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AOCS
September 2006 Volume 17 (9) 553–616

inform September 2006 Volume 17 (9) 553–616

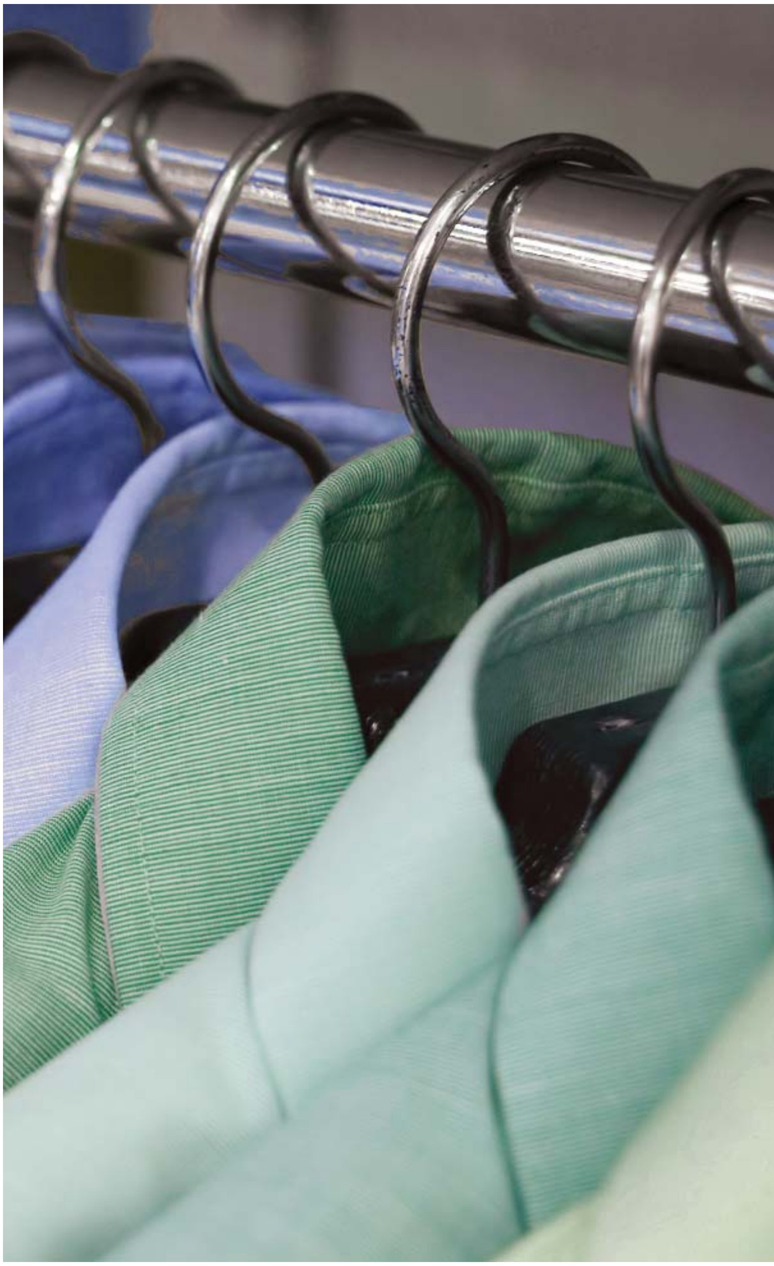
Silicones in Fabric Care

Is the silicone "roller coaster" on its way back up?

Silicones in fabric care

Silicone use has seen its share of ups and downs, but where is this "roller coaster" headed?

Fiona Case



Silicones in fabric softeners

Fabrics that have been softened drape and flow: they have a better hand. The earliest "cotton softeners," in the 1900s, were simple emulsions of corn, olive, or tallow oil in soapy water. The oil deposited onto cotton lubricated the fibers allowing them to slip past each other, preventing them from sticking together to create a dense, hard material.

By the 1960s, several commercial products were available. Common ingredients were quaternary ammonium salts of tallow oils (organic quats). The positively charged quats had a higher affinity for negatively charged fiber surfaces (such as cotton) than the simple oils. They did a good job of softening, but they also made the fabric hydrophobic. "You could have a soft bath towel," explains Meyer Rosen, a consultant with more than 35 years experience in silicones. "But you couldn't dry yourself with it."

Part of the solution to this problem was the addition of silicones. Surprisingly, the addition of low molecular weight poly(dimethyl siloxane) (PDMS) dramatically improves the water absorbency of fabric. And formulators were not limited to dimethyl siloxane.

"They could modify the siloxane backbone to introduce pendant amine groups, which aid deposition," explains Rosen. "Hydrophilic groups such as short polyglycol chains could be added as branches to aid water absorbency. That was the breakthrough in the early 1980s," he says.

So, silicones became widely used ingredients in fabric softeners. As might be expected from their physical properties, they lubricated the fibers and gave a wonderful softness to fabric. But, success didn't last.

"It was like a roller coaster," recalls Russ Elms, Global Industry Manager, Household & Cleaning Products, Dow Corning Corporation, Midland, Michigan, USA. "The main issues were cost and build-up," he explains. "These materials were not suitable for repeated use." The pendant amines caused problems, too. Softened fabric yellowed when it was heated during ironing. Use of silicones in fabric softeners plummeted. "By the mid '90s, very few silicones were used in laundry applications," says Elms.

Undaunted, the researchers and formulators kept working. "The biggest change in the late '90s was new silicone structures that produced low yellowing," says Elms. "For example, capping the amine to make an amide group gave orders of magnitude improvement." Formulations that enhanced the synergy between organic quats and silicones allowed smaller amounts of polymer to be used (reducing cost). The roller coaster was on its way up again.

H. Miyasaka, of Lion Corporation, Tokyo, Japan described this trend during the 2005 AOCS Annual Meeting in Cincinnati, Ohio: "A clear liquid softener that contained silicone as a main ingredient was released on the Japanese market in 1998; since then the use of silicones in domestic fabric softeners has accelerated," he said. "Now, about 20 softeners containing silicone are sold in this market." Silicones became popular ingredients again because they could offer new benefits, benefits that consumers were beginning to appreciate around the world.

"Procter and Gamble looked at shape retention starting in early 2000, as did Lion Corporation," recalls Elms. "Unilever focused on ease of ironing, and then on products that enhanced drying time. Companies were at aiming at niche benefits."

Each of these value-added features provides a considerable challenge to suppliers and formulators. "Shape retention can be achieved by using a two component silicone fluid: the two components react when heated," claim developers at Wacker Chemie AG, Munich, Germany, in their online magazine.

After the treated material has been ironed, it is "less likely to crease when worn, and much less wrinkled the next time it emerges from the washing machine," they say. Because of the flexibility of the silicone-oxygen bond, the fabric can remain soft and pliable even with the crosslinking.

A silicone coating on the surface of the fibers reduces the friction between cloth and the iron leading to improved ease of ironing. One challenge was to ensure a sufficient concentration on the fibers closest to the surface—where the iron was about to pass—without overloading the entire material. A solution was to provide the silicones in spray-on ironing aids.

The key to enhanced drying time is to reduce the amount of water left in the fabric after the spin cycle. Russ Elms and Benoit Hénault (Dow Corning S.A., Belgium) found that a softener containing 1% of an amido functionalized silicone reduced water content by a third, relative to the water-rinsed fabric. Almost half of this improvement could be attributed to the silicone. They suggest that the fabric surface is made partially hydrophobic, and that the low surface tension of the silicone aids water spreading. The combination of these two effects allows more water to be removed during the spin cycle.

Research into new silicone structures for fabric softeners continues. Researchers at Wacker Chemie are introducing a new material in which polyglycol chains, attached to positively charged anchor groups, form part of the polymer backbone rather than branches.

"The hydrophilic polyglycols lie directly against the surface of the fibers. The silicone loops remain very mobile. As a result, the fabric has the pleasant soft hand typical of silicone but also readily absorbs water," they claim.

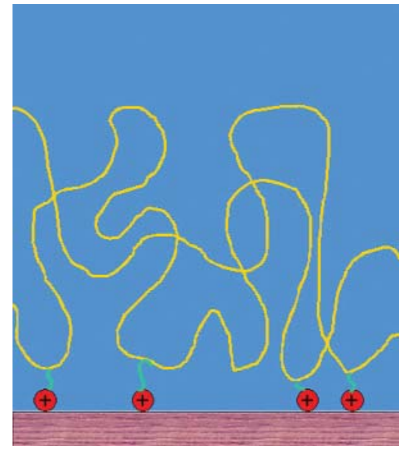


FIG. 1. Silicone polymers (yellow) coat the surface of a fiber. Positively charged species attached to the polymer (red) enhance the deposition of the polymer and its adhesion to the fiber surface. The coated fiber is able to slide past other fibers enhancing the flexibility and softness of the fabric.

Formulating silicone products: Getting the oil into water

Oil and water do not mix. Silicones are emulsified to facilitate their incorporation into water-based fabric softeners or laundry detergents. Part of the art of creating a good formula is control of the size and charge of the emulsion droplets to ensure their stability and compatibility with the other components of the product.

"The emulsion droplets need to be fairly large for anti-foam applications," say Rosen. "You often need to thicken the water phase with polymer to maintain the stability of the system."

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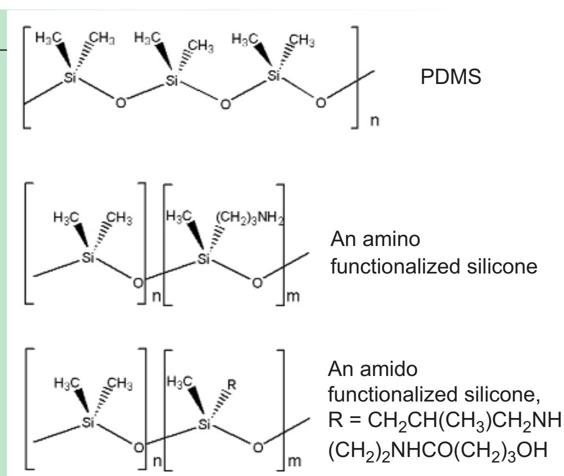
Silicones at a glance



Silicones are polymers with backbones that consist of alternating oxygen and silicon atoms. The silicon-oxygen bonds are strong and very flexible compared to the carbon-carbon bonds found in the backbones of other polymers. One of the simplest silicone examples is poly(dimethyl siloxane) (PDMS), in which the remaining bonding sites on the silicon atom are taken by methyl groups (see figure). The flexibility of the siloxane backbone means that at an interface the methyl groups can always be presented to the outside world, creating a very low surface energy material. Nothing really likes to stick to a siloxane surface (not even other siloxane molecules). Many of the applications of silicones are based on their low surface energy: barnacles cannot stick to the bottom of ships that are coated with silicone-based anti-fouling paint; gears and bearings in motors move more smoothly against each other with a squirt of silicone oil. Silicones are stable and unreactive, which allows them to be used as lubricants in food and medical applications. They are also flexible and do not crystallize: silicone-based bathroom sealants can flex and maintain a seal between the tub and the tile; medical implants made of silicone remain soft over years of use. These same physical properties motivate the use of silicones in fabric care applications: in fabric softeners, as defoaming agents in liquid detergents, in spray on ironing-aids, and in dry cleaning.

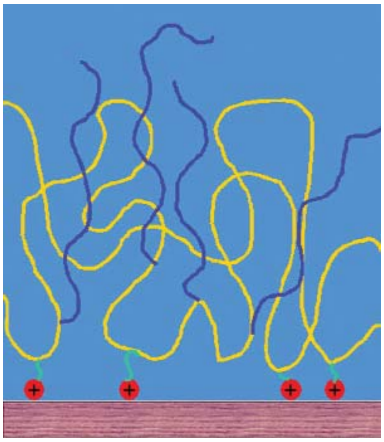


FIG. 2. The addition of hydrophilic branches (blue) to the silicone backbone provides a path for water to penetrate through the silicone coating and enhances the water absorbancy of the fabric.

In fabric softeners, microemulsions with particle sizes below 100nm can penetrate into yarns and deposit onto fabric fibers deep within the weave. Larger macroemulsions deposit on the surface of the fabric.

Anionic emulsions generally show good compatibility with laundry detergents (which contain anionic surfactants)—they are not stable with positively charged quats in a fabric softener. Nonionic emulsions can be stable in both detergents and in fabric softeners, and cationic emulsions can have very good stability in fabric softeners.

A positively charged emulsion is also more likely to deposit the silicone on the fabric (rather than carrying it away with the rinse water). Deposition of the silicone in fabric softeners is also aided by "carry over" of anionic surfactant from the wash cycle, presumably because this helps to destabilize the emulsion, releasing the silicone.

"Deposition can be reduced by more than half if you don't wash the clothes first," explains Elms. "Aiding deposition is particularly important in U.S. washing machines with high-water usage," he comments. "High dilution makes deposition even harder to achieve."

"Customers and dry cleaning professionals can be very comfortable with the safety profile of this material [D5]."

Silicones in dry cleaning

Legend has it that dry cleaning was discovered by accident in France in the late 1800s. Turpentine was spilt on a tablecloth. Remarkably, the areas where the turpentine soaked into the cloth became cleaner: even stubborn stains that had not been removed by washing were gone. The idea of cleaning fabrics in solvents other than water was born. In the early 1900s, the petroleum-based "Stoddard solvent" was widely used. It worked well and was cheap, but it had a low flash-point. After numerous fires and explosions at dry cleaning facilities, perchloroethylene was introduced as an alternative in the 1930s. "Perc" is non-flamable and it is a better cleaning agent. It rapidly became the solvent of choice for dry cleaning. But, perc has its own problems.

The National Institute of Environmental Health Sciences state that "in high concentrations in air, single exposures can cause central nervous system (CNS) effects leading to dizziness, headache, sleepiness, confusion, nausea, difficulty in speaking and walking, and possibly unconsciousness and death." On May 25, the California Air Resources Board voted to phase out the chemical, which has also been linked to cancer. Perc has cost manufacturers, and the owners of dry-cleaning plants, huge sums of money for cleanup when it has leaked into groundwater.

Clearly the dry cleaning industry needs to move to a different solvent. A strong candidate is the five repeat-unit PDMS ring: decamethylcyclopentasiloxane, or D5. It works well and doesn't leave an odor on clothing.

"Customers and dry cleaning professionals can be very comfortable with the safety profile of this material," explains Tim Maxwell, president of GreenEarth Cleaning (Kansas City, Missouri, USA), the company that is developing D5-based dry cleaning. "Personal care applications for this material are already extensive, from moisturizers to shampoo. There is already a significant body of testing on this product," he says.

The chemical basis for the low flammability of D5 is the remarkable stability of the silicone-oxygen bond and the material's low intermolecular interaction energy. The small D5 molecule is sufficiently volatile to allow the solvent to be distilled, but the vapor will not burn. A mixture of D5 and a silicone compatible surfactant (usually a nonionic) is used to clean fabric. The spent solution is then filtered and distilled to separate the D5. The mixture of dirt and surfactant is disposed of and the D5 reused.

"You can clean 1500 lbs of clothing per gallon of D5, compared with only 800 lbs per gallon of hydrocarbon, or 800–1000 lbs of chlorinated hydrocarbon," says Maxwell.

The new silicone-based technology is catching on.

"We now have more than 1000 affiliate machines in the U.S., U.K., and Japan," says Maxwell. "Including 25 near Houston, Texas, where Men's Wearhouse dry-clean more than 1350 tuxedos per hour!" It is another successful application of silicones in the fabric care industry.

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Further reading:

■ "How products are made: fabric softener," Randy Schueller, Enotes.com

■ "Easy care thanks to novel silicones," *Wacker World Wide Corporate Magazine*, Issue 1, June 2006.

■ "Silicone provides new opportunities for high-performace laundry products," Russ Elms and Benoit Hénault, *Household and Personal Care Today*, supplement to *Chemistry Today*.

■ *Silicone surfactants*, (Surfactant Science Series), edited by Randall M. Hill, CRC Press, 1999.