SILICONE SURFACE IMPREGNATION & COATING

Paper
label-release, bakery paper...

Textiles
airbags, sportswear, lingerie...

Building Materials
stones, concrete, wood...

but also:
tires, ships, corks, etc.
**GENERAL PROPERTIES**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si – O</td>
<td>106 kcal/mol</td>
</tr>
<tr>
<td>C – C</td>
<td>85 kcal/mol</td>
</tr>
</tbody>
</table>

Chain Valence angle

<table>
<thead>
<tr>
<th>Chain</th>
<th>Valence angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O-Si</td>
<td>130-140°</td>
</tr>
<tr>
<td>O-Si-O</td>
<td>110-115°</td>
</tr>
<tr>
<td>C-C-C</td>
<td>110°</td>
</tr>
</tbody>
</table>

Chain flexibility – Lubrication, hydrophicity, release properties

- low Tg (-123°C)
- low surface energy (~20 mN/m)

Thermal stability, weathering resistance

Durability well above organic polymers
Environmental Profile

- **SiO$_2$ (sand)**
- **Elemental Silicon**
- **Chlorosilanes**
- **Manufacturing**
- **Degradation**
- **Silicones**
- **Use**
WATER REPELLENTS
Risks
- Degradation (frost, moss, mold...)
- Appearance (efflorescence, spotting..)
- Economic (insulation loss…)

Exposure
- Infiltration,
- Raising Damp,
- Condensation

Substrates
- Roofing (Tiles…)
- Facades (Stones, Bricks, Concrete, Mortar, Stucco)
- Walls (Plaster…)
- Wood

Solutions
- Surface treatment
- Injection
Silicones Advantages

- Hydrophobia
- Low surface tension → spreadability
- UV Resistance → durability
- Water vapor permeability
Silicones Properties

- Molecular treatment (inside of the capillaries)
  - water proof (liquid water)
  - water vapour permeability (open pores)
  - No surface modification

\[
\text{deep penetration} = \text{durable treatment}
\]
Contact angle (°) for silicone resins on glass.

Few molecular layers are sufficient to provide optimum water-repellency.
Building protection with emulsions

Factors affecting penetration

Need a compromise (too reactive if too concentrated)
Substrate pore size vs. emulsion droplet size

Mercury Porosimetry
Cumulated volume (mm$^3$/g)

Pore diameter (µm)

solvent-based and water-based will penetrate differently
Building protection with emulsions

Should we adapt droplet size to pore size?

- $R_{\text{droplet}} > R_{\text{pore}}$ => no penetration?
- $R_{\text{droplet}} < R_{\text{pore}}$ => penetration?

... not only a matter of relative size!
Building protection with emulsions

Should we adapt droplet size to pore size?

When pores are too small:

Favorable for capillarity

Importance of water/oil interfacial tension (droplet deformability) and droplet/solid interfacial tension (=> wetting)

\[ R_{\text{droplet}} > R_{\text{pore}} \]

=> no penetration?
Building protection with emulsions

Impregnation of a porous material with an emulsion:

Important parameters are:

- $R_f$ mean pore size at front
- $\theta_{ws}$ water/solid contact angle
  $\Rightarrow$ capillary driving force
- $L$ droplet “position”
- $R_L$ mean pore size along $L$
  $\Rightarrow$ pressure loss along pore
- $R_d$ droplet size
- $R_p$ pore size
- $\theta_{os}$ oil/solid contact angle
  $\Rightarrow$ droplet wetting and deformation
Impregnation of a porous material with an emulsion:

\[ x(t) = A \sqrt{1 - \beta \sqrt{t}} \]

modified Washburn’s Law, with:

\[ A = \sqrt[4]{\frac{4 \gamma_w \cos \theta_{ws} R_w^2}{K R_f^2}} \]

\[ \beta = \frac{\gamma_{oil}}{\gamma_w \cos \theta_{ws}} \left[ - \frac{R_f \cos \theta_{os}}{R_p} - \frac{R_f}{R_d} \right] \]

Allows to describe different penetration regimes (depending on \( \beta \))

Washburn, *Phys Rev.* (1921), 17, 273
Marmur et al. *JCIS* (1989), 189, 299
Regimes of penetration:

Relative droplet size ($R_d/R_f$)

- Impossible
- Slower
- Accelerated
- Unhindered

Relative pore size ($R_p/R_f$)

- $\theta_{o/s} > 90^\circ$
- $\theta_{o/s} < 90^\circ$
- No obstacle

Not enough surfactant to deform the droplets

$R = R_p \cdot |\cos \theta_{o/s}|$

$\gamma_{w/o} / \gamma_w$
Building protection with emulsions

Penetration depth of different silicone formulations:

![Bar chart showing penetration depth for St Vaast Sandstone and Concrete, comparing in solvent, Emulsion, NanoEmulsion, and MicroEmulsion forms.](chart_de.png)

(2x1mn impregnation of 10% active material solutions, allowed to dry out for 48h)

**Importance of droplet size + derformability**
Building protection with emulsions

Analysis of silicone penetration:

Excess surfactant help droplet penetration
Should we adapt droplet size to pore size?

When pores are bigger:

Penetration might still be hindered, if affinity between surfactant and solid is too strong

\[ R_{\text{droplet}} < R_{\text{pore}} \]

\( => \) penetration?
Importance of interactions between surfactant and substrate:

- High retention
- Low retention => deeper treatment
Building protection Basic principles

Macroscopic protection: put enough silicone at macroscopic level

**Water Uptake on St Vaast**

- **need ≥ 4% silicone**

**Water Uptake on Tuffeau**

- **need > 10% silicone**
Building protection Basic principles

Macroscopic protection: put enough silicone at macroscopic level

Porous Substrate:
- Specific Surface, $S$
- Specific Porous Volume, $V_p$

Mean Thickness, $h$
Solution concentration, $C$

$$h = \frac{V_p}{S} \cdot C$$

<table>
<thead>
<tr>
<th>Examples</th>
<th>$S$</th>
<th>$V_p$</th>
<th>$h$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>St Vaast Stone</td>
<td>2 m²/g</td>
<td>0.25 cm³/g</td>
<td>50Å</td>
<td>4%</td>
</tr>
<tr>
<td>Tuffeau Stone</td>
<td>15 m²/g</td>
<td>0.31 cm³/g</td>
<td>50Å</td>
<td>24%</td>
</tr>
</tbody>
</table>

knowing basic substrate characteristics can help provide a suitable treatment
Treating porous materials with emulsions can be tricky, but formulations can be optimized:

- Importance of surfactant type and proportion
- Importance of droplet size but also deformability (play on interfacial tension to allow large droplets to enter smaller pores)
- Importance of surfactant interaction with solid (avoid chromatographic retention of surfactants on solids)
WATER REPELLENT (different forms)

- **Creams and pastes**: are designed more particularly to ensure better penetration of the silanes in concrete. Two problems inherent to this type of formula are identified: form of application in thick coats, which seems restrictive, and the risk of losing active material through volatilisation.

- **Microemulsionable concentrates**: appear to be fairly economical solutions (100% active, hydrodispersible but without the need for any excess agitation). Main disadvantage is their very low stability after dilution.
**SILOXANES VERSUS SILANES**

**SILANES**
- small molecules penetrate deeper and more easily
- very high reactive site
- not necessarily require a perfectly dry surface for application;
  …but also numerous downsides:
  - volatility
  - toxicity (often irritants)
  - need for humidity and a catalyst to react
  - low beading effect
  - risk of leaching where insufficient cross linking.
  - So as to attenuate these disadvantages, possible to use oligomerised or “advanced” silanes. (= siloxane oligomers )have the following advantages:
    - less volatile
    - less toxic
    - less alcohol salted out;
    - …but:
      - the silane’s functionalities are less well distributed throughout the network;
      - less penetration in non-porous materials.
SILOXANES

- non volatile
- very low toxicity
- good beading effect as of the first hours
- no risk of leaching

...with the following downsides:
- high viscosity: sometimes have to be diluted in solvents;
- require very dry surface for application;
- molecular weight of several thousand g/mol => poor penetration

That means silane content must be modulated according type of
surface/ application conditions. For example a low-porosity surface
such as fresh concrete is very reactive, requiring the high
penetration of silanes, . On the other hand, a much lower level of
silane content is recommended for treating neutral and porous
materials
WATER REPELLENT DILUTION (solvent based products)

- Generally: aliphatic (white spirit, isoparaaffin) and aromatic hydrocarbons. Some products (with high silane content) can also be diluted in anhydride alcohols, typically ethanol or 2-propanol (anhydride aspect is essential because of the cross linking before it is applied). These alcohols are suitable for formulations, better compatibility with materials which are sensitive to aromatic solvents potentially exposed during application (tar seals, or polystyrene for example).

- The type of solvent used will affect the product’s penetration capacity: low-polarity solvents tend to be considered more effective. Their low superficial tension makes them easier to spread on a varied range of surfaces, and their relatively low density is a benefit in the case of treatments by capillarity.
WATER REPELLENT DILUTION (water based product)

- Recommending demineralised water gets round local water hardness variations (content of calcium and magnesium ions). The presence of electrolytes modifies interactions between water and surfactants, and can lead to the destabilisation of droplets and therefore the destruction of the emulsion.

- This risk is in fact fairly limited since most water repellent emulsions tested tend to be non-ionic surfactant based.
• **Rhodorsil H224 (69% AM) & Rhodorsil BP 9400 (100% AM)**

**Rhodorsil BP 9400** is versatile: it can be used on many porous substrates and is particularly recommended for the treatment of stone, brick, and « old » concrete (carbonated).

**Rhodorsil BP 9400** has been certified by CSTC: HD-340/133-150

Generally these products are applied diluted down to 6 - 8% into solvent.
RHODORSIL BP 9710 (44% AM)

BP 9710 is an emulsion of an alkylpolysiloxane oligomer designed to protect buildings against moisture.

BP 9710 is versatile: it can be used on many porous substrates, particularly on lime stones, sand stones, mortars, renderings or bricks.

Rhodorsil BP 9710 has been certified by CSTC: HD-340/133-151

Generally, RHODORSIL BP 9710 is diluted between 4% and 8% of active material in water.
RHODORSIL BP 97XX Range

- **Rhodorsil BP 9710**: Ready to use water based water repellent:
  - versatile (performances on many different porous substrates)
  - good storage stability (12 months concentrated / 12 months diluted)
  - controlled reactivity

- **Rhodorsil BP 9705**: Ready to use water based water repellent:
  - low reactivity
  - Designed as an additive for various formulations
  - Stability 12 month
PRODUCTS POSITIONNING

• Technology

![Diagram showing product positioning with axes for Reactivity, Durability, Oil Repellency, Water Repellency, Beading Effect, and Penetration Depth. Different product types are color-coded: Solvent based (blue), Water based (pink), Fluorinated (green), and Waxes (cyan).]
Building Protection: Water based products

- BP9710 - 4% on wall
- BP9710 - 4% in mortar
- BP9710 - 4% on cement
BP water repellents after 3 years outdoor exposure

TUFFEAU : lime stone north exposure

SAVONNIERE : lime stone south exposure

All products have been diluted down to 8% in the appropriate solvent
Damp-proof course system

The aim is to make the capillary network of the material water-repellent to avoid water working its way upwards.

• When the degree of humidity is very high, solvent based Rhodorsil H 224 makes it possible to quickly achieve the required results.

• Standard dilution: 1 part of H 224 for 10 parts white spirit
Building Protection : Solvent based products

- **BP 9600 : for lime paints**
  
  Surface treatment to protect lime paints against water damages (stains ....)
Inorganic material loses its binder and cohesion under the action of water and harmful elements, mainly acid, which penetrate it, causing reactions.

RHODORSIL RC are designed to treat materials which show signs of damage

- Formation of a new binder to recover the mechanical properties of the substrate.
- Reduction of the water absorption (RC 80)
Building Protection – stone consolidation

- The Rhodorsil RC70-80-90 Range:

  - RHODORSIL RC 70: based on ethyl silicate
  - RHODORSIL RC 80: based on ethyl silicate + polysiloxane resin
    = Consolidation + water repellent action
  - RHODORSIL RC 90: based on ethyl silicate + methylphenylpolysiloxane resin
    = Consolidation: more flexibility and binding effect

Under the action of the residual water in the pores and a catalyst, it is transformed into silicic acid gel.

\[
\begin{align*}
\text{Si (OC}_2\text{H}_5\text{)}_4 & + 4 \text{H}_2\text{O} \rightarrow \text{Si (OH)}_4 + 4 \text{C}_2\text{H}_5\text{OH}
\end{align*}
\]
Building Protection – stone consolidation

• The Rhodorsil RC70-80-90 Range

After consolidation, the porosity of initial stone is recovered (filling of holes and grain joints).
Thermal Insulation with Silicone Paints and Water Repellents
In France, Building contributes to 43% of the total consumed energy

Thermal regulations in Europe, (2000, 2005, ...) comes into a range in France:
- 2012 => new building energy consumption = 50kw/m2/year.
- 2020 => Buildings with positive energy

HQE (france) & BREEAM (UK) should be joined in 2012
Studied systems:

*Breeze blocks + cement render + water repellent*

- **Cement render:**
  - 400 kg of cement / m$^3$ dry sand,
  - water/cement = 0.5.

- **Application of 2 coats of render:**
  - 1st coat thickness: 13mm - Drying: 7 days at 23°C and 60% RH
  - 2nd coat thickness: 7mm - Drying: 7 days at 23°C and 60% RH
APPLICATIONS

For water repellents:

- Application with a brush until substrate saturation.
- Drying 7 days at 23°C 60% RH

Systems are then:

- Coated with wax
- Dried at 45°C during 48h,
- Weighted,
- And placed onto the rain apparatus
Rain test:

- Water is pulverized with the help of compressed air
- 2 blocks can be tested at the same time
- Good repeatability of the results (% water uptake +/- 0.2%)
Results of rain test for water repellents

Breeze block + cement

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Water uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>15</td>
<td>1.5</td>
</tr>
<tr>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>25</td>
<td>2.5</td>
</tr>
</tbody>
</table>

- Blank
- BP 9400 8% (SB)
- BP 9710 8% (WB)
- BP 9500 8% (SB)
- BP 9600 8% (WB)
Comparison rain test / capillarity test

Water repellents

Note:
capillarity test = immersion of the treated face into 3 mm of water
THERMAL LOSS CALCULATION

- \[ Q = U \times S \times \text{delta}T \times h \]
  
  \[ = \text{coeff thermal transmission} \times \text{Surface} \times \text{Delta T}^{\circ}C \times \text{time (h)} \]

With \( U = 1 \) / termal resistance = \( \lambda/e = \text{termal conductivity} / \text{thickness} \)

And \( \lambda = \lambda_0 \times e^{0.08 \times \text{humidity}} \)

And \( \lambda_0 = \text{termal conductivity of dry material} \)

Postulates (individual house)

- Total surface = 80 m² of façade, exposed surface= 40 m².
- Chosen place= Nan Yueh in China (1874mm rain/ year)
- Number of days with maximal humidity for our system = 50 days for Nan Yueh
- Internal comfort temperature : 19°C.
- External temperature when heating (October – April) is 6°C in Nan Yueh.
- Price: 1kW.h chinois= 0.0479 euros
- \( \lambda_0 = 1 \)
**THERMAL LOSS COST / IMPACT OF SILICON**

- Calculation

\[ Q_{TOT} = Q_{\text{exposed wet wall}} + Q_{\text{exposed wall during drying}} + Q_{\text{dry exposed wall}} + Q_{\text{non exposed wall}} \]

<table>
<thead>
<tr>
<th>With water repellent BP9400</th>
<th>Breeze block alone</th>
<th>Breeze block with cement render</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saving for one year ( / breeze block without cement render )</td>
<td>reference</td>
<td>4.3%</td>
</tr>
<tr>
<td>Breeze block + cement render untreated</td>
<td>Breeze block + cement render Treated with BP9400</td>
<td></td>
</tr>
<tr>
<td>Saving for one year ( / breeze block with cement render without treatment)</td>
<td>reference</td>
<td>13.3%</td>
</tr>
</tbody>
</table>
Photos hydrofugation

terra bricks hydrofugation

photos hydrofugation consolidation

photos rofugation consolida