SOME TRENDS IN WOOD ADHESIVES FOR LOW OR NO FORMALDEHYDE EMISSION

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UFs of LOW FORMALDEHYDE EMISSION

- Not yet a problem in Europe, BUT
- JAPAN’s F**** standard is far more severe
- If JAPAN’s F**** spreads to other countries are there ways to satisfy easily the standards, or better?
- The answer is YES, with a variety of different technologies, new and/or old.

Technologies to decrease/eliminate formaldehyde content and emission

- Phenol-formaldehyde (PF) and phenol-urea-formaldehyde (PUF) resins
- UF/isocyanate, MUF/isocyanate, PF/isocyanate
- MUF resins of low formaldehyde content
- Tannin adhesives without formaldehyde
- Isocyanates
- M, U and MU resins with non-toxic, non volatile aldehyde
- New Entries

MOST OF THESE RESINS ALREADY EXIST AND ARE ALREADY USED INDUSTRIALLY TO-DAY
AND UF RESINS?

• UF resins of formaldehyde emission low enough to satisfy F**** can be produced. It seems one major adhesive manufacturer already produces them for the Japanese market.
• But they are more expensive and higher amounts used.
• And Japanese standard intends tightening further formaldehyde emission regulation: towards an effective formaldehyde emission ban? (note, not a ban of formaldehyde).

IF JAPAN’S F**** TAKES HOLD

• ONLY PF RESINS, PUF, hybrid PF/MDI, UF/MDI resins, top range MUF resins and Tannin adhesives WILL SURVIVE SHORT TO MEDIUM TERM.
• NEW RESINS AND TECHNOLOGIES WILL PENETRATE MORE DEEPLY THE MARKET. AMONG THEM, BUT NOT ONLY, NATURAL ADHESIVES AND SOME OF THE ABOVE.
• ISO CYANATES ALONE MIGHT HAVE EVENTUALLY THE SAME POLLUTION PROBLEMS OF FORMALDEHYDE.

FAST-CURING PF RESINS

• Today as fast pressing as UF and MUF by
• 1. use of ester accelerators
• 2. alkaline setting PUF resins
• 3. alkaline setting PF/MDI hybrid resins
• Extremely low emission as these resins are completely stable
HYBRID ISOCYANATE RESINS

by DECREASE/ELIMINATION OF TOXIC -NCO GROUPS IN ISOCYANATES

• BY CO-REACTION OF ISOCYANATES WITH TRADITIONAL WATER-BORN ADHESIVES

Melamine and Urea resins without any formaldehyde

• A major chemical group has developed M and U formulations based on a non-toxic, non-volatile aldehyde.
• Press time is still slower but will be improved
• This aldehyde is still relatively expensive, but if industrial demand increases dramatic shifts in prices will result

SHIFT TO NATURAL ADHESIVES

• Tannin Adhesives NEW TECHNOLOGIES (not the old ones)
• Protein Adhesives
• Carbohydrate Adhesives
• Unsaturated Oils Adhesives
• Hybrid glyoxylated lignin adhesives
TANNIN ADHESIVES

1. IMPROVEMENT OF TRADITIONAL SYSTEMS
2. NEW HARDENERS
3. AUTOCONDENSATION
2005-2006 Japanese Use of Tannins: EFFECTIVE EMISSION = 0.0

BONDING BY TANNINS
AUTOCONDENSATION
ENVIRONMENT FRIENDLY GLUING
WITHOUT ANY ALDEHYDE
ALTERNATIVE HARDENERS

- Methylolated Nitroparaffins, i.e. Trishydroxymethyl nitromethane
- Glyoxal
- Hexamethylenetetramine (HEXAMINE)

IN PRESENCE OF FAST-REACTING COMPOUNDS: HEXAMINE IS NOT A FORMALDEHYDE-YIELDING COMPOUND

- In presence of MELAMINE
- In presence of RESORCINOL
- In presence of TANNINS
PROTEIN ADHESIVE (SOY)

Properties of soy-PF40 and commercial PF random strand laboratory panels:

<table>
<thead>
<tr>
<th></th>
<th>Thickness swell (%)</th>
<th>Internal bond (MPa)</th>
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</thead>
<tbody>
<tr>
<td>Face resin</td>
<td>Density (kg/m³)</td>
<td>24-h Boil</td>
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<tr>
<td></td>
<td></td>
<td>2-h Borst</td>
</tr>
<tr>
<td>PF control</td>
<td>677</td>
<td>62.8 (4.8)</td>
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<tr>
<td>Soy-PF40</td>
<td>696</td>
<td>65.1 (3.8)</td>
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</tbody>
</table>

CARBOHYDRATE ADHESIVES

- As modifiers of existing PF and UF adhesives
- By forming degradation compounds that can be used to form resins for adhesives: i.e. FURANIC RESINS (but furanic monomers are toxic)
- Directly as wood Adhesives: i.e. Liquefied Wood (phenol present)

UNSATURATED OILS

- Epoxidized unsaturated oils: acceptable results for panels but pressing times are far too long. They are relatively expensive
- Cashew nut shell liquid

\[
\text{RO} + \text{Ar} \xrightarrow{\text{O}_3 \text{ in methyl spirit}} \text{CH}_2 \xrightarrow{\text{an hydroperoxide}} \text{O}_3 \text{O}_{\text{HOH}} \xrightarrow{\text{reduction (pinnos or Zizane acid)}} \text{OHC} \xrightarrow{\text{Phenol/aldehyde network}} \text{resinified network}
\]
Hybrid Glyoxylated Lignin Adhesives

- Non-traditional technology
- Must watch out not to be drawn in traditional lignin/PF resins
- Hybrid MDI/PF/glyoxylated lignin and MDI glyoxylated lignin adhesives, with lignin up to 65% of total
- Glyoxal is classified as non-toxic (LD50 > 7000 mg/kg) and non-volatile
- Pressing times industrially significant

WOOD WELDING WITHOUT ADHESIVES

1. Vibrational
2. Dowel rotation
### RESULTS - PARAMETERS

<table>
<thead>
<tr>
<th>Welding Time (s)</th>
<th>Welding Pressure (MPa)</th>
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<th>Holding Pressure (MPa)</th>
<th>Number of specimens tested</th>
<th>Tensile Strength (MPa)</th>
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<tbody>
<tr>
<td>3</td>
<td>1.3</td>
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<td>1.3</td>
<td>No</td>
<td>10.4 ± 1.2</td>
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<tr>
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<td>1.3</td>
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<td>10.4 ± 1.2</td>
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**BUT ONLY FOR JOINING**

- Solid Wood to Solid Wood
- Solid Wood to Wood Panel
- Wood panel to Wood Panel
- CANNOT BE USED FOR BOARDS
## Dowel Welding

<table>
<thead>
<tr>
<th>Test</th>
<th>Grain orientation</th>
<th>Wood species</th>
<th>Dowel type</th>
<th>Hole diameter (mm)</th>
<th>Rotation rate (rpm)</th>
<th>Insertion time &amp; holding time</th>
<th>Average tensile strength (N)</th>
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</thead>
<tbody>
<tr>
<td>Welding Best combination</td>
<td>T+R Beech Fluted groove</td>
<td>9</td>
<td>1200</td>
<td>400mm/min</td>
<td>&gt;3134*</td>
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<td></td>
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<tr>
<td>PVAc control</td>
<td>T+R Beech Fluted groove</td>
<td>10</td>
<td>0</td>
<td>24 hours</td>
<td>&gt;3190*</td>
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<td></td>
</tr>
</tbody>
</table>

* Dowel shaft bond failure occurred in all cases. R = radial section. T = tangential section.

### Conclusions

- Accelerated PFs, PUFs resins
- Mixed PF/pMDI, UF/pMDI, PUF/pMDI
- Top of the range MUFs
- M and U resins with other aldehyde
- New adhesives, as yet unknown
- Wood Welding without adhesives
- Natural adhesives
  - tannin autocondensation
  - hexamine (for synthetic adh. too), and other hardeners
  - protein adhesives
  - carbohydrate adhesives
  - Unsaturated oil adhesives

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10 µm
THANK YOU

FOR YOUR KIND ATTENTION