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Section 4 Processes and properties

Corrosion of fasteners in furfurylated wood – final report after 9 years exposure outdoors

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Abstract
Corrosion of some common fastener materials – mild steel, stainless steel, zinc-coated steel, brass and Sanbond Z (nickel, zinc and chromate) coated steel – has been evaluated after nine years’ exposure outdoors in untreated Scots pine and furfurylated beech and Southern yellow pine (SYP).

The furfurylation was carried out according to a process that resulted in approximately 40 % Weight Percent Gain (WPG).

The results show that the corrosion of fasteners in furfurylated wood according to the particular specification is considerably more severe than in untreated wood and very similar to the corrosion caused by thermally modified wood. Mild steel and zinc coated steel have been most susceptible. Stainless steel has not been attacked at all and is therefore strongly recommended for furfurylated wood in outdoor applications.

Keywords: furfuryl alcohol, furfurylation, corrosion, fasteners, nails, screws

1. INTRODUCTION
The properties of furfurylated wood in interaction with other materials is an important aspect of the performance in a construction of furfurylated wood and its overall durability. The aim of this study has been to investigate the effect of furfurylated wood on different types of metal fasteners in comparison with untreated wood.

The work was initiated within the framework of the European project ECOBINDERS (2006-2008), a project that focused on developing new processes and products based on furan and/or lignin chemistry. One of the main objectives was to develop durable wood as a sustainable alternative to wood treated with traditionally biocide-based wood preservatives.

2. MATERIALS AND METHODS
Furfurylated Southern yellow pine (*Pinus* sp., SYP) and European beech (*Fagus sylvatica*) was provided by the Norwegian ECOBINDERS partner WPT, now Kebony ASA. The wood was treated according to a Weight Percent Gain (WPG) of approximately 40%. Scots pine (*Pinus sylvestris*) was used as a reference wood species.

Three types of nails and two types of screws were chosen for the study, see Table 1. The surface areas were calculated based on the given fasteners’ dimensions and were considered to be as accurate as possible.
Table 1. Types of fasteners studied.

<table>
<thead>
<tr>
<th>Type</th>
<th>Material</th>
<th>Dim. [mm]</th>
<th>Area [cm²]</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nail</td>
<td>Mild steel, quality CD9 (EN 10016-2)</td>
<td>2.3 x 60</td>
<td>5.8</td>
<td>Gunnebo Fastening AB</td>
</tr>
<tr>
<td>Nail</td>
<td>Hot-dip galvanised steel (zinc coating &gt;50 µm) quality CD9 (EN 10016-2)</td>
<td>2.3 x 60</td>
<td>5.8</td>
<td>Gunnebo Fastening AB</td>
</tr>
<tr>
<td>Nail</td>
<td>Stainless steel, quality A4 (SS 2347)</td>
<td>2.3 x 60</td>
<td>5.8</td>
<td>Gunnebo Fastening AB</td>
</tr>
<tr>
<td>Screw</td>
<td>Brass, quality according DIN 7997</td>
<td>4.0 x 40</td>
<td>5.4</td>
<td>Bårebo Nordic AB</td>
</tr>
<tr>
<td>Screw</td>
<td>“Cobra” Sanbond Z-coated steel (nickel, zinc, chromate coating &gt;16 µm)</td>
<td>4.3 x 51</td>
<td>7.3</td>
<td>Arne Thuresson Byggmaterial AB</td>
</tr>
</tbody>
</table>

The fasteners were all washed in ethanol, weighed and installed upright in rigs consisting of samples of 22x100x400 mm (reference rigs 28x120x400 mm), standing as in Figure 1 at SP’s (now RISE) field test site in Borås, Sweden in mid-September 2006. The ground of the test site was covered with gravel and maintained free of vegetation. The annual average of rainfall in Borås is approximately 970 mm and the average temperature is approximately +7 °C.

The test set-up was originally used by Boliden AB in a trial carried out in the 1970s (Berglund and Wallin 1978) and later by SP (now RISE) for corrosion trials with fasteners in preservative-treated wood (Larsson Brelid et al 2011) and thermally modified wood (Jermer and Andersson 2005 and 2012, Schalnat et al 2016). In 2004, the set up was acknowledged by Nordtest for testing the corrosion of fasteners in fire-retardant treated wood, NT Fire 056 (2004).

![Corrosion test set up.](image)

The first inspection was carried out after five years’ exposure in 2011. The results from that inspection were never published in an official report, but presented at the Nordic Wood Protection Conference in Oslo in 2012 (Jermer 2012). The trial was then terminated in mid-September 2015, i.e. after 9 years’ exposure and it is thus communicated in this report.

The samples were visually inspected before and after they were chiselled out of the wood. A grading system according to Table 2 was applied for rating the amount of attack on the surface coating and the basic material. The more severe the attack, the higher the rating.
Table 2: Rating scale for visual assessment of corrosion attack.

<table>
<thead>
<tr>
<th>Rating</th>
<th>Description</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>No attack</td>
<td>&lt; 5 % attacked</td>
</tr>
<tr>
<td>1</td>
<td>Insignificant attack</td>
<td>&lt; 5 - 50 % attacked</td>
</tr>
<tr>
<td>2</td>
<td>Slight attack</td>
<td>50 - 95 % attacked</td>
</tr>
<tr>
<td>3</td>
<td>Serious attack</td>
<td>&gt;95 % attacked</td>
</tr>
<tr>
<td>4</td>
<td>Completely attacked</td>
<td></td>
</tr>
</tbody>
</table>

The rating of the basic material was more important for the performance of the fastener and therefore the weighted rating was based on 75 % basic material and 25 % surface coating:

\[
Weighted \text{ rating} = \frac{\text{rating surface coating} + (3 * \text{rating basic material})}{4}
\]

To determine metal loss and depth of corrosion, the corrosion products had to be removed by pickling in acid and cleaned with water and ethanol according to the following procedure:

1. 5 min pickling in an ultrasonic bath (pickling solutions are listed in Table 3)
2. 2 min cleaning in hot water in an ultrasonic bath
3. 10 s rinsing in hot running water
4. Drying with a clean paper tissue
5. 30 s dipping in 96 % ethanol
6. Drying with a clean paper tissue
7. Steps 1 to 6 repeated once
8. Storage for at least one hour in a desiccator. To equalise the temperature, this was carried out in the same room as the weighing

Table 3: Pickling solutions and temperatures according to the material of the fasteners.

<table>
<thead>
<tr>
<th>Metal/Surface treatment</th>
<th>Temperature</th>
<th>Pickling solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>25 °C</td>
<td>Hydrochloric acid 1:1 in de-ionised water with an additive of hexamethylene chloride (3.5 g/l)</td>
</tr>
<tr>
<td>Brass</td>
<td>25 °C</td>
<td>Amidosulphuric acid, 5 %</td>
</tr>
<tr>
<td>Zinc containing materials</td>
<td>25 °C</td>
<td>Glycine (5 g/l) in de-ionised water</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>-</td>
<td>No treatment</td>
</tr>
</tbody>
</table>

At the 5 year inspection, corrosion products were removed after one pickling with glycine only for the zinc containing materials (galvanised steel and Sanbond Z). However, after 9 years an additional pickling in hydrochloric acid was performed to see if any corrosion was present on the base material and to check the thickness of the zinc coating of the galvanised samples.

After pickling, the fasteners were weighed and the difference between the original weight (prior to exposure in the trial) and the weight after pickling was determined. To calculate the metal loss/surface unit and the depth of corrosion the following formulas were used:

\[
\text{Metal loss} \left( \frac{mg}{cm^2} \right) = \frac{\text{Original weight (g)} - \text{Weight after pickling (g)}}{\text{Fastener area (cm}^2)} \times 1000
\]

\[
\text{Depth of corrosion (\mu m) = } \frac{\text{Metal loss (mg/cm}^2)}{\text{Density (kg/dm}^3)} \times 10
\]
The following densities were used:

- Mild steel: 7.8 kg/dm³
- Zinc coating: 7.1 kg/dm³
- Brass: 8.5 kg/dm³
- Stainless steel: 7.9 kg/dm³

3. RESULTS

Results from the inspections are shown in Figures 3 to 5. Figure 3 shows the result of the visual inspection before pickling. The corrosion rate after 9 years’ exposure, expressed as average metal loss (mg/cm²) is summarised for the wood materials and fasteners in Figure 4. Figure 5 shows the visual appearance of the fasteners exposed for 9 years in furfurylated and untreated wood after extraction and pickling.

![Ranking according to visual inspection after 9 years exposure](image1)

Figure 3. Results of visual inspection and rating of the corrosion of different fasteners in furfurylated and untreated wood after 9 years of exposure before pickling.

![Average metal loss after 9 years exposure](image2)

Figure 4. Average metal loss in mg/cm² after 9 years for the different fasteners tested in furfurylated and untreated wood after pickling.
Figure 5. Appearance of the different fasteners after 9 years' exposure in untreated Scots pine, furfurylated SYP and furfurylated beech after pickling.
4. DISCUSSION OF RESULTS

4.1 Comparison of visual assessment and calculated corrosion
When comparing the visual assessment (Figure 3) against the calculated metal loss (Figure 4), it appeared that the actual corrosion in the untreated material for all materials but galvanised steel and stainless steel (no corrosion at all) was somewhat over-estimated. The corrosion of galvanised steel and brass in the two furfurylated materials was also over-estimated.

4.2 Mild steel
The corrosion of the mild steel nails was greater than the corrosion of the other materials in the test. Furfurylated beech showed the greatest corrosion rate. The corrosion rate expressed as µm/year decreased over time for furfurylated SYP, increased somewhat for furfurylated beech and was constant for the untreated material, as can be seen in Figure 6.

Usually, the corrosion of mild steel shows a typical waistline formation 15-20 mm below the nail head owing to aeration cells and different electrochemical potential along the nail. In this test, the corrosion of mild steel in Scots pine was most severe at the tip of the nail which indicated that air has reached all the way down to the tip through cracks in the wood (Figure 7).

![Figure 6. Depth of corrosion of mild steel samples](image)

Figure 6. Depth of corrosion in µm/year in the first five years of exposure and the following four years.
4.3 Hot-dip galvanised steel

After pickling of the samples in glycine, which removes zinc corrosion products only, followed by pickling in hydrochloric acid with inhibitor (hexamethylene chloride), which removes all zinc and steel corrosion products, metal losses according to Table 4 were obtained.

Table 4. Metal losses after pickling hot-dip galvanised steel nails in glycine and hydrochloric acid after 9 years exposure.

<table>
<thead>
<tr>
<th>Wood sample</th>
<th>Metal loss after pickling in glycine, µm</th>
<th>Metal loss after pickling in HCl, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Scots pine</td>
<td>19</td>
<td>95</td>
</tr>
<tr>
<td>Furfurylated beech</td>
<td>61</td>
<td>100</td>
</tr>
<tr>
<td>Furfurylated SYP</td>
<td>58</td>
<td>100</td>
</tr>
</tbody>
</table>

The original coating thickness for the hot-dip galvanised nails was just below 100 µm. Approximately 80 % zinc remained on the samples of the untreated Scots pine, whilst approximately 40 % zinc remained on the other samples. Some basic metal corrosion may have occurred on fastenings of the furfurylated samples. As was found with mild steel, the corrosion rate decreased over time for furfurylated SYP. For furfurylated beech it was nearly constant, but for the untreated wood there was a remarkable increase during the last 4 years, see Figure 8.
4.4 Sanbond Z
Sanbond Z coating consists of a layer of nickel which is heat-treated onto which an electrolytic zinc layer with conversion coating (yellow chromate) is applied. Pickling of the samples in glycine removes zinc corrosion products only, whilst pickling in hydrochloric acid with inhibitor removes all zinc and steel corrosion products. After pickling in glycine and hydrochloric acid, metal losses according to Table 5 were obtained.
Table 5. Metal losses after pickling Sanbond Z coated screws in glycine and hydrochloric acid after 9 years exposure.

<table>
<thead>
<tr>
<th>Wood sample</th>
<th>Metal loss after pickling in glycine, µm</th>
<th>Metal loss after pickling in HCl, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Scots pine</td>
<td>12</td>
<td>17</td>
</tr>
<tr>
<td>Furfurylated beech</td>
<td>46</td>
<td>68</td>
</tr>
<tr>
<td>Furfurylated SYP</td>
<td>41</td>
<td>64</td>
</tr>
</tbody>
</table>

A typical Sanbond Z coating thickness is 16 µm zinc. After 9 years, approximately 25 % zinc remained on samples from untreated Scots pine, whilst on the other samples all zinc had corroded away.

Figure 10. Sanbond Z coated screws after pickling with glycine.
4.5 Brass
The brass screws and Sanbond Z coated screws in the furfurylated wood showed similar corrosion patterns, i.e. a metal loss (mg/cm²) that is approximately 5 times higher than for the untreated Scots pine. They also had a reddish appearance after pickling, which indicated selective corrosion commonly referred to as de-zincification.

4.6 Stainless steel
All stainless steel nails were unaffected after 9 years exposure. However, stainless steel had a tendency to pop out of the wood over extended time.
5. GENERAL ASPECTS AND CONCLUSIONS

Nails and screws to be used in outdoor wood construction or otherwise in wood constructions where there is a high risk of corrosion should be made of a material that will provide reasonable resistance against corrosion in combination with the wood or wood-based materials.

The results showed that the corrosion of fasteners in furfurylated wood according to the particular specification was considerably more severe than in untreated wood. The degree of corrosion attack for identical fasteners in furfurylated wood was comparable to the corrosion obtained on fasteners in thermally modified wood (TMT) (Schalnat et al 2016) after a similar exposure time.

This study has confirmed results from previous studies, in that stainless steel has a superior performance compared to any other fastener material tested. A disadvantage with stainless steel is the tendency to pop out of the wood with time.

The Sanbond Z coated screws and the brass screws performed relatively well, and much better in the untreated wood than in the furfurylated materials. In the furfurylated materials, the brass screws were subject to severe corrosion caused by de-zincification. According to experience, the loss of zinc will affect the strength properties of the brass more than the weight loss indicated.

Not surprisingly, mild steel showed the poorest performance in both furfurylated materials. The typical waistline formation could not be observed, most likely due to crack formation that allowed air to reach all the way down to the tips of the nails.
To summarise the results of the study in terms of corrosion prevention, the following ranking applies:

stainless steel > Sanbond Z coated steel > hot-dip galvanised steel > brass > mild steel

Brass is ranked after galvanised steel, mainly because the dezincification and strength loss.

Stainless steel has not been attacked at all and is therefore strongly recommended for furfurylated wood in outdoor applications.

6. REFERENCES


Nordtest 2004: Corrosion test for fire retardant treated wooden products. Nordtest Method NT Fire 056