COST E22 MEETING, TUUSULA, FINLAND

Modification of wood with silicon compounds

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Overview

- General Aspects and Chemistry of Silicon
- State of the Art of silicon treatment
    - Inorganic silicates (“water glass”)
    - Wood-inorganic composites by sol-gel process
    - Organo-functional silanes (sol-gel process)
    - Micro-emulsions (WACKER SMK® Technology)
    - Trimethylsilyl Derivatives
    - Chlorosilanes
    - Surface modification and hexametyldisiloxane-plasma coating
- EU project “HYDROPHOB”

General Aspects of Silicon

- Silicon makes up one forth (27.5%) of the earth's crust
- Silicon in nature is found as polymeric SiO_2

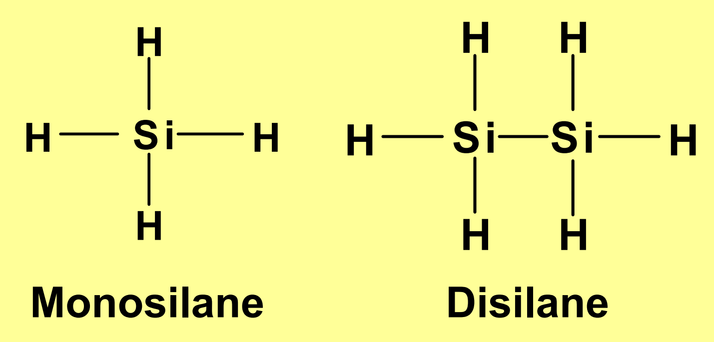
  $m\ SiO_2 \cdot n\ H_2O$ - $[Si(OH)_4]$
- Two forms: crystal (most frequent is quartz)

  amorphous
- SiO_2 in plants (bamboo, blades of grass, thorns, palm leaves) and in lower organisms (diatoms, sponges, nudibranchs) is amorphous
- Health Aspects: **Silicosis -** Pneumoconiosis caused by inhalation of crystalline SiO_2 dusts

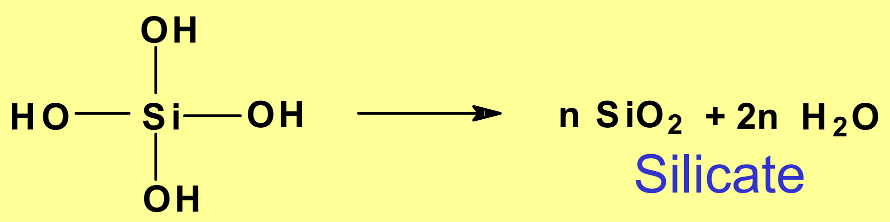
Chemistry and Nomenclature of Silicon Compounds

- Silanes: Hydrogen compounds of silicon

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

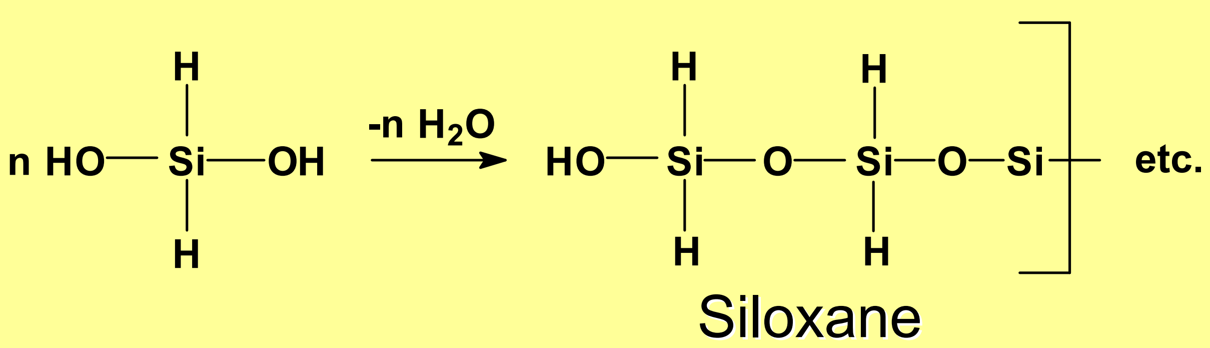


- Halogen silanes: **SiH_3Cl; SiH_2Cl_2, $SiHCl_3$**
- Silicic acid:

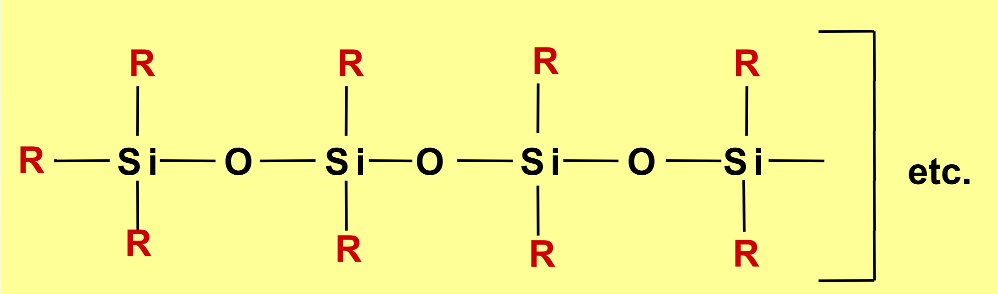


Chemistry and Nomenclature of Silicon Compounds

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



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



R = Alkyl

  – Si-C bond is stable towards acids and bases

Silicon Treatment of Wood

Aims

1. **Improvement of properties related to moisture and weathering**
   - → Swelling /shrinkage
   - → adhesion of coatings and varnish
   - → UV degradation
   - → decay and moulds protection

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

2. **Improvement of elasto-mechanical properties**
   - → hardness
   - → tensile strength
   - → fire resistance

→ **Could be achieved by storage of silicon compounds into the lumina of the wood cells**

“Water glass”

- Furuno et al., Faculty of Agriculture, Shimane University, Japan
- Matthes et al., University of Applied Science, Erfurt, Germany
- MASID umwelterhaltende Produkte GmbH, Dreieich, Germany

What is “water glass”?

- water-soluble K or Na-silicates or their solutions
  - 2-4 mol SiO_2 to 1 mol alkali-oxide ($M_2O \cdot nSiO_2$, n = 2-4)
- Solution: colloidal, clear; produced at elevated temperature and pressure
  - Insoluble in cold water
  - Alkaline (pH over 12)
- Precipitates as silicate in presence of acids and metals

"Water glass"

Furuno et al. (1991 - 2001)

- Impregnation of hinoki and kaba veneer (2.4 mm)
  - Na-water glass ($Na_2O{\cdot}nSiO_2$, n = 2.06 - 2.31) in 5% conc.
  - Vacuum impregnation as well as under atmospheric pressure
  - Precipitation with metals $Al_2(SO_4)_3$ or $CaCl_2$, $BaCl_2$, boron compounds
  - Drying: 60°C (24 h), then *in vacuo* (P_2O_5)

Matthes et al., Erfurt (1998 – now)

- Na-, K-, Li-silicates
  - No specific precipitation; alkaline pH of wood

"Water glass"

Results

- 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
- Decay resistance (EN 113)
  - High
    - Due to high pH
    - boron precipitation

“Water glass”

MASID umweltenhaltende Produkte GmbH

- Woodbliss (aqueous solution, pH >12)
  - More than 10% silicate (water glass), up to 10% silicic acid (to improve penetration)
  - Abietinic acid, cellulose, terpenes, Na-carbonate wood sugars etc.

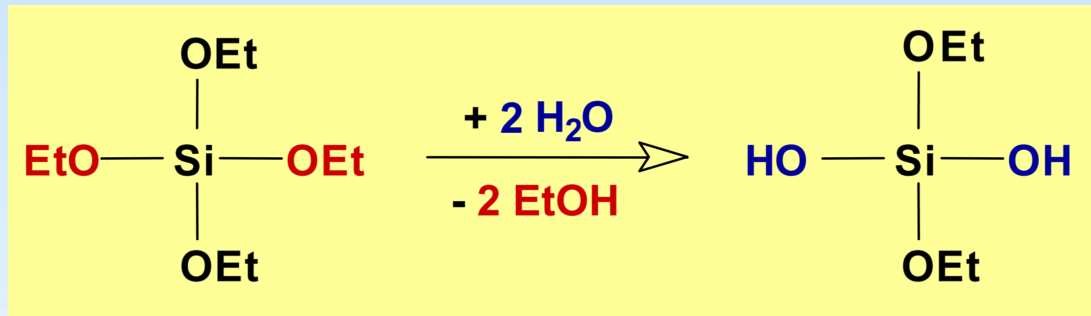
- HM 1 (aqueous solution, pH < 2)
  - siliceous earth (SiO_2)
  - Silicic acid
  - Al_2O_3, CaO, K-palmitate, NaCl, MgO, plant pigments, etc. all ingredients in concentration of < 10%

Wood-inorganic composites by sol-gel process

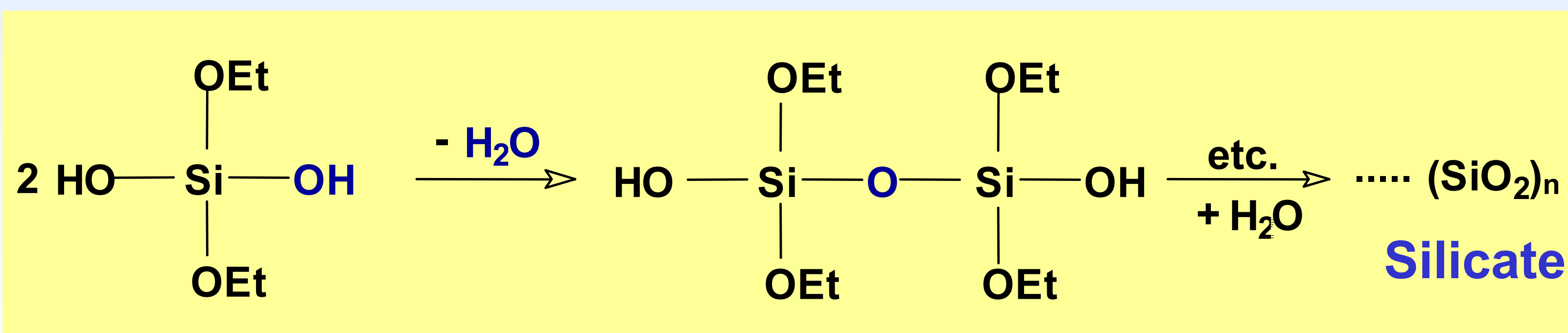
- Saka et al., Graduate School of Energy Science, Kyoto University
- Böcker et al., Bundesanstalt für Materialforschung, Berlin
- Feinchemie Sebnitz (H. Böttcher, German Patent, 2000)

Wood-inorganic composites by sol-gel process

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



  - **Condensation**



- End product is an amorphous silicate (glass)

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Wood-inorganic composites by sol-gel process

Shiro Saka et al. (1992 - 2001)

- Impregnation of veneer with tetraethoxy silane (TEOS)
  - Pre-conditioning high moisture content (up to 98%) or water saturated

Aim: Hydrolysis should occur only within the cell wall

- ASE: up to 42%
- Water absorption ratio was not reduced

Wood-inorganic composites by sol-gel process

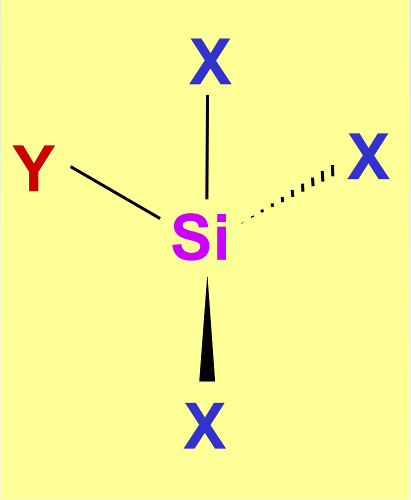
Böcker et al. (2001), BAM
Böttcher et al. (1999), Sebnitz

Soles based on tetraethoxy silane (TEOS) are prepared before the impregnation

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

Organosilanes

Silanes are <u>bifunctional</u> molecules



Silanes act as

- adhesion promoters
- surface modifiers
- cross-linking agents
- ...

Y = “Organofunctional group”

X = “Silicon-functional group, OCH_3, OC_2H_5 etc.

Aim: To increase hydrophobicity and fixation by organo-functional group

Organosilanes applied in the sol-gel process

Impregnation performed in one step

- **Hydrophobation**
  - Decyltrimethoxysilane + TEOS (0.001:1)
  - 2-Heptadecafluorooctylethyltrimethoxysilane + TEOS (0.004 or 0.001:1).
    - Water absorption ratio reduced to 25%
- **Fixation to the cell wall**
  - 3-Isocyanatpropyl-triethoxysilane (acetone, pyridine)[1]
    - Approx. 60% ASE at 20% WPG
  - γ-Methacryloxypropyltrimethoxysilane (methanol)[2]
    - Approx. 54% ASE at 22% WPG[2]

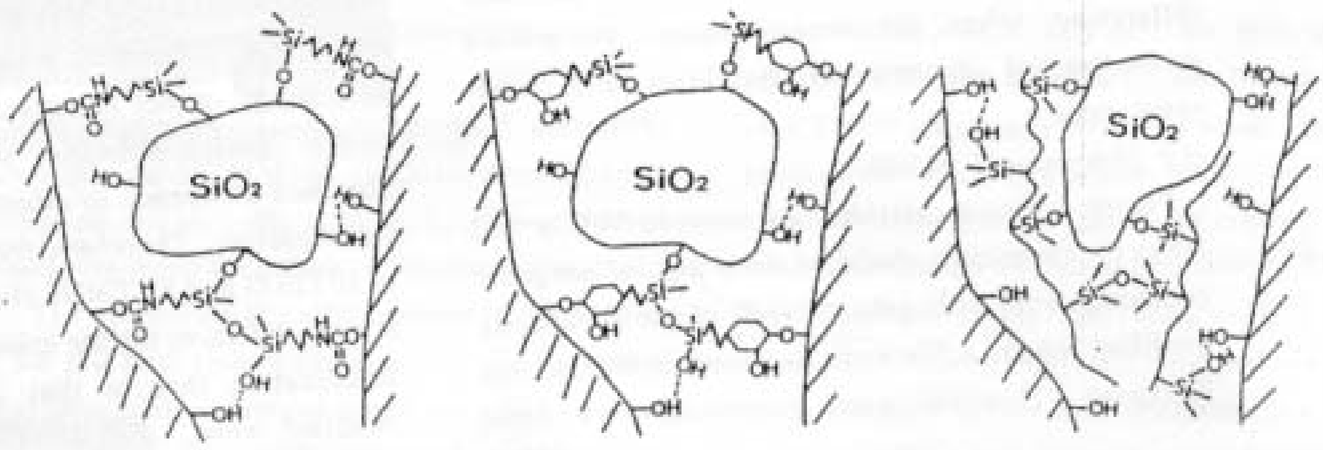
[1]Saka et al.
[2]Schneider et al.

Organosilanes

Impregnation performed in two step

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

Aim: Set an anchor to fix the silicate network to the cell wall



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

Micro-Emulsion Technology

Micro-emulsions of some 10 nm diameter

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

Good water repellent effect, but no increase of ASE

Chlorosilanes

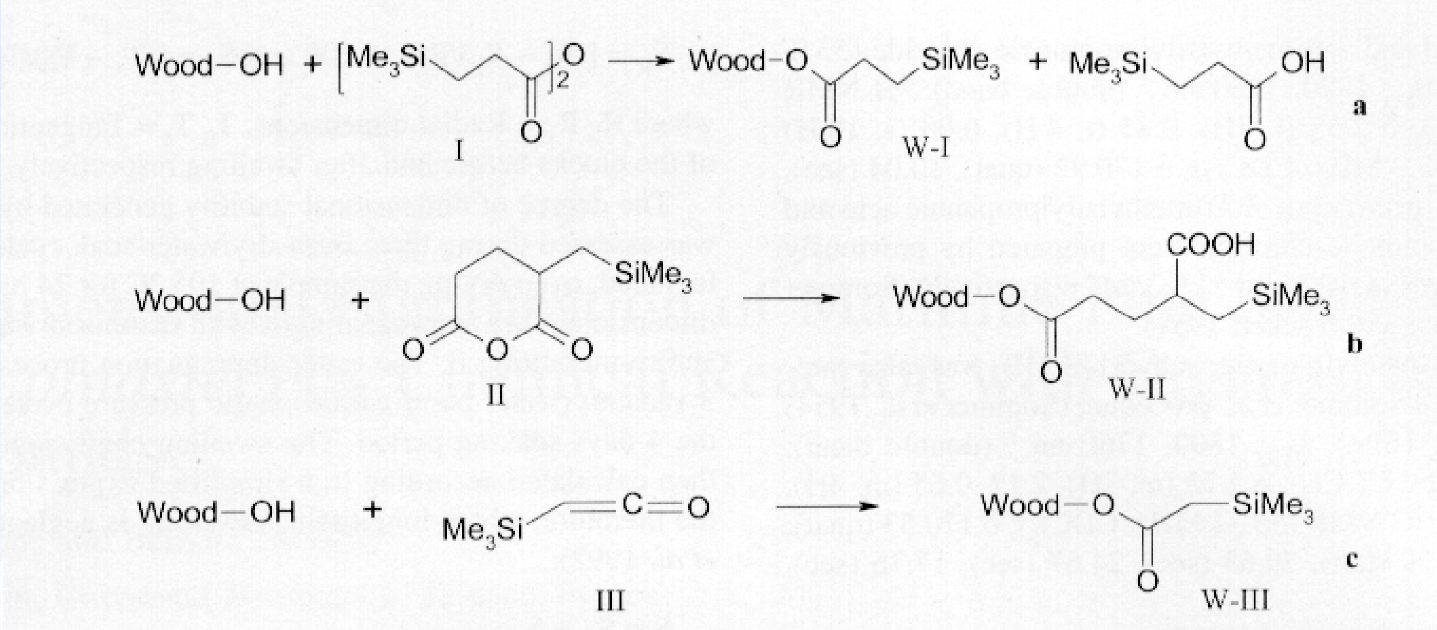
Stevens (1981-1985)
Zollfrank (2001, 2001)

$SiCl_4$
CH_3SiCl_3
CH_3SiHCl_2
$(CH_3)_3SiCl$

- Need of dry conditions during treatment
- Covalent bonds are hydrolysable
- Low performance as wood preservative

Modification with Trimethylsilyl Derivatives

Sèbe and De Jéso (2000)



I: 3-trimethylsilylpropanoic anhydride
II: 2-trimethylsilylmethylglutaric anhydride
III: trimethylsilylethenone

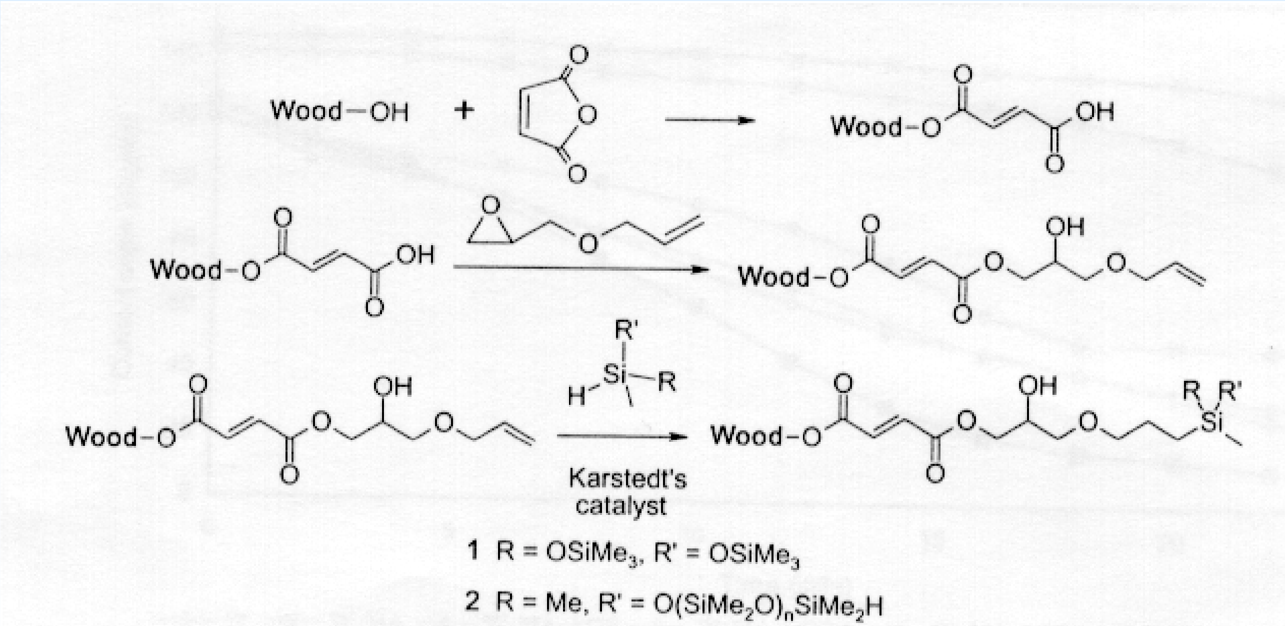
High ASE due to bulking

Surface Modification by Sililation

Sèbe and Brook (2001)

Hydrophobisation in three steps

1. Maleic anhydride
2. Allyl glycidyl
3. Hydride terminal silicon



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Hexametyldisiloxane - Plasma Coating

Cho and Sjoblom (1990)
Mahlberg et al., VTT (1998)
Denes et al., Univ. Wisconsin (1999)

- Hexametyldisiloxane was “polymerised” on the surface of wood in a cold plasma
- Si-O-Si and Si-O-C bonds were detected
- Strong water repellence
  - Contact angle = 130° (≤ 15° on un-treated wood)
- High thermal stability of the coating

Conclusions

- Wide range of chemical 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 hazard class III

Eu-Project, 5. Framework

“Improvement of Wood Product Properties by Increased Hydrophobicity Obtained by the Use of Silicon Compounds”

Partners

1. VTT, Fi, Antti NURMI (co-ordinator)
2. University of Ghent (RUG), B, Joris VAN ACKER
3. BioComposites Centre, Bangor, UK, Jeremy TOMKINSON
4. Institut Du Pin, Bordeaux, F, Gilles SÈBE
5. University of Göttingen, D, Holger MILITZ
6. SHR Timber Research, NL, Dennis JONES
7. Dow Corning, UK, Stuart KEEPING
8. Lappset, Fi, Hannu YLINENPÄÄ
9. Masid, D, Elfi RUNKEL

Eu-Project, 5. Framework

Work packages

1. Identification of suitable compounds and type of bonding
2. Bioassays
3. Optimisation of processes to meet requirements of final products
4. Testing material properties of treated wood
5. Feasibility of developed product systems to meet market and environmental requirements

Thank You
for Your Attention!