Silicone: Expanding Opportunities for a Performance-Enhancing Material in the Detergent Industry

Ir. Benoît Hénault
Dow Corning S.A.
Seneffe, Belgium

Russ A. Elms
Dow Corning Corporation
Midland, Michigan USA
After the introduction of the first synthetic surfactants in laundry products more than 50 years ago, silicones have been used in the detergent industry for the last 35 years to provide effective foam control in consumer washing machines. Silicone antifoams are also well known and used as process aids in numerous industrial processes involving foaming medium, synthetic surfactants or both.

Within the textile industry, silicone products have been used for nearly that long. However, the primary textile benefits and applications from silicones have been as antistatic agents, fibre and thread lubricants during fabric production, and antifoaming and fabric softening agents during the fabric-finishing step. Additional textile finishing benefits derived from silicones also have been introduced. These include antimicrobial properties, water repellence characteristics, elastomeric finishes, antistatic properties and, surprisingly, improved hydrophilicity. Actual and potential contributions of silicones to today’s garment needs can be grouped in three categories:

- **Garment comfort** including benefits such as fabric elasticity, softness, breathability, static-free properties, water absorbency and perfume release characteristics.
- **Garment protection** including benefits such as water resistance, wind-proofing, abrasion resistance and antimicrobial properties.
- **Easy care** including benefits such as wrinkle resistance, ease of ironing, fabric dewatering, shrinkage control, durable press, finish durability, strength retention and soil release compatibility.

It is known from both the textile and laundry industries that the laundry wash cycle process removes most of these fabrics finishes. It is considered that about 10 wash cycles are sufficient to remove most of the initial garment fabric care attributes.

With ever-demanding consumers having less time for clothing care, wanting clothing to look better and as new as possible after repeated washing, and expecting clothes to be comfortable directly from the dryer, it became a market need to deliver the known textile industry technology into consumer laundry benefits. Dow Corning has been working in the recent years to identify and develop technologies to meet some of the above benefits when applied into laundry products.

The distinctive physicochemical properties of silicone polymers and the ability to tailor their architecture and functionality can bring a variety of consumer relevant benefits when correctly formulated. Softness improvements, ease of ironing, water absorbency and to a lesser extent, antiwrinkle characteristics, have been demonstrated and commercially implemented. New science and technologies that bring improvements in fabric dewatering, fabric elasticity, shape retention and perfume release are amongst the new areas of developments described in this paper.

### Fundamental Properties of Silicones Related to Fabric Care Benefits

The chemical structure of a silicone polymer or polydimethylsiloxane (PDMS) is typically characterised by an inorganic Si-O backbone on which organic side groups are attached (Figure 1). In most cases, these are methyl moieties. The degree of polymerisation varies from n=1 to several thousands. The polymer spatial conformation is helicoidal.

Knowing some of the fundamental properties of siloxane \(^1\) and how they translate to macroscopic properties is key to understanding why silicones provide unique fabric care application benefits. Chemical bond characteristics of Si-O-Si compared to organic C-C-C or C-O-C bonds provide to siloxane the flattest and longest bond angle, while having a much higher bond energy and a lower rotation activation energy (Figure 2).

The consequences are for PDMS to exhibit unique chain flexibility with a versatile orientation of the molecule versus different substrates, and to have a helicoidal molecular conformation due to the orientation of the methyl moieties toward the outside. Among the important resulting macroscopic properties of PDMS are:

- Low viscosity due to low intermolecular interactions even at high molecular weight
- Extremely low surface tension and high spreading ability
- High hydrophobicity
- High gas permeability
- High refractive index

All these properties account for the distinctive application benefits of silicones:

- Excellent lubricity
- Non-adherence properties
- Softness
- Surface property modification, hydrophobisation or hydrophilisation

![Figure 1. Molecular structure of polydimethylsiloxane (PDMS).](image)

\[
R = \text{OH or CH}_3 \\
n = 64 \quad 100 \text{ cps} \\
n = 320 \quad 1,000 \text{ cps} \\
n = 730 \quad 10,000 \text{ cps} \\
n = 1300 \quad 50,000 \text{ cps}
\]
Silicone technologies were selected based on silicone polymer types and emulsion properties that suggested useful fabric care benefits.

The main technical parameters of silicone product technologies affecting fabric care application benefits are based on the following elements:

- Polymer functionality and architecture
- Type of delivery vehicle
- Particle size properties of emulsion vehicle
- Surfactant systems used with emulsion vehicle

**Polymer Functionality and Architecture**

The polymers of interest are mainly methyl, hydroxy, amino, amido, polyether and alkylmethyl functionalised silicone polymers. These functionalities can be a termination or a pendant group, and this will be important regarding the molecule interactions with the substrate and the subsequent surface properties modification, their substantivity, the molecule conformation and susceptibility to further polymerise on the substrate. Some polymers can be cyclic, but the majority are linear with various molecular weights, from volatile to high consistency gums. They can also be cross-linked to variable levels to provide higher substantivity, controlled spreading and elastomeric properties.

**Type of Delivery Vehicle**

The active polymers may be delivered in a variety of ways depending on the specific requirements of the application formulation. Typically the active can be either:

- Self emulsified in the formulation (polyethers)
- Emulsified in situ (low molecular weight polymers, amino)
- Pre-emulsified (most polymers)
- Volatile silicone used as a secondary delivery system within the emulsion and active while on the substrate

**Particle Size Properties of Pre-emulsified Actives**

Silicone emulsions are available either as microemulsions (<100 nm) or macroemulsions (>100 nm) depending on the polymer functionality or architecture selected. The emulsion particle size is often related to the properties ultimately observed on a fabric.

Microemulsions are able to penetrate into the yarns and deposit onto the fabric fibers, bringing a soft, dry feel to fabric. Studies by Dow Corning suggest that the deposition of silicone is internal, which provides dry lubrication of individual fibers against each other with a very thin coating of silicone, probably reducing the static coefficient of friction.

Macroemulsions deposit on the external surface of the fabric, causing superior lubrication through reduction of the dynamic coefficient of friction. They provide relatively good fabric softening performance.

**Surfactant Systems Used With Emulsion Vehicle**

Silicone emulsions may be formulated with adequate anionic, nonionic or cationic surfactants, the choice being driven by the compatibility with the application formula and the mechanism of silicone action or deposition. To demonstrate its benefits, the silicone must generally deposit on the fabric. This deposition is triggered either by the polymer functionality, the emulsion surfactant system or both used in synergy with the application formulation. Some internal studies have demonstrated high levels of silicone deposition onto fabric when delivered through fabric softener application. We suggest the following mechanism of deposition.

**Proposed Silicone Deposition Mechanism**

Fabric softeners are typically a water dispersion of dialkyl ester ammonium compound including other ingredients such as nonionic surfactants, fatty acid, alcohols and perfume. The product pH is generally acidic for chemical stability reasons, and the application occurs during the last rinse of a wash cycle at around pH=7. The contact time with treatment solution does not last for more than five minutes. Cotton fabric was selected as the study substrate.

Measurement of silicone deposition levels onto fabric is delicate but accessible through an extraction method using trimethyl pentane as an extraction solvent and quantifying the concentration using FTIR between 1140 cm\(^{-1}\) and 1000 cm\(^{-1}\) in hexane. In Figure 3, results for silicone are expressed in terms of the percent of the maximum theoretical deposition concentration on the fabric.

These results suggest that a synergy in deposition exists between nonionic emulsions and quats, while this synergy is less important or negligible with cationic emulsions.
In this particular system, the deposition mechanism of silicone emulsion is believed to be essentially a charge-driven mechanism. The surface potential of wet cotton measured using the streaming potential method gives an average value of zeta potential of \(-30\) mV. Silicone emulsion zeta potential can also be measured through electrophoretic mobility. As such, a nonionic emulsion has a neutral potential while a cationic emulsion shows a +35 mV potential.

The ability of nonionic emulsions to deposit is to be found in the occurrence of cross contamination of emulsion particle sizes with free cationic surfactant from the softener and the modification of its surface potential. It has been measured that the zeta potential of a nonionic emulsion can be increased up to +15 mV, which could explain the synergistic mechanism. Deposition levels above 80% can be easily achieved with cationic emulsions or using the right type of ammonium compound.

Modelisation of deposition pattern suggests a patchy deposition of actives where the silicone polymer will subsequently spread to a thin film onto the quat hydrophobised cotton surface (Figure 4).

**Fabric Care Benefits Delivered by Silicones**

**Fabric Softening**

Panel testing on towel swatches is typically used to evaluate softening benefits. Dow Corning’s internal test considers 16 panelists and focuses on paired-comparison tests between a reference treatment based on a 16% active triethanolamine-based diesterquat softener and the same with the addition of a silicone additive. Figure 5 shows that a first evaluation at 3% active silicone gives the following results. Performance data in subsequent figures uses these same codes and samples.

Subsequent extensive internal and external evaluation (Figure 6) including paired comparisons and numerical tests show that particular technologies are susceptible to delivering a perceivable softening benefit at much lower silicone concentration when added to a softener composition.

Numerous patents have been filed on this application since 1976, and many commercial product implementations exist, mainly in fabric softeners but also in liquid detergents. The fundamental properties of silicones behind this application benefit are their low surface tension, low intermolecular interactions, high spreading and non-adhesion characteristics.

**Ease of Ironing - Friction Coefficient**

The ease of ironing benefit can be subjectively assessed through paired-comparison panel tests but can also be objectively measured by friction coefficient (FC) measurements. Several protocols exist to measure static and dynamic FC. IEC 60311 Clause 24 describes measuring the force needed to pull a standard iron over a fabric on a horizontal axis at a constant speed. A selection of results comparing water-rinsed with softener-rinsed fabric show that highly significant lubrication (C.L. > 95%) can be achieved with a fairly low level of silicone (Figure 7).

**Figure 3. Levels of silicone deposition in fabric softening applications.**

**Figure 4. Silicone deposition pattern during rinsing and drying.**

**Figure 5. Softening performance summary by technology.**

<table>
<thead>
<tr>
<th>Code</th>
<th>Polymer Technology</th>
<th>Emulsion Technology</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Low MW PDMS</td>
<td>Anionic microemulsion</td>
<td>=</td>
</tr>
<tr>
<td>B</td>
<td>Low MW amino</td>
<td>Nonionic microemulsion</td>
<td>••</td>
</tr>
<tr>
<td>C</td>
<td>Medium MW amido</td>
<td>Nonionic microemulsion</td>
<td>••••</td>
</tr>
<tr>
<td>D</td>
<td>Medium MW PDMS</td>
<td>Cationic microemulsion</td>
<td>••••</td>
</tr>
<tr>
<td>E</td>
<td>Medium/high MW Elastomeric PDMS</td>
<td>Cationic macroemulsion</td>
<td>••••</td>
</tr>
<tr>
<td>F</td>
<td>Medium MW Elastomeric amino</td>
<td>Cationic macroemulsion</td>
<td>N.A.</td>
</tr>
</tbody>
</table>
Here again several patents exist and are actually practiced in the fabric softener market.\textsuperscript{6,7} The fundamental properties behind this application benefit are the same as softening, with the proviso of higher levels or external deposition of the silicone.

In laundry liquid, sample C provides significant ease of ironing benefit at 1.5\% active without an issue of stability or appearance. High molecular weight silicone polyethers are of interest in nonaqueous liquids.

Easy iron spray trigger and aerosol are other commercial product forms.\textsuperscript{8}

**Fabric Dewatering**

There is an interest in terms of consumer convenience to accelerate fabric drying, matching wash and drying cycle times, and also to contribute to a reduction of tumble dryer consumption. The approach to reduce the amount of water left in the fabric after the wash/spin cycle directly correlates with a reduction of drying time/energy. Because most water loss occurs during the spin cycle, Dow Corning concentrated on this step and evaluated several technologies.

The weight of fabric load is measured after full wash cycle and compared to initial weight to give the water pick-up level. Figure 8 shows that when dosed at 1\% active in the softener, up to a 13\% further reduction of water content can be achieved with the tested silicones over quat-rinsed fabric, which is already reduced by 23\% over the water-rinsed fabric.

It is believed that the fundamental silicone properties behind this benefit are hydrophobisation of the fabric surface and its subsequent dewetting, as well as its low surface tension, which allows fast spreading.

Several patents were issued and are commercially practiced.\textsuperscript{9,10}

**Water Absorbency**

Fabric softeners have the side effect of hydrophobizing fabric, which is a concern for consumers who want a soft, bulky towel with good drying properties. Surprisingly, in the middle 1980s, it was found that the addition of silicone polymer in a fabric conditioner composition actually improves the water absorbency of fabric.

Water absorbency is evaluated by a Drave’s wetting test, which measures the time required for a fabric sample to sink to the bottom of a 1L beaker filled with demineralized water. Results are relative to a given quat type and are arbitrarily stopped after 300 s.

Several patents\textsuperscript{11} were issued from the mid 80s until recently for a variety of silicone structures and compositions, but...
so far no clear, convincing interpretations of this phenomenon have been published. Because low molecular weight PDMS is known to be the most effective in water absorbency studies, we suspect that the versatile orientation of the silicone molecule and its ability to modify surface hydrophobity/hydrophilicity as well as its low viscosity and high spreading rate are involved.

Figure 9 summarizes the results of water absorbency tests for treated fabrics.

Wrinkle-Related Benefits
Perhaps the most critical objective of fabric care is to reduce garment wrinkling after the wash cycle and during ironing, and also to improve wrinkle resistance during wear. It is not surprising that this is a difficult technical challenge, because the mechanism of wrinkle formation is complex and not easy to access from a laundry application perspective. The textile industry has been able to meet this challenge to some extent through the application of “easy care” finishes. These treatments are based on a high-temperature cure of crease resist resins (DMDHEU), quat and silicone. However, its use is not compatible with consumer washing processes and safety. The current opportunity is extensive for technical improvements that can bring satisfactory performance.

Based on internal panel tests, a specific cationic emulsion of elastomeric amino silicone (F) dosed at 3% active is relatively effective (>95% C.L.) in anti-wrinkling and wrinkle removal compared to pure softener only.

Wrinkle resistance evaluation has been based on externally generated data (CTTN-Lyon) using the empty cylinder wrinkle tester (NF G07-125). Fabrics were panel tested and compared after a standard fabric pretreatment and conditioning, followed by a standard wrinkling. Dosed at 1.5% active levels for samples B and C, and 1.7% for sample F, all silicone products gave significantly better results at 95% C.L. than the pure softener, with F being directionally superior.

Many patents12-15 have been published in this field for various product formats (e.g., sprays, fabric softeners and detergents), and they always combine silicone with other ingredients or polymers. It is suspected that at this stage that fibre lubrication is most likely to be the added benefit in this process together with the silicone’s softening touch.

Fabric Mechanical Property Modifications
External investigations performed by the WfK textile institute in Krefeld-DE for Dow Corning found that silicone products E and F have a positive impact on fabric strength when formulated into a fabric softener, compared to water-rinsed or pure softener-rinsed fabric.

The method used is called “tear crack propagation” and follows the DIN ISO 13937-1:2000 protocol. This test consists of measuring the force needed to break a standard fabric sample that contains a controlled crack. The test results after 10 and 25 wash and drying cycles are given in Figure 10, and they clearly show a reinforcement of fabric against crack propagation with samples E and F. See Figure 5 for a description of these samples. It is suspected that the elastomeric nature of the silicone polymer and its lubrication properties are involved in this phenomenon.

It is believed that treating fabric with silicone lubricants can reduce fabric wear abrasion and consequently improve color definition, reduce pilling and fuzziness, and help to maintain fabric shape retention.

Fabric shape retention was internally evaluated with silicones E and F formulated at 3% active into a standard liquid detergent. The shape retention method consists of applying tear strength to a 5x2 cm knitted cotton T-shirt sample until 80% deformation is reached (=9 cm) and maintained for 1 minute. The remaining fabric elongation is measured after a 2 minute relaxing time. The lower the value, the better the shape retention of the fabric. Results in Figure 11 show that significantly (95% C.L.)
higher fabric elasticity could be obtained with silicone. Several patents have been filed with regard to this new claim.\textsuperscript{16}

Silicones as Perfume Release Modifiers

Fragrances are present in almost any consumer surfactant-based product in the personal care and home care segments. The use of perfume is first to cover the residual odour of raw materials and also to provide consumer benefits and well-being. The protection and release of fragrances in these applications have been an area of growing development in recent years, with patent activity by perfume houses, major users of fragrances and key raw material producers, including Dow Corning.

The key characteristic of silicones that makes them valuable in fragrance delivery is derived from their high gas permeation properties compared to organic materials. In addition, product compatibility with fragrances can be tailored due to the variety of physicochemical and barrier properties exhibited by silicone materials as different as volatile silicones, polymers, functional polymers, elastomers, rubbers and silicone wax. The delivery form depends on the final application requirements, and in particular, the effective deposition on the substrate. The form can be dispersion (i.e., volatile silicone), an emulsion, a particulate (i.e., wax), a film or a bulky material such as an elastomer.

A small sample of the patent activity is given in the reference section of this paper.\textsuperscript{17-21}

Figure 12 shows an example of the bulk weight loss of a single fragrance note in a mixture of fragrance and silicone wax, compared to the pure fragrance note. This demonstrates the prolonged release benefit (lasting fragrance) possible using the silicone.

Conclusions

This paper provides a view of the unique physicochemical properties of silicone polymers and the ability to tailor their architecture and functionality to bring a variety of consumer-relevant fabric care benefits when correctly formulated.

The development and use of these technologies is applicable within the laundry industry primarily in fabric conditioners. The development of innovative and cost-effective solutions for powder and liquid detergent applications is a logical and important extension. However, these latter applications require generally a specific delivery system to obtain deposition during the wash cycle.

Dow Corning continues to investigate new applications and benefits of silicones based on its expertise in personal care and textile applications. This ongoing effort to reapply silicone technologies to fiber treatment demonstrates that silicones hold growing potential as performance-enhancing materials in the detergent industry. Capitalizing on the benefits of silicones can potentially be useful in other industrial processes or in applications where fibre treatments are made.
References

12. Coffindaffer, T. et al., “Aq. compsns. contg. curable amine-functional silicone(s) - and opt. additives e.g. quat-ammonium cpd. fabric softener, useful for wrinkle-proofing laundered fabrics e.g. polyester(s)” EP0300525, Procter & Gamble, 1989
13. Fox, D. et al., “Fabric softening formulation for reducing wrinkles in laundered clothing comprises agents selected from e.g. ethoxylated organosilicones and polyalkyleneoxide modified polydimethylsiloxane” EP1124925, Unilever, 1999
19. Krzysik, D. et al., “Anhydrous emulsifier-free perfume oil compsn. in which vehicle comprises a linear or cyclic alkylmethyl siloxane” US5160494, Dow Corning, 1992

LIMITED WARRANTY INFORMATION - PLEASE READ CAREFULLY

The information contained herein is offered in good faith and is believed to be accurate. However, because conditions and methods of use of our products are beyond our control, this information should not be used in substitution for customer's tests to ensure that Dow Corning's products are safe, effective, and fully satisfactory for the intended end use. Suggestions of use shall not be taken as inducements to infringe any patent. Dow Corning's sole warranty is that the product will meet the Dow Corning sales specifications in effect at the time of shipment. Your exclusive remedy for breach of such warranty is limited to refund of purchase price or replacement of any product shown to be other than as warranted. DOW CORNING SPECIFICALLY DISCLAIMS ANY OTHER EXPRESS OR IMPLIED WARRANTY OF FITNESS FOR A PARTICULAR PURPOSE OR MERCHANTABILITY. DOW CORNING DISCLAIMS LIABILITY FOR ANY INCIDENTAL OR CONSEQUENTIAL DAMAGES.

Dow Corning is a registered trademark of Dow Corning Corporation.

WE HELP YOU INVENT THE FUTURE is a registered trademark of Dow Corning Corporation.

©2004 Dow Corning Corporation. All rights reserved.

Printed in USA