Poznań University of Life Sciences

Commercial biobased wood coatings – the current market position

Ewelina Depczyńska

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Biobased – what does it mean?

"amount of bio-based carbon in the material or product as a percent of the weight (mass) of the total organic carbon in the product"*

*The United States Department of Agriculture (USDA)

Wood coatings – non-film forming

1) Wood preservatives – priming oils and stains

- registration in each EU country (BPR), where will be sold
- protection of wood against rot/blue stain (wood preservation)
- main components: biocides, solvent, binder

2) Wood oils

- non-film-forming products for garden furniture and terraces
- main components: binder, solvent, biocides

3) Non-film-forming wood stains

- form a film of about 5-20 microns, solid content max. 25 - 30% vol.
- garden furniture, log houses, fences and structures
- main components: binder, solvent, biocides, pigments, additives

Wood coatings – Film forming

4) Film-forming wood stains

- form a film of higher then 20 microns, solid content min.25-30% vol.
- fences, wooden claddings, window and door joinery,
- Main components: binder, solvent, biocides, pigments, additives

5) Lacquers

- film-forming product on wood surface
- main components: binder, solvent, biocides, pigments, additives

6) Opaque products – primers, enamels, putty

- window and door joinery, furniture, floors
- main components: binder, solvent, biocides, pigments, fillers, additives

7) Others - adhesives

Main binders in wood coatings:

- Oxopolymerized oils
- Polyesters:
  - alkyd resin
  - high-solid alkyd resin
  - water-soluble alkyd resin
  - modify alkyds (acrylic, urethane, silane, styrene)
- Polyurethanes:
  - SB polyurethanes
  - water-soluble polyurethanes
- Polyamides, Vinyl polymers, Epoxy resins, Polyesteramides, Polynaphtols

Polyesters

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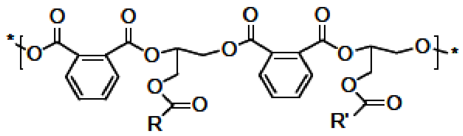
Alkyds – old binder with brilliant future

- 1920s – first synthesis of alkyd resin from glycerol and phthalic anhydride. Classification in three groups: short, medium long oil resin
- 1933s – commercial production of alkyd binder
- 1950s – starting point for development of environment friendly alkyds
- 1970s – water soluble alkyd resins
- 1980s – 1990s – WB alkyd emulsion



Alkyd Resin

Where R and R' are different combinations of these acids depending on oil choice

Stearic Acid	$CH_3(CH_2)_{16}COOH$
Palmitic Acid	$CH_3(CH_2)_{14}COOH$
Oleic Acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ (9c)
Linoleic Acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ (9c 12c)
Linolenic Acid	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ (9c 12c 15c)

Figure 1: General structure of alkyd resin.

Alkyds – synthesis and bio-recourses

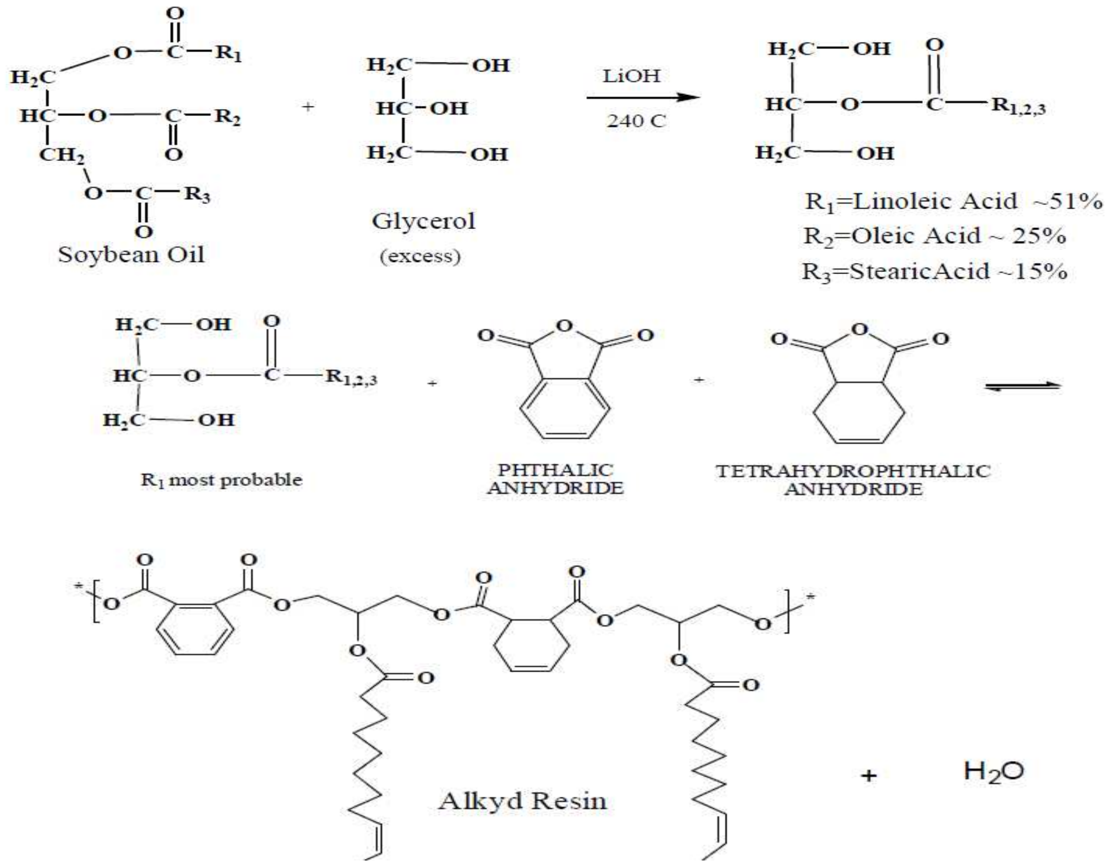


Figure 2: Synthesis of alkyd resin.

Alkyds – synthesis and bio-recourses

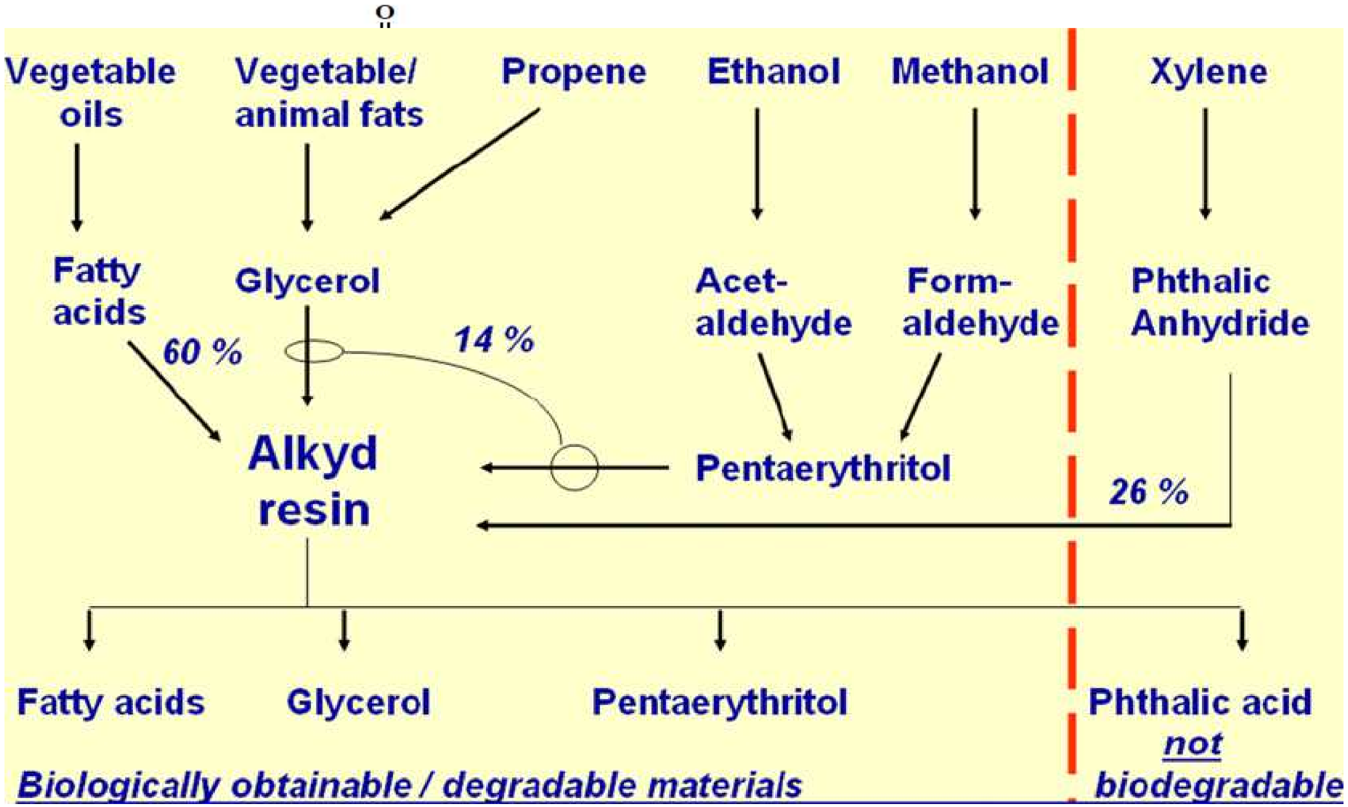


Figure 3: Biobased raw materials in alkyd's synthesis.

Alkyds – based on biobased oils

	Oil							
Property	Raw Linseed Oil	Raw Castor Oil	Dehydrated Castor Oil	Tung Oil	Soya Bean Oil	Safflower Oil	Crude Tall Oil	Fish Oil
Acid No.	2-4	5-12	3-6	-	0.5-6.0	1-4	165-170	0.5-8.0
Sap. No.	188-196	172-182	188-194	190-195	189-195	188-194	170-180	185-195
Specific Gravity	0.931-0.934	0.963	0.938-0.941	0.940-0.942	0.924	0.924	0.960-0.984	0.923-0.933
Wt/gal	7.76	8.08	7.81	7.85	7.70	7.70	8.11	7.73-7.78
Iodine no.	170-190	85	125-140	160-165	130-140	142	143-170	165-195
Color	11-12	8-9	4-6	9-12	9.5-10.5	10-10.5	10-dark	12-14
Viscosity	A	U	G-H	H-J	A	A	S-V	A
Saturated Acids (%)	5.0	2.0	2.0	5.5	13.2	6.6	7	20
Oleic Acid (%)	5	8.6	8.6	15	30.2	16.4	16-25	10
9-12 Linoleic Acid (%)	40	3.5	57		51.2	76.7	16-25	15
9-11 Linoleic Acid (%)	-	-	25.5	-	-	-	-	-
Linolenic Acid (%)	50	-	-	-	5.4	0.3	-	-
Ricinoleic Acid (%)	-	85.9	6.9	-	-	-	-	-
Eleostearic Acid (%)	-	-	-	79.5	-	-	-	-
Refractive Index	1.4775	-	1.4873	1.5160-1.5200	1.4734-1.4740	-	-	-

*Drying Index = %Linoleic acid + 2 *%Linolenic acid*

Figure 4: Properties of common oils used in alkyd preparation.

Bio - Alkyds and their properties

- **Soybean, sunflower and linseed oil** in alkyd synthesis:
  - first, traditional oils used in alkyd synthesis
  - excellent autooxidative, chemical and mechanical properties
  - problem with yellowing and loss of gloss during the time
- **Nahar seed oil** in synthesis of polyester resin:
  - plant in India with high oil contents seeds (~75%)
  - three different types of resins were prepared with yield (80 – 90%)
  - parameters (like hardness) increase with increase of phthalic anhydride
- **Yellow oleander seed oil** – based alkyds:
  - ever-green tree in North-East India
  - non-drying index (lower then 70%) – oil has to be mixed with epoxy resin
  - alkyd resin with satisfying mechanical properties (gloss, hardness, adhesion), chemical resistance and thermal stability

Bio - Alkyds and their properties

- Alkyd resins based on **Ricinodendron heudelotii oil**:
    - fast growing tree in tropical forest in Africa
    - three different resins were prepared with different molar ratio anhydrides
    - good drying time, adhesion, gloss and contact angle
    - satisfying mechanical, properties, chemical resistance and thermal stability
- **Palm oil** in synthesis of alkyd resin:
    - three different resins were prepared with different molar ratio anhydrides
    - depending of molar ratio with phthalic anhydride: high gloss, good hardness
    - resistance to water, alkali and acid
- Polyester resin based on **castor oil**:
    - advantages: low cost, biodegradability and unique molecular structure
    - better physical, mechanical and thermal properties then petroleum-based polymer
- Others oils used in alkyd production with good results: **coconut oil , tobacco seed oil , karawila seed oil and ricinodendron heudelotii oil**

Polyurethanes

References 18 - 27

Polyurethanes

- High quality binder very popular in wood coatings

- The main feature of polyurethanes:
  - availability
  - good mechanical properties: abrasion resistance, high elasticity (in different range of hardness)
  - great chemical and thermal properties
  - possible modification in properties and structure
  - low and stable cost
  - SB binders (right now mostly HS) and Water soluble PU
  - From petroleum sources - linear structure
  - From biobased material – hyperbranched structure (more durable)

Polyurethane formation

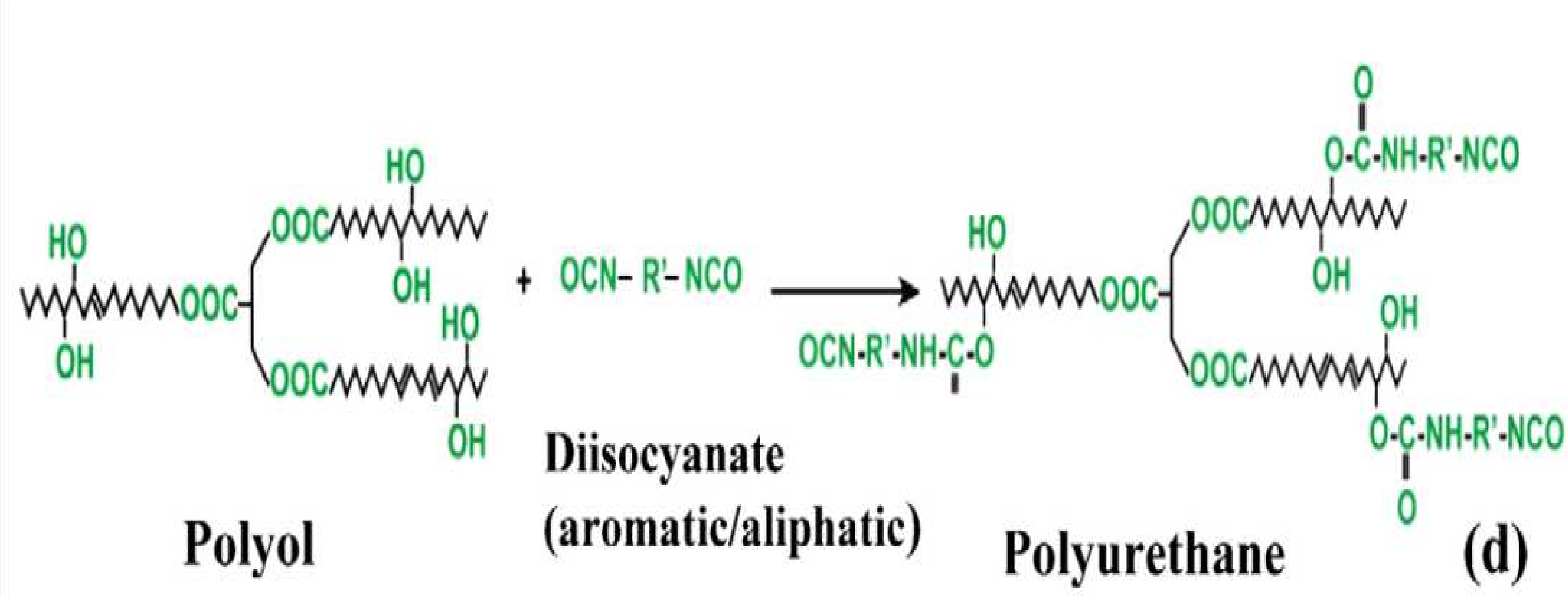


Fig. 4. Alam et al (2014): Arabian J. Chem 7: 469-479

Polyurethanes – bio-resourses

From seeds like:

- cashew nut
- natural rubber
- Pongamia glabra
- karanja
- rapeseed
- Annona squamosa
- Moringa oleifera
- Nahar (Mesua ferrea L.)
- Jatropha
- canola

Traditional oils:

- linseed
- soybean
- coconut
- castor
- sunflower
- palm
- tung
- cardanol
- cotton
- fish
- camelina

Bio-polyurethanes - properties

- PU based on jatropha oil:
  - good properties: pendulum hardness, water repellence and thermal stability
  - possible application: wood and decorative coatings
- HBPU from sunflower oil:
  - better then linear counterpart
  - very good mechanical, chemical and thermal properties
  - biodegradation properties
- Linseed oil – based PUD (UV/air dual-cured system):
  - several benefits: higher- molecular- weight but with lower viscosity, lower toxicity/odour, easy to clean up and conventional application method
  - depending on curing system different properties e.g. higher hardness and gloss, lower yellowing than in air/UV dual-cured system

Bio-polyurethanes - properties

- High- solid PU from canola, camelina and sunflower oils:
  - good mechanical and thermo-mechanical properties
  - biobased content higher then 60% - good mechanical and thermal properties
  - conclusion: the highest linolenic acide content the most similar to petroleum PU, good abrasion resistance, hardness and high contact angle with water
- Waterborn PU based on rapeseed fatty acid methyl esters:
  - great opportunity to be use commercial
  - possibility to modify – lower level of unsaturation less yellowing
  - good chemical resistance and hydrophobicity
- Cardanol PUD:
  - low particle size, good viscosity
  - Improvement in hardness, water and solvent resistance, corrosion resistance
- BIO- PU based on soybean oil:
  - good mechanical properties
  - cheaper and more available then from petro-sources

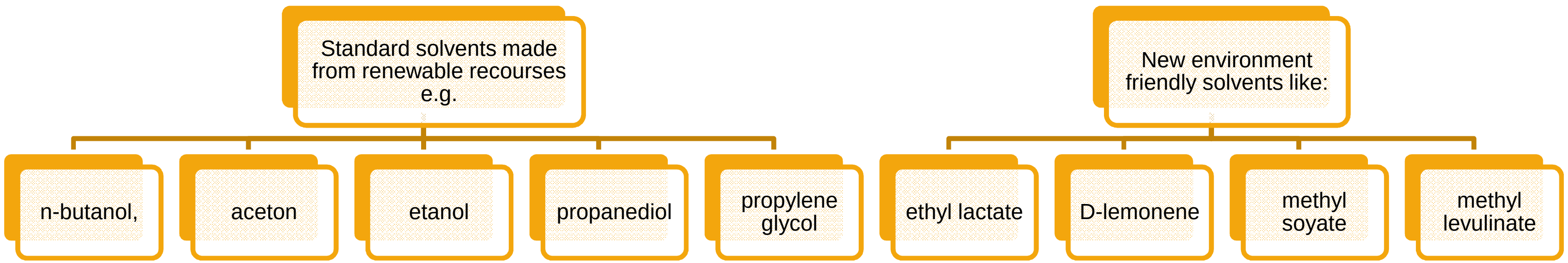
Solvents

References 28 - 30

Solvents

Water – the most important, ecofriendly solvent. WB products started to be very important, because of e.g. VOC regulations, healthy issue;

Two main direction in bio-solvents:



Solvents - sources

- **n-butanol, acetone and ethanol** can be achieved in ABE fermentation from maize and wheat (mostly in the past), lignocellulosic biomass and syngas
- **propylene glycol** is produces from glycerol deriving from biodiesel production
- **propanediol,** receive via fermentation of corn glucose, can be a replacement for propylene glycol or butylene glycol
- **ethyl lactate** – environment friendly solvent, which can replace conventional solvents, is produce from agricultural material
- **methyl soyate** is produced from soybean oil. It has very good compatibility with many resins. Mostly use as a cleaning agent
- **D-lemonene**, receive from orange or lemon, can replace mineral spirit, methyl ethyl ketone, acetone, toluene, glycol ethers and halogenated solvent
- White spirit, the most popular solvent in paint industry, can be replace via **methyl levulinate** (from glucose)

Bio-solvents

Attribute	Chlorinated	Hydro-carbon	Methyl Ethyl Ketone	Ethyl Lactate	D-Limonene	Methyl Soyate
Good solvency	Y	N	Y	Y	Y	Y
Low VOC	Y	N	N	Y	Y	Y
Non HAP	N	N	Y	Y	Y	Y
Nonflammable	Y	N	N	N	N	Y
Low toxicity	N	N	Y	Y	Y	Y
Fast evaporation	Y	Y	Y	Y	Y	N
No surface residue	Y	Y	Y	Y	Y	N
Biodegradable	N	N	N	Y	Y	Y
Low odor	N	N	N	Y	N	Y
Material compatibility	Y	Y	N	Y	Y	Y
Competitive cost	Y	Y	Y	Y	N	Y

Biocides

References 31 - 33

Biocides

Bio-oils an their lignin fraction:

- from pine and oak (wood and bark) were pyrolyzed
- more effective against the brown-rot fungus then the white-rot
- better weathering resistance and water repellency
- potencial candidates to exchange traditional biocides

Natural oil (linseed and tung oil) modified with with organosilanes:

- chemical reaction between cellulose and silane
- very low toxicity, high hydrophobicity
- diminishe water uptake, good weathering resistance
- does not form a coating
- good alternative for traditional biocides

Additives

References 34 - 35

Additives

Biosilica can be synthesized from cogon grass or rise

- very important as a matting agent in wood coatings
- from cogon grass (cellulose) we can get high purity amorphous silica
- very smooth surface
- very low concentration 2,9%

Cellulose nanofibres as fillers:

- improved mechanical properties of wood coatings
- higher hardness, but no improvement in abrasion resistance
- matting effect because of surface roughness

Organosolv lignin (from maize stalks and spruce wood):

- Many potancial application in paint as e.g.: dispersing, hydrophobic, plasticization, antybacterial agents and flame retandant

Adhesives

References 36 - 38

Wood adhesives

- Soya protein and wheat gluten:
  - inexpensive industrial product
  - combination of properties of both adhesive
- Phenolic resol resin from cornstalk-derived bio-oil:
  - lower price and "green" recourse
  - very easy controlled viscosity
  - very similar to standard phenolic resin
- PU adhesive from canola oil:
  - environmental friendly product
  - great adhesion, strength and flexibility
  - better performance then conventional adhesive
- Tung oil improved water resistance and adhesion of adhesive

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Contact details:

SP Technical Research Institute of Sweden, SP Sustainable Built Environment, Drottning Kristinas väg 67, 114 28 Stockholm, Sweden

dennis.jones@sp.se

[2]Tikkurila Polska S.A., Mościckiego 23,

39-200 Dębica, Poland

Ewelina.Depczynska@tikkurila.com

[3]Poznan University of Life Sciences, Institute of Wood Chemical Technology, Wojska Polskiego 28,

60-637 Poznan, Poland

bartsimp@up.poznan.pl

[4]SP Technical Research Institute of Sweden, SP Sustainable Built Environment Laboratorgränd 2, SE-931 77 Skellefteå, Sweden

bror.sundqvist@sp.se


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