البوليمرات السليكونية ..... تحضيرها وتطبيقاتها الصناعية والطبية

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كلية العلوم – قسم الكيمياء
جامعة البصرة

1- Introduction

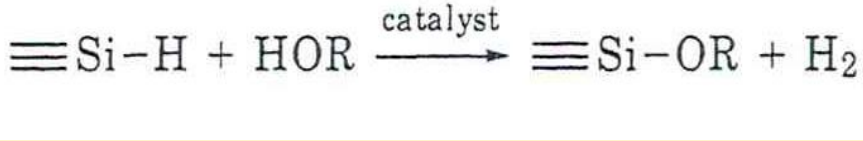
Property	Carbon	Silicon
Atomic Radius A	0.7	1.1
Covalent Radius A	0.77	1.16
Electron Effinity ev	1.12	1.39
Electronegativity	2.74	2.13

Saul Patai, Z. R. *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; The Chemistry of Functional Groups; John Wiley & Sons, Ltd: Chichester, UK, 1998; Vol. 2.

Cont.

Si-H Bond

Cat.NaOH,KOH



Cat.$ZnCl_2$,$SnCl_2$

CH_3-H + H_2O → No Reaction

Cont.

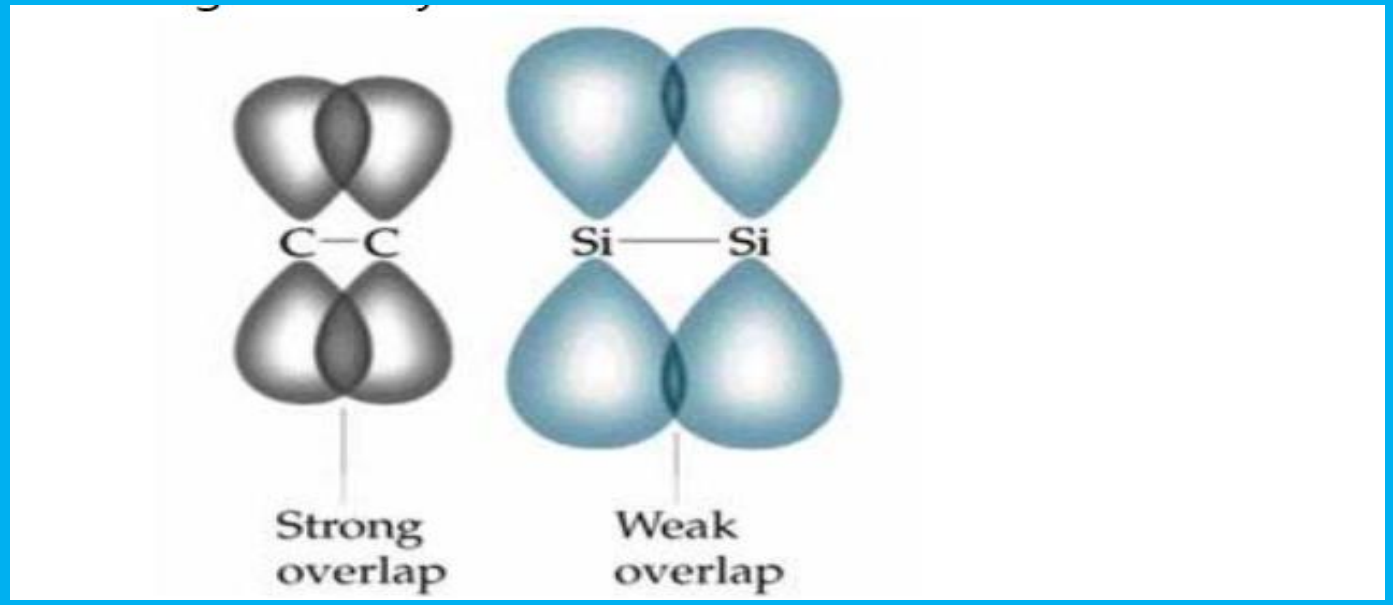
Si-Halogen Bond

Silicon-halogen bond is more reactive and more ionic than the Carbon –halogen bond. The silicon halide toward active hydrogen compounds is a susceptible and very fast reaction, especially in the case of silicon chloride.

$SiCl_4 + H_2O \rightarrow Si(OH)_4$ Silicic acid

$CCl4 + H2O \rightarrow$ No reaction


Si
SiO_2
CO_2

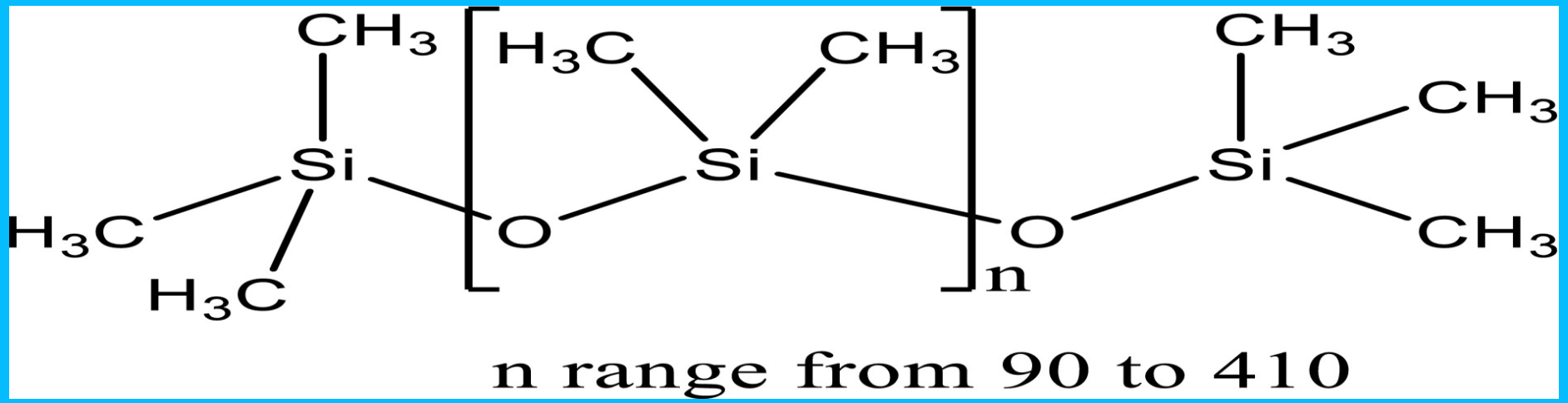

C—C
Si—Si
Strong overlap
Weak overlap

Reaction Hydrolysis SiCl4

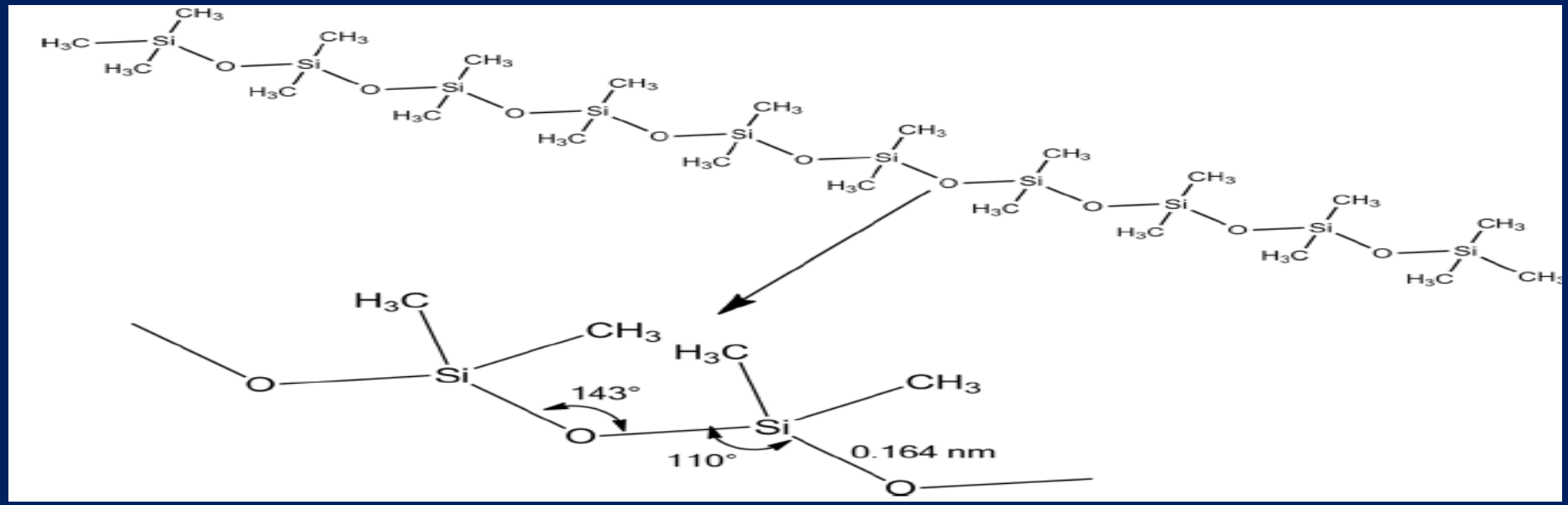
Reaction of water with silicon tetrachloride

RSC | Advancing the

2-General Chemical Structure of Polysiloxane



The Si-O bond- The Key to Silicones Unique Properties



The Si-O bond is longer and flatter than C-O bond,------ In comparison to C-C bonds (1.53 Å), the significantly longer Si–O skeletal bond (1.64 Å) reduces steric interference and intramolecular congestion.

The Si-O bond has Higher bond energy than C-O bond , so the thermal stability is higher .

The Si–O–Si bond angle (~143°) is much more open than the common tetrahedral bonding (~110°).
------As a result, polysiloxane chains are in elastic, random coil structures. Due to the high flexibility and mobility of the chains.

3- History

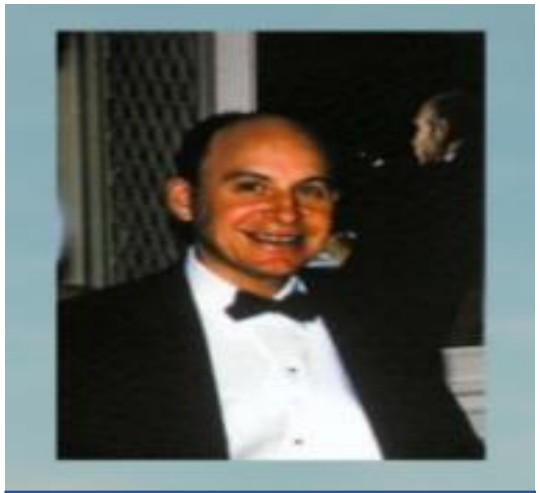
Fredric Kipping

In 1904 Kipping was the first to achieve the synthesis of silicon compounds. While Hyde In 1931 was the first successful research leading to commercial production of silicones

James Hyde

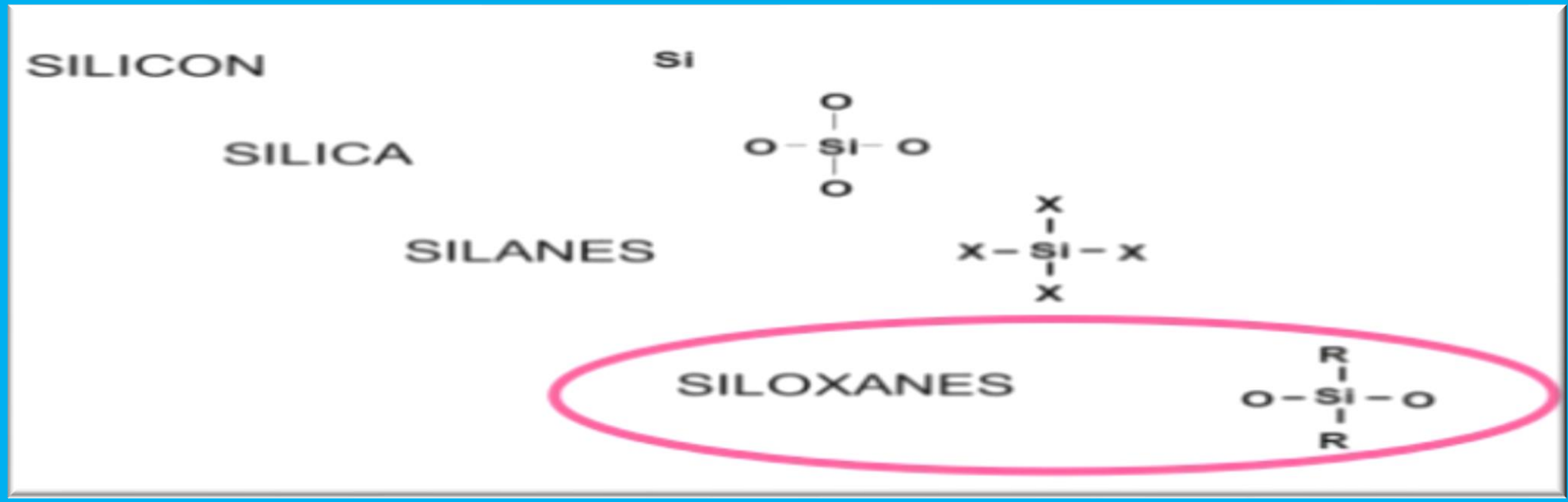
Richard Muller

In 1940 Richard Muller and Eugen Rochow develop a direct methods for synthesis of silicones on an industrial scale.



Eugen Rochow

4- Preparation of Polysiloxane
From Silcon to Silicones.



The production of silicones takes place in three stages :-

1- Synthesis of chlorosilane from silicon metal (Direct Methods).
2- Hydrolysis of chlorosilanes .
3- Condensation of silanols.

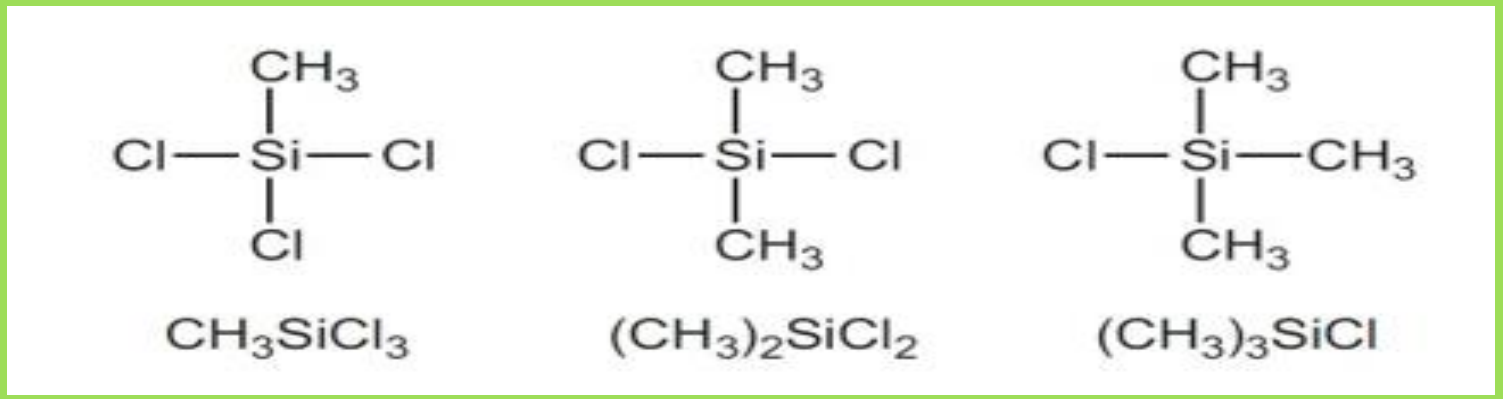
4-1- Synthesis of chloro silane

Silicones are manufactured from pure silicon which has been obtained by the reduction of silicon dioxide (silica) in the form of sand with carbon at high temperatures (1200 ^{0}C) :-

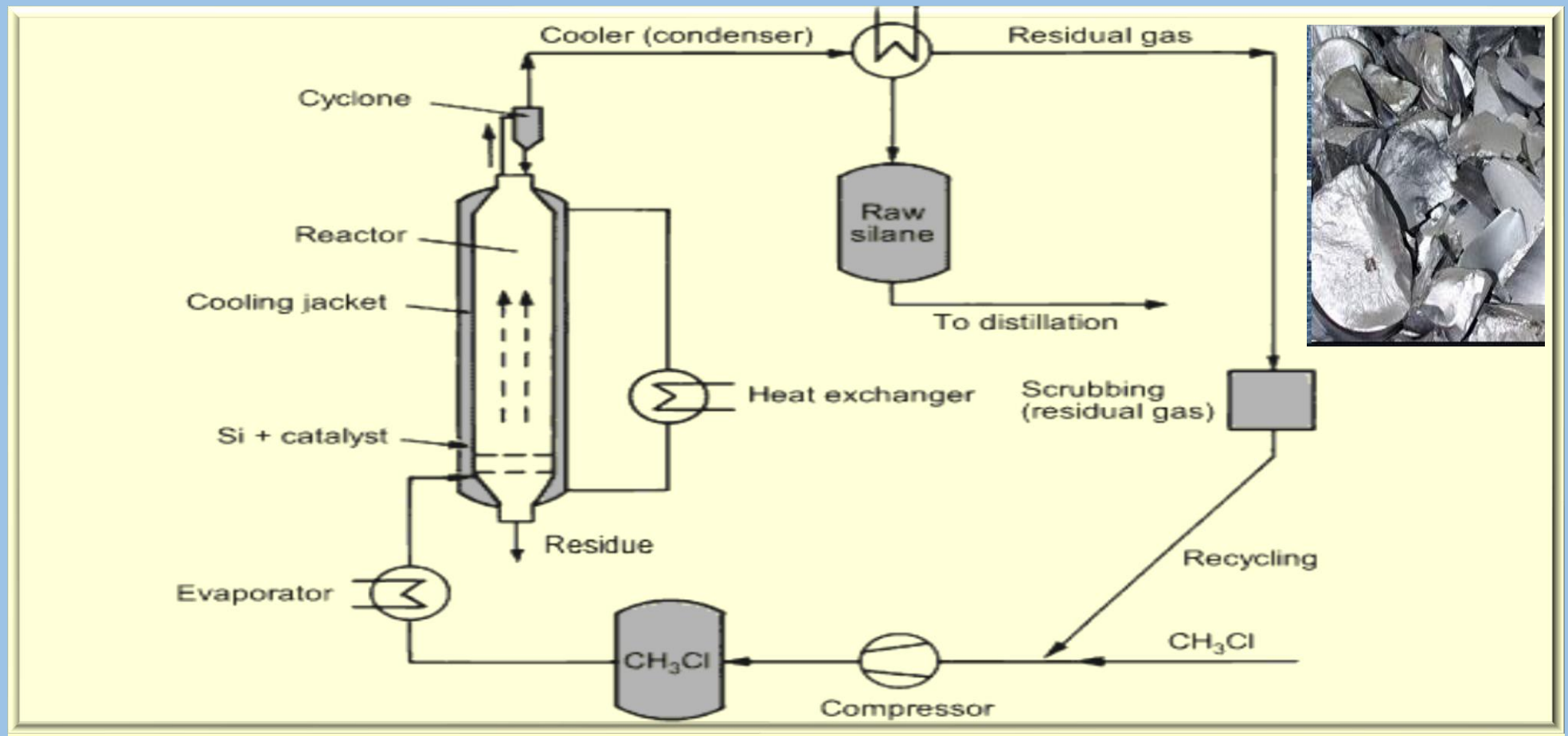
$$SiO_2\ (s) + 2C(s) \longrightarrow Si + 2CO_g$$

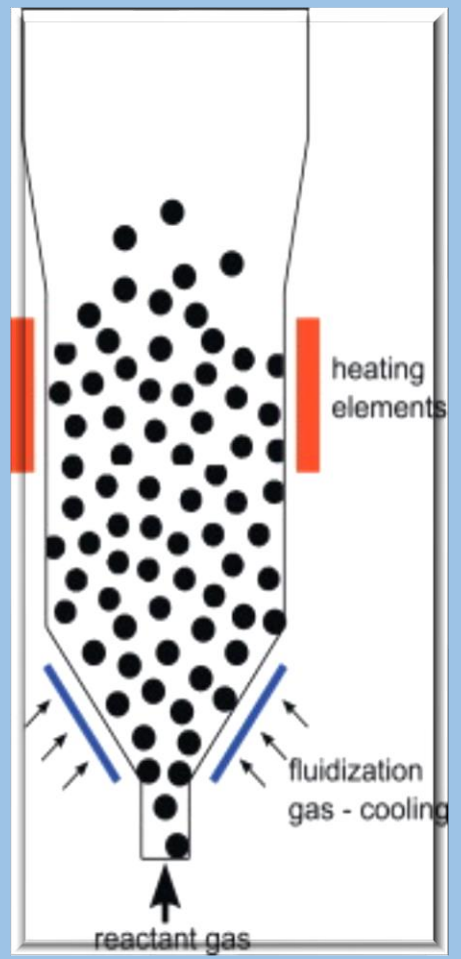
In the second steps the silicon was converted into chlorosilane , e.g $RSiCl_3$, R_2SiCl2, R_3SiCl
Where R is an organic groups .When chloromethane is passed through heated silicon at about 350^{0}C ,in the presence of catalyst (copper chloride) , a volatile mixture of chlorosilane distils over .for example :-

$$Si\ (s) + 2CH_3Cl\ (g) \longrightarrow (CH_3)_2SiCl_2$$



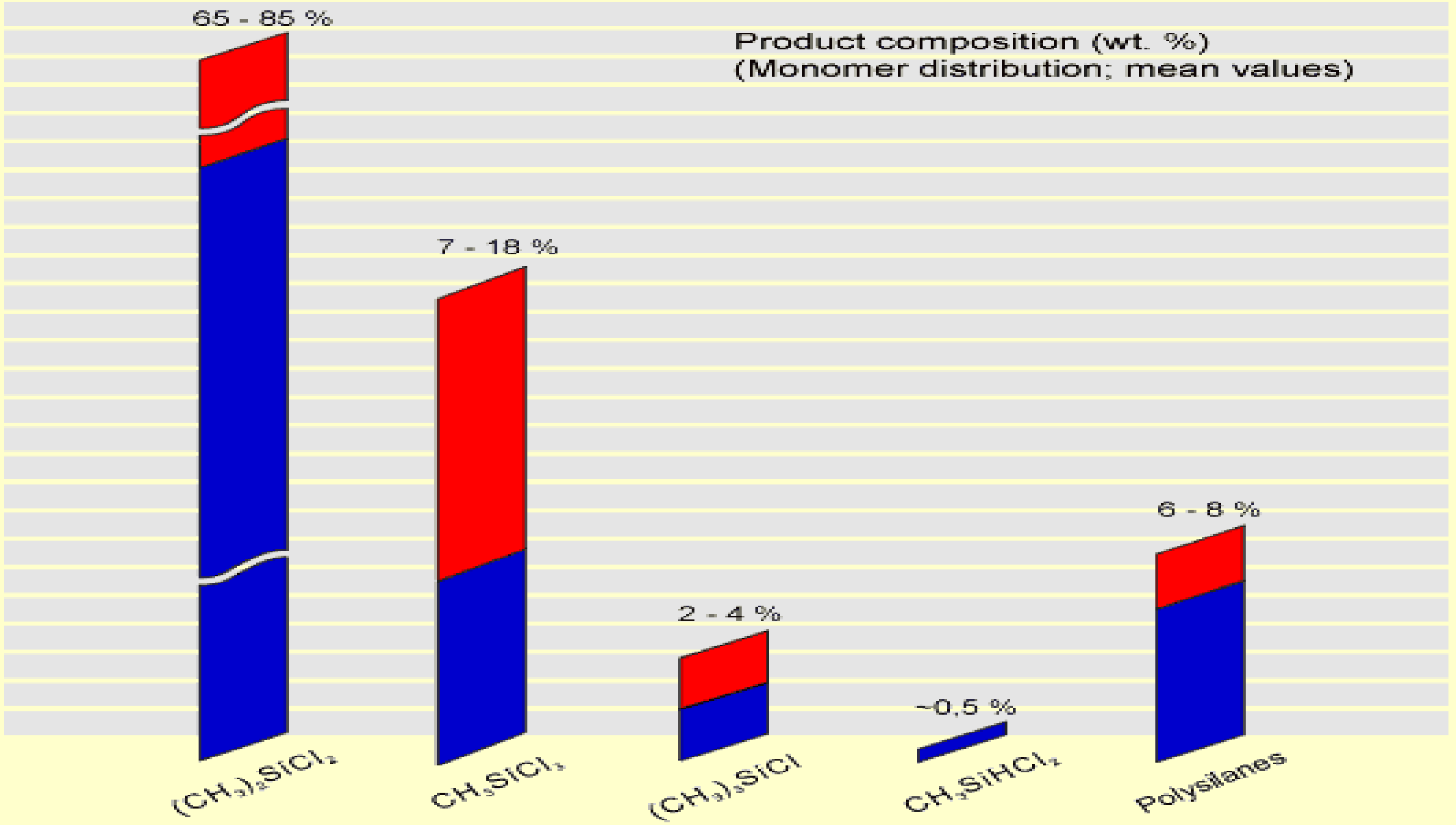
Flowsheet diagram of the synthesis of chlorosilanes





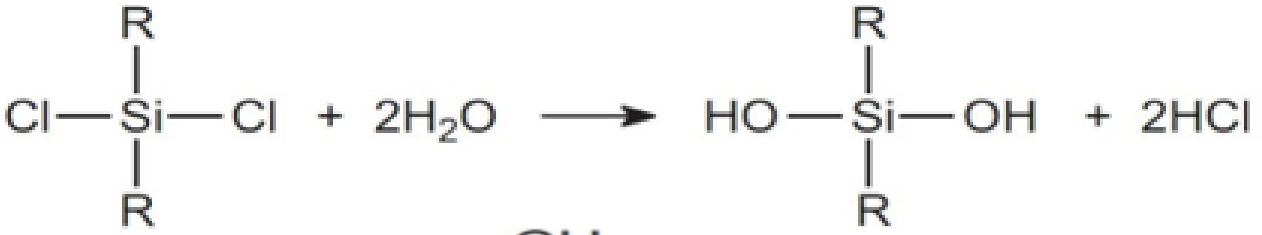
$$Si---Cu + CH_3Cl \longrightarrow -Si(CH_3)(Cl)---Cu- \longrightarrow CH_3-Si(Cl)-Cl + Cu--$$

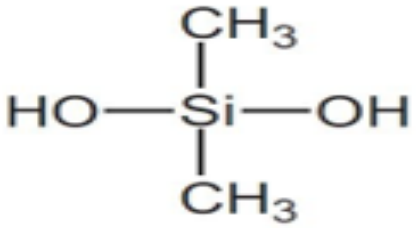
Fluidized bed reactors


Product composition (wt. %)
(Monomer distribution; mean values)
65 - 85 %
7 - 18 %
2 - 4 %
~0,5 %
6 - 8 %
(CH3)2SiCl2
CH3SiCl3
(CH3)3SiCl
CH3SiHCl2
Polysilanes

4-2- Hydrolysis of chloro silane

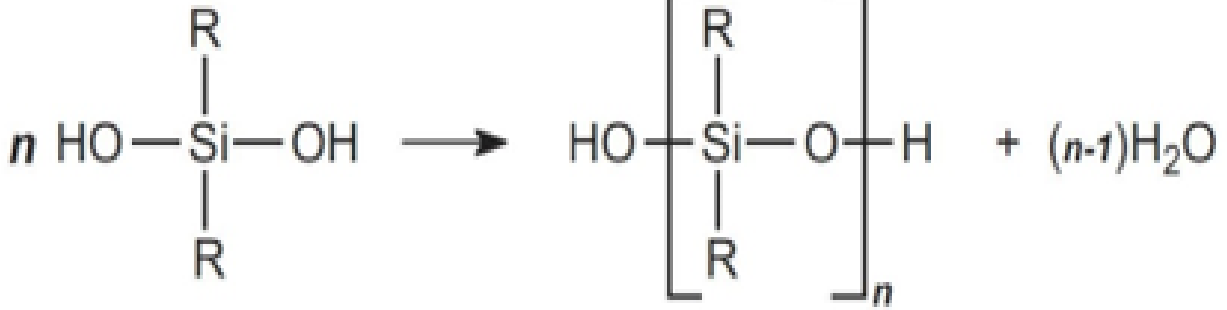
A dichloro dimethyl silane is hydrolysis to a molecule having two hydroxyl group (Silanol).



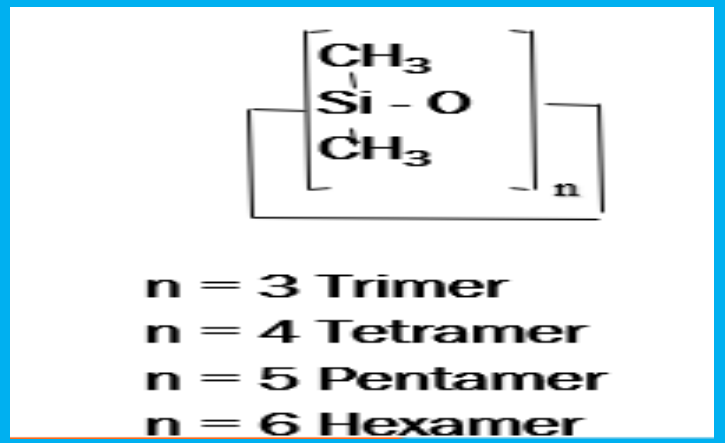


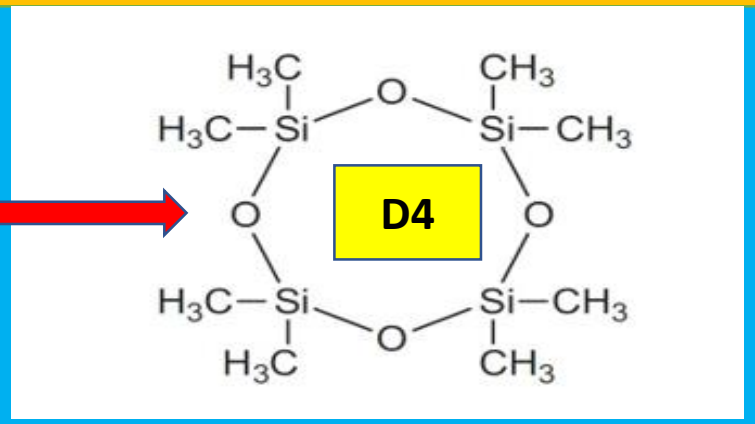
dimethyldisilanol

The hydroxyl groups of the silanol react spontaneously to form siloxane backbone.



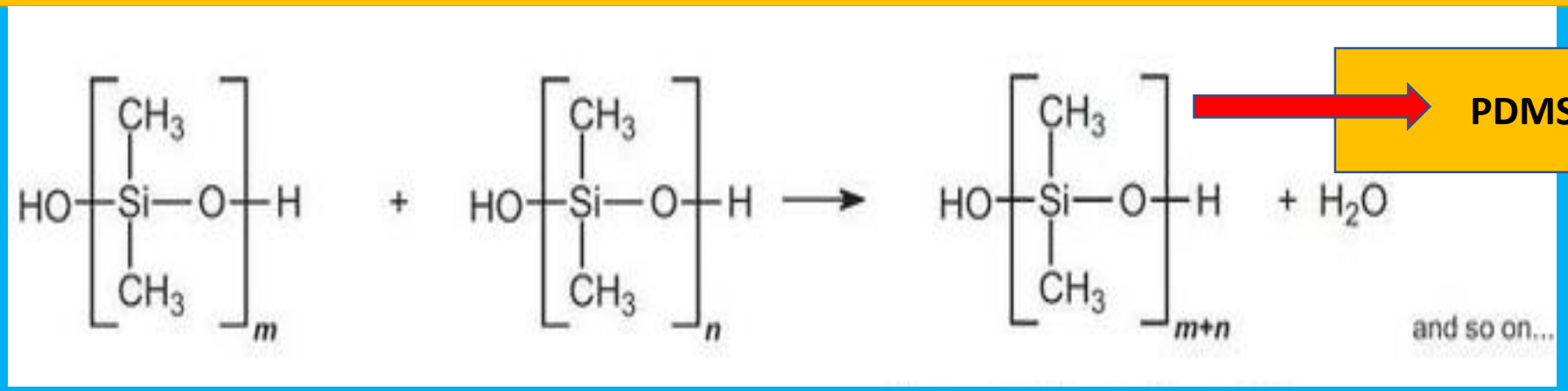
Low molecular weight cyclic polysiloxane are produced throughout the hydrolysis of chlorosilane and then separated.

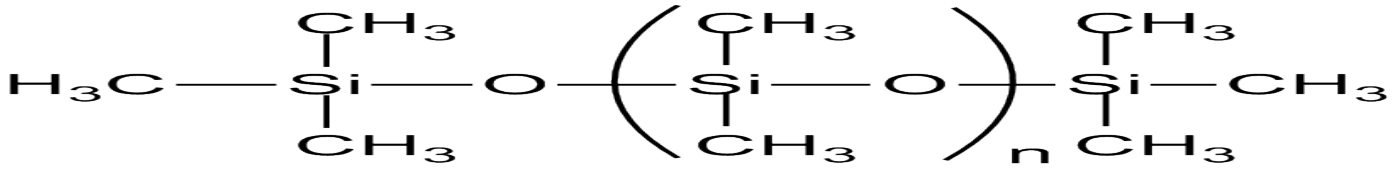




4-3- Condensation of silanols

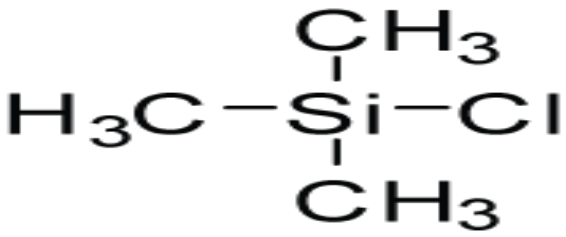
The oligomers condense rapidly in the presence of an acid catalyst to form long chain polymers





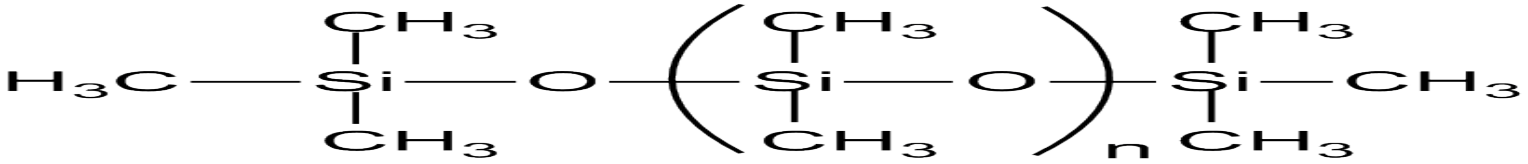
PDMS

Chain Stopper



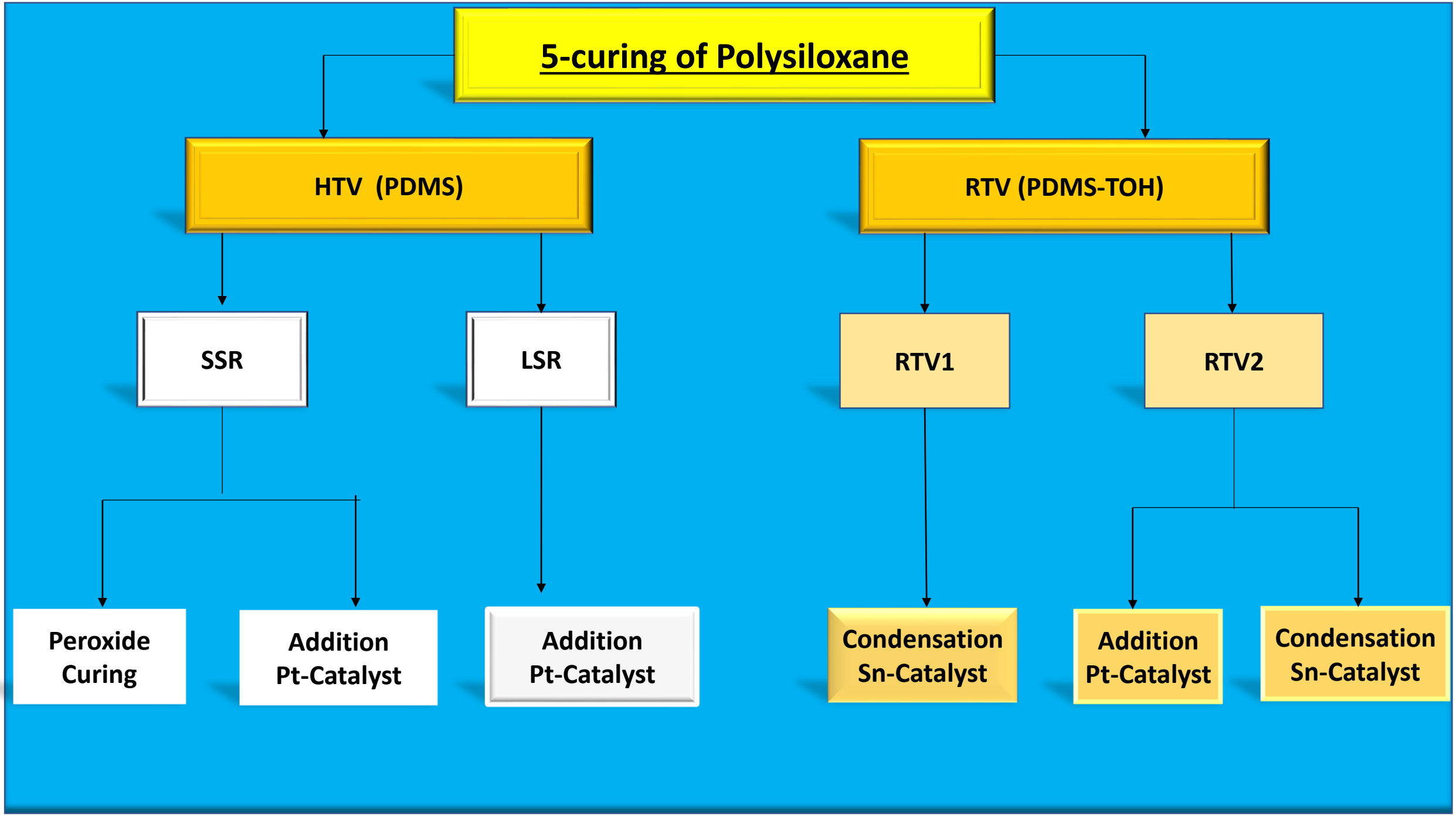
PDMS-TOH

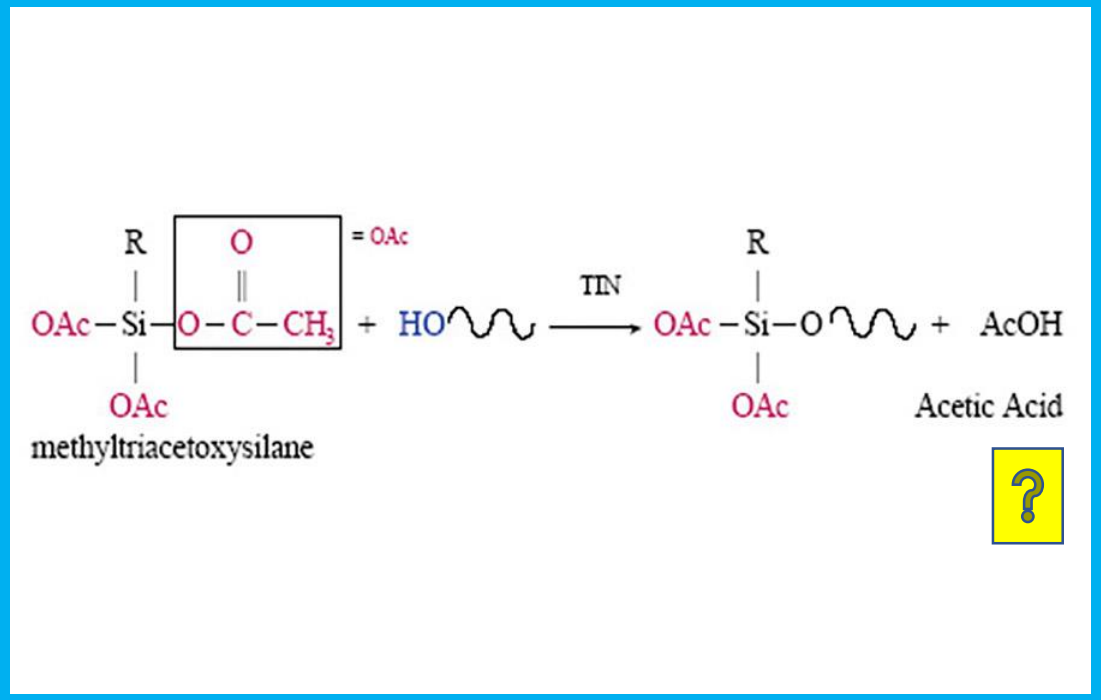
RTV

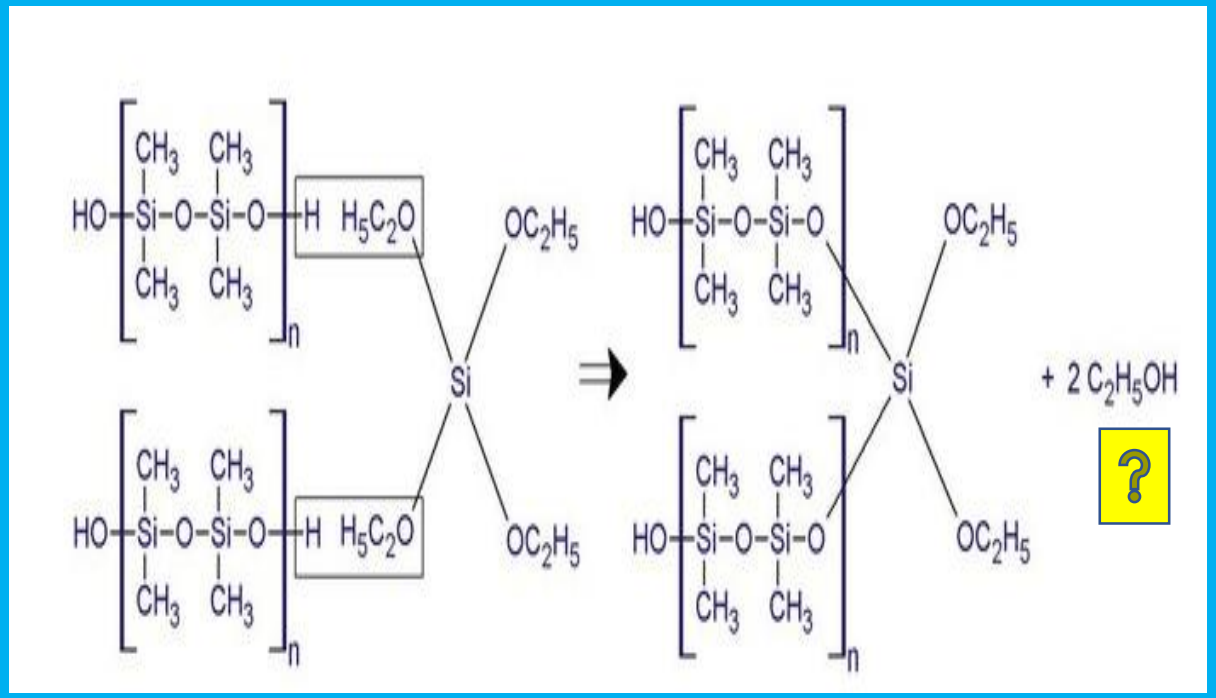


PDMS

HTV

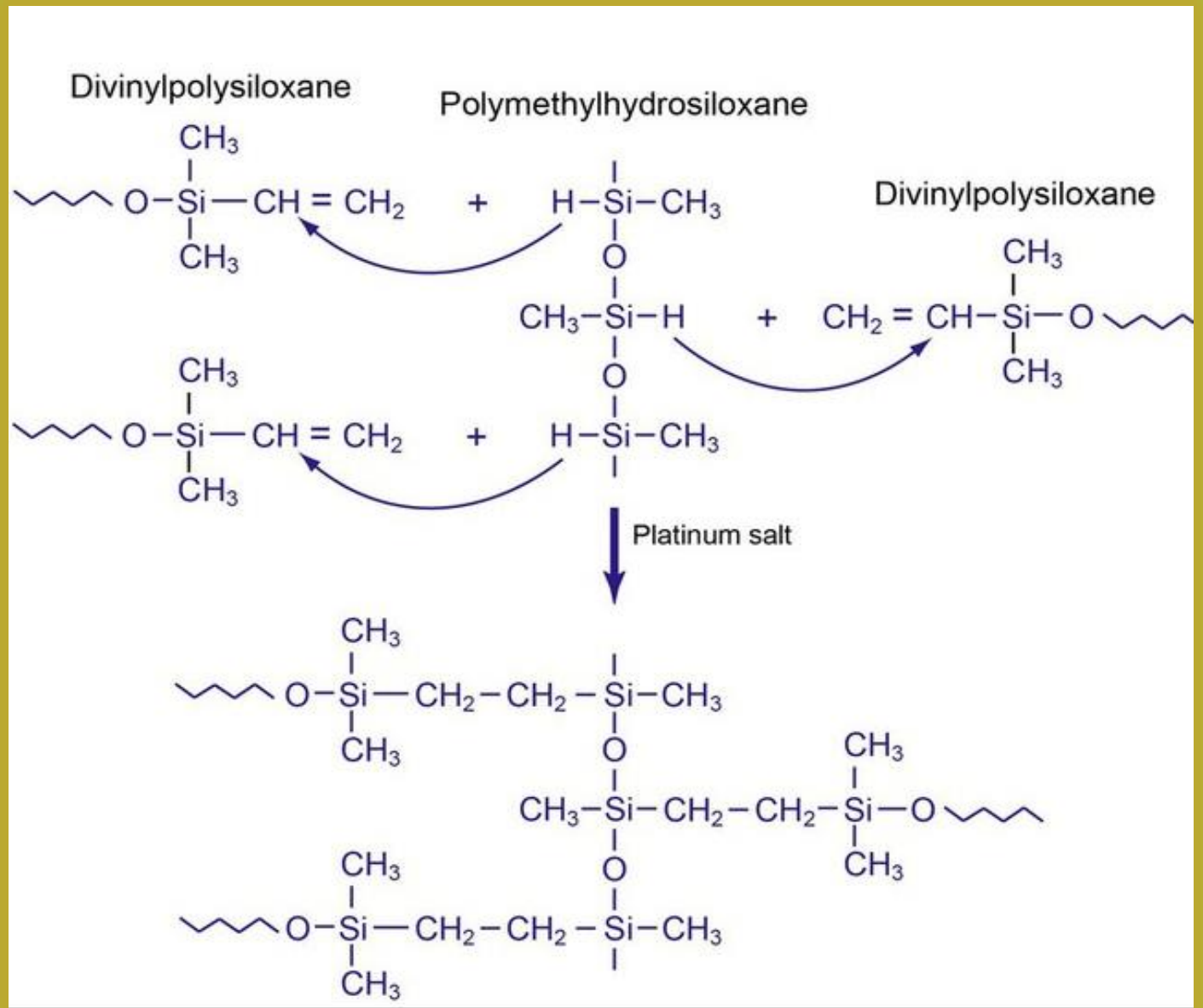

5-curing of Polysiloxane
HTV (PDMS)
RTV (PDMS-TOH)
SSR
LSR
RTV1
RTV2
Peroxide Curing
Addition Pt-Catalyst
Addition Pt-Catalyst
Condensation Sn-Catalyst
Addition Pt-Catalyst
Condensation Sn-Catalyst





RTV1-Mosture Cure Mechanism

RTV2-Condensation Cure Mechanism



RTV2-Addition Cure Mechanism

Properties of Siloxane

1-Flexibility.

2-Chemical inertness.

3-Permability to gases.

4-Water repellency.

5- Resistance to oxidation.

6-Thermal stability.

7-Low Glass transition temp.,Tg

8- Low surface energy .

Application of Siloxane Polymers

Non Medical Applications

Typical non medical applications include

----High –performance rubbers
-----Membrane
-----Electrical insulators
------Water repellency
------Antifoaming agents
------Adhesives
-----Mold-Release agents
------Protective coating
------Encapsulation media
-------Heat transfer fluids
----------Hydraulic fluids

Medical Applications

Midical applications as aresult of their inert nature ,stability and flexibility . include:-

----- Artificial organs
----- Facial reconstruction motifs
------ Vitreous substitutes
------ Tubing and Catheters
------ Contact lenses
------ Drug Delivery system.

Non Medical Applications/Industrial applications.

Silicone Fluide

Silicone fluids posses a variety of useful properties

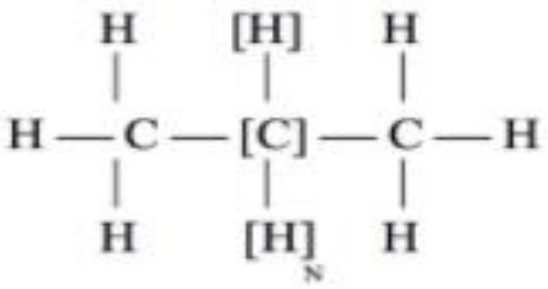
-- Thermal Stability.(150-300 C^0

--- High Hydrophobicity

----Dielectric properties.

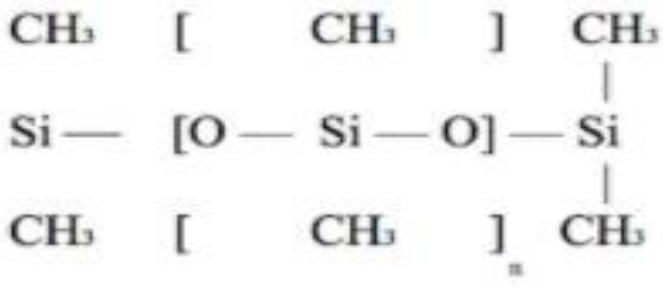
---Resistance to radiation.

Organic Fluid

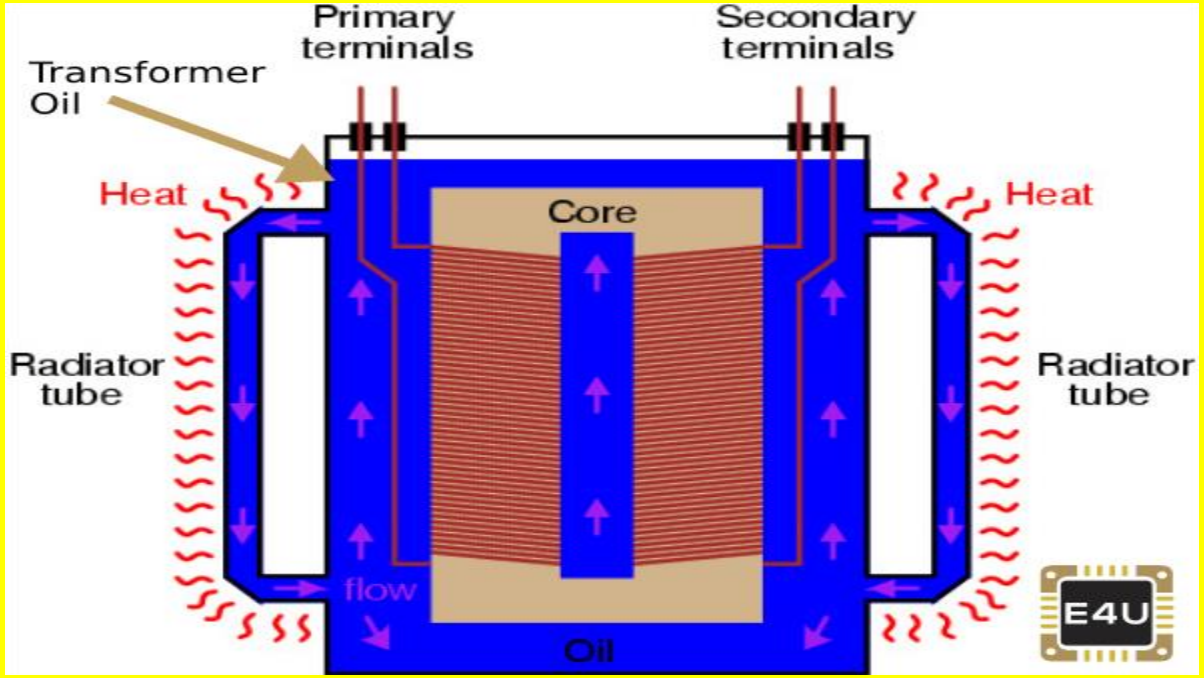


(Hydrocarbon Polymer)

Silicone Fluid



(Polydimethylsiloxane)



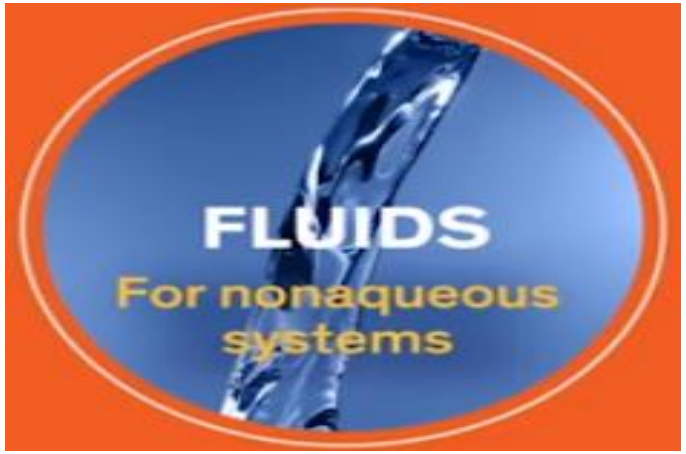
Silicone oil not biodegradable , it was <u>not –flammable</u> , the <u>price point</u> was good , it <u>has afire point</u> above 572 F (300^0) and <u>resist to oxidation</u>

Mineral Oil 3 mins

Mineral Oil 4 mins

Silicone Oil as antifoaming agents


MORE
PERSISTENT
LESS
REACTIVE
WHY
SILICONES
WIN
LOWER
SURFACE
TENSION
STABLE

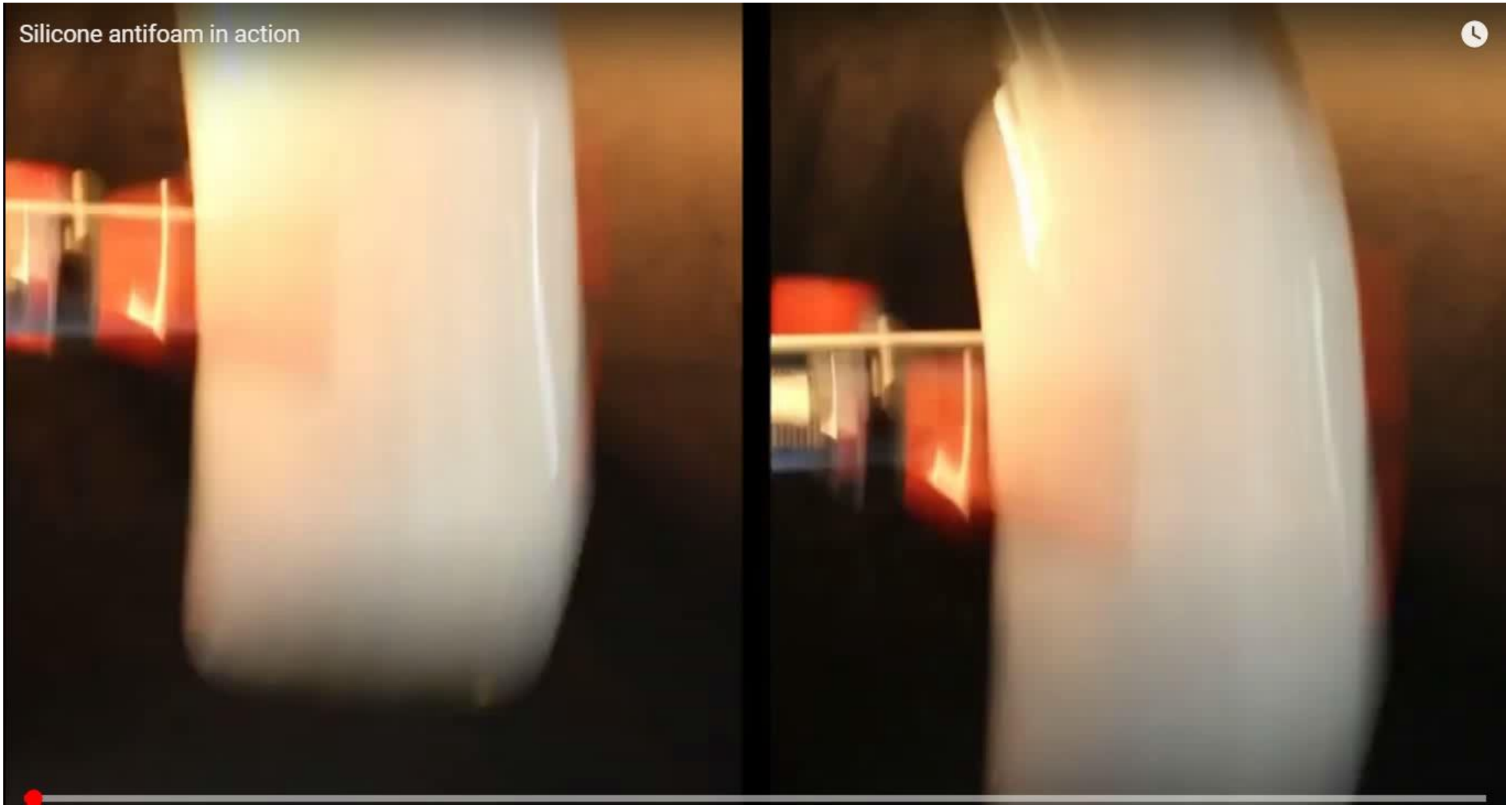

FLUIDS
For nonaqueous systems


COMPOUNDS
For nonaqueous systems


EMULSIONS
For aqueous systems


POWDERS
For use in dry products


DISPERSIONS
For oil and gas applications


Silicone antifoam in action

Used of silicoes in PU Productions

Silicone Release Agents

Silicone Rubbers

Silicone Damping Materials

Insulator for noise damping in disk break

Silicone rubber sheet for gasket

Silicone rubber tubes

Shock absorber silicones

Silicone as Electrical Insulators

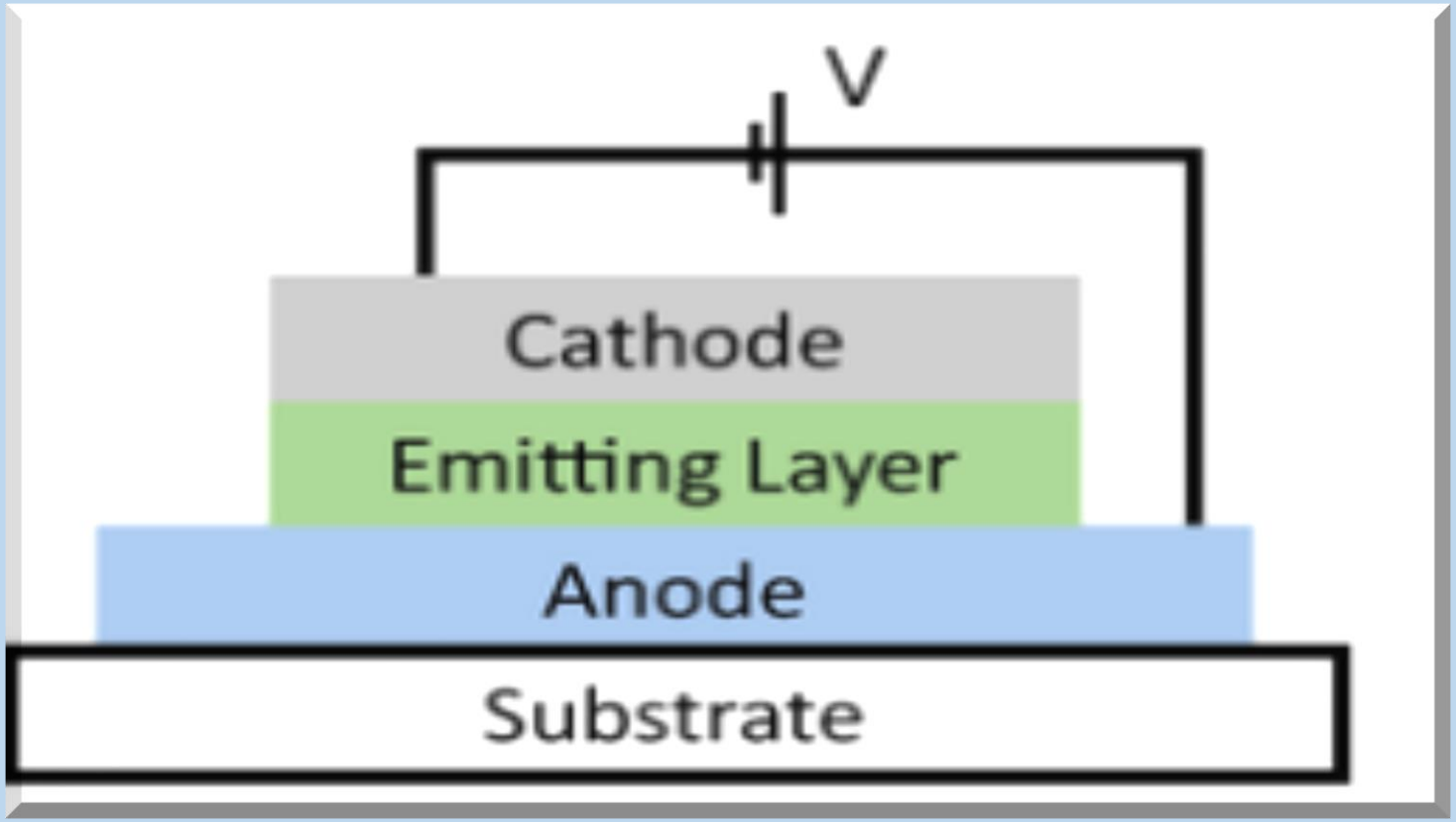
the bonding energy of Si-O bonds is 444 kJ/mol versus only 348 kJ/mol for C-C bonds. Shortwave sunlight at 300 nm has an energy content of about 6.2×10^{-22} kJ (i.e. 398 kJ/mol) and can therefore cleave C-C bonds but not the Si-O bond that remains stable.

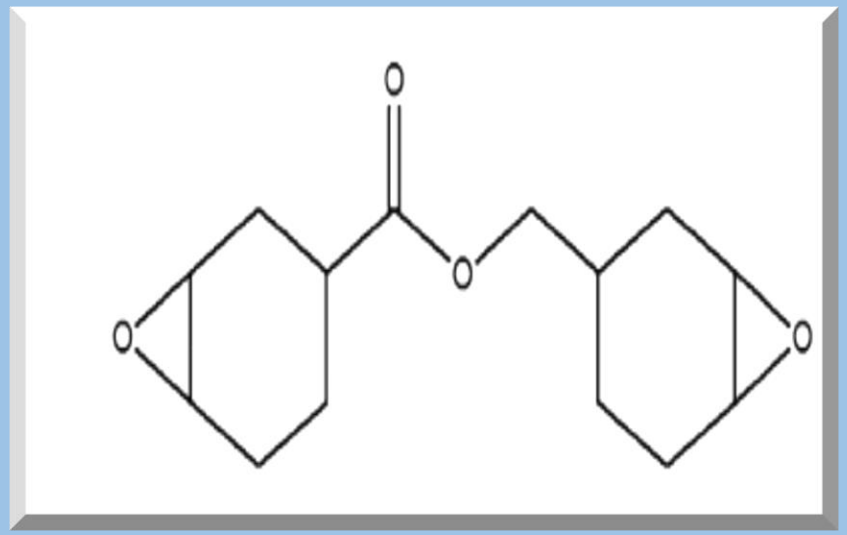
RTV-coated line insulators

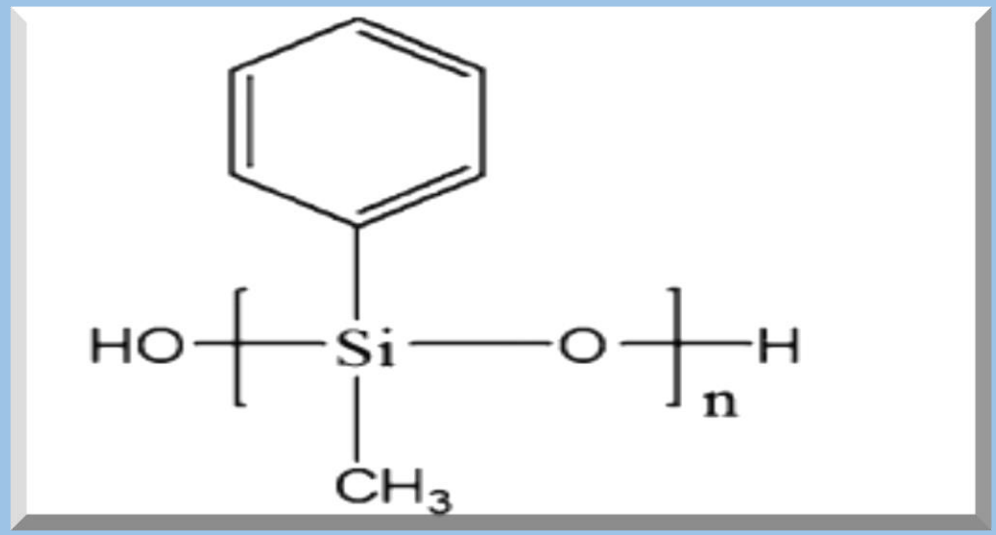
Composite polymer insulator silicon rubber .Tensile strength:40 to120kn. Polymer insulator. Silicone rubber insulator. Range. Of composite insulators:. 10kv to 220kv suspension insulators, pin insulators, post insulators, crossarm insulators. 220kv to 400kv.

Heat Resistant Wire 600V Silicone, Rubber Insulated Glass Braided Cable

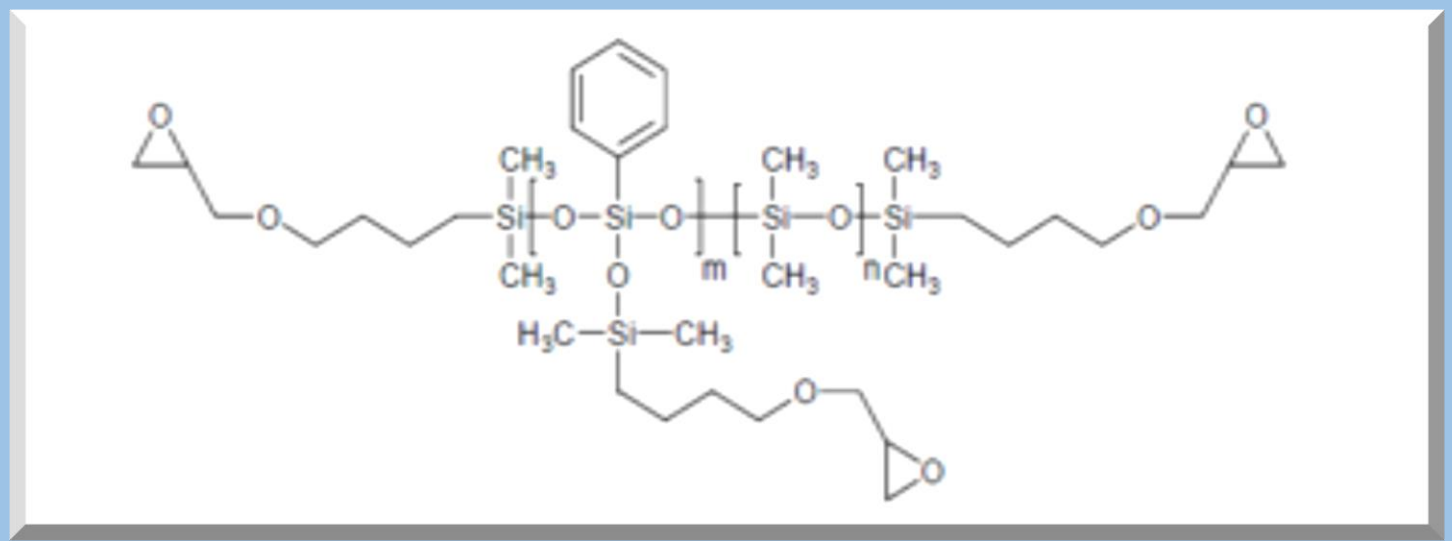
Use of siloxane polymers in capsulated LED

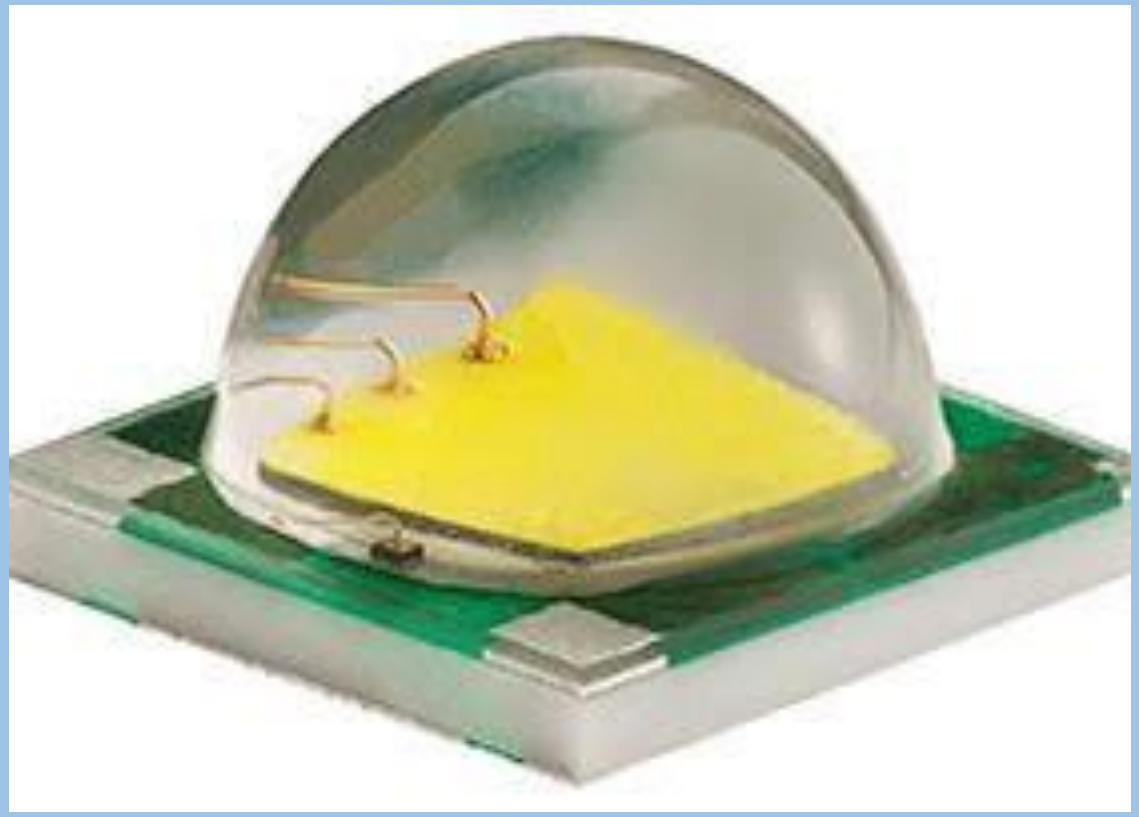






Cycloaliphatic epoxy resin was modified by phenyl methyl silicone resin to investigate the influence of silicone content on the performance and reliability of epoxy packaged light-emitting diode

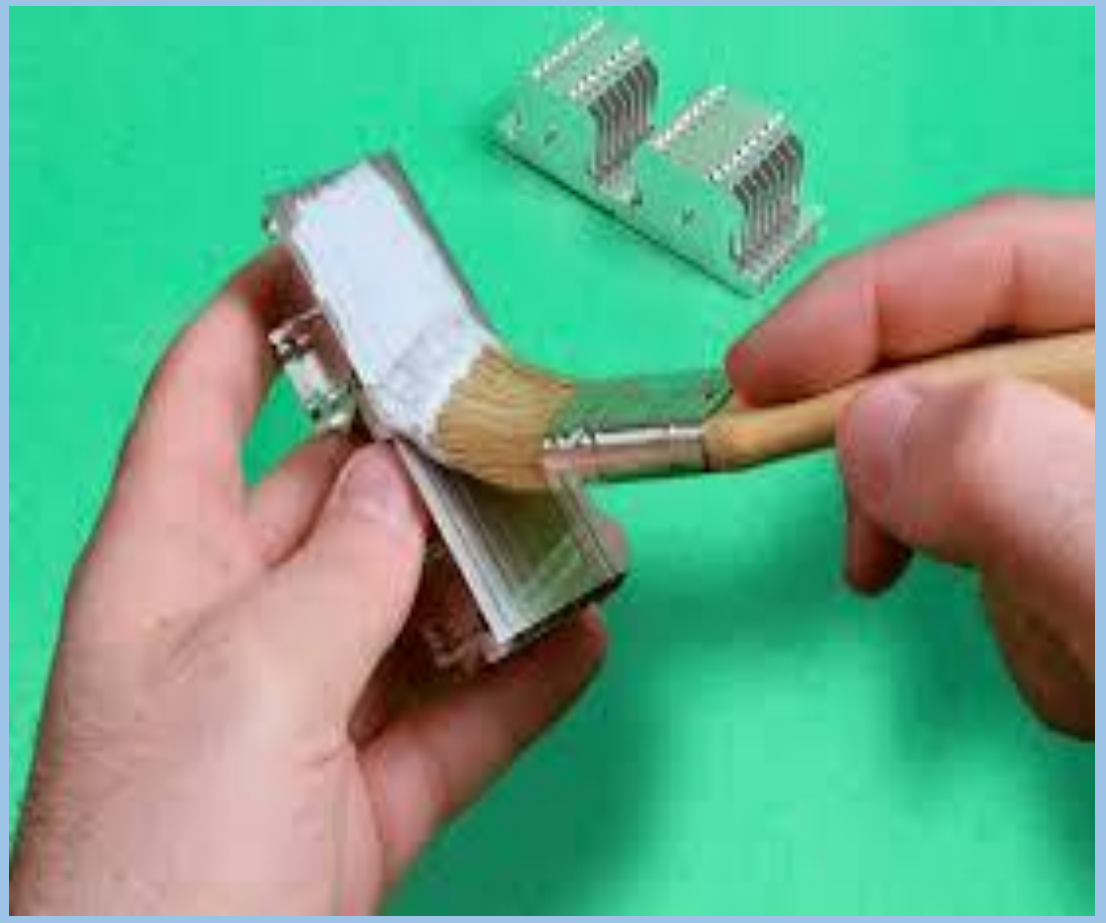




Siloxane polymers gives better transmittance ,Refractive index and thermal stability

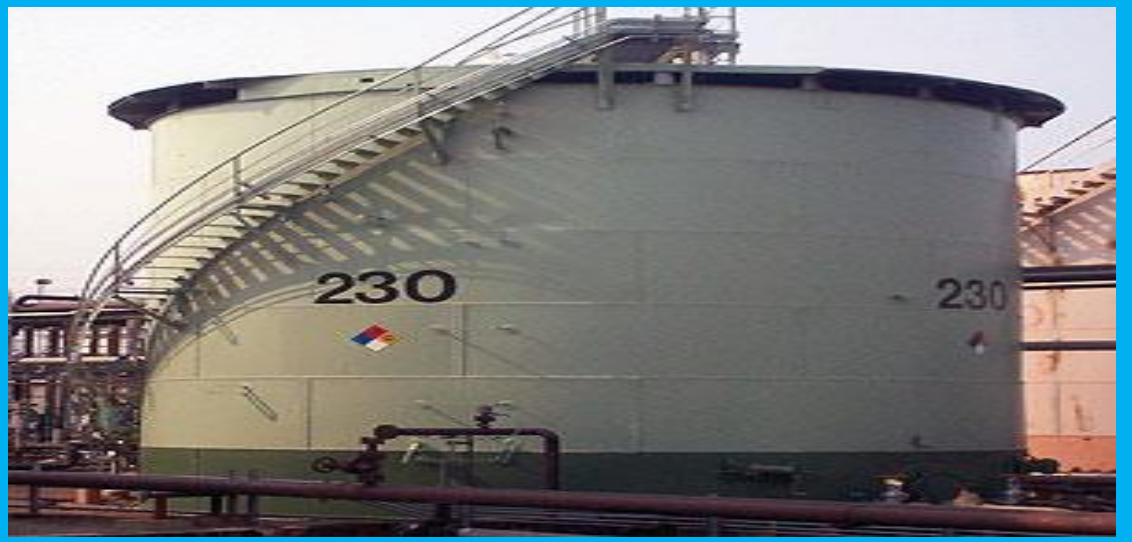
Silicone as Coating

Silicone Coating is a solvent-based, single component, moisture cure, high solids, silicone roof coating. Containers are filled with dry nitrogen gas to prevent premature cure.



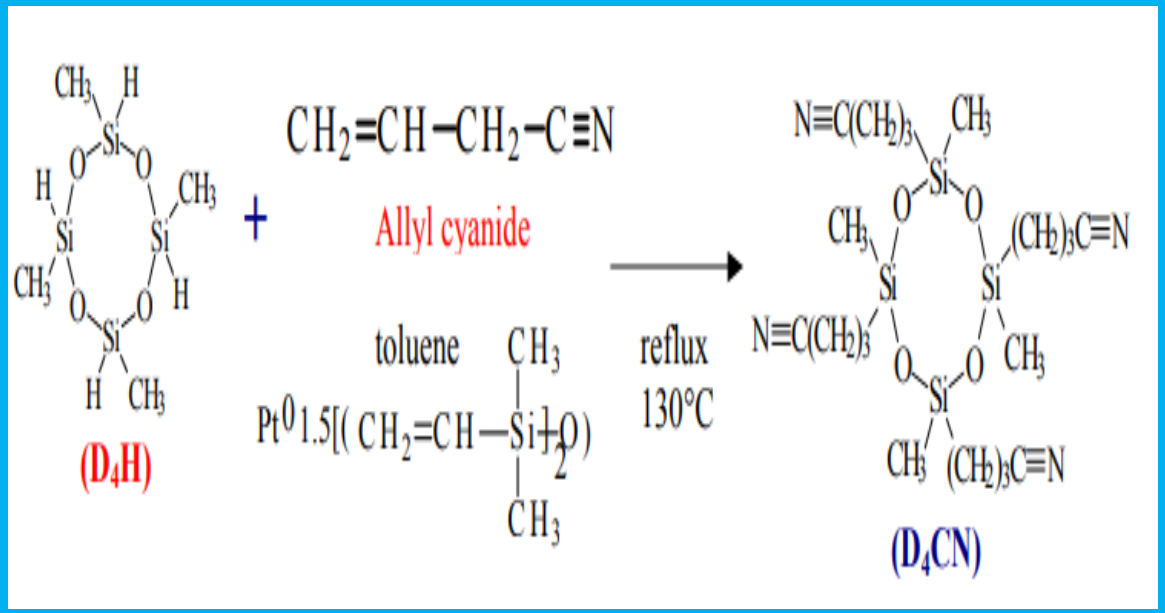
One component, non-corrosive silicone for bonding, sealing & coating.
Key Futures : Thermally conductive, Electrically Isolating
Room Temp.Curing and Servicable from -65F to 400F

Silicone containing trifluoro groups



Silicone containing a pendent cyano groups

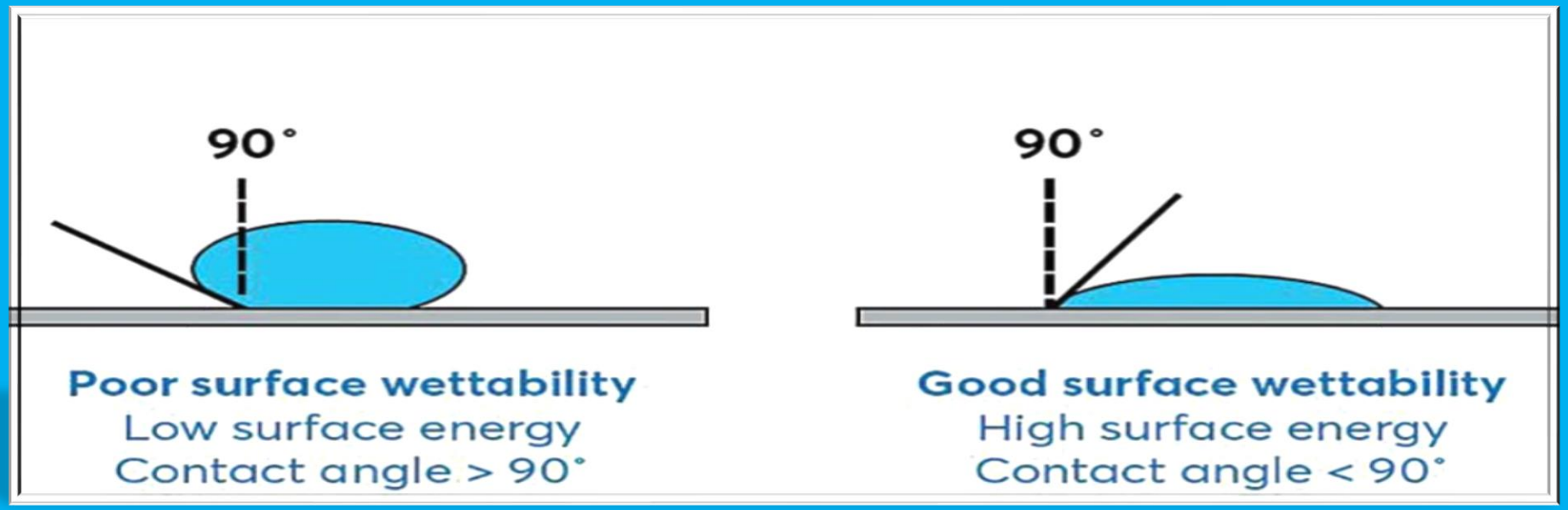
Silicone containing trifluoro groups

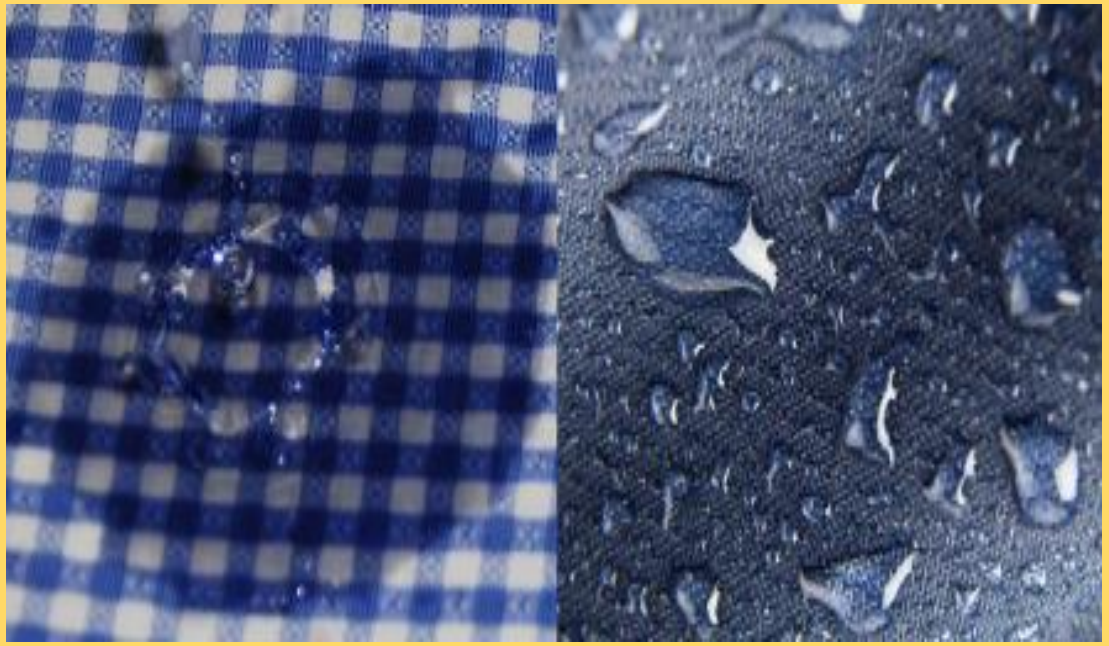


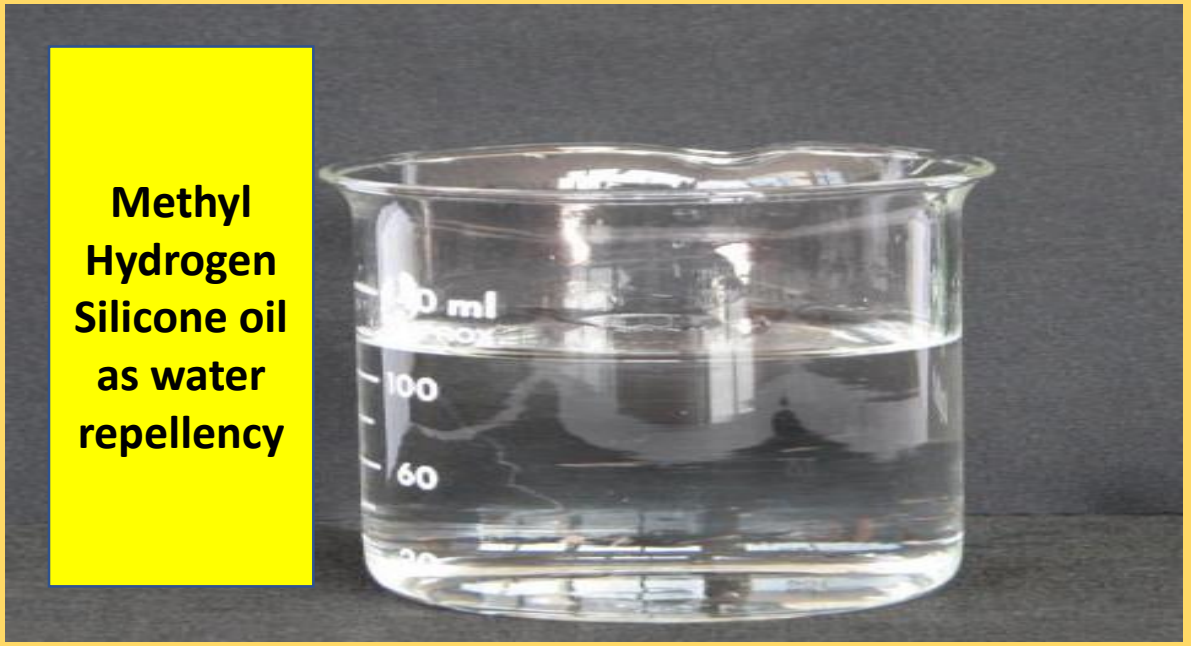
Silicone as Water Repellency

Water-resistant: able to resist the penetration of water to some degree but not entirely. Water-repellent: not easily penetrated by water, especially as a result of being treated for such a purpose with a surface coati

methyl hydrogen siloxane polymer with low viscosity , there for this polymers used as coating materials






Methyl Hydrogen Silicone oil as water repellency
100
60

Use some types of silicone resin water repellency with concerete

RTV-silicone mobile covers

(Left)23 years of use exposure to pullitions against retained sample kept at room temp.(right) .

use of structural glazing silicone adhesive

Medical Applications

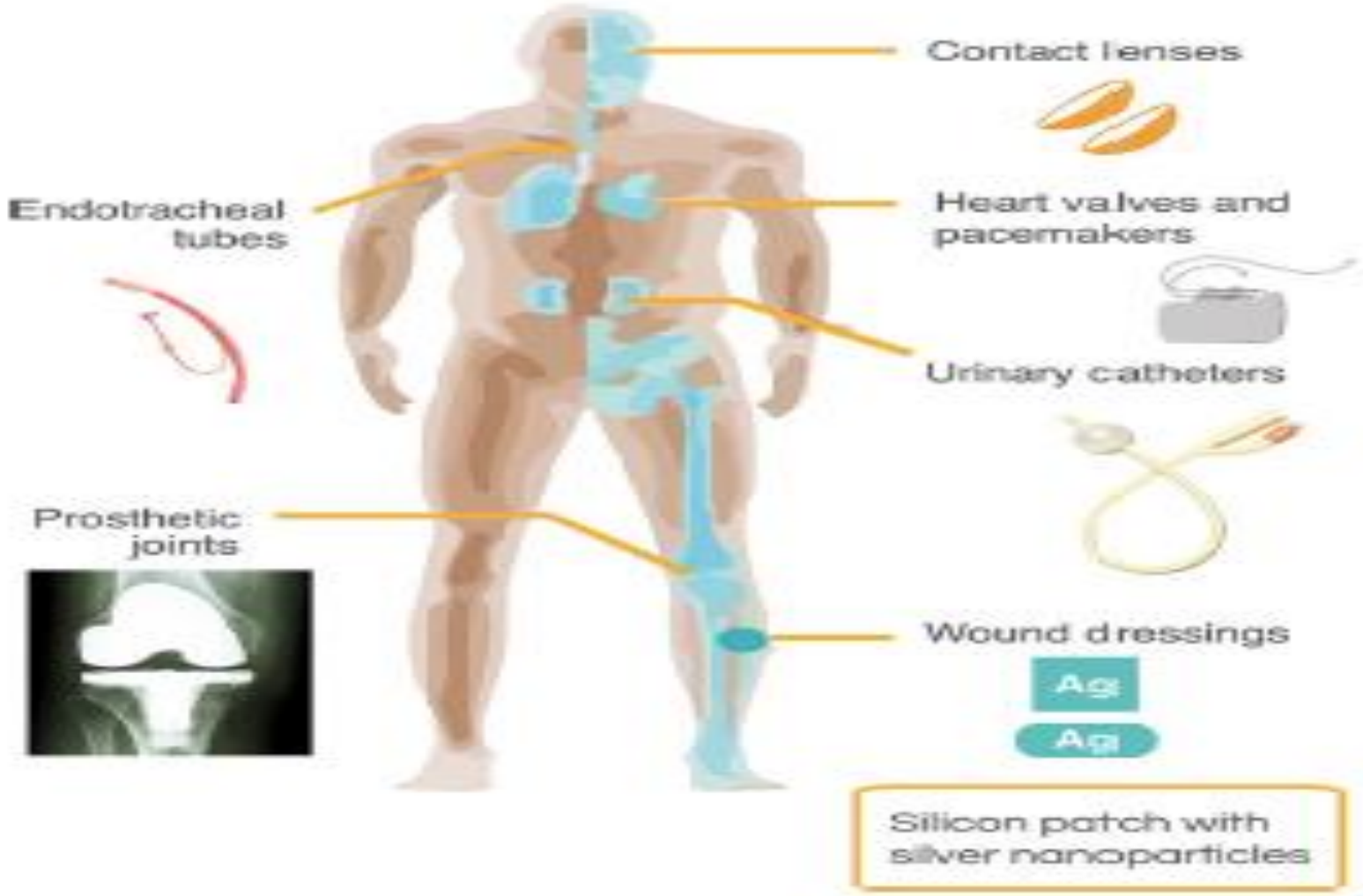
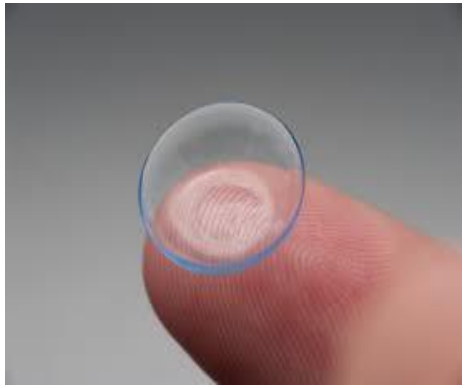
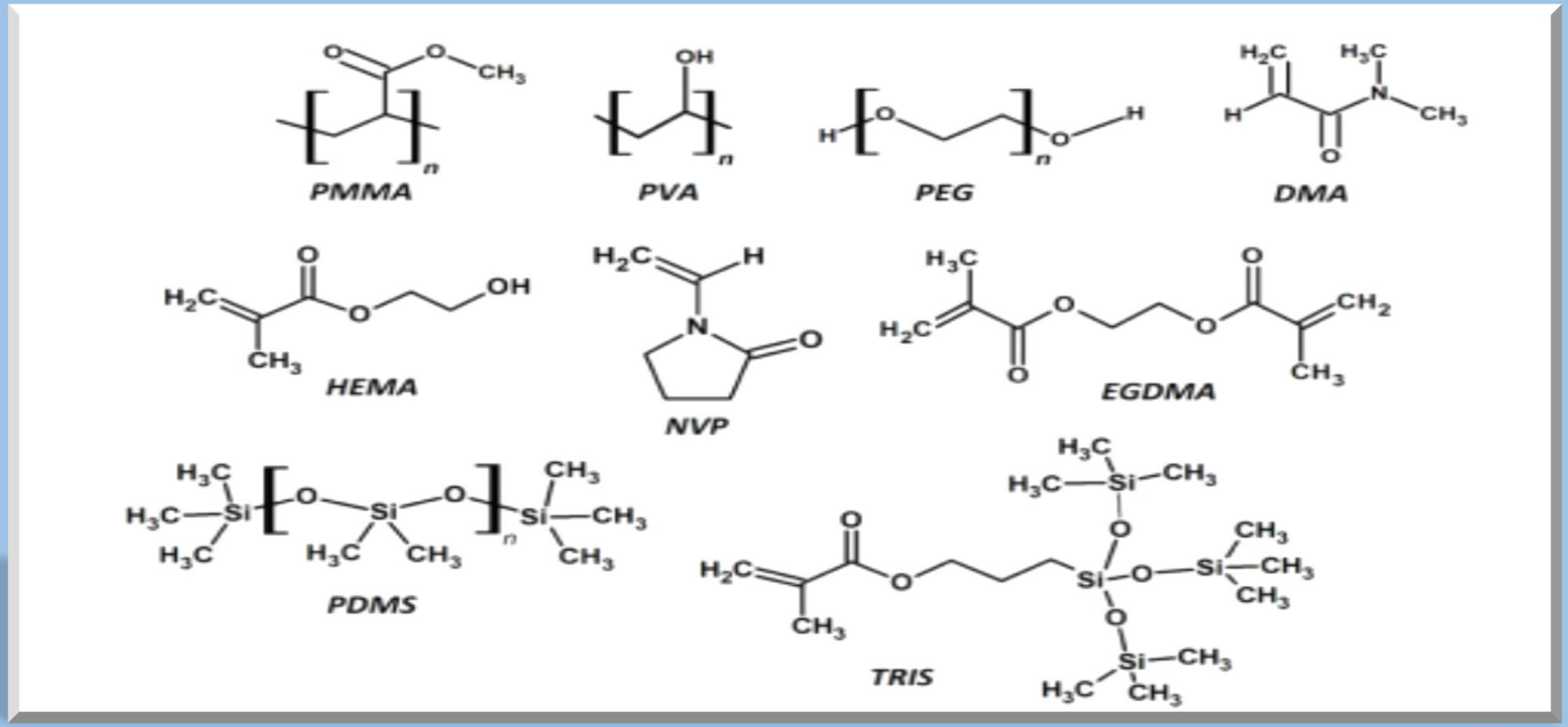


Fig. 10 Illustrative scheme of several silicon-based biomedical implants and devices

Contact Lenses



Contact Lenses



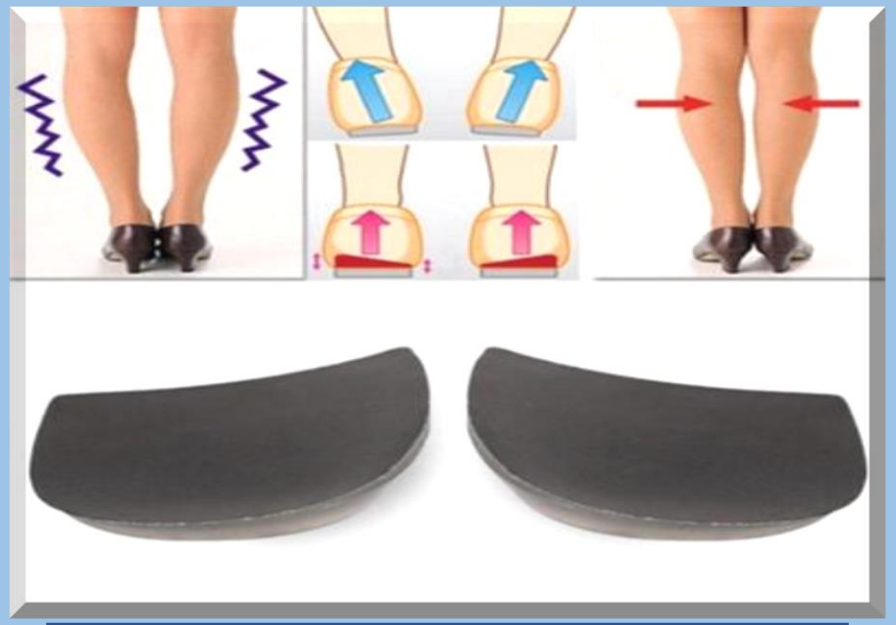
The chemical structures of common monomers and polymers used to produce CLs.

Orthopedic Application of Silicones

The most significant orthopedic applications of silicones are the hands and foot joint implants

Photograph and X-ray of arthritic right hand

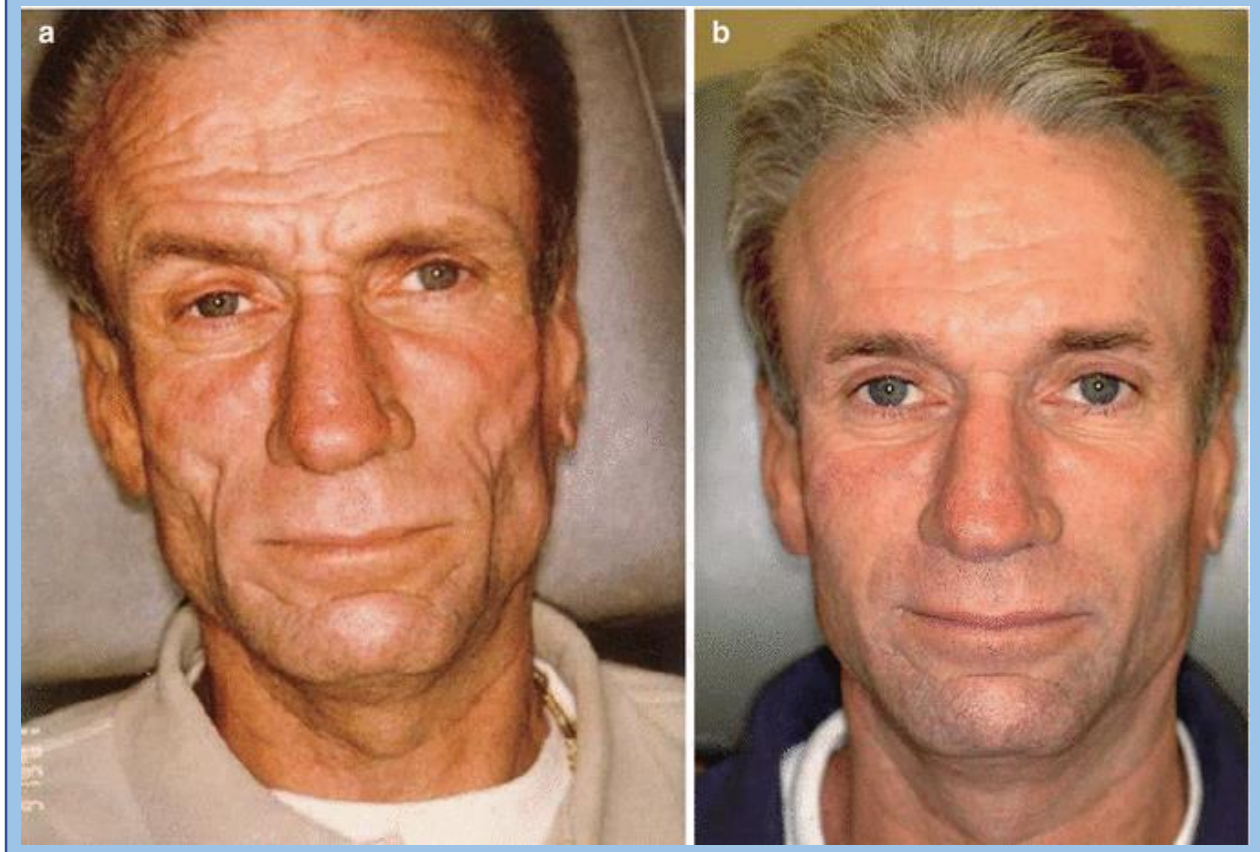
Toe corrector



Orthopedic silicone correction core

Orthopedic silicone Correctors

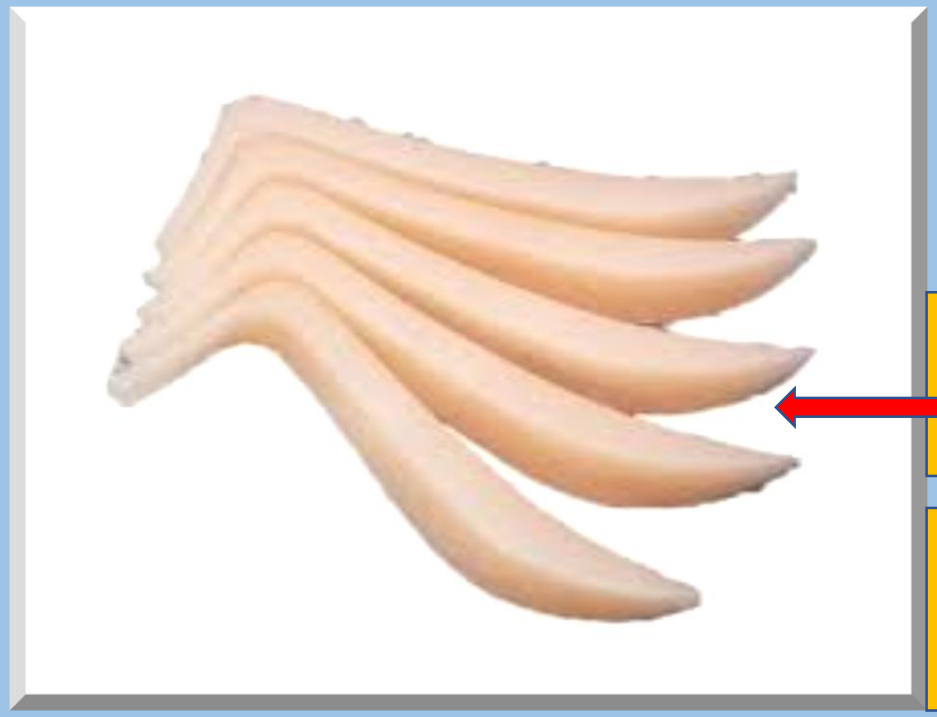
Orthopedic Bunion Correction



Liquid injectable silicone , PDMS gel is slightly crosslinking with silca or without silica , some times use other fillers

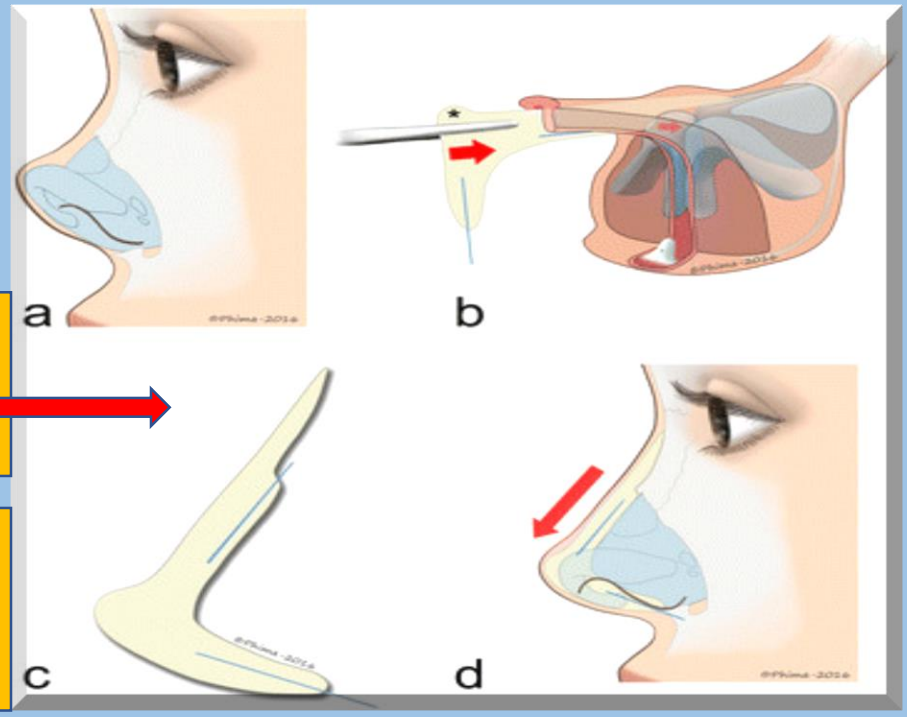
Medical gel silicone to make fake breast

Body parts silicone rubber



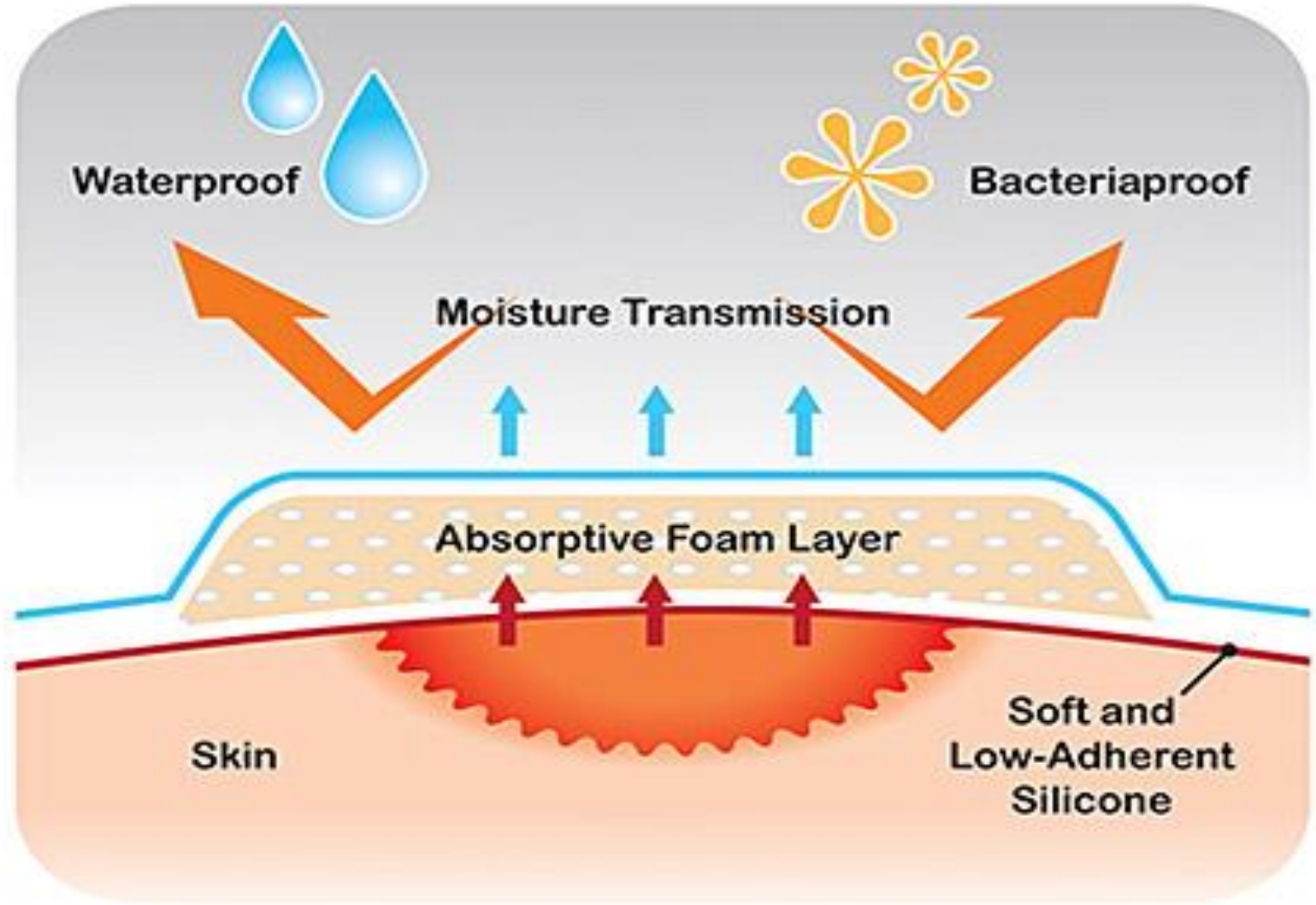
Orthopedic silicone surgical nasal implants

polyvinyl siloxane: novel material for external nasal



Orthopedic silicone heel protectors

Silicone wound dressing



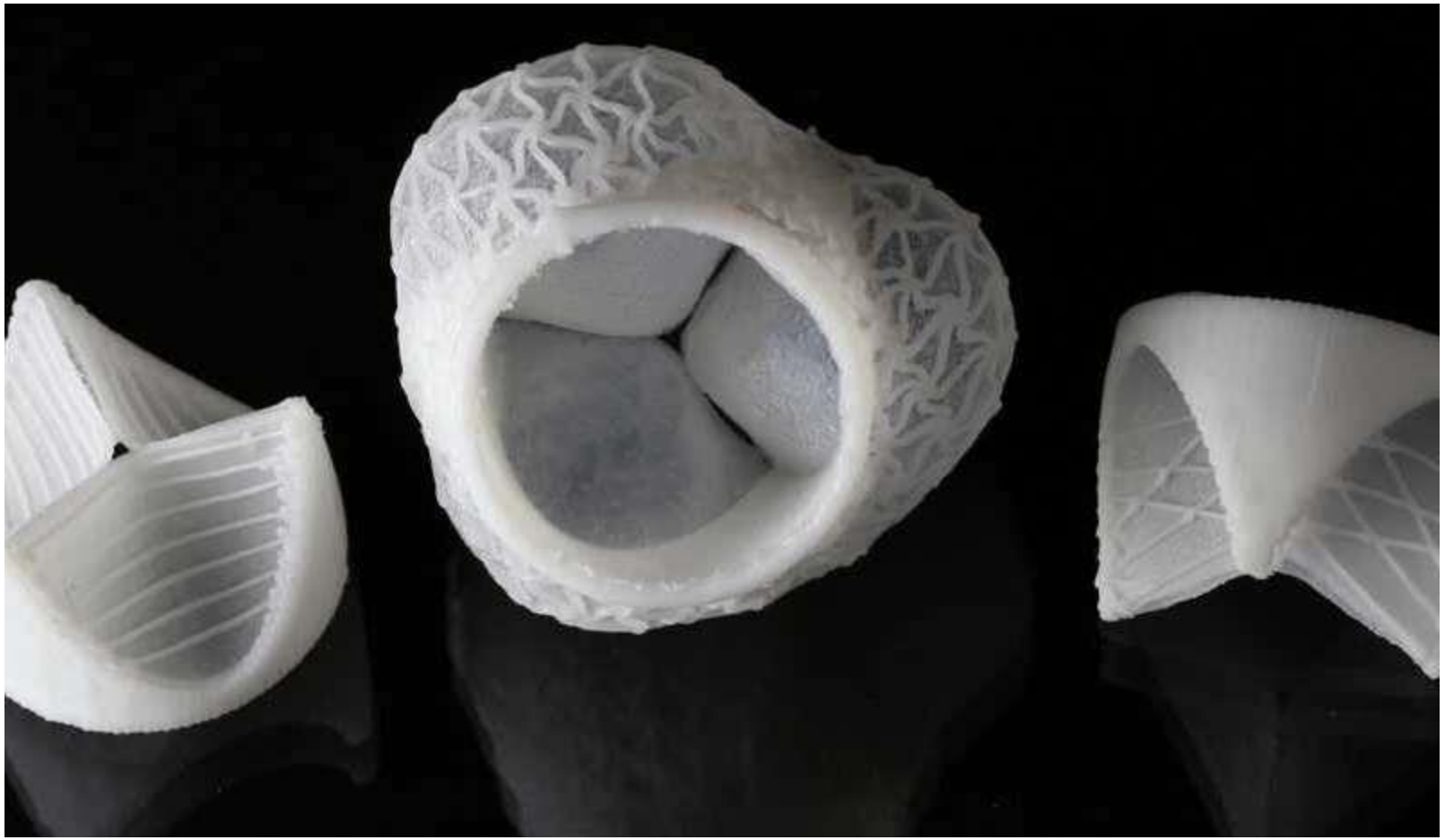
华卫®
HUAWEI

Sterile Silicone Foam Wound Dressing Silicone Gel Adhesive for Burn Wounds

Medical Silicone Gel Dressing for Wound Care to Promote Wound Healing

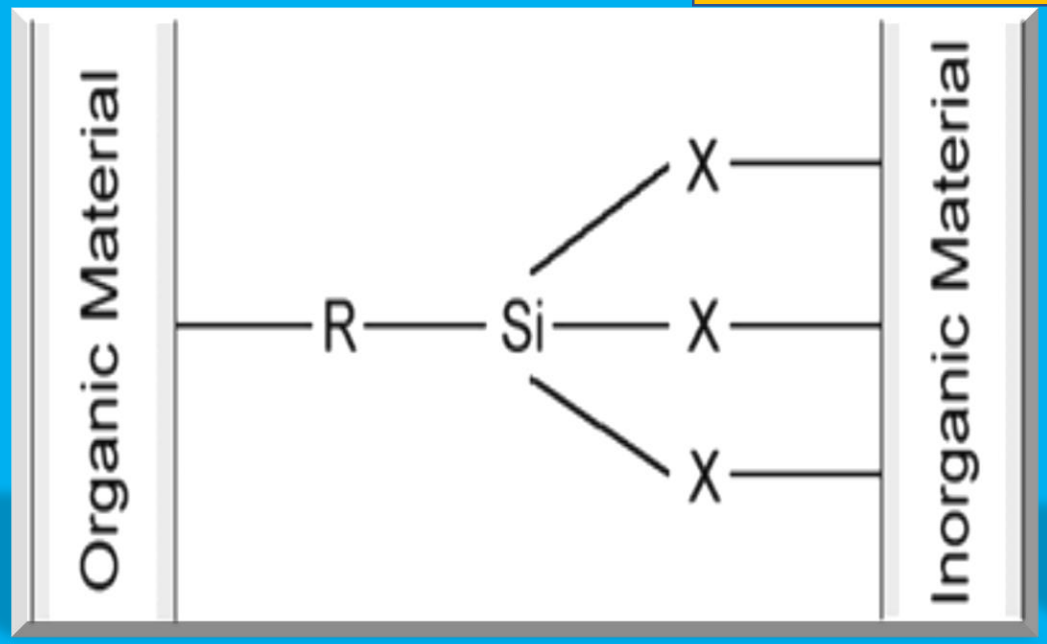
New siloxane Polymer Successfully Smooths Wrinkles,

silicon heart valves

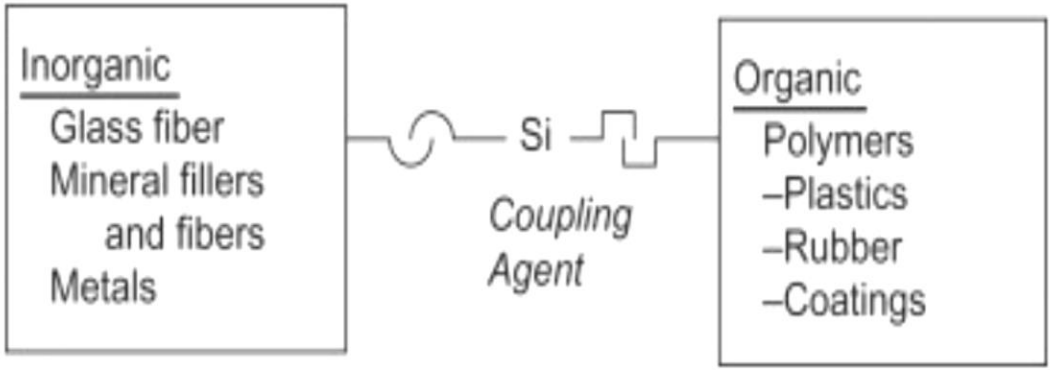


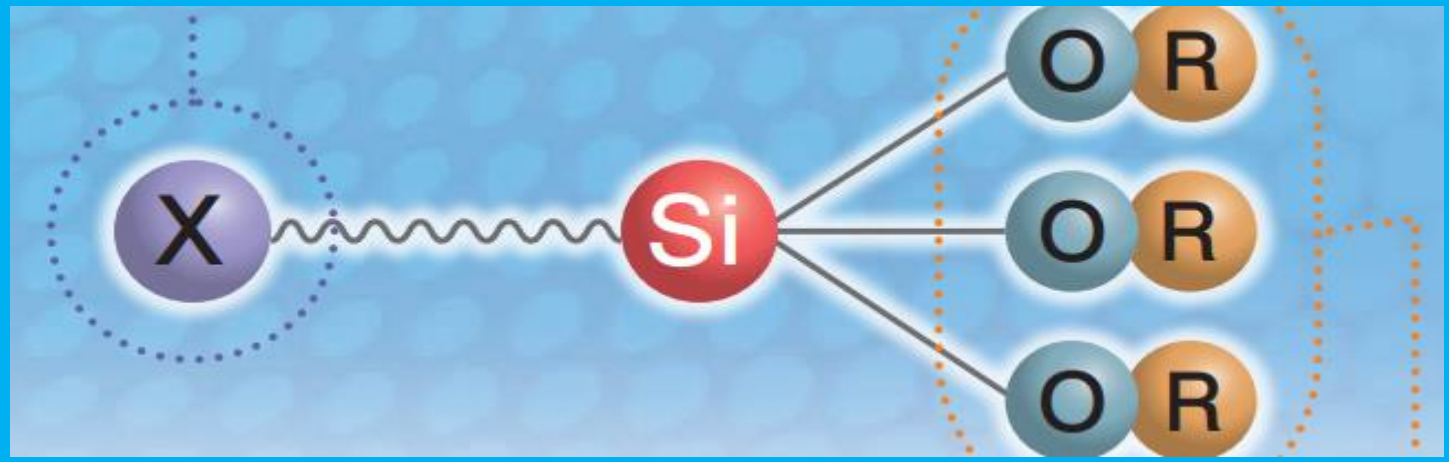
3-D printed custom silicon heart valves

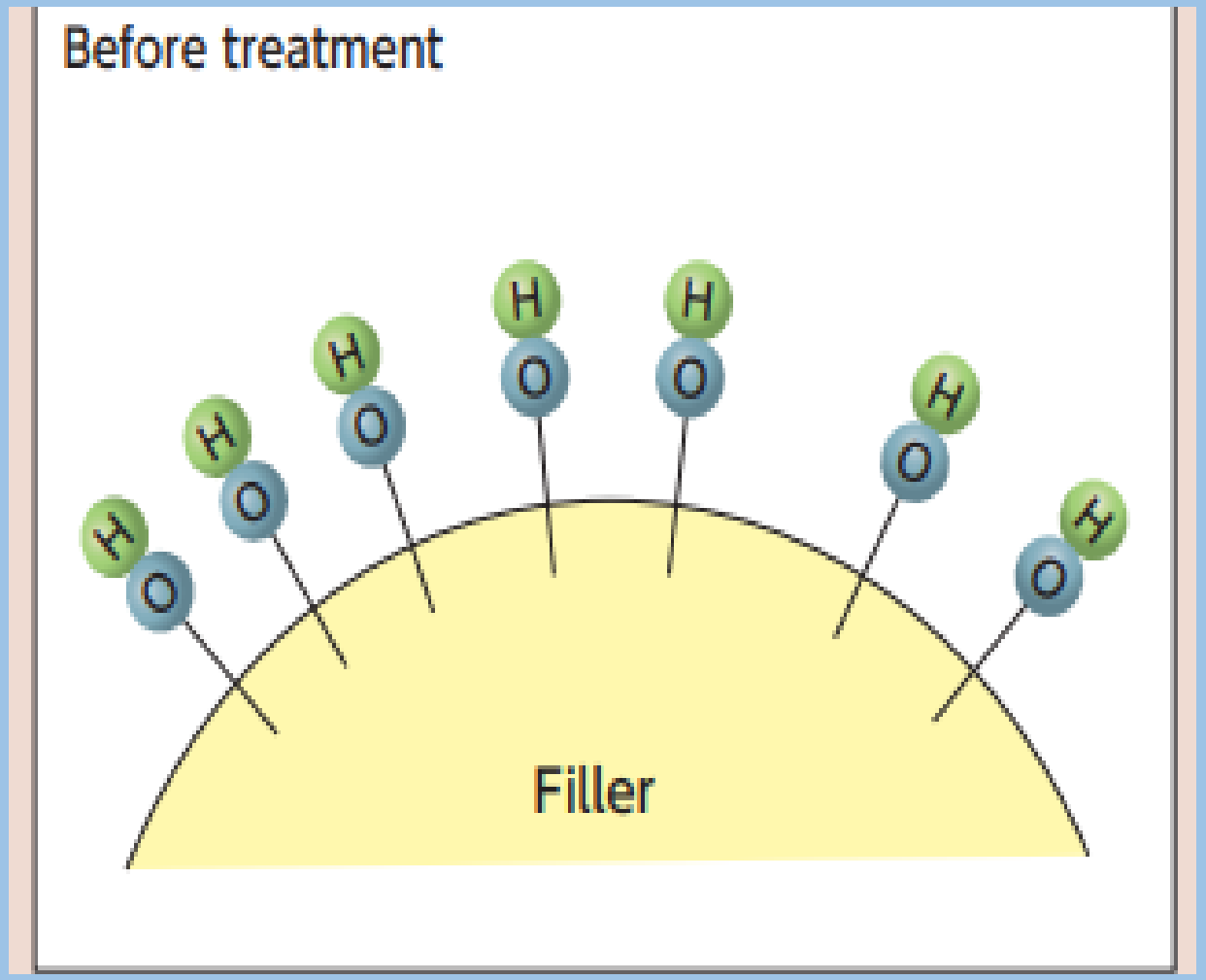
Silane coupling agents

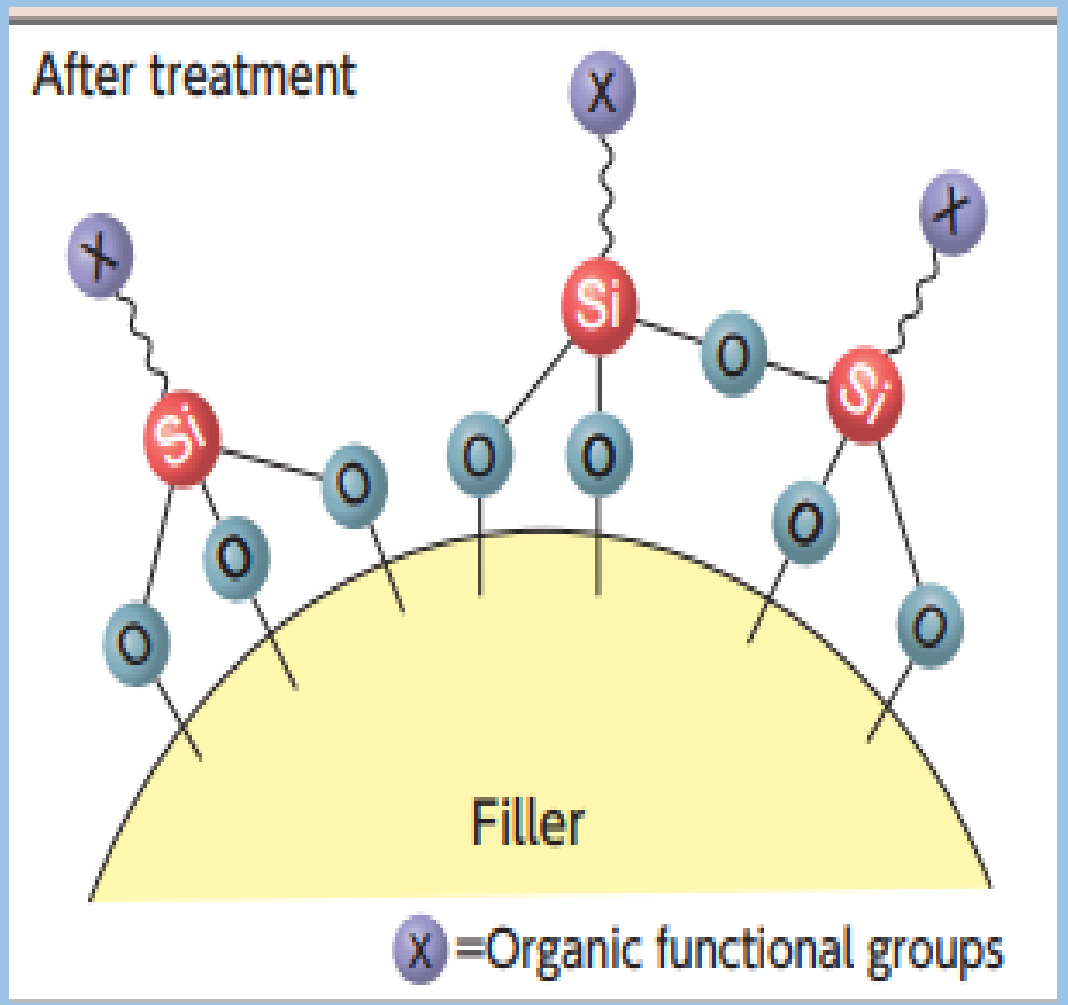


- Improve adhesion through dual reactivity
  - Alkoxysilane–inorganic reactivity
  - Organic group – reactivity and compatibility





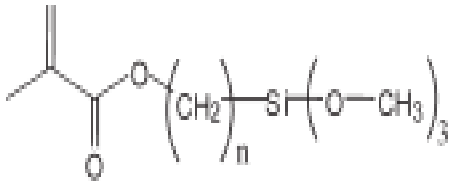

Before treatment
H
O
Filler


After treatment
X
Si
O
Filler
X =Organic functional groups

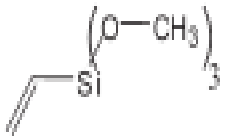
Functional Organotrialkoxysilanes (silane coupling agents)

amino silane

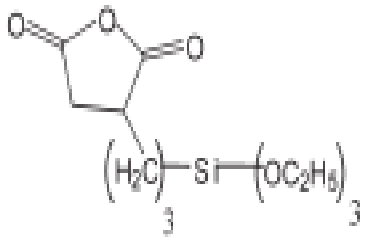
oxirane silane



MPTMS n = 3
MDTMS n = 10

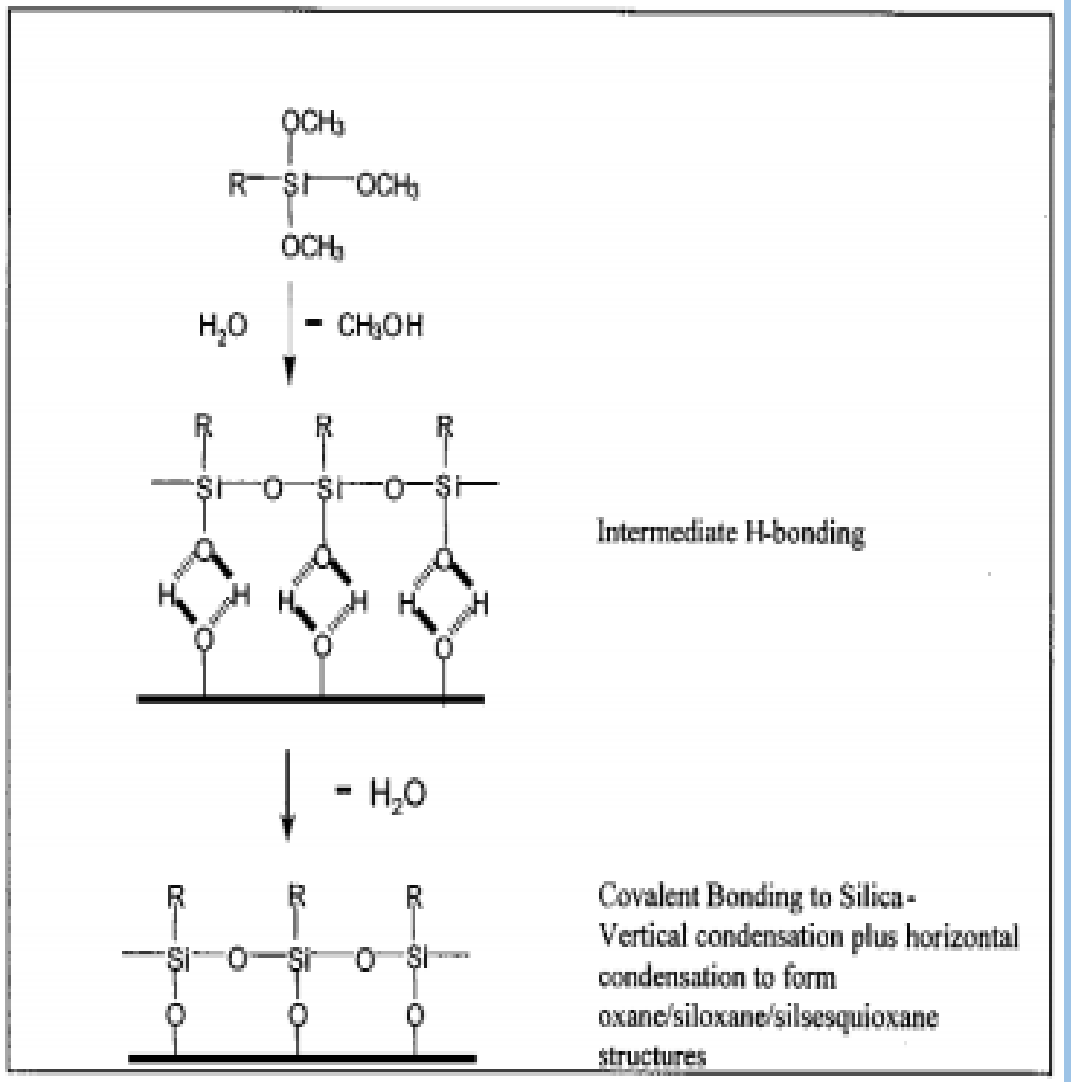


vinyl silane



anhydride silane

mercapto silane



Asian Journal of Applied Sciences (ISSN: 2321 – 0893)
Volume 04 – Issue 02, April 2016

Synthesis and Polymerization of New silane Coupling Agent and Used it as Impact Modifier of Silica Filled Unsaturated Polyester

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Basrah-Iraq
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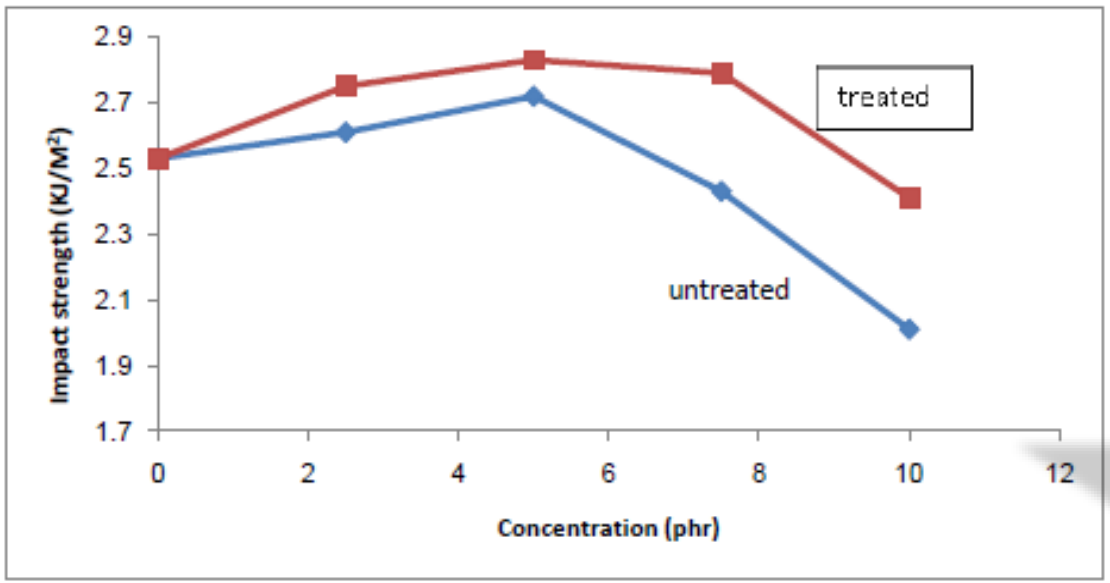
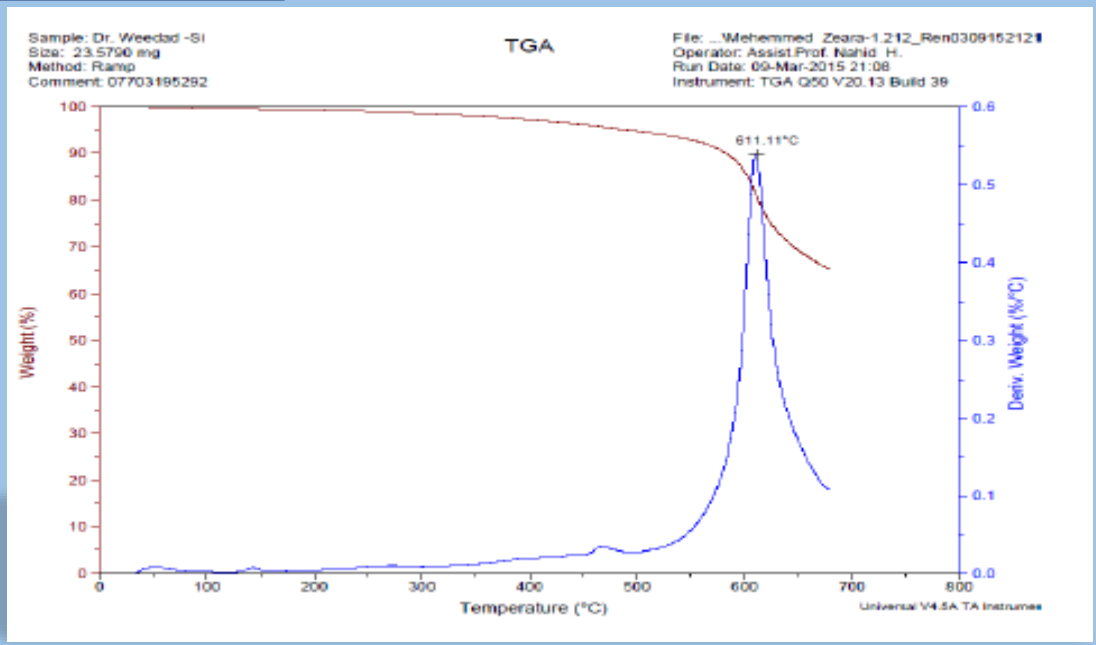
$$CH_2=CH-Si(O-CH_2CH=CH_2)_3$$





تحضير وتقييم اغشية بوليمرية للاستخدامات الطبية

(19) IQ
جمهورية العراق
مجلس الوزراء
الجهاز المركزي للتقييس والسيطرة النوعية
قسم الملكية الصناعية

براءة اختراع

(12)

(11) رقم البراءة : 3041
(21) رقم الطلب : 99/204
(22) تاريخ تقديم الطلب : 1999/9/1
(30) تاريخ طلب الاسبقية - بلد الاسبقية - رقم طلب الاسبقية
(45) تاريخ منح البراءة : 2002/A/10
(51) التصنيف الدولي
C01F13/02
C01G31/74
C08J 31/695
(52) التصنيف العراقي 6
صورة طبق الاصل

(72) اسم المخترع وعنوانه :
١ـ السيد رائد كاظم زيدان / جامعة البصرة / كلية العلوم
٢ـ الاستاذ الدكتور كوركيس عبدال ادم / جامعة البصرة / كلية العلوم
٣ـ الاستاذ الدكتور ظبي احمد حمدان / جامعة البصرة / كلية العلوم
٤ـ ب. وداد صالح حنوش / هيئة التصنيع العسكري / مركز ابن سينا
٥ـ الاستاذ الدكتور مؤيد كاصد جلهوم / هيئة التصنيع العسكري / مركز ابن سينا
٦ـ الاستاذ الدكتور حكمت نعيم الجلو / شركة ابن سينا للصناعات الدوائية

(73) اسم صاحب البراءة :
جامعة البصرة / كلية العلوم
وهيئة التصنيع العسكري
والشركة العامة للصناعات الدوائية

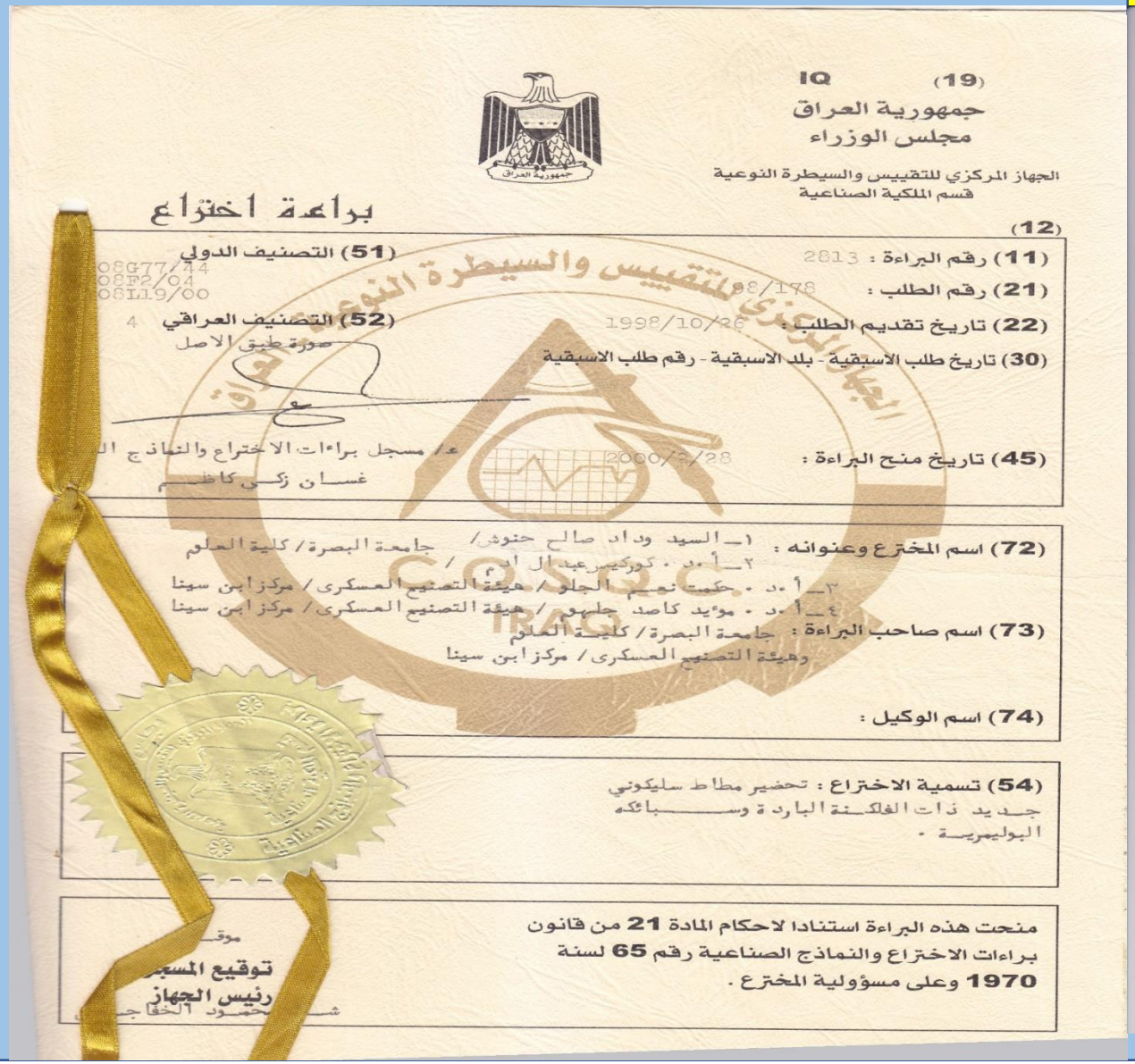
(74) اسم الوكيل :

(54) تسمية الاختراع : تحضير وتقييم أغشية بوليمرية نفاذة لاستخدامات طبية .

منحت هذه البراءة استنادا لاحكام المادة 21 من قانون براءات الاختراع والنماذج الصناعية رقم 65 لسنة 1970 وعلى مسؤولية المخترع .

موقع
توقيع المسجل
رئيس الجهاز
شاكر محمود الخفاجي

تحضير مطاط سليكوني جديد ذات الفلكنة الباردة وسبائكه البوليمرية



(19) IQ
جمهورية العراق
مجلس الوزراء
الجهاز المركزي للتقييس والسيطرة النوعية
قسم الملكية الصناعية

براءة اختراع

(12)

(11) رقم البراءة : 2813
(21) رقم الطلب : 98/178
(22) تاريخ تقديم الطلب : 1998/10/26
(30) تاريخ طلب الاسبقية - بلد الاسبقية - رقم طلب الاسبقية
(45) تاريخ منح البراءة : 2000/2/28
(51) التصنيف الدولي
C08G77/44
C08F2/04
C08L19/00
(52) التصنيف العراقي 4
صورة طبق الاصل

(72) اسم المخترع وعنوانه :
١ـ السيد وداد صالح حنوش / جامعة البصرة / كلية العلوم
٢ـ أ.د. كوركيس عبدال ادم /
٣ـ أ.د. حكمت نعيم الجلو / هيئة التصنيع العسكري / مركز ابن سينا
٤ـ أ.د. مؤيد كاصد جلهوم / هيئة التصنيع العسكري / مركز ابن سينا

(73) اسم صاحب البراءة :
جامعة البصرة / كلية العلوم
وهيئة التصنيع العسكري / مركز ابن سينا

(74) اسم الوكيل :

(54) تسمية الاختراع : تحضير مطاط سليكوني جديد ذات الفلكنة الباردة وسبائكه البوليمرية .

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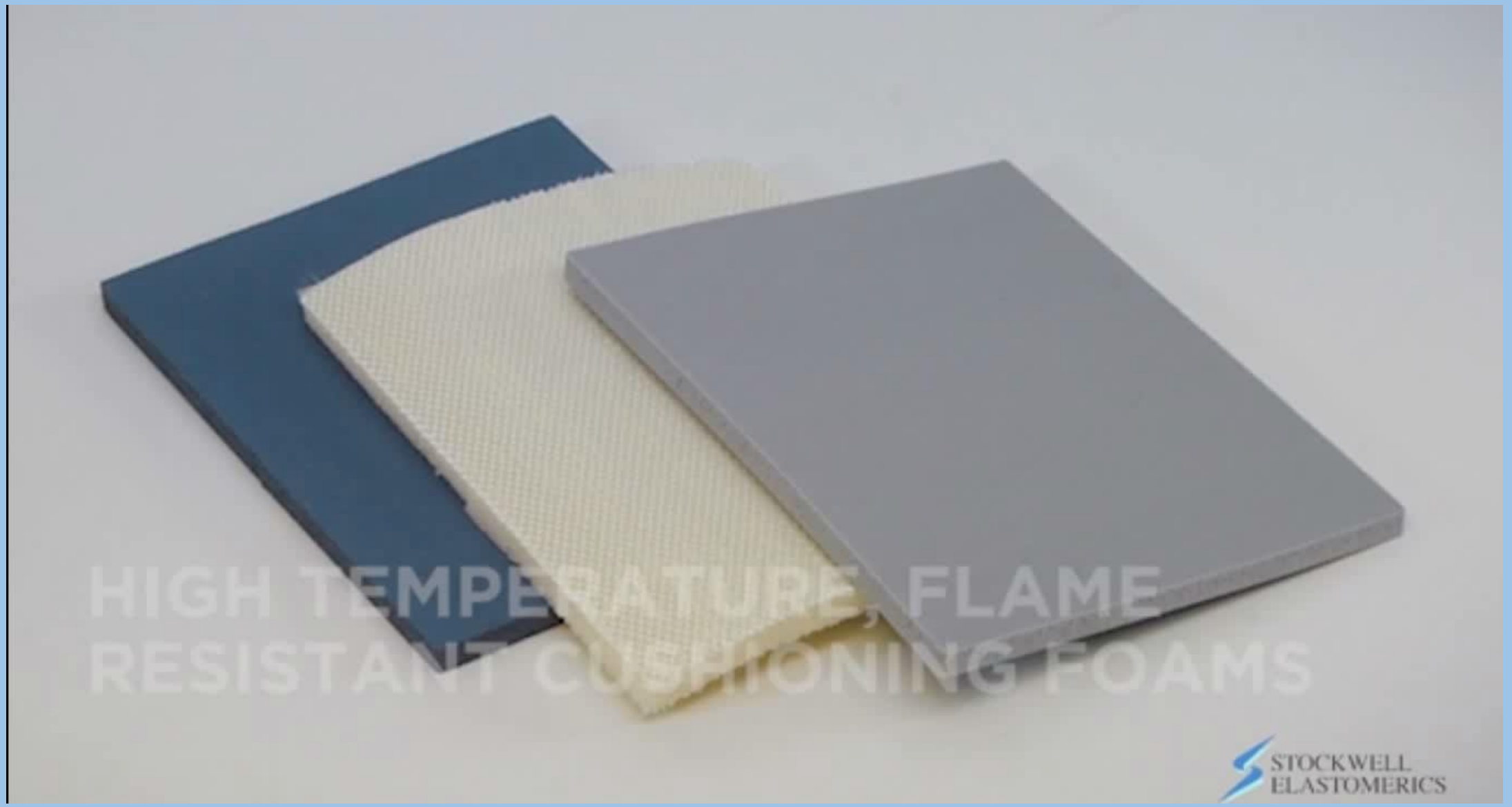
رئيس الجهاز
شاكر محمود الخفاجي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Dr.Widad