

## **Siloxane chemistry boost performances to eco-friendly leather finishing**

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### **Introduction**

Manufacturing industry is divided in 20 different categories. The 13<sup>th</sup> describe the chemicals industries and that ones related to petroleum derivatives, which include 31 sub-categories. Among them we find the so called Sector of Chemicals Derivates describing the industry whose production of chemicals is mainly purposed to other industries and agriculture (eg. gas, fatty acids and synthetic oils, soaps, fragrances and essences, extracts for tanning and dyeing, varnish, and many others).

Without taking particular and deep care of the economical and financial structure of chemicals industries, we can say that, within the Sector of Chemical Derivates, plastics and elastomers or, more generally, polymer chemistry (macromolecular) account for the highest weight in total production value and it is the segment in which innovation is mainly concentrated.

### **Historical hints**

The pioneering work on polyurethane polymers was conducted by Otto Bayer and his colleagues in 1937 at the laboratories of I.G. Farben in Leverkusen, Germany.

This Team recognized that using the polyaddition principle to produce polyurethanes from liquid diisocyanates and liquid polyether or polyester diols seemed to point to special opportunities, especially when compared to already existing plastics that were made through polymerization of olefins, or by polycondensation.

Initially, work has been concentrated on fibers and flexible foam and, because of the constrained of the World War II, it was not until 1952 that polyisocyanates became commercially available.

Commercial production of flexible polyurethane foam began in 1954, based on toluene diisocyanate (TDI) and polyester polyols.

The first commercial available polyether polyol, poly(tetramethylene ether) glycol, was introduced by Du Pont in 1956 by polymerizing tetrahydrofuran and, subsequently, in 1957 less expensive polyalkylene glycols were introduced by BASF and Dow Chemical.

These polyether polyols offered big technical and commercial advantages such as low cost, ease of handling, and – the most important- they showed a much better hydrolytic stability.

Further development have been possible thanks to the introduction of methylene diphenyl diisocyanate (MDI) which heralded the development and use of polyurethane rigid foams as high performance insulation materials : rigid foams based of MDI offered better thermal stability and combustion characteristics if compared with those based on TDI and on 1969 Bayer exhibited an all plastic car in Dusseldorf, Germany, using an innovative process to manufacture that car : the so called RIM, Reaction Injection Molding.

Better to stop at this point the PU history, because if not and due to the enormous number of new developments, we should write an Encyclopedia on this theme.

What we should say is that in the tanning industry polyurethanes started to have a certain success when they replaced flax oil in the production of patent leathers.

In a second time, PU have been used as solvent top coat together and/or as replacement of nitrocellulose and, only in a third time, water dispersed PU have been introduced in finishing leather technology.

Already during the '40 Schlack founded the possibility to disperse PU in water, but only during the '70 PU emulsions started to be used with success in leather finishing.

PU dispersions can be obtained essentially in two different way :

- a) emulsifying pre-polymers with low molecular weight dissolved in organic solvent
- b) preparing PU ionomers

By using the first system we obtain emulsion like O/W, which still contain organic solvent, while with the second system obtained emulsion are solvent free and film formed by these PUD show physical-chemicals characteristics similar to solvent polymers.

## Polyurethane Technology

Which kind of raw materials do we need to manufacture PU ?

Two group of at least bifunctional substances are needed as reactant ; compound with isocyanate groups, and compound with active hydrogen atoms. The physical and chemical character, structure, molecular size of these compound influence the polymerization reaction and additive like catalysts, surfactants, cross-linkers, flame retardant, light stabilizer, etc. are used to control and modify the reaction process and the performances of the polymer.

**Isocyanates** with two or more functional group are needed for the formation of PU polymers.

In a global point of view, volume wise, aromatic isocyanates account for the most commonly produced, but aliphatic and cycloaliphatic ones are also important building block for PU materials.

The two most important aromatic isocyanates are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI).

TDI consist of a mixture of the 2,4 – and 2,6 – diisocyanate isomers and the most important product is TDI-80 which consist in 80% of the isomer 2,4 and 20% of the isomer 2,6.

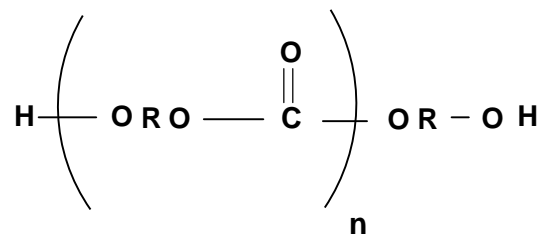
MDI has three different isomers.

The most important aliphatic and cycloaliphatic isocyanates are 1,6 – hexamethylene diisocyanate (HDI) and 1 – isocyanato – 3 – isocyanomethyl – 3,5,5 – trimethyl – cyclohexane (also called isophorone diisocyanate, IPDI).

They are used to produce light stable, non yellowing polyurethane coatings and elastomers.

**Polyols** are higher molecular weight materials manufactured from an initiator and monomeric building block. Essentially we can count three different family of polyols :

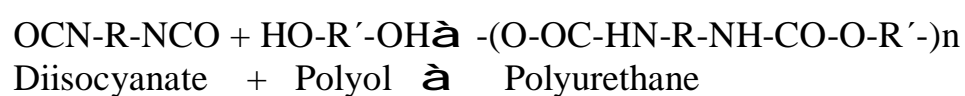
- Polyester** which contain **-CO-O-** group . While quite costly and difficult to handle because of their high viscosity, they offer superior solvent, abrasion and cut resistance.
- Polyether** which contain **-(-CH<sub>2</sub> -O-)-** group. As already seen, PU manufactured using such kind of polyols show better hydrolytic stability
- Polycarbonates** which contain functional group as showed below :



This kind of materials are used in all kind of application that require superior performances like better weatherability, resistance to chemicals and environment attack.

An urethane linkage is produced by reacting an isocyanate group,  $-\text{N}=\text{C}=\text{O}$  , with an hydroxyl (alcohol) group,  $-\text{OH}$ . The reaction product is a polymer which contain the urethane linkage,  $-\text{RNHCOOR}'$ - as following described :

### Polycondensation polymerisation



If reaction is conducted with stochiometric equivalent quantities of poliisocyanate with polyalcohol in ratio 1:1, obtained polymer show a very high molecular weight.

With ratios NCO / OH higher than 1 is possible to obtain polymer (or pre-polymer) with terminal group NCO, while with ratio lower then 1 polymers have terminal group OH .

PU with high molecular weight show better technological performances but, in the same time, adhesion and solubility are worsening.

Polymers with ratio NCO / OH lower then 1 form very flexible film but less resistant to organic solvent and to chemicals in general and do not have good adhesion ; on the contrary, polymers with ratio NCO / OH higher then 1 have a better resistance to chemicals and, due to the NCO group, show an excellent adhesion.

## Silicone Polymers (Siloxanes)

Silicones are used today in most leather applications: footwear, home upholstery, automotive upholstery, garments and other leather goods. 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, and scratch resistance.

But what kind of chemistry are they based on?

Silicones are macromolecules comprised of a polymer backbone of alternating silicon and oxygen atoms.

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.



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.

## Organoreactive Polysiloxanes.

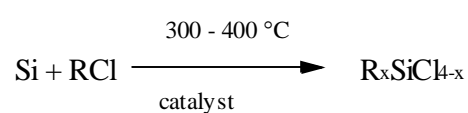
By adding a number of organoreactive groups to a polysiloxane, it is possible to create a silicon-based organoreactive molecule with the chemical characteristics of a carbon-based reactive molecule and the physical properties of a polysiloxane.

So, by blending the chemistry of silicon with the chemistry of carbon, it is possible to create polymers with unique properties and superior performance characteristics.

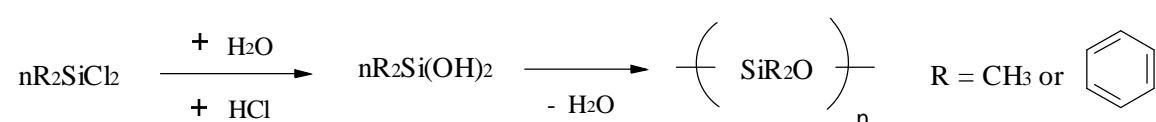
This organoreactive silicon-based molecule can be made to any size. Any number of reactive groups can be designed into it.

Organoreactive groups can be attached to polysiloxanes in a number of ways. The industrial process which lead to the organo-polysiloxanes is the Muller-Rochow Synthesis:

Organochlorosilanes are obtained directly from elemental silicon.



By hydrolysis organo-polysiloxanes are obtained.



By adjusting -Si-O- chain lengths, the functionality of the side groups and the crosslinking between molecular chains, silicones can be synthesized into an almost infinite variety of materials, each with unique chemical properties and performance characteristics.

The types of organic groups attached to the silicon atoms can be controlled to create a hybrid chemistry capable of imparting important organic characteristics to the silicone, including hardness, tack and flexibility:

Monomer	Polymer structure
(R)3SiCl	Chain termination
(R)2SiCl2	Linear polymer
RSiCl3, SiCl4	Branched polymer

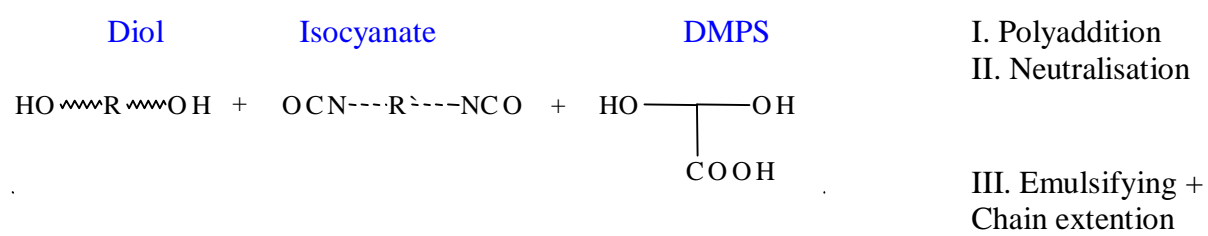
Property	CH3SiCl3	PhSiCl3	(CH3)2SiCl2	CH3PhSiCl	(Ph)2SiCl2
Hardness	+	+	--	--	--
Tack	--	----	+	+	+
Flexibility	--	--	+	+	+

### Innovative polymer technology

As already mentioned, silicones can be formulated into customized emulsions or blended with organic polymer emulsions to provide a wide variety of performance properties.

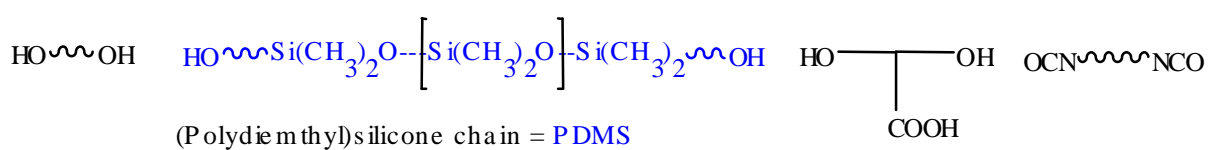
Starting from the classical polyaddition reaction, we can manipulate it by adding silicone polymer backbone as described :

### Common Polyurethane Dispersion

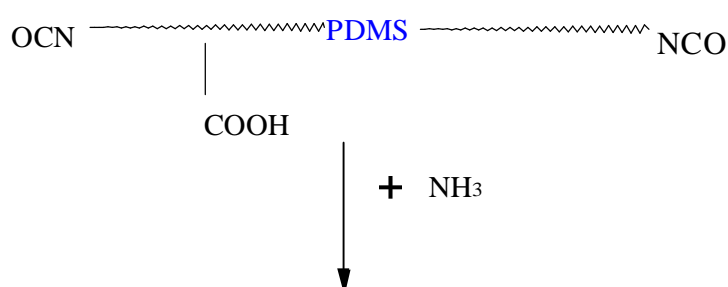


### Silicone Reinforced Polyurethane Dispersion

#### I. Polyaddition



#### II. Neutralisation





We can clearly see that increased amount, from 0 to 10% on PUD top coat weight, of the new silicone based polymer increase all physical performances till reaching an average of 125,000 flexes in trials #3 without addition of any cross-linker. A subsequent addition up to 20% allow to reach almost 20,000 cold flexes but we do not see considerable further increases in flexes.

Comparable performances can be seen in trial #6, where conventional top coat has been added of 5% of polyisocyanate and 5% of the new silicone back bone PU, while trial #5 – which is the most conventional one – show a little lower performances.

Increasing amount of both cross-linker and PDMS-PU lead to even better flexes (over 150,000) but we see a deterioration on Taber test.

UV fastness and heat resistance are not affected

As conclusion we can say that postulate was valid and that obtained results are extremely encouraging, because they open the door to further development in order to produce more eco-friendly leathers with a better respect of the environment.

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