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Treatment of timber with water soluble dimethylol resins to improve their dimensional stability and durability *

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Summary. European Beech (*Fagus silvatica* L.) was impregnated with a dimethylol resin to improve its dimensional stability and durability. Different catalysts were evaluated in combination with the resin. Depending on the range of relative humidity, the resin improved the shrinkage and swelling by approximately 50%. The use of an acid (citric or tartaric) catalyst lead to improved resin curing. A curing temperature of 100 °C is necessary.

Introduction

Efforts have been made for many years to improve the swelling- and shrinking properties of wood as well as its resistance to fungal and insect attack. This can be attained by modifying the reactive parts of cellulose, hemicellulose and lignin in the cell wall. In recent years results with non-catalysed acetic acid anhydride have shown improved durability and dimensional stability of various timber species (Rowell 1975, Militz 1991). In view of these tests, an investigation on the effect of a water soluble synthetic resin, based on dimethylol, was carried out (DMDHEU = Dimethylol dihydroxy ethylenurea). DM is used industrially for the up-grading of cellulose fibres in the textile industry. It can be diluted in cold water in different proportions and, based on its viscosity, it has the ability to penetrate well into the cell wall of wood.

In the textile industry, DM is used because its ability to cross-link the cotton of textile thus improving the quality of textiles (Kullman & Reinhard 1978). Adding catalysts such as acids or metals causes acceleration and improvement of the cross-linking. Suitable catalysts are tetracarbon acids, citric acid (single or in combination with metals) and metals. Using strong acids can cause the collapse of fibres.

Initial tests to use dimethylol-components to improve the dimensional properties of wood were carried out by Nicholas & Williams (1987). They impregnated pine species with DM in combination with different catalysts. The best results (60% ASE = Anti Shrink Efficiency) were achieved with a 10–20% aqueous solutions of DM, with the addition of an $AlCl_3$ and tartaric acid catalyst. They pointed out, however, that the bending strength decreases considerably at increased curing temperatures of the resins.

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Videlov (1989) carried out fungal decay tests on *Pinus sylvestris* treated with DM. He reported that no attack by *Coniophora puteana* occured at 10% weight gain of resin. This increased resistance was still present even after repeated leaching. He thereupon concluded that the dimethylol-components fix to the fibres of the wood and that they cannot be simply leached out.

In the above studies, there were no results presented on alternative catalysts, optimum curing temperatures, and on hardwood species. The work on European Beechwood (*Fagus silvatica*) was therefore executed to verify the results of the other authors and to get more information on the process technology of DM-treatments.

Material and methods

Selection of suitable catalysts

DM will cross-link wood cell wall polymers in the presence of catalysts more quickly and completely. Therefore a catalyst had to be selected which cross-linked best with the available DM-resin in wood. On the one hand, the catalysts should be selected from a cost point of view and only environmentally justifiable catalysts should be used. After consulting the manufacturing firms, the following agents as catalysts in combination with the DM resin Arkofix NG (Hoechst) were examined:

Catalyst	Description of ingredient
Hoechst 3282	mixture from metal salts
Hoechst NKA	amine salt
Citric acid	organic acids

In order to obtain an impression of the curing speed of combinations of DM and the different catalysts at various temperatures, small quantities of the DM resin "NG" (10% in water) mixed with catalysts (1.5 by weight %) were hardened in petri dishes at different temperatures (80 °C–100 °C–120 °C) for 30 minutes. After 10 and 20 minutes the first assessments of the curing condition took place. In the tests it became clear that a 30 minutes treatment at a temperature of 80 °C, the catalyst 3282, with citric acids added, caused the resins to harden well. The concentrated Hoechst DM resin ("NG concentrate", contains 70% DM in water), reacts in the same way than the non-concentrated DM ("NG" contains 50% DM in water).

Increasing the temperature to 100 °C resulted in almost all combinations hardening within 20 minutes. A further rise in temperature to 120 °C accelerated the reaction, so that after 10 minutes almost all resins were hardened. Pure DM without catalyst also cured within 20 minutes at temperatures above 100 °C.

All the petri dishes were then stored at 20 °C/65% RH for some weeks. A second assessment of the curing condition of the resin proved that only the NG resins with the citric acid catalyst, were still hard. All the others were, at the time of assessing, soft and sticky. We presume that this softening is to be attributed to the strong hygroscopic properties of the resins.

Determination of the anti-shrink-efficiency (ASE)

Material

Wood: Non-steamed german beechwood (*Fagus silvatica* L.) was used. Sound material was dried, planed and cut into specimens, measuring 20 × 20 × 10 mm. Ten replicates were introduced in each treatment.

DM: The DM resin "Hoechst NG" was dissolved in various concentrations in water (5%, 10%, 20%). The following agents were added as catalysts (20% related to the quantity of NG): Hoechst NKA, Hoechst 3282, citric acid. At some treatments a supplementary 1% tartaric acid (related to NG quantity) was added.

Methods

The specimens of beech were vacuum impregnated with the aqueous solutions DM + catalyst. The uptake of agents and the dimensions in swollen state were determined. Subsequently the specimens were treated for 1 h in the drying oven at different temperatures (80 °C, 100 °C) in order to cure the resins. Some of the specimens were dried at 20 °C as controls.

After this all specimens were carefully equilibrated above $CaCl_2$ to ca. 0% m.c. After conditioning till the constant weight was reached, the specimens were weighed, measured once more and then conditioned consequently under the following relative humidities: 30%–60%–90%–100% relative humidity. For each condition the following values were calculated:

- absolute change of radial and tangential dimensions between climate x and y
- relative change of the radial and tangential dimensions between climate x and y [%]
- comparison of changes in dimensions of non-treated and treated specimen of beech; assessment of the ASE (Anti Shrink/Swelling Efficiency) from the following formula:

$$ASE = (\beta_{untreated} - \beta_{treated}) \cdot 100/\beta_{untreated}\ [\%].$$

Determination of the effect of DM on fungi

The determination of the effect of the DM-resin on wood attacking fungi was carried out according to the European Standard EN 113. The specimens were impregnated in a dessiccator with the following solutions and subsequently stored at a relative humidity of 60% and a temperature of 20 °C:

Solution 1: 20 % NG in water
4 % Cat. 3282
0.2% tartaric acid

Solution 2: 20% NG in water
4% Cat. 3282
5% Hoechst Arkophob (anti-wetting agent).

The non-treated specimens were dried at 103 °C for 24 hours, before being tested. The following fungi were used: *Coriolus versicolor* and *Gloeophyllum trabeum*.

Results

Anti-shrink-efficiency (ASE)

It is well known that resins can influence the ASE in different ranges of relative humidity in a different way. For this reason the ASE has been separately calculated for the three different ranges.

Dimensions maximally swollen till dry condition

Table 1 gives the ASE data of the most successful treatments. The non-treated material shrank 9–10% from the saturated to the dry condition. All treatments with the DM-resin lead to a lower shrinkage. The level of improvement depended on DM concentrations, curing temperature and catalysts.

Concentration DM: The higher concentrations (20% NG) of the DM resin yielded better results than the lower concentrations (5% NG). With some of the concentrations with 20% NG, good ASE could be attained (70–75%). However, good ASE was also attained with the lower concentrations. The most prominent treatment with 10% NG reaches an ASE of 50–60%, the most prominent with 5% NG an ASE of 40–45%.

An explanation for this effect is that – at treatment with 20% NG – the weight gain of the specimen by absorption of DM resins is ca. 10%. At treatment with 10% NG, this is only 5%, at the solution with 5% the weight gain is only 2% approx. Convert-

Table 1. ASE of the most successful treatments with NG in the range "dimensions saturated till dimensions dry" (the tangential dimensions of the specimens were used for determination)

Conc. NG	Catalyst	Temp. [°C]	ASE [%]
20%	3282 + Tart.	100	75%
20%	Citr-Tart.	100	70%
20%	NKA + Tart.	100	70%
20%	Citr + Tart.	100	65%
10%	Citr – Tart.	80	60%
10%	NKA + Tart.	100	55%
10%	3282 + Tart.	100	52%
10%	Citr + Tart.	100	45%
5%	Citr + Tart.	100	45%
5%	NKA + Tart.	100	43%
5%	3282 + Tart.	100	43%
5%	Citr – Tart.	100	40%
20%	Citr – Tart.	80	45%
20%	Citr – Tart.	80	40%
5%	3282 – Tart.	80	5%

ing these (numerical) values to kg/m^3 results in the following resin retentions: With a 20% NG the retention of DM is approx. 57 kg NG/m^3, which corresponds to 28 kg/m^3 at 10% NG and 14 kg/m^3 at 5% NG concentration.

Curing temperature: The fact that the temperature had a major effect, can clearly be seen in all the treatments. The treatments with resins were best at a curing temperature of 100 °C. A temperature of 80 °C was in almost all cases must less effective. At curing without raised temperature (20 °C) the resins improved the stability in about the same order as at 80 °C.

Catalyst: Without adding tartaric acid, citric acid was the better catalyst in the higher concentrations with NG. The catalysts NKA and 3282 without addition and acids were, depending on the treatment, less effective. On the other hand, when tartaric acid was added, both these catalysts were equally effective as citric acid without tartaric acid. Citric acid looses some of its effect when tartaric acid is added.

Dimensions from 30% r.h. to 100% r.h.

An important r.h.-range in the assessment of the effect of treatment of wood is the range to which wood in exterior use is exposed to (varying between ca. 30% and 100% r.h.). In this range only the specimens treated with a concentration of 20% NG were measured.

Table 2 illustrates the ASE achieved through treatment with DM. The best results were obtained with a curing temperature of 100 °C. The improvement (ASE 40–50%) in this range of r.h. was nevertheless far less than in the range "swollen-dry" (see above).

It becomes very clear that in order to obtain good results the addition of the acid catalyst was necessary. No adding acids (citric acid, tartaric acid), in general give poor results (ASE 0–25%).

Dimensions from 30% r.h. to 60% r.h.

For wood in interior use, the range of 30–60% relative humidity is important. Table 3 shows the ASE of the better treatments. Treatments with DM and citric acids as catalyst proved again to be the most successful.

EMC (equilibrium moisture content) of the timber

Figure 1 illustrates that due to the treatment with DM, the moisture content of the wood – in all zones of relative humidity – is higher than that in the non-treated specimens.

This was particularly clear in the treatments with DM whereby "3282" without added acid was used as catalyst. When adding tartaric acid to "3282", it lay in the range of the other treatments. An interesting fact is that all those treatments which

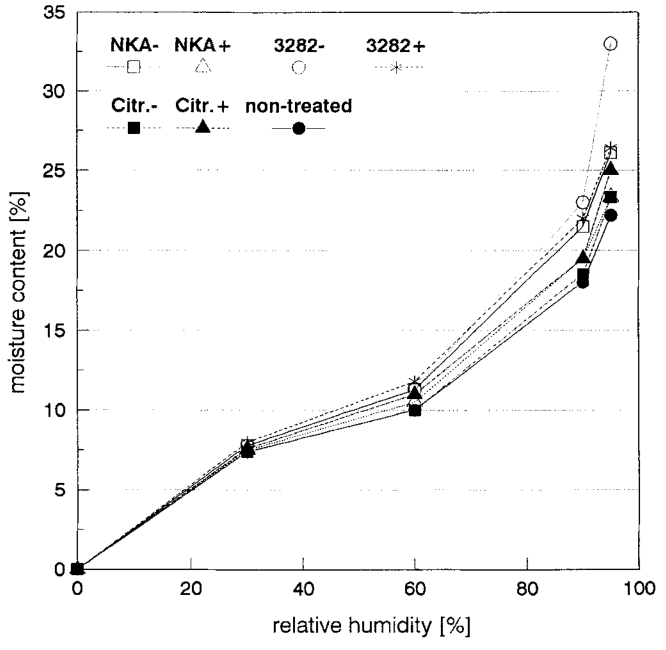

Fig. 1. Equilibrium moisture content of resin treated (20% NG) an untreated wood

Table 2. ASE of the most successful treatments with NG (20% NG) in the range 30%–100% relative humidity (tangential dimensions were taken for determination)

Catalyst	Temp. [°C]	ASE
3282 + Tart.	100	50%
Citr. + Tart.	100	40%
Citr. – Tart.	100	40%
NKA + Tart.	100	40%
3282 + Tart.	80	35%
3282 – Tart.	100	18%
3282 + Tart.	20	20%
Citr. + Tart.	20	16%

strongly increased the e.m.c did not improve the swelling/shrinkage properties of the wood in a very effective way. This can be explained by the fact that hygroscopic resins and catalysts attract moisture, partly causing the swelling of the cell wall.

Resistance to fungal attack (EN 113)

Figure 2 shows the weight loss of the specimens in the fungi test. During the 16 weeks' testing period *Coriolus versicolor* attacked the non-treated specimen by approx. 30%. Both treatments with DM increased the resistance of the wood. The resistance

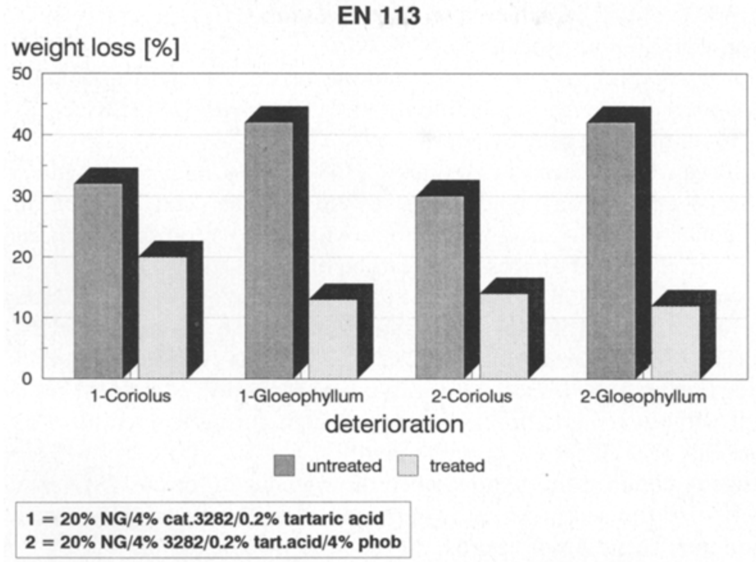

Fig. 2. Weight loss of treated and untreated specimens in fungal test EN 113 with *Gloeophyllum trabeum* and *Coriolus versicolor*

Table 3. ASE of the most successful treatments with NG in the range 30%–60% relative humidity (the tangential dimensions were used)

NG	Catalyst	Temp. [°C]	ASE [%]
20%	Citr. – Tart.	100	50
10%	Citr. – Tart.	100	43
20%	Citr. – Tart.	80	35
20%	3282 + Tart.	100	35
5%	NKA + Tart.	100	30
20%	NKA + Tart.	100	22
20%	3282 + Tart.	80	22
10%	NKA + Tart.	100	22
10%	Citr. – Tart.	80	22
5%	3282 + Tart.	80	22

to attack by *Gloeophyllum* resulting from treatment was greater than with *Coriolus*. Adding an anti-wetting agent even improved the resistance against the fungi tested.

Discussion

Anti-shrink-efficiency

The present tests with small specimens of beechwood proved, that treatment of wood with DM improves the dimensional stability of the wood considerably. An improvement of these properties can be achieved in all the examined ranges of relative humidity, however to a different extent.

In applications of wood for interior use, fluctuations between a relative humidity of 30% and 60% appear. Under these conditions, a treatment with DM (citric acids as catalyst) leads to an improvement by approx. 50%.

A similar result can be achieved in the range (30%–100% relative humidity) important for exterior applications. Under these conditions, the catalyst based on metal salts (3282) added to tartaric acid proves to be superior to citric acids without a metal salt. An improvement of approx. 50% can be obtained too.

However, in general it can be concluded that the resin NG requires the addition of an acid (either citric or tartaric acid). In comparing the toxic properties of the catalysts, the citric acid versus the metal salts (3282, NKA) is more useful and should be recommened for further tests. Because of the hygroscopic nature of the DM resin it is not certain, if without the addition of a catalyst, high curing temperatures or longer curing time will be sufficient to get a good ASE.

The best results are obtained throughout when the ingredient (Hoechst NG) in a concentration of 10–20% mixed in water, is impregnated in the wood. This corresponds with a minimum retention of approx. 30–60 kg DM/m^3.

From the tests it became also evident that an increased curing temperature (100 °C) leads to far better results than curing at room temperature. In further research this should be investigated with larger timber dimensions.

The improvement of the dimensional stability of beechwood through treatment with DM supports the results from Nicholas & Williams (1987). They found, on pine, an ASE of 40–60% depending on the curing temperature.

Resistance to fungal attack

The treatment of beech with DM and the metal salt catalyst "Hoechst 3282" led, at a weight gain of 20%, to improved resistance against *Coriolus versicolor* and *Gloeophyllum trabeum*. However, in comparison to the well-known commercial wood preservatives the protective effectiveness of the DM resins is not sufficient.

These results with beech do not correspond with the very satisfactory results from Videlov (1989) who obtained with a 15% weight gain of DM in pine a complete protection from attack by *Coniophora puteana*. Further research work has to be done to clarify these differences in results.

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