Silicones for textiles

By Dr. Naresh M. Saraf,
F.T.I., F.S.D.C., F.A.I.C.
Sarex Overseas, India.

Silicon is the most abundant element in nature after oxygen and makes up more than 25% of the earth's crust. Silicones, known to chemists as poly-organosiloxanes, have a backbone of alternating silicon and oxygen atoms. The backbone can be modified in various ways through the incorporation of carbon-based side groups, resulting in various types of silicone fluids.

Silicon emulsions are known to produce far superior handle than any organic softener. Polydimethylsiloxane (PDMS) imparts a full soft handle, but with the progress of technology of emulsion polymerisation, higher viscosity silicone fluids could be emulsified to give better softness. But the greatest breakthrough in fabric softening was achieved by the introduction of aminofunctional polysiloxane in the late 1970s. of these amino-functional polysilicones (AFS), those bearing amino ethyl amino propyl groups have yielded the best results. The amino groups are linked to the polymer by short hydrocarbon chains and are stable to hydrolysis and to high temperatures. These (AFS) impart an incomparable permanent soft handle to fabrics due to the affinity of the amino groups to the fibres which promotes optimum orientation of the silicone molecule on the substrate, thus ensuring an ideal soft handle. The amino silicones, due to their polar nature, develop a positive cationic charge under acidic conditions. These highly polar, partly protonated amino ethyl amino propyl groups in the polysiloxane are strongly attracted to the negatively charged surface of cellulosic fibres and protein fibres, providing points of anchorage via electrostatic forces and hydrogen bonding.

Classification of silicones

Silicones for textiles may be broadly classified into three categories.

- Non-reactive Silicone Polymers
- Reactive Silicone Polymers
  - Methyl ended methyl hydrogen polysiloxane
  - Hydroxyl ended PDMS
  - Alkoxy ended PDMS
  - Epoxy modified silicone (This is produced by hydrosillation of allylgycidyl ether)
- Organo functional silicone polymers
  - Amino modified silicones
  - Carboxyl modified silicones
  - Polyether modified silicones

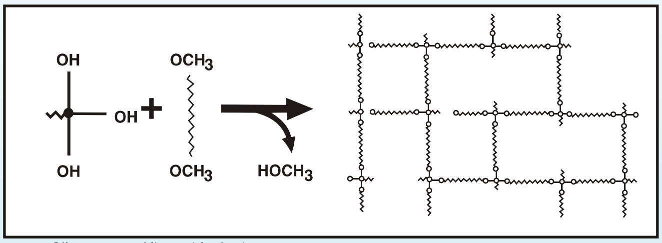
Amino modified slicones (AFS) are essentially linear PDMS with pendant amino functional group. The most popular amino functional modified fabric softener is amino ethyl amino propyl poly siloxane.

Reactive elastomeric silicones

Silicone fluids, which have a terminal mehtyl group, have no reactivity but those with the hydroxyl (-OH) group are reactive. The advantage with these -OH groups is that they are capable of undergoing further condensation.

Further, amino ethyl amino propyl polysiloxanes with reactive endgroups (i.e. -OH, -OCH3) also exhibit reactivity allowing chain extension especially in presence of stannous chloride-based catalysts and silanol functional polydimethyl siloxane.

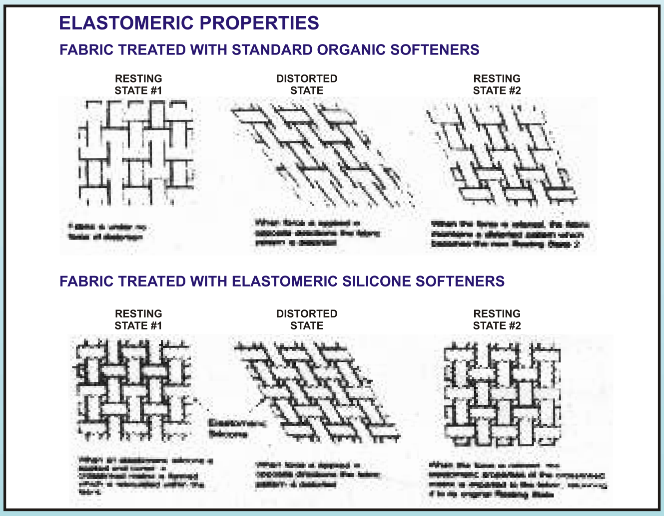
The reactive form of hydroxyl-ended PDMS is capable of undergoing chain extension/polymerisation, especially in presence of silanic hydrogen or alkoxy silanes to improve the fabric physical properties such as tear strength, tensile



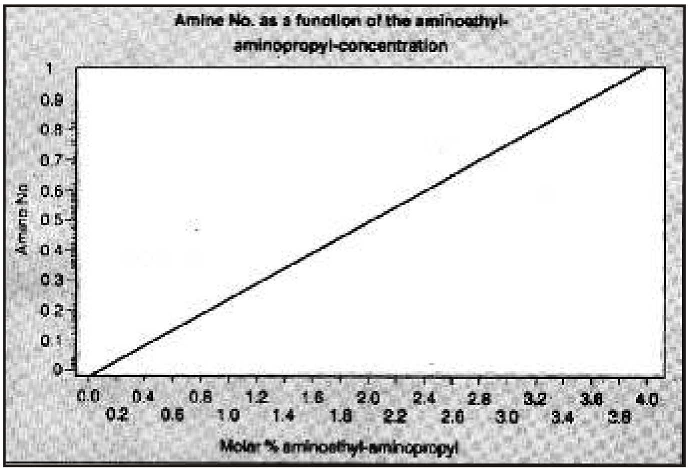
Silane Crosslinker

Alkoxy blocked PDMS

Figures 1 and 2. Silicones crosslinks provide a range of fabric properties



Reprinted from International Dyer April 1998



Figures 3. Correlation between the amine number and the molar percentage of an AFS.

strength and fabric cut and sew performance. It also enhances the crease recovery property of the treated fabric.

It is used to give elastomeric finishes and when coupled with a silane crosslinker to form an elastomeric crosslinked network which results in increased fabric bounce and resilience(1) (Fig 1).

When a force is applied to the matrix it becomes distorted. After removing this force, the elastomeric properties of the matrix will restore the crosslinked polymer to its original resting state and hence the treated fabric exhibits excellent shape retention and crease recovery(2) (Fig 2).

Amino silicones

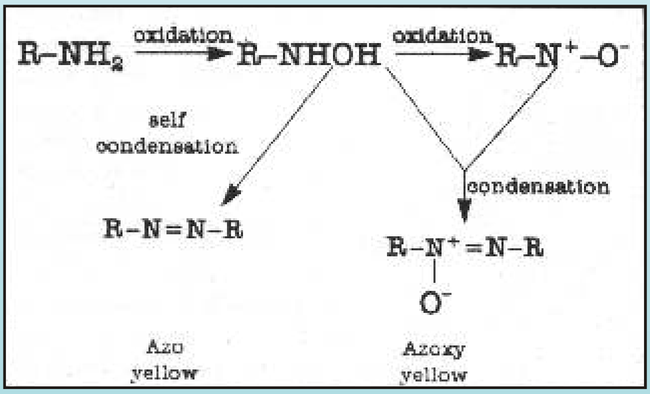
The properties conferred by amino-silicones, such as handle, smoothness and suppleness, are a product of the content of the amino groups in the polymer. The amino content of a silicone fluid is expressed by the amine value, which is defined as the number of millilitres of 1 NHCl that are required to neutralise 1 gm of the amine. The amine value is directly proportional to the percentage mole fraction of amino groups in the silicone(3) (Fig 3).

Generally speaking the higher the amine content, the better is the softness. But higher amine content also means more yellowing. Hence, an optimum balance has to be struck between amine content and yellowing behaviour.

The viscosity of the amino silicone fluid is a direct function of the polymer chain length. This has to be adroitly selected in such a way that given a gaussian distribution, each should bear at least one amino group. Amino silicones have the tendency to crosslink with each other during the process of fabric drying on the stenter; hence the initial viscosity of the silicone formulation may be different from the final viscosity on the textile fabric. One can get varying amount of softness and surface smoothness by changing the viscosity of the fluid. In fact, the viscosity can be varied from 50 cSt to 2,00,000 cSt.

Lower viscosity fluids are far easier to emulsify into a stable emulsion than higher viscosity fluids. But there is a direct co-relation between viscosity and surface lubricity on the fabric surface, i.e., higher the viscosity, greater is the surface smoothness.

Figures 4. Mechanism of yellowing.



The particle size of amino silicones can play a pivotal role in satisfying the finishers varying market requirement. A micro emulsion could be difined as an emulsion where the radius of the particles is less than ¼ the wavelenght of light, or <40 nanometers.

As a result of this, fine particles become "invisible" due to their lack of impendence of light and the emulsion appears clear. Such products give good internal softness as the particles travel to the depth of the fabrics, i.e. the interstices of the fabric. This softness is also more permanent along with drapability. This is particularly so when the particles of the emulsion have a radius of 100 to 50,000 nm since these particles are longer than the wavelength of light, they block the passage of light and as a direct consequence of this, the emulsion appears milky. These are called macroemulsions and they give extremely good surface smoothness(4).

During the process of textile finishing on the stenter, the drying conditions and presence of the amino silicone cause yellow discolouration, which can be perhaps attributed to the oxidation of the amino group in the presence of air, heat and metal cations. In this oxidation process, azo and azoxy compounds are formed, which cause yellowing(5) (Fig 4). The degree of yellowing increases with increase in amine content or increasing amino functionality in the polymer.

Functional modifications made in the silicone like alicylic modified amino silicone, modified piperidine functional amino silicone can reduce the yellowing tendency to a very great extent. Conventional amino ethyl amino propy silicone, being a primary amine has a very great tendency to yellow. The alicyclic: modified amino silicone and the modified piperidine functional amino silicones being secondary amines(6) do not tend to yellow to the same extent due to steric hinderance caused by bulky organic group which prevents azo/azoxy formation.

References

1. *Rhone-Poulenc Technical Application bulletin.*
2. *Rhone-Poulenc Technical Application bulletin.*
3. *Wacker – Textiles and silicones literature.*
4. *Wacker – Textiles and silicones literature.*
5. *Cray, Stephen; Budden, Graham, International Dyer, Jan 1997. p19*
6. *Saraf, Naresh, International Dyer, Sept. 1997. p39*

Reprinted from International Dyer April 1998