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The ongoing quest for a D5 replacement

KEYWORDS: D5, cyclopentasiloxane, D4 cyclotetrasiloxane, dimethicone, methicone, ethyl methicone, butyl methicone, surface tension, spreadability, hydrocarbon, natural hydrocarbon, regulations, wetting.

ABSTRACT

As the regulatory pressure continues on the use of cyclomethicone compounds, it is looking increasingly that silicone will continue to be needed to achieve the combination of properties needed to make a truly functional product. The set of requirements for a functional product appear to be mostly physical (surface tension, spreading, wetting and volatility) rather than chemical.

REGULATIONS

The regulations that are imposed on the use of D5 continue to grow. These are outlined in Table 1.

D4 (cyclotetrasiloxane)
The European Commission has classified D4 as a reprotoxic substance, category 3 [ECB 2006]. The NOAEL for systemic toxicity (150 ppm) used for this risk assessment also covers reprotoxic effects (NOAEL = 300 ppm) (1).
D5 - Cyclopentasiloxane
The European Commission has published Regulation (EC) 2018/35 to restrict the use of Octamethylcyclotetrasiloxane (D4) and Decamethylcyclopentasiloxane (D5) in "wash-off cosmetic products" as defined in Article 2(1)(a) of Regulation (EC) No 1223/2009 (2)

Table 1. The Regulations.

This increased regulation will put more pressures on to find suitable replacements, what originally sounded like a reasonable task has proven to be a difficult undertaking.

D5 Sensory

What gives D5 its feel? This turns out to be a rather complex question, related to both physical chemistry and structure.
Cyclomethicone compounds possess a cyclic structure rather than the chain structure of linear dimethyl silicones (dimethicone). Likewise, D5 has a low heat of vaporization and low vapor pressure has led their use as cosmetic vehicles. Volatility has some impact on the feel. It is quite interesting that D4 is appreciably more volatile than D5.

Volatility is but one aspect of the complex phenomenon that contributes to a dry feel in a solvent used in cosmetics. Other considerations that impact upon selection of a D replacement include viscosity, surface tension reduction (which affects spreadability), flammability of the solvent, effects of the solvent on skin and cost. Clearly, a D replacement that is flammable, defatting and expensive is unacceptable. Table 2 outlines what we think are the properties replacement materials for D require.

1. Dry feel.
2. Volatility at ambient temperature meaningless.
3. Lack of flammability.
4. Cost effective (compared to D5).

Table 2. D5 Replacement – Desirable Properties.

This article will address several recent approaches taken in the market and the progress made recently.

Volatility

Volatility is the ability of the compound being tested to evaporate under the temperatures at which the compound is used in formulation. For cosmetic products, this temperature is ambient (~25° C). It has generally been accepted that cyclomethicone compounds provided this feel because they evaporate quickly after helping to carry oils into the top layer of the epidermis.

The ability to provide a product that (1) has the dry feel, (2) is cyclomethicone free, (3) is not capable of making cyclomethicone when exposed to catalyst and (4) is not flammable is a long felt need, unsatisfied need in the cosmetic industry.

Since we have long called D4 and D5 volatile silicones this appears to be a good point to start the investigation. Just how volatile are D4 and D5 and the recommended materials which are recommended to replace them.

STANDARD SILICONE PRODUCTS

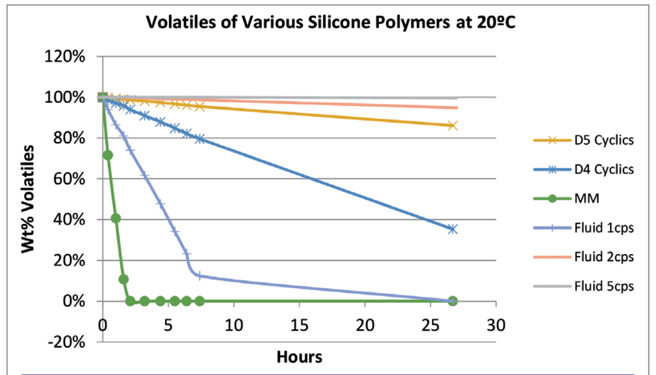
One of the most common product suggestions to replace D5 are silicone compounds that are well known and commercially available. The compounds shown in Table 3 include D5, D4, 0.65 Cst fluid, 1 and 2 Cst dimethicone.

We firstly wanted to compare volatility, that is the % the weight lost over time. Table 3 shows the results in tabular form and Graphic 1 shows them in graphic form.

VOLATILITY

Hours	D5	D4	MM	Fluid 1cps	Fluid 2cps
0	100.00%	100.00%	100.00%	100.00%	100.00%
0.4	99.80%	98.60%	71.60%	94.00%	99.90%
1	99.40%	97.10%	40.60%	86.50%	99.90%
1.6	99.10%	95.80%	10.70%	81.00%	99.80%
2.1	98.70%	94.00%	0.00%	74.00%	99.70%
3.2	98.10%	91.00%	0.00%	61.60%	99.50%
4.4	97.40%	87.90%	0.00%	47.70%	99.30%
5.5	96.70%	84.80%	0.00%	34.20%	99.10%
6.4	96.10%	82.20%	0.00%	23.30%	98.90%
7.4	95.50%	79.60%	0.00%	12.40%	98.70%
24.0	86.10%	35.30%	0.00%	0.00%	94.90%

Table 3. Volatility of Standard Silicone Polymers (20°C).



Graphic 1. Volatility of Standard Silicone Polymers (20°C).

Conclusions on volatility

1. The most volatile of all materials tested was MM (0.65 Cst dimethicone). It virtually evaporated over the first 2 hours. Table 4 shows that MM is flammable, while all others were combustible.
2. Despite the fact the most common substitute for D4 since it was regulated cosmetic products in 2005 is D5. D5, D5 is much less volatile that D4. (D4 at 65.7% and D5 at 13.9%).
3. 1 Cst dimethicone is not flammable, it is 100% volatile.
4. 2 Cst fluid is 5.7% volatile and not flammable.

Material	Bp (°C)	MP (°C)	CAS	EINECS	Hazard	Volatility (20°C) (Loss @ 24 hrs)
D4	175	17.5	556-67-2	209-136-7	Combustible	64.7%
D5	210	-38	69430-24-6	209-136-7	Combustible	13.9%
MM (0.65)	153	12	107-46-0	203-492-7	Flammable	100%
1 Cst	194	-80	107-51-7	203-497-4	Combustible	100%
2 Cst	112	-70	141-63-9	205-492-2	Combustible	5.1%

Table 4. Properties of Standard Silicone Compounds.

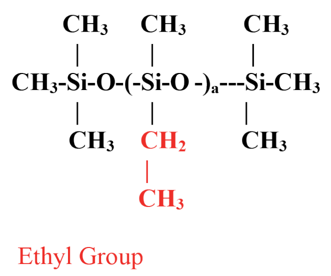
Based upon the above information it is not difficult to see why low viscosity silicone fluids (1 Cst and 2 Cst) are recommended as replacements for D5. Interestingly, nothing but MM (including D5) is as volatile as D4.

It is quite likely that if volatility were the only factor, or the salient factor controlling the feel, the big difference in volatility between D4 and D5 would probably made us choose another replacement for D4.

ALKYL DIMETHICONE COMPOUNDS

Lower alkyl (C2 and C4) were also evaluated as replacements for D5, looking at volatility.

Compounds evaluated have the structure shown in Structure 1. As the "a" value increases the % by weight of ethylene in the molecule increases.

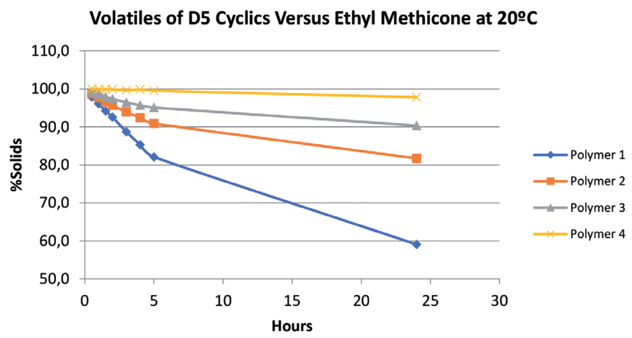


Structure 1. Ethyl Methicone.

Table 5 shows the volatility of ethyl methicone compounds based upon the % by weight ethyl group present. This data isshown in a graphic as Graphic 2.

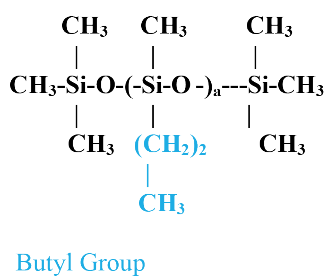
Hours	0.5	1	1.5	2	3	4	5	24	% Ethylene
Polymer 1	97.9	96.1	94.2	92.6	88.7	85.3	82.1	59.1	11.1
Polymer 2	98.7	97.7	96.5	95.6	93.9	92.4	90.9	81.7	16.5
Polymer 3	99.1	98.6	97.9	97.4	96.4	95.7	95.1	90.3	19.7
Polymer 4	100.0	100.0	99.9	99.9	99.6	99.9	99.5	97.8	21.7

Table 5. Volatility Ethylene Based Methicone.



Graph 2. Volatility Ethylene Based Methicone.

Compounds evaluated having butyl groups as shown in Structure 2. As the "a" value increases the % by weight of ethylene in the molecule increases.



Structure 2. Butyl Methicone.

The volatility of compounds with butyl groups are shown in Table 6.

Hours	0.5	1	1.5	2	3	4	5	24
Polymer 5	99.6	99.1	98.5	97.9	96.7	95.8	94.7	79.6
Polymer 6	99.5	99.3	98.9	98.7	98.2	97.7	97.2	90.6
Polymer 7	99.8	99.6	99.5	99.34	98.9	98.8	98.4	94.8
Polymer 8	99.9	99.7	99.5	99.27	99.1	98.8	98.6	95.2

Table 6. Volatility Butylene Based Methicone.

Polymer 1 and Polymer 4 have been recommended as potential replacements for D5 and have some commercial applications, but the dry feel associated with D5 is much more complex that simply volatility. A material that is completely volatile like MM does not give the same dry feel as D4. In fact, it is more like ethanol in that there is substantially no feel left upon evaporation. There is a pleasant non sticky feel on the skin, which we attributed to spreading on the skin. D5 has a different feel upon drying than does D4 or MM. The replacement of D5 requires more than a volatility match.

Surface Tension

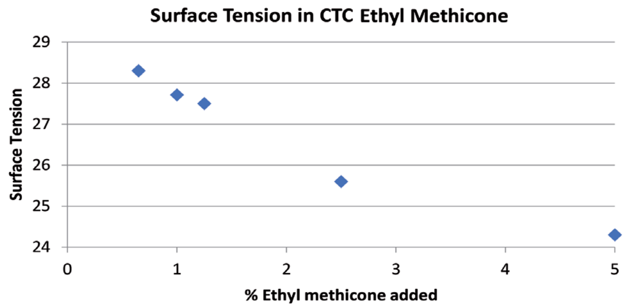
One of the key properties that make silicone interesting in personal care products is its ability to lower surface tension. Fatty compounds have a surface tension of about in the 30 dynes/cm² .area. Silicone compounds have a surface tension of about in the 20 dynes/cm² area. This is because the fatty compounds have primarily methylene groups (-CH_2-) at the interface, while silicones have methyl groups (-CH_3). In fact, the compounds shown above all have surface tension values between 22 and 25 dynes/cm. Surface tension reduction which improves spreadability is considered critical to make an acceptable feeling D5 replacement.

To the formulator interested in obtaining the dry effect on the skin provided must look to the fact that silicone compounds listed above function in part by the efficient reduction of surface tension of an ester using low concentrations of alkyl silicone is an important concept.

SILICONE / ESTER COMBINATIONS

Some carefully selected silicone compounds when added to low cost esters result in clear low surface tension solutions. This lower surface tension together with low viscosity, results in a dry skin feel because of efficient spreading. Graphic 3 shows the effect of adding ethyl methicone to caprylic / capric triglyceride. Certain highly branched esters do in fact have a low surface tension but are too expensive to provide the desired functionality in a cost effective manner.

The quest for a D5 replacement that meets the established requirements of feel, cost and lack of flammability will almost certainly be achieved using a low concentration of a silicone that can efficiently lower the surface tension of an inexpensive ester.



Graphic 3. Ethyl Methicone (Polymer 1) in C8-10 Triglyceride.

Not only has the approach of replacing D5 with combination of natural oils and a small amount of alkyl silicone is approach been used to replace D5, the replacement is greener than D5 (due to the fact that natural oils are present), not flammable, effective in many formulations, and is cost effective because the majority of the material used is a relatively inexpensive natural oil. Additionally, properly chosen ethyl methicone chosen for low viscosity, spreadability and low surface tension in the organic chosen, have the following properties making them of interest when used in combination together with esters or triglycerides as D5 replacements.

Silicone Blends

The blending of silicone polymers into fluids has been widely investigated in an attempt to develop products that would be clear and lower the surface tension, which in turn would improve spreadability. There are two difficulties with this approach. Firstly, the dimeticone may not be soluble in the oil causing separation, or it may be too soluble in the oil leading to poor surface reduction efficiency.

This approach has been successful and has demonstrated that surface tension reduction is more important than volatility in achieving a D5 replacement. Table 7 shows the solubility of 20% by weight of several dimethicone polymers diluted in olive oil.

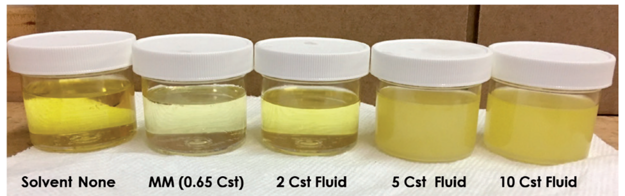


Table 7. Solubility of 20% Silicone Polymers in Olive Oil.

Finding a particular silicone that will effectively lower surface tension of the ester or hydrocarbon to achieve the desired effect and that remains soluble in the ester or oil remains a challenge.

One commercially available product, Siltech DOSA is a mixture of sweet almond oil and ethyl methicone. The surface tension is shown in Table 8. Properties are outlined in Table 8.

Product	Surface Tension (mN/m)	Standard deviation (mN/m)	Viscosity, cps, 60 rpm@25C	Appearance
Sweet Almond Oil	31.028	±0.118	110	Clear
Siltech DOSA	25.373	±0.093	100	Clear
10% Siltech DOSA in Sweet Almond Oil	29.350	±0.133	110	Clear.

Table 8. Blends of Ethyl methicone and Sweet Almond Oil.

Synthetic Hydrocarbons

A number of vendors recommend hydrocarbons and hydrocarbon blends as D5 replacements. These specifically include; Isododecane (flammable (7)), dodecane (flammable (8)), and tetradecane (flammable(8)). Polyalphaolefins is a polymer made by polymerizing an alpha-olefin. They are designated at API Group IV and are a 100% synthetic chemical compound (9). They are highly branched oils.

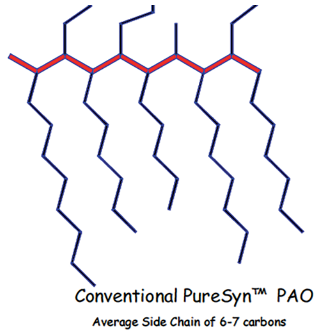


Table 9. PAO Structure (10).

Hydrogenated PAO (n poly alpha olefins) are a good material to which silicone can be added in an attempt to develop a D5 replacement. Not only will the surface tension be reduced by addition of the silicone to the PAO, the spreadability will also improve. Table 10 shows the incredibly fast spreading rate of Dimethicone 5cSt. Nothing in the table comes close.

Using the most efficient silicone additive to the other less spreading materials will likely give a more D5 like feel.

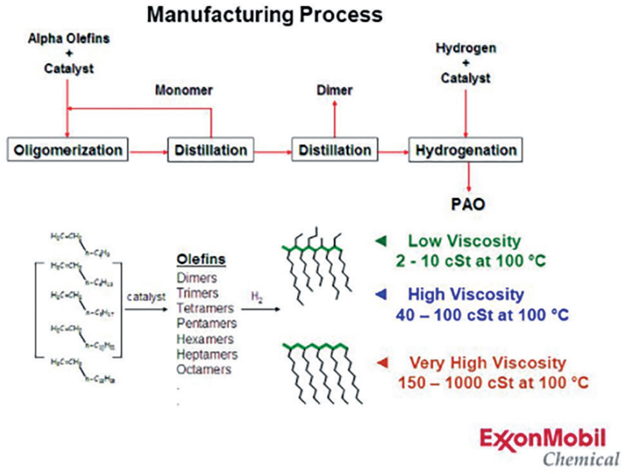


Table 10. Polyalphaolefin (10).

PAO while much less able to spread on artificial skin, has fast spreadability and is low viscosity and dry. Table 11 shows the results.

Material	mm² @ 5 minutes	Relative Rate
Dimethicone 5cSt	651	Very Fast
Isopropyl Myristate	371	Fast
C12-15 Benzoate	314	Fast
PAO (Pursyn 2)	301	Fast
Caprylic Capric Triglyceride	288	Medium
Dimethicone 350 Cst	127	Slow
Mineral Oil	83	Slow
Castor Oil	27	Slow

Table 11. Spreadability on Vitro Skin*.
*VITRO-SKIN® (Innovative Measurement Solutions, Inc., Milford, CT) was first hydrated at 23°C and 60% relative humidity for 24 hours. Five microliters of the test material were placed on the hydrated VITRO-SKIN® and the spreading area was measured after 5 minutes. The relative spreading rate of the test materials was then classified based on an established emollient classification system (11).

Addition of the ethyl methicone or butyl methicone will also lowed the surface tension and lead to a better match for D5. Table 12 shows the surface tension reduction.

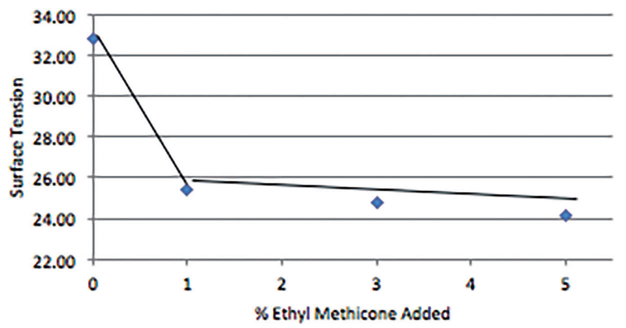


Table 12. Surface Tension Reduction PAO.

NATURAL OIL DERIVED HYDROCARBONS

A product has been developed by Elevance that makes olefins from natural oils via a process called Metathesis (11). The process allows for the conversion of natural oils into decene, which is then polymerized into polydecene, then hydrogenated. U.S. Patent 7,960,599 (12) describes a process for producing industrially "biobased" products using fatty acids rather than exploiting fossil sources, such as coal and petroleum. A flow diagram is shown in Table 13 (13).

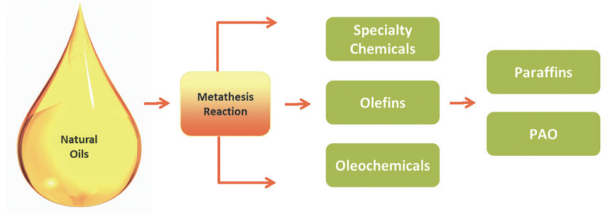


Table 13. Metahesis Reaction (13). Elevance Renewable Sciences' energy-efficient biorefinery process affords paraffins and PAO through conventional transformations of its bio-based olefins.

An additional approach is to evaluate lower molecular weight methyl esters on natural oils. One such product is PELEMOL® EC which has an INCI name of Ethyl Canolate. When a drop is placed on the skin and slowly spread the product the feel like D_5. It penetrates the strateum cornium and disappears from the surface. So, whether the product is volatile or not is not relevant. Perception is reality.

CONCLUSION

It appears that a combination of properties related to volatility, spreadability, low surface tension, and low viscosity are needed to make a real mimic of D5. At the current time it appears that the best candidates will be formulated blends. The best candidate will be the blend that can approximate all of these parameters in one composition.

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ABOUT THE AUTHOR

***Tony O'Lenick** is President of Siltech LLC. Tony has published six books, numerous articles and has over 300 patents. He received the 1996 Samuel Rosen Award, the 1997 Innovative Use of Fatty Acids Award and the 1996 Partnership to The Personal Care. Tony was President of the U.S. SCC in 2015 and is currently Education Chair of IFSCC.*