

The benefits of silicones in leather finishing

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Silicon is a natural substance, constituting 27.7% of the earth's crust. It can be converted into an array of silicon based polymers called silicones. Many of these silicone polymers are of interest to the leather industry, in both wet end chemistry and finishing.

Silicones: composition, generic properties and versatility

The most basic silicone polymer is polydimethylsiloxane (PDMS), which is composed of an inorganic backbone of repeat Silicon-Oxygen units, and two organic methyl side groups attached to each silicon atom (*Figure 1*). The degree of polymerisation (x) can vary between 0 and > 10,000. Often the basic silicone polymer, PDMS, is referred to as siloxane.

Figure 1

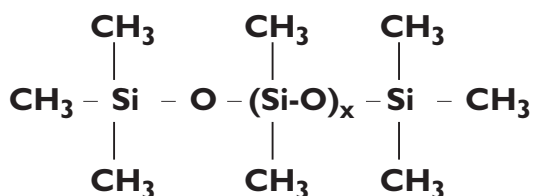
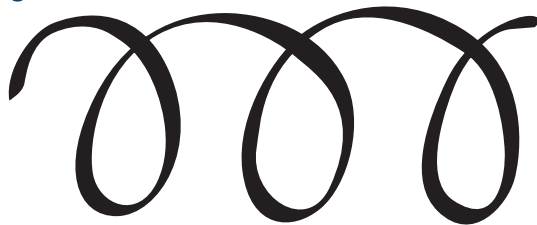


Figure 2



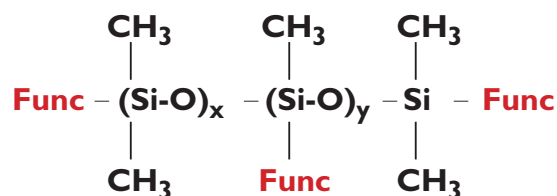
The PDMS chain is a highly open, flexible and mobile species, adopting a helical structure (*Figure 2*). The extremely flexible and mobile backbone permits the polymer to easily re-orientate itself to adopt the lowest energy configurations. Interchain interaction is very low which means that high molecular weight polymers are still flowable. In contrast the Si-O bond is very strong, 435 kJ mol⁻¹ (cf 350 kJ mol⁻¹ for C-C), which is the reason why silicones are stable at very high temperatures and extreme conditions. These characteristics give PDMS a low surface energy and high spreading and wetting capabilities and as such they perform as

very good lubricants. PDMS has low polarity, is permeable to gas and water vapour, is heat stable, compatible with organic materials and has high weather resistance. The lubricating properties are one of the key reasons why silicones are used widely in the personal care industry. Silicones are used in hair conditioners and skin creams to enhance the feel, touch and aesthetics of hair and skin, providing a smooth and silky finish.

The basic PDMS structure can be modified to give silicones in either fluid, gum, elastomeric or resin form. Fluids have molecular weights in the 200 - 250,000 range. Gums have molecular weights of around 10⁶. Elastomers are lightly crosslinked gums or fluids, usually reinforced for enhanced properties. Resins are highly crosslinked three dimensional species.

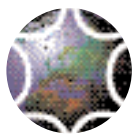
Instead of having methyl side groups, other organic functional groups can be introduced onto the PDMS backbone, (*Figure 3*). These can either be pendant, so as to give a rake structure, or terminal to give an ABA structure, or a combination of both. In addition these functional groups can either be reactive or non-reactive.

Figure 3



The reactive groups will either react to a surface, react with other chemicals or may react with other silicones to form a crosslinking network on the desired surface. By carefully selecting the functional group it is possible to modify properties such as hydrophobicity, surface tension, solubility, compatibility, permeability and reactivity.

For example a polyether group will increase hydrophilicity whereas a long chain alkyl group e.g. C₁₆ will increase



hydrophobicity. Adding a fluoroalkyl group will reduce surface tension. Adding an amino group invariably enhances substantivity. The range of functional groups that can be attached to the silicone backbone is vast. The most common commercial ones include polyethers, aminos such as $\text{RNHCH}_2\text{CH}_2\text{NH}_2$, hydroxyl groups, fluoroalkyls, phenyls, alkyls, alcohols, epoxys and carboxyls.

Silicones are used today in many very diverse applications thus demonstrating their versatility. A few examples include beauty products, cosmetics, shampoos, laundry powders, bathroom sealants, paint coatings, oil and gas, pressure sensitive adhesives, textiles, construction industry, structural glazing, airbags, mould making and leather.

There is a perception that silicones in general are more expensive than their organic counterparts. Whilst this may be true for some specialty polymers with unique structures, functionalities and benefits, two points should be noted. Firstly basic silicone structures have come down significantly in price as demand has increased and economy of scale has kicked in. Secondly, and probably more importantly, the amount of silicone required for a particular benefit, is often very low and usually significantly less than an organic alternative. This makes the cost in use generally far more attractive.

Silicones in Leather Finishing

Silicones are used today in most leather applications - footwear, home upholstery, automotive upholstery, garments, and other leather goods (Figure 4). It is the feel, lubricating effects, low surface tension, hydrophobicity and durability of silicones that make them of particular benefit to the leather industry. Incorporated into the topcoat, silicones have an important influence on the protection, feel, comfort and appearance of finished leather. The touch and look can be modified by both the type and amount of silicone employed. Certain silicone types will impart abrasion resistance, scuff resistance, mar resistance and scratch resistance. These properties are of particular relevance to shoe leather and automotive leather. Hydrophobic silicones can be used to give a water repellent treatment.

Figure 4: Contribution of silicones to today's leather needs

Garments	Shoes	Automotive
Comfort Rain protection Aesthetics Softness	Water Resistance Comfort Scuff Resistance Aesthetics Flexibility Breathability	Scratch Resistance Mar Resistance Durability Water Resistance Aesthetics

The use of silicones in leather finishing can be divided into three principal categories namely protection, look and comfort (Figure 5).

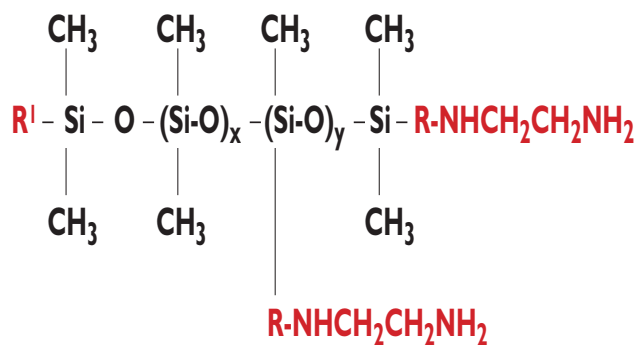
There is no one silicone polymer which will give all desired properties for leather. The main types of silicones used in leather finishing today and the key benefits they provide are given in Figure 6.

Silicones can be applied either by direct incorporation into the topcoat or can be post sprayed onto the topcoat (See Legend).

Figure 5: Needs in natural leather finishing satisfied by silicones

Need	Key Features/Benefits Provided by Silicones
Protection	Water resistance, Scratch, Mar, Abrasion resistance, Scuff resistance (<i>shoes</i>), Low temperature flexibility (<i>prevents cracking</i>)
Look	Gloss Matt
Feel Comfort	Soft, Silky, Slippery, Oily, Supple, Flexible, Breathable, Dry

Figure 6: Main silicone types in natural leather finish

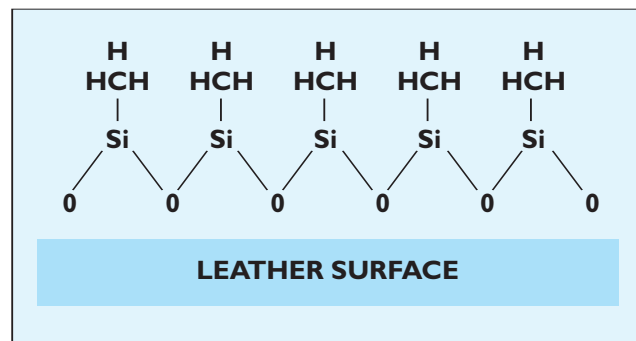


Hydrophobicity

Silicones provide hydrophobicity due to their ability to orientate on the surface of the leather with the hydrophobic methyl groups orientating away from the surface (Figure 7). Non-functional silicones i.e. PDMS or gums will give hydrophobicity.

Functional silicones like aminofunctional silicones will also give hydrophobicity because the amino group will orientate itself to the leather surface, thus exposing the hydrophobic methyl groups (Figure 8). The advantage with the aminofunctional groups is that there will be better binding of the silicone and thus enhanced durability and protection of the leather.

Figure 7:



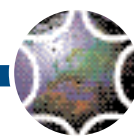
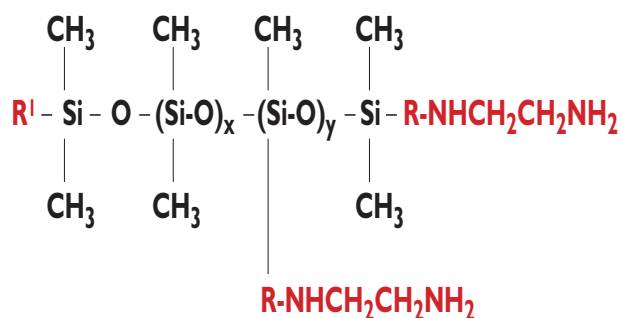


Figure 8



Silicones can provide water repellency on both full grain leather and nubuck, as shown in *Figures 9 & 10*.

FULL GRAIN LEATHER

Test: European norm IUF420, using ethyl alcohol 95° instead of water for a more severe and discriminating test condition.

Figure 9: Time for alcohol droplet to penetrate the leather (minutes)

Silicone Type	Silicone product concentration in solvent (methyl ethyl ketone). Applied onto the PU Topcoat				
SOLVENT BASED	0%	0.5%	1%	2%	4%
Aminofunctional Silicone ¹	4	8	10	12 *	12 *
Silicone Resin ²	4	6.5	6.5	7	9
Silicone Resin ³	4	5	5.5	6	7
	Silicone product concentration in the PU Topcoat				
AQUEOUS BASED	0%	1%	2%	4%	8%
High Molecular weight special silicone emulsion ⁵	1.30	5 #	6 #	6.30 #	7 #

0% PU fixation with no Silicone
 * Droplets evaporate without penetrating the support
 # Droplets do not spread

NUBUCK LEATHER

Test: European norm IUF420, using ethyl alcohol 95° instead of water.

Figure 10: Time for alcohol droplet to penetrate the leather (seconds)

Silicone Type	4% Silicone Product in Water		
AQUEOUS BASED	No application	1 application	2 application
High Molecular weight special silicone emulsion ⁵	20	20	50
Comments	Dark spots after drying	Slight spots after drying	Slight spots after drying

Abrasion Resistance

The lubricating and wetting properties of silicones are believed to be key for achieving abrasion resistance. The outward

orientating methyl groups will present a low energy surface. The best results are typically achieved with very high molecular weight silicones with possibly some degree of crosslinking. Functionality does not seem to be crucial. Also it is noted that there is a threshold concentration above which the performance will not improve further. A wet rub test has been performed with the leather evaluated after 50 rubs.

Figure 11: Wet Rub Resistance - European norm IUF450

Silicone Type	Silicone product concentration applied after the PU fixation							
	0%	1%	2%	3%	4%	6%	8%	11%
High Molecular weight silicone with special silicone additive ⁴	1	2	2		3			
High Molecular weight special silicone emulsion ⁵	2	2	3		4		4	
Elastomeric Silicone Particles ⁶	1			5		5		5

European norm IUF450 standard using Veslic equipment. 50 rubs.
 Grading is as follows:-
 5: neither degradation of appearance or transfer of pigment to pad.
 4: slight degradation of the appearance
 3: average degradation of appearance
 2: clear degradation of appearance
 1: complete degradation of the finish

Appearance

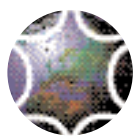
Silicones can be employed to modify the brightness of the leather surface without repolishing. Of particular interest for automotive leather is a matt finish but at the same time abrasion resistance is required. It can be difficult to achieve the two because often the properties that are important for abrasion resistance - wetting, spreading and lubrication - will normally give a very smooth flat surface which will have a high degree of gloss. Certain silicones however can be used to give a matt and abrasion resistant finish. The format and delivery of the silicone is important to achieve this. Either a special silicone additive is used or the silicone is delivered in particulate format. Generally though the base silicone is of the high molecular weight, non-functional variety.

Figure 12: Brightness of finish

Silicone Type	Silicone product concentration applied onto the PU fixation								
	0%	1%	2%	3%	4%	6%	8%	11%	18%
High Molecular weight silicone with special silicone additive ⁷	7	7	5		4	4	3		
Elastomeric Silicone Particles ⁶	15			10		6		4	0.5

Touch

Different touches can be achieved on both full grain and



nubuck leather using silicones with different chemical structures, molecular weights and functionalities. There are no strict rules for touch and feel because these are subjective and the desired feel will vary as an application develops. Traditionally standard PDMS and particularly aminofunctional silicones have been widely used in leather finishing and the textile industry due to their lubricating properties which provide a soft, smooth and silky surface touch.

These traditional feels though can be enhanced and in some cases completely altered through clever combinations of novel functionalities and silicone formats. Elastomeric silicone particles for example give a dry feel to a finish which is very different to what one would expect from a silicone. The range of touches that are accessible from silicones is really dependent on the creativity

and willingness of the silicone chemist and the leather chemist to try different combinations. 

Legend

Silicone additives were either used with Polyurethane top coats on full and corrected grain or simply diluted for nubuck applications. Topcoats are either Bayderm® 80 UD 30% dry extract, cured with a polyisocyanate, Aqualen® DA 80, or Aqualen® 2004 at 25% dry extract cured with Aqualen® DA 80.

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** Aqualen is a registered trademark of Clariant International Ltd.*

Leather samples have been prepared and tested by Centre Technique Cuir Chaussure Maroquinerie, 4 Rue Hermann Frenkel, 69367 LYON Cedex 07, France.

Products

1. Dow Corning® 531
2. Dow Corning® 477
3. Dow Corning® 593
4. Dow Corning® 3289
5. Dow Corning® 5-7222 emulsion
6. Dow Corning® 33 Additive
7. Dow Corning® 3238
8. Dow Corning® 2-8818

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Figure 13: Tactile properties

Silicone Type	Nubuck	Full Grain
High Mwt silicones with special silicone additive ⁴		Silky
Aminofunctional silicones ⁸		Slip
High Molecular Weight special silicone emulsion ⁵		Slip
Aminofunctional Silicones ¹	Velvety	Oily