

Biodegradable lightweight construction boards based on tannin/hexamine bonded hemp shaves

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Interior grade hemp shave lightweight construction boards of about 0.260 g/cm^3 , with a dry I.B. strength of up to 0.34 MPa, a formaldehyde release well within the emission class E1 and certificate as normal flammable and not burning dripped off (DIN 4102-B2) were fabricated by mixing hemp shaves with a borate-modified mimosa tannin-hexamine binder and press the masses as fast as 6 s/mm thickness at 70°C to one-layer boards. Different drying processes indicate that fast drying at $\sim 100^\circ\text{C}$ is needed both for satisfactory strengths and for a sufficient dimension stability performance of soaked samples, but, as well for a lower boron leaching during soaking. For dry environments the resistance to fungal attack is sufficient enough to have boards for interior application.

Biologisch abbaubare Leichtbauplatten basierend auf Tannin/Hexamin gebundenen Hanfschäben

Hanfschäben wurden mit Borat modifizierten Mimosa Tannin-Hexamine Bindern gemischt und bei 70°C und Presszeiten von 6 s/mm Dicke zu einlagigen Leichtbauplatten mit Dichten von etwa 0.260 g/cm^3 verpresst. Querkzugfestigkeiten bis zu 0.34 MPa, Formaldehyd-Emissionen die innerhalb der Emissionsklasse E1 liegen und Brandschutzeinstufungen als normal entflammbar und

nicht brennend abtropfend (DIN 4102-B2) wurden bestimmt. Verschiedene Trocknungsprozesse zeigen, dass schnelles Trocknen bei $\sim 100^\circ\text{C}$ zu höheren Festigkeiten und, nach wässern der Proben, zu ausreichender Dimensionstabilität bei geringerer Borauswaschung führt. Für trockene Umgebungen ist die Resistenz gegen Pilzbefall ausreichend genug um die Bretter für Innenanwendungen einzusetzen.

1 Introduction

Hemp has successfully proven its qualities as paper, textiles, fleeces components etc. since 6000 years BC (Herer 1993). Presently the raw material is utilized not only in paper and textile industries but also for automobile and building materials as well as in the field of agrarian techniques (Herrmann et al. 1998; Kozłowski 2000). Whereas long and short fibres are used for example for the processing of fibre reinforced plastics and components for several years (Satlow et al. 1994; Hanselka et al. 1995), the fibrous waste in great quantities finds its application in nonwovens since the 1940s (Kozłowski 2000). Shives and shaves are commonly used only in small amounts as an addition or filler to medium density fibre boards (MDF) (Kozłowski et al. 1994; 1996).

This gave us the motivation to develop board materials consisting of compressed resinated shaves. Because of the low bulk density of loose hemp straw of about 120 kg/m^3 (15% moisture content; Kozłowski 2000) such boards should offer applications in the area of lightweight constructions e.g. for mobile homes, ship building, packing material etc. as well as for floor acoustic insulation, closets, shelves and so on. In addition, using a biodegradable adhesive like tannin and additives which should not lead to a release of formaldehyde a biocomposite is given particularly suitable as component for interior fittings for buildings based on natural material e.g. for people with allergies. Due to the products being completely fabricated of biological renewable resources the possibility is offered to recycle the boards or having a convenient removal after the end of a lifetime by composting.

Fabricating these boards involves a mixing of the binder system to shortened hemp shaves and press the resulting mass to one-layer boards. With respect to mechanical properties the pressed components should be comparable to particleboards, and utilizing polyphenolic tannin which is well-known for its resistance to fire (Knop et al. 1985; Meikleham et al. 1994a) can result in flame retardant boards. To protect the material against fungal attack a

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wood preservation is necessary (Yalinkilic et al. 1999). This will be done by boron compounds which are capable of acting as both as an insecticide and a fungicide (Thevenon et al. 1997). In addition, using borates should lead to boards with higher strengths compared to a non addition boards (Pizzi et al. 1995a) and offer great advantages for applications including no or very low mammalian toxicity, low volatility, they are colourless and odorless (Yalinkilic et al. 1999; Murphy 1990). Because, the boards thought to be used in particular in dry environments a possibly small but sufficient addition of the fungicide should be used. However, tests on the dimension stability and leaching of fungicide have to be carried out to characterize the board-quality for a short-time contact with water (Thevenon et al. 1997; Yalinkilic et al. 1999).

2 Materials and methods

2.1 Chemicals and board preparation

An aqueous boric acid solution of 13.9 wt.% boric acid and 30.6 wt.% NaOH-solution (33 wt.% in water) was premixed. As an adhesive/hardener mixture a solution of 37.9 wt.% mimosa tannin extract powder (0.75 kg; Weibul, Brazil), 5.3 wt.% NaOH-solution (33 wt.% aqueous solution) and 2.5 wt.% powder of the hardener hexamethylenetetramine (0.05 kg; as 40 wt.% aqueous hexamine solution) was prepared at pH 9 giving 0.8 kg of dry admixed adhesive/hardener solids in water. Besides the tannin powder all chemicals were received as technical grade by Zschimmer und Schwarz, Germany. To get the desired borate-modified adhesive (BMA) 16.9 wt.% of the boric acid solution – with respect to the adhesive/hardener mixture – was added to it and stirred for 5 min at 500 rpm. For control samples (CS) water was added to the adhesive/hardener mixture instead of the boric acid solution.

Shortened hemp shaves with a mean shave length of approximately 30 mm and a bulk density of 100 kg/m³

were used to prepare the wood/adhesive mixtures. These hemp shaves yield a water content of approximately 15 wt.% measured by oven-drying of 5 charges (each 1 kg) for 24 hours at 105°C. To each of the 5 kg sample of hemp shaves (67.8 wt.%) 2.37 kg of the adhesive/hardener solution (32.2 wt.%) was mixed, giving a ratio of adhesive/hardener solids to dry wood of 1:5.3 for both adhesive/hardener mixtures (BMA or CS). The mixing was carried out in an Eirich-mixer-system (R09 W, Hardheim, Germany; capacity: 0.15 m³/240 kg) for 5 min at the slowest possible rotation speed. The wood/adhesive mixtures were then pressed to one-layer hemp shave boards (HSB) of a dimension of 1250 × 625 × ~25 mm for 2.5 min (6 seconds/mm thickness) at a pressure of 100 bar (102 kg/cm²) using a modified Erlenbach system, Lautert, Germany. The temperature at the press form was adjusted at 180°C and a controlled flow of hot gas (heated by the press form) through the form and boards did not exceed a temperature of 70°C inside the boards which was measured by a thermocouple.

2.2 Drying process of boards

Because different drying processes are supposed to affect the quality of the boards respective five samples of HSB of dimensions of 200 × 200 × ~25 mm were dried for 36 hours in flowing dry air at (A) 25 or (B) 30°C followed by a drying process in an oven (Memmert, Germany) for 24 hours at 105°C. In addition, five HSB samples (C) with or (D) without boron compounds of the same dimensions were dried for 36 hours in flowing dry air at 45°C, respectively. Subsequently, all samples were stored for 7 days (15°C, 70% air moisture). A dried sample which is processed by (B) is shown in Fig. 1.

2.3 Dimension stability and boron leaching

For dimension stability specimens of (A), (B), (C) and (D) of dimensions of 50 × 50 × ~25 mm were soaked in water

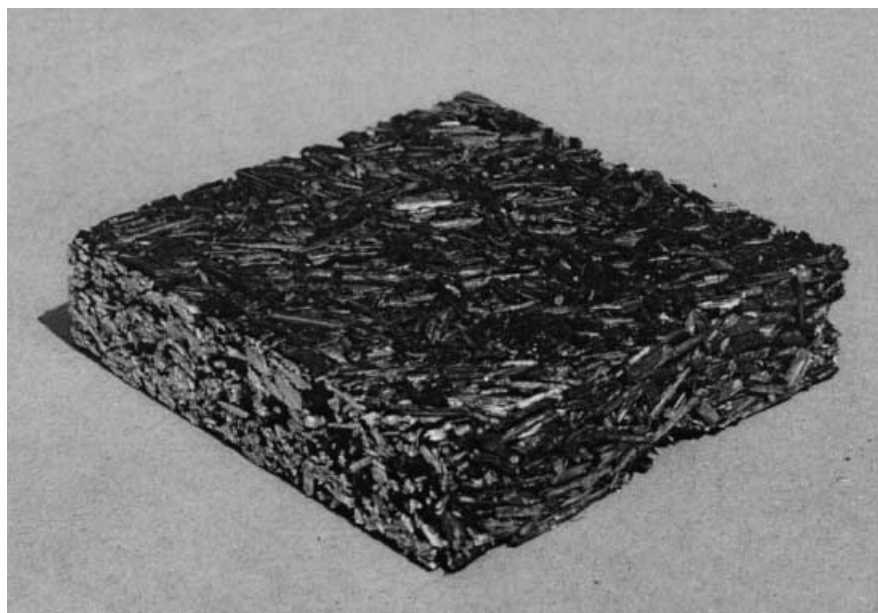


Fig. 1. Sample of a fabricated one-layer-board consisting of tannin-hexamine bonded hemp shaves after drying for 36 h in flowing dry air at 30°C followed by a drying process in an oven for 24 hours at 105°C. The sample was then stored for seven days (15°C, 70% air moisture)
Bild 1. Probe eines einschichtigen Brettes aus Tannin-Hexamine gebundenen Hanfschäben, nach 36 Std. Trocknen in umflutender trockener Luft bei 30°C und weiteren 24 Std. Trocknen bei 105°C in einem Ofen. Anschließend wurde die Probe für sieben Tage gelagert (15°C, 70% Luftfeuchte)

for 4 days and then oven-dried at 60°C (Mettmert, Germany) for 3 days. Swelling values both in water-swollen and oven-dry state were determined using a ruler to calculate the volumetric change.

Samples of (B) and (C) of dimensions of 40 × 40 × ~25 mm were leached by placing each specimen in 150 ml distilled water at 20°C and changing the water every day over period of 4 days. The leaching waters were then analysed on their boron contents according to EN 11885 (E22) by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). This method is used for the quantitative determination of trace elements in solutions and allows the detection of boron up to 1.5 µg/L (Tyler 1991).

2.4

Properties of strength, formaldehyde emission and resistance to fire

Samples of (B), (C) and (D) were investigated for their dry internal bond (I.B.) strength after the drying process and after a sequence of leaching the samples for 4 days in water and subsequent drying for three days at 60°C (Mettmert, Germany), respectively. The measurements were carried out according to EN 319.

For formaldehyde emission specimens of (B), (C), (D) and control samples (only borate bonded hemp shaves) were tested by the WKI-method (Muratzky 1989).

For fire properties, samples of all prepared HSB were tested according to DIN 4102-1.

2.5

Biological resistance

Four unleached samples of (B) and of (C) (90 × 90 × ~25 mm) were exposed to pure cultures of the wood destroying fungal species *Aspergillus niger*, *Aspergillus terreus*, *Aureobasidium pullulans*, *Paecilomyces variotil*, *Penicillium funiculosum*, *Penicillium ochrochlo-* *ron*, *Scopulariopsis brevicaulis* and *Trichoderma viride* by

spraying an aqueous spores solution containing a mixture of all 8 fungi in equal shares onto the specimens. As a control each kind of fungal solution was placed on a Petri dish separately and was incubated at room temperature (positive control 1). A sterile filter paper was sprayed with the spore mixture (positive control 2) and respective two samples of (B) and (C) were sprayed with distilled water (negative control). Finally, all samples and the filter paper were placed above an aquatic surface in closed plastic dishes and stored in an incubator at 29°C for 28 days. The experiments were conducted according to DIN IEC 68, where a quality class rating between 0 (= no attack seen by a loop) and 3 (= more than 25% of the samples surface is covered by the fungi and seen to the naked eye) is assigned to specimens.

3

Results and discussion

3.1

Drying process and strength properties

Densities, differences of mass loss and dry I.B. strengths after drying and storage of samples in different ways are given in Table 1. Different temperatures during air drying (25-, 30- and 45°C) for 36 hours expectedly lead to different mass losses by water. The reduced water content in samples dried at 45°C is higher than that of drying at lower temperatures. But, after drying samples (A) and (B) in an oven for 24 h at 105°C and store them for 7 days as well as storage of the samples (C) and (D) for 7 days at 15°C (70% moisture), respectively, led to a mass loss which is nearly the same for all treatments, except for (D). Because, samples (D) were fabricated without borates a lower adhesive force between the binder and the shaves can lead to a more open structure of the samples. Thus, the shaves can adsorb higher amounts of water during storage. This assumption is confirmed by results of Pizzi et al. (1995a) who fabricated tannin bonded particle boards by adding

Table 1. Densities, mass losses and dry I.B. strengths of tannin bonded hemp shave samples fabricated with or without boron compounds after drying and storage in different fashions

Tabelle 1. Dichten, Masseverluste und Querzugfestigkeit (trocken) von Tannin gebundenen Hanfschäben-Proben, die mit oder ohne Borzusätze produziert und anschließend getrocknet und gelagert wurden

Samples [#]	Density in [g/cm ³] after				Difference of mass loss [wt.%]		Ave. I.B. strength dry (MPa) ^{&}
	Production	Air drying [*]	Oven drying, storage [§]	Storage [§]	Production – air dried	Production – stored	
A	0.362 (0.036)	0.309 (0.033)	0.279 (0.022)	–	14.6	22.9	Not measured
B	0.355 (0.018)	0.277 (0.015)	0.271 (0.013)	–	22.0	23.7	0.338
C	0.341 (0.017)	0.244 (0.013)	–	0.258 (0.014)	28.4	24,3	0.026
D	0.310 (0.022)	0.225 (0.020)	–	0.255 (0.017)	27.4	17.7	0.009

Values in parenthesis: standard deviation

[#] Sample D: control (without boron compound)

^{*} For 36 hours in dry air at (A) 25°C, at (B) 30°C and (C, D) at 45°C

[§] After air drying the samples were oven dried (24 h, 105°C) and then stored for 7 days (15°C, 70% air moisture)

[§] After air drying for 36 hours the samples were stored for 7 days (15°C, 70% air moisture)

[&] After drying and storage the samples

weak Lewis acids. Their measurements of I.B. strength have led to higher values if they added boric acid to mimosa tannin compared to a non addition.

To discuss the big differences in strengths between the samples (B), (C) and (D) (Table 1) the addition of boron compounds and the different drying processes have to be taken into account. Because, samples (C) and (D) were similarly dried and stored the addition of boron compound to HSB (C) during fabrication can lead to higher values of strengths compared to (D). By boron, the adhesive force between hemp and tannin is increased by an accelerating of the process of creating a cross-linked network of tannin-tannin and tannin-hemp shave bonds, whereas boron acts as a catalyst during the condensation of tannin (Meikleham et al. 1994b). But, the addition of the boron compound alone does not lead to maximum possible strengths if one compares the results for (B) and (C). The need for drying HSB after processing implies an uncompleted reaction of the tannin-hexamine system to fully condensed and cross-linked phenolic polyflavonoids. Using tannin-hexamine binders processing or drying temperatures of $\sim 100^\circ\text{C}$ inside the boards are needed for a fast and complete curing and hardening of the adhesive in the boards (Heinrich et al. 1996). Thus, different temperatures during drying lead to different amounts of desorbed water and, therefore, to different advanced stages of the condensation. In addition, at temperatures up to 100°C hexamine reacts at an intermediate decomposition stage to high amounts of methylen bridges and low amounts of benzylamine bridges between the mimosa flavonoids (Pizzi et al. 1995b; Heinrich et al. 1996; Wang et al. 1997). Thereby mono-benzylamines are predominant among the benzylamines not leading to interflavonoid bridges. This species remains single bonded in the network of tannin-tannin and tannin-hemp shaves or will – as a detached high reactive molecule – immediately react either with negatively charged or electrophilic compounds in the framework. This depends on the stage of protonation of the molecule. Due to the high pH of the adhesive/hardener solution deprotonated mono-benzylamines will be predominant leading to bonds with electrophilic compounds. Finally, this affects the curing and hardening of the adhesive by being more sensitive to water attack and by the

more open structure of the adhesive/wood network. In addition, the open framework leads to higher amounts of water in the boards (Pizzi et al. 1995b) and lower strengths are the result.

3.2

Leaching – residual boron and properties of dimensional stability and strength

The results for residual boron in wood after leaching the samples (B) and (C) are given in Table 2. Decreased boron concentrations for both samples (B) and (C) are measured but, the rate of concentration decrease is more pronounced for (C) and tends to zero after 4 days of leaching. A similar behaviour was observed by Thevenon et al. 1997 who dipped wooden samples in boric acid solutions. By soaking the specimens no boron was left in the wood after 2 days. But, in comparison to (C), nearly 45% of the boron is left in (B) after 4 days. Because, samples (B) and (C) were fabricated under the same conditions these results are somewhat surprising. Naively one would expect a similar boron leaching. But, if one takes into account that a very high $\text{B}(\text{OH})_4^+$ -concentration exists near and at the reacting tannin-monomer sites a partial or complete intersystem precipitation of the boron compound may take place that in turn is stabilized by condensed and cross-linked phenolic polyflavonoids. The latter becomes more and more probable the higher the temperatures are during drying, accelerating curing and hardening of the adhesive in the boards. In what fractions boron is present as enclosed borate or bonded at organic compounds was not measured. But this could be determined by X-ray diffraction and NMR-spectroscopy.

Figure 2 shows the volumetric increase of samples leached for 4 days. There is a fast increase of the volume within the first 2 h followed by a reduced increasing of the volume from 2–7 h and a time interval from 7–96 h where the volumetric increase of the samples tend to a limiting value, except for samples (D). The final volumes of the samples after leaching and after drying (72 h, 60°C) are given in Table 2. The results indicate that the pretreatments for (B) are best for giving dimensional stability within the experiments. Whereas the pretreatments for (D) (without boron addition) lead to the highest values of volumetric increase

Table 2. Residual boron left in hemp shave samples and the change of sample-volume after soaking them for 4 days in water as well as the volumetric change and properties of I.B. strength after drying the soaked samples for 3 days at 60°C

Tabelle 2. Verbleibendes Bor und Volumenänderung von Proben aus Tannin gebundenen Hanfschäben nach viertägigem Wässern sowie die Volumenänderung und die Querkzugfestigkeit nach dreitägigem Trocknen der gewässerten Proben bei 60°C

Sample [#]	Residual boron left in wooden compound (%)					Change of sample-volume (%)		Ave. I.B. strength dry (MPa) [§]
	Unleached	After 1 day	After 2 days	After 3 days	After 4 days	Before – after leaching*	Before leaching – after drying [§]	After drying
A	100	n.m.	n.m.	n.m.	n.m.	19.61	7.82	n.m.
B	100	67.92	56.77	49.82	44.88	17.81	7.18	0.042
C	100	37.52	16.23	6.47	1.26	21.13	9.11	0.005
D	–	n.m.	n.m.	n.m.	n.m.	23.17	10.58	0.005

n.m.: not measured

[#]Sample D: control (without boron compound)

*After leaching for 96 h

[§]After drying leached samples for 72 h at 60°C

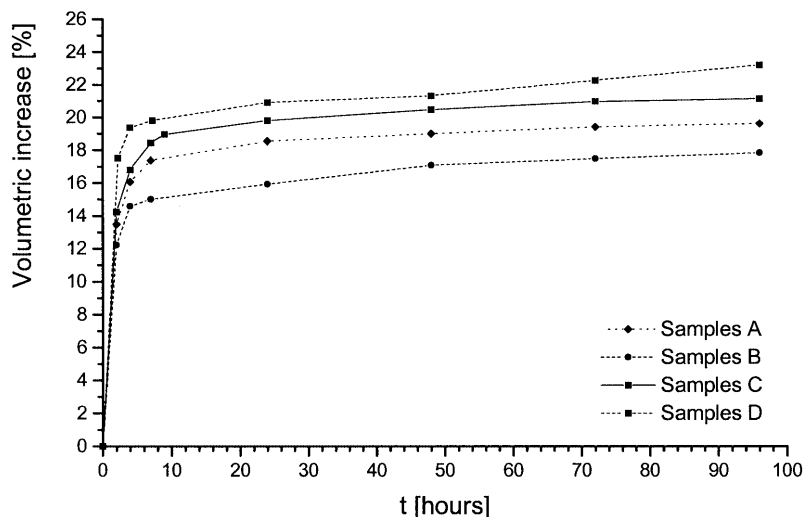


Fig. 2. Volumetric increase of tannin-hexamine bonded hemp shave samples during soaking them in water for 4 days. For description of sample-pretreatments (A)–(D) see section 2.2

Bild 2. Volumenzunahme von Tannin-Hexamin gebundenen Hanfschäben Proben während 4 tägigem Wässerns. Zur Vorbehandlung der Proben (A)–(D) siehe 2.2

and, which is assumed, to an increased detach of hemp shaves between 48 and 96 h. But, this is not surprising taking the results into account mentioned above. The absence of boron compounds and the increased amounts of monobenzylamines through decreased drying temperatures for samples (D) lead to an accelerated sensitivity to water attack in the boards compared to samples (B). Finally, the drying temperature is more important for giving higher dimension stability as adding a borate and is verified by the comparison of (A) and (C).

Although, the strength is drastically decreased in comparison to unleached samples (Table 1) showing that the mimosa-hexamine systems are not capable to reach exterior application quality (Pizzi et al. 1994), decreased strengths correlate with decreased dimension stability (Table 2). After all, for a distinctive dimension stability and high strengths temperatures $\sim 100^\circ\text{C}$ are important during fabrication or a subsequent drying of the mimosa-hexamine bonded HSB. Thereby, boron helps in catalysing the reaction (Meikleham et al. 1994b).

3.4

Release of formaldehyde and fire protection

Due to the formaldehyde (CH_2O) toxicity (Yusuf et al. 1995; Yalinkilic et al. 1999) the release of formaldehyde was investigated after drying the HSB. For HSB samples and control samples (borate bonded hemp shaves) the measured values of formaldehyde emission are on average:

sample (B): 1.8 mg/100 g board,
 sample (C): 0.9 mg/100 g board,
 sample (D): 2.1 mg/100 g board and
 control sample: 0.95 mg/100 g board.

This indicates very low release of CH_2O -molecules (Pizzi et al. 1994; Pizzi et al. 1995a; Heinrich et al. 1996) and that the boards are well within the limits of the E1 emission class (Marutzky 1989). Comparing samples (C) and the control samples shows that the used mimosa tannin has no influence on the formaldehyde emission. The relatively high value of samples (D) is probably due to the more open structure of the fabricated HSB and, therefore, increased concentrations of formaldehyde were

measured. But in comparison to the compact samples (B) the differences are rather small which implies that higher temperatures used during drying, e.g. samples (B), results in higher emission of formaldehyde. Heinrich et al. (1996) found that temperatures above approximately 100°C in boards during fabrication leads to an accelerated release of formaldehyde. By increasing the temperature a forced decomposition of hexamine to formaldehyde occurs. This is verified by comparing the results for samples (B) and (C) considering an additional drying of (B) at 105°C for 24 hours. Finally, a further decrease of formaldehyde emission can be achieved if fabrication and/or drying processes for compact samples take place at temperatures $\leq 100^\circ\text{C}$ (Heinrich et al. 1996). But this is not urgently necessary because, the measured release of formaldehyde is very low and there is practically no risk for ones health.

A very important criterion of the produced HSBs are their behavior in the case of fire. That applies particularly using them for interior fittings for buildings. Because tannins do not burn (Knop et al. 1985) they should ensure that the boards either will not or will burn only for a short time. The investigations of samples (B), (C) and (D) according to DIN 4102-1 were conducted by setting a flame onto the edge of each sample for 20 seconds. The inflammability of all samples was less than 5 s. After removing the flame source the samples burnt for 16–23 s and then the flames self-extinguished. All samples smouldered than for more than 25 s and non of them had to be quenched. Thereby, only very small amounts of smoke were formed and burning parts did not detach from any sample. After all, the investigated samples perform DIN 4102-B2 and are certificate as normal flammable and not burning dripped off. Therefore, the fabricated HSB are suitable for interior application.

3.5

Biological resistance

After 4 days of exposure of the wooden specimens, the filter paper and Petri dishes to fungi the typical growth of the respective isolate could be observed on the Petri dishes (positive control 1), only. The filter paper was completely covered by fungi after 14 days (positive control 2) and a

visible growing of fungi was observed after 14 days at samples for the negative control. Also after 14 days, a first visible growth of fungi at the test samples was noticed. According to DIN IEC 68 the tested controls and samples were allocated to the quality class 3 (see section 2.7). Because, the negative control as well as the test samples show the same grade of fungal growth after 14 days of exposure it is assumed that the HSB and, in particular, the hemp shaves are already contaminated by fungi. In addition, the chosen amount of boron compounds as wood preservative is not enough to implement the boards in moist climates. To minimize the fungal attack higher amounts of the wood preservative or more efficient fungicide compounds have to be used. Several approaches deal with this problem and have led to preservatives indicating excellent results. There are protein borates (Thevenon et al. 1998a, 1998b) and a wide range of boron formaldehyde or boron polymer reagents (Yalinkilic et al. 1999). In addition, the application of fungicide used for e.g. in cosmetics or technical bio-products should also be considered. But, finally, for dry environments the amount of fungicide addition is sufficient enough to have boards for interior application.

4

Conclusions

Hemp shave boards with densities of about 0.260 g/cm^3 , dry I.B. strengths up to 0.34 MPa and a formaldehyde emission much lower than the limits for a E1 quality standard were fabricated by mixing hemp shaves (water content $\sim 15 \text{ wt.}\%$) with a borate-modified mimosa tannin-hexamine binder and pressing as fast as 6 s/mm thickness at 70°C to one-layer boards. In addition, the pressed boards are certificate as normal flammable and burning parts did not detach from any sample (DIN 4102-B2). Different drying processes indicate that flowing dry air at temperatures up to 45°C are not sufficient both for satisfactory strengths and for performing sufficient dimension stability of soaked samples. A possibly fast drying at temperatures $\sim 100^\circ\text{C}$ is needed to decrease the amounts of monobenzylamines created by hexamine in conjunction with mimosa-tannins to have higher strengths and dimension stabilities, at the end, but as well a lowered boron leaching. The resistance to fungal attack by borates is sufficient enough for dry environments and boards for interior application.

5

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