Formulation of Silicones: why and how?

Bridging the gap between science and industry

Dr Gilbert Schorsch
Former R&D Director of Rhône-Poulenc Specialities

The « world of silicones »
A guided tour

- Section 1

  Historical background
  Silicones: what and why?

- Section 2

  The “science of PDMS*”
  Why PDMS* need to be formulated?

- Section 3

  The main “industrial applications of PDMS”
  How are PDMS* formulated?

* PDMS=Polydimethylsiloxane

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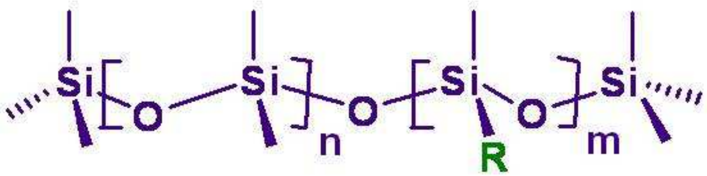
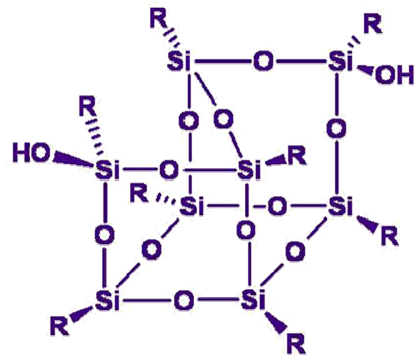
Section 1 What are silicones?

- Si, C, O containing organo-mineral polymers

- Two types:

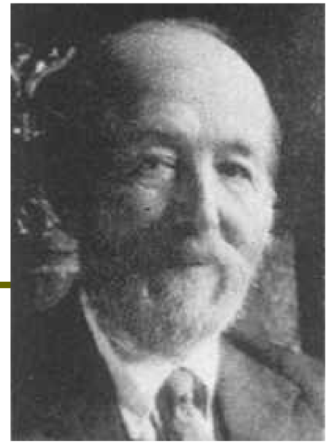




Linear macromolecules   Tri-dimensional networks

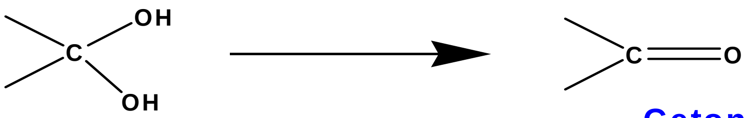
- Two possibilities: non reactive & reactive

Silicones: How and Why?
The “fruitful mistake”

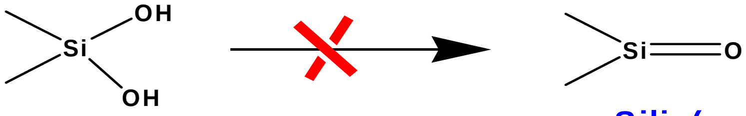


Stanley Kipping
(1863-1949)
Nottingham U.

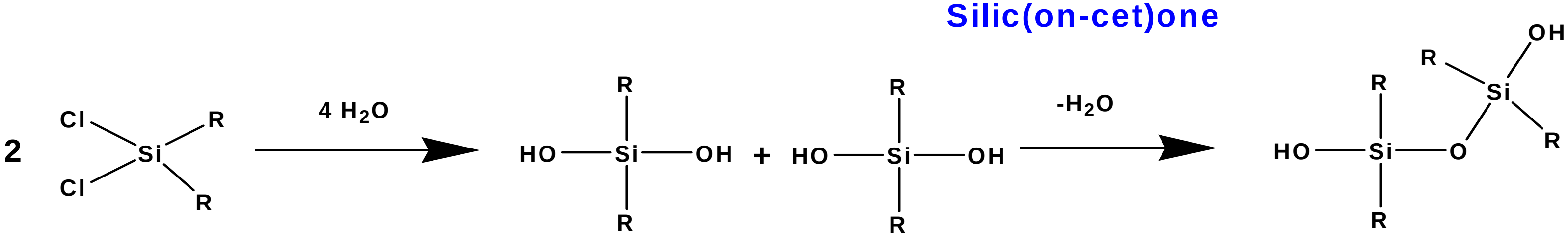
Intramolecular dehydratation



Cetone

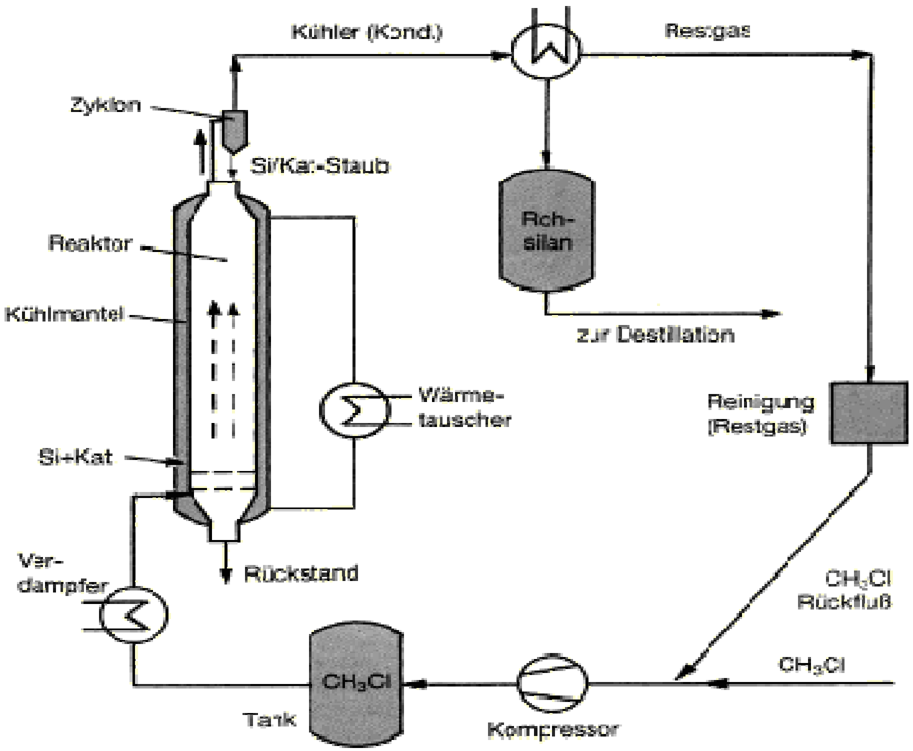


Silic(on-cet)one



Intramolecular dehydratation

Rochov-Müller's « Direct Synthesis »



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    The main industrial applications of PDMS*

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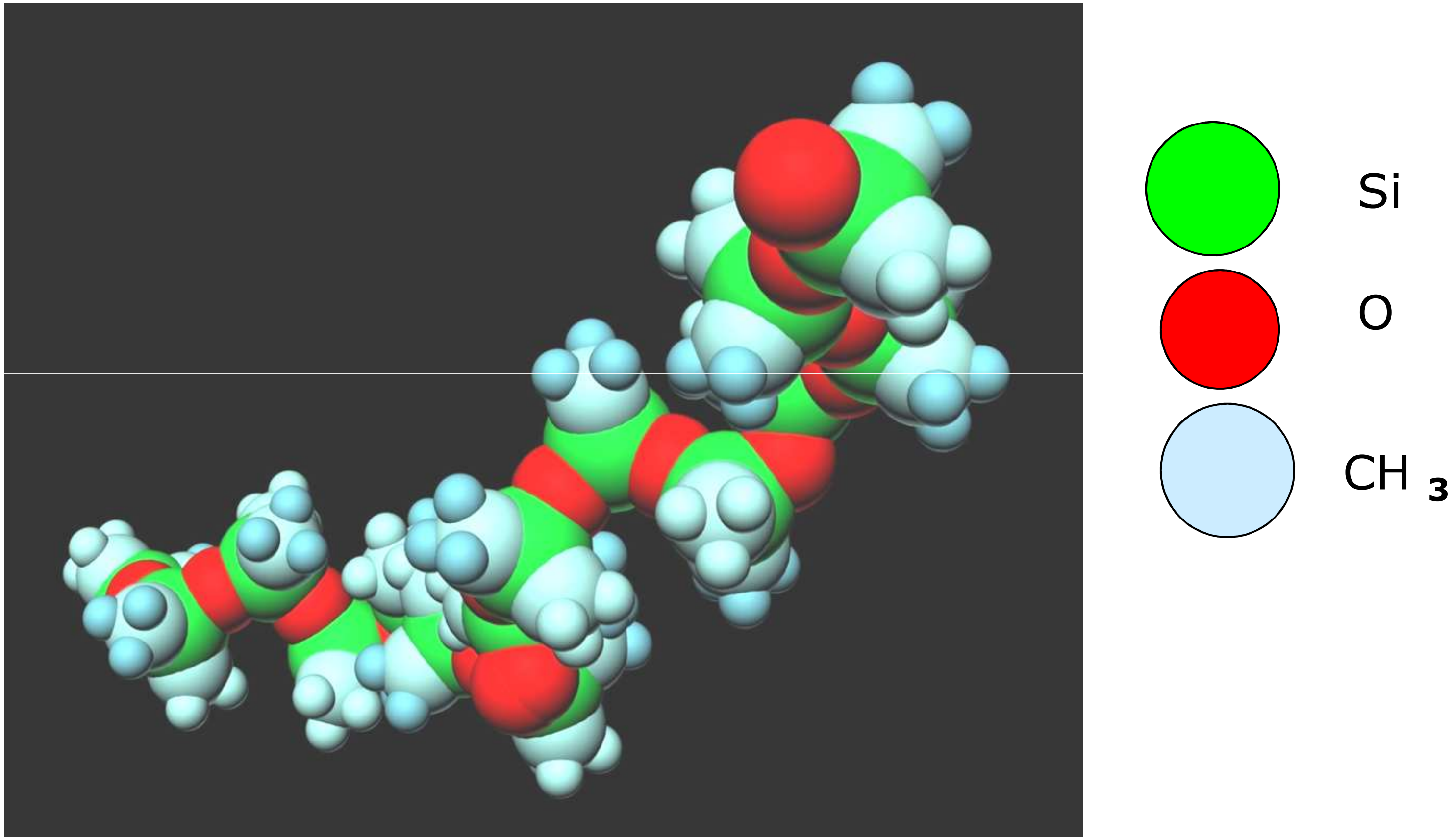
*PDMS= Polydimetylsiloxane

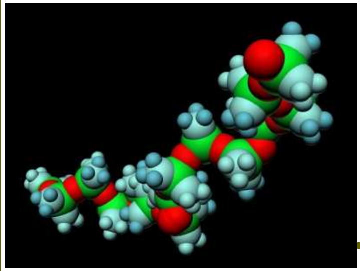
Section 2 The « Science » of PDMS

- The real face of PDMS?
- Structure/properties relationship?

Lorenzo Lippi (1606-1665)
«Allegory of the Simulation»
Museum of Art, Angers (F)

PDMS: a 3D simulation

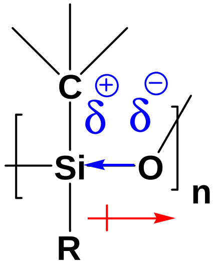




Structure/properties relationship

Exploring the ambivalence
at 3 complementary levels

- ***Atomic level***: Comparing the Si-O et Si-C energy bonds for evaluating the overall **stability ?**
- ***Molecular level***: Analysing the composition of the « dimer » for **solubility/compatibility issues ?**
- ***Macromolecular level***: Anticipating the overall behaviour & **the physical/mechanical properties ?**



Si(+) - O(-) : a iono-covalent bond

- *Origin*

  Electro-negativity differences between Si (1.8) & O (3.5)

- *Consequences*

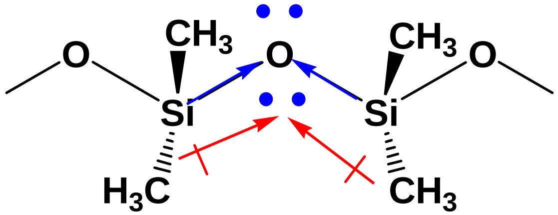
  Physical stability (T, XR, EB…)

  Chemical sensitivity(to elec.acceptors & donors)

- *Comments*

  Good ageing performances

  Amphoteric: OH-& H+=scissors & glues

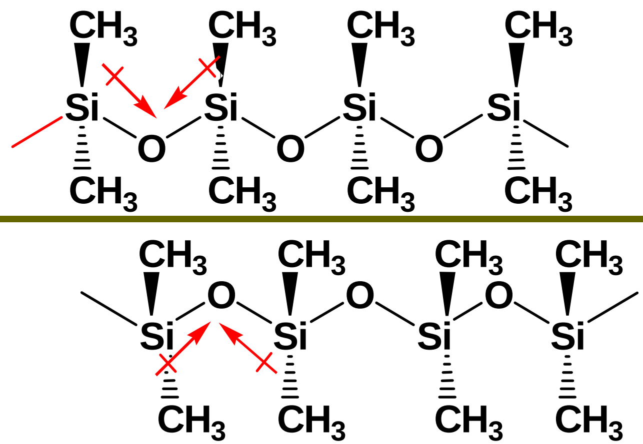


$-Si(CH_3)_2-O-Si(CH_3)_2$ a slightly amphiphilic dimer

- *Origin*: small "mean dipole" & 2 CH_3 groups
- *Consequences*
  - ✓ Hydrophobic and lipophobic
  - ✓ Non soluble/Incompatible in aqueous & apolar media. Only a very limited number of solvents
  - ✓ Low dielectric constant
- *Comments*
  - ✓ Water-repellent but tests in dry cleaning
  - ✓ Importance of interfaces: Location at interfaces and interfacial reactions

PDMS

a very «mobile» chain



- *Origin*
  - Flexibility of the linear chain
  - Low attractive intermolecular interactions
- *Consequences*
  - Low critical temp. (Tc = -55°C, Tg = -125°C...)
  - Low vicosities § surface tensions (21mN/m)
  - High molar vol.= solubility & permeability of gases...
- *Comments*
  - An « adaptable » amphiphile
  - Foam-regulators (stabilizers & defoamers)

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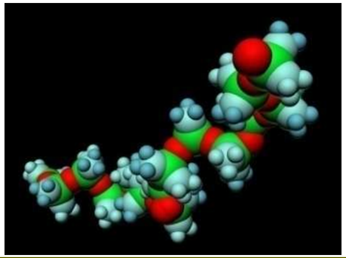


PDMS needs to be formulated. Why?

➢ ***1st Reason ?*** Absence of mechanical properties

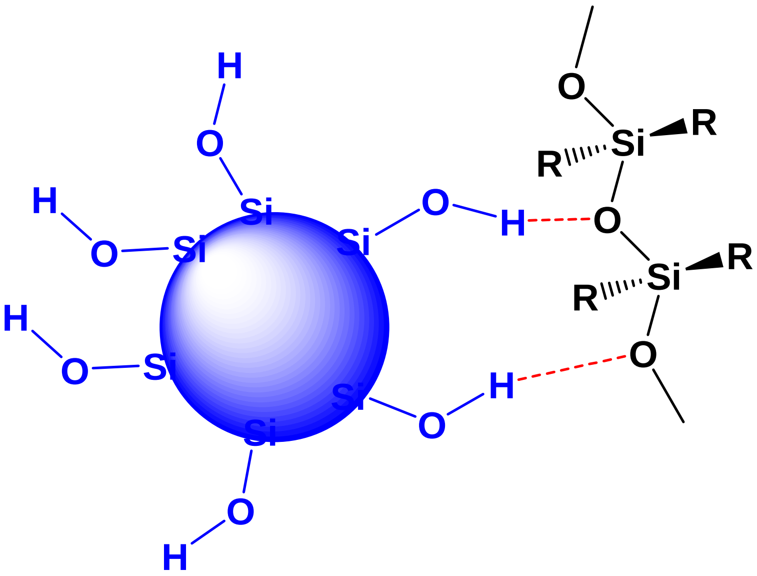
❖ ***Remedy ?*** Reducing the mobility of the chain by

✓ Introducing fillers

Physical adsorption

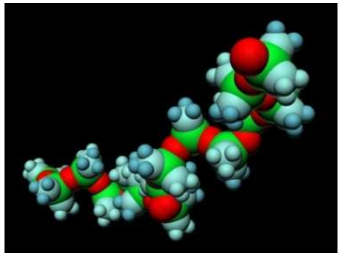
of PDMS on SiO2

by Hydrogen bonding



✓Chemical crosslinking

- **Silicone elastomers**
  - H.C.E.
    - Heat Cured Elastomers
    - 1940
    - Peroxydes
    - Vinyl functionalized gums
    - Reinforcing agents (Silica)
    - → Analogy with hydrocarbon elastomers…
  - RTV — Room temperature vulcanized crosslinked
    - RTV I — 1956
    - RTV II — 1958
    - → Polycondensation



Why PDMS needs to be formulated?

➢ ***2nd Reason*** ? Speed up the spreading of hydrophobic PDMS on hydrophilic substrates!

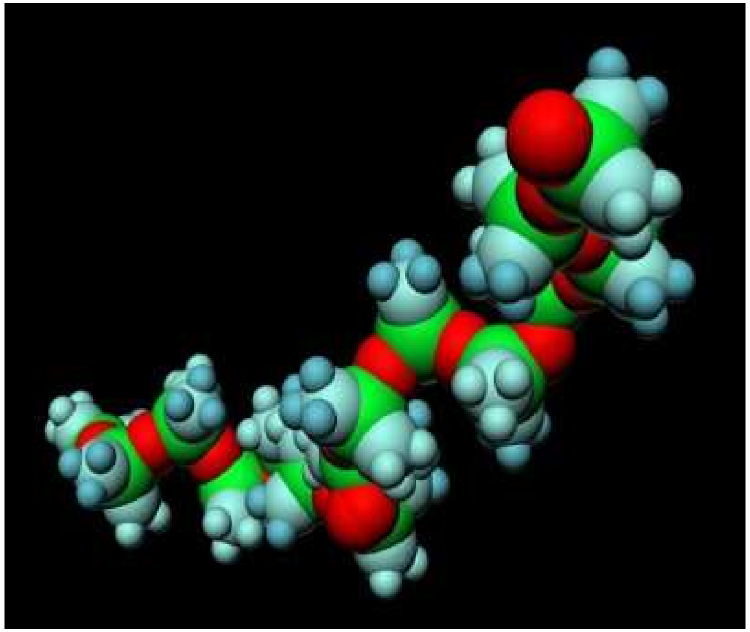
❖ ***Remedy ?*** PDMS/ Water emulsions (from top/down to bottom/ up)

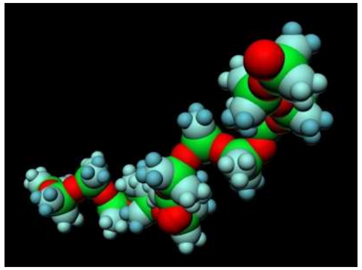
❖***Applications ?*** Demoulding fluids, lubricants in textile processing, cosmetic creams, anti-foams...

From physical caracteristics to *applications*

Two examples:

- based on an adequate combination of **two unique physical properties**





A large temperature range

(as a first example)

❖ *Origin*

➢Macromolecular liquid from Tg to Td

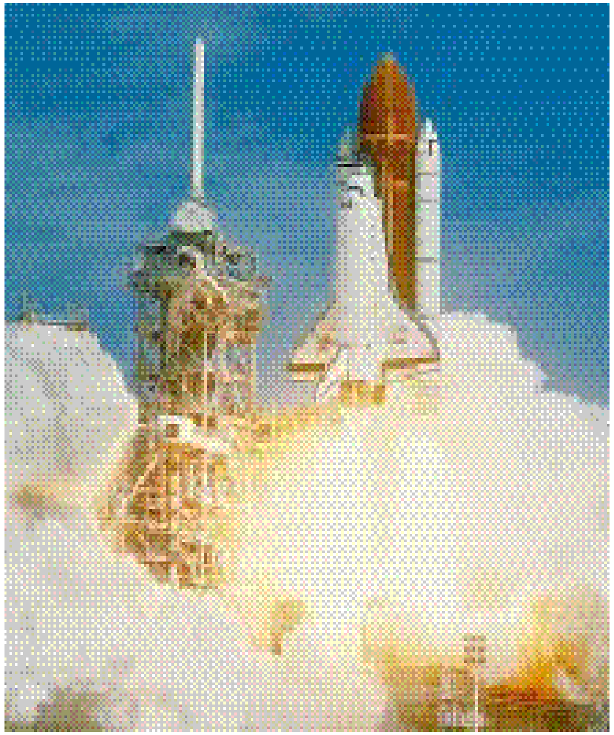
➢No phase transition i.e. no drastic changes of major physical constants (viscosity, elasticity, electrical propetrties…)

❖*Applications*

➢*Damping & heating oils , hydraulic & dielectric fluids... …*

A "negative" illustration

- The **shuttle crash** :
  Challenger
  1986, january 28
  7 astronauts died



- The reason:
  Use of sulfur based Sealants (leading to cracks) **instead of silicone ones**

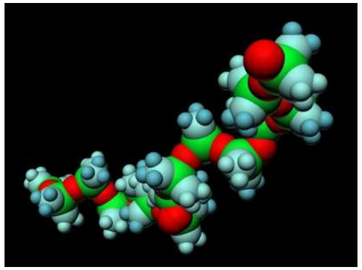
Positive illustrations

Kitchen ware

From freezer (- 18 °C) to micro-oven (+200 °C)

Sealants for photovoltaïc cells

From aerospace (-50°) to desert (+70°)



Water-permeable water-repellent coatings (as a 2nd example)

❖ Origin

Hydrophobicity and a high molar volume (=gas permeability) of PDMS contact with two states of the water (liquid and vapour)

❖ Applications

- *Eliminating capillary water (in façades) and swet (in K-Ways) while protecting against rain!*

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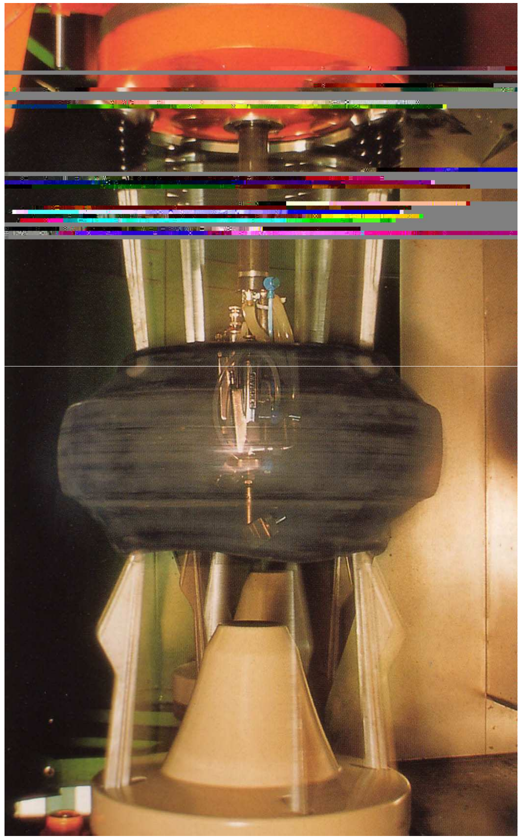
PDMS
The main industrial applications

- Pomegranate:
  A symbole of fertility

- Four «Interface-related» applications

- Learning from practice

Application 1/ Demoulding fluids in polymer processing

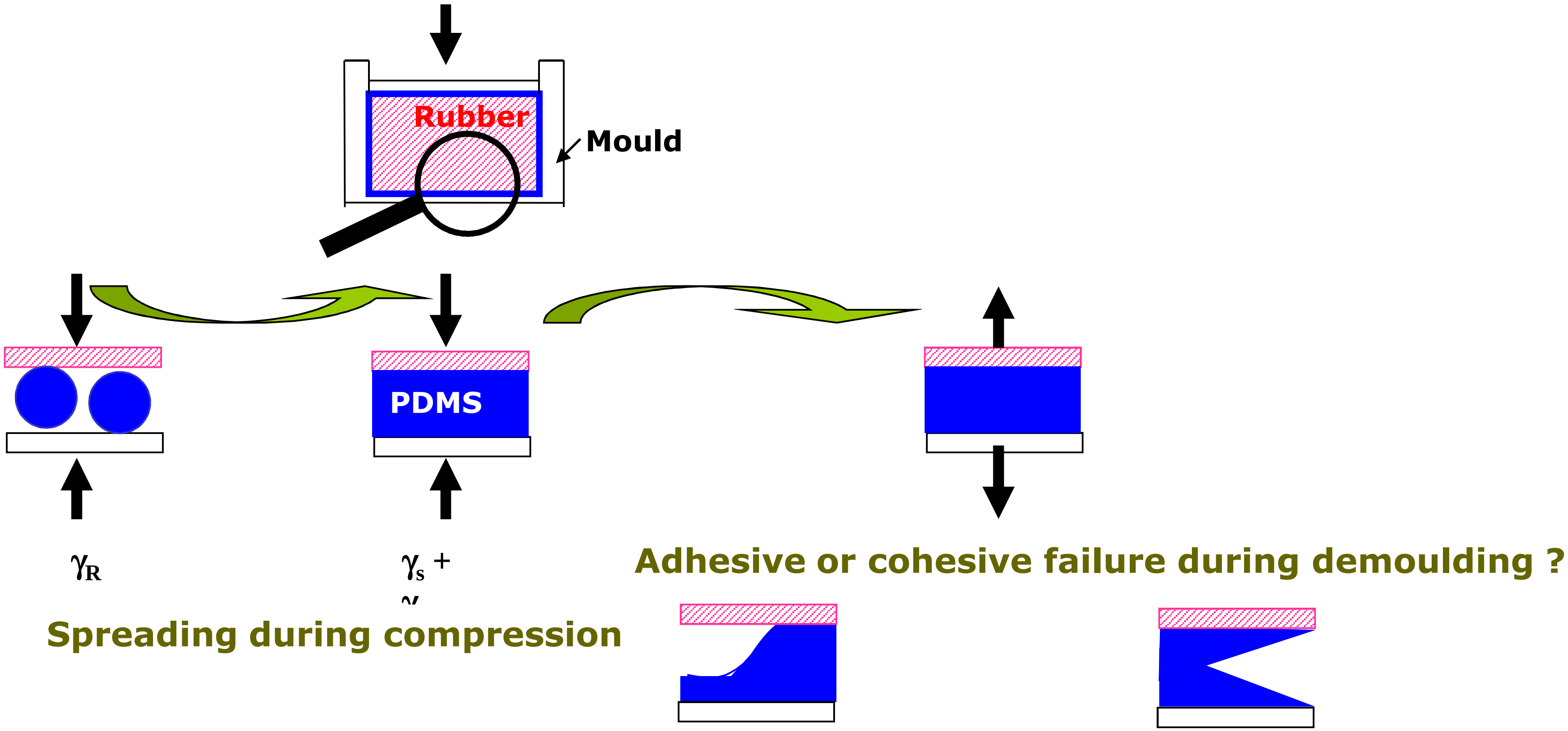


Formulations (Aerosols)

non reactive PDMS

- ***pure or solvant based***
- ***emulsions***

Compression moulding:
A theoretical similation



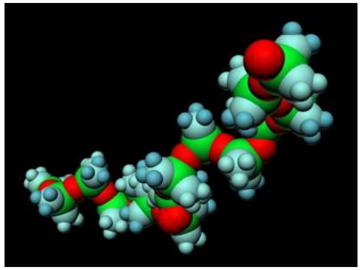
$W_A = \gamma_R + \gamma_s - \gamma_{RS}$

$W_B = 2\,\gamma_S$

$$\sigma_{SR} = \gamma_R - \gamma_s - \gamma_{RS} > 0$$

$$W_B - W_A = \gamma_S - \gamma_R + \gamma_{RS}$$

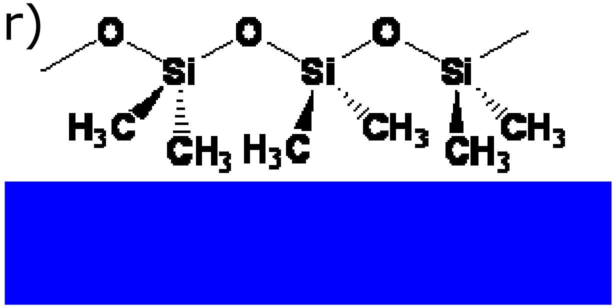
$$W_B < W_A$$



Wetting/ spreading of PDMS on liquids and solids surfaces

➢PDMS/Surface adhesion> PDMS/PDMS cohesion

❖ PDMS spreads on water and oil surfaces (cf Liliane Léger)



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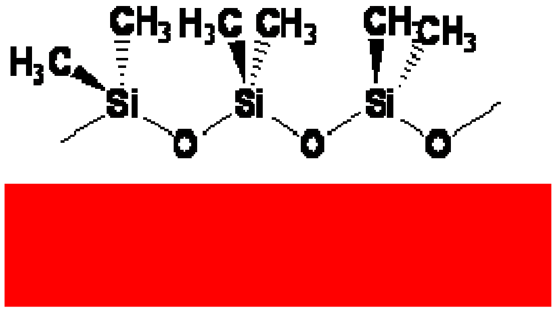
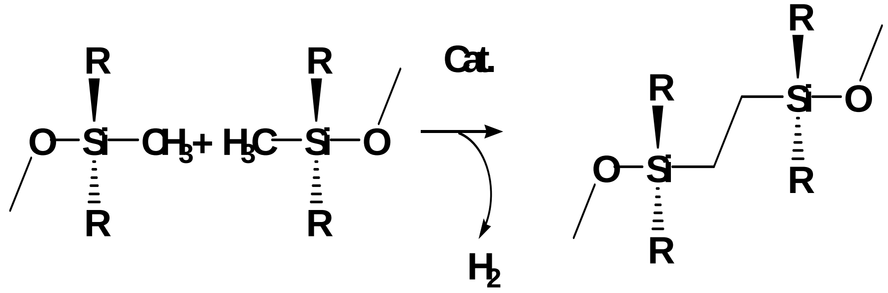
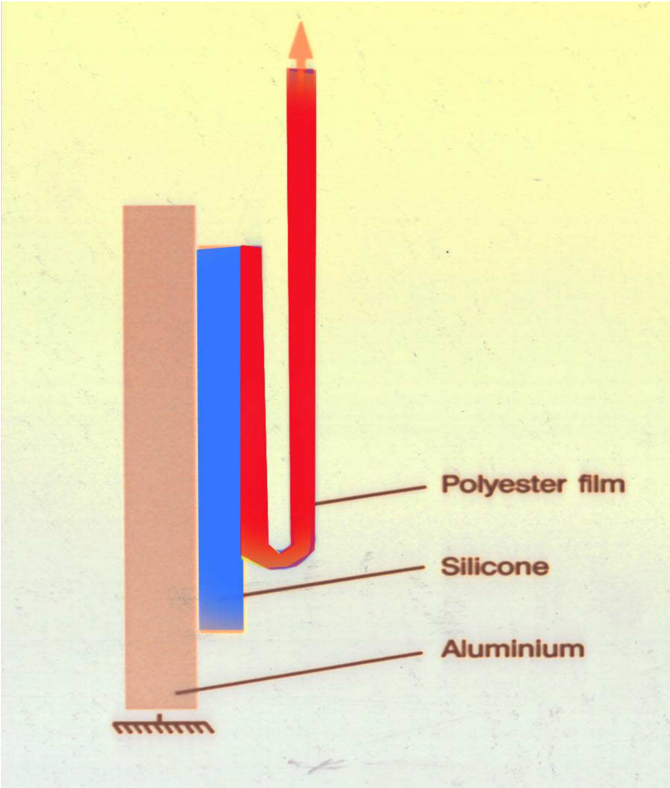


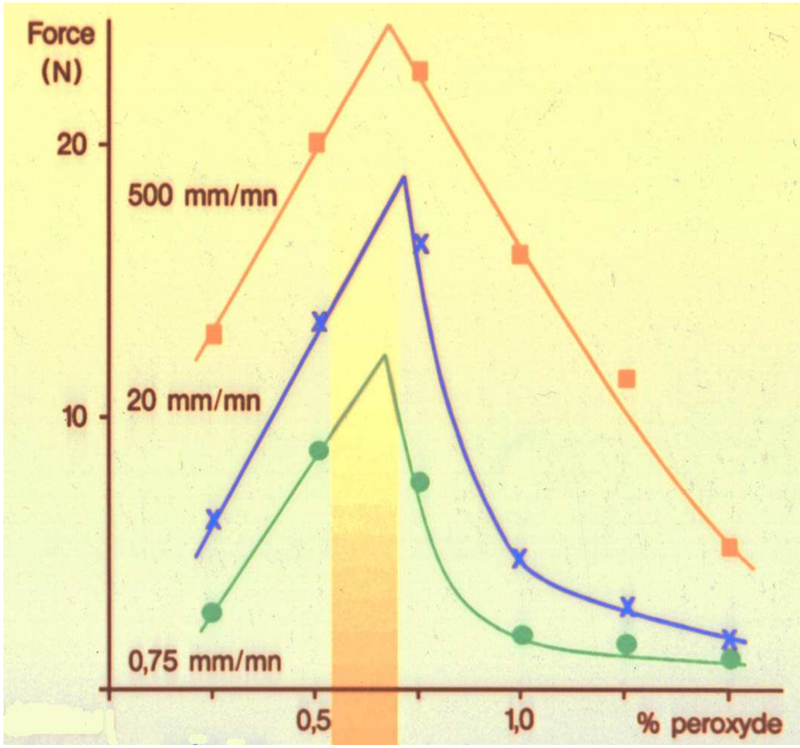
❖ The kinetics depends upon the treatment of the surface and the size ofthe drop (cf Anne-Marie Cazabat)

❖ May explain the « hand- feel » of PDMS in textiles § cosmetics? (cf Liliane Léger)

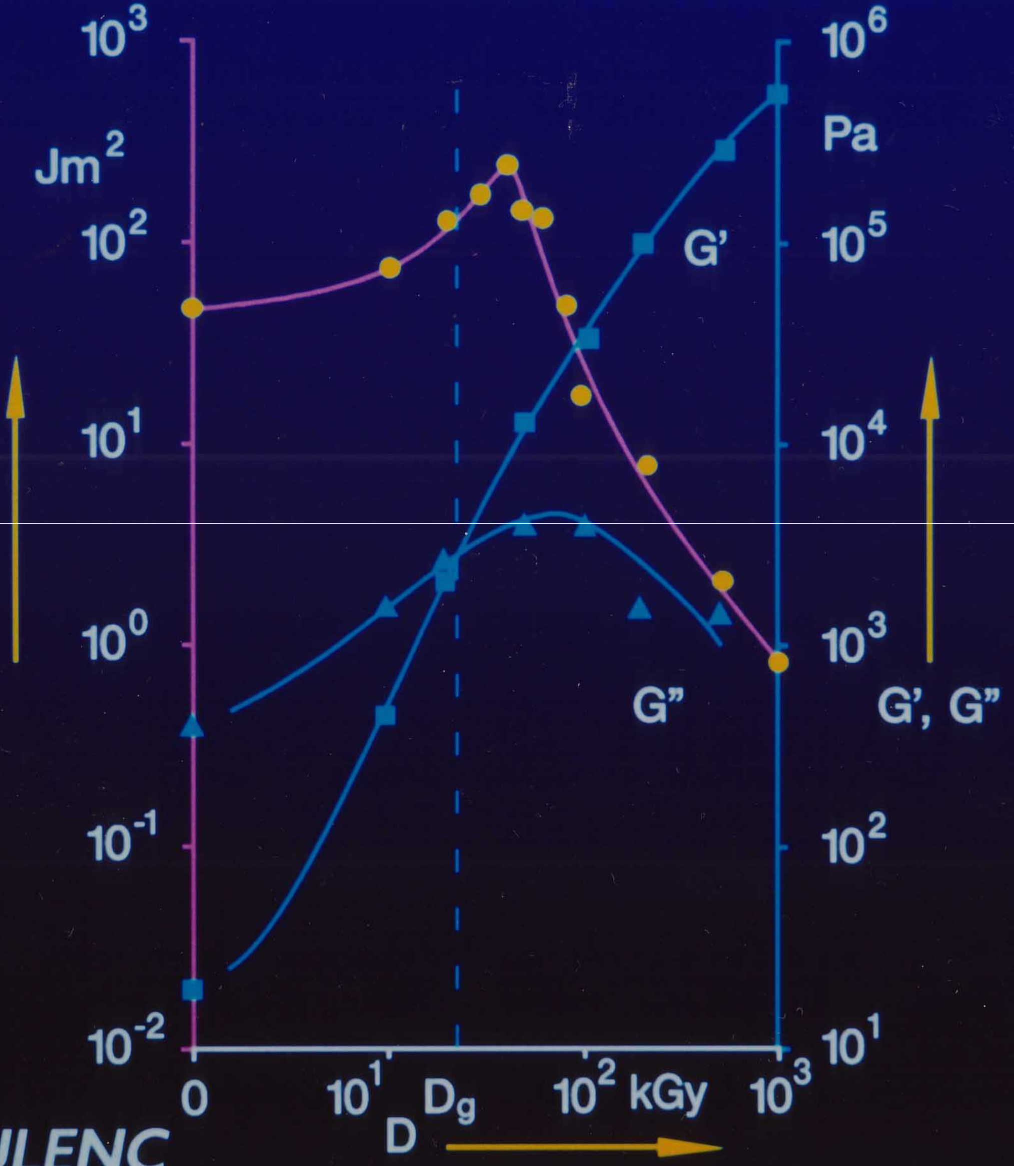
Preparing an adhesive by cross-linking: a practical simulation







E.B. Cured PDMS

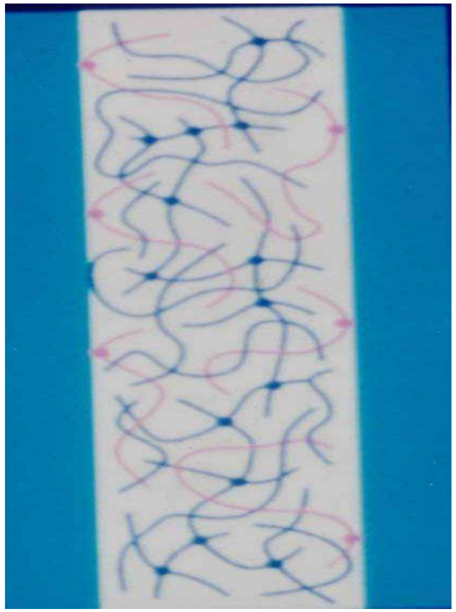


RHÔNE-POULENC

(From A. ZOSEL EUROCOAT 1991-Nice, 19-28)

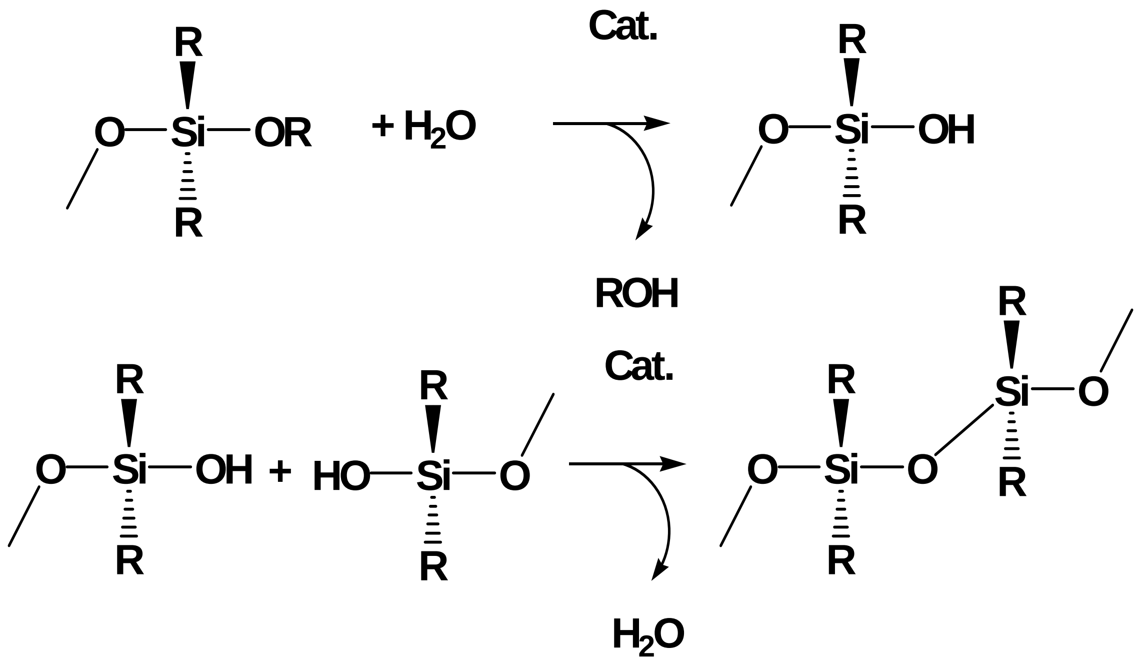
Maximizing adhesion ?

- Clearly an *optimised situation*
  - where « ***cohesion*** » is assured by the ***connectivity of a network*** throughout the bulk of the material
  - where « ***adhesion*** » is favoured by *free chains adsorbed* at the surface, acting as ***connectors.***



Applications 2 & 3

Water catalysed cross-linking



Application 2/An example
« Moulding with silicones »

Guillaume Coustou (1745)
The Marble at the Louvre

A copy in cement at the
Concorde (since 1984)

Two types of situations

Silicone moulds

Moulding of silicones

Formulations for « mouldings »

- **RTV *2 components***

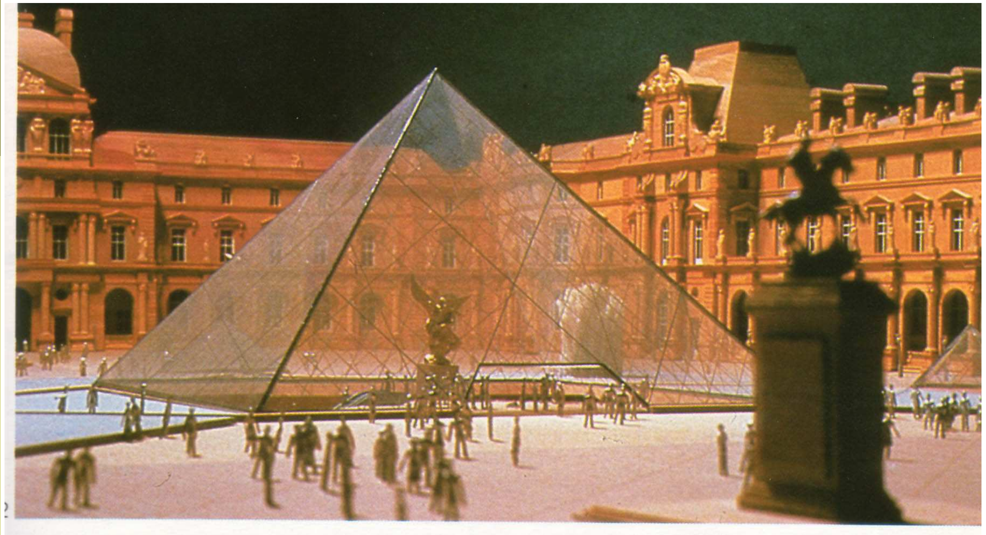
  1. Di-Alkoxy-terminated PDMS oils

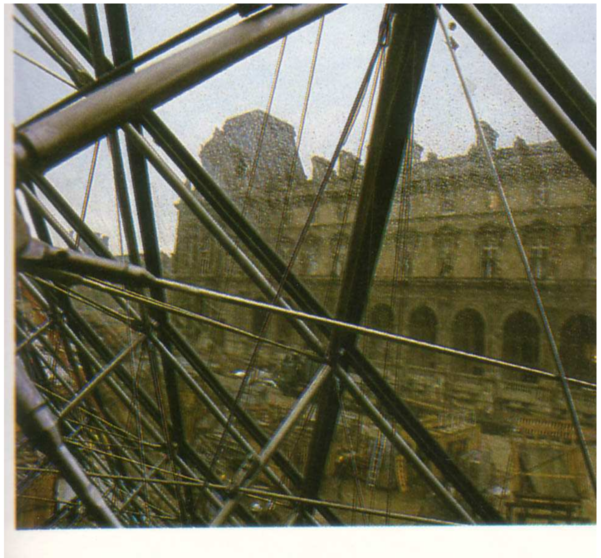
  + Silica+ Catalyst

  2. Water /PDMS oils Emulsions

Easy mixing,
Short pot-life

Application 3/Silicone « Sealants »





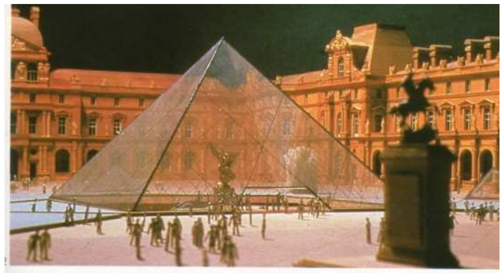
Application 3/Formulations for Sealants

➢ **RTV *one-component systems*:**

□ ***Di-alkoxy-terminated PDMS oils***

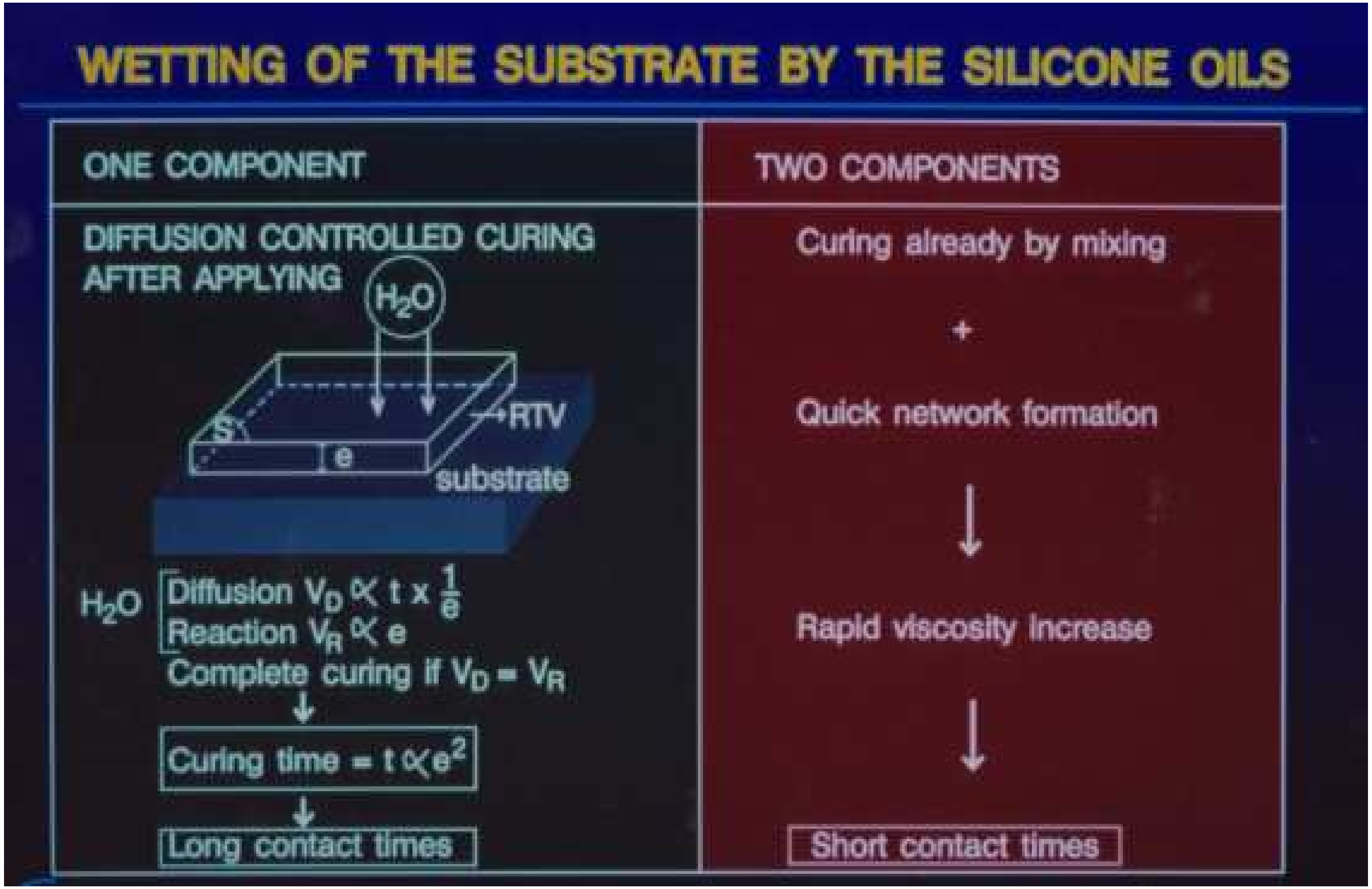
+Silica

+Catalyst



➢ ***Applications: Glazing, framing, caulking…***

Comparing Sealing /Moulding



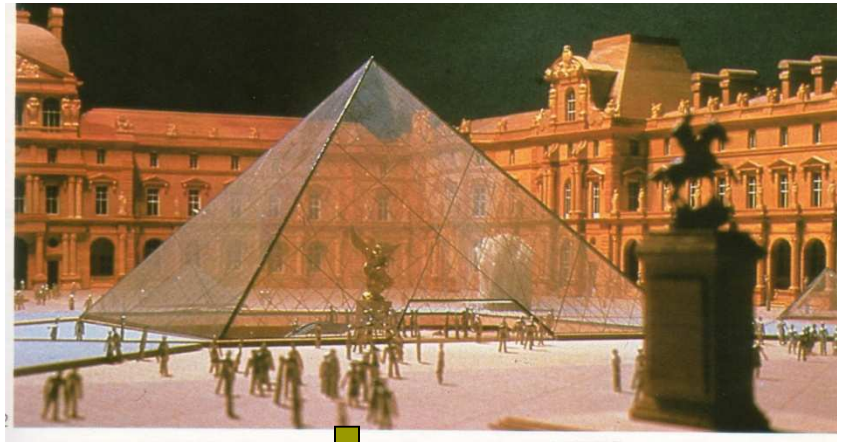
Comparing Sealing/Moulding

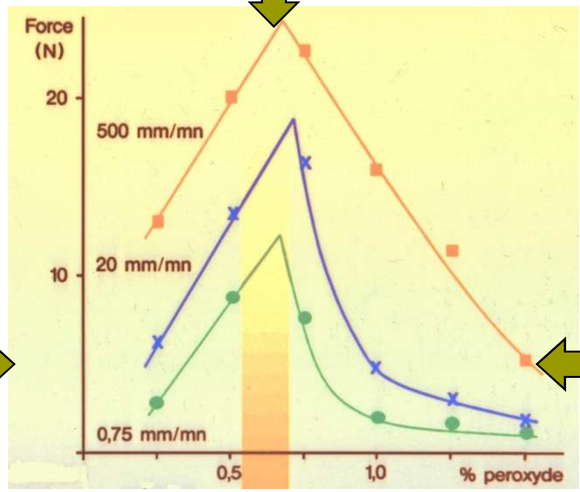
- ***RTV 1*** **= *« sealant case » : slow and heterogeneous diffusion-controlled crosslinking* by the humidity in the air**

- ***RTV 2*** **= *« moulding case » : quick and homogeneous crosslinking* by the added water during mixing**

- **« Adhesion » determined by the *crosslinking kinetics***

Summarizing the three applications





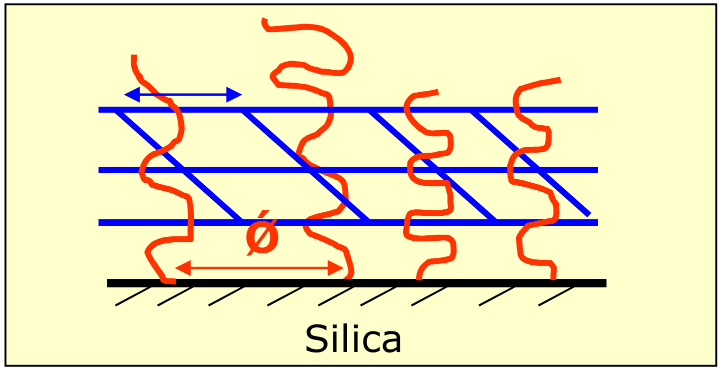
A molecular simulation

Liliane Léger & co /Collège de France

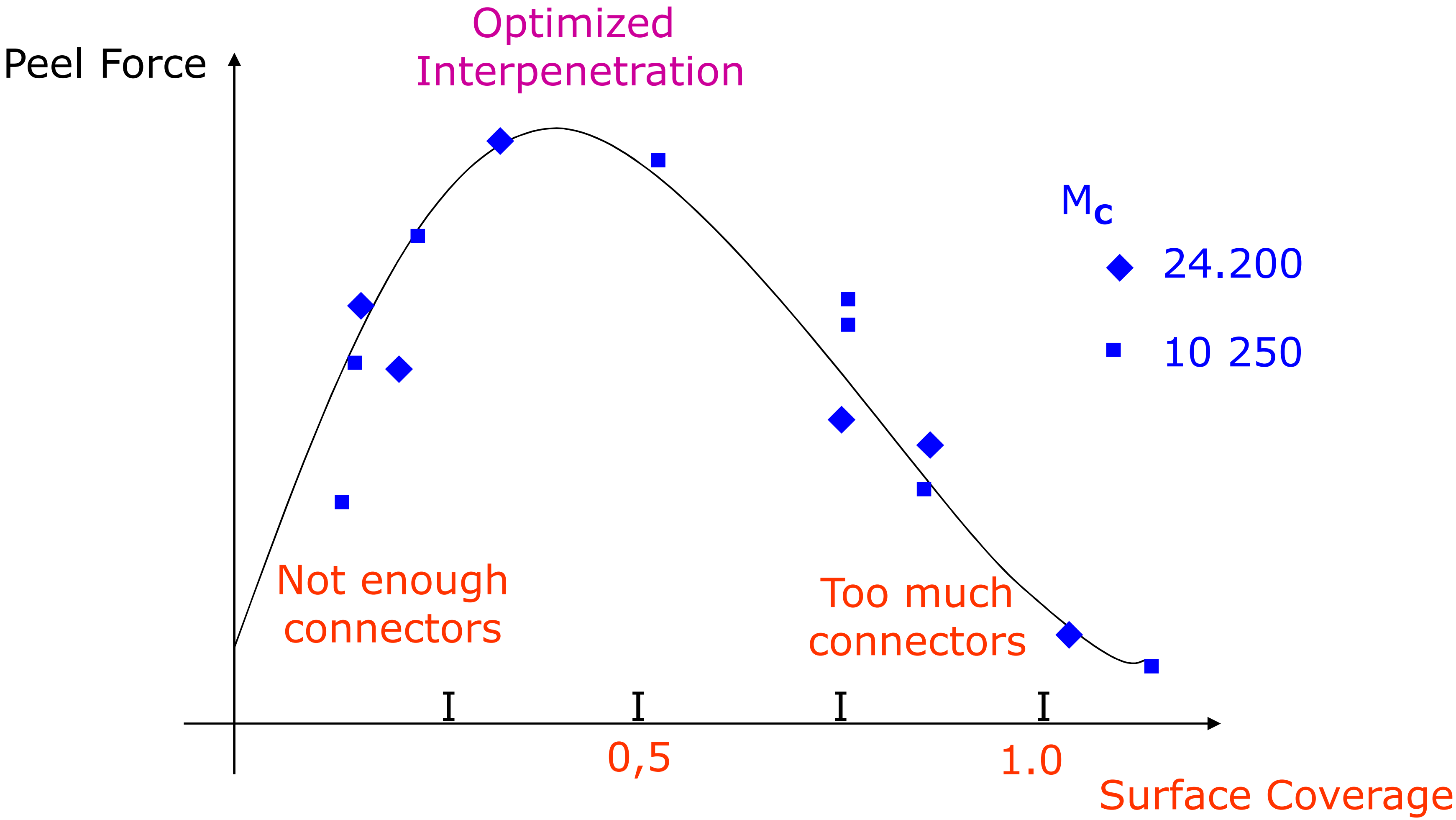
•**Connectors**	PDMS (M=250.000) grafted on silica at various concentrations (ϕ)
•Adsorption time	10 days (from solution)
•**Network**	PDMS with various Cross Linking Densities (M_c=10.250 and 24 200)
•Film thickness	200 μm on PDMS treated Silica

Measurements ?

•What ?	Adherence energy
•How ?	Peel Test (90 °)



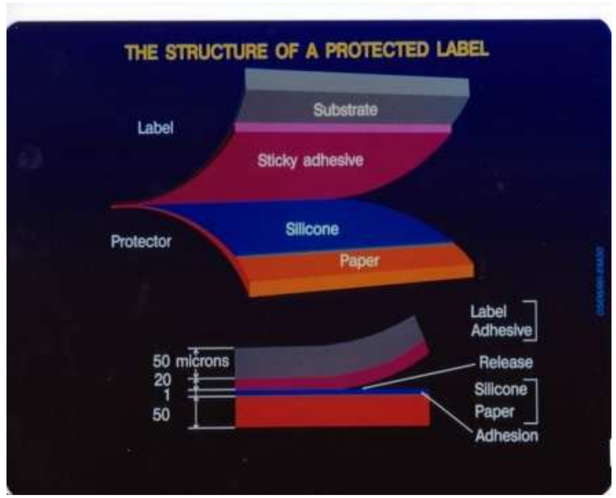
Connectors/Network interpenetration



Application 4/ « Release papers »

- An emulsion of ***two reactive oils based on***
  - ***Vinyl-modified PDMS oils*** **containing a catalyst (Pt 0)**
  - ***H-modified PDMS oils***

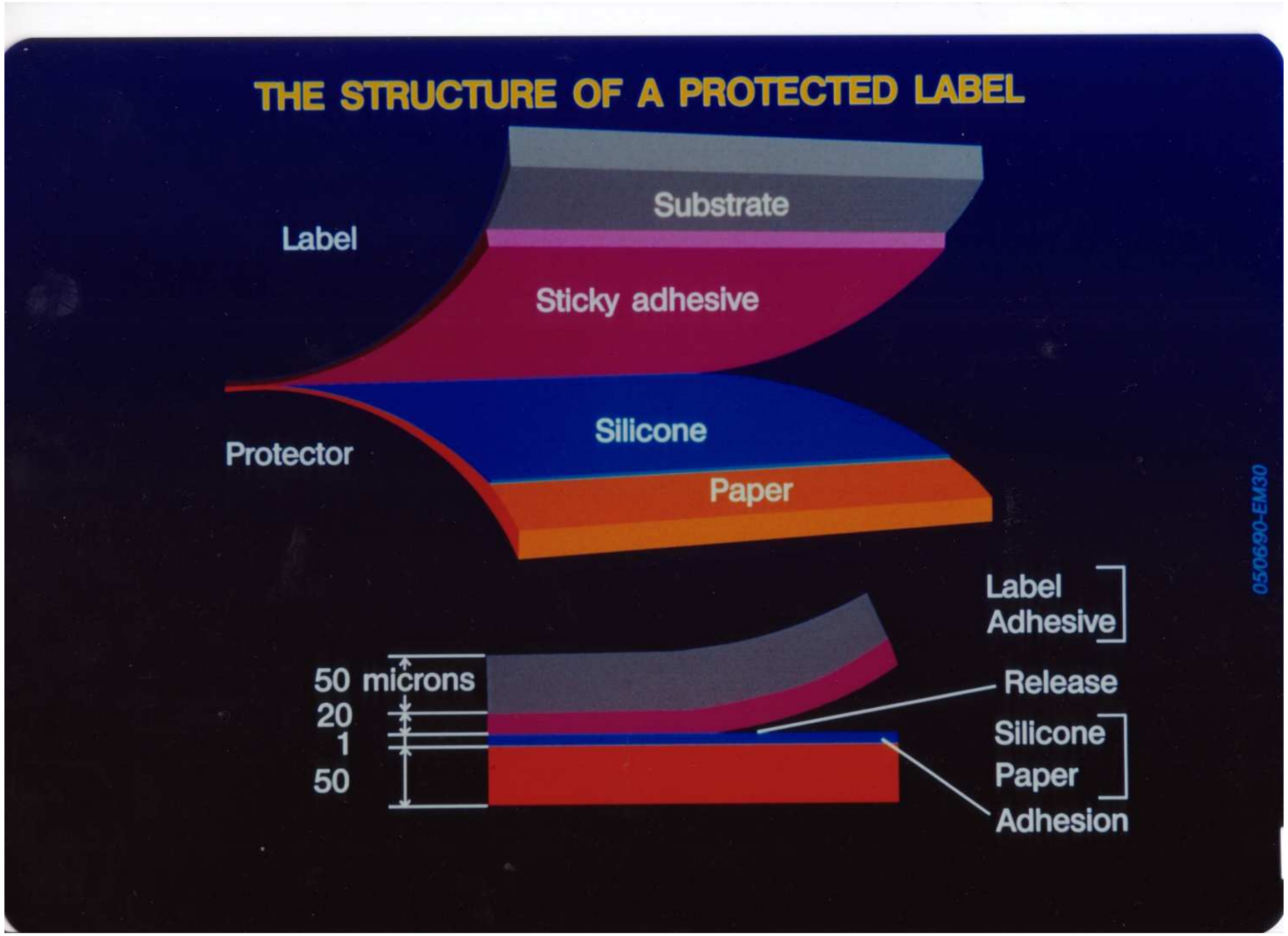
  blade-coated on paper



Applications

Stickers (Post-it), wallpapers, labels ….

A « Release paper »

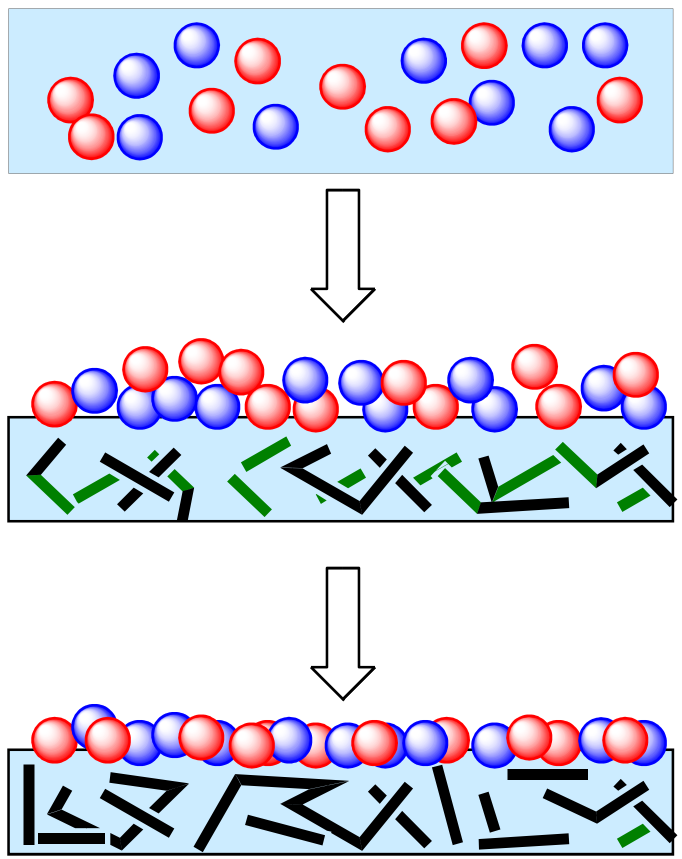


Why emulsions for release papers ?

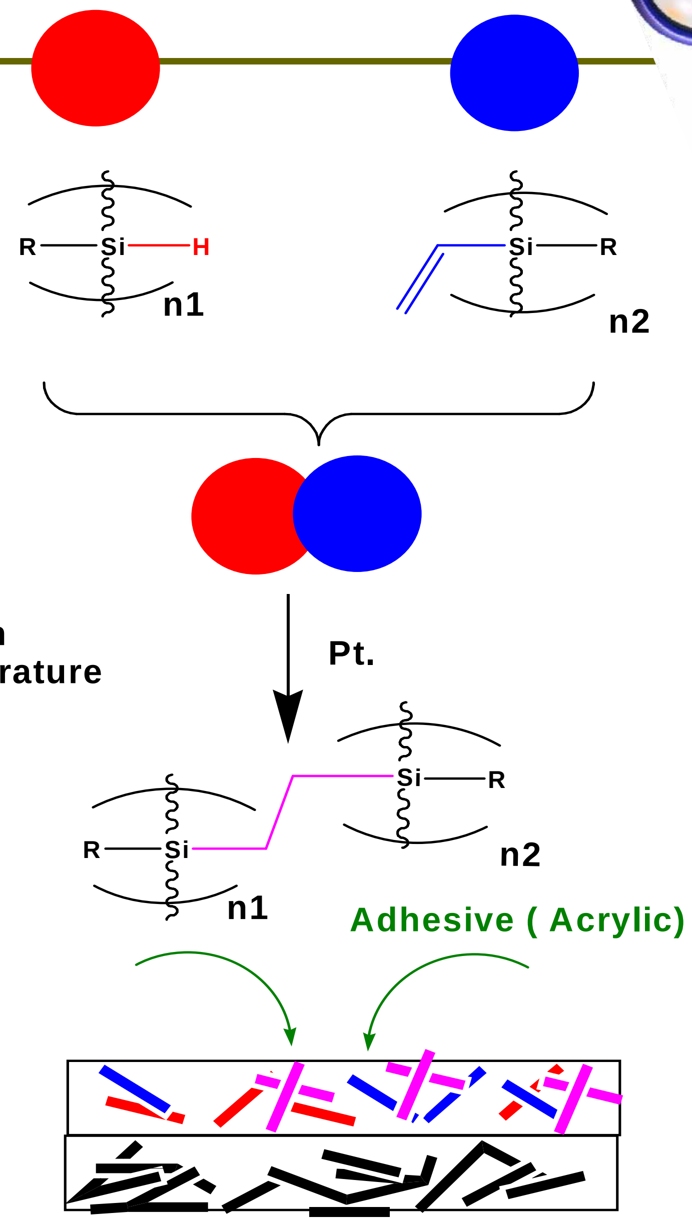
Water insolubility of PDMS

Surface retention of the droplets

Good –filmification of the droplets



Change of the cross-linking system......



Polyaddition
room temperature

Pour finir: Etat des lieux et perspectives?

- Que faut-il retenir, en l’état actuel?
- Que faut-il « creuser » davantage?
- Quelles propositions éventuelles pour de futurs stages pédagogiques du CNRS?

Que faut-il « retenir » de la structure du PDMS ?

PDMS: une macromolécule à caractéristiques ambivalentes:

- **Stable "physiquement" mais instable "chimiquement"**
Conséquences: bon "vieillissement" et recyclable

- **Hydrophobe mais aussi lipophobe.**
Conséquences: nombre limité de solvants, à l'aise qu'aux interfaces

Très grande mobilité
Conséquences: un liquide macromoléculaire, de faible tension superficielle, filmogène, adaptable par formulation.

Que faut-il retenir de la formulation du PDMS?

- **PDMS non réactif**
  = agents de démoulage
  Adhesion>Cohesion

- **PDMS réactif monocomposant**
  = « Mastics »
  Interpénétration Connecteurs/ réseau optimisée

- **Bicomponent reactive PDMS formulations**
  = Moulage de/avec PDMS
  Cohesion > Adhesion

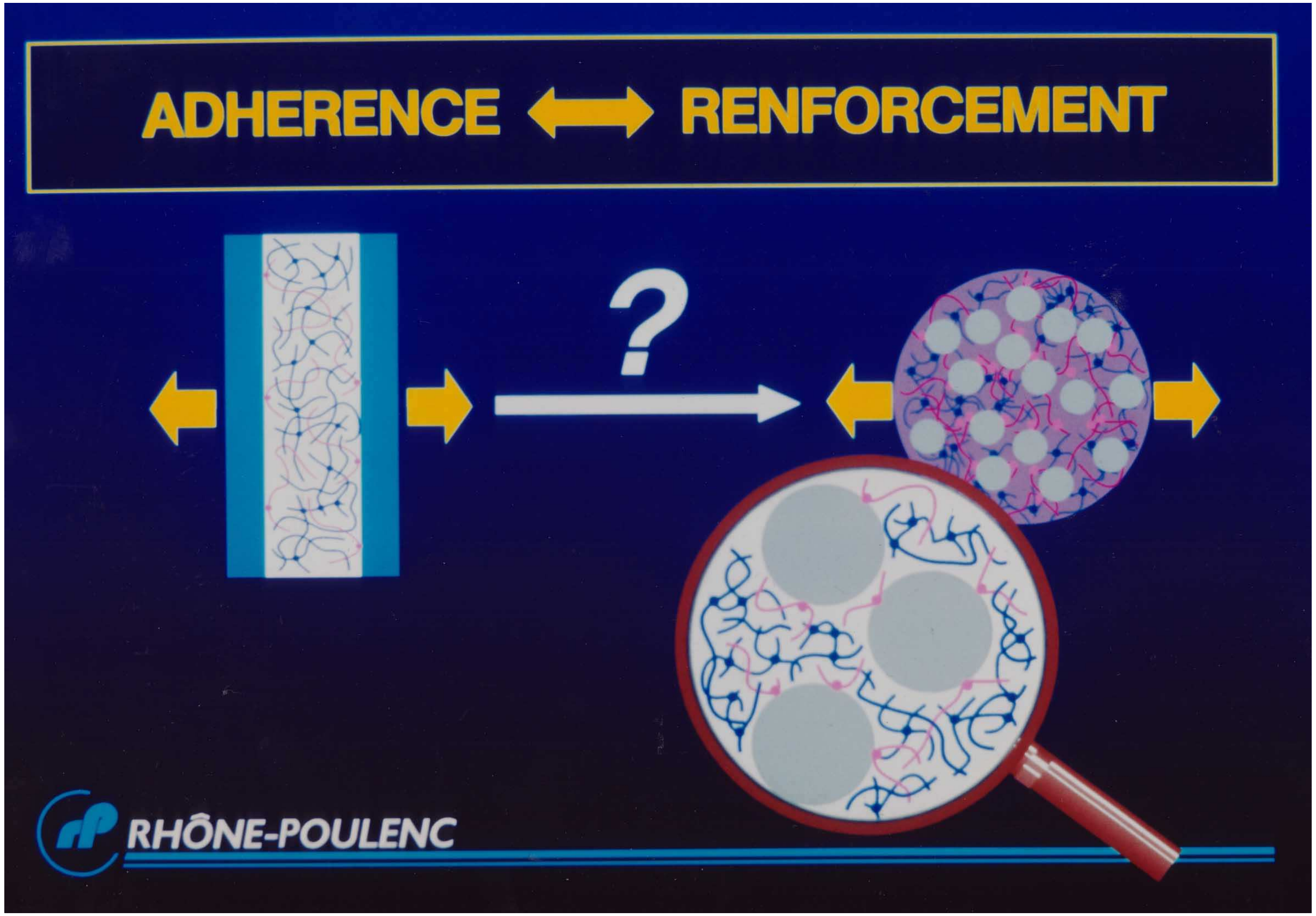
Les « polymères en couches minces »
Que faut-il « creuser »?

« Mixing and Comparing »

for stimulating creativity

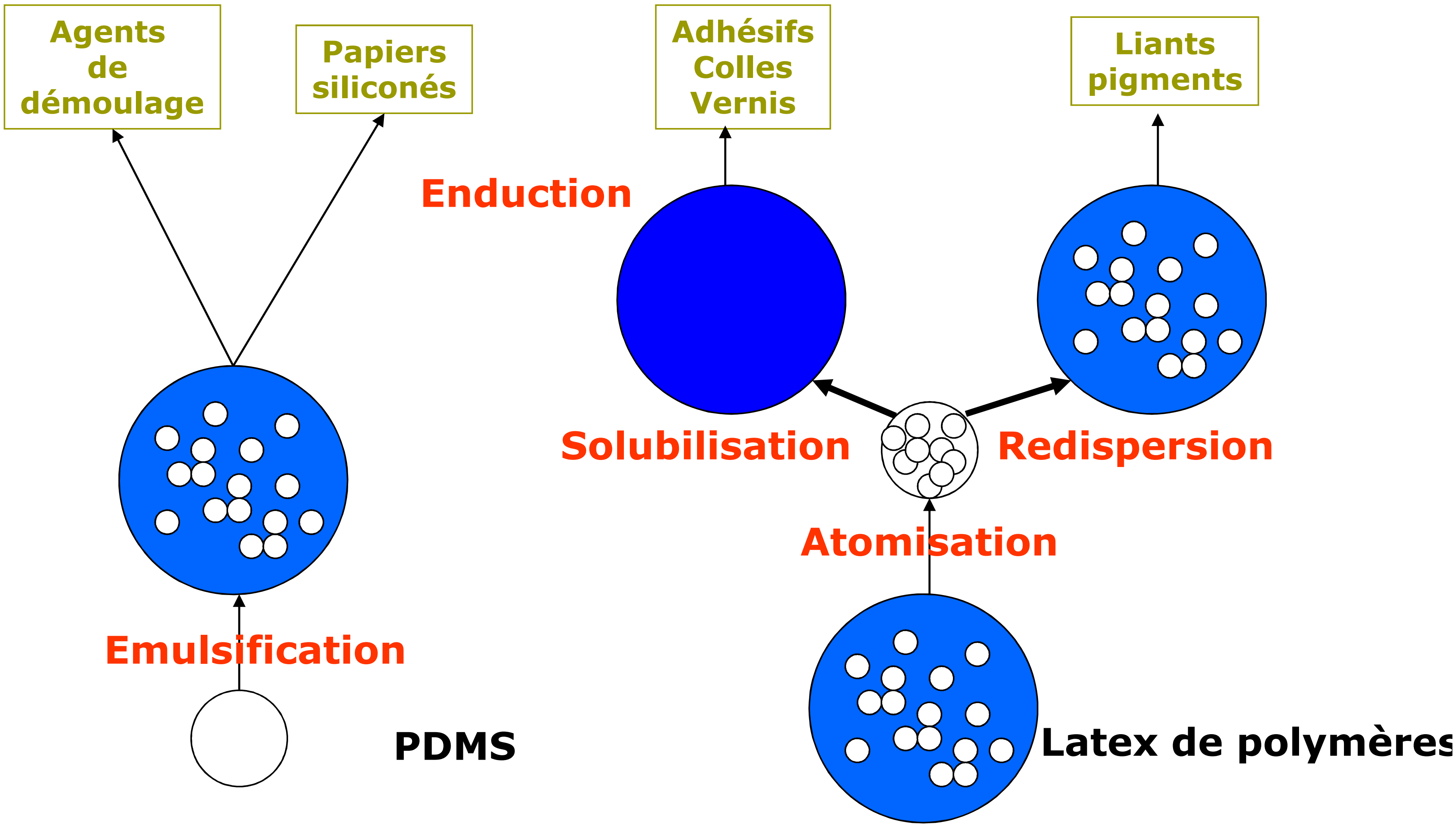
« Picasso and his masters » Paris, Louvre
June to december,2008

De l'adhérence au renforcement
Du macroscopique au « mésoscopique »



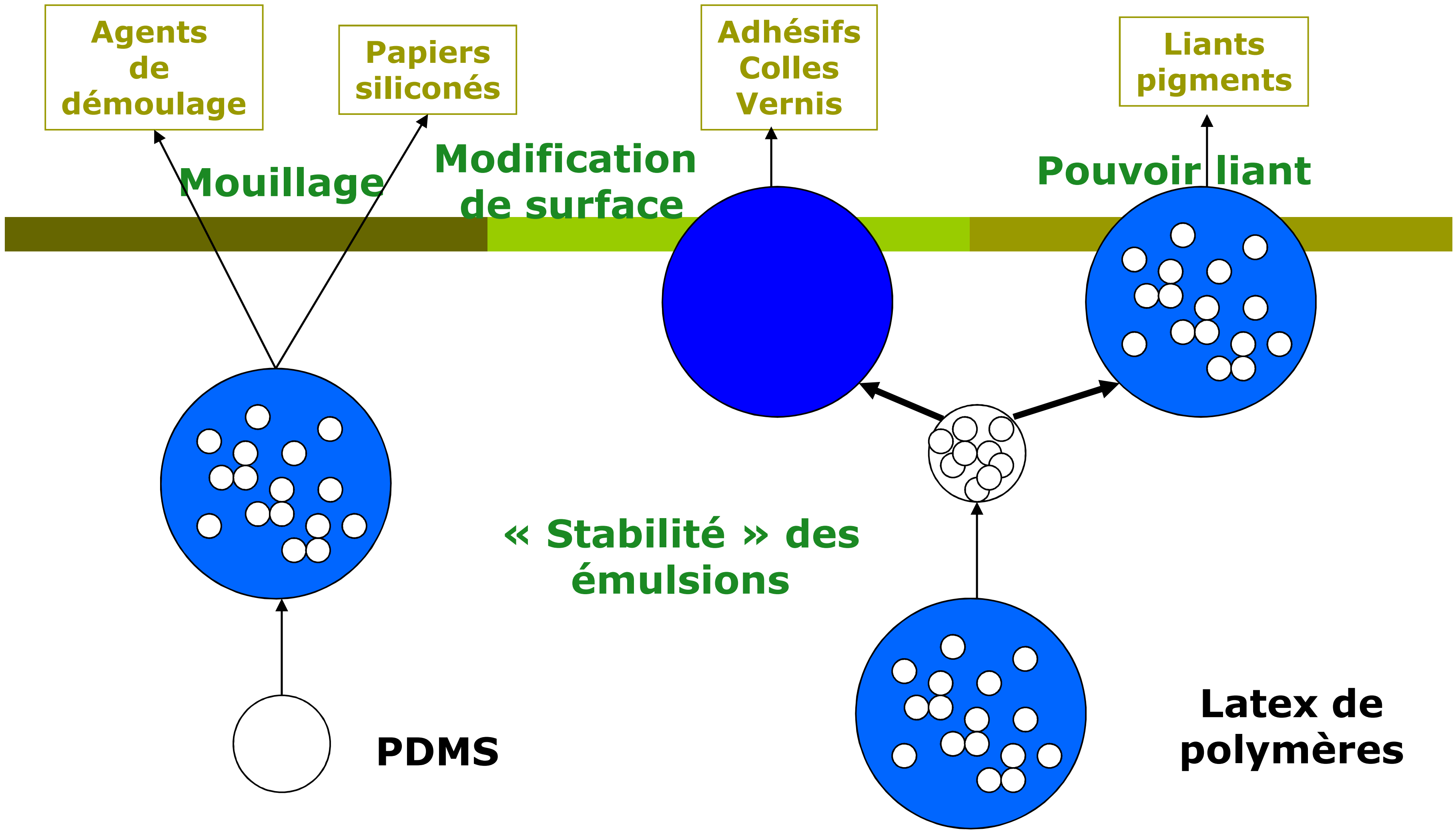
Comparaison PDMS/Latex

Applications « couches minces »: les technologies



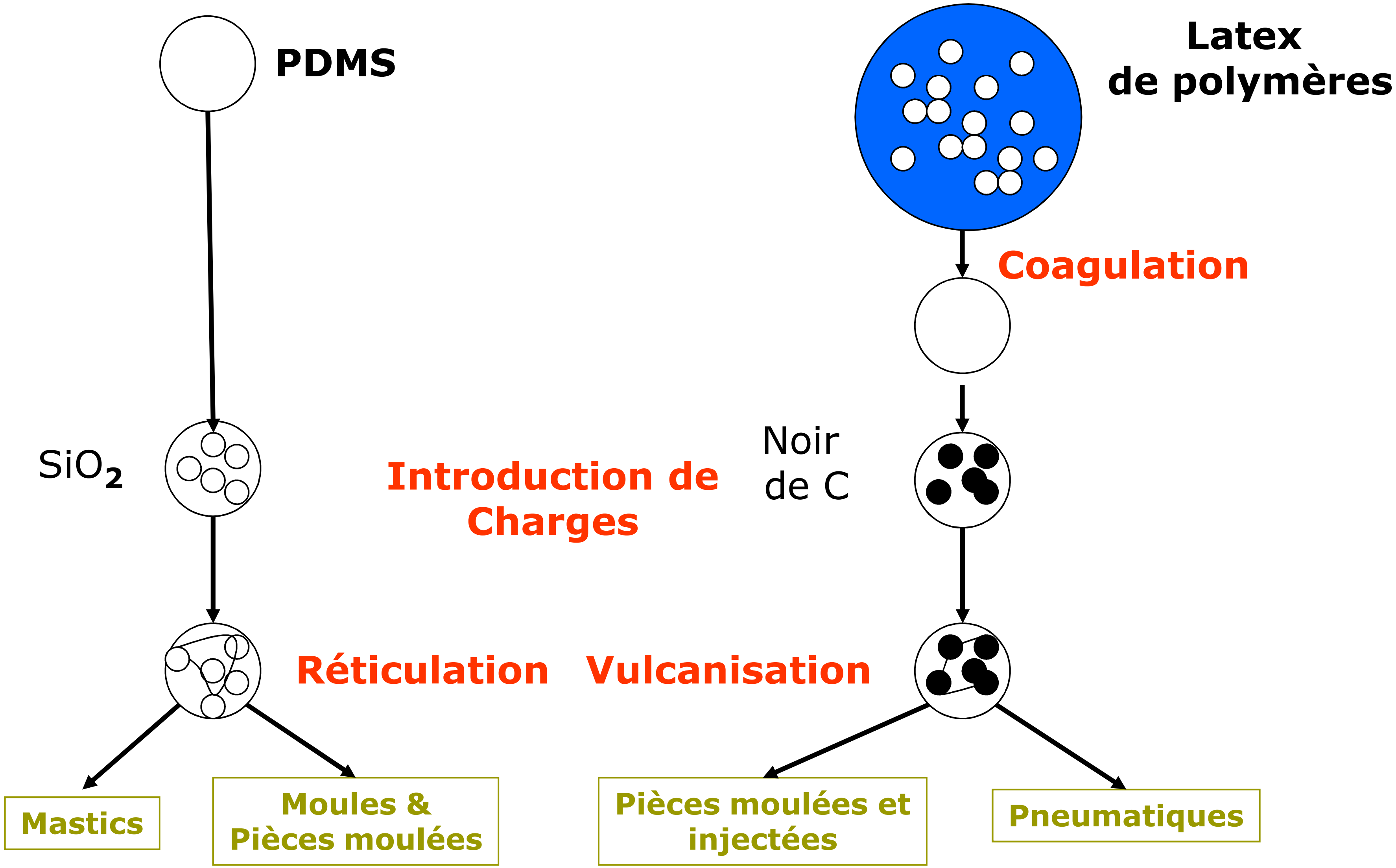
Applications « couches minces »

Des problématiques communes d'interfaces



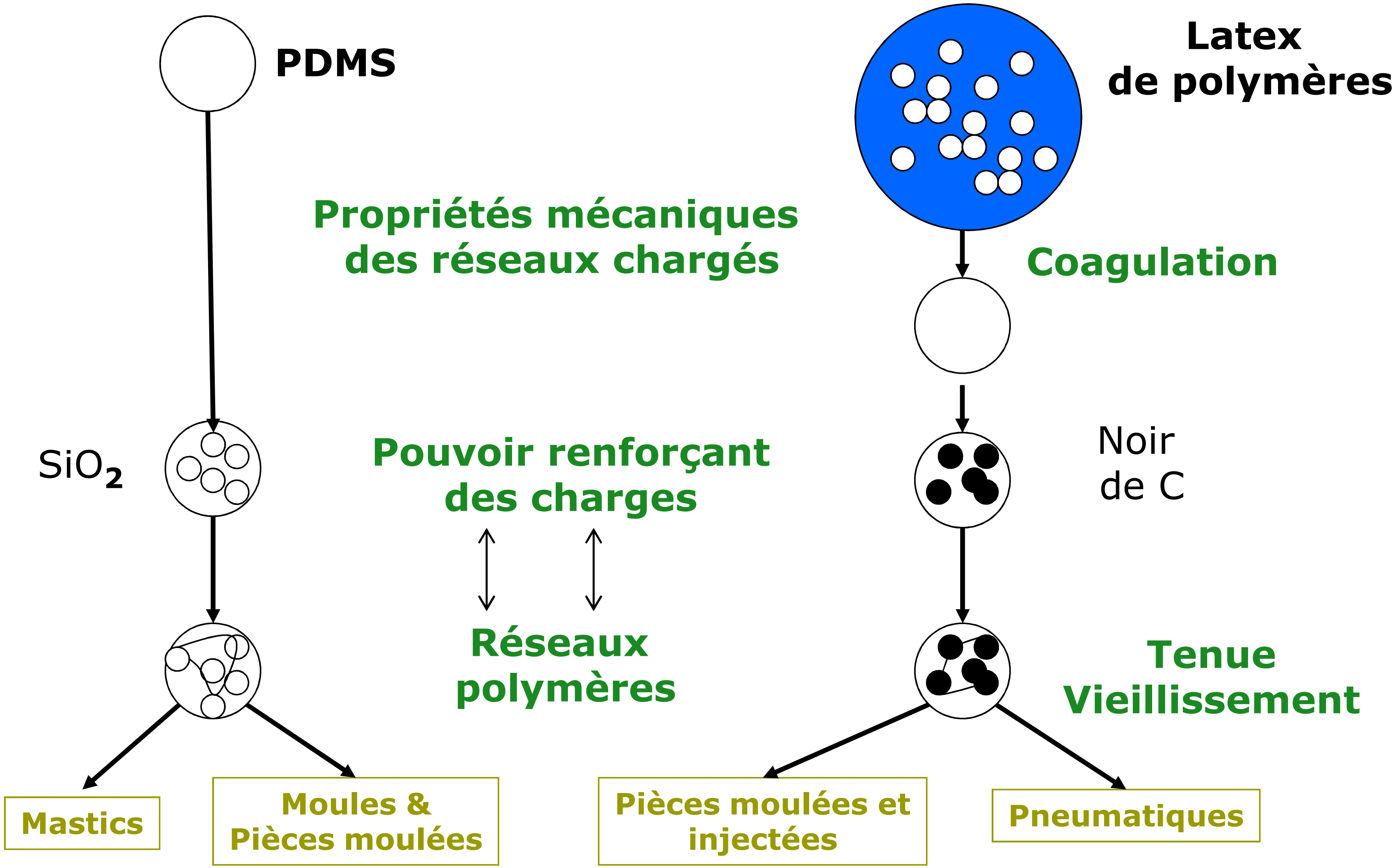
Comparaison PDMS/Latex

Applications « matériaux »: les technologies



Applications matériaux

Des problématiques communes



Réunir des communautés qui se rencontrent guère : 2 propositions

- Pouvoir liant des latex?
  - Le revêtement routier (granulat/bitume)
  - Couchage du papier (talc/latex)
  - Encre d’impression (pigment/résine)…
- Pouvoir renforçant des charges?
  - Charges pour élastomères
  - Charges pour thermoplastiques

Merci pour votre attention

et bon appétit…..