SILICONE CHEMISTRY FOR FABRIC CARE

M.Muthu Manickam.

ABSTRACT:

Silicone softeners have a firm place in final finishing for a very important reason. A piece of fabric which has been subjected to pretreatment ,dyeing and fixing processes is almost impossible to be appealing to any one without taking a corrective measures of handle. The Application of silicone softeners turns hard and a brittle fabric into a soft pleasant textile with which the buyer can expect a high degree of wearing comfort. Silicone have wide spread applications in the textile industry from fiber, yarn and fabric production to final product finishing.Thier distinctive chemistry imparts a range of characteristics. A variety of silicone technologies have application in the textile industry. They include,

- Polydimethylsiloxanes.
- Amido, Amino Functional Silicones.
- Methyl Hydrogen Silicones.
- Epoxy Functional Silicones.
- Hydroxy functional Silicones.
- Silicone Polyethers.
- Epoxy Polyether Silicones.

INTODUCTION:

Silicones are the most versatile polymer known. This chemical adds value to the fabric by transforming the fabric handle to the match the customer perception. Silicones are the organo metallic polymers derived from the abundant raw material on earth, sand. Silicone is a generic term that refers to a class of man made polymers based on a frame work of alternating silicon and oxygen (Siloxane Bonds) with organic subtituents attached to the silicon.Methl groups are the most important organic substituents used in the commercial silicones. The Vast majority of which are Poly dimethyl Siloxanes.Because of their Inorganic – Organic structure and the flexibility of the silicone bonds, silicones have some unique properties including thermal oxidative stability , low temperature flow ability , low viscosity change vs. temperature , high compressibility , low surface tension , hydrophobicity,good electric properties and low fire hazard. A feature shared by many silicone materials is effectiveness at very low concentartions.Very small amounts are required to achieve the desired properties, which can improve the cost of textile operations and ensure a minimum environmental impact.

Silicones are developed from Silicon metals. Silicon is represented by the formula Si which has 14 protons in its nucleus. The structure is given as below,

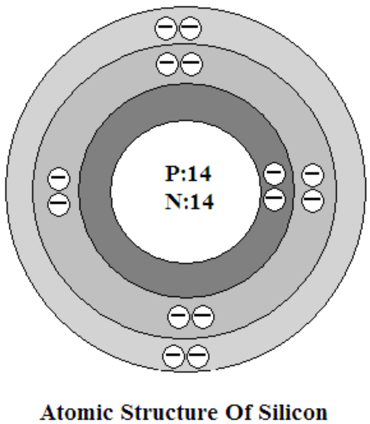

Fig 1: Atomic Structure of Silicone.

SYNTHSIS OF SILICONES:

Silicon is not found as a free element. It is found as sand (SiO_2) or silicates of metals. The Silicon metals are separated from sand (SiO_2) by oxidation method. Silicones are then prepared from silicon metals by the following three step process,

- Synthesis of chlorosilane.
- Hydrolysis of chlorosilane.
- Polymerization and poly condensation

CHLOROSILANE SYNTHESIS:

Chlorosilane are synthesized by treating silicon metal powder (prepared by Direct Rochow’s reduction of sand at high temperature) with a stream of methyl chloride (Obtained by the condensation of hydrochloric acid with methanol) at 250°C to 350°C at 1-5 bar pressure in fluid bed reactor. This process yields a complex mixture of methyl choloro silanes with following distribution of products,

Rochow’s Direct Process:

$$SiO_2 + 2\,C \longrightarrow Si + 2\,CO$$

Preparation of Methyl chloride:

$CH_3OH + HCl \longrightarrow CH_3Cl + H_2O$

$Si + CH_3Cl \xrightarrow{300°C / Cu} CH_3SiCl_3 + (CH_3)_2SiCl_2 + (CH_3)_3SiCl +$ Other Silanes

(Methyl Chloro Silane) (Dimethyl Chloro Silane) (Trimethyl Chloro Silane)

The proportions of methyl chloro silanes yielded are given below,

Methyl Chloro Silanes	App Proportion
$(CH_3)_2SiCl_2$	70-90%
CH_3SiCl_3	3-15%
$(CH_3)_3SiCl$	3%
CH_3HSiCl_2	1-3%
$(CH_3)_2HSiCl$	0.50%
$(CH_3)_4Si$	0.10%
Poly Chloro Silanes	1-6%

Table 1: Methyl Chlorosilane Yield Table.

These products were distilled in a long distillation columns and the primary product dichloro dimethyl silane is separated.

CHOLROSILANE HYDROLYSIS:

Polydimethyl siloxanes are obtained by the hydrolysis of the dimethyl dichloro silane in presence of excess water. These exothermic reaction yields a disilanol $(CH_3)_2Si\ (OH)_2$ which readily condenses with HCl acting as a catalyst to give a mixture of linear and cyclic siloxanes by inter molecular or intra molecular condensation as follows,

$$X\ CH_3SiCl_2 \longrightarrow Y\ HO\ (Me_2\ SiO)_n H + Z\ (Me_2Sio)_m$$

POLYMERIZATION:

Opening and polymerizing of (R_2SiO) m to form long linear chains is catalyzed by many acid and base compounds and gives at equilibrium a mixture of cyclic oligomers plus a distribution of polymers. The Proportion of cyclics will depend on substituents along the chain, the temperature and the presence of solvent. Polymer chain length will depend on the presence of substances capable of giving chain ends.

$$Me_3SiOSiMe_3 + (Me_2SiO)_4 \longrightarrow Me_3SiO\ (Me_2SiO)_n SiMe_3.$$

The Ratio between the D and M units will define the average molecular weight of the polymer formed. The Structure of silicone polymer is illustrated below,

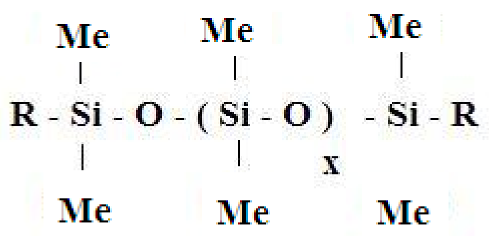

Fig 2 : Structure of PDMS

R = -OH, - CH_3

In general the structure can be derived as follows,

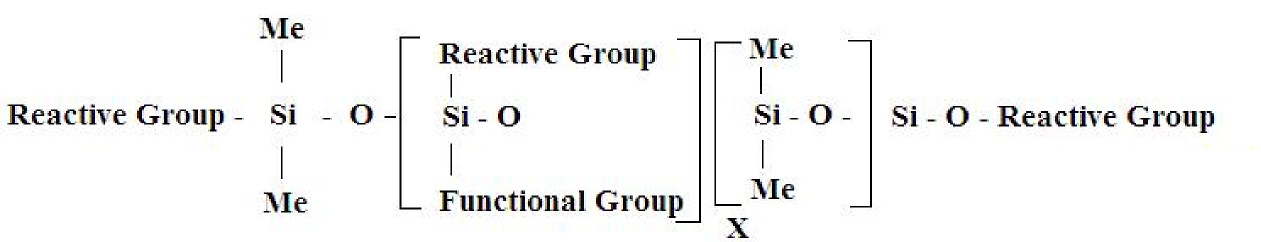

Fig 3 : General Structure Of a silicone softener.

Functional Group = Amino Ethyl, Amino Propyl, Amido, Glycol, Vinyl, Quaternary, Hydroxyl
Reactive Group = Methoxy, Ethoxy, OH, H
X, Y = number of monmeric units

PDMS are available in viscosities ranging from 0.65 cSt to 1,000,000 cSt for methyl terminated polymers and from 70 cSt to 330,000 for polymers terminated with hydroxyl groups. The Addition of PDMS to fabric softener formulations dramatically improves the water absorbency of softened cotton fabric. This effect is true for ester – quat based softeners. The Diverse property of the silicone can be changed by changing the R group in the structure. Given below are the properties derived by incorporating different modifications,

SILICONE MODIFICATIONS	PROPERTES DERIVED
Amino Group	Highly exhaustible and durable softness
Hydrophilic Group	Water adsorptive
Methyl Group	Water repellence and antistatic finish
Hydrogen Group	Water repellence and soil resistance
Other Organo modifications	Drapery and wrinkle recovery property.

Table 2 : Silicone Modifications Table.

AMINO & AMIDO SILICONES:

Mostly amino modified silicones are used in textile industry as amino groups provide better affinity to textile fibers. For further reactivity the end group of the amino silicone polymer needs to be hydroxyl, methoxy, ethoxy, but if the end group is methyl group then the polymer is called as non reactive or terminated one. The high bonding affinity of the amine polymers makes them more substantive to fabrics than the other silicone polymers. In general the amino functional silicones reach their best performance after 2- 3 washes.Amido functional silicones have limited range of viscosities and nitrogen content. The benefits of amido silicones are highly effective softening, ease of ironing, water absorbency and low yellowing. They are more substantive to fabrics than polydimethylsiloxanes.

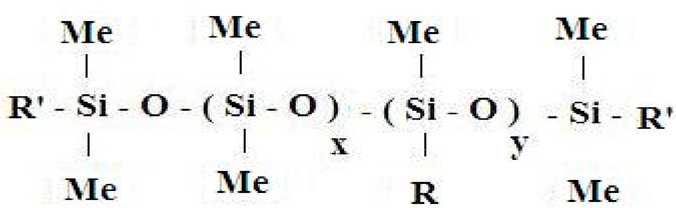

Fig 4: Structure of Amino / Amido Silicones

If R = - $(CH_2)_3NH_2$ or $-CH_2CH(CH_3)CH_2NH(CH_2)_2NH_2$ then Amino Silicone
If R = $-CH_2CH(CH_3)CH_2NH(CH_2)_2NHC(O)(CH_2)_3OH$ then it is Amido Silicone

Yellowing may be resulting when amino silicones are used on white garments due to the oxidation of amino radicals in the presence of air, heat and light energy which results in the formation of azoxy compounds.

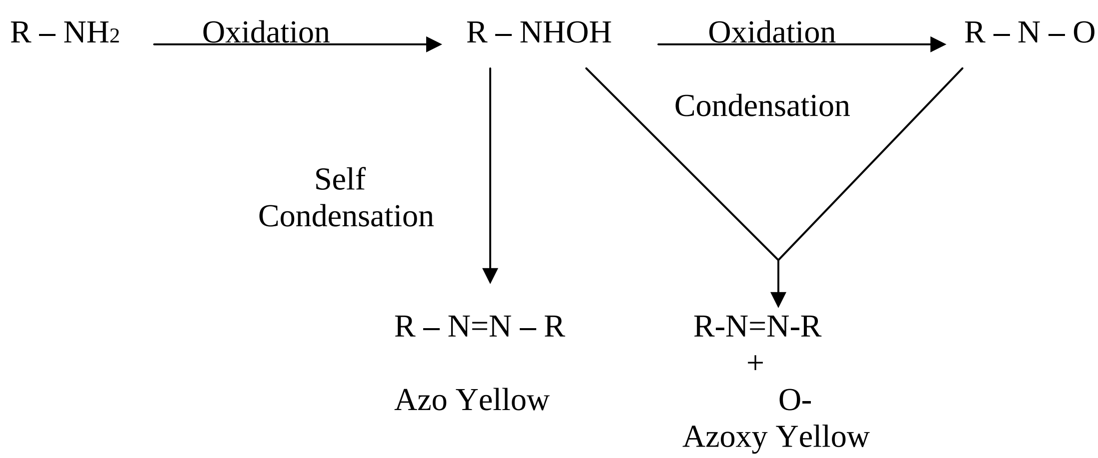

Fig 5 : Mechanism of Amine Yellowing

This kind of yellowing can be prevented by the use of amido silicones here the amines are hindered from yellowing.

EMULSIFICATION:

Polydimethyl silicones, amino and amido functional silicones are stabilized by adding an emulsifier or emulsifying agents. All emulsifying agents concentrate at and are located adsorbed onto the oil water interface to provide a protective barrier around the dispersed droplets. In addition to this protective barrier, emulsifiers stabilize the emulsion by reducing the interfacial tension of the system. Some agents enhance the stability by imparting a charge on the droplet surface thus reducing the physical contact between the droplets and decreasing the potential for coalescence. The Emulsion characteristics in particular their particle size and the surfactant system used play a critical role both in terms of deposition on the fabric and the stability in the final product. Micro emulsions typically have a particle size below 100 nm which can penetrate into the yarns and can deposit onto fabric fibers. In Contrast macro emulsions deposit on the external surface of the fabric. Cationic emulsions have a very good compatibility with fabric softeners and provide very high level of silicone deposition. Non Ionic Emulsions have good stability. Anionic emulsions generally show good compatibility with standard detergent but have an uncertain deposition. The Emulsification of silicones can be done in two methods as below.

- Thick Phase Method.
- Non Inversion Method.

Thick phase method involves the initial mixing of poly siloxanes, surfactants and the water to form a thick phase and then the addition of water gradually in a series of time gradually. Whereas the Non-Inversion phase method involves the initial addition of surfactant with water and then the polysiloxanes are added gradually in series of time gradually.

HLB SYSTEM:

A system was developed to assist in the decisions about the amounts and the types of surfactants needed in stable products. The System is called the HLB (Hydrophile Lipophile Balance) system and has an arbitrary scale of 1- 18.HLB numbers are experimentally determined for the different emulsifiers. If an emulsifier has a low HLB number, there is a low number of hydrophilic groups in the molecule and it will have more of a lipophilic character. The Higher the HLB number would indicate that the emulsifier has a large number of hydrophilic groups on the molecule and therefore should be more hydrophilic in character. Combinations of emulsifiers can produce more stable emulsions than using a single emulsifier with the same HLB value. Emulsifiers with low HLB value are considered water in oil emulsifiers. Emulsifiers with high HLB values are considered oil in water emulsifiers. High temperatures and the alkaline p-H values have a very negative influence. Alkaline medium leads to instabilization through deprotonation of the primary amino groups and the high temperatures promote the coalescence by increasing the kinetic energy. To prevent the softeners from breaking due to shearing forces the following points has to be observed.

- Apply in a weakly acid pH range (5-6).
- Select a liquor temperature in such a way that the turbidity point of the emulsifier system is not exceeded. Generally it should be below 50°C.

ENVIRONMENTAL EFFECTS OF SILICONES:

Non Volatile PDMS fluid is essentially insoluble in water. These materials become a minor component of the sludge in the treatment plant. If the sludge is incinerated, the silicone content converts to amorphous silica, water and carbon dioxide. Silicone materials are highly resistant to bio degradation by micro organisms, but they undergo very effective degradation via natural chemical process such as catalyzed hydrolysis and oxidation.PDMS breaks down into siloxanols and silanols.PDMS is ecologically inert and has been found to have no effect on aerobic or anaerobic bacteria. It does not inhibit the biological process by which waste water is treated. In the world of eco friendly chemicals in the processing, silicones can offer the best solution to cater the multi dimension demands of the customers.

REFERENCES:

1). Benoit Henault and Russ Elms, “New Silicone Technologies for Fabric care”, Giornate CD in Venezia (June2001).

2). Blondine Van Roy, chritel Simon and Dirk Soontjens,”Silicone Technologies for liquid laundry tablet detergents”, annual meeting in Valencia (March 2003).

3). A. Colas “Silicone Chemistry Overview”, Chimie Nouvelle, vol.8 (30), 847(1900).

4). Rochow, E.G”silicon and Silicones”, springler-verlag, 1987.

5). STARK, F.O”Silicone Comprehensive Organo metallic Chemistry”, vol.22, 305, Pergamon Press, 1982.

6). Noll.W”Chemistry and technology Of Silicones”, Acamedic Press, 1968.

7). M.Brook, silicon In Organic, Organometallic and Polymer Chemistry, Hon Wiley and Sons.Newyork (2000).

8). J.W.White, R.C.Treadgold”Organo Functional siloxanes”, in Siloxane Polymers (edited by S.J.Clarson and J.ASemlyen), p193-215, Prentice hall, New Jersey (1993).

9). W.Gardiner, J.W.White”Speciality Silicones as building blocks of organic polymer modification in high value polymers” (edited by A.H.Fawcett), Royal Society Of chemistry, Cambridge.

10). Joyner, M., “Amino functional Polysiloxanes: A New Class of Softeners”, Textile Chem. Color. 18(3), 34 (1986).

11). Joyner, M., “Development of Silicone Micro emulsion- Based Softeners”, Am. Dyest. Rep. 77(8), 36 (1988).

12). Rooks, R. J., “New Development in Silicone Emulsion Polymers as Textile Finishes”, Textile Chem. Color. 4(1), 47(1972).

13). Henault, B. et al. “A fresh look at fabric softeners. New silicone technologies offer formulating opportunities” Soap Cosmet. (2001), 77(6), 34-36, 38, 40.