48th Annual Convention
Society of Wood Science and Technology

# New Protection Systems With Silicones and Silanes

C. Mai, S. Donath, O. Weigenand, H. Militz

Institute of Wood Biology and Wood Technology
University of Göttingen

# General Aspects

- Si is the second most frequent element on earth
  - Makes up 27.5% of the earth‘s crust
  - Is predominantly found as polymeric $SiO_2$ :

$$m\ SiO_2 \cdot n\ H_2O \quad - \quad [Si(OH)_4]$$

- Si occurs in higher concentration in tropical wood species

# General Aspects of Silicon

## Natural process of silification:

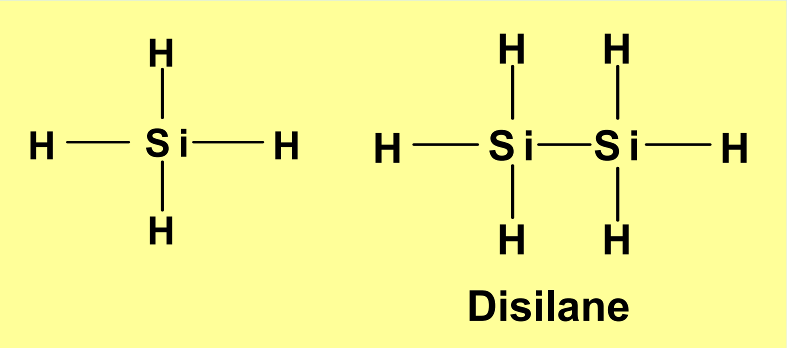
## Petrified wood

From: Museum of natural history, Vienna

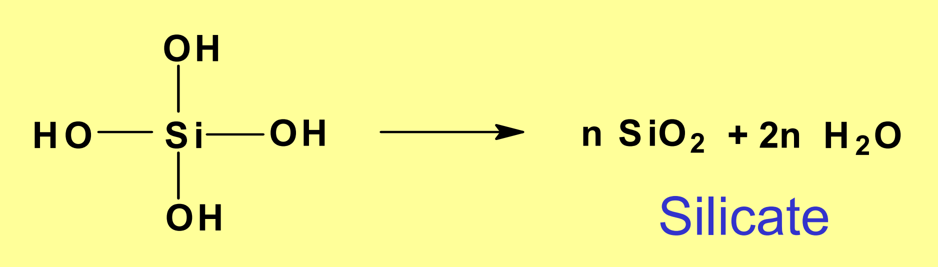
# Chemistry and Nomenclature

- Silanes: Hydrogen compounds of silicon

  $Si_nH_{2n+2}$ (n=1-15)

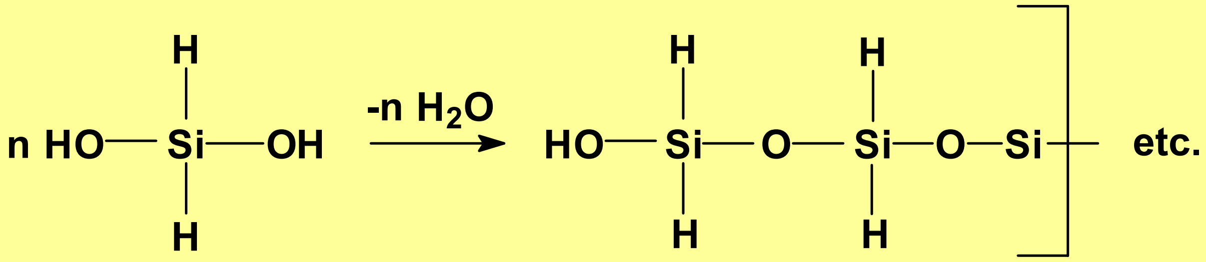



- Halogen silanes: $SiH_3Cl$; $SiH_2Cl_2$, $SiHCl_3$
- Silicic acid:



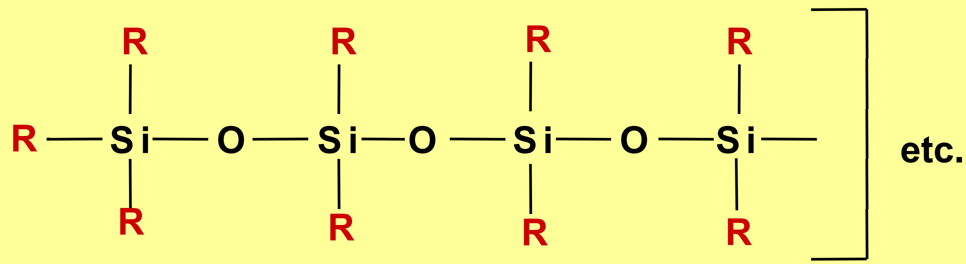
# Chemistry and Nomenclature of Silicon Compounds

- **Silanol: $H_3SiOH$ Silanediol: $H_2Si(OH)_2$ etc.**




Siloxane

- **Silicone (polyalkylsiloxane): Organic derivatives of poly(silicic acid)**




**R = Alkyl**

  - Si-C bond is stable towards acids and bases

# Aims of Silicon-Treatment

1. **Protection against degrading and staining fungi and insects**
   - Basidionmycetes / Moulds
   - No biocide
2. **Improvement of properties related to moisture and weathering**
   - Swelling /shrinkage
   - adhesion of  coatings and varnish
   - UV degradation

**⇧ Incorporation of silicon compounds into the cell wall**

# Aims of Silicon-Treatment

3. **Improvement of elasto-mechanical properties**

   - hardness
   - tensile strength
   - fire resistance

**⇑ Can be achieved by deposition of silicon compounds into the lumina of the wood cells**

# Treatments

- Inorganic silicates ("water glass")
- Silanes (sol-gel process)
- Silicones
- Micro-emulsion technology

# "Water glass"

## What is "water glass"?

- Water-soluble K or Na-silicates or their solutions
- Alkaline (pH over 12)

- **Problem: Fixation:**
  - Precipitation in the wood through acids
  - Precipitation with salts ($CaCl_2$, $Al_2(SO_4)_3$, borax)

# “Water glass”

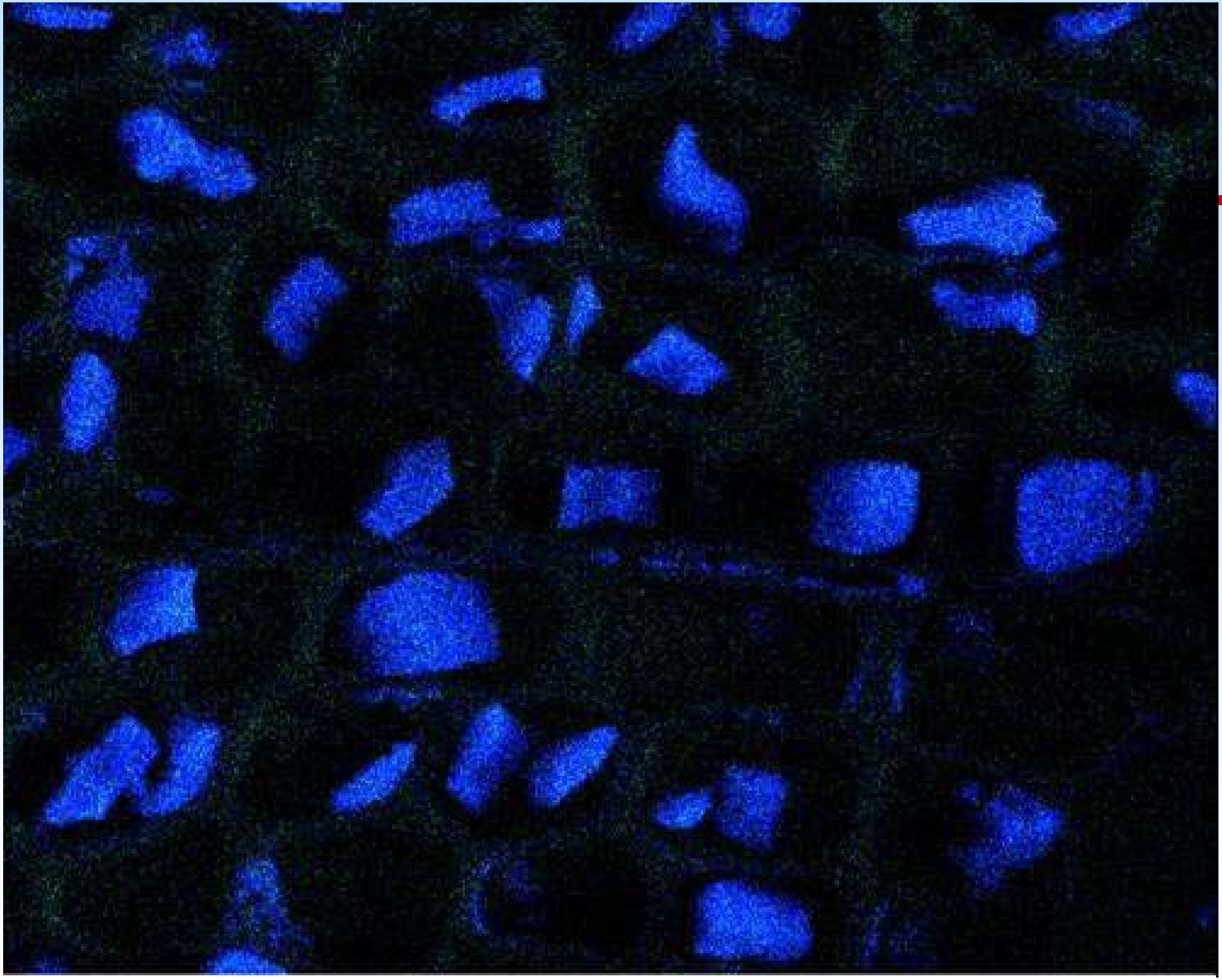
## Fixation:

### Matthes et al., Erfurt (1998 – 2003)

- Precipitation through $CO_2$ from air
- Needs several weeks for curing

### Furuno et al. (1991 - 2001)

- Precipitation through salts (2 impregnation steps)
  - E.g. boron compounds, $Al_2(SO_4)_3$ or $CaCl_2$, $BaCl_2$



# „Water glass“: white / brown rot

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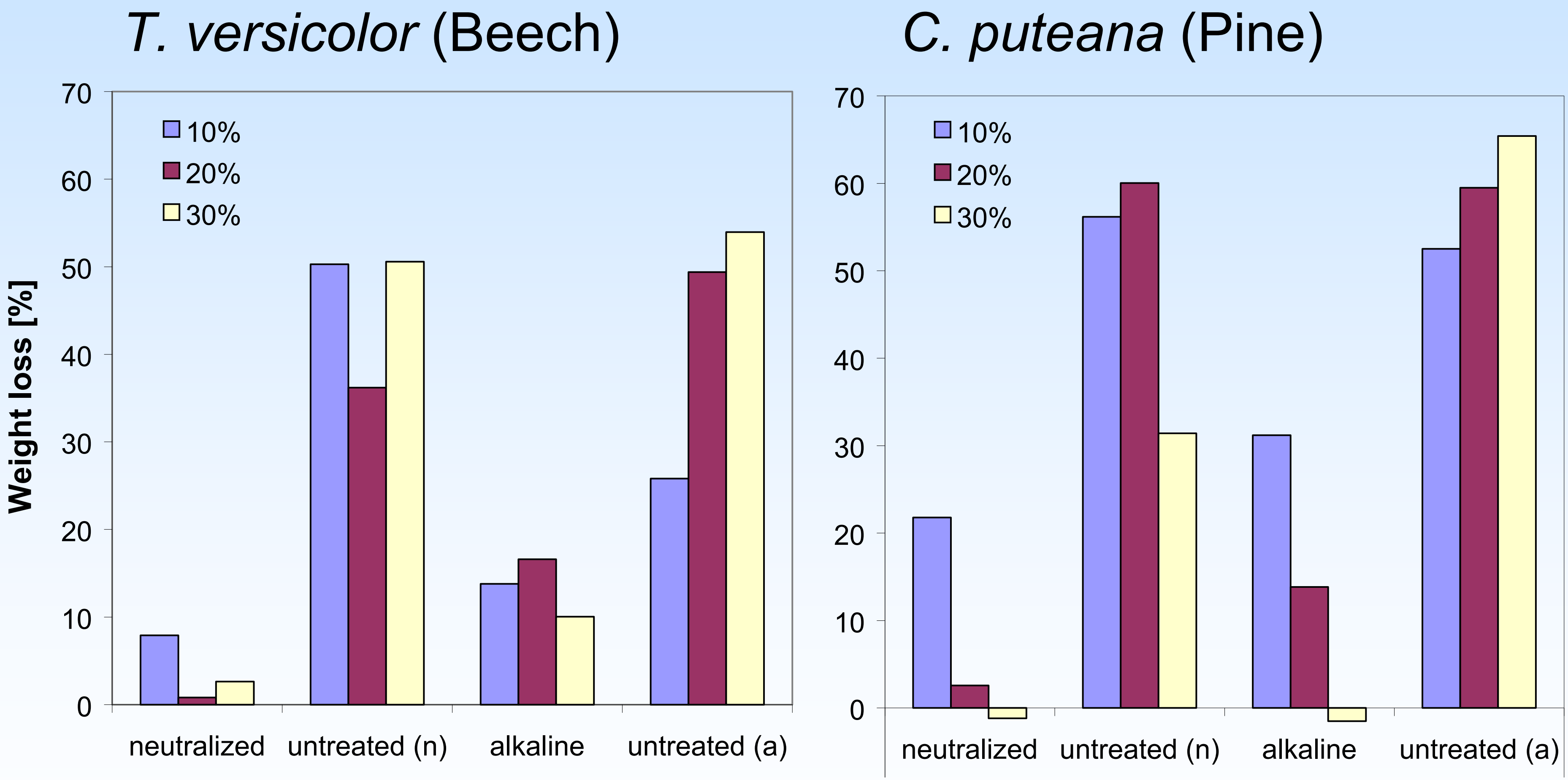


# "Water glass"

## Results

- Decay resistance (EN 113)
  - High
    - Because of high pH
- Enhanced fire resistance
- Increased hygroscopicity
- High pH (problems at high drying temperature)
- Mechanical
  - ASE low increase
  - Hardness unchanged or increased
  - Strength is significantly reduced
  - Dynamic MoE un-changed

# “Water glass”

## MASID umwelterhaltende Produkte GmbH

- “Woodbliss”: (aqueous solution, pH >12)
  - More than 10% silicate (water glass), up to 10% silicic acid (to improve penetration)

## Timbersil (Springfield, VA)

- „Sodium Silicate Technology (SST)“

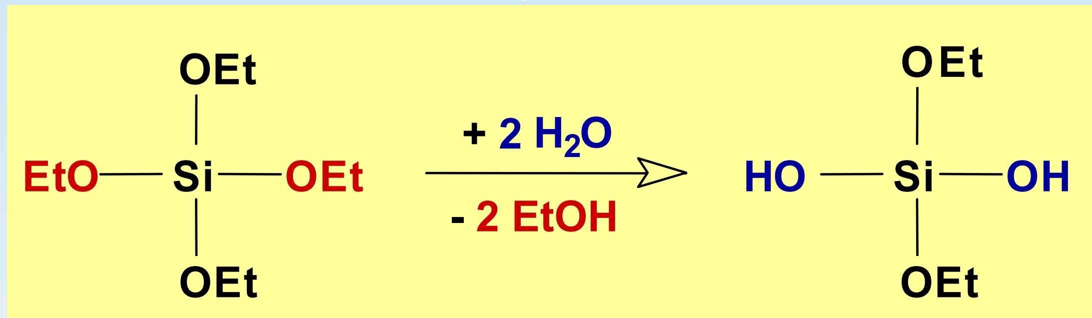
# Treatments

- Inorganic silicates ("water glass")
- **Silanes (sol-gel process)**
- Silicones
- Micro-emulsion technology

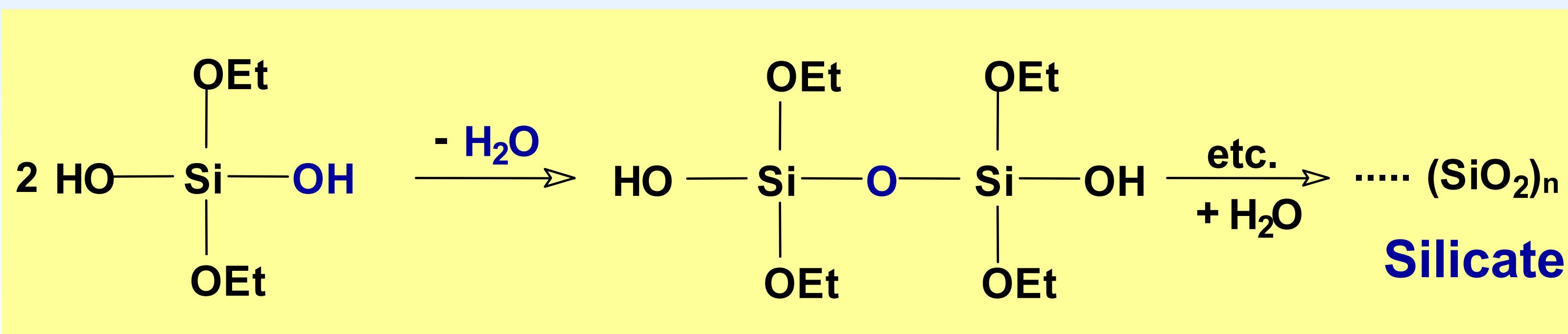
# Wood-inorganic composites by sol-gel process

- Two stage process
  - **Hydrolysis** (here Silicic Acid Esters)

Tetraethoxy silane (TEOS)




  - **Condensation**

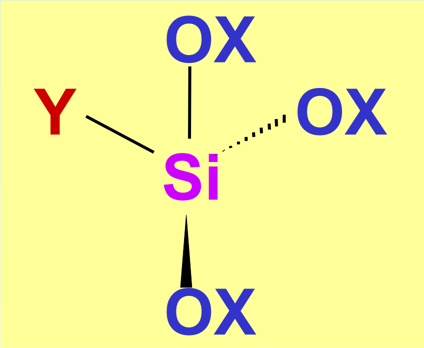



- End product is an amorphous silicate (glass)

# Silane Types

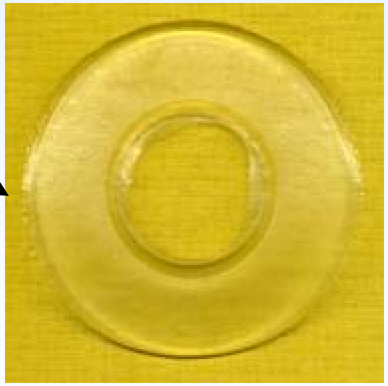
Y = "Organo-functional group"

OX = "Silicon-functional group, $OCH_3$, $OC_2H_5$ etc.




TEOS → $SiO_2$

MTES → $Me\text{-}SiO_{3/2}$



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# Wood-inorganic composites by sol-gel process

Saka et al. (1992 - 2001)

How to treat?

<u>Si must incorporated into the cell wall!!</u>

- Pre-conditioning of wood to fibre saturation point
  - Impregnation with TEOS in ethanol (free of water)
  - Condensation in the cell wall
- ASE: about 42%
- Water uptake is reduced

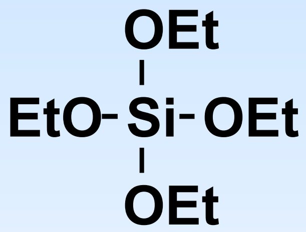
# Wood-inorganic composites by sol-gel process

Böcker et al. (2001), Böttcher et al. (1999)

Silanes are hydrolysed before the impregnation. Impregnation is performed with pre-condensed sols (in ethanol)

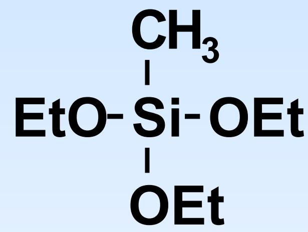
- Properties:
  - WPG: 5 – 50%
  - Reduced moisture content
  - ASE: 60% (at 45% WPG)
  - Low decay resistance
    - Enhanced by boron addition ("controlled release")

# Alkoxysilanes



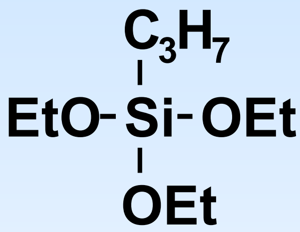

TEOS

Tetraethoxysilane




MTEOS

Methyl-
Triethoxysilane




PTEOS

Propyl-
Triethoxysilane

# Impregnation Methods

**"Sol impregnation"**

1. Conditioning of Wood Samples at 65% r.H.
2. Hydrolysis of the silane (Pre-hydrolysis)
3. Impregnation with Sol
4. Curing at 103°C

**"Silane impregnation"**

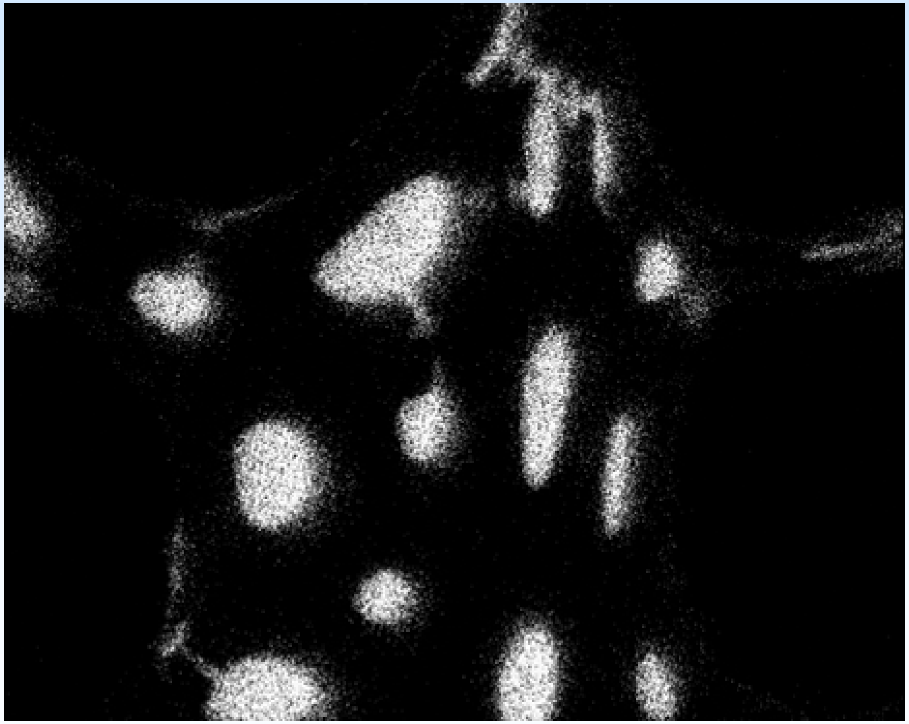
1. Conditioning of wood samples at 100% r.H. (fibre saturation)
2. Impregnation with silane/catalyst mixture
3. Curing at 103°C

# Wood Samples

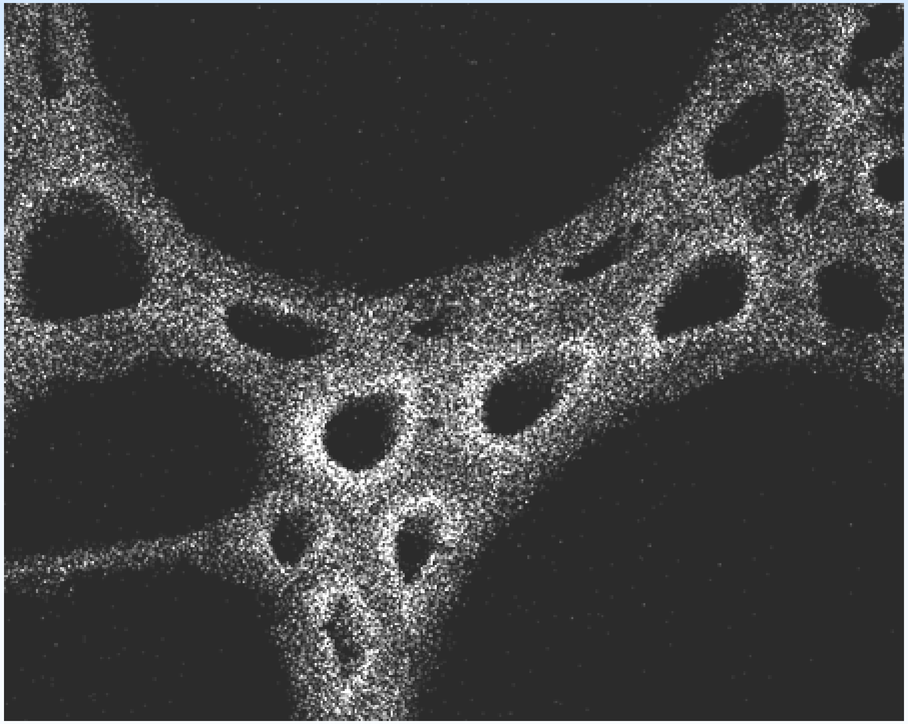
| Examination | Wood Species | Sample Size |
| --- | --- | --- |
| Water Uptake,<br>Dimensional stabilization | Beech | 25 x 25 x 10 mm<br>(rad x tang x long) |
| Soil Bed Test<br>(ENV 807) | Pine Sapwood | 5 x 10 x 100 mm |
| Basidiomycete Test (Mini-block)<br>(*T. versicolor, C. puteana)* | Beech<br>Pine Sapwood | 5 x 10 x 30 mm |

# Penetration of Silanes

**Sol** (pre-hydrolysed)



**Silane** (monomer)



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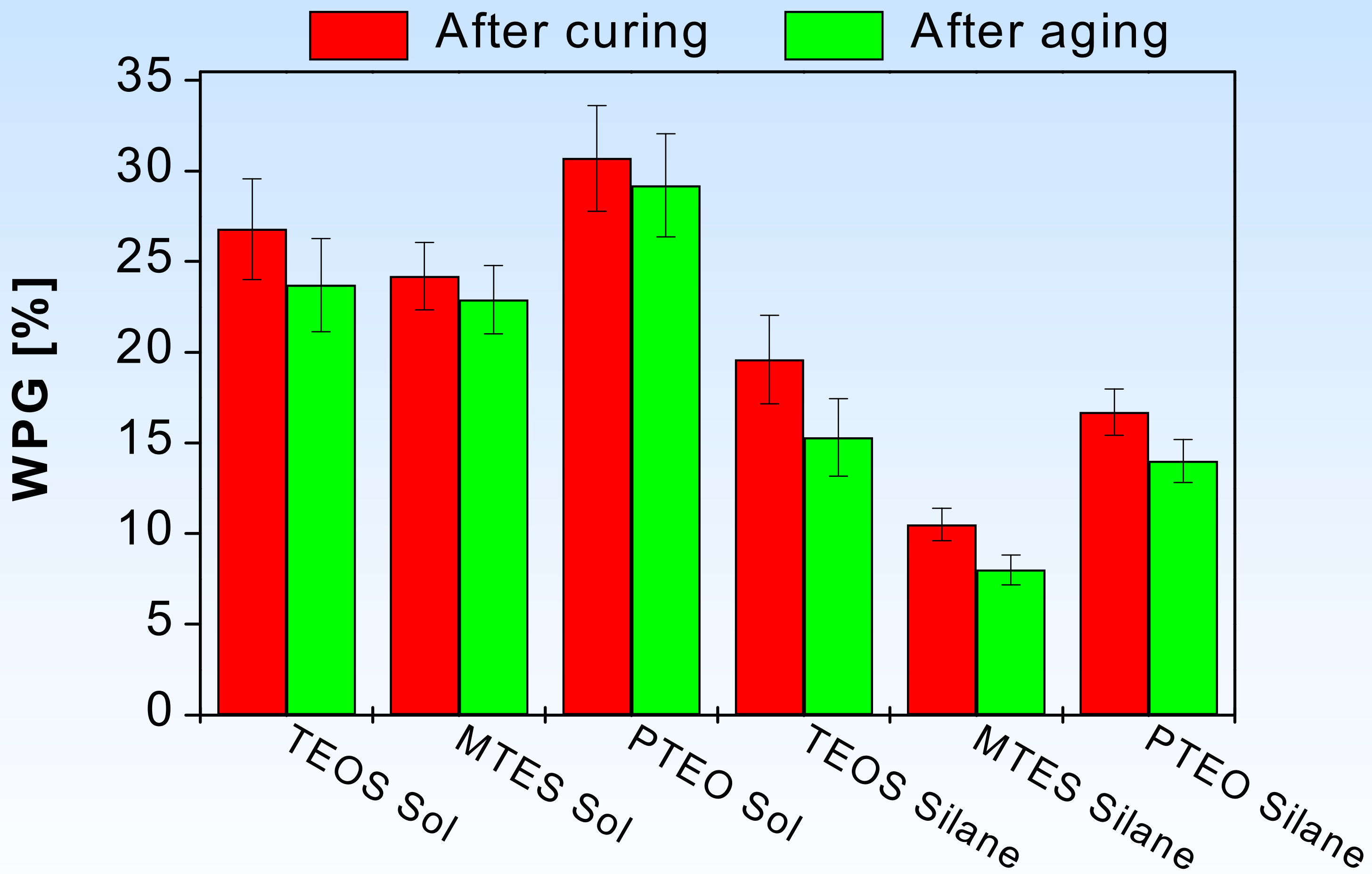
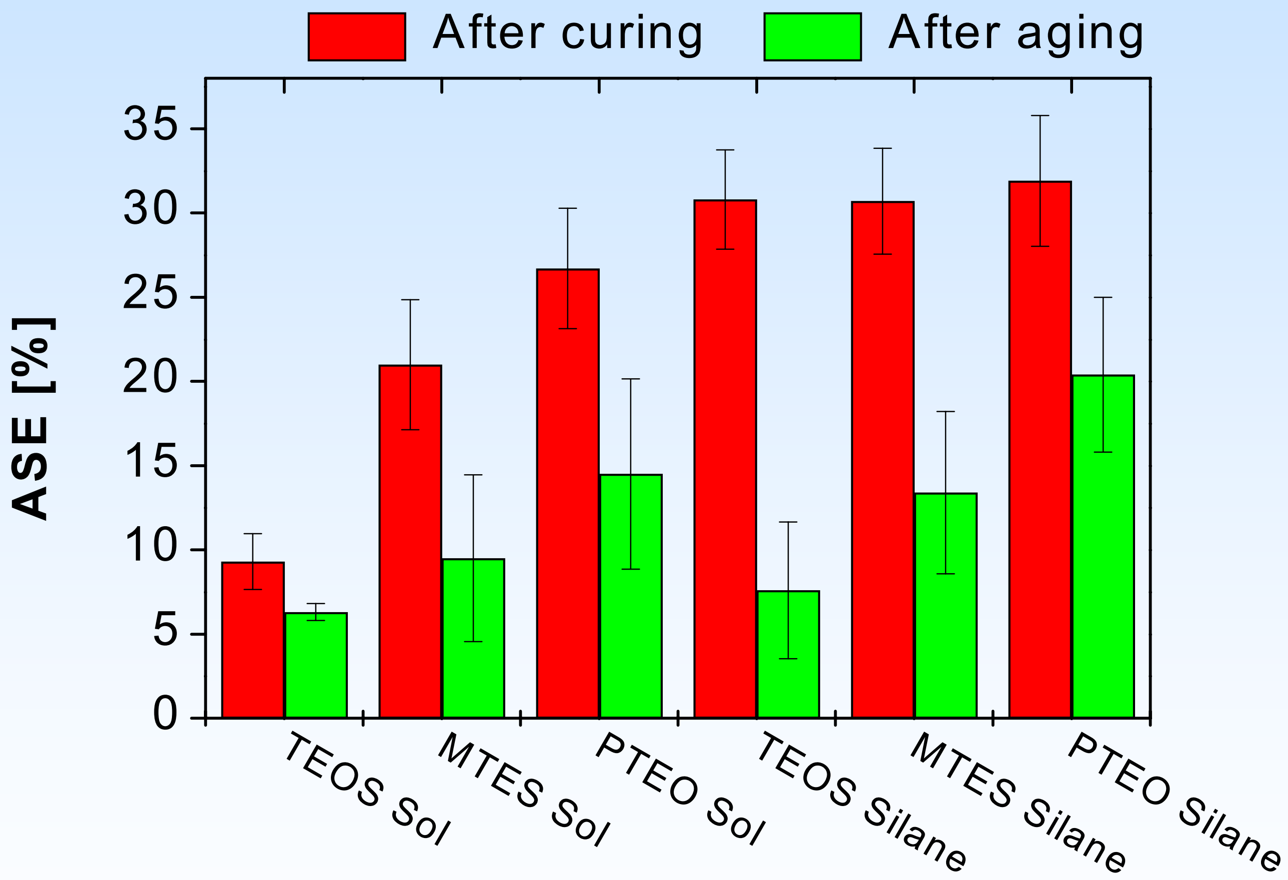
# WPG (beech)

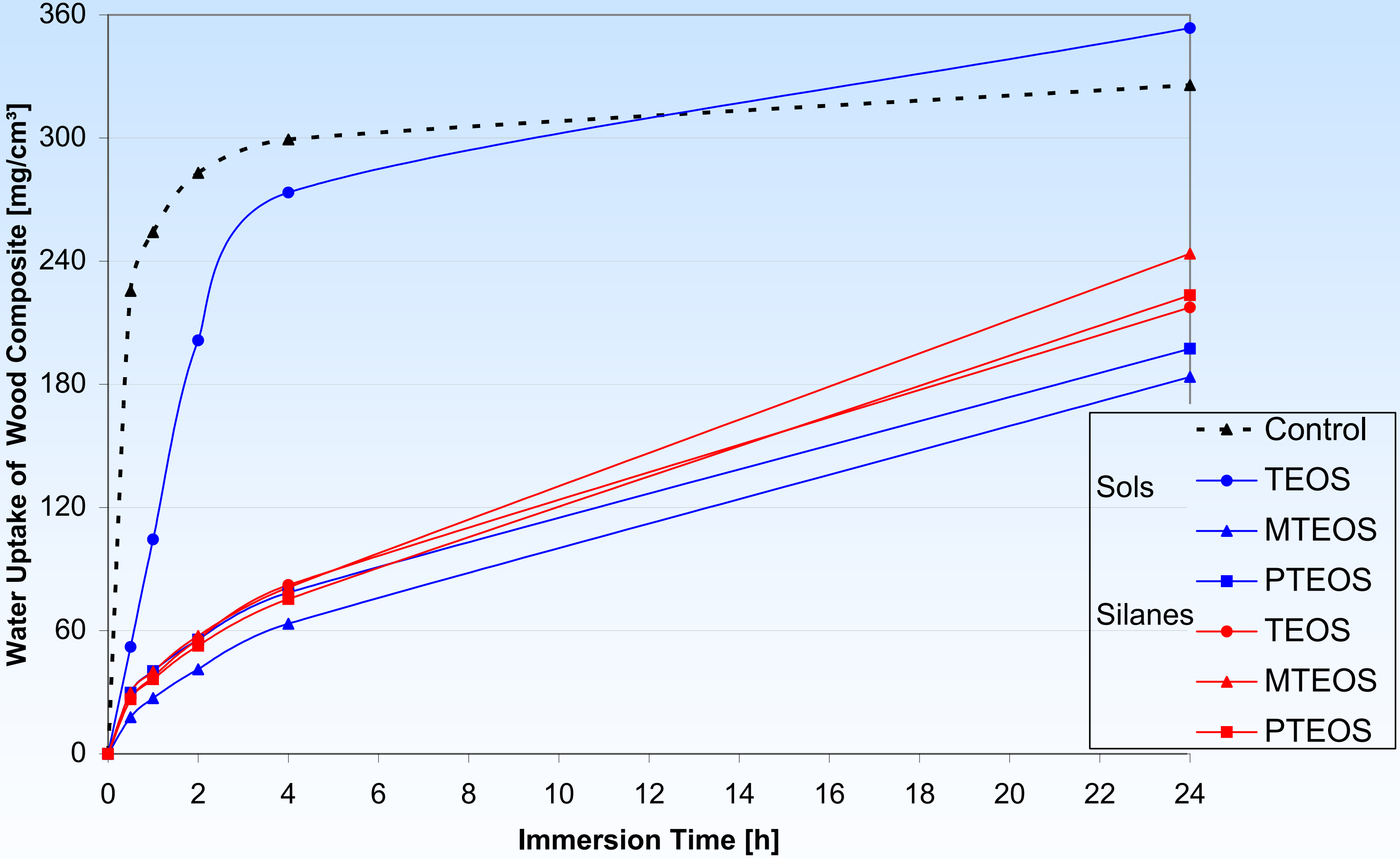


After curing
After aging
WPG [%]
35
30
25
20
15
10
5
0
TEOS Sol
MTES Sol
PTEO Sol
TEOS Silane
MTES Silane
PTEO Silane

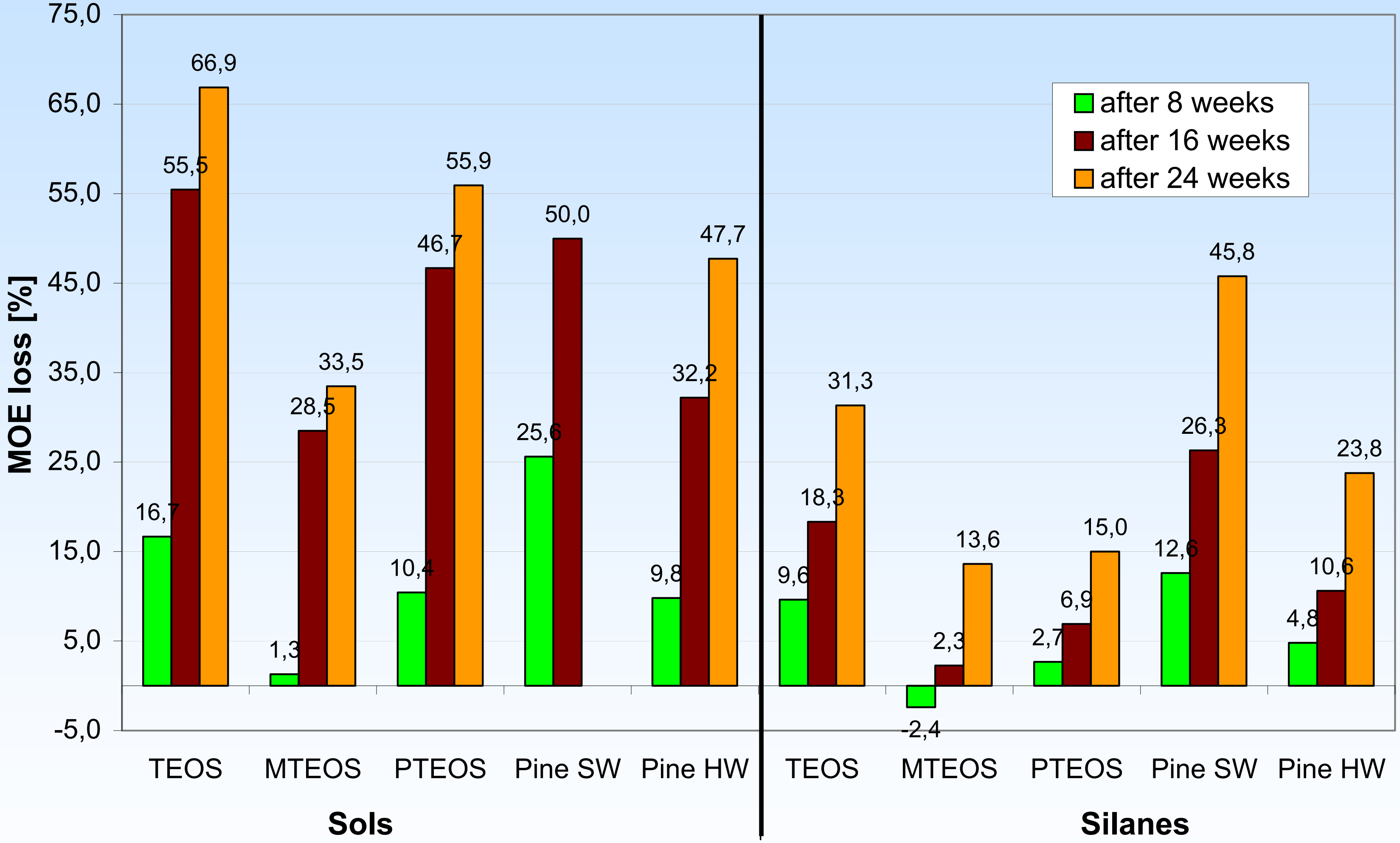
# Dimensional stabilisation (beech)



# Water Immersion Test

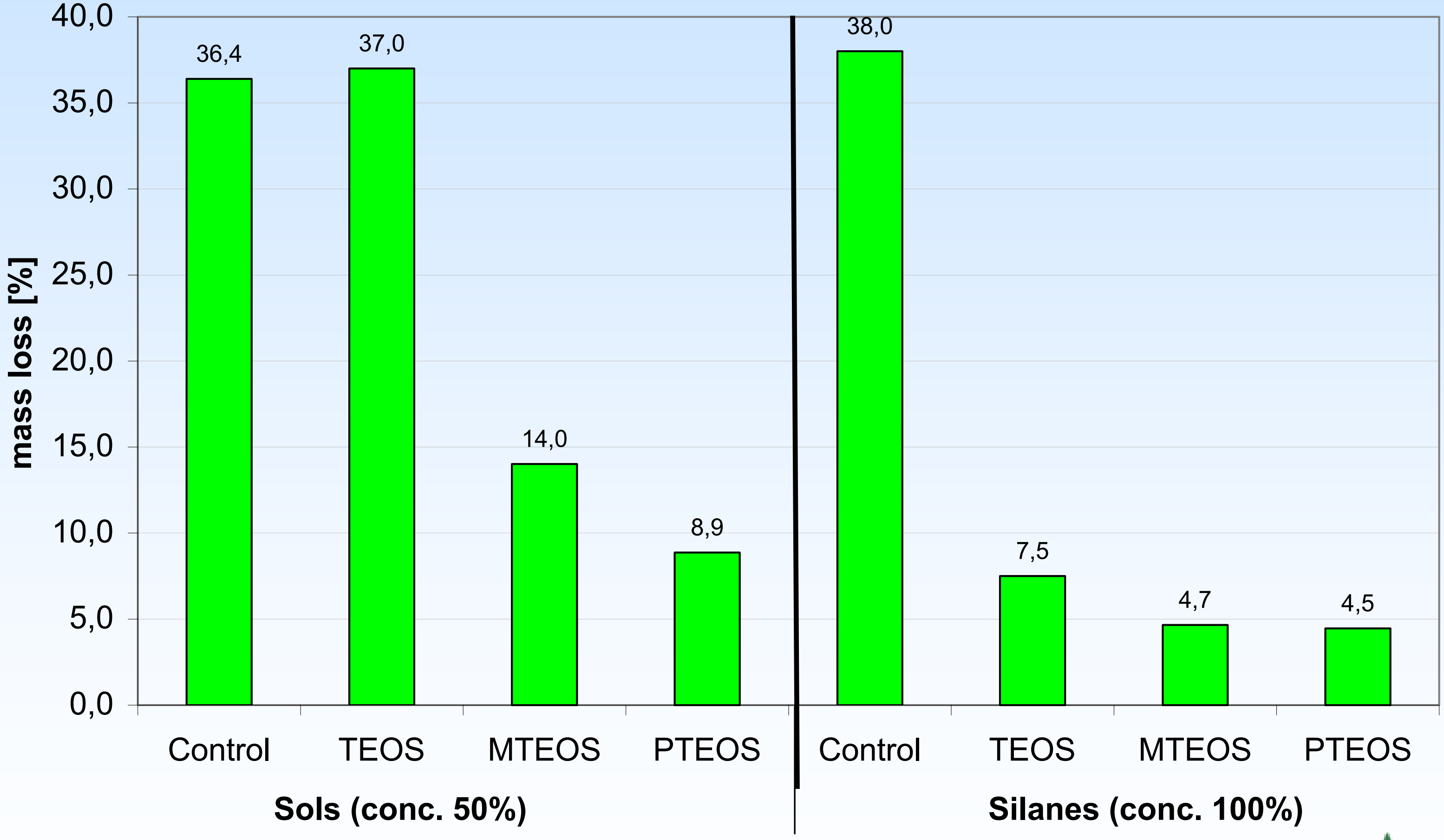


# Soil Bed Test (ENv 807)



# Basidiomycete Test (mini-block)

## Mass Loss of Beech after 6 Weeks Exposure to Trametes *versicolor*



# Weathering

## Reverse sides of wood samples after 1 year of weathering in Göttingen


**untreated** **oligomeric silane systems**

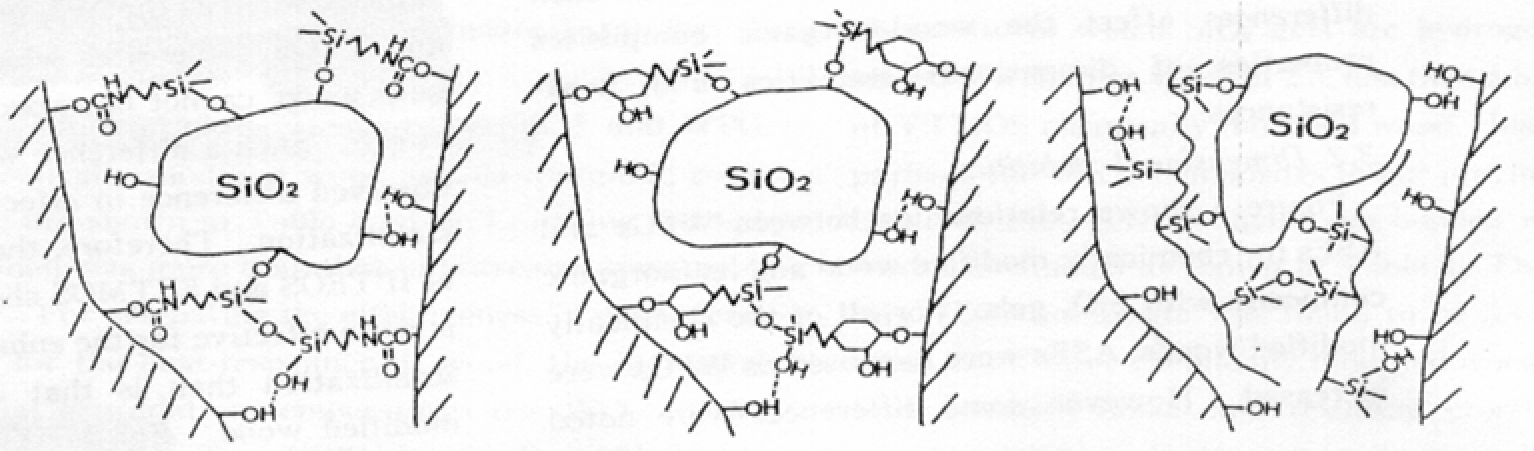
# Conclusions (Silanes)

- Good penetration of monomeric silane in pine and beech
- Ageing during several weeks
- Slight or no reduction of moisture uptake
- Slight dimensional stabilisation
- Good hydrophobation effects with alkyl-silanes
- Alkyl-silanes improved resistance against fungal attack only initially

# Silanes – Two-step Processes

## Covalent Fixation to the cell wall

1. Reaction with organo-silanes
2. Reaction with TEOS




| IPTEOS-TEOS | EETMOS-TEOS | VTMOS-TEOS |
|---|---|---|
| **3-Isocyanatpropyl triethoxysilane** | **β-(3,4 epoxycyclohexyl) ethyl trimethoxysilane** | **vinyl trimethoxy silane** |

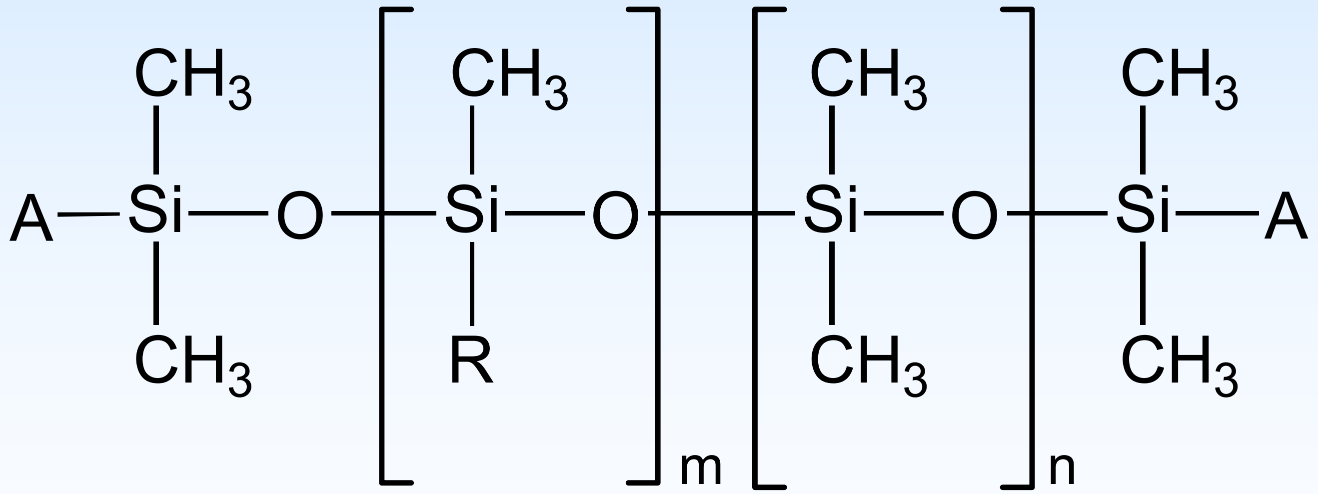
**High ASE !**

# Treatments

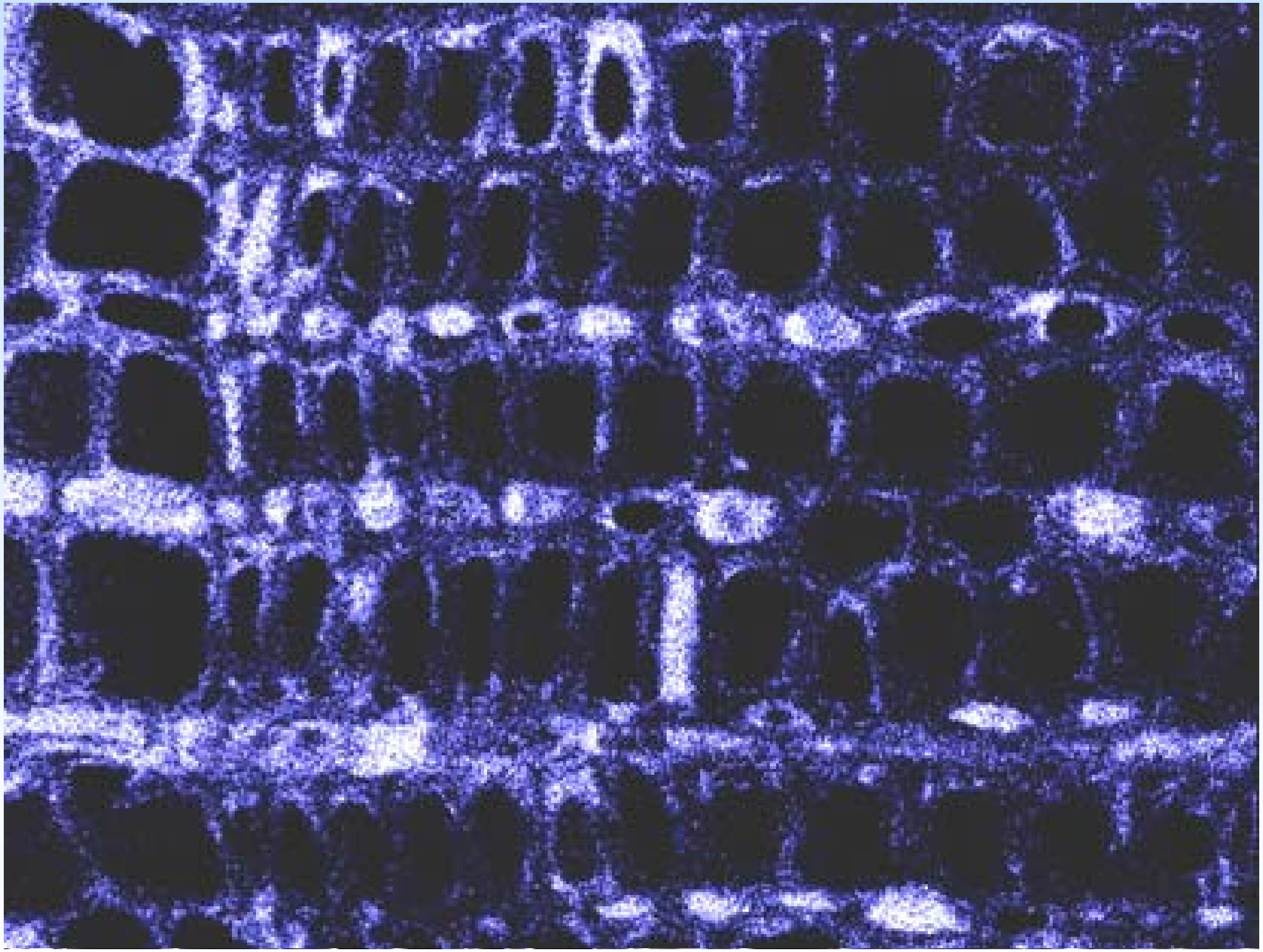
- Inorganic silicates (“water glass”)
- Silanes (sol-gel process)
- **Silicones**
- Micro-emulsion technology

# Silicones

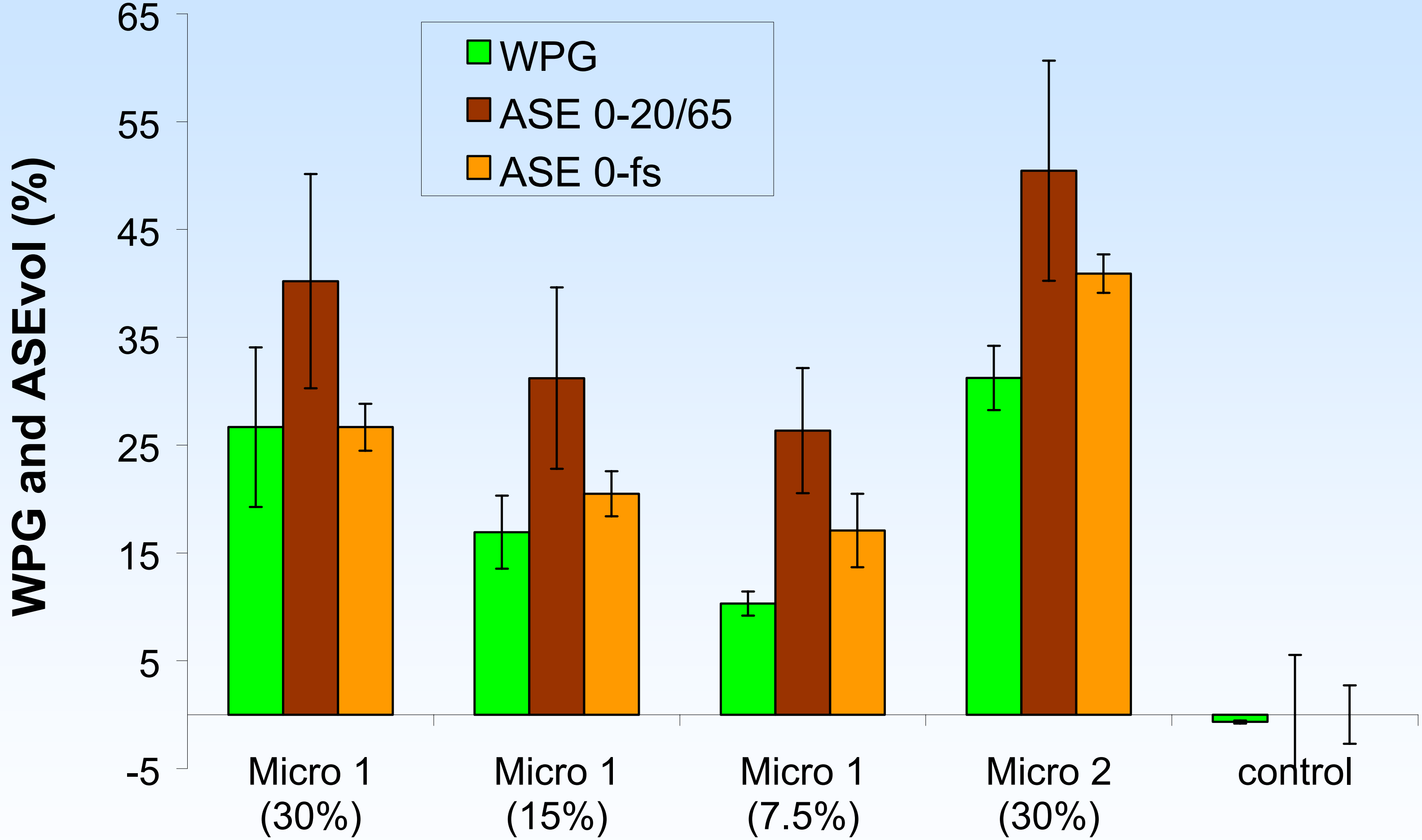
**Silicones are polydimethyl siloxanes!**



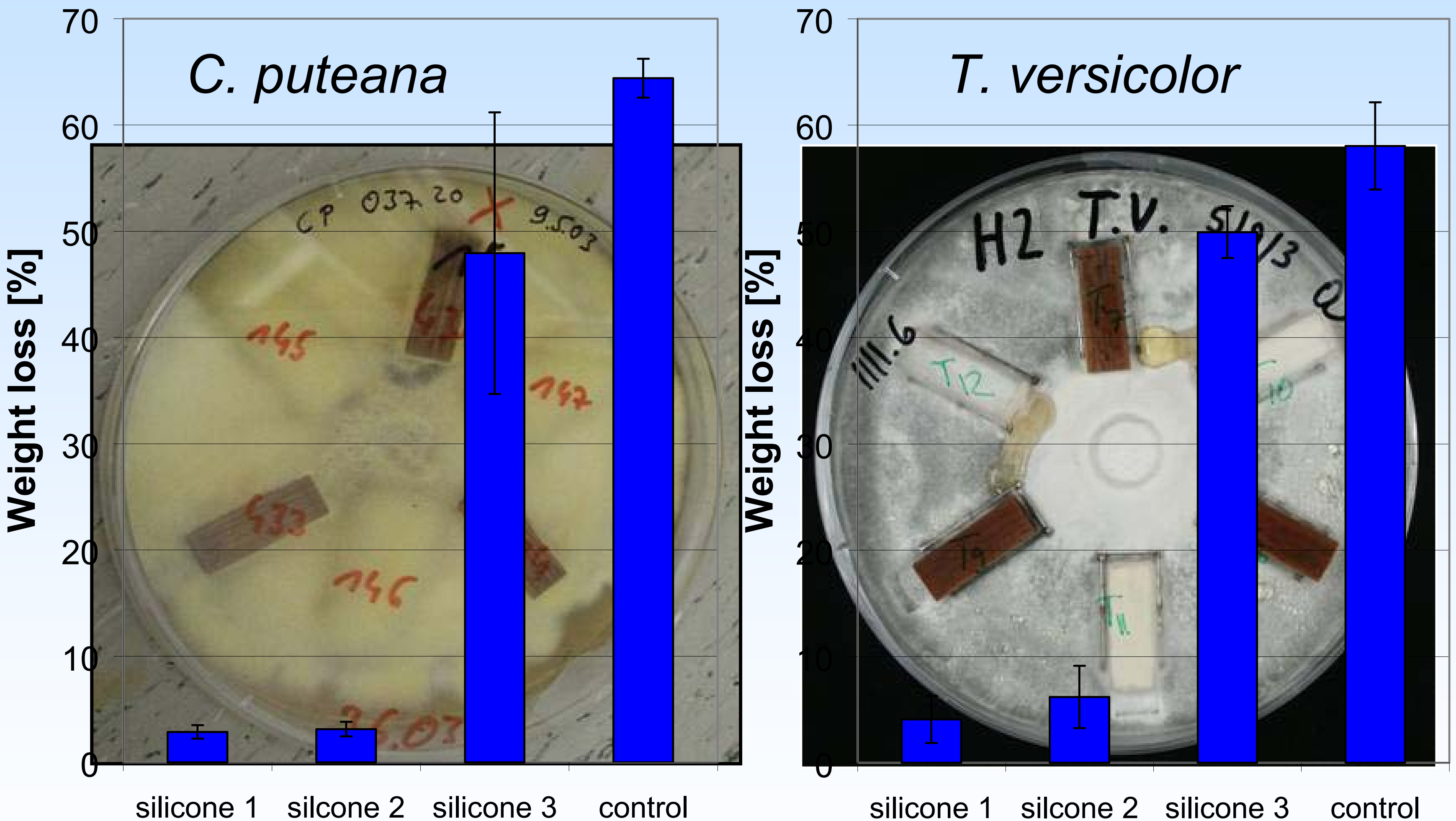
# Silicones Emulsions - Penetration



# Dimensional stability (Pine)



# Silicones - Decay Fungi (12 weeks)

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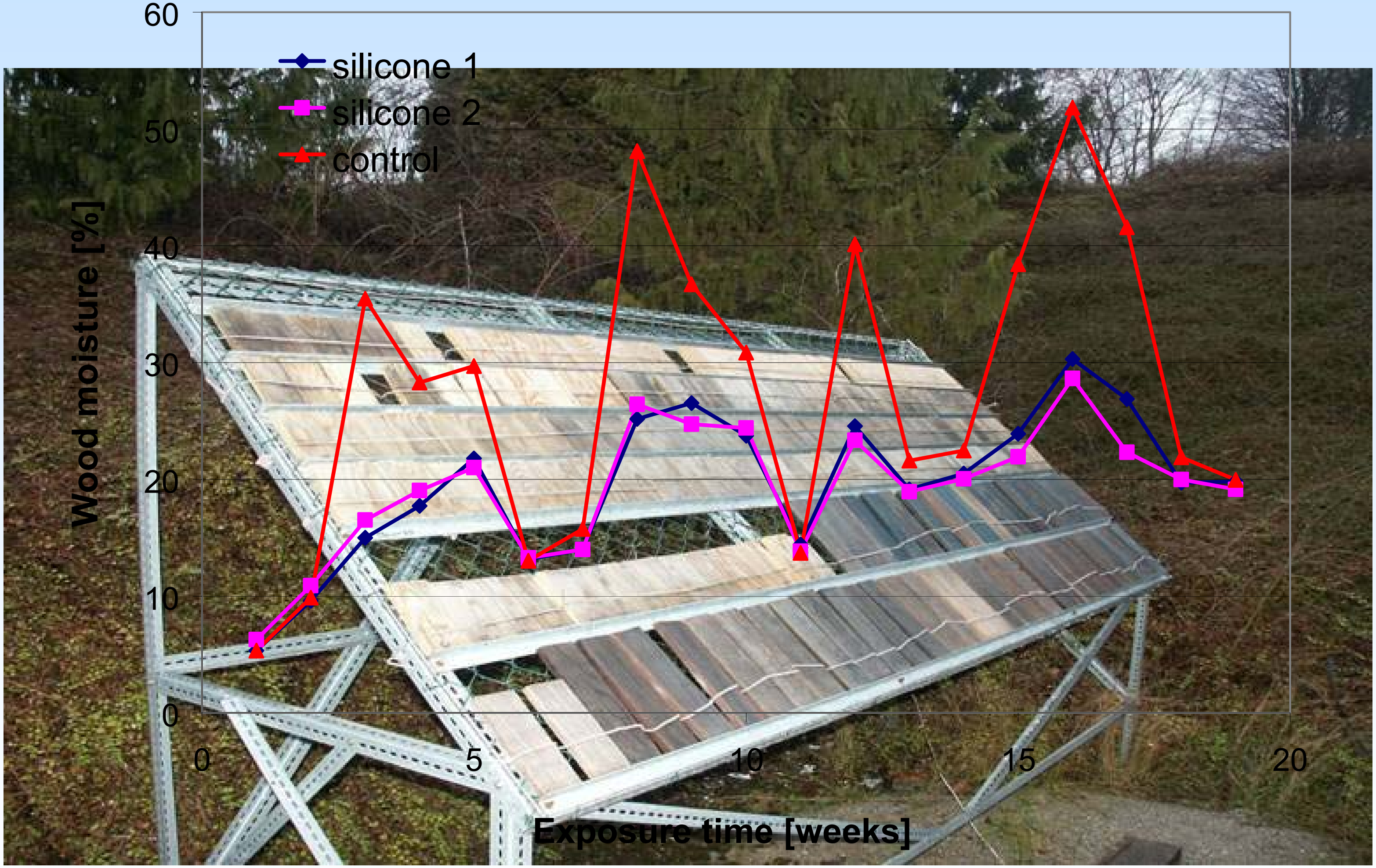
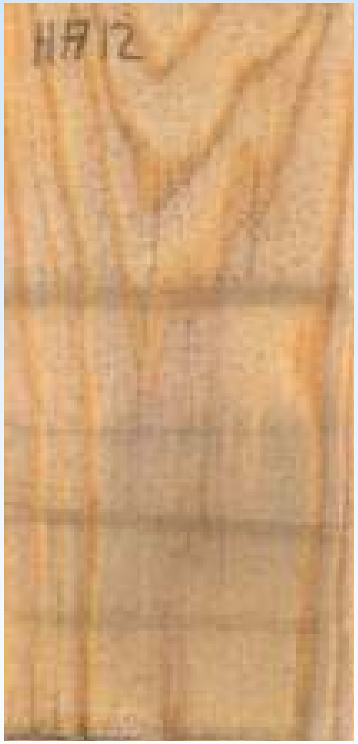
# Silicones - Outside Weathering



# Silicones - Outside Weathering (6 month)

## Front side

untreated



treated

## Reverse side

untreated

treated

# Conclusions (Silicons)

- Penetration was dependent on the particle size of silicone emulsions
- Micro-emulsions enhanced the dimensional stability
- Reduction of moisture uptake and increase in weathering stability
- Decay resistance was dependent on functional groups on the siloxane backbone

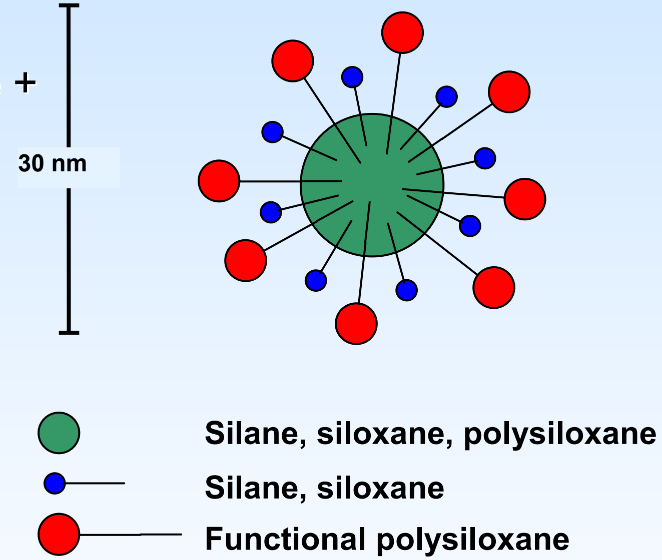
# Treatments

- Inorganic silicates (“water glass”)
- Silanes (sol-gel process)
- Silicones
- **Micro-emulsion technology**

# WACKER SMK® Technology

## Micro-emulsions of some 10 nm diameter

- **Emulsifier:**
  - N-(2-aminoethyl)-3-aminopropyl trimethoxysilane + α,ω-dihydroxy-methylpoly siloxane +KOH
- **Co-Emulsifier:**
  - Isooctyltriethoxy silane
    [15g + 80g A + 4g propionic acid]
- **Hydrophobic compound:**
  - Silane, siloxane, polysiloxane




**Good water repellent effect, but no increase of ASE**

# Conclusions (general)

- Wide variety of chemicals is available
- Various wood properties can be improved
- Improvement of decay resistance is low
- Decay resistance can be enhance by combination with other compounds (“controlled release”)
- High water repellence
- Application in use-class III (EN 335)

# Thank you for your attention!