has a low cushion and play time. Abandon that view. Alkyl dimethicone polymers properly chosen will allow you to apply a blend that will have a great cushion and minimal play time.

CMC

Another very important observation made when studying alkyl silicone polymers in oils is that despite their being soluble (that is clear when added), the molecules function as surfactants. That is they first lower surface tension by increasing their concentration at the interface, then form micelles. It is this property that makes them amphiphilic, and allows them to function at low concentrations. Figure 3 below shows what happens when behenyl dimethicone is added to soybean oil.

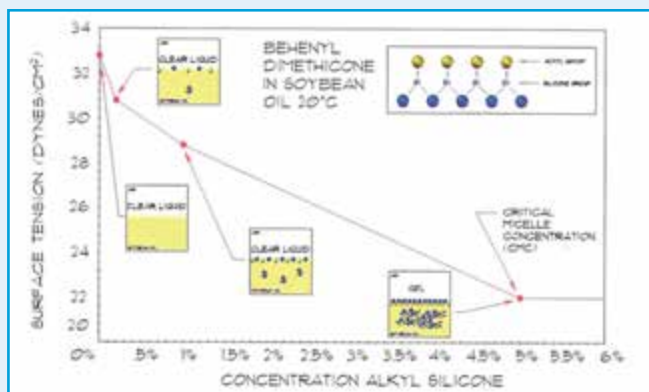


Figure 3. Addition of Surfactant Silicone to Soybean Oil (8).

The reduction of surface tension makes the oil feel like silicone, in fact because of the low surface tension the oil feels like D5. As one increases the concentration, micelles form. If an alkyl silicone with a melting point above ambient is chosen, a gel will form upon cooling. The gel is reversible, liquefying upon heating and re-solidifying upon cooling. The gel is thixotropic that is it liquefies under pressure.

This ability to lower surface tension is seen in a number of organo-functional silicone polymers as seen in Table 4. The reduction of surface tension is important to the performance in altering the aesthetics of oil phases modified by the addition of alkyl dimethicone polymers. The question becomes, do alkyl dimethicone polymers have a classical CMC (critical micelle concentration) curve as observed looking at traditional surfactants in water?

Solvent	Surface Tension (as is) Dynes/cm ²	Silicone Added (0.5% weight)	Surface Tension Dynes/cm ²
Toluene	28.9	C-26 alkyl dimethicone	25.0
2-butoxy ethanol	29.1	Stearyl dimethicone	22.0
Methanol	23.4	Octyl PEG-8 dimethicone	22.2
Water	72.3	PEG-8 dimethicone	20.1

Table 4. Reduction of surface tension of oils with silicone derivates.

If one looks at a surface tension vs. concentration graph of for cetyl dimethicone added as a surfactant to soybean oil, she/he would observe the results shown in figure 4. While not a perfect match for a graph like sodium lauryl sulfate in water, it is not too bad. It is at least possible to read an approximate "CMC".

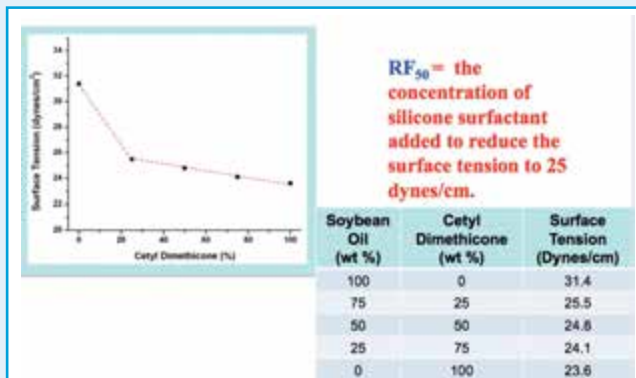


Figure 4. Cetyl Dimethicone in Soybean Oil (9).

There are however other CMC analysis that are far less like standard CMC graphs. Consider the information presented in Figure 5. Wherein the same cetyl dimethicone added to soybean oil above is added to mineral oil. The graph while having an inflection point does not have minimum viscosity over the range of addition.

The ability to find the lowest concentration of alkyl dimethicone that provides a reduction in surface tension is critical to the economics of lowering surface tension. It will be the salient property to alkyl silicone selection and will vary with type of oil phase or mixtures of oil phases.

Since a clear critical micelle concentration cannot be determined by the above graph, we suggest that for mixed systems the RF₅₀ be evaluated in order to compare effectiveness of surface tension reduction. The RF₅₀ is the **Reduction Factor 50%** for each silicone surfactant in each system. The definition is as follows (11):

RF₅₀ = the concentration of silicone surfactant added to reduce the surface tension to 25 dynes/cm

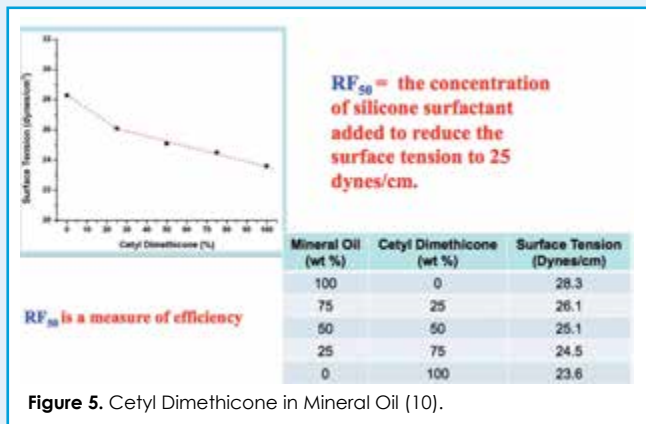


Figure 5. Cetyl Dimethicone in Mineral Oil (10).

The lower the RF₅₀, the better able is the silicone surfactant to compete with the fatty surfactant for surface and the more efficient the silicone surfactant will be. This technique allows one to design molecules that will be optimized for a particular formulation. Not only can surfactant systems be evaluated but also complex formulations can be evaluated, by simply defining the Fatty Surfactant's Surface tension as the formulation's initial surface tension. Not only surface tension, but also foam and the like can be tested and optimized by evaluating foam as the property rather than surface tension.

The so-called RF₅₀ value is a measure of the effectiveness in lowering surface tension in mixed systems. The lower the RF₅₀ value the lower the concentration needed to reach 25 dynes/cm in surface tension when a silicone surfactant is added to an oil.

The ability to lower surface tension is dependent upon the type of oil chosen and how it interacts with the alkyl silicone added. Ethyl methicone, a low molecular weight silicone is much more effective in lowering surface tension than is Cetyl dimethicone in soybean oil. Ethyl methicone has an RF₅₀ of 2% in soybean oil, while Cetyl dimethicone has an RF-50 of 20% in soybean oil. Figure 6 shows the graph.

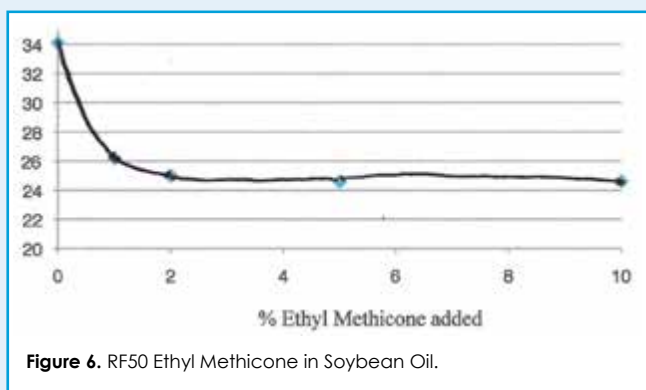


Figure 6. RF₅₀ Ethyl Methicone in Soybean Oil.

Formulator tip

In determining which alkyl dimethicone should be used to obtain both the lowest surface tension and the desired aesthetics, pick the alkyl dimethicone, which provides the best aesthetics along with the lowest the RF₅₀. The polarity of the oils and the interaction between will in part affect the outcome. Minimizing the amount of alkyl silicone lowers cost and gives an overall greener product.

Oil gelation (12)

Thus far, alkyl dimethicone has been recommended to the formulator to improve aesthetics and lower surface tension to improve spreadability and thickness of the oil on the skin. As the number of carbon atoms in the alkyl group increases above 18, the alkyl dimethicone polymer becomes a solid at room temperature. This added factor provides a number of new possibilities.

The number of carbon atoms in the alkyl dimethicone is the salient factor in determining the melting of the alkyl silicone. In order to make gels, the alkyl silicones must be solids at room temperature. The oil and the alkyl silicone are added together and heated to 80°C, upon which they become clear (solutions). Upon cooling gels form. The gels range from soft non-flowable solids to hard non-flowable solids. These gels liquefy under pressure of the finger, spread well no the skin and provide an excellent cosmetic feel. In instances where delivery is desired, the active is added.

Table shows the effect of increasing the % of alkyl group on the alkyl dimethicone polymer. This is accomplished by increasing "a" to "b" ratio in the structure provided. Figure 7 shows the effect.

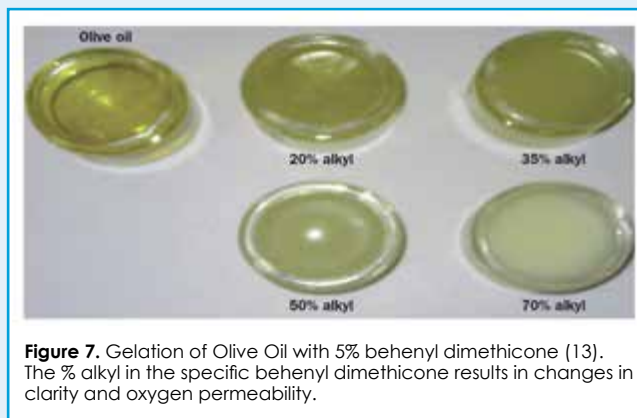


Figure 7. Gelation of Olive Oil with 5% behenyl dimethicone (13). The % alkyl in the specific behenyl dimethicone results in changes in clarity and oxygen permeability.

Olive oil shown in the upper left hand corner is a yellow liquid. When 5% of a behenyl dimethicone is added to it a translucent, almost clear gel results. As the 35% alkyl blend is made using a different a:b ratio the resulting gel is a little more translucent. Next 5% of the alkyl dimethicone having 50% alkyl is added. That product is opaque. Finally when the 5% solution of the alkyl dimethicone having 70% alkyl is added a opaque gel is obtained.

Typical of the effects that can be achieved is the incorporation of behenyl dimethicone into olive oil is shown in table 12. The higher the concentration of alkyl group the closer to clear the resulting gel, and the more occlusive the oil. As the concentration of silicone in the alkyl silicone increases the resulting gelled structure becomes more breathable and is no longer occlusive. Clear systems can be engineered by selecting an alkyl silicone with the proper refractive index.

Formulator tip

U.S. Patent 7,875,263 discloses a gel composition that comprises an specific solid alkyl silicone polymers combined with specific low viscosity liquid including natural oils, glyceryl esters, trimethylolpropane esters, and pentaerythritol esters.

These gels provide an emolliency to the skin by applying and allow for altering cushion and play time of these esters. Finally, the invention is also directed to application of sun screen actives, hydroxy acids, antioxidants, flavonoids, tocopherol, vitamins and the like to the skin in gelled form. By choosing very dry low viscosity esters and forming a gel using the proper solid alkyl dimethicone polymer and different concentrations, cushion and play time of the oil can be altered independently.

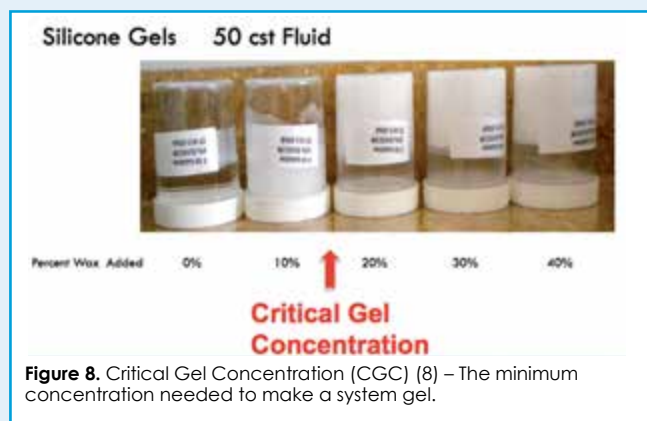
Gelation Concentration (14)

When selecting the alkyl dimethicone to produce an oil gel, one generally wants the most efficient product that is one wants to produce the gel using the lowest concentration of alkyl silicone possible. In order to evaluate the efficiency of gelation, we have coined a term "Gel Concentration".

Gel Concentration = The minimal concentration of alkyl silicone that can be added to an oil resulting in a gel at ambient temperature that does not flow.

The procedure for the determination of Gel Concentration is as follows:

Four separate 100 gram solutions having 0, 10, 20, 30 and 40 percent by weight alkyl silicone in tested oils are added to a 250 ml beaker. The reaction mass is heated to 80°C. If the clear solution is not obtained, the test is terminated. If a clear solution is achieved, the solution is allowed to cool in a 250 ml beaker at 25°C. The cooled beakers are then examined, for the lowest concentration of alkyl dimethicone which solid. That beaker is inverted for five minutes. If the material continues to cling to the beaker with no breakage the Gel Concentration is the lowest concentration that remains solid under inverted conditions. The test can be re-run if desired with concentrations just below the gel concentration to more definitively determine the gel concentration. Typical results are shown in Figure 8.



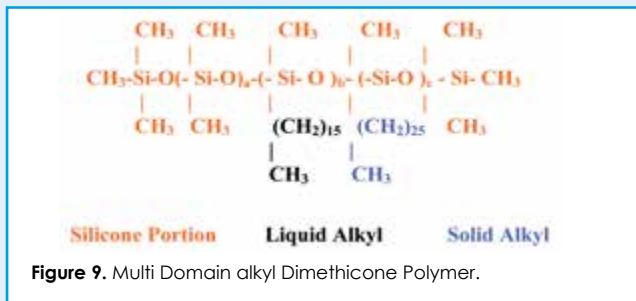
The above process can be repeated using a ranges between 10 and 20 to further narrow down the concentration at which a gel forms.

Formulator Tip

When determining the desired content to make a gel using alkyl dimethicone, consider both the critical gel concentration and the aesthetics of the gel to optimize the formulation using your combination of oils.

Multi domain silicones

The alkyl silicone surfactants that have been discussed until now have had a single alkyl group on the silicone backbone. A series of patent pending alkyl dimethicone polymers have been developed which contain two different alkyl groups, one liquid at ambient temperatures and another that is solid at ambient temperatures. These polymers provide unique aesthetics to cosmetic formulations. One such polymer is shown in Figure 9.



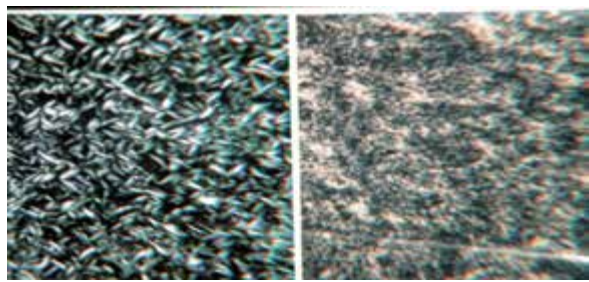
The specific structures of the "R" groups of the solid and liquid domain have a profound effect upon the rheology and aesthetics of the product, Products of this family are thixotropic solids that liquefy under pressure. The ability to define the polymers results in the ability to vary cushion and play time in formulations that contain this class of polymers.

The differences between a Multi Domain silicone and a single domain silicone are easy to ascertain by looking at the picture in Figure 10. The two polymers shown in the figure have exactly the same composition of C22 and C16, one a blend of two single domain alkyl silicone polymers, and the other a multi-domain alkyl silicone polymer having the two types of alkyl group on the same molecule.

The presence of the liquid portion of the molecule inhibits the products from becoming hard solids. Instead a soft, thixotropic gel forms. The resulting translucent gel liquefies under pressure has a cushion effect, but has a short playtime.



In addition, photo microscopy of the two materials above show that the multi domain silicone polymer is highly structured, while the blend of the two single domain silicone polymers is quite random and lack structure. This is seen in Table 16. It is this structure that accounts for the different functionality seen in the polymers. The INCI names also recognize the difference. The blend of the two single domain silicone molecules has the INCI name behenyl dimethicone and acetyl dimethicone, whilst the multi domain silicones have the INCI name behenyl / cetyl dimethicone.



Multi-domain silicone Blend of two single domain silicones

Figure 11. Photomicrograph of a blend of two single domain silicones multi-domain silicone.

A study was conducted on the above materials by Microtrace LLC, their results state:
 "Sample 1 and 2 are entirely different from one another. Sample 2 is an opaque, waxy, white, crystalline solid at room temperature. Its color and solid phase structure are a direct result of the fact that it is composed entirely of colorless, interlocking crystals. These crystals melt at 56°C (132.8°F) when the solid becomes liquid. This transformation is entirely reversible. Sample 1 is, at room temperature, a translucent, gel that flows under pressure. It is composed of two phases. The liquid phase is liquid at room temperature. The solid phase is crystalline and the relatively large, elongated crystals scatter light just enough to make the product translucent instead of white and opaque like sample 1 or entirely transparent and colorless as would be the case if the crystals were absent. The crystalline phase melts entirely at 38°C (100.4°F) but recrystallizes when the temperature drops below this.


It also appears that the crystals in sample 1 are liquid-crystals rather than ordinary crystals such as those that form the waxy solid comprising sample 2. This would take some time and effort to confirm but the initial observations seem to point in this direction. The most compelling evidence for this is the disappearance of most of the birfringent crystals in a thin film of sample 1 when pressure is applied to the cover slip and their immediate reappearance once the pressure is released."

Formulator tip


Making emulsions using alkyl dimethicone polymers that are solid when at room temperature, but liquid at the processing temperature can provide added emulsion stability.

"Structured" Emulsion

Addition of a solid alkyl dimethicone to an emulsion heating to above the melt point of that alkyl dimethicone and making the emulsion provides structure to the oil and improved emulsion stability



Cetyl dimethicone



Multi Domain

Material	Non-Structured Gel (%)	Structured (%)
Olive Oil	36.0	36.0
Water	56.0	56.0
Lauryl PEG 8 Dimethicone	4.0	4.0
Cetyl Dimethicone (Liquid)	4.0	
Cetyl Behenyl Dimethicone (Solid)		4.0

Figure 12. "Structured" emulsion.

In order to demonstrate this a formula was prepared as shown in Figure 12. Both oils were heated to 60°C then the emulsion was prepared using the standard process. The olive oil emulsion was a white stable emulsion with a blue tint. The product made with cetyl dimethicone, a liquid alkyl dimethicone that provides no structure, resulted in an unstable emulsion.

Whenever possible, make a structures oil phase in an emulsion to increase stability.

CONCLUSIONS

1. Many of the most interesting properties that are found in oil soluble silicone compounds are found are based upon one or both of two "surfactant" properties.
2. One salient property is surface tension lowering and can include give rise to wetting, emulsification, and foaming, depending upon the specific structure of the alkyl silicone chosen.
3. The other salient property is gelation of oil. Producing a gelled oil depends upon having a melt point above room temperature and when an alkyl dimethicone polymer with a melting point above room temperature is incorporated into the oil a reversible thermal gel occurs. That is when heated the gel melts (unlike elastomer gelled systems that are thermally insensitive).
4. Multi domain alkyl silicone polymers are a new class of material that include both liquid and solid domains that provide a unique aesthetic in the form of a gel that also can be used to improve emulsion stability by structuring the oil phase.
5. Since silicone polymers are almost never the sole ingredient in the formulation, it is critically important to evaluate the interaction of the various components in formulations. We have presented tools that allow for such testing including RF50, and Critical Gel Concentration. These are always used in conjunction with aesthetic modification to meet the formulation's required properties.
6. The evaluation of the effect of silicone surfactants in formulation is an ideal candidate for computer-assisted evaluation of many different formulations.

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