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PEG/PPG dimethicone structure and function

PEG/PPG dimethicone compounds should be used in instances where they provide benefits that cannot be obtained by organic compounds. These properties include:

● Lowering of surface tension (into the range of 25 dynes/cm).
● Provide unique skin feel.
● Provide unique emulsification properties (especially in invert emulsions).
● Provide film formation.
● Provide foaming of non-traditional formulations.

These properties are a direct result of the structure, but the structure needs to be carefully selected. PEG/PPG dimethicone polymers have increased polarity, by virtue of their polyoxyalkylene groups. It is important to note that these modifications are done by chemical reaction between a reactive silicone and a vinyl containing compound. A very common structure is shown in Figure 1.

There are several variables that can be modified to change the performance of the DMC polymer. One of the most important is the ratio of a (silicone soluble portion) to b (water soluble portion) as well as the total number of a and b, both of which are important to functionality. The higher the ratio of a to b the less water soluble the product. Also, the molecular weight of the DMC polymer can drastically change properties. The studies presented in this paper keep the ratio of D/D* constant (that is the ratio of a/b is kept constant relative to each other).

ABSTRACT

Despite the increasing usage of silicone polymers in personal care products, the selection of the proper polymer for a particular application remains somewhat elusive. This directly results in inefficiency of formula development. This problem is exacerbated by the reliance upon INCI names in selection of compounds. While helpful in placing polymers in a generic class, it is of limited help in optimising formulation efficiency. Compounds that are water insoluble, water dispersible or water insoluble can all share a common INCI name. Likewise polymers that provide wetting, emulsification, or conditioning can share a common INCI name. This article is intended to clarify selection of products for formulation.
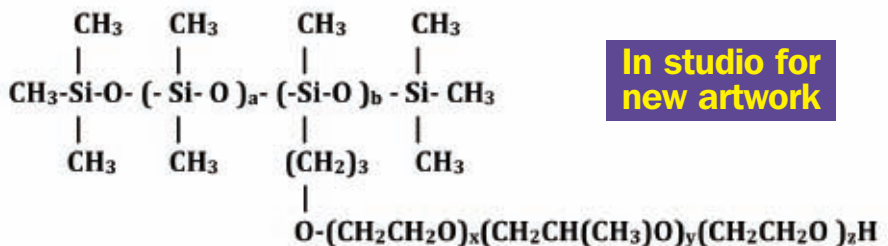
Figure 1: *PEG/PPG dimethicone structure.*

Surface tension

When added into water at low concentrations, PEG/PPG dimethicone (DMC) migrates to the air/water interface. As more DMC is added into the water, the interface becomes saturated and a critical point is achieved. When additional DMC polymer is added, it cannot migrate to the interface, so they start to form micelles. This critical point where the interface is saturated and micelles start to form is called the critical micelle concentration (CMC). Critical micelle concentrations are
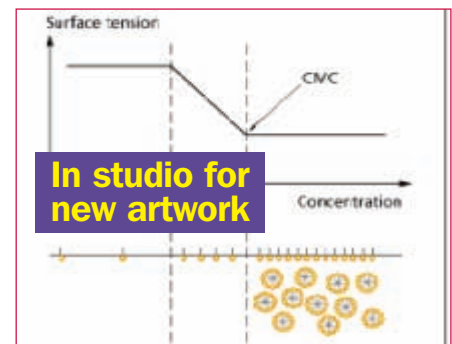

Figure 2: *Illustration of CMC.*[1]

Table 1: Surface tension and molecular weight.		
PEG 8 dimethicone (0.5 wt% solution)		
Product	Molecular weight	Surface tension (dynes/cm)
A	607	21.0
B	808	21.9
C	1108	23.1
D	1610	24.8
E	2111	26.3
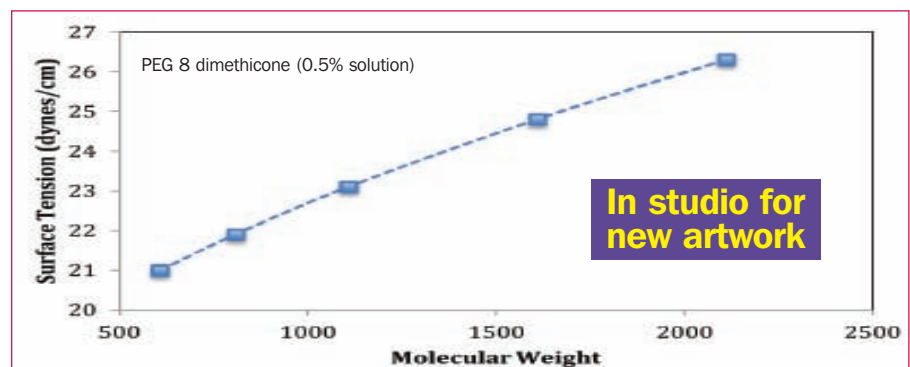
Figure 3: *Graphic surface tension and molecular weight.*

Young's Equation

$$\gamma^{sv} = \gamma^{sl} + \gamma^{lv}\cos\theta$$

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- γ^{lv}
- LIQUID θ
- γ^{sl} γ^{sv}
- SOLID

is the contact angle

is the solid/liquid interfacial free energy

is the solid surface free energy

is the liquid surface free energy

ramé-hart instrument

Figure 4: *Contact angle.[2]*

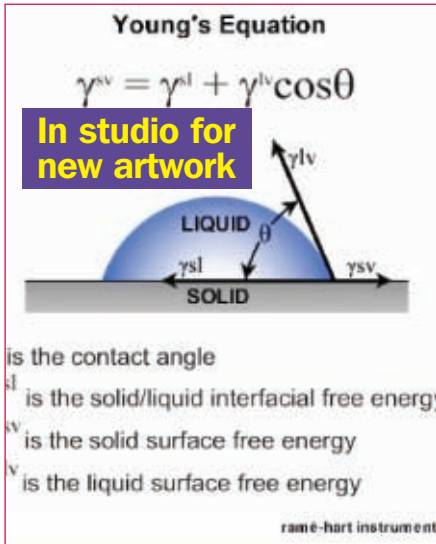In studio for new artwork

Figure 5: *Wetting time (seconds) versus molecular weight.*

determined by monitoring surface tension. Figure 2 shows an illustration of what happens upon addition of a surfactant into bulk solution.

The surface tension starts to decrease in a linear relationship with the amount of surfactant added. The moment the interface gets saturated, the surface tension stops decreasing.

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 that interface. This maximisation of free volume at the interface and its affinity for the interface makes the DMC extremely effective at lowering surface tension. This leads to DMC being used at very low concentrations to drastically change the properties of a solution. The molecular weight is a key concept in determining CMC. As the molecular weight increases, the CMC decreases. This is due in part to the fact that the surface can accommodate fewer 'large molecules' than small molecules. The CMC of a DMC is a key property to be determined before using a specific DMC in formulation, this is based upon the observation that if the DMC cannot get to the interface, it will not provide desired properties to the
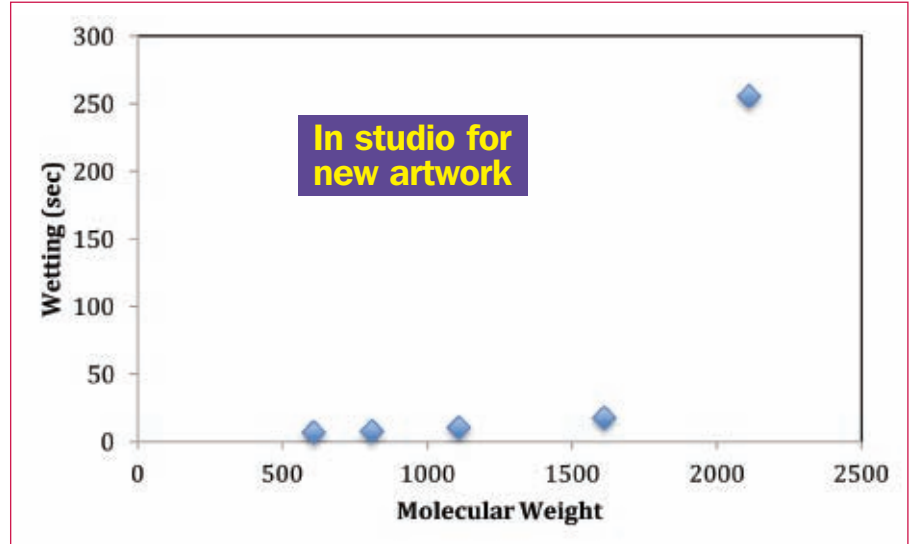
formulation. As will become clear subsequently, interaction with other raw materials in the formulation needs to be considered as well.

The surface tensions are related to the molecular weight of a series of PEG 8 dimethicone in which the ratio of silicone units to polyoxyalkylene units (a:b) are kept constant but increases. The results are shown in Table 1 and Figure 3.

The structure/function relationship is seen in these same compounds in both wetting times and eye irritation as shown below.

Wetting properties as a function of molecular weight

The term 'wetting' refers to how a material coats a surface. For example, if a water drop is placed onto a lotus leaf, the water will minimise the interaction with the leaf and have a high contact angle. If a good wetting agent is added either to the surface of the leaf or in the water solution that same drop will spread out coating the surface of the leaf, in turn making the leaf 'wet', and this is where the term wetting comes from. Figure 4 illustrates the Young's equation and how the contact angle is defined.

Table 2: Function of dimethicone copolyol versus molecular weight.

Molecular weight (Da)	Function
500	Wetting
2500	Emulsification
10000	Conditioning
50000	Waterproofing

Table 3: Draves wetting.

Sample	M.W.	Wetting time (Seconds)
A	607	7.0
B	808	8.0
C	1108	10.7
D	1610	18.0
E	2111	256.0

Table 4: PEG 8 dimethicone 1% foam test.

Sample	M.W.	Immediate	3 minutes
A	607	90	62
B	808	90	63
C	1108	95	67
D	1610	90	62
E	2111	90	61

Table 5: Foam height.

PEG 18/PPG 18 dimethicone 1% in water			
Sample	M.W.	Immediate	3 Minutes
F	7600	97	50

Table 6: Surface tension

Sample	Molecular weight	Surface tension (dynes/cm)
E	211	26.3
F	7600	31.3

$$CH_3\text{-}Si\text{-}O\text{-}(\text{-}Si\text{-}O)_a\text{-}(\text{-}Si\text{-}O)_b\text{-}Si\text{-}CH_3$$

with CH_3 groups and $(CH_2)_3$ chain leading to

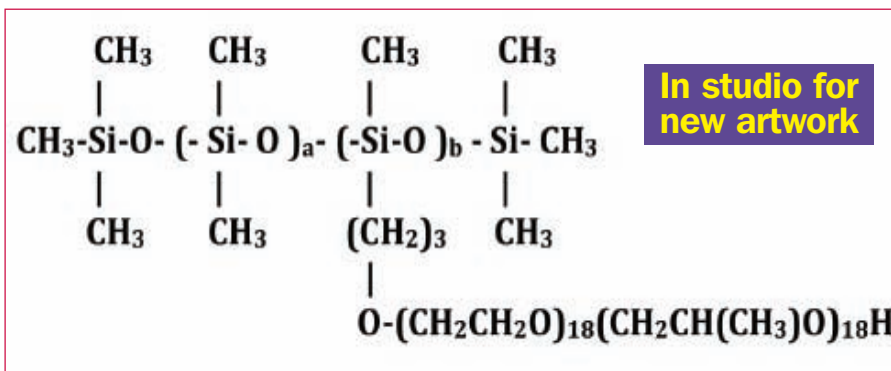$$O\text{-}(CH_2CH_2O)_{18}(CH_2CH(CH_3)O)_{18}H$$

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Figure 6: *Sample F – PEG 18/PPG 18 dimethicone structure.*

Table 7: Property comparison.

Property	Sample E	Sample G Star Product
Surface tension (0.5% aqueous)	26.2	30.5
Foam height (1% aqueous)	90	185
Cloud point (˚C)	58	89
Wetting time (seconds)	>200	>200

Figure 7: *PEG 8 dimethicone structure.*

The contact angle is defined as the angle the water makes with the surface. In this illustration, a low contact angle (θ<90˚) means the surface is hydrophilic. Large contact angles (θ>90˚) lead to a surface that is hydrophobic.

Another measure of wetting is the time required for a standard skein of fibre, or of hair to drop in an aqueous solution. This type of wetting time is called Draves Wetting (ASTM D2281). The lower molecular weight DMC polymer has faster wetting times than their high molecular weight counterparts. The lower molecular weight polymers allow for more efficient packing and dynamics. The materials with lower molecular weight were extremely effective at the higher concentration of 1.0% w. Their wetting speeds were almost instantaneous meaning it is controlled by the diffusion of the DMC polymer to the air/water interface. The interesting finding is that the wetting speed is lost slowly as the molecular weight is increased. The slope increases once one gets to a molecular weight over 2000. This implies that a rapid wetting conditioner can be prepared by proper selection of molecular weight. As the molecular weight of a polymer is increases, its ability to function in different capacities changes. This is due to hydrogen bonding and achieving lowest free energy.

If the ratio of a to b is held constant, the molecular weight of the polymers controls its wetting properties. As shown in Table 3, as molecular weight increases, the wetting ability decreases. Table 3 shows in tabular form the effect of molecular weight on wetting time and Figure 5 shows the same data in graphic form.

Foam

Ability to generate foam is an important functionality in any surfactant, including silicone surfactants. The ability to generate foam results from the balance of silicone portion to water soluble portion, which includes as an important variable the amount of PEG/PPG. The cylinder shake foam test data is shown in Table 4.

The data in Table 4 indicates that changes to the PEG-8 dimethicone with the D/D* ratio evaluated has really no effect upon foam, either initial or after 3 minutes. A change was made to Sample E replacing the PEG 8 group with PEG 18/ PPG 18. This material was designated Sample F and is shown in Figure 6.

Table 5 shows the result of the foam testing on Sample F. Table 6 shows the result of the surface tension testing on Sample F.

The inclusion of more EO and PO lowered foam, but interestingly also raised the surface tension. Simply put, the highly alkoxylatyed DMC polymer had a surface tension like a fatty alkoxylate, not like a silicone.

Star silicones

Knowing that molecular weight as shown above has little effect upon foam properties when the D/D* is kept constant, and that inclusion of EO/PO did not improve foam, a new series of products have been made and patented (US Patent 7,951,893 to O'Lenick *et al*, issued May 31, 2011). This class of compounds, referred to as Star Silicones, have unique properties and are a model useful in explaining the properties observed above. The structure of PEG 8 Dimethicone is shown in Figure 7.

The structure of the Star compound (Sample G) is evaluated in shown in Figure 8 and a comparison of the properties of Sample E and G are shown in Table 7.

It is noteworthy that the surface tension of Sample G is more reminiscent of a fatty compound than of a silicone (30s dynes/cm not 20s dynes/cm). It is also quite significant that the foam level

Table 8: Draize primary ocular irritation scale.

Moderately irritating	25.1 – 50.0
Mildly irritating	15.1 – 25.0
Minimally irritating	2.6 – 15.0
Practically non-irritating	0.6 – 2.5
Non-irritating	0.0 – 0.5

Table 9: Eye irritation of PEG 8 dimethicone by molecular weight.

Sample	M.W.	1-day irritation	7-day irritation
A	607	28	4
B	808	13	2
C	1108	5	2
D	1610	4	0
E	2111	2	0
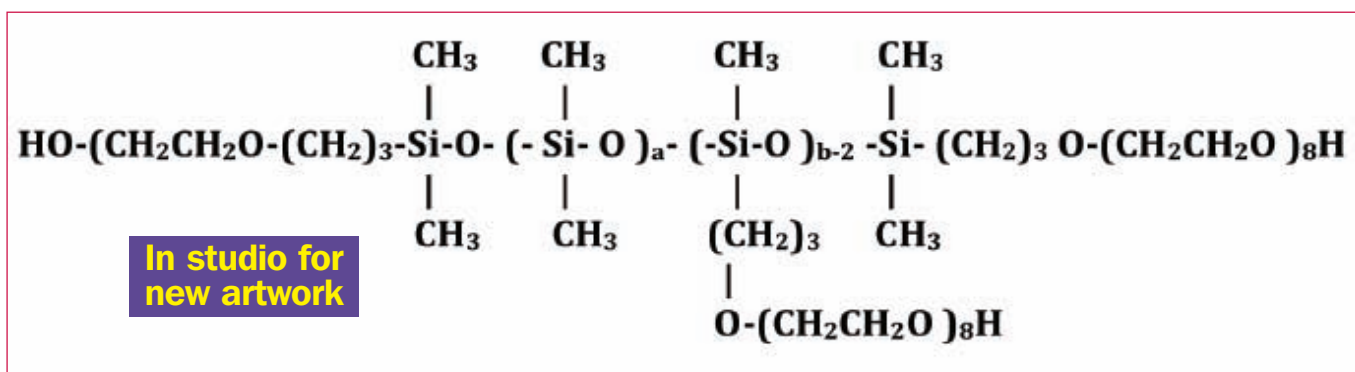
Figure 8: *PEG 8/Bis PEG 8 dimethicone (Sample G).*

is more than twice the non-star version. Most significantly is the cloud point, the temperature at which a 1% solution in water of the product becomes hazy while heating. It is significantly higher. This is an indication that the water is tenaciously held to the EO group.

Eye irritation as a function of molecular weight

Not only do wetting properties depend upon molecular weight, but the molecular weight is also a controlling factor in eye irritation. Lower molecular weight polymers penetrate into the eye, causing more irritation to the eyes. As molecular weight increases, irritation decreases. However, there is a very definite molecular weight effect over which irritation becomes little or no problem (Table 8).

The data in Table 8 was generated on a series of PEG 8 dimethicone polymers with the same a to b ratio, by increasing the total number of a and b units. The eye irritation was run at 20% active and was evaluated over one and 7 days. The data is presented graphically in Figure 9.

Formulation interactions

One of the most important factors facing the formulator of cosmetic products is how additives to formulations will interact with each other. This complication can include hydrophobic/hydrophilic interactions between ingredients, hydrogen bonding between ingredients, insolubility or limited solubility of ingredients, micelluar interactions, just to name a few. This explains why there is a great deal of trouble for the formulator to adapt raw material supplier data on function of products in a
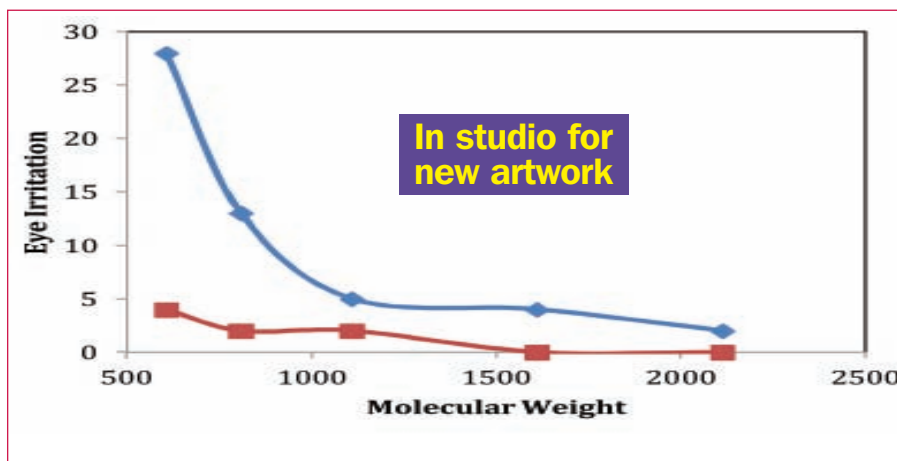

Figure 9: *Eye irritation of PEG 8 dimethicone by molecular weight.*

Table 10: RF_{50} definition.[3]
RF_{50} = the concentration of silicone surfactant added to reduce the surface tension to 25 dynes/cm.

pure aqueous environment with data obtained in the real world. Figure 9 shows the effect of adding PEG-8 dimethicone into an aqueous solution of DI water. The graph is quite ordinary and looks like what one might expect for a CMC. Notice, however, that the surface tension is significantly lower than for fatty surfactants (i.e. below 30 dynes/cm).

When the same PEG-8 dimethicone is added to a 1% solution of sodium lauryl sulfate, a completely different result is obtained. Figure 17 does not look like a CMC (critical micelle concentration) graph. This shows an interaction effect between the two surfactants as they compete for

surface at the air water interface. While not a CMC graph in the classical sense, this graph and its shape are very enlightening as to the effectiveness of the silicone surfactant when added to the surfactant. Since there is no clear break point as is seen with the CMC graph, we created a new point so the effectiveness of the addition of a silicone surfactant to another surfactant *vis-à-vis* surface tension reduction can be determined. That term is RF_{50} and it is described in Table 10.

Table 11 shows the results of addition of two different PEG-8 dimethicone molecules being added to 1% solution of two different sulfated fatty surfactants.

It is interesting to see from Table 11 that when SLS is used as a co-surfactant, the of the higher MW dimethicone copolyol has a RF50 of 1.5 %, while the lower molecular weight dimethicone copolyol has a RF50 of 1.2%. This shows that the low molecular weight polymer is more efficient at lowering the surface tension when a co-surfactant is involved. When comparing the RF50 in the samples containing SLES-2, the results are more dramatic. The RF50 for the low molecular weight PEG/PPG dimethicone polymer is 1.2, while the higher molecular weight PEG/PPG dimethicone polymer is 3.5%. This is much more significant and is driven by the hydrogen bonding between the 2 moles of polyoxyalkylene on the SLES, making getting to the surface of the solution much harder for the larger C-208 molecule.

How can this be applied when putting together a cosmetic formulation?
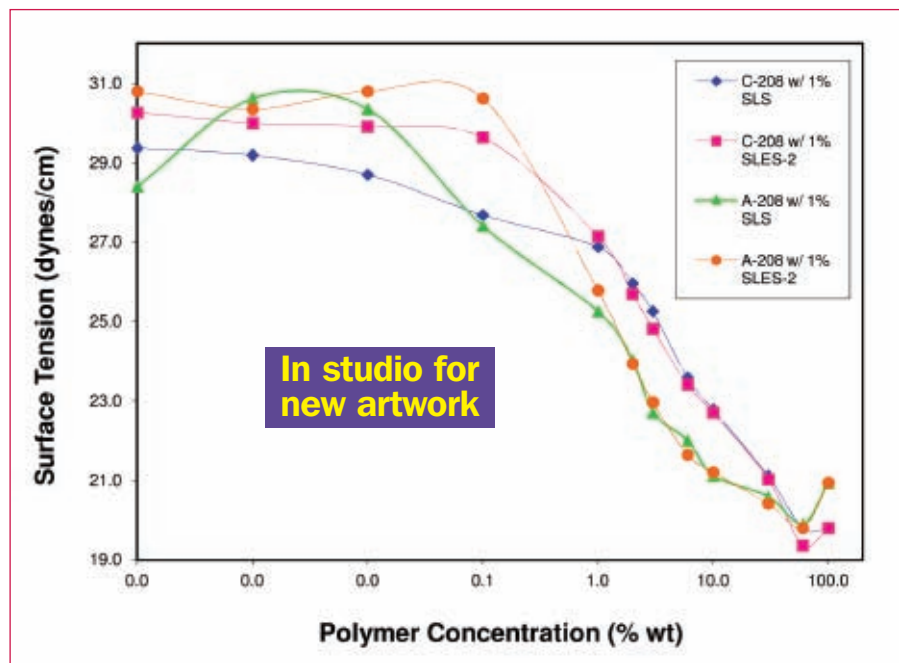
Figure 10: *CMC curve with SLS and SLES-2.*

Table 11: SLS/SLES-2 comparison.			
Silicone surfactant	Molecular weight	Co-surfactant	RF_{50} (%)
A-208	616.3	SLS	1.2
A-208	616.3	SLES-2	1.2
C-208	1556.5	SLS	1.5
C-208	1556.5	SLES-2	3.5

Table 12: $\Omega = (0.17)x + 1$			
Where as; Ω is the minimum number of D* units and x is the number of D units.			
Solubility in 10% H_2O			
D	D*	Calculated	Observed
5	1.0	Insoluble	Insoluble
5	2.0	Soluble	Soluble
10	2.0	Insoluble	Insoluble
10	2.5	Micro	Micro
10	3.0	Soluble	Soluble
20	3.5	Insoluble	Insoluble
20	4.0	Micro	Micro
20	4.5	Soluble	Soluble
24	4.0	Insoluble	Insoluble
24	4.5	Micro	Micro
24	5.0	Soluble	Soluble
40	6.0	Insoluble	Insoluble
40	7.0	Micro	Micro
40	8.0	Soluble	Soluble

Figure 11: *Water tolerance.*

It will be less efficient to use a higher molecular weight copolyol to lower surface tension effectively in SLES-2 based systems. It would be more efficient to use a lower molecular weight dimethicone copolyol.
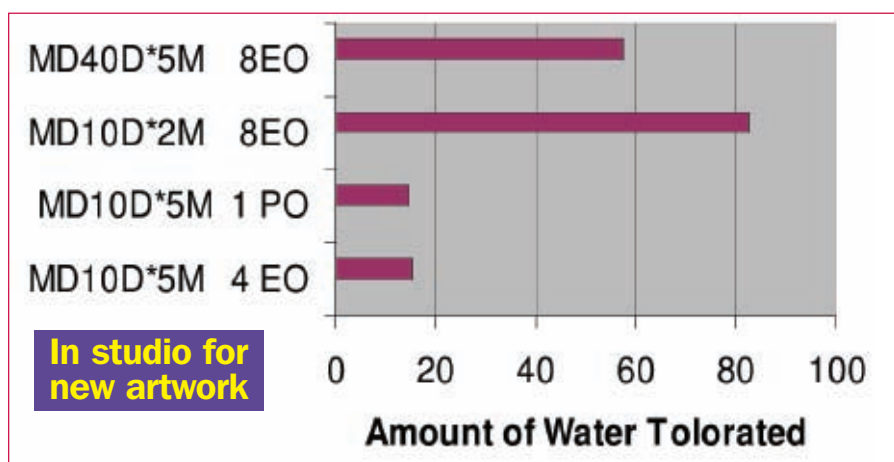
The evaluation of surface tension reduction in formulation needs to be determined to maximise the effectiveness of formulations. There is simply no other alternative.

Delivery of the silicone to the surface (interface) is a prerequisite to obtaining consumer perceivable advantages in formulations. The consumer can easily feel a difference in a formulation where there is a surface tension difference. As shown above, silicones when added into a surfactant solution with other surfactants affects the efficiency. Efficiency can be measured by RF_{50}.

Another mostly neglected structural variable that can dramatically change RF_{50} is the solubility of the silicone being added. Insoluble materials cause formulation problems, and too soluble materials result in the expensive silicone ingredient going down the drain. Products that form micro-emulsions (i.e. are thick and blue in colour when added to water) are most efficient. Consider the structure in Figure 7.

Table 13: Water tolerance test
1 Dissolve 2.0 g of dimethicone copolyol in 100.0 g of Isopropanol.
2 Slowly titrate in deionised water into the isopropanol solution.
3 Record the number of grams of water needed to produce the first haze.

As the ratio of a to b changes, the water solubility changes. This is because the 'a' subscript is related to a group that lowers water solubility, and the 'b' group to one that improves water solubility. A polymer with an a:b ratio of 100:1 will be insoluble in water and one with an a:b ratio of 1:100 will be very water soluble. Somewhere in between there will be a polymer that forms a microemulsion. It will be that polymer in the series that will offer the best effectiveness in solution. Using a wide range of a to b ratios, the polymer can be determined which provides a microemulsion. Knowing the a:b ratio (D:D* ratio) provides a means to calculate the ratio at which a microemulsion can be formed. From the formula, shown in Table 12, we can calculate the critical ratio needed to make a microemulsion.

It is always recommended that microemulsion forming polymers can be used in formulation, since these will be most effective at getting to the surface.

Water tolerance[4]

In the previous section water soluble silicones and silicone surfactants were discussed. In this section we will be discussing another important phenomenon to formulating chemists. To start our discussion we will have to first consider what happens when water is added into an anhydrous formulation. Most commonly, formulations will split or separate when water is added. Typically this is because the addition of water changes the HLB of the system, thus decreasing the solubility of one of the components in the formulation. A new concept has emerged and it is called water tolerance. Basically, water tolerance is a measure of how much water can be added into a formulation before the formulation splits.

PEG/PPG dimethicone polymers are in interesting polymer in the fact that they can be utilised to increase the water tolerance of a formulation. To test how the PEG/PPG dimethicone polymers effects the formulation, the water tolerance of the formulation has to be determined. The determination of water tolerance is based upon the fact that PEG/PPG dimethicone polymers are soluble in anhydrous isopropanol, independently of their solubility in water. Water can be added to the isopropanol solution until a haze develops. This haze signifies the water tolerance of the solution, this allows for the concentration of water tolerated by the formulation and is called 'water tolerance'. A common procedure for determining the water tolerance is described in Table 13.

Figure 11 shows the water tolerance of specific silicone compounds. As the D:D* ratio (a:b ratio), i.e. the number of D units (hydrophobic) compared to the number of water soluble groups (D*), goes up the materials become more water insoluble and the water tolerance drops. What is very interesting and warrants consideration is the fact that 1 mole of propylene oxide will increase water tolerance as much as four moles of ethylene oxide does.

Conclusion

PEG/PPG dimethicone polymers can be effective additives to cosmetic formulations if the formulator is careful to use the proper polymer for achieving the proper effect. One can simply not choose a product by INCI name for matching the label as it is unlikely that the products from different manufacturers will be identical chemically or functionally. Only by evaluating the effect in formulations can the formulation be optimised. **PC**

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