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'Greening with silicones' examined

Today's consumer has very sophisticated if not contradictory attitudes when it comes to the selection of cosmetic products.

On one hand, the consumer will neither accept products that are not formulated to minimise the impact on the environment. On the other hand, the consumer will not accept products that fail to meet performance expectations. This results in a basic contradiction: how does one achieve the performance that one has come to expect, while having concern for the environment? This has been a problem for marketing over the last decade and will become a defining problem for our industry.

One simplistic approach, favoured by some, is the complete banning of all materials that do not meet a specific definition of green. This approach, while simple, fails to consider the fact that successful products need to have the proper combination of consumer and environmental acceptability. Simply put, consumers will not wash their hair with simple soap despite it being green, because it lacks many other attributes demanded by the consumer. The other approach is to simply accept all products regardless of ingredients.

The approach that appears to offer the best possibility is the so-called Hybrid Formulation Model. This approach[1] compares the cosmetic formulation to the hybrid car and speculates that the optimised consumer product is one that will be as green as the category can be (the electric part), while using a minimal quantity of materials that are not green only in special instances where performance demands it (the gasoline portion). This approach results in a metric system, referred to as the Green Star System[2], that allows one to consider both the environmental and performance aspects of the product. This concept encourages the use of minimal concentrations of raw materials that offer unique consumer benefit while keeping the green aspect uppermost in formulations. The result is a process as much as a product. The process is one of continuous re-evaluation of formulations ever increasing the green efficiency of raw materials.

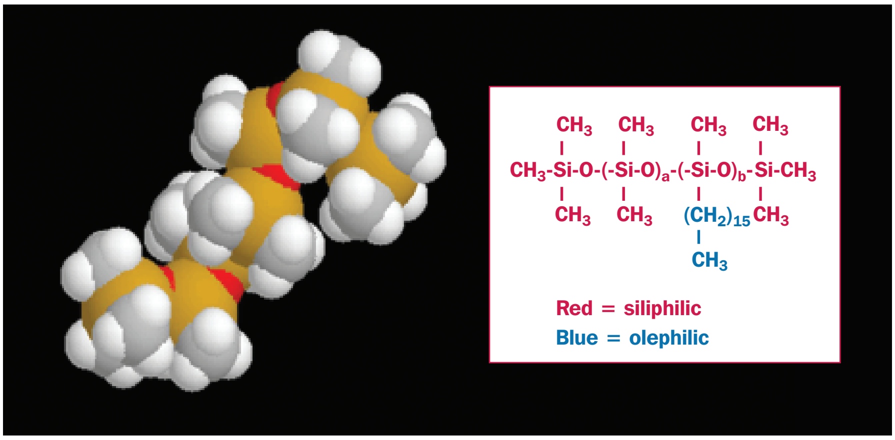

Figure 1: *Polydimethylsiloxane model (white groups are methyl). Inset: Cetyl dimethicone structure.*

Role of silicones

Silicones are found in cosmetic formulations primarily because they have a unique surface tension relative to both water (72 dynes/cm^2) and oil (32 dynes/cm^2). Silicone provides surface tensions in the 20 dynes/cm^2 area. It is this surface tension reduction that leads to many of the desirable properties of silicones, such as: spreading; foaming of materials that cannot be foamed with fatty surfactants; creating invert emulsions; and elegant aesthetics.

The Hybrid Formulation Model (HFM) approach results in an understanding that silicone raw materials offer a benefit demanded by consumers that can only be provided by raw materials that would traditionally be left out of formulations in the quest for greenness. Silicones are unique in a number of areas including the elegant aesthetics they contribute to a formulation.

Initially, the concept that silicone compounds can contribute to the formulation of green products is confusing and somewhat contradictory. However, applying the Hybrid Formulation Model, silicone compounds should be selected to use the lowest possible concentration that provides the desired benefit. It is under this criterion that "Greening with silicones" is meaningful.

Amphilic silicones

Surface tension of a liquid is a result of internal attractive forces. These forces cause the liquid's surface to act as if it were a stretched elastic membrane, thus causing it to form spherical droplets.

Amphilic materials have two or more groups in the same molecule that in pure form are insoluble in each other. The groups that are mutually insoluble are:

- Water.

Table 1.

Group	Surface tension	Dominant group
Water	72 dynes/cm^2	H_2O
Oil	30-35 dynes/cm^2	$-CH_2-$
Silicone	20-25 dynes/cm^2	$-CH_3$
Fluoro	Below 20 dynes/cm^2	$-CF_2-$

- Oil phases.
- Silicone phases.
- Fluoro phases.

Each group in pure form has a surface tension associated with the predominant moiety present. The surface tension is determined by the surface tension of the group that is found at the interface (Table 1).

Surfactants

Surface-active agents (also called surfactants) possess at least two of these groups on the same molecule. Consequently, they orientate themselves in solution to obtain the lowest free energy. Initially this is at the air/solvent interface. As the concentration of surfactant is raised above the so-called *critical micelle concentration*, aggregations called micelles form. It is very interesting to note that these organised structures are soluble. This is because the structures are below the size that effects clarity. Solubility and homogeneity of concentration cannot be confused. Oil soluble silicones first lower surface tension, then form micelles as shown in Figure 2.

Alkyl silicones conform to the structure shown in Figure 1.

Considering the salient properties of the wax:

- Ratio of a to b determines the solubility in a specific solvent.
- Total molecular weight determines the skin feel.
- Alkyl chain length determines melting point.

As the value of ‘a’ increases relative to ‘b’ the percentage of silicone in the molecule increases. As the value of ‘b’ increases relative to ‘a’ the percentage of alkyl in the molecule increases.

When added to oils like triglycerides, natural oils, and simple or complex esters these amphilic materials organise themselves at the interface and lower surface tension as shown in Figure 2.

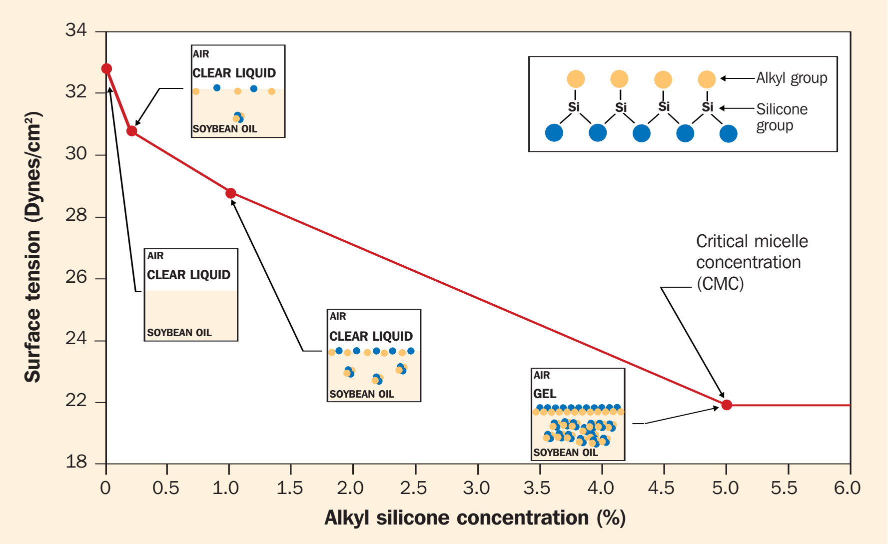

Figure 2: *Behenyl dimethicone in soybean oil at 20˚C.*

This ability to lower surface tension results in improved cosmetic aesthetics, making the oil feel like silicone. The ability to efficiently lower surface tension is dependent on two factors: the solubility of the silicone in the oil, and the ease of the silicone to reach the interface.

If a silicone is too soluble in the oil it will stay in solution and be very inefficient in lowering surface tension. The silicone needs to be soluble enough in the oil to remain clear, but insoluble enough to be driven to the surface. It is the balance of these two contradictory phenomena that results in making organic materials feel like silicone.

One area in which silicones can make a dramatic impact in cosmetic formulation is in their ability to make natural oils, triglycerides and esters more cosmetically elegant. This is achieved by the use of alkyl silicones. Alkyl silicones are a class of compounds that are clear in organic oils (therefore soluble) and are amphilic, that is surface active. These materials go first to the interface, lowering surface tension, then form micelles. These two properties, lowering surface tension and forming micelles, result in two key formulation benefits. The former is referred to as siliphilisation (literally making oils feel more like silicone) and gellation (forming cosmetically elegant gels). It is the ability to select materials that optimise the efficiency of materials to provide these properties that is key to “Greening with silicones”. The materials that provide the desired effect at the lowest concentration will result in the greenest product.

An example is the reduction of surface tension of soybean oil using cetyl dimethicone. Figure 3 shows the effect.

Efficiency (RF_{50})

The shape of the curve will allow for the determination of the efficiency. In clear systems, the lower the concentration needed to reduce surface tension the more efficient the oil. The graph of Figure 3 does not have the break point observed with traditional surfactants, like PEG 8 dimethicone shown in Figure 4.

Since there is no clear break point

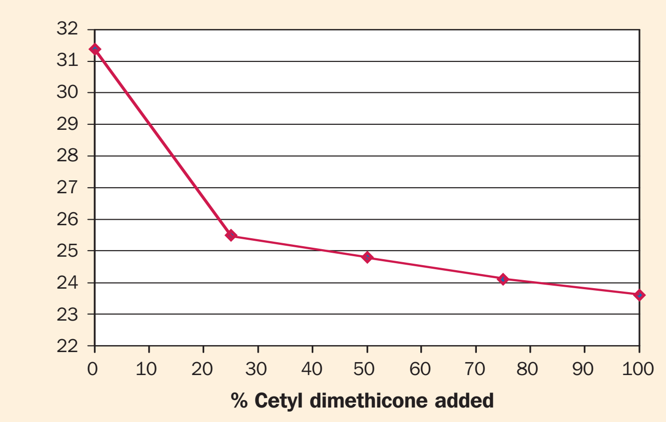

Figure 3: *Surface tension of soybean oil with added cetyl dimethicone.*

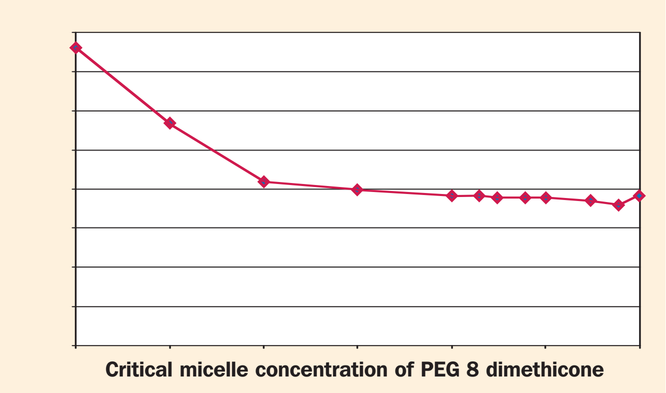

Figure 4: *A break point is observed with traditional surfactants such as PEG 8 dimethicone.*

when cetyl dimethicone is added to soybean oil, we have created a value RF_{50} that is a measure of the ability of the additive to drop the surface tension from 30 to 25 or a Reduction Factor of 50%.

RF_{50} = the concentration of silicone surfactant added to reduce the surface tension to 25 dynes/cm²

The particular cetyl dimethicone used in the graph of Figure 3 is not very efficient, having a RF_{50} of 25% by weight. This means that in order to obtain a surface tension of 25 dynes/cm² the ratio of soybean oil to cetyl dimethicone is 75:25. By properly altering the structure of the silicone (by the alkyl length, and/or the 'a' and 'b' values in the structure), RF_{50} values on 1% can be achieved.

There is a great deal of oil specificity in the RF_{50} value, that is the solubility of the silicone in the oil and the RF_{50} differ with different classes of oil.

Gellation

Alkyl silicones having 20 or more carbon atoms are solids at room temperature. The number of carbon atoms in the alkyl chain determines in large part the melting point. (Fig. 5)

Alkyl	Melt point
C22	37˚C
C26	50˚C
C32	60˚C

Figure 5: *Typical melting point of alkyl silicones.*

When an alkyl silicone that is soluble (clear) in a particular oil and solid at ambient temperature is added to an oil at a concentration above the critical micelle concentration, it will form micelles and make gel structures. The melt point of the gel is determined by the alkyl chain length and the clarity of the gel determined by how much silicone is present in the molecule. More silicone will result in opaqueness. The way the amount of alkyl is modified in the behenyl dimethicone is alteration of the 'a' to 'b' ratio.

Figure 6 shows an example. Behenyl dimethicone was added to olive oil at 5% concentration.

Molecules that are principally alkyl result in a gel that is almost clear. As the percentage of alkyl group is decreased, by increasing the amount of silicone in the molecule, the gelled oil becomes translucent, then opaque. Gels made with compounds having a high percentage of alkyl in the molecule tend to provide stiff gels, while those with high amounts of silicone provide softer gels. A solid is a state of matter in which the material shows resistance to deformation and changes in volume. Solids have their molecules closely packed together in fixed positions. If the molecules are fixed in repeating groups a crystalline group occurs. A liquid is a state of matter in which molecules are fluid – that is they can move easily around, assuming the shape of the container.

Alkyl dimethicone compounds have been around for many years. They are soluble in a variety of oils such as mineral oil, and esters. The length of the alkyl chain determines the melt point of the traditional alkyl dimethicone. Consequently, cetyl (C16) dimethicone is liquid and behenyl dimethicone (C22) is solid.

Another interesting difference is that alkyl waxes with a high content of alkyl in them are occlusive, and decrease transepidermal water loss, while the same molecular weight alkyl wax with high silicone content does not affect transepidermal water loss.

Cosmetic elegance – multi-domain

The physical form of traditional alkyl silicone compounds are determined by the length of the alkyl chain. They are either

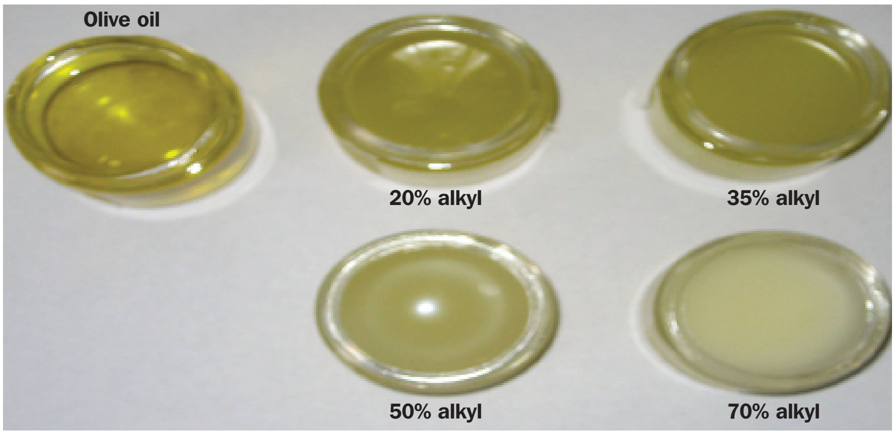

Figure 6: *Gelled olive oil (5% behenyl dimethicone added).*

In principle, the same.

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solid or liquid at ambient temperature. Figure 7 shows an example of a solid and liquid alkyl dimethicone.

A new patent pending class of alkyl silicones called multi-domain alkyl silicone has both liquid and solid alkyl groups in the same molecule. This results in an ability to manage cushion and play time in compounds resulting in cosmetic elegance and ease of formulation.

Unlike products described previously, multi-domain silicone polymers (Fig. 8) are carefully engineered materials that have segments called domains that have both solid and liquid alkyl groups placed on the same silicone backbone. The result is an inability to form a hard wax. The reason for this is that the molecule takes on the lowest energy confirmation in which there are solid domains and liquid domains within the matrix. The presence of these different domains within the polymer results in unique properties. The liquid and solid domains within the same molecule limit the ability to form hard solids and result in soft, cosmetically elegant, wax.

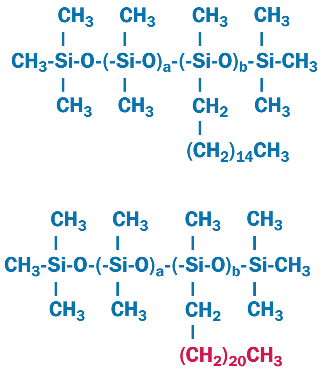
The reaction of two different alkyl groups, one liquid and one solid results in a substantially different product than blending two separate alkyl silicones having different alkyl groups. Figure 9 shows a blended C22/C16 alkyl silicone and a co-reacted C16/C22 silicone (one with the two different alkyl groups on the same molecule). A comparison of the multi-domain silicone polymer and product made by blending two silicone polymers on which there is one alkyl group each is illustrated. The two products have the same *average* composition, but the multi-domain product is clearly different. This difference is because of the structuring provided by the multi-domain design – not only are the appearances different, the rheological and aesthetics are vastly different.

The multi-domain product is a soft translucent thixotropic material, while the blend is a hard opaque solid. The multi-domain product when spread on the hand exhibits significant cushion, resembling petrolatum. As it is rubbed, it spreads rapidly and results in a dry feel. The blend cannot be applied by hand at room temperature.

Multi-domain silicones have been found to be excellent additives to serums. Hydrophobic serums spread better and feel more hydrophilic. This can be done at concentrations of 1% to 2% by weight.

Multi-domain silicones have been used in emulsions where they significantly alter the cushion and play time of these products. Multi-domain alkyl silicones also promote the formation of liquid crystals, improving feel and slip.

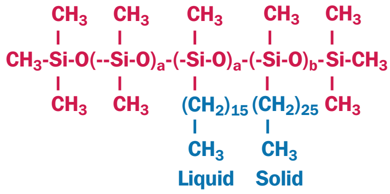
The addition of a multi-domain silicone to an oil phase lowers the surface tension of the oil into the range of 20-25 dynes/cm^2, making the oil feel like silicone and, at the same time, providing a greener formulation. Addition of the proper silicone to the water phase results in *matched surface tension emulsion* products that feel more elegant because the drag encountered in using emulsions of different surface tension is eliminated.



Cetyl dimethicone
Liquid domain only

Behenyl dimethicone (mp 37˚C)
Solid domain only

Figure 7: *Example of a solid and liquid alkyl dimethicone.*



Red = siliphilic
Blue = oleophilic

Figure 8: *Multi-domain alkyl silicone.*

Multi-domain alkyl silicone. **Blend of two alkyl silicones.**

Figure 9: *Comparison of multi-domain alkyl silicone and blend of two different alkyl silicone polymers (having the same ratio of alkyl groups).*

Conclusions

- Amphilic silicones offer the ability to make oil-based formulations more silicone-like.
- Properly selected amphilic silicones allow for the formulation of cosmetically elegant products using very low concentrations of silicone.
- Formulations using amphilic silicones at low concentrations allow for a significantly lowering of the total silicone present in the formulation, and consequently allow for greener formulations.
- Amphilic silicones can be used to make formulations containing oils, triglycrides and esters more siliphilic (silicone-like), lower the surface tension and provide cosmetically elegant gels.
- Amphilic silicones are formulator friendly.

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