Organofunctional Siloxanes: The Best of Both Worlds

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Dow Corning Ltd

Chemsource 2006 Symposium
14th June 2006

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Outline of Presentation

- Overview of Dow Corning
- Brief History
- From Sand to Silicones
- Properties of Silicones
- Organofunctional Siloxanes
  - New developments

Dow Corning

The Silicone Technology Pioneer

- **A joint venture of The Dow Chemical Company and Corning, Inc.**
- **Organised to explore the potential of the silicon atom**

Dow Corning and Silicones

- **The market leader in the silicones industry**
- **More than 8,000 products and services**
- **More than 25,000 customers world-wide**
- **Sales of $3.88 billion in 2005**
  - **60% of the Sales outside the US**
- **Approximately 9,100 employees world-wide**
- **4,500+ active patents globally**

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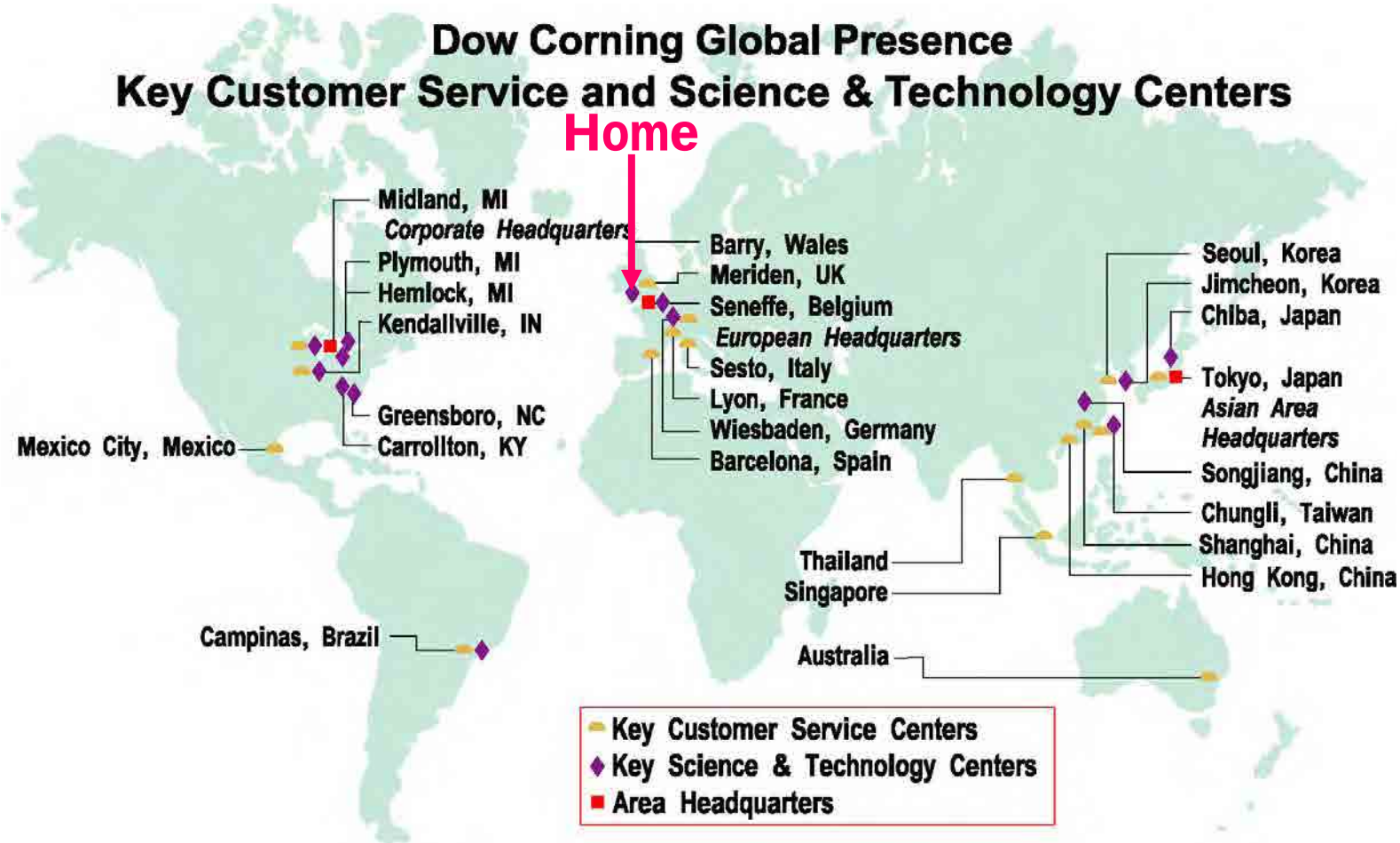
Dow Corning is Innovating around the World



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History of Silicones

Silicone and silicone compounds do not occur naturally

- **Neolithic- flint, quartz, sand, granite**
- **B.C.-sand+potash+minerals=glass**
- **1771-Scheele makes first silicone compound, SiF_4**
- **1811-Gay-Lussac & Thenard, isolate silicon metal**
- **1828-Berzelius, Si metal**
  SiF_4
  $SiCl_4$
- **1846 Ebelman, $Si(OEt)_4$**

The ability to make and isolate silicon metal was the key to making silicones

History of Silicones

1857	**Wohler, $SiHCl_3$**
	SiH_4
	Introduced the term silicone $R_2Si=O$
	Analogue to Ketone $R_2C=O$
1863	**Friedel and Crafts, $SiEt_4$**
1900	**Grignard, RMgX**
1900-1940	**Kipping and Dilthey, R_2SiCl_2**
	Uninviting glues and oils……

"The prospect of any immediate and important advance in this section of organic chemistry does not seem very hopeful"

1930-1950	**Hyde, Rochow, McGregor**
	Established the basis for silicone technology

Silicones become a Commercial Reality

Dr. Eugene Rochow

- Direct process for the synthesis of chlorosilanes
- Production of methyl silicone
- Silicone Rubber

Dr. Frank Hyde

1903-1999

- Design and control (polymerisation) of polymers containing silicon and oxygen chains
- Some of the first industrial applications of silicone fluids, gums and resins
- RTV sealants

Modern Day Uses of Silicon Compounds

Dow Corning's products are used by customers in virtually every major industry.


Laundry Detergents


Cosmetics


Textile

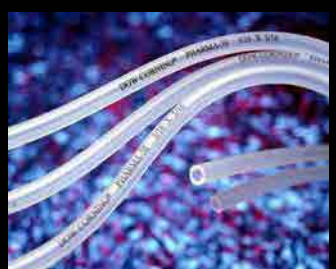

Construction

Paper/Labels


Coatings


Automotive


Electronics


Medical Materials


Lubricants

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Silicon in Nature

- **Diatom Unicellular alga**
- **Silica structures 50um wide**
- **Produce gigatons of silica annually-3km^3**
- **Industry achieves only several billion kg of silicones annually**

From Sand to Silicon

Overall Composition of the Earth:
Iron-56 34.6%
Oxygen-16 29.5%
Silicon-28 15.2%
Magnesium-24 12.7%
Nickel-56 2.4%
Sulphur -32 1.9%

Composition of the Earth's Crust:
Oxygen - 46.6%
Silicon 27.7%
Aluminium 8.1%
Iron 5.0%

From Sand to Silicon

- Reduction of sand into silicon metal :

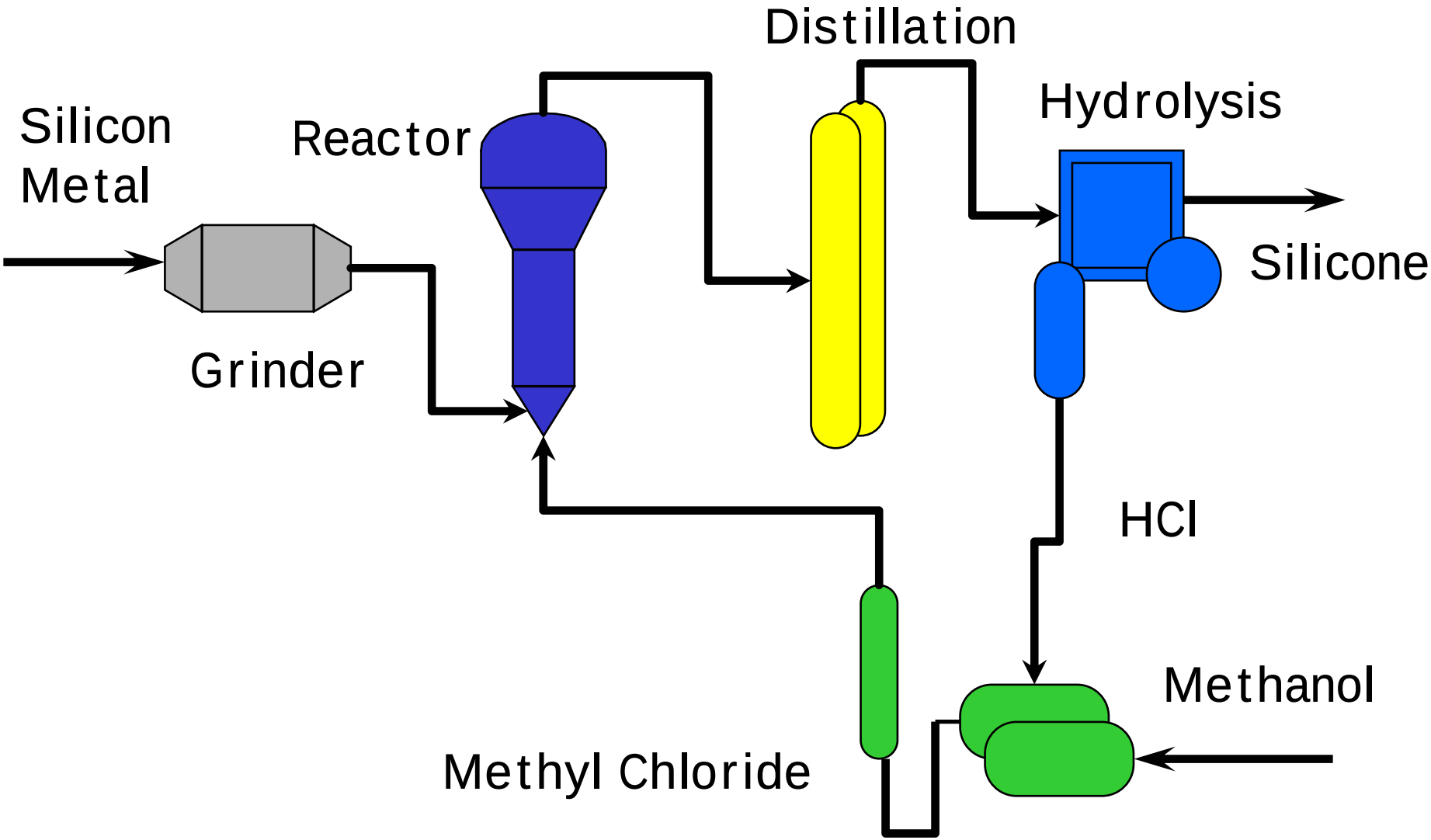
$$SiO_2 + 2\,C \longrightarrow Si + 2\,CO$$

Sand (silica) Carbon Silicon Carbon monoxide

- Hyper pure silicon

$$HSiCl_3 + H_2 \longrightarrow Si + 3HCl$$

The Basic Production Process



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From Silicon to Silanes (Chlorosilane Production)

Direct Process (Mueller-Rochow Process)

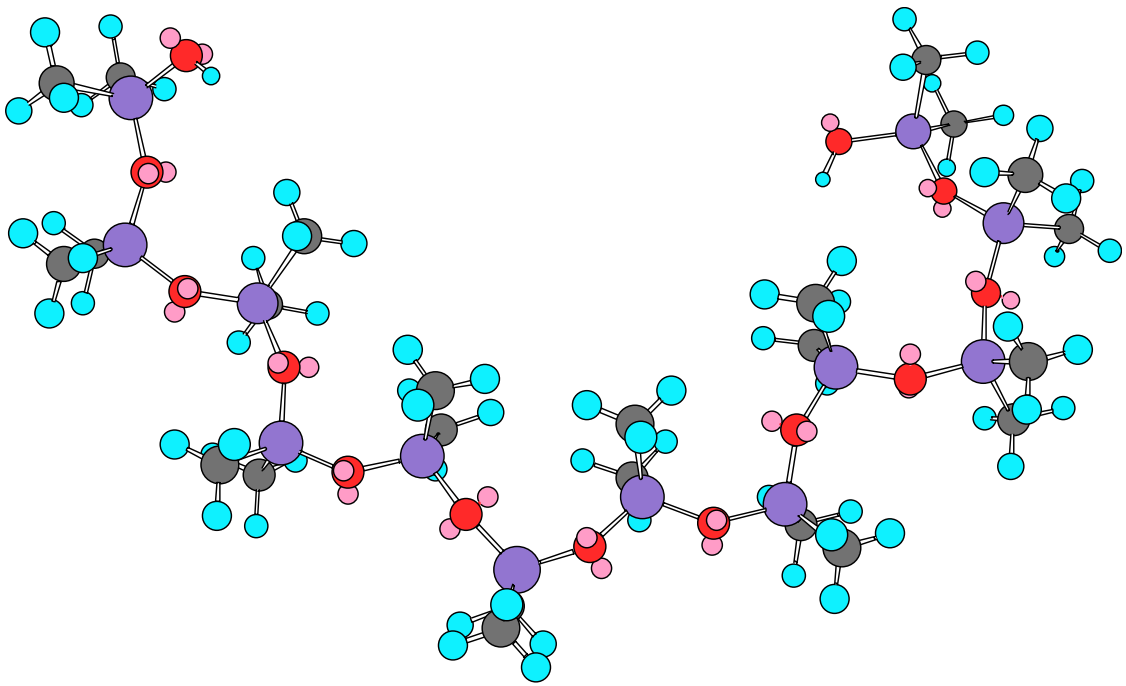
$$Si + 2\,MeCl \xrightarrow[300°C]{Cu} \begin{cases} MeSiCl_3 & \text{bpt: } 66°C \\ \mathbf{Me_2SiCl_2} & \text{bpt: } 70°C \\ Me_3SiCl & \text{bpt: } 57°C \end{cases}$$

Chlorosilane Hydrolysis

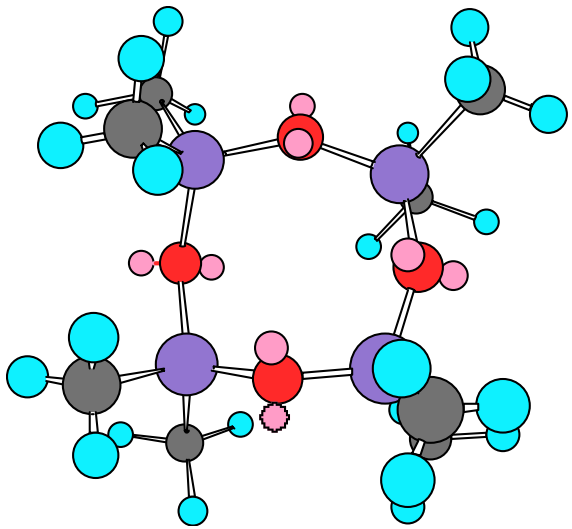
$$x\ Me_2SiCl_2 + H_2O \longrightarrow y\ HO(Me_2SiO)_nH + z\ (Me_2SiO)_m$$

n = 20 - 50 m = 3, 4, 5,6

linears **cyclics**



+HCl



Polymerisation

- **Ring opening polymerisation/equilibration**

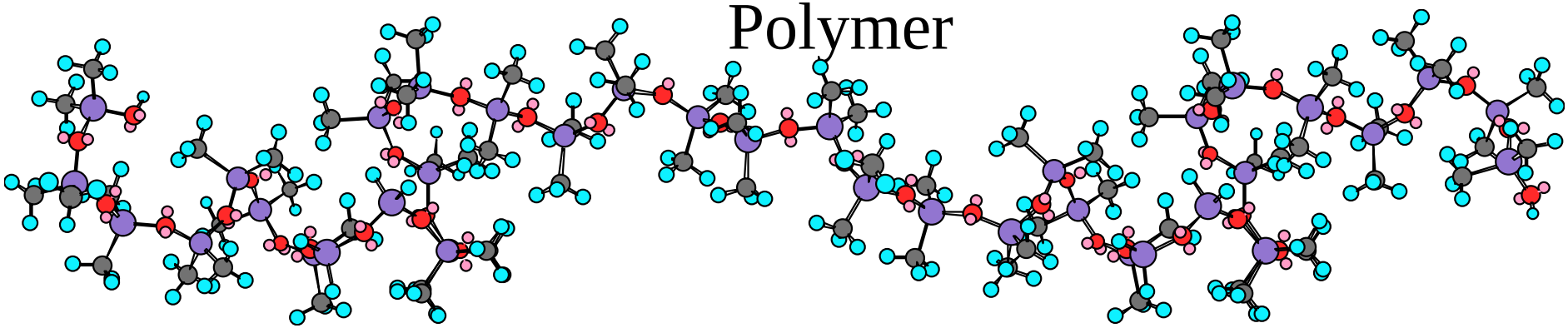
$$\text{Cyclics} + Me_3SiOSiMe_3 \xrightarrow[\text{Catalyst}]{} Me_3SiO\text{-}(Me_2SiO)_n\text{-}SiMe_3$$

endblocker Polymer

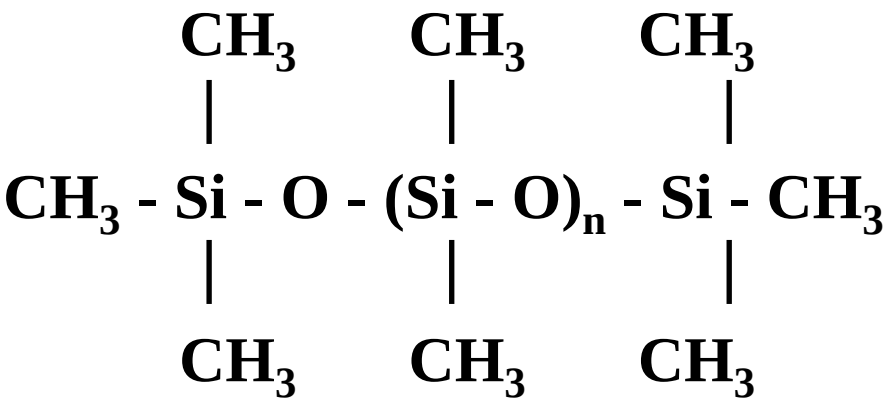
- **Condensation polymerisation**

$$\text{Linears} \xrightarrow[\text{Catalyst}]{} HOSiMe_2O\text{-}(Me_2SiO)_n\text{-}SiMe_2OH + H_2O$$

Polymer



POLYDIMETHYLSILOXANES

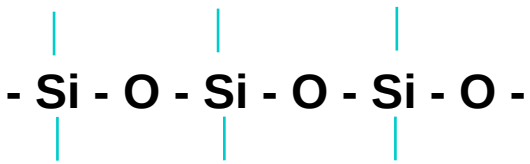


- Silicones typically have a back bone which is inorganic like glass
- The side groups are organic: in most case methyl
- The degree of polymerisation varies from n=0 to several thousand
- Silicones show low viscosity, even at very long chain lengths

Chain has spiral shape

n	Viscosity (cSt)
64	100
320	1000
730	10000
1570	60000

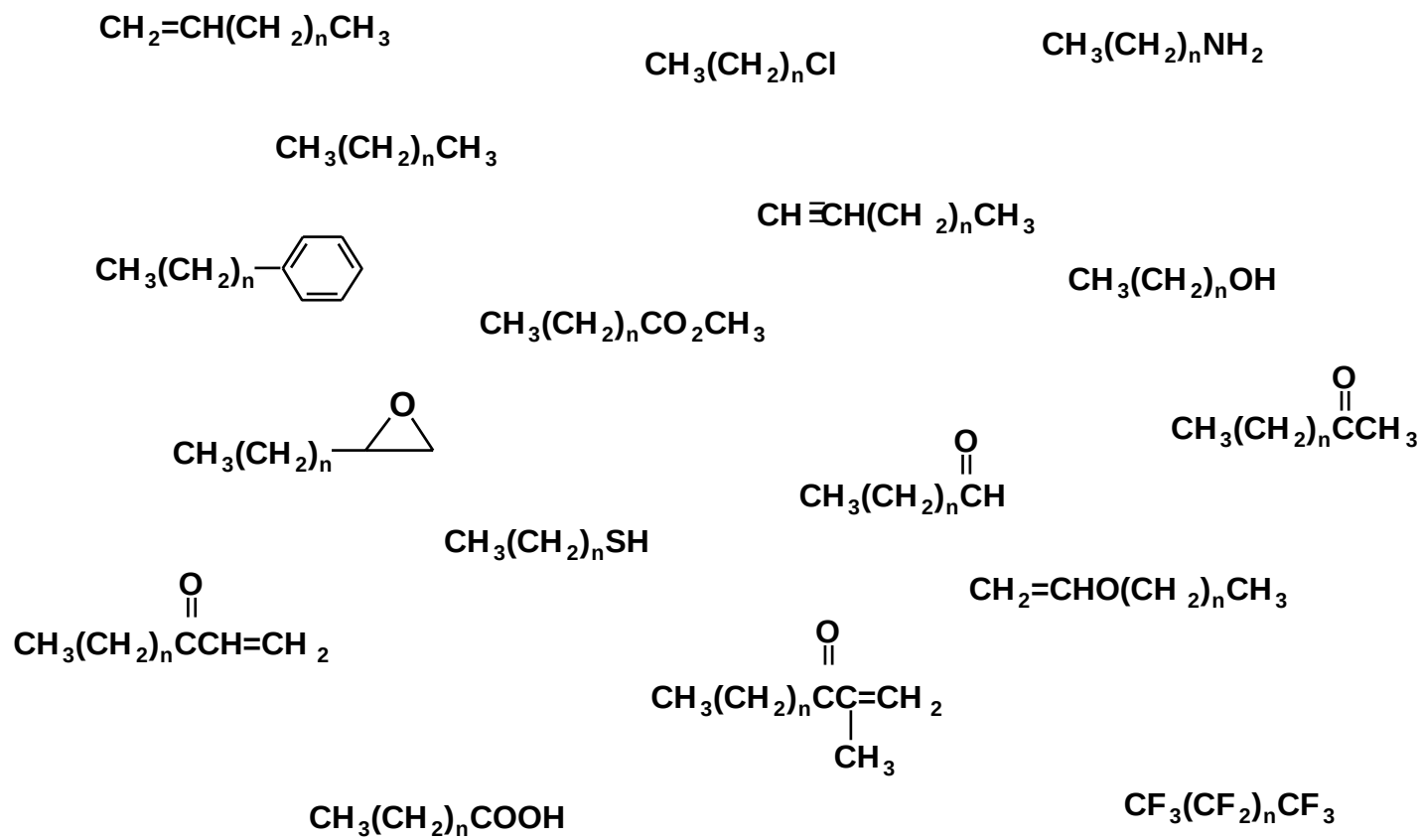
The Unique Properties of Silicones

Molecular Characteristics	Physico-chemical Properties	Applications
- highly open, flexible and mobile siloxane backbone  - high bond strength 435 kJmol^{-1} Si-O (cf. 350 kJmol^{-1} C-C)	- low surface tension & energy - high spreading and wetting capabilities - permeable to gas and water vapour - heat stability - degradability - compatibility with organics - weather resistance	- lubricant - antifoaming - release agent - aesthetic feel (softness) - comfort - high temperature processing - can be sterilised - hydrophobic / hydrophilic - breathable

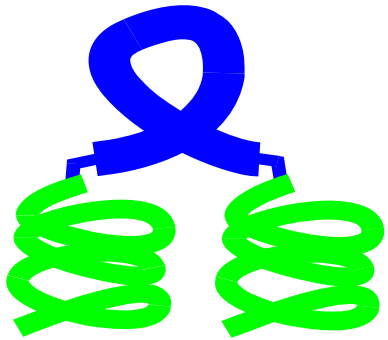
Why Organofunctional Silicones?

- Unique properties of silicone
  - flexible backbone, surface properties, UV/oxidative stability, etc.
- Compatibility with other fluids
- Reactivity with organics
  - physical (hydrogen bonding)
  - chemical
- Increased Deposition/Substantivity

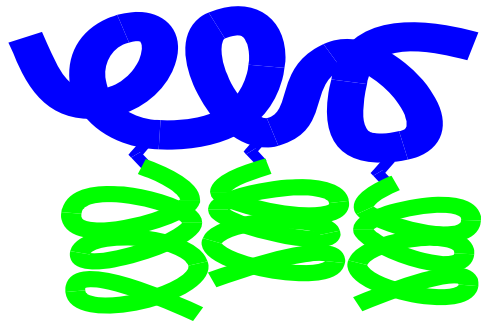
The World of Organic Chemistry



The Versatility of Siloxanes

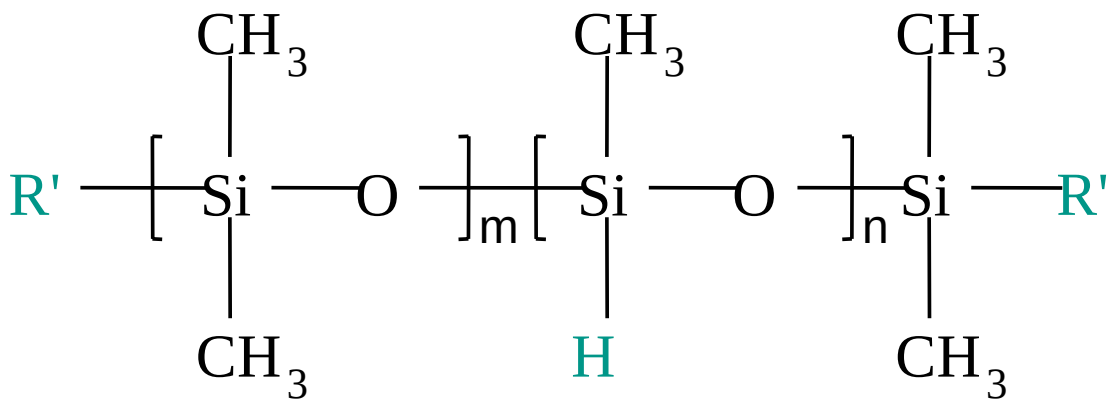


- ABA Block Copolymers
- Graft or “Rake” Copolymers
- Combination ABA/Graft



SOME EXAMPLES……

Methyl Hydrogen Siloxanes



R': H, Me

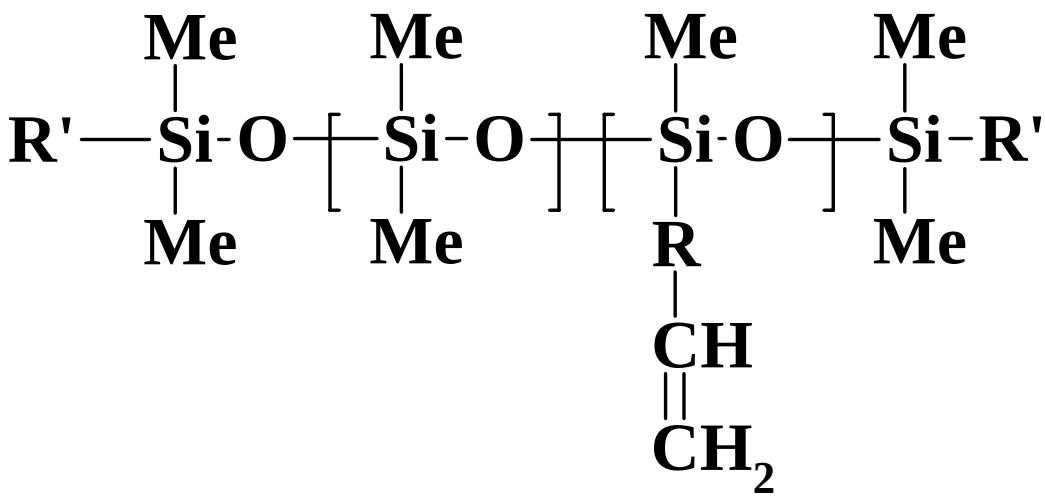
Properties

- Reactivity
  - Crosslinking *via* hydrosilylation
- Durability/substantivity

Applications

- Elastomers/gels
- Coatings
- Waterproofing
- Organofunctional siloxanes

Methyl Alkenyl Silicones



R: CH_2, $(CH_2)_4$,
R': Me, $RCH{=}CH_2$, OH

Methyl Alkenyl Silicones

- Properties
  - Reactivity:
    - Crosslinking via free radical & hydrosilylation
- Applications
  - Elastomers/gels
  - Coatings

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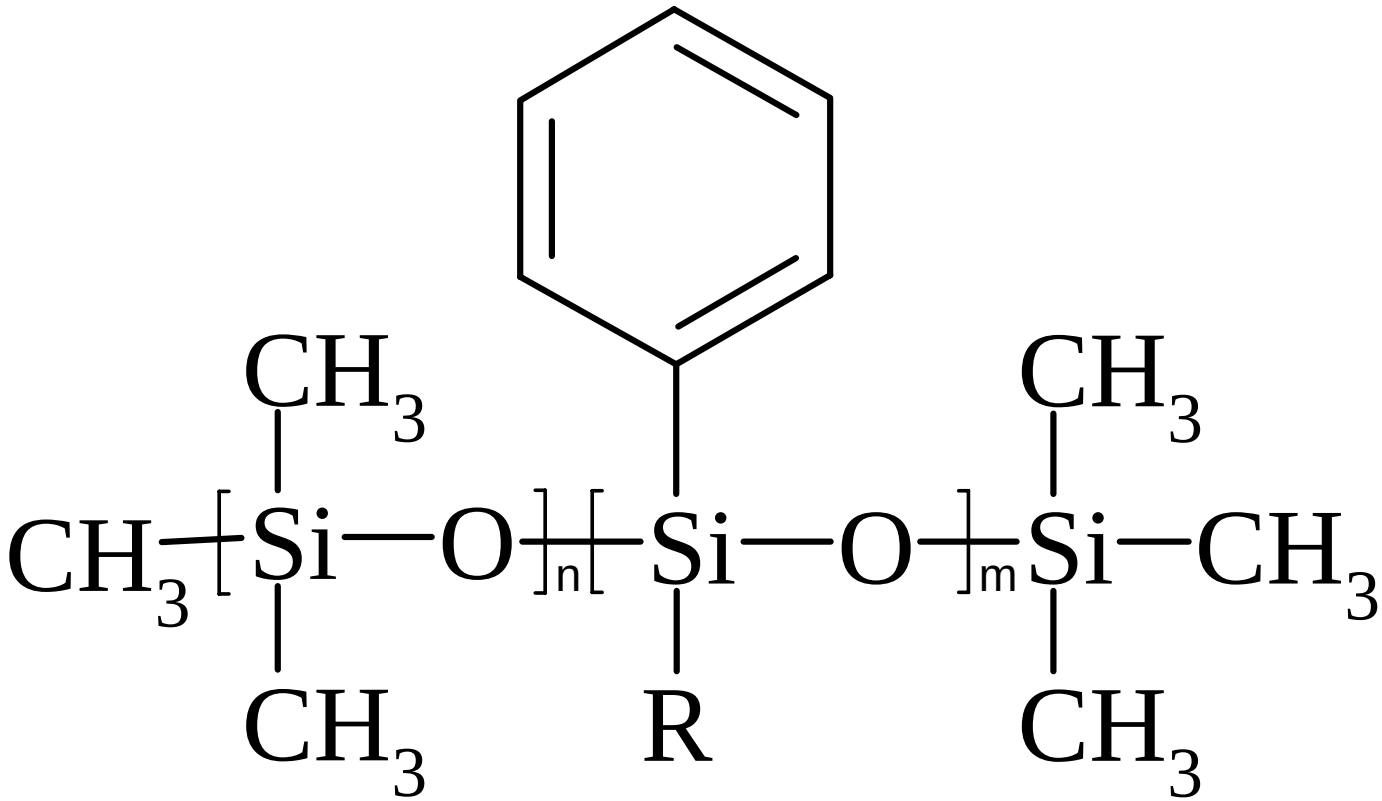
Phenyl Functional Siloxanes



$R = CH_3, OSi(CH_3)_3$

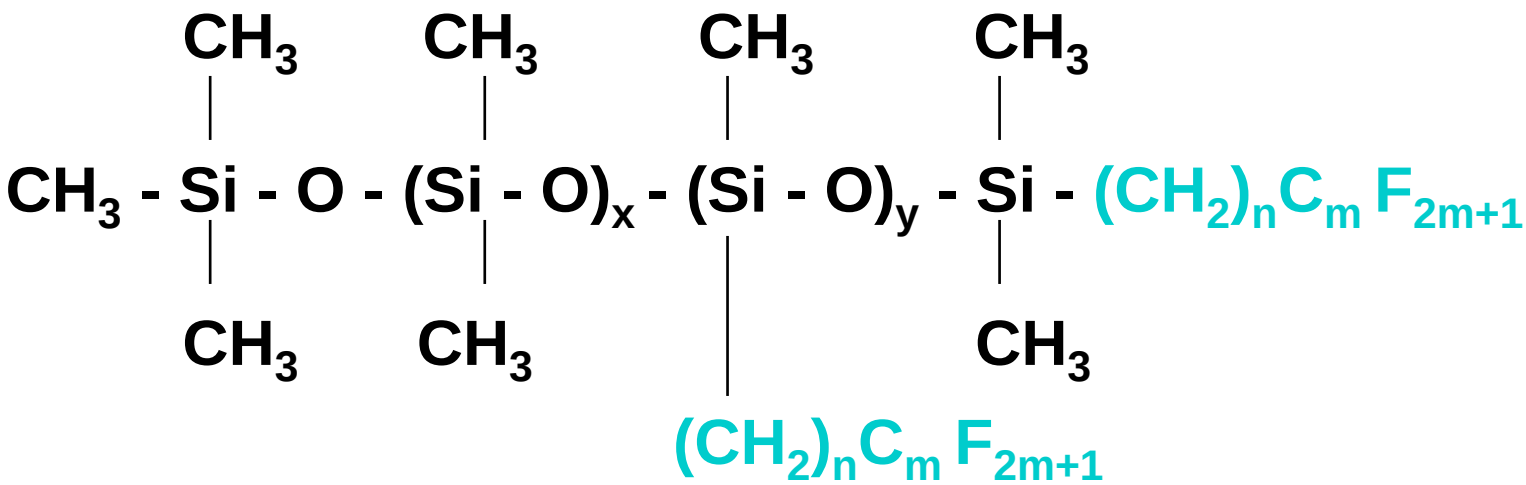
Phenyl-functional Siloxanes

PROPERTY/BENEFIT	APPLICATIONS

- Good compatibility with organics / alcohol
- Durable water repellency
- Gloss
  - High refractive index
    - (RI = 1.46)
- Softness
- Manageability to hair
- Non oily, easy to spread

- Hair/skin care
- Cosmetics
- Auto/home care

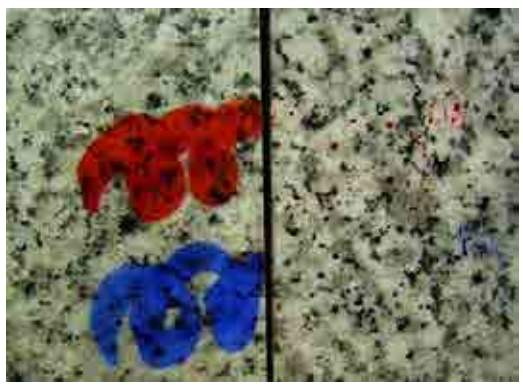
Fluoroalkyl-functional Siloxanes



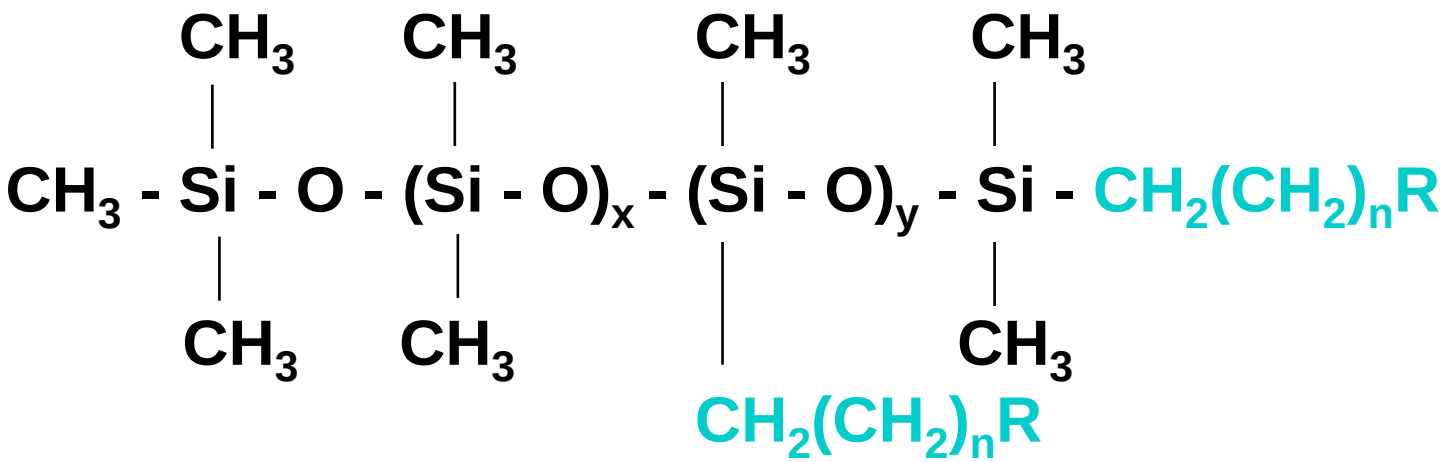
Fluoroalkyl-functional Siloxanes

PROPERTY/BENEFIT	APPLICATIONS

• Low surface tension
• Incompatibility with aqueous and non-aqueous media
• Aesthetics
	• Release
	• Stain resistant and easy clean coatings
	• Non-aqueous antifoams
	  • crude oil
	  • solvent borne coatings
	• Coating special effects
	  • hammer finish
	• Oil resistant elastomers
	  • auto parts
	• Oil resistance/chemical resistance



Alkylmethyl-functional Siloxanes



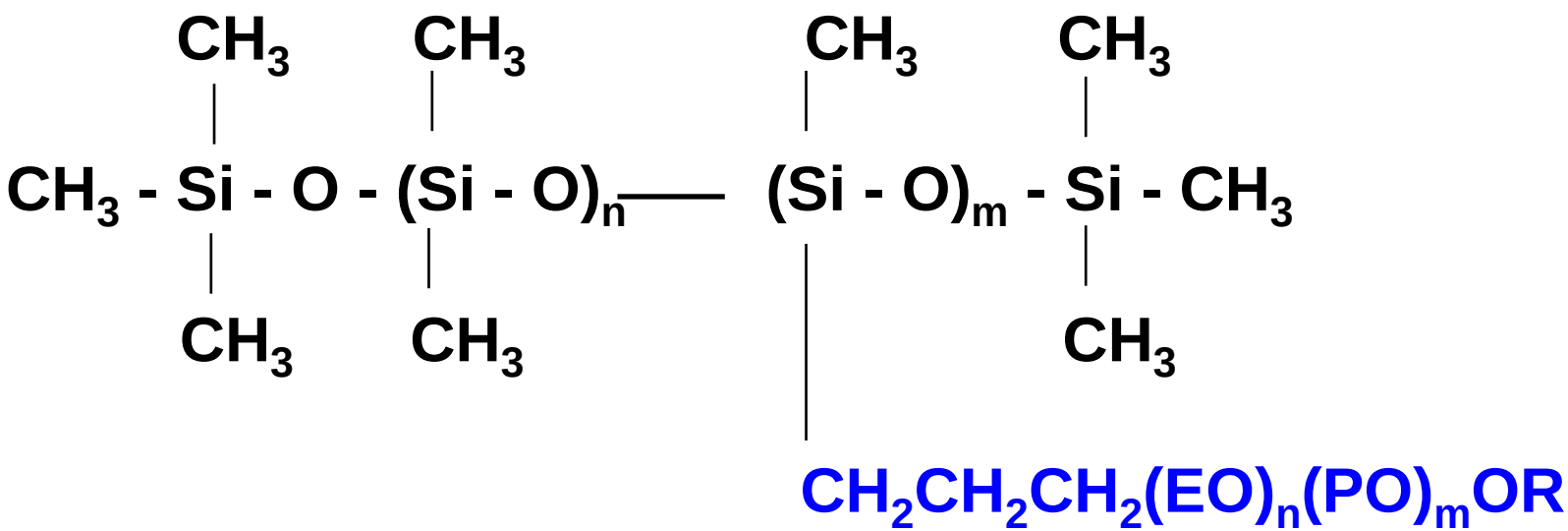
Alkylmethyl-functional Siloxanes

PROPERTY/BENEFIT	APPLICATIONS

- Viscous fluid - low m.pt. wax
  - Length of alkyl chain
- Improved compatibility with organics
- Controlled permeability
- Substantive
- Spreadable

- Emulsion, formulation
- Skin care
- Shower gels
- Auto polish

Silicone Polyethers (SPEs)



R = H, Ac

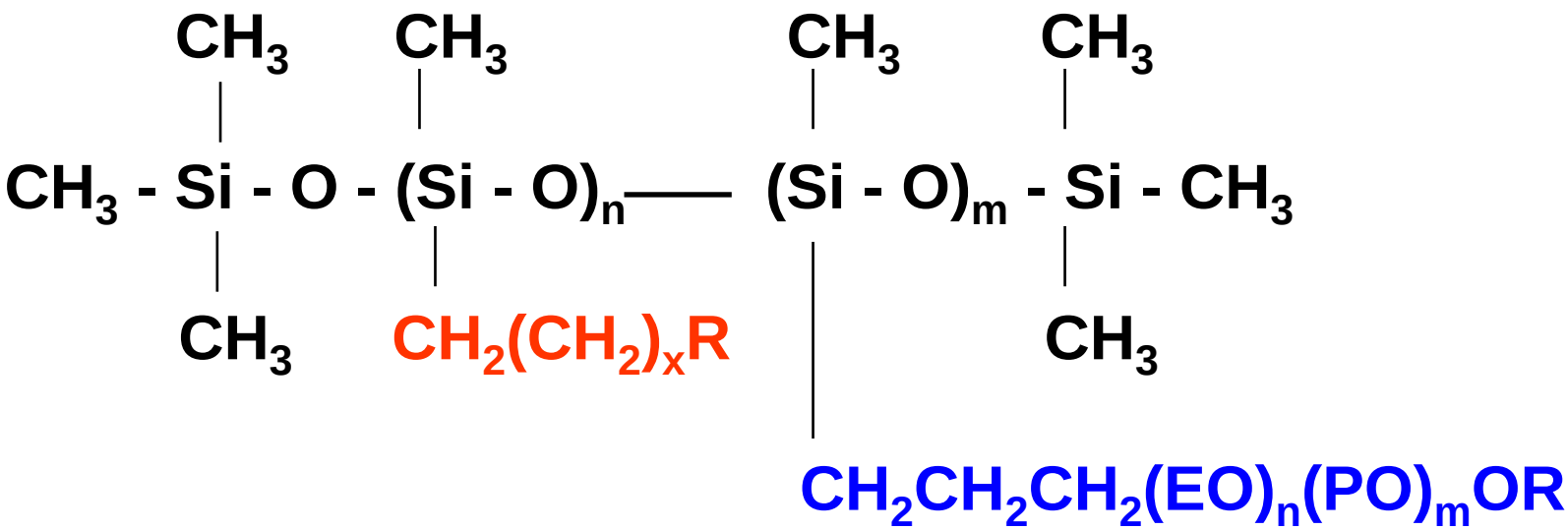
Silicone Polyether Copolymers

Foam Control in High Speed Printing

APPLICATIONS

- **Water dispersible, formulated products, emulsions**
- **Hair/skin care**
- **Paint/ink additive**
- **Polyurethane foam additive**
- **Antifoam**
- **Thread lubricant**

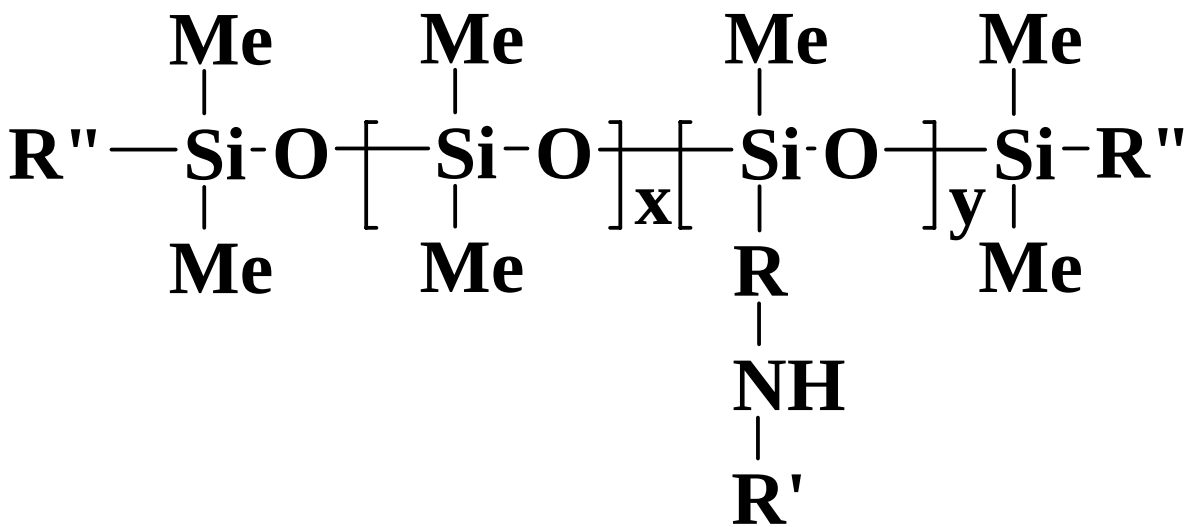
Alkylmethyl-co-polyether Siloxane Copolymers



Alkylmethyl-co-polyether Siloxane Copolymers

PROPERTY/BENEFIT	APPLICATIONS
• Stable W/O emulsions • Moisturising & protective • Non-greasy feel • Spreadable • High water content	• Emulsifier • Facial care • Hand & body creams & lotions

Amino Silicones



R = $(CH_2)_3$, $CH_2CH(CH_3)CH_2$

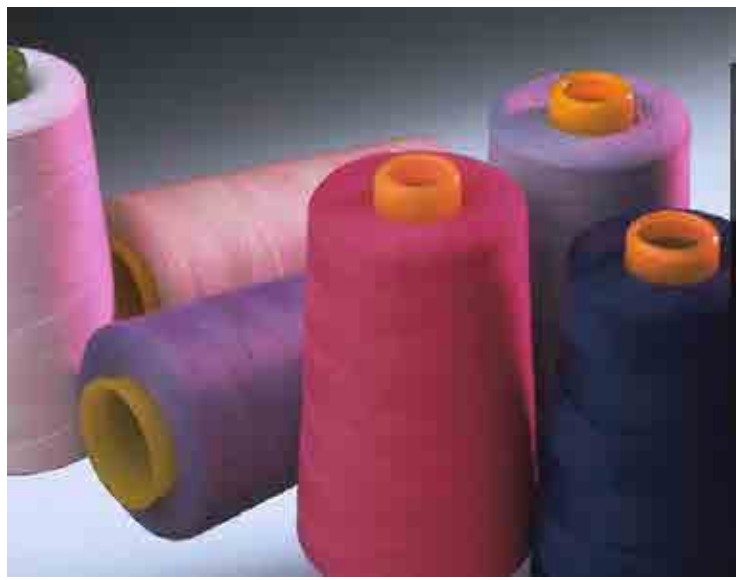
R’ = H, $CH_2CH_2NH_2$

R” = Me, RNHR’

Applications of Aminosiloxanes

The feel-good factor for textiles

- **Leather and textile fabric softeners for softening**, water repellancy and stain resistance
- Nonwoven fabric treatments
- Fibre and thread lubrication
- Automotive safety air bag coatings



Applications of Aminosiloxanes

In the Home…

Hair Care

Other !

Key property is SOFTNESS

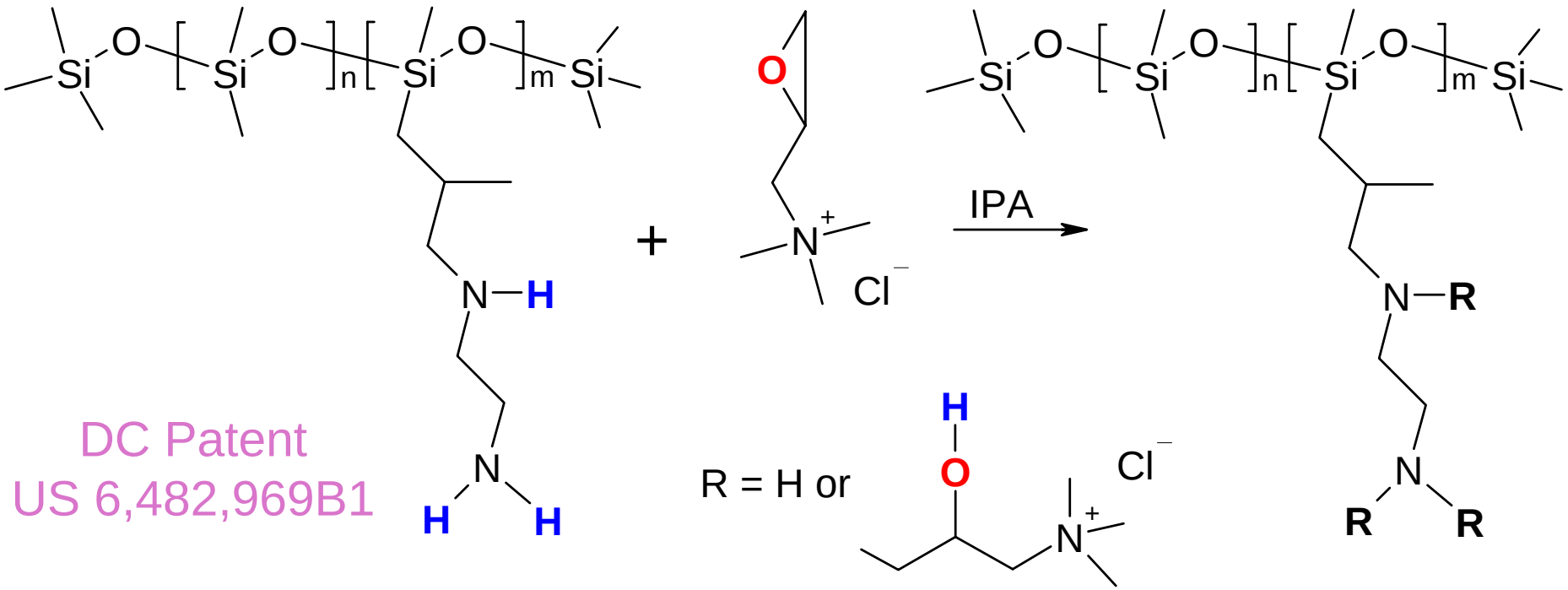
- **Shampoo[illegible]itioners**
- Cos[illegible]oisturisers and [illegible]preparations
- **[illegible]ssue (face & bathroom)**
- Automatic washing powder
- Furniture polishes

Amino Derivatives: Quaternary Ammonium Salts

- Quaternaries in general are highly substantive to negatively charged surfaces (hair, textiles, *etc*).
- Polymeric quats should offer the benefit of even higher substantivity.
- Improved delivery of a low surface energy material (silicone) to a surface.
- Depending on the structure, quats can be made to impart:
  - conditioning, feel, body, slipperiness, hydrophobicity, hydrophilicity, *etc*.

Quaternary Ammonium Functional Silicones

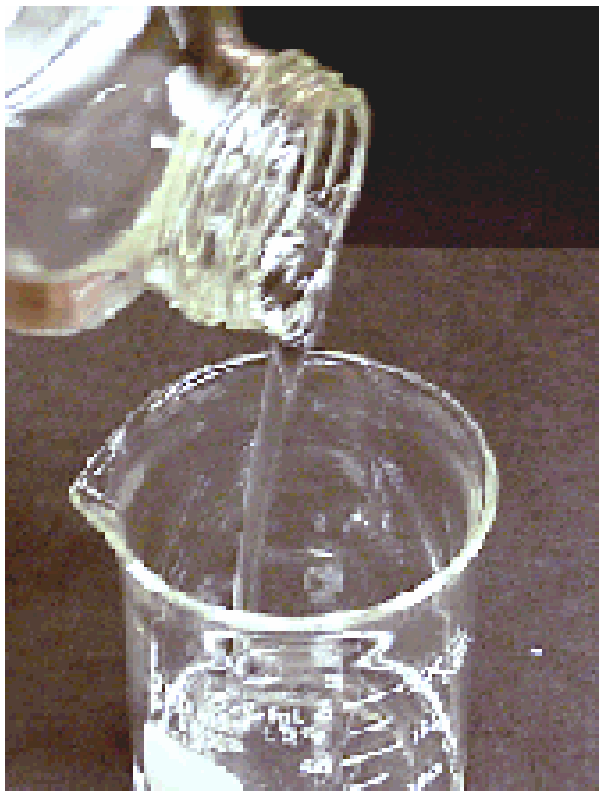
– Cationization of amine functional silicones with glycidyl trimethyl ammonium chloride (GTMAC).



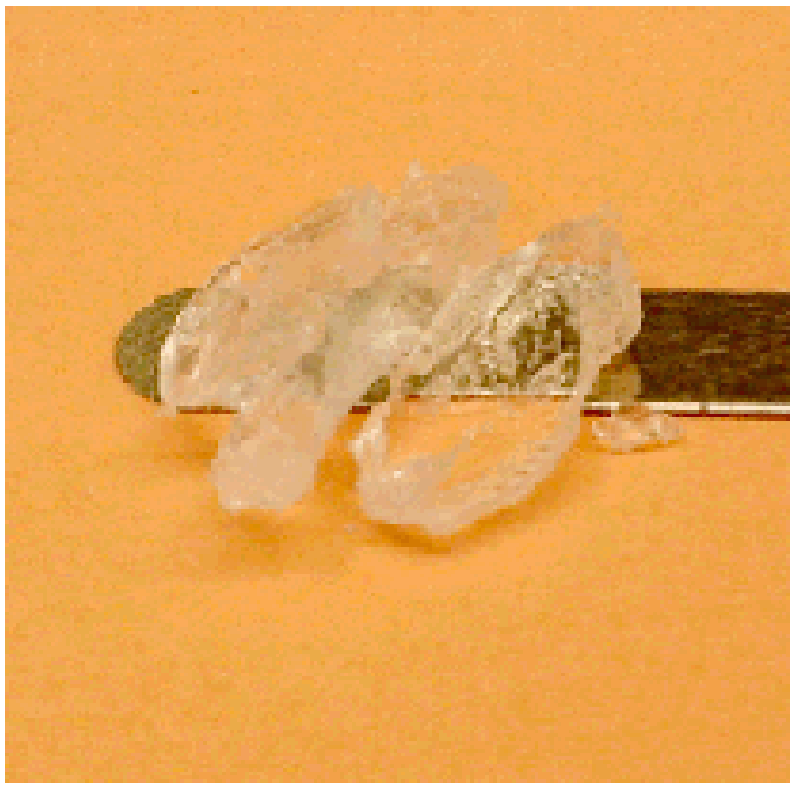
DC Patent
US 6,482,969B1

Comparison of Amine Fluid and ‘Quat Fluid’

Amine Functional Fluid



Quat “Fluid”



Dow Corning® 5-7113 Silicone Quat Microemulsion

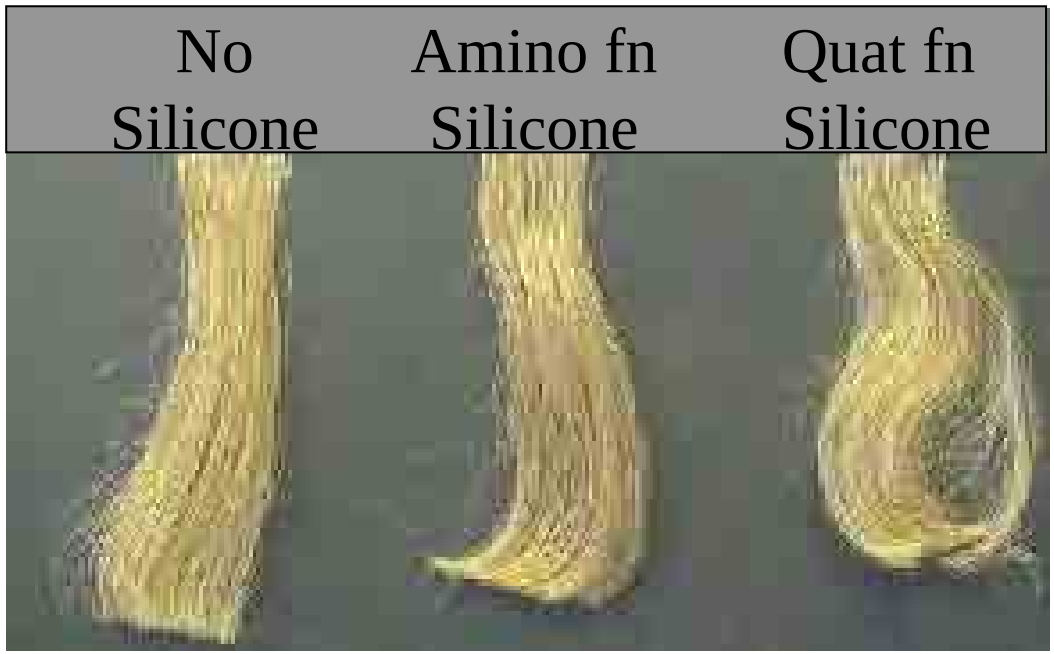
- Process Overview
  - Amino Inversion Emulsification

- Key Product Characteristics
  - Actives: 28% 7-6030 Polymer (25% Actives)
  - Appearance: Translucent to transparent
  - Particle size: < 20nm microemulsion
  - Odor: Low (surfactant/amine)
  - Stability: Good heat-aged and shelf

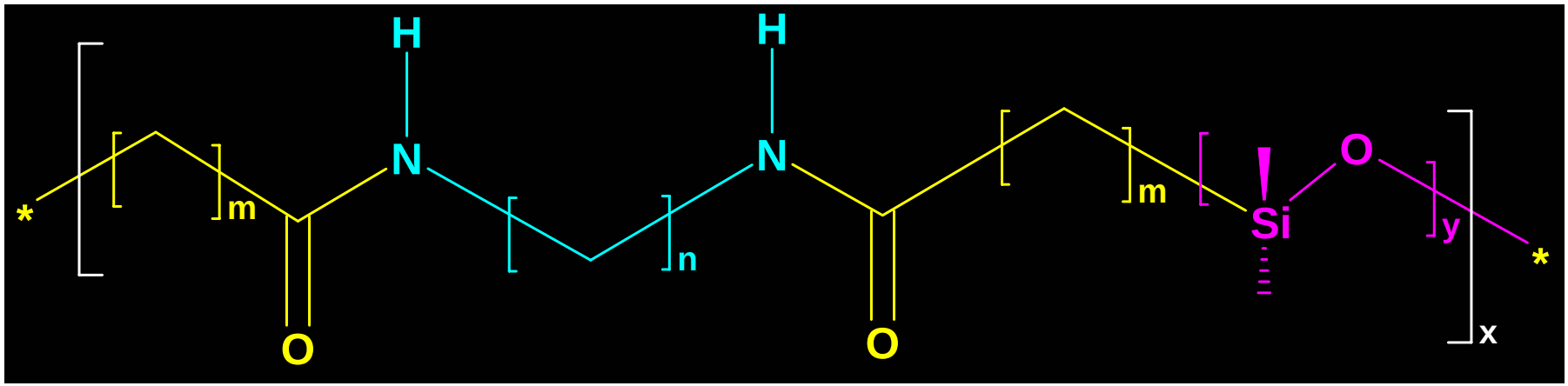
- INCI Name: Silicone Quaternium-16 (and) Undeceth-11 (and) Butyloctanol (and) Undeceth-5

Multiple Benefits ….

- Heat Protection
- Hair Colour Protection
- Hair Body/Volume Enhancement
- Superior Conditioning
- Clear Formulations Possible



Amino Derivatives: Silicone Polyamide
Dow Corning® 2-8178 Gellant

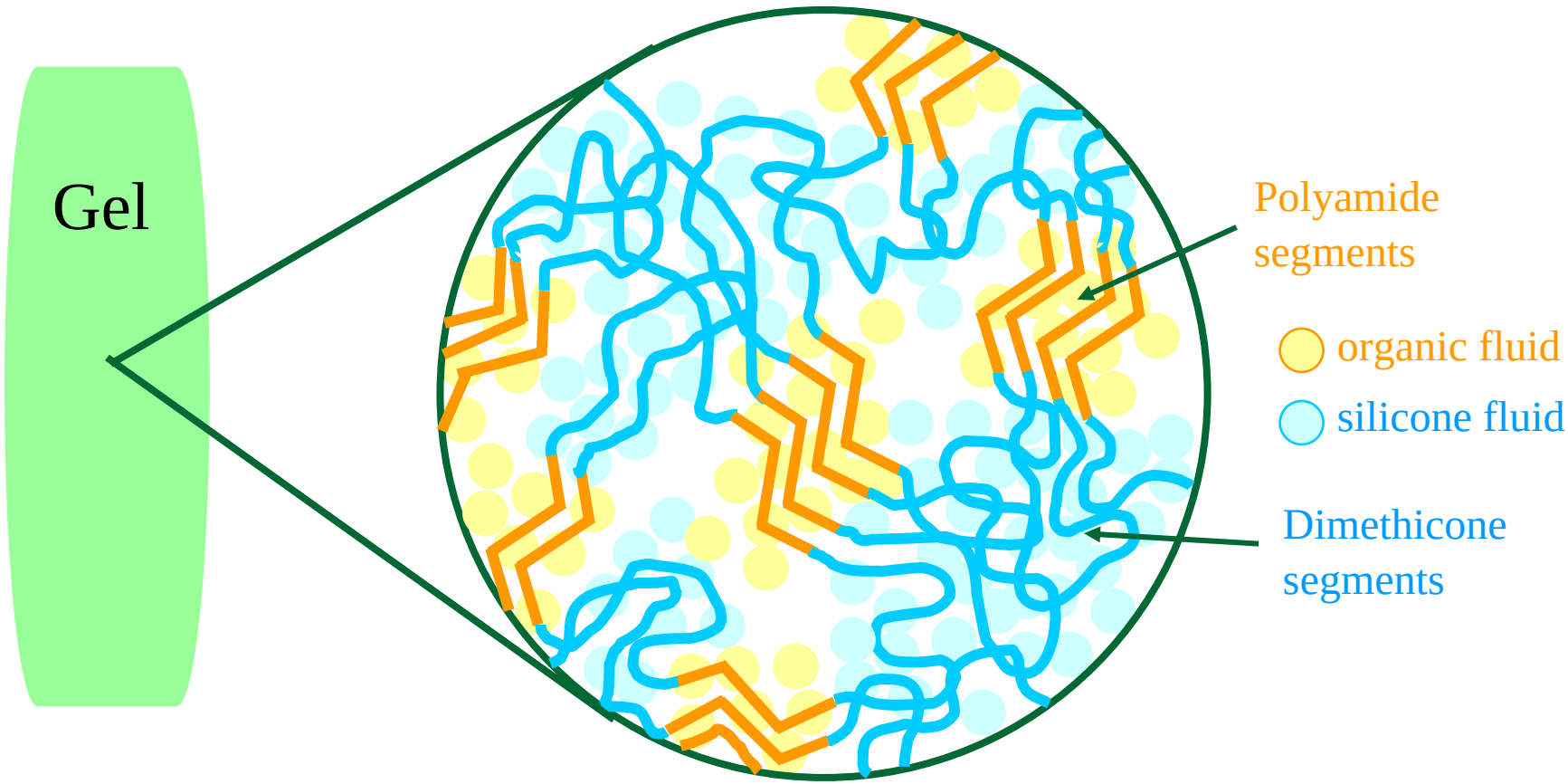


- Thicken or Structure Silicone and Organics
  - Formulate soft gels to rigid solids
  - Formulate clear or opaque systems

- Can be used in anhydrous or emulsion systems.

Mixtures of 2-8178, silicone, and organic oil form Microphase Separation Gels

Association of the polar polyamide segments led to thickening and gellation when the mixture is cooled below the phase transition temperature (melting point)



Summary

- Silicones combine many properties of organic and inorganic materials and are tremendously versatile
  - many forms from low viscosity liquids to elastomers or solids
  - may be delivered neat or as dispersions, blends, solids, gels, emulsions
- Structures may be modified to yield a range of organofunctional species
  - almost any organic group can be placed on a silicone or a silane
- They may be very inert or highly reactive, dependent on structure

Thank You for your Attention

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