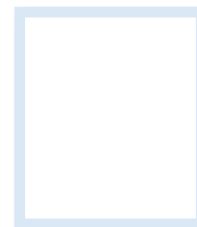


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Altering organic oils with Silicones

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ABSTRACT: Alkyl dimethicone polymers are a class of oil soluble materials that can provide surface-active properties when added to oils. Addition of the proper alkyl silicone can alter feel, lower surface tension, and or provide gels. This article looks at these interesting materials in a new way, hopefully making them more interesting to the formulation chemist.

Silicone polymers have become a common additive to personal care products; in fact there are few cosmetic categories in which silicones are not an ingredient. The fact that this class of polymers has become so widely used in so many different applications is a testimony to both the versatility of silicone chemistry and the adaptability of the formulator to use these new materials.

Despite the fact that the basic technology that resulted in commercial success for silicones goes back to Rochow in the 1940s, the explosion of technology in the cosmetic industry really did not happen until the early 1990s. It was during this time that organofunctional silicones developed rapidly. Organofunctional silicones are interesting since they possess desirable properties of both silicone and organic polymers.

In order to understand why silicones have become so important in today's personal care market, chemists need to look at the special properties that silicone polymers possess. One of the salient properties of silicone compounds is their low surface tension. Silicone compounds have surface tensions in the 20-25 dynes/cm range, water around 72 dynes/cm and fatty surfactants 30-55 dynes/cm. This ability to lower surface tension gives silicone polymers many unique and desirable properties.

There are several misnomers that exist about silicone compounds. The first is that all compounds that have silicone present have the same surface tension. This is simply not true. The ability of a molecule to lower surface tension is determined in part by how it orientates at the surface. For example, silicone compounds that have a lot of polyoxyalkylene (polyoxyethylene or polyoxypropylene) at the surface will have the surface tension of the polyoxyalkylene portion. This is because at the surface the polyoxyalkylene groups are dominant. Another misnomer is that the surface tension of the silicone polymer in pure solvent will be the same as the surface tension in formulation. Many silicone companies provide data on surface tension of PEG/PPG dimethicone compounds in water. The interaction of other ingredients in the formulation with the silicone will determine if the silicone even gets to the surface at all. Hydrogen bonding, surface adsorption in formulations with particulates, and micellar considerations are but two of the reasons that silicone may not provided the same effect in

formulations as are seen in pure solvent.

Amphilphilic Silicones are compounds that have two or more groups in the same molecule that in pure form are insoluble in each other. Amphilphilic Silicone Polymers

are polymers that contain two or more groups with different solubility covalently bonded to the same polymer backbone.

Group Solubility

Oil Soluble	(oleophilic)
Water Soluble	(hydrophilic)
Silicone Soluble	(siliphilic)
Fluoro Soluble	(fluorophilic)

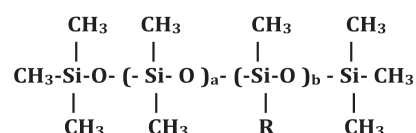
At low concentrations, amphilphilic silicones migrate to the interface. When the interface becomes saturated and the critical micelle concentration (CMC) reached, micelles are formed. The key to surface tension efficiency is the ability of a polymer to migrate to the interface and take up the maximum free volume on the surface. This means that there will be much more silicone found at the interface rather than in the solution. The fact that there is more silicone located at the surface than in solution makes silicone polymers extremely effective. Under very low concentrations, silicone polymers can drastically change the properties of a solution.

Silicone polymers can provide many unique and desirable properties:

- function as emulsifiers
- function as wetters
- function as form films
- function to alter foam
- construction/destruction
- function to provide conditioning and skin feel (1)

OIL SOLUBLE SILICONES – ALKYL DIMETHICONES

The incorporation of an alkyl group into the silicone backbone results in a surface-active oleophilic silicone polymers. These alkyl dimethicone polymers lower surface tension in oil from 30-35 dynes/cm to 20-25 dynes/cm and form micelles with siliphilic cores capable of encapsulating and releasing siliphilic small molecules. These two phenomenon make these alkyl dimethicone polymers extremely interesting in the formulation of personal care products.



R is $-(\text{CH}_2)_n\text{CH}_3$ where n is at least 1.

Silicone to alkyl ratio

These alkyl dimethicone polymers not only have the ability to form solid and liquid products, they also have the ability to change the physical properties of the solid. By tuning, or changing, the silicone to alkyl ratio (changing the "a" to "b" ratio in the structure), the physical properties of the solid can range from a very brittle opaque solid to a translucent wax. Increasing the percentage of silicone will result in a softer wax with minimal effect upon melting point. This ability to control the tensile strength applies not only to the polymer in bulk but also when it is added into a products formulation. The addition of a silicone with the correct silicone to alkyl ratio provides a formulation chemist the ability to "stiffen" or "soften" a solid.

Alkyl effects

Along with the ability to lower surface tension and increase the solubility of the silicone in oil, alkyl dimethicone polymers can also change the physical properties of the materials that they are added to. By changing the alkyl group attached to the silicone backbone, a wide variety of products can be obtained. Attaching alkyl groups containing 16 or less carbons atoms in their alkyl chain will result in a liquid product at ambient temperature. Alkyl groups with 18 or more carbon atoms in their alkyl chain are solid at ambient temperatures. Adding alkyl dimethicone, with a long carbon chain in the pendant group (≥ 18 carbons), to a liquid product will cause the products melting point to increase and under high enough concentrations the product will gel. The opposite is true for a product that has a high melting point. Adding alkyl dimethicone, with a small carbon chain in the pendant group (≤ 18 carbons), can drastically lower the melt point of the product and add liquidity.

Surface effects

Alkyl dimethicone, in oil, is a surface active agent or surfactant. When alkyl dimethicone is added to a solvent (polar or non-polar) the polymer chains migrate to the air-oil interface. As the concentration of alkyl dimethicone increases, the surface tension of the oil drops from 30-35 dynes/cm (surface tension of the pure oil) to 20-25 dynes/cm (surface tension of pure silicone). This effect is shown in Figure 1. The selection of the alkyl dimethicone and the oil phase can drastically change the shape of the surface tension curve.

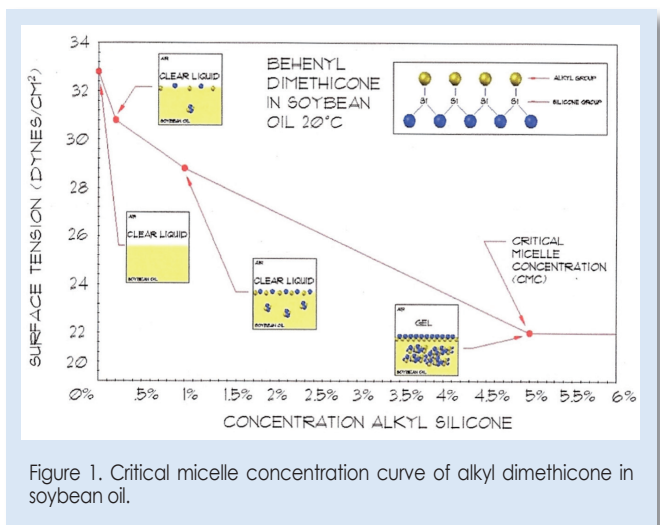


Figure 1. Critical micelle concentration curve of alkyl dimethicone in soybean oil.

Migration of the alkyl dimethicone is based largely on the interactions of the polymer with the oil. If the alkyl dimethicone polymer has a strong interaction with the oil, i.e. Intermolecular forces, the curve will flatten out. This will result in a higher concentration of polymer needed to reduce the surface tension to the desired level. Figures 2 and 3 show the effect of

changing the oil for cetyl dimethicone. The goal is to get the largest drop in surface tension with minimal alkyl dimethicone added.

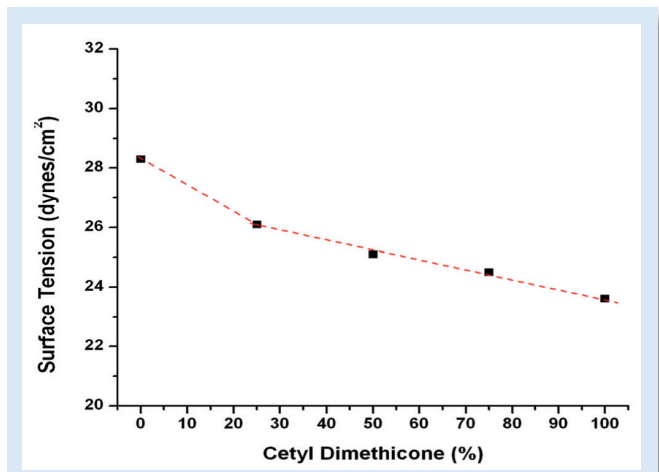


Figure 2 shows that cetyl dimethicone is relatively ineffective in lowering the surface tension of mineral oil, needing 50 percent to achieve the desired 25 dynes/cm.

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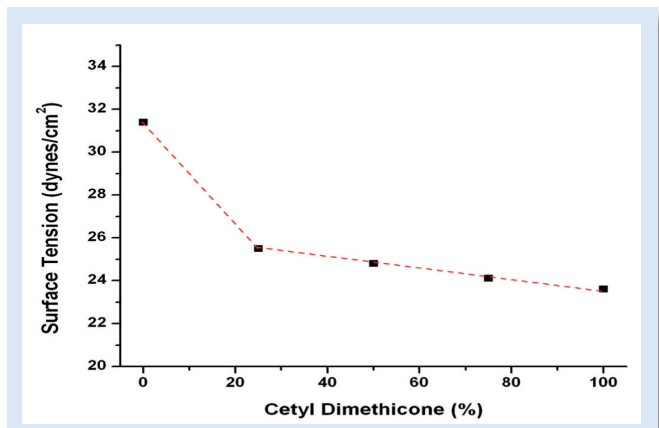


Figure 3. RF50 curve of cetyl dimethicone in soybean oil.

Figure 3 shows that cetyl dimethicone is more effective in lowering the surface tension of soybean oil, than it is does in mineral oil. The RF₅₀ of cetyl dimethicone in soybean oil is 22, 50 percent in mineral oil. A study was undertaken to look at the efficiency of lowering the surface tension of olive oil using various silicone additives. The results are summarized in Table 1.

Alkyl Dimethicone	RF ₅₀ (%)
Silfilm DC-70	0.15
Silwax D02	0.20

Table 1. RF50 values of different silicone additives in olive oil.

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

Since the addition of amphiphilic silicone to oils can but does not always result in a typical critical micelle concentration curve, a new measure of efficiency needed to be developed. This new measure of efficiency is called RF₅₀. The term is Reduction Factor 50 percent. Since oils have a surface tension of around 30 dynes/cm and silicone around 20 dynes/cm, the concentration at which the surface tension reaches 25 dynes/cm is the RF₅₀.

FORMULATION

The lower the RF_{50} the lower the concentration needed to get the surface tension to the desired level and the more efficient the material. This ability to lower surface tension of oil at low concentrations is a very attractive because it allows for the precise tuning of surface tension. Lowering of the surface tension, in oil, is very attractive to the cosmetic industry because it makes oils feel more like silicone.

Gelation (2)

Alkyl silicones with long pendant alkyl chains ($C \geq 16$) will be solid at ambient temperatures. As the concentration of alkyl silicone is increased in oil, it reaches a critical gelation concentration (CGC). At concentrations greater than the CGC, the long alkyl chains will overlap and form a physical cross-linked gel. Since physically cross-links are not permanent, these gels are reversible and will flow under stress. If the gel is heated, the gel will flow. Upon cooling, the gel will reform. This is in stark contrast to oils thickened with silicone resins, which are irreversibly gelled and are independent of temperature. This is a very desirable property because it makes the gels much easier to process. This gelation of organic solutions is not limited to just oils; the gelation of liquid esters and triglycerides is the topic of U.S. Patent 7,875,263 and several others pending.

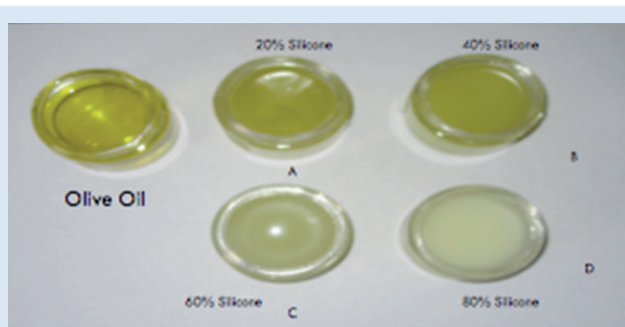


Figure 4. Optical images of alkyl dimethicone in olive oil with altering ratio of silicone to alkyl chains: (a) 20 percent silicone, 80 percent alkyl, (B) 40 percent silicone, 40 percent alkyl, (c) 60 percent silicone, 40 percent alkyl and (D) 80 percent silicone, 20 percent alkyl chains.

Alkyl dimethicones can also be used to gel silicone fluid. Figure 5 shows the effect of adding an alkyl silicone to 50 cSt viscosity silicone fluid.



Figure 5. Alkyl dimethicone added in 50 viscosity silicone. Percent Added: 0%, 10%, 20%, 30%, 40%.

MULTI DOMAIN SILICONES

A new patent pending class of compounds has been developed that contain two different alkyl chains as pendant groups on the same silicone backbone. One alkyl group is a short chain (C_{12} to C_{16}). This chain has a low melt point and is liquid at ambient temperatures. The other alkyl chain is a longer alkyl chain (C_{20} and above).

This alkyl chain has a high melt point and is solid at ambient temperatures. Figure 6 shows the general structure of such compounds:

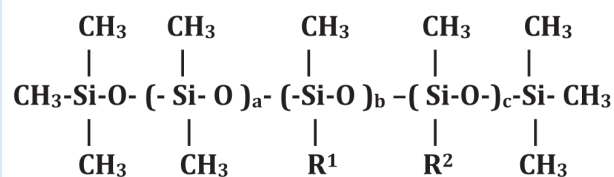


Figure 6. Multi domain alkyl silicone structure

R^1 is $-(CH_2)_mCH_3$ where m is 7 to 15

R^2 is $-(CH_2)_pCH_3$ where p is 21 or greater.

These systems can self-assemble into organized networks with the long alkyl chains forming solid domains surrounded by a liquid domain of the smaller alkyl chain. The gels formed with these multidomain polymers have very interesting properties. Under shear the gel will flow. When the stress is removed, the gel domains will reform and the gel will solidify. The addition of multidomain polymers in a cosmetic product drastically changes the rheology and aesthetics. There is a new class of INCI names that go with this unique class of compounds, they have both alkyl groups in the name, for example behenyl cetyl dimethicone.

PHOTOMICROGRAPH EVALUATION

In order to further study these multidomain polymers, photomicroscopy was employed (3). These photomicrographs show the differences in the structure of the wax. Two different materials were evaluated, the 1st is the multidomain product a blend having the same percentages of alkyl groups but on different molecules. The results are shown in Figure 7 and Figure 8.

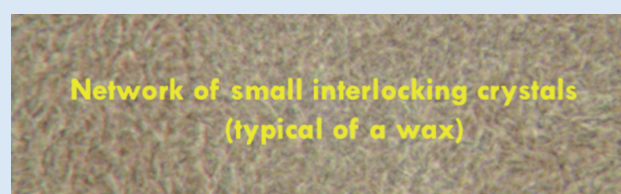


Figure 7. Photomicrographic evaluation polymer blend.



Figure 8. Photomicrographic evaluation multidomain silicone.

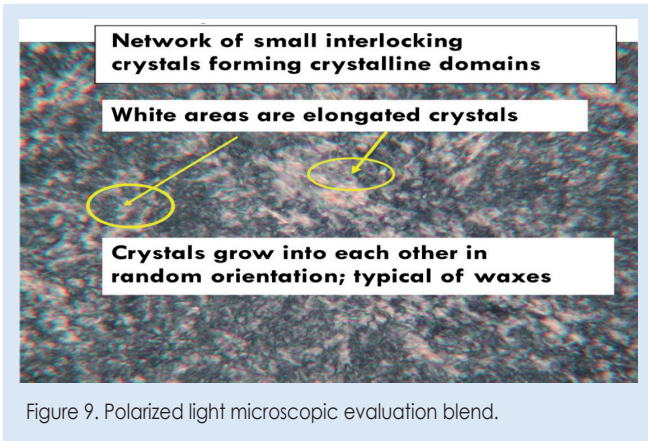


Figure 9. Polarized light microscopic evaluation blend.



Figure 11. Co-reacted di-alkyl dimethicone and blend of two alkyl dimethicone polymers (same ratio).

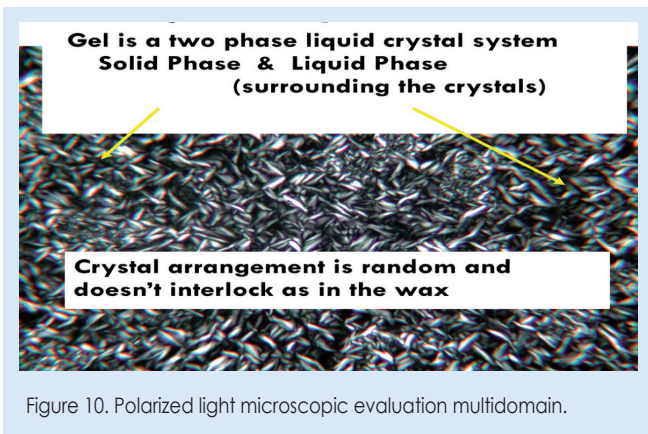


Figure 10. Polarized light microscopic evaluation multidomain.

	Multidomain	Polymer Blend
Melt Point (°C)	34 - 38	56
Visual Appearance	Translucent gel	Opaque waxy solid
Gel Shear	Flow under shear	No Flow

Figure 15. Visual appearance.

As seen from the polarized micrographs, multidomain silicones are drastically different from a polymer blend of the same composition. In the multidomain silicone, both alkyl chains are covalently bonded to the same silicone backbone. This restricts the degree of freedom of each alkyl chain and drastically affects the properties of the solid. As two long alkyl chains (in the multidomain silicone) come into contact with one another, they "stick together" and form a solid domain. As the long alkyl chains get incorporated into these solid domains, the small alkyl chains get excluded and start to form small liquid domains. Since both domains are attached to the same polymer backbone it is impossible for them to completely separate. This causes each solid and liquid domain to be confined into small regions and causes each solid domain to be surrounded by a liquid domain. The small domain size leads to many of the different properties of the solid, from scattering light (large domains scatter more light and are opaque to smaller domains that don't scatter much light and are translucent) to low melt point. The fact that the solid domain is surrounded by the liquid domain allows for the solid to flow under pressure. When a stress is applied to the

solid, the solid domains can slide past one another more easily. This allows the solid to flow without breaking. In the polymer blend, the domains are not limited in size. Each domain can be very large size, this accounts for greater light scattering (opaque solid) and the solid becomes brittle. Since these multidomains are highly organized compared to the blend and can provide specific properties need they have been classified into a new category called high definition silicone polymers™.

CONCLUSIONS

1. Alkyl silicone compounds offer the formulator a number of opportunities to alter the feel, consistency and rheology of oil-based formulations.
2. Alkyl silicones can be used for the desirable attributes they provide in oil phases in the oils themselves, serums, emulsions and any other form that the oil is present. Adding structure to the oil phase will stabilize emulsions.
3. Alkyl silicones will provide (a) lower surface tension, (b) gelation, and (c) tactile changes.

REFERENCES AND NOTES

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3. Microtrace LLC 790 Fletcher Drive Elgin, IL 60123.