UNIVERZA V LJUBLJANI

BIOTEHNIŠKA FAKULTETA

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INTERAKCIJE BOROVIH SPOJIN IN EMULZIJ VOSKOV Z LESOM IN LESNIMI GLIVAMI

Doktorska disertacija

INTERACTIONS OF BORON COMPOUNDS AND WAX EMULSIONS WITH WAX AND WOOD DECAY FUNGI

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KLJUČNA DOKUMENTACIJSKA INFORMACIJA

ŠD	Dd
DK	UDK 630*841.1:630*844.41
KG	borova kislina/boraks/emulzije voskov/glive razkrojevalke/izpiranje/sorpcijske lastnosti vodoodbojna sredstva/vlažnost lesa
AV	LESAR, Boštjan, univ. dipl. inž. les.
SA	HUMAR, Miha (mentor)
KZ	SI-1000 Ljubljana, Rožna dolina, c. VIII/34
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IN	INTERAKCIJE BOROVIH SPOJIN IN EMULZIJ VOSKOV Z LESOM TER LESNIMI GLIVAMI
TD	Doktorska disertacija
OP	X, 198 str., 3 pregl., 6 sl., 144 vir.
IJ	sl
JI	sl/en
AI	Za zaščito lesa se zelo pogosto uporabljajo pripravki na osnovi borovih spojin. Borovi pripravki so zelo učinkoviti insekticidi in fungicidi. Njihova slaba lastnost je, da se v vlažnem okolju iz lesa izpirajo. Vlažnost lesa in s tem tudi izpiranje borovih spojin smo skušali zmanjšati s hidrofobnimi sredstvi. Vzorce smo impregnirali z različnimi emulzijami voskov in jih izpirali v skladu s kontinuirnimi in nekontinuirnimi postopki izpiranja. Ti določajo vlažnost vzorcev med izpiranjem. Vlažnost je bila najpomembnejši dejavnik, ki je vplival na končni delež izpranega bora. Na vlažnost lesa med izpiranjem vplivata tudi delež in vrsta voska, s katerim je bil les impregniran. Emulzije voskov z manjšim deležem suhe snovi so med impregnacijo prodrle globlje v les in so bile bolj učinkovite pri zmanjševanju izpiranja kot emulzije z večjim deležem suhe snovi. S sorpcijskimi testi smo ugotovili, da večji ko je suhi navzem voska v lesu boljša je vodoodbojna učinkovitost ter počasnejše navlaževanje in nižja stopnja ravnovesne vlažnosti lesa, impregniranega z emulzijami voskov med uravnovešanjem bodisi v laboratoriju bodisi na prostem. V nadaljevanju smo določali odpornost lesa, zaščitenega z borovimi spojinami in emulzijami voskov, proti lesnim glivam. Z laboratorijskimi in terenskim testom smo ugotovili, da emulzije voskov upočasnijo razgradnjo lesa z glivami razkrojevalkami, vendar je ne preprečijo. Po drugi strani pa voski niso zaščitili lesa pred delovanjem gliv modrivk in plesni. Ocenjujemo, da bi vodne emulzije voskov lahko uporabljali za zaščito lesa, vendar ne v 4. in 5. razredu izpostavitve.

KEY WORDS DOCUMENTATION

DN Dd

DC UDC 630*841.1:630*844.41

CX boric acid/borax/wax emulsion/wood decay fungi/leaching/sorption properties/water repellent/moisture content

AU LESAR, Boštjan

AA HUMAR, Miha (supervisor)

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TI INTERACTIONS OF BORON COMPOUNDS AND WAX EMULSIONS WITH WAX AND WOOD DECAY FUNGI

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LA sl

AL sl/en

AB In wood protection, boron compounds are among the most frequently used ingredients in wood preservatives. Boron compounds are excellent fungicides and insecticides. Their drawback is that they leach from wood in a humid environment. The moisture content of wood and boron leaching were reduced with selected hydrophobic agents. Specimens were impregnated with various wax emulsions and leached according to continuous and discontinuous leaching procedures. During leaching,the moisture content which is the key factor influencing the final proportion of leached boron, was determined. The concentration and type of wax emulsion used for the impregnation of the wood also affect the moisture content during the leaching. Wax emulsions with a lower share of dry content penetrated deeper during the impregnation and were more effective in lowering the boron leaching than emulsions with a higher dry content. Sorption tests showed that wood with a higher dry content of wax had higher water repellent effectiveness. They slowed down the increase in moisture content and reduced the equilibrium moisture content of the impregnated wood during conditioning in both the laboratory and in outdoor experiments. Subsequently, the resistance of wood impregnated with boron compounds and wax emulsions to wood decay fungi were subsequently determined. The laboratory and outdoor tests showed that wax emulsions slowed down the fungal degradation of the wood but do not stop it. On the other hand, treatment of the wood with waxes did not prevent staining. Wax water emulsions can thus be presumed to have the potential to be used for wood protection but not in the 4th and 5th use class.

KAZALO VSEBINE

KAZALO PREGLEDNIC

KAZALO SLIK

Str.

OKRAJŠAVE IN SIMBOLI

Oznaka	**Opis**
LGE	Emulzija montanskega voska (proizvajalec Samson d.o.o.)
MW1	Emulzija montanskega voska (proizvajalec BASF)
WE1	Emulzija polietilenskega voska
WE3	Emulzija etilen kopolimernega voska
WE6	Emulzija oksidiranega polietilenskega voska
BA	Borova kislina
BAE	Boric acid equvalent (ekvivalent borove kisline)
CCB	Zaščitno sredstvo na osnovi bakrovih, borovih in kromovih spojin
CIELAB	Sistem za numerično vrednotenje barve Mednarodne komisije za svetlobo CIE (*Commission Internationale d'Eclairage*)
L*	Svetlost barve po sistemu CIELAB
a*	Lega barve na rdeče(+)-zeleni(-) osi sistema CIELAB
b*	Lega barve na rumeno(+)-modri(-) osi sistema CIELAB
ΔE*	Sprememba barve po sistemu CIELAB
EN 113 vzorci	Vzorci dimenzij 1,5 cm × 2,5 cm × 5,0 cm
EN 252 vzorci	Vzorci dimenzij 2,5 cm × 5 cm × 50 cm
#	Oznaka dodana pri slikah pomeni, da smo prosili za dovoljenje za objavo, vendar negativnega odgovora nismo prejeli

SLOVARČEK

Preventivna zaščita lesa	zaščita lesa pred njegovo uporabo oziroma vgradnjo pred delovanjem biotskih in/ali abiotskih dejavnikov razkroja z namenom, da povečamo njegovo kvaliteto, uporabnost in trajnost
Kurativna zaščita lesa	zaščita lesa, ki so ga že okužile glive oziroma napadli insekti
Kontinuirni postopek izpiranja	vzorci so ves čas izpiranja namočeni v vodo, vodo menjamo po naprej določenih intervalih
Nekontinuirni postopek izpiranja	vzorce namakamo v vodo v naprej določenih časovnih intervalih za določeno časovno obdobje, ko vzorci niso namočeni v vodi se sušijo pri sobnih pogojih

1 UVOD

1.1 OPREDELITEV RAZISKOVALNEGA PROBLEMA

Les je izpostavljen biotskim in abiotskim dejavnikom razkroja. V naravi so ti procesi nujno potrebni, kadar pa les uporabljamo v komercialne namene, želimo te procese čim bolj upočasniti. Želimo, da je uporabnost lesa čim daljša. Zato se uporabljajo različni načini zaščite. Prvi je uporaba naravno odpornih lesnih vrst, predvsem tropskih. Posledica uporabe eksotičnih lesnih vrst je krčenje tropskih gozdov, kar pomembno prispeva h globalnemu segrevanju ozračja. Prav zaradi tega in povečane okoljske ozaveščenosti evropskih potrošnikov se povečuje uporaba domačih drevesnih vrst, ki pa imajo praviloma slabšo naravno odpornost kot tropske lesne vrste. Naslednji ukrep za povečevanje trajnosti lesa je konstrukcijska zaščita, pri kateri z ustrezno konstrukcijo preprečimo navlaževanje lesa in s tem kar najbolj zaščitimo les pred lesnimi glivami, ki so v našem podnebnem pasu največje uničevalke lesa. Žal lesa vedno ne moremo zaščititi samo s konstrukcijo, zato je potrebna tudi biocidna zaščita. Razmere na področju kemijske oziroma biocidne zaščite lesa se zadnja leta močno spreminjajo. Leta 2006 je začela veljati direktiva o biocidih (Biocidal Products Directive, 98/8/EC), ki prepoveduje ali pa močno omejuje uporabo številnih klasičnih biocidov. Alternativa klasičnim pripravkom na osnovi težkih kovin je uporaba novejših biocidnih pripravkov ter nebiocidna zaščita lesa. K nebiocidni zaščiti prištevamo med drugim tudi modifikacijo in hidrofobizacijo lesa. Predvsem za les, obdelan s hidrofobnimi sredstvi, žal nimamo na voljo dovolj podatkov, kako se ta rešitev obnese v dejanskih razmerah ter kakšni so mehanizmi fungicidnega ter fungistatičnega delovanja. Razumevanje in dobro poznavanje teh lastnosti nam bo omogočilo razvoj optimalnih postopkov zaščite. Po drugi strani pa bomo lažje napovedali tudi življenjsko dobo zaščitenega lesa ter se izognili okolju, v katerem uporaba tako zaščitenega lesa ni primerna.

Obdelava lesa z vodoodbojnimi sredstvi je v praksi zelo pogosta in se uporablja za zaščito pred navzemom tekoče vode ter za preprečevanje razvoja in rasti gliv. Največkrat uporabljene hidrofobne snovi so emulzije voskov (predvsem parafinskih). Vodoodbojna sredstva za zaščito lesa poleg voskov vsebujejo še biocide in smole. V zadnjem času se kot dodatek za povečevanje vodoodbojnosti v površinskih premazih namesto parafina zelo pogosto uporabljajo drugi sintetični voski. Sintetični voski so najpogosteje sintetizirani iz etena oz. etilena. Lastnosti voskov določijo v procesu sinteze in so prilagojene za določeno uporabo. Uporaba sintetičnih voskov pri zaščiti lesa je še zelo slabo raziskana. Zelo malo je podatkov o tem, kako impregnacija z voski vpliva na navlaževanje in sušenje lesa, kakšno je fungicidno in fungistatično delovanje ter kakšen je vpliv teh voskov na staranje lesenih površin. S praktičnega vidika je predvsem pomembno, kako dolgo ostane površina hidrofobna. Na to precej vpliva tudi obstojnost na ultravijolično in infrardeče sevanje, ki ju povzroča izpostavitev sončni svetlobi.

V praksi zaščita lesa s hidrofobnimi sredstvi pogosto ne zadostuje, zato je emulziji treba dodati okolju prijazne biocide. Med okolju sprejemljivejše in po drugi strani stroškovno ugodnejše biocide uvrščamo borove učinkovine. Njihova uporaba je dovoljena tudi po uvedbi direktive o biocidih. Žal se borove spojine iz lesa izpirajo in se vanj skoraj ne vežejo. Borove spojine se za zaščito lesa uporabljajo že vse od začetka 20. stoletja. Večina raziskav fungicidnega in insekticidnega delovanja je bila narejena že v 50. in 60. letih prejšnjega stoletja. Mejne vrednosti v teh raziskavah pa so bistveno višje od mejnih vrednosti, ki smo jih mi določili v preliminarnih testih. Nižje mejne vrednosti pomenijo manjše obremenjevanje okolja in nižji strošek zaščite lesa.

Kljub zelo dolgi uporabi borovih spojin za zaščito lesa in desetletjem raziskav raziskovalcem do sedaj še ni uspelo vzpostaviti stabilnih kemijskih vezi med borovimi spojinami in funkcionalnimi skupinami lesa. Menimo, da bi fiksacijo bora v les lažje dosegli, če bi borove spojine primešali hidrofobnim sredstvom, kot so to naravni in/ali sintetični voski. Na ta način bi bor stabilizirali v matriksu, kar bi preprečilo ali vsaj zmanjšalo mobilnost borovih spojin. Nepoznane so tudi številne druge interakcije med borom in voski. Pomembno bi bilo raziskati, kakšno je fungicidno delovanje zmesi bora in voskov ter kam se voski in bor med impregnacijo odložijo v lesu, kar bi nam lahko pomagalo pojasniti vezavo bora.

1.2 NAMEN RAZISKAVE IN DELOVNE HIPOTEZE

Namen raziskave je preučiti interakcije borovih spojin ter emulzij montanskih in polietilenskih voskov z lesom in lesnimi glivami. Osvetliti želimo vpliv borove kisline in emulzij voskov ter njihovih kombinacij na glive rjave in bele trohnobe, ki povzročajo razkroj lesa. Z dodatki voskov nameravamo zmanjšati izpiranje borovih spojin. S temi postopki bo podaljšana trajnost zaščitenega lesa. Končni cilj raziskave je razviti sredstvo na osnovi borovih spojin in emulzij voskov, primerno za zaščito lesa v tretjem razredu izpostavitve.

Postavljene so naslednje delovne hipoteze:

- *Voski z borovimi spojinami delujejo proti glivam razkrojevalkam in glivam modrivkam sinergistično*

Borove spojine že pri nizkih koncentracijah delujejo kot učinkovit fungicid. Menimo, da bo dodatek voskov te koncentracije še znižal. Sklepamo, da voski tako kot na površini lesa tudi na površini celičnih sten tvorijo tanko odporno plast, ki omejuje dostop encimov do celične stene, kar se bo pokazalo v manjših izgubah mase glivam izpostavljenega lesa.

- *Les, zaščiten z voski, bo imel nižje ravnovesne vlažnosti od nezaščitenega lesa ali lesa, zaščitenega z borovimi spojinami, in se bo počasneje uravnovešal*

Predvidevamo, da se med impregnacijo lesa z vodnimi emulzijami voskov tako na površini vzorca kot tudi na površini celičnih sten tvori tanka zaščitna (za vodo odbojna) plast, ki vodi preprečuje dostop do prostih hidroksilnih skupin v lesu.

- *Dodatek voskov borovim spojinam za zaščito lesa bo zmanjšal izpiranje bora*

Sklepamo, da bosta navlaževanje in končna vlažnost lesa, impregniranega z vodnimi emulzijami voskov in borovimi spojinami, nižja od tistih pri lesu, impregniranem le z borovimi spojinami. Pri nižji vlažnosti lesa poteka difuzija bora počasneje, kar pomeni počasnejšo migracijo borovih ionov na površino lesa in tako zmanjšano izpiranje bora iz lesa.

- *Dodatek borove kisline lepilu ne zmanjša trdnosti lepilnega spoja; ko se les navlaži, bor difundira iz lepilnega spoja in zaščiti les*

Menimo, da dodatek borove kisline lepilu ne vpliva na trdnost lepilnega spoja. Predvidevamo, da med borovo kislino in lepilom ne poteče kemijska reakcija, kar pomeni, da se bor ne veže v strukturo lepila, ampak ob povečani vlažnosti lesa difundira iz lepilnega spoja v les in ga zaščiti.

2 PREGLED OBJAV

2.1 NARAVNA ODPORNOST IN TRAJNOST LESA

Razgradnjo lesa lahko povzročijo abiotični in biotični dejavniki. Abiotični dejavniki so dejavniki nežive narave, med katere prištevamo ogenj, vremenske vplive (UV-žarki, visoke ter nizke temperature, vlaga in veter), mehanske sile, kemikalije … Med biotične dejavnike prištevamo bakterije, glive in insekte. Največji abiotični destruktor lesa je ogenj, saj se v požarih uničijo zelo velike količine lesa. Najpomembnejši biotični vzrok za razvrednotenje lesa v našem podnebnem pasu pa so glive, prave razkrojevalke lesa.

Naravna odpornost je v najširšem pomenu definirana kot odpornost lesa proti delovanju fizikalnih, kemijskih ali bioloških dejavnikov (Dinwoodie, 2000). Daleč najpomembnejši so biološki dejavniki razkroja, zato standard (EN 335-1/2, 1992) definira naravno odpornost kot lastnost, ki jo ima les v naravnem, zdravem stanju in označuje dovzetnost na škodljivce. Izraz naravna odpornost se uporablja zgolj za nezaščiten les, medtem ko se za zaščiten ali modificiran les uporablja izraz odpornost lesa. Življenjska doba lesa je obdobje, v katerem les ohrani mehansko trdnost in stabilnost, ki je zahtevana za določeni proizvod. Ko so te lastnosti manjše oziroma slabše od zahtevanih, je treba proizvod zamenjati, tako da se zagotovi varnost uporabnikov skozi celotno dobo uporabe (Brischke in sod., 2006). V slovenščini se poleg življenjske dobe uporablja še drug podoben strokovni izraz: trajnost lesa. Ta je definirana kot obdobje, v katerem les obdrži vse svoje naravne lastnosti in je odvisna od (naravne) odpornosti lesa ter mesta in načina vgradnje oziroma konstrukcije ter mesta uporabe (Pohleven, 2008). Naravne lastnosti lesa, trdnost, odpornost, barva itd., se lahko s časom uporabe spreminjajo, a ne vplivajo na zmanjšanje mehanske trdnosti in odpornosti, ki sta najbolj pomembni za zagotavljanje varnosti skozi celotno obdobje uporabe lesa. Takšna lastnost je na primer barva lesa, ki ne vpliva na mehansko trdnost in odpornost, kljub temu, da se s časom spreminja.

Na trajnost lesa lahko vplivamo z izbiro drevesne vrste, lokacijo rasti drevesa ter časom sečnje. Na naravno odpornost lesa posamezne drevesne vrste najbolj vplivajo ekstraktivne snovi, vendar samo z ekstraktivi ni možno pojasniti naravne odpornosti. Poleg ekstraktivov vplivajo na naravno odpornost še hidrofobnost sestavin celične stene, zgradba lesa, gostota idr. Naravna odpornost lesa iste vrste ni vedno enaka, ampak se spreminja tako v drevesu kot tudi med posameznimi drevesi (Panshin in De Zeeuw, 1980; Aloui in sod., 2004). Zaradi velike variabilnosti naravne odpornosti lesa se močno razlikuje tudi njegova življenjska doba. Življenjska doba lesa je za uporabnika pomembnejša od same naravne odpornosti, saj pove, koliko časa bo les oziroma leseni izdelek služil svojemu namenu, ob tem, da se nekatere lastnosti lahko spremenijo oziroma celo poslabšajo. Da bi zagotovili ustrezno življenjsko dobo tudi slabše naravno odpornemu lesu, ga je treba zaščititi. Največkrat se uporablja zaščita z biocidi, v zadnjem času pa se vedno bolj uveljavlja tudi nebiocidna zaščita (konstrukcijska zaščita, modifikacija, hidrofobizacija …) (Evans, 2003; Freeman in sod., 2003; Schultz in sod., 2007a; Humar, 2008).

Kadar delovanja škodljivcev ne moremo preprečiti na drug, okolju prijaznejši način, moramo uporabiti biocidne pripravke. Zaščitne pripravke lahko uporabljamo v preventivni, poznejši in tudi kurativni zaščiti lesa. Uporabo biocidnih učinkovin v EU obravnava Direktiva o biocidih (Biocidal Products Directive, 98/8/EC). Direktiva natančno predpisuje, katere aktivne učinkovine lahko uporabljamo za zaščito lesa. Veliko klasičnih učnkovin, ki so se uporabljale več desetletij , je že umaknjenih s trga. Po uveljavitvi direktive je dovoljenih še 40 biocidov, pričakovati pa je, da se bo to število po preverjanju vseh okoljsko toksikoloških dosjejev še zamnjšalo (Leithoff in Blancquaert, 2006). Kljub temu biocidna zaščita še vedno predstavlja osnovo preventivne zaščite lesa. V EU letno zaščitimo okoli 24 mio m^3 lesa, od tega več kot 95 % z biocidnimi zaščitnimi sredstvi (Sutti in Englund, 2008). V zaščitnih pripravkih, registriranih na slovenskem tržišču, je 20 od 40 dovoljenih aktivnih učinkovin (Humar, 2010). Večina zaščitnih pripravkov je sestavljena iz več kot ene aktivne učinkovine, od katerih ima vsaj ena ali več aktivih učinkovin fungicidno delovanje in ena ali več učinkovin insekticidno delovanje. Pripravki za zaščito lesa v drugem in tretjem razredu izpostavitve najpogosteje vsebujejo IPBC, permetrin, propikonazol in borovo kislino. V pripravkih za zaščito lesa v tretjem in četrtem razredu se najpogosteje uporabljajo bakrove učinkovine v kombinaciji z borovimi. Bakrovi pripravki so znani fungicidi, borove spojine pa imajo vlogo insekticidov in sekundarnih fungicidov (Humar, 2010). Borove spojine so močno navzoče tudi v zaščitnih pripravkih, proizvedenih v drugih članicah EU. V Nemčiji namreč več kot 90 % zaščitnih sredstev za les na vodni osnovi vsebuje borove spojine (Peylo in Willeitner, 2001).

2.2 BOROVI PRIPRAVKI ZA ZAŠČITO LESA

2.2.1 Splošno

Bor je zelo razširjen kemijski element. V naravi se ne nahaja v čisti elementarni obliki, ampak v spojinah s kisikom in drugimi elementi. Najpogostejši obliki sta borova kislina in boraks. Poznanih je več kot 80 različnih mineralnih tipov boraksa, med njimi je najpogostejši tinkal ($Na_2B_4O_7 \cdot 10H_2O$, natrijev tetraborat dekahidrat), za katerega se največkrat uporablja kar splošno ime boraks (angl. borax). Komercialno boraks pridobivajo v rudnikih oziroma kamnolomih v ZDA, Turčiji, Tibetu in Čilu. Boraks uporabljajo za sintezo drugih borovih spojin. Svetovna proizvodnja znaša približno 2 milijona ton letno (Boron B, 2006).

Do devetnajstega stoletja so se borove spojine redko uporabljale, zdaj pa jih srečujemo na vsakem koraku, le da za to največkrat sploh ne vemo. Bor je prisoten v rastlinah, prehrani ljudi, z njim se srečujemo tudi doma, kjer se uporablja kot dodatek najrazličnejšim izdelkom, ki jih uporabljamo v gospodinjstvu. Moderne industrije si enostavno ne moremo predstavljati brez borovih spojin.

V vsakdanjem življenju se borove spojine uporabljajo v kozmetičnih in farmacevtskih izdelkih kot so: mila, pralni praški, hladilne kreme, krema po britju, kapljice za oči in še mnogih drugih. Posoda, ki jo uporabljamo v mikrovalovni pečici, prav tako vsebuje borove spojine, ki izboljšajo toplotno odpornost plastike. Borove spojine se uporabljajo še pri proizvodnji steklenih vlaken, ki se med drugim uporabljajo za izdelavo športne opreme. Ta element je razširjen tudi v industriji. Uporablja se v transportnem sektorju kot dodatek gorivom, motornemu olju, hladilni tekočini … Velik porabnik je tudi sodobna »high tech« proizvodnja mikroelektronike, računalnikov ... Borove spojine se že dolgo časa uporabljajo tudi v gradbeništvu in lesarstvu za zaščito lesa in lesnih tvoriv (Woods, 1994; Richold, 1998).

Borove spojine so ene izmed najstarejših aktivnih učinkovin, ki se še vedno uporabljajo za zaščito lesa. Njihova uporaba je dovoljena tudi po uvedbi direktive o biocidih (Biocidal Products Directive, 98/8/EC, 1998; Humar, 2004). Glavna lastnost borovih spojin je poleg dobre difuzivnosti, ki omogoča dobro zaščito slabo permeabilnih lesnih vrst, še širok spekter delovanja proti insektom in glivam. Ne nazadnje je ena od pomembnejših lastnosti boratov tudi nizka toksičnost za ljudi. Slaba stran dobre difuzivnosti je, da se borove spojine iz lesa izpirajo, zato je uporaba borovih spojin za zaščito lesa omejena na uporabo v suhih razmerah oziroma dovoljuje občasna zvišanja vlažnosti.

2.2.2 Zgodovina uporabe borovih spojin za zaščito lesa

Borove spojine spadajo med najvarnejše biocide za zaščito lesa. Ob običajni uporabi v industriji ni poročil o nobeni nesreči ali drugem škodljivem vplivu na okolje (Lloyd, 1998). Dobre lastnosti borovih spojin so že dolgo znane, zato se že dolgo časa uporabljajo v pripravkih za zaščito lesa. Prva industrijska uporaba borovih soli se je začela leta 1913 z Wollmanovim sredstvom Wollmanit CB (kromove in borove spojine), ki se je uporabljalo za zaščito lesenih drogov in pragov. Dodatek kromovih spojin je izboljšal antikorozivno delovanje in fiksacijo sredstva v les. Poleg tega so kromati do določene mere zavirali tudi gorenje. Dve desetletji kasneje se je bor uveljavil kot zamenjava dikromatov v sredstvih za zaviranje gorenja lesa.

Prva industrijska uporaba se je začela leta 1949 z uporabo dobro difuzne mešanice borove kisline in boraksa, podobne dinatrijevemu oktaboratu tetrahidratu (DOT). Nekaj let kasneje se je pojavilo sredstvo Timbor®, ki je imelo podobne lastnosti kot dinatrijev oktaborat tetrahidrat in je bilo primerno za nanašanje z brizganjem. Postopek zaščite se je imenoval timborizacija. Zdaj je ta sistem splošno sprejet za globinsko impregnacijo lesa (Lloyd, 1998).

V Evropi so se prve raziskave glede borovih spojin pričele ob povečani nevarnosti pred napadom insektov iz skupine kozličkov (*Hylotrupes spp.*) in trdoglavcev (*Anobium spp.*). Ugotovljeno je bilo, da je učinkovitost boratov podobna učinkovitosti fluoridov (Freitag in Morrell, 2005).

Zelo dobra difuzivnost borovih zaščitnih sredstev je neposredno povezana z eno največjih slabosti teh pripravkov, to je izpiranje učinkovin iz lesa. Zato so ob koncu štiridesetih let prejšnjega stoletja razvili zaščitno sredstvo na osnovi bakra, kroma in bora (CCB) (Lloyd, 1998). V tem sistemu sta bor in baker aktivni učinkovini, krom pa služi za vezavo aktivnih učinkovin v les. Žal ta rešitev ne prepreči izpiranja borovih spojin iz lesa, temveč jih le upočasni. Sredstvo se je uporabljalo predvsem za kotelski postopek impregnacije lesa za zunanjo uporabo, kjer je možnost pogostega močenja. CCB se je predvsem v Evropi uveljavil kot nadomestek za CCA (baker, krom, arzen) zaradi velike toksičnosti arzena. Zdaj se sredstvo v EU zaradi škodljivosti kromovih spojin skoraj ne uporablja več (Leithoff in sod., 2008).

2.2.3 Toksičnost

Bor je v majhnih količinah v naravi povsod prisoten. Je v zemlji, vodi in hrani (Woods, 1994; Howe, 1998). Povprečna koncentracija bora v zemlji znaša med 10 mg/kg in 20 mg/kg zemlje (Woods, 1994; Gentz in Grace, 2006). Morska voda vsebuje v povprečju 4,5 mg/kg (Jenkins, 1980), sladka voda pa od 0,1 mg/L do 0,5 mg/L bora (Howe, 1998). Koncentracije so lahko tudi višje, odvisno predvsem od lokacije (Yazbeck in sod., 2005). Na primer, koncentracija bora v pitni vodi na obrobju rudnikov bora v Turčiji znaša (21 do 29) mg/L (Sayli in sod., 1998). Po podatkih Javnega podjetja Vodovod-Kanalizacija o kakovosti vode v Ljubljani za mesec februar 2011 znaša količina bora v pitni vodi manj kot 0,04 mg/L (Anonymous, 2011). Evropska direktiva o pitni vodi iz leta 1998 (98/83/EC) določa mejno vrednost bora pri 1 mg/L.

Bor se kot konzervans uporablja tudi kot dodatek k prehrambenim izdelkom. Ocene o dnevnem navzemu se močno razlikujejo. Odvisne so od lokalnih prehrambenih navad in uporabe konzervansov v prehrani. Povprečni dnevni vnos bora v telo s prehrano v ZDA znaša vsaj 1,5 mg/dan/prebivalca (Murray, 1995). Medtem pa Roper (1992) navaja še višje količine borovih spojin, ki jih dnevno vnesemo v telo (10 mg/dan do 25 mg/dan). Uporabnik dnevno konzumira bor predvsem s hrano oz. z uživanjem sadja in zelenjave. Najbolj znana jed, ki jo konzerviramo z borovo kislino, je kaviar. Šele uporaba borove kisline je omogočila transport kaviarja v oddaljene kraje. Na srečo pa povprečni prebivalec Slovenije letno poje le manjše količine kaviarja.

Bor lahko pride v človeško telo tudi preko kože in dihalnih poti. Vdihovanje zraka, v katerem je 4,1 mg/m^3 bora, povzroča draženje nosu, žrela ali oči. Bor draži oči, a le tedaj, ko smo mu izpostavljeni daljše časovno obdobje (Roper, 1992). Maksimalna delovna koncentracija borovega oksida in boraksa v zraku znaša 10 mg/m^3. Študije uporabe boratov v praksi po drugi strani dokazujejo, da se inhalatorni vnos boratov ne odraža v nobenem zaznavnem kroničnem učinku, prav tako dermalni kontakt ni povzročal draženja, občutljivosti ali vnetja kože (Culver in sod., 1994).

Akutna oralna toksičnost (LD_{50}) borove kisline znaša pri podganah 3000 mg/kg do 4000 mg/kg telesne mase, boraksa pa 4500 mg/kg do 6000 mg/kg telesne mase (Weir in Fisher, 1972). Razlike nastanejo zaradi različne vsebnosti bora, 1 mg bora (B) je enakovreden 5,7 mg borove kisline ali 8,8 mg boraksa (natrijev teraborat dekahidrat). V preglednici 1 so prikazane vrednosti akutne oralne toksičnosti (LD_{50} mg/kg) pri podganah za spojine, ki se uporabljajo za zaščito lesa in še nekaterih drugih splošno uporabnih materialov. Iz teh podatkov je razvidno, da je akutna toksičnost borovih spojin primerljiva s toksičnostjo kuhinjske soli, po drugi strani pa je bistveno nižja od toksičnosti ostalih biocidov, ki se uporabljajo za zaščito lesa.

Študije toksičnosti bora na sesalcih (miši, podgane in psi) kažejo, da ta vpliva na moške spolne organe (reproduktivna toksičnost). To se je pokazalo še posebej pri testih, kjer so živali krajše ali daljše časovno obdobje zaužile večje količine borove kisline (Roper, 1992). Podobne raziskave na brejih miših, podganah in zajcih so pokazale manjši razvojni učinek na mladiče (Fail in sod., 1998). Weir in Fisher (1972) poročata, da 8,8 mg bora/kg/dan, ki so ga dodajali hrani psom dve leti, ni učinkovalo na njihovo reproduktivnost. Škodljiv učinek bora na reproduktivnost sta ugotovila pri podganah, ki so bile kronično izpostavljene bistveno višjim koncentracijam (58,5 mg bora/kg/dan). Podatki raziskav reproduktivne toksičnosti bora na ljudeh ne kažejo škodljivega učinka na moške (Whorton in sod., 1994; Sayli in sod., 1998). Kljub temu je Evropska komisija borove spojine označila kot reprotoksične druge kategorije po direktivi o nevarnih snoveh (67/548/EEC, 1967). To pomeni, da bo uporaba borovih spojin v biocidnih pripravkih s koncentracijo, višjo od 5,5 % ekvivalentov borove kisline (BAE), v široki potrošnji močno omejena (Anonymous 2010). Prav tako ni na voljo podatkov, ki bi potrjevali teratogenost borovih spojin. Po drugi strani študije na živalih (oralna izpostavljenost boru) potrjujejo škodljivost bora za zarodek (Moore in sod., 1997). Na anketi zasnovana študija, izvedena na 542 zaposlenih moških v proizvodnji boraksa (rudniki in predelava bora), ki so bili več kot pet let dnevno izpostavljeni visokim koncentracijam bora (vsaj 23,2 mg boraksa/m^3, 0,48 mg borove kisline/kg telesne mase/dan), ugotavlja, da ni moč zaznati statistično značilnih učinkov na njihovo reproduktivnost. Moški so bili plodni približno toliko, kolikor je povprečje za ZDA (Whorton in sod., 1994). Do podobnih zaključkov so prišli tudi Sayli in sodelavci (1998), ki ugotavljajo, da visoka koncentracija bora v pitni vodi (od 21 mg/L do 29 mg/L) ne vpliva na plodnost in reprodukcijo. Tako visoka koncentracija bora v pitni vodi je bila določena v bližini naravnih nahajališč bora, tako da je bila večina udeležencev raziskave izpostavljena boru tudi poklicno. Izpostavljenost visokim koncentracijam bora kitajskih delavcev v predelavi bora je vplivala na visok delež bora v krvi in urinu, medtem ko ni bilo zaznanega škodljivega vpliva na količino in kakovost moških semenčic (Robbins in sod., 2010).

Preglednica 1: Akutna oralna toksičnost (LD$_{50}$) nekaterih kemikalij in biocidov za podgane (Rainer, 1993).

Table 1: Acute oral toxicaty LD$_{50}$ in rats (Rainer, 1993).

Spojina	*Akutna oralna toksičnost LD$_{50}$ (mg/kg)*
Sladkor	29700
Boraks	4500–6000
borova kislina	3000–4000
sol (NaCl)	3000–3320
Aspirin	1000–1200
bakrov sulfat	960
kloroform	908
kofein	192
DDT*	113
nikotin	10–53
PCP**	27

*DDT – diklordifeniltrikloroeten: včasih se je uporabljal za zaščito lesa, sedaj prepovedan

**PCP – pentaklorofenol: včasih se je uporabljal za zaščito lesa, sedaj prepovedan

Tudi podatki o rakotvornosti borovih spojin so obetajoči. Študije na podganah, ki so jih dve leti hranili z borati, so pokazale, da tako borova kislina kot tudi boraks nista kancerogena (Weir in Fisher, 1972). Tudi eksperimenti z borovo kislino na miših so pokazali, da borova kislina ni mutagena ali genotoksična (Roper, 1992; ECETOC, 1995).

Bor se v človeškem telesu ne skladišči. Raziskave mobilnosti bora v telesu so pokazale, da se 50 % zaužitega bora izloči z urinom v 21 urah. Ostala količina se izloči v 95 urah po zaužitju bora (Rainer, 1993; Sutherland in sod., 1999).

2.2.4 Borove spojine in rastline

Bor je bistveno pomemben za rastline. V majhnih količinah ga potrebujejo za rast, nadzor cvetenja, produkcijo cvetnega prahu, kalitev in pri razvoju plodov ter semena. Pomaga pri prenosu sladkorjev iz starejših delov rastline v na novo nastajajoče dele in koreninski sistem (Lloyd, 1998; Letho in sod., 2010).

Biokemični učinki bora se kažejo v vplivu bora na metabolizem in olesenitev rastlin. Pomanjkanje bora povzroča povečano akumuliranje fenolnih spojin in drugih komponent lignina (Lloyd, 1998; Letho in sod., 2010), kar vodi v odmiranje rastlinskega tkiva in pretirano olesenitev. Pomanjkanje bora se odraža tudi v zmanjšani odpornosti rastlin na zmrzal, kar potrjujejo študije, izvedene na jablanah in trti (Lloyd, 1998).

Pomanjkanje bora v rastlinah povzročajo padavine, ki izpirajo dobro topne borate iz vrhnjih plasti zemlje in s tem iz dosega korenin rastlin. Kljub množični uporabi boratnih gnojil v svetu na kar 205 milijonov hektarjih kmetijskih površin primanjkuje bora. Letna poraba boratnih gnojil presega 60000 ton in se povečuje za 5 % letno (Lloyd, 1998).

Bor pa ne vpliva le na fiziološke procese rastlin, temveč izboljša tudi odpornost rastlin na plesni in listne uši. Že dolgo je znano, da bor učinkovito deluje tudi proti koreninskim boleznim, ki jih povzročajo patogene glive (Lloyd, 1998). Bor se uporablja tudi v gozdarstvu. Predvsem iglavci, ki rastejo na podlagi, bogati z apnencem, so močno izpostavljeni koreninski trohnobi, ki jo povzroča jelov koreničnik (*Heterobasidium annosum*). Najpogosteje so vir okužbe sosednji štori, ki ostanejo po poseku dreves, iz katerih se razraste micelij na zdrava drevesa. Za preprečevanje okužb se je kot zelo učinkovita in ekonomsko upravičena pokazala zaščita čelnih površin panjev z borovimi spojinami. V Evropi se je uveljavil predvsem dinatrijev oktaborat tetrahidrat (DOT – $Na_2B_8O_{13}\cdot 4H_2O$). Zaradi dobre difuzije bor že v nekaj urah prodre do globine 5 cm in več. Po dveh mesecih se njegova koncentracija skoraj izenači s koncentracijo bora v okolici in panj postane dovzeten za okužbo gliv, ki so odporne na višjo koncentracijo bora (npr. *Peniophora spp.*). Omenjena gliva ima antagonističen učinek na rast jelovega koreničnika (Lloyd, 1998).

2.2.5 Delovanje proti glivam razkrojevalkam, modrivkam ter plesnim

Borove spojine že pri nizkih koncentracijah delujejo kot učinkovit fungicid in insekticid. Poznano in dobro raziskano je delovanje bora proti glivam, insektom in tudi termitom. Po do sedaj znanih podatkih nobena gliva razkrojevlka ni tolerantna na borove spojine in ne more razkrajati z borovimi pripravki zaščitenega lesa (Findlay, 1956; Jonge, 1987).

Mejna vrednost, določena z laboratorijskimi testi, je za različne glive primerljiva in znaša 2,0 kg/m^3 BAE (boric acid equivalent) (Beachler in Roth, 1956; Becker, 1959; Carr, 1964; Drysdale, 1994), medtem ko Jonge (1987) navaja, da je pisana ploskocevka (*Trametes versicolor*) relativno odporna na borove pripravke. Mejna vrednost za to glivo je nekoliko višja od prej omenjene in znaša med 1,8 kg/m^3 BAE in 3,0 kg/m^3 BAE. Iz tega lahko sklepamo, da mora les vsebovati vsaj 3,0 kg/m^3 BAE, da dosežemo odpornost lesa proti glivam razkrojevalkam (Jonge, 1987). Po drugi strani Freitag in Morrell (2005) navajata, da mejne vrednosti za pisano ploskocevko (*Trametes versicolor*) ni bilo mogoče določiti, saj so bile izgube mase pri vseh testiranih koncentracijah zanemarljivo nizke. O podobnih rezultatih poroča tudi Tsunoda (2001), kjer vzorci kriptomerije (*Crypotomerija japonica*), impregnirani z najnižjo koncentracijo 0,9 kg/m^3 BAE (0,26 % BAE), med poskusom niso izgubili mase, medtem ko so pri kontrolnih vzorcih določili 52,9-odstotno izgubo mase. Kakorkoli, pri interpretaciji teh rezultatov se moramo zavedati, da sta Freitag in Morrell (2005) teste izvajala na vzorcih jelke, medtem ko Jonge (1987) poroča o rezultatih poskusa na hrastu. Razlika med vzorci tako nastane tudi zaradi različne lesne vrste vzorcev, saj glive bele trohnobe veliko bolje razkrajajo les listavcev kot iglavcev.

Mejne vrednosti (preglednica 2), ki jih navajajo različni raziskovalci, se med seboj nekoliko razlikujejo. Do razlik prihaja tudi zaradi različnih eksperimentalnih metod, s katerimi so določali mejno vrednost. Iz preglednice 2 razberemo, da so s testi, ki so potekali v stiku z zemljo, ugotovili nekoliko višje mejne vrednosti. Becker (1959) navaja, da znaša povprečna mejna vrednost za borovo kislino med 0,5 kg/m^3 in 1,0 kg/m^3, za boraks pa med 0,5 kg/m^3 in 1,6 kg/m^3. Mejna vrednost, določena po ameriški laboratorijski metodi, pri kateri so vzorci med testiranjem v stiku z zemljo, znaša za borovo kislino med 0,9 kg/m^3 in 1,5 kg/m^3, za boraks med 1,6 kg/m^3 in 2,8 kg/m^3 lesa.

Učinkovitost borovih spojin je odvisna predvsem od deleža bora v posamezni spojini. Delež bora v borovi kislini znaša 17,48 %, v boraksu (natrijev tetraborat dekahidrat) pa 11,34 %. Zato je mejna vrednost za boraks višja od mejne vrednosti borove kisline (Jonge, 1987). Poleg deleža bora na učinkovitost vpliva tudi vrednost pH. Najbolj učinkovite so raztopine borovih spojin z visokim pH, zato je natrijev tetraborat relativno bolj učinkovit kot borova kislina (Richardson, 1978).

Borove spojine delujejo tudi proti glivam modrivkam in plesnim. Mejna vrednost za plesni je veliko višja kot za glive razkrojevalke. Za preprečevanje rasti plesni je potrebno med 15 kg/m^3 in 17 kg/m^3 borove kisline ali boraksa (Becker, 1959). Po drugi strani so na srečo glive modrivke nekoliko bolj občutljive kot plesni. Lloyd (1996) za glive modrivke in plesni navaja veliko nižjo mejno vrednost (2 kg/m^3 BAE).

Lloyd in sodelavci (1990) so skušali osvetliti fungicidni mehanizem delovanja borovih spojin. Hipoteza je bila, da primarni način delovanja temelji na splošni presnovi z interakcijo boratnega aniona z biološko aktivnimi polioli in z interakcijo z oksidiranimi koencimi NAD$^+$, NMN$^+$ in NADP$^+$. Borati v vodni raztopini tvorijo mono- in diestre s *cis*– sosednjimi hidroksilnimi skupinami in α-hidroksi karboksilnimi kislinami in najverjetneje delujejo ekstracelularno in intracelularno, poleg tega pa vplivajo na vitamine in koencime ter membrane (Lloyd in sod., 1990) (slika 1).

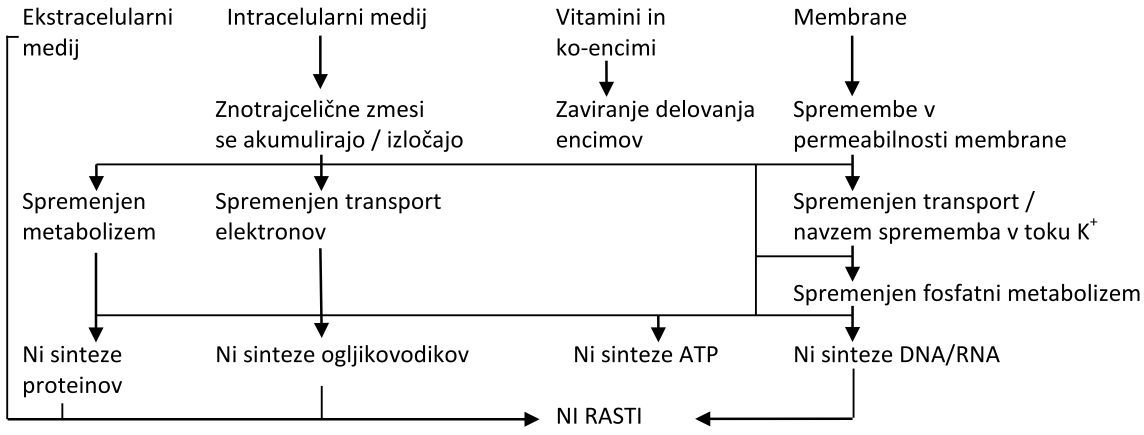
Preglednica 2: Mejne vrednosti raztopin borove kisline (H_3BO_3) za različne glive.

Table 2: Thresholds values of boric acid (H_3BO_3) against selected decay fungi.

Gliva	Koncentracija (%)	Navzem (kg/m^3) BAE*	Vrsta lesa	Test	Vir
Navadna tramovka (*Gloeophyllum trabeum*)	0,075 - 0,1	0,52 - 0,72	-	razkroj lesa na agarju	Becker (1959)
	0,1 - 0,13	0,52 - 0,72	-	**	Carr (1964)
	0,17 - 0,27	0,80 - 1,28	bor	v kozarcu z zemljo	Beachler in Roth (1956)
	0,23 - 0,60	1,12 - 2,88	hrast	v kozarcu z zemljo	Beachler in Roth (1956)
	0,48	2,0	bor	v stiku z zemljo	Harrow (1950)
	< 0,3	< 1,6	bor	v kozarcu z zemljo	Findlay (1956)
		0,40 - 0,44	jelka	razkroj lesa na agarju	Freitag in Morrell (2005)
Bela hišna goba (*Antrodia vaillanti*)	0,3	1,60	bor	v kozarcu z zemljo	Findlay (1956)
Bela hišna goba (*Postia placenta*)	0,24	1,0	bor	v stiku z zemljo	Harrow (1950)
	0,1	0,5	bor	v kozarcu z zemljo	Findlay (1956)
	0,07 - 0,17	0,32 - 0,80	bor	v kozarcu z zemljo	Beachler in Roth (1956)
	0,10 -0,13	0,48–0,64	hrast	v kozarcu z zemljo	Beachler in Roth (1956)
Pisana ploskocevka (*Trametes versicolor*)	0,10 - 0,20	1	bukev	v kozarcu z zemljo	Findlay (1956)
	0,23 - 0,40	1,12 - 1,92	hrast	v kozarcu z zemljo	Beachler in Roth (1956)
Kletna goba (*Coniophora puteana*)	0,48	2,0	bor	v stiku z zemljo	Harrow (1950)
	0,2	1,0	bor	v kozarcu z zemljo	Findlay (1956)
	0,075 - 0,1	0,53 - 0,73	-	razkroj lesa na agarju	Becker (1959)
	0,1 - 0,17	0,53 - 0,75	-	**	Carr (1964)
Siva hišna goba (*Serpula lacrymans*)	< 0,3	< 1,6	bor	v kozarcu z zemljo	Findlay (1956)
	0,05 - 0,075	0,36 - 0,54	-	razkroj lesa na agarju	Becker (1959)
	0,07 - 0,10	0,36 - 0,54	-	**	Carr (1964)
Luskasta nazobčenka (*Lentinus lepideus)*	0,10	0,50	bor	v kozarcu z zemljo	Findlay (1956)
	0,17 - 0,27	0,80 - 1,28	bor	v kozarcu z zemljo	Beachler in Roth (1956)
	0,075 - 0,2	0,54 - 1,4	-	razkroj lesa na agarju	Becker (1959)
	0,10 - 0,30	0,54 - 1,4	-	**	Carr (1964)
Vrsta iz družine luknjičark (*Polyporus rugulosus)*	0,25 - 0,30	1,5 - 1,6	bukev	v kozarcu z zemljo	Findlay (1956)

*BAE (boric acid equivalent – enakovredno borovi kislini, BAE kg/m^3 izračunana na podlagi gostote lesa 450 kg/m^3)

**Nemška standardna metoda iz leta 1959



Slika 1: Predlagani fungicidni mehanizem delovanja boratov (pripravljeno po Lloyd in sod., 1990).

Figure 1: Proposed fungicidal mechanisms of actions of borats (adapted from Lloyd et al., 1990).

2.2.6 Delovanje proti insektom

Za lažjo primerjavo toksičnih vrednosti med posameznimi testi so vsi opisani eksperimenti izvedeni na popolnoma prepojenih vzorcih z enakomerno porazdelitvijo zaščitnega sredstva po celotnem prerezu. To sicer ne ustreza vedno realni porazdelitvi zaščitnega sredstva v praksi, kjer se pogosto uporablja le površinska zaščita.

Bor je za insekte želodčni in ne kontaktni strup, zato učinkuje počasneje (Becker, 1959). Za njegovo delovanje je nujen prehod skozi črevesje. Na insekticidnost močno vpliva tudi starost larv insektov. Becker (1959) je ugotovil, da je zelo težko uničiti štiri mesece stare larve hišnega kozlička (*Hylotrupes bajulus*) (preglednica 3). Pri poskusu, ki je trajal štiri tedne, se je izkazalo, da niti 10 kg borove kisline oziroma boraksa na kubični meter lesa ni dovolj. Pri štiritedenskem poskusu je razlika v mejni vrednosti za jajčne larve in štiri mesece stare larve hišnega kozlička (*Hylotrupes bajulus*) precejšnja. Glavni vzrok za to razliko se skriva v dejstvu, da so srednje velike larve sposobne preživeti štiri tedne brez hrane. Poleg tega se larve v lesu premikajo naprej in nekako prepoznajo impregniran les. Jajčne larve lahko brez hrane preživijo krajši čas (Jonge, 1987; Peylo, 2005), zato je mejna vrednost nižja – med 3,6 kg/m^3 BAE in 5,6 kg/m^3 BAE.

Pri daljših eksperimentih (12 tednov) je bilo dovolj že 0,36 kg/m^3 BAE (64 g B/m^3) (preglednica 3) za 100-odstotno smrtnost srednje velikih larv. Če se trajanje eksperimenta podaljša na 6 mesecev, se mejna vrednost znatno ne zmanjša (Jonge, 1987).

Enako kot za glive velja tudi za hišnega kozlička (*Hylotrupes bajulus*), da je borova kislina nekoliko bolj toksična od boraksa. Ti podatki potrjujejo, da je učinkovitost borovih spojin v največji meri odvisna od vsebnosti bora.

Za preventivno zaščito lesa pred hišnim kozličkom je zadostna mejna vrednost 5,6 kg/m^3 BAE. V praksi je namreč majhna verjetnost, da bi bil zaščiten les izpostavljen srednje starim larvam. Za kurativno zaščito pa je potrebna višja koncentracija (10 kg/m^3 BAE), saj so v lesu tudi starejše larve, ki lahko dalj časa preživijo brez hrane oziroma lahko tolerirajo večje količine bora.

Poleg hišnega kozlička so trdoglavci najpomembnejši terciarni insekti v Srednji Evropi. Spiller (1948) je za jajčne larve navadnega trdoglavca (*Anobium punctatum*) določil mejno vrednost 0,2 kg/m^3 BAE. Starejše larve so pri 16-tedenskem poskusu poginile šele pri približno 5 kg/m^3 BAE. Becker (1959) je pri 12-tedenskem poskusu določil mejno vrednost celo pri 17 kg/m^3 BAE (preglednica 3). Pri šestmesečnem poskusu je mejna vrednost padla na približno 4 kg/m^3 BAE.

Očitna višja odpornost larv navadnega trdoglavca (*Anobium punctatum*) je posledica dejstva, da lahko preživijo larve brez hrane celo do enega leta. Larve ostanejo v impregniranem lesu, ga prepoznajo, obglodajo, a se z njim ne prehranjujejo (Spiller in Danne, 1948).

Poleg hišnega kozlička in trdoglavca les v svetu ogrožajo tudi termiti. Ksilofagnih vrst termitov je okoli 400 in vsaka vrsta se na bor odziva drugače. Običajni priporočeni navzem borove kisline za zaščito pred termiti znaša 4,5 kg na 1 m^3 lesa. V Veliki Britaniji, kjer je znatno manjša možnost za napad termitov, je zahtevani navzem nižji (1,8 kg/m^3 BAE), medtem ko je v Nemčiji minimalni zahtevani navzem še nekoliko manjši 1 kg/m^3 BAE globinsko impregniranega lesa (Kartal in sod., 2007). Za zatiranje termitov (*Coptotermes formosanus*) je potrebno v les vnesti vsaj 0,5 % BAE (2,25 kg/m^3 BAE), medtem ko je Greace s sodelavci (1992) v laboratorijskem testu ugotovil, da navzem 0,35 % BAE (1,6 kg/m^3 BAE) zadostuje za pogin vseh termitskih delavcev po treh tednih trajanja poskusa. Pri terenskem poskusu je pri najvišji koncentraciji 1,02 % BAE (4,6 kg/m^3 BAE) še vedno prišlo do izgube mase (2,5 %). Kljub temu je bila dobro vidna poškodba le kozmetična in ni vplivala na strukturne lastnosti vzorcev. Novejše borove spojine z vodoodbojnim učinkom (aluminijev borat oleat) prav tako kažejo dobro termicidno delovanje, saj mejna vrednost znaša le 2,0 kg/m^3 BAE (Lyon in sod., 2007). Tsunoda (2001) poroča, da razlike v termicidnem delovanju bora med vzorci, impregniranimi s TMB (trimetil borat; plinski postopek), in vzorci, impregniranimi z vodno raztopino borove kisline, ni.

Borove spojine so se izkazale za zelo učinkovite tudi pri zaščiti nekaterih vrst listavcev v Avstraliji, ki so bili dovzetni za napad insektov iz skupine parketarjev (*Lyctus* sp). Raziskave so pokazale, da je beljava listavcev, impregnirana z borovo kislino, popolnoma odporna na njihov napad (Hunt in Garratt, 1953). Difuzija borove kisline v furnir in žagani les je bila dobra, zato se je njena uporaba zelo razširila.

Poudarili smo že, da so spojine bora želodčni strup in ne kontaktni, zato delujejo počasi. Kot je opisano, lahko larve dolgo časa preživijo v lesu brez hrane in se v njem premikajo. Tako lahko prečkajo zaščiteno plast in pridejo globlje v nezaščiteni predel. Tudi pri insekticidih s hitrejšim delovanjem je razvoj larv mogoč, kljub površinsko zaščitenem lesu, zaradi tanke zaščitne plasti. Vodna raztopina borove soli ne prodre globlje kot 2 mm do 3 mm (Peylo, 2005). V tankem zaščitenem delu je koncentracija bora največkrat nad mejno vrednostjo, vendar larve to tanko plast hitro prečkajo. Zato ostaja sorazmerno tveganje, da larve v zaščitenem lesu preživijo in tudi izletijo (Peylo, 2005). Domnevno pomanjkljivost, počasnejše delovanje, lahko opravičimo z manjšim učinkom na okolje, čemur dajemo veliko prednost (Peylo, 1998).

Preglednica 3: Mejne vrednosti borove kisline in boraksa po standardu DIN 52165 za jajčne larve in 4 mesece stare larve hišnega kozlička (*Hylotrupes bajulus*) ter srednje velike larve navadnega trdoglavca (*Anobium punctatum*) (Becker, 1959)

Table 3: Thresholds values of boric acid and borax according to the standard DIN 52165 for egg larvae and 4 months old larvae of old house borer (*Hylotrupes bajulus*) and middle age larvae common furniture beetle (*Anobium punctatum*) (Becker, 1959).

		Trajanje poskusa					
borova spojina	Vrsta insekta	4 tedne		12 tednov		6 mesecev	
		% raztopina	Kg soli na m^3 lesa	% raztopina	Kg soli na m^3 lesa	% raztopina	Kg soli na m^3 lesa
borova kislina	*Hylotrupes* jajčna larva	1,0 -0,63	5,6 -3,6	0,063 - 0,050	0,45 -0,36	0,040 -0,025	0,29 -0,18
	4 mesece stare *Hylotrupes* – larve	>1,6	>10	0,10 -0,05	0,70 -0,36		
	srednje velike *Anobium* – larve			>2,5	>17	0,63 -0,40	4,2 -2,6
boraks	*Hylotrupes* jajčna larva	1,0 -0,63	6,0 -3,8	0,100 - 0,050	0,65 -0,32	0,050 -0,025	0,36 -0,18
	4 mesece stare *Hylotrupes* – larve	>1,6	>10	0,20 -0,10	1,4 -0,7		
	srednje velike *Anobium* – larve			>2,5	>18	>0,4	>2,6

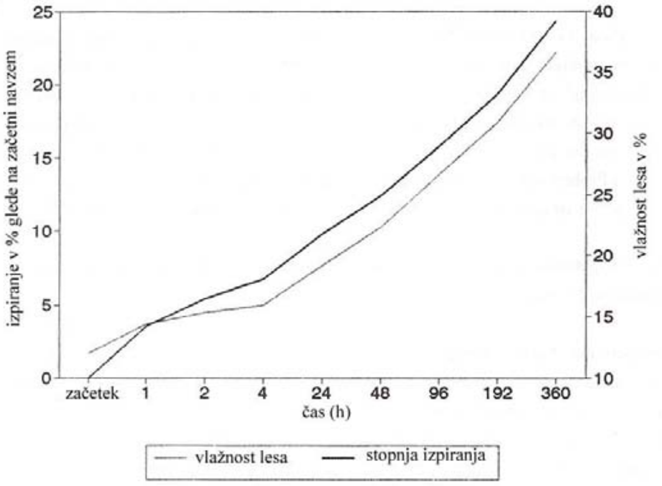
2.2.7 Difuzivnost in izpiranje bora

Uporaba borovih spojin kot sredstev za zaščito lesa je omejena zaradi slabe fiksacije bora v lesu in naravne topnosti v vodi. Posledica je intenzivno izpiranja bora iz lesa. Zato se borove spojine uporabljajo samostojno le za prvi in drugi razred izpostavitve, kjer ni nevarnosti močenja in izpiranja. Pomembno je upoštevati, da bor v že impregniranem lesu ni dobro fiksiran, ampak zaradi vlage difundira z mesta višje koncentracije na mesta z nižjo (Lloyd, 1998; Obanda in sod., 2008).

Na difuzijo vplivajo različni dejavniki: vlažnost lesa, temperatura, koncentracija raztopine in čas trajanja difuzije. To so dejavniki, ki jih lahko kontroliramo. Poleg njih vplivajo tudi nekontrolirani dejavniki, ki so tesno povezani z anatomskimi, fizikalnimi in kemičnimi značilnostmi lesa (Ra in sod., 2002). Za difuzijo bora je potrebna vsaj 20-odstotna vlažnost lesa. Bor najbolje difundira pri vlažnosti med 40 % in 60 %, medtem ko se hitrost difuzije pri višjih stopnjah vlažnosti nekoliko upočasni (Morrell in sod., 1990; Morrell in sod., 1992; Morrell in Freitag, 1995). Pri vlažnosti, ki je nižja od točke nasičenja celičnih sten (26 %), se difuzija bistveno zmanjša (Schoeman in sod., 1998). Zaradi dobre difuzivnosti globina penetracije s časom narašča, maksimalna globina penetracije znaša približno 4 cm in jo dosežemo po 25 dneh (Ra in sod., 2002). Dobra difuzija bora omogoča dobro penetracijo v les, kar pomeni dobro globinsko zaščito. Po drugi strani pa je dobra difuzija slabost, saj vpliva na izpiranje bora.

Bor se že dolgo časa uporablja v mešanicah anorganskih pripravkov za zaščito lesa. Kot smo že omenili, je eden takšnih pripravkov CCB (mešanica kromovih, bakrovih in borovih spojin). Peylo in Willeitner (1997) sta ugotovila, da se je v treh letih in pol na prostem (nad zemljo) iz droga, impregniranega s pripravkom CCB, izpralo približno 30 % bora, medtem ko je bilo izpiranje bakra veliko manjše (1,3 %) in kroma (0,05 %). Po petih letih preskusa pa se je izpralo 35 % bora, 2 % bakra in 0,1 % kroma (Peylo in Willeitner, 1999). CCB je pripravek, ki se uporablja za kotelski postopek zaščite lesa. Ta zaščita se uporablja v tretjem in četrtem razredu izpostavitve. Zdaj se namesto kroma uporabljajo amini. Novi pripravki so na osnovi bakra in aminov, kjer pa se borove spojine uporabljajo kot sekundarni fungicid in insekticid. Humar in sodelavci (2006) navajajo, da dodatek bora k baker/etanolaminski raztopini nekoliko poveča izpiranje bakra in izboljša odpornost na glive razkrojevalke, predvsem na tiste, ki so odporne na bakrove učinkovine.

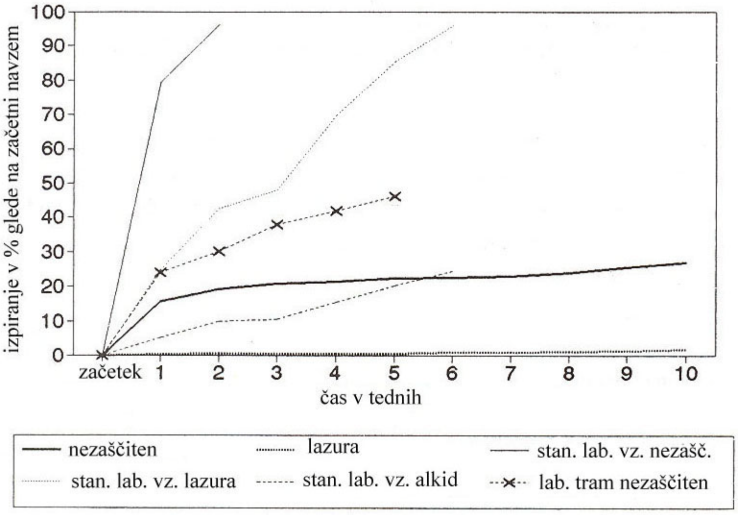
Izpiranje bora je v dobri korelaciji z vlažnostjo lesa. Čim višja je vlažnost, tem več bora se izpere iz lesa (Peylo, 1995; Peylo in Willeitner, 1995; Kartal in sod., 2004; Baysal in sod., 2006) (slika 2). Takoj, ko je vlažnost lesa dovolj visoka, se začne izpiranje (Peylo in Willeitner, 1995). Zato je ena od možnosti, kako zmanjšati izpiranje bora, uporaba hidrofobnih sredstev ali površinskih premazov, ki so sposobni upočasniti navlaževanje lesa. Toda tudi premaz v celoti ne zaustavi izpiranja bora (Orsler in Holland, 1993). Peylo in Willeitner (1995) sta ugotovila, da imajo hidrofobna sredstva (parafin, alkidni premaz, firnež, mešanica naravnih smol, olj in zelišč, mešanica naravnih smol in sintetičnih polimerov) zaviralni učinek na navlaževanje. Ta učinek je večji na začetku izpiranja, po daljšem času pa se zmanjšuje, saj difuzije vode ne moremo preprečiti, ampak jo lahko samo upočasnimo. Najbolj se je izpiranje bora zmanjšalo z alkidnim premazom (Peylo, 1995; Peylo in Willeitner, 1995). Prosta voda v lumnih celic ne vpliva na izpiranje bora, saj boratni ioni difundirajo v vlažnih celičnih stenah v smeri koncentracijskega gradienta. Zato izpiranja ne moremo zmanjšati z zapolnitvijo lumnov celic (Peylo, 1995; Peylo in Willeitner, 1995).



Slika 2: Odvisnost izpiranja bora od vlažnosti borovega (*Pinus sylvestris*) impregniranega trama (#Peylo, 1995).

Figure 2: Dependence of boron leaching from moisture content of impregnated pine (*Pinus sylvestris*) beam (#Peylo, 1995).

Poleg dodatkov na rezultat močno vpliva tudi postopek izpiranja. Primerjava kontinuiranega in nekontinuiranega izpiranja (čas namakanja enak času namakanja pri kontinuiranem izpiranju) je pokazala, da je količina izpranega bora večja pri kontinuiranem izpiranju. Iz vzorcev, impregniranih z 0,1-odstotno raztopino borove kisline se je po 24 ciklih nekontinuiranega izpiranja (96 ur namakanja) izpralo približno 50 % bora glede na začetno količino v lesu, medtem ko se je pri kontinuiranem izpiranju izpralo približno 75 % bora, ki so ga v les vnesli z impregnacijo (Peylo 1995; Peylo in Willeitner, 1995). V primerjavi z laboratorijskimi testi je izpiranje na prostem manjše (slika 3). Po 38 tednih izpiranja na prostem se je iz vzorcev, impregniranih z borovo kislino, brez površinske zaščite, izpralo približno 40 % bora (Peylo, 1995). Les v drugem in tretjem razredu izpostavitve ni izpostavljen kontinuiranemu izpiranju, tako kot les v četrtem in petem razredu. Zato bi bilo za določanje vezave borovih ionov verjetno bolj smiselno uporabiti nekontinuirne metode.

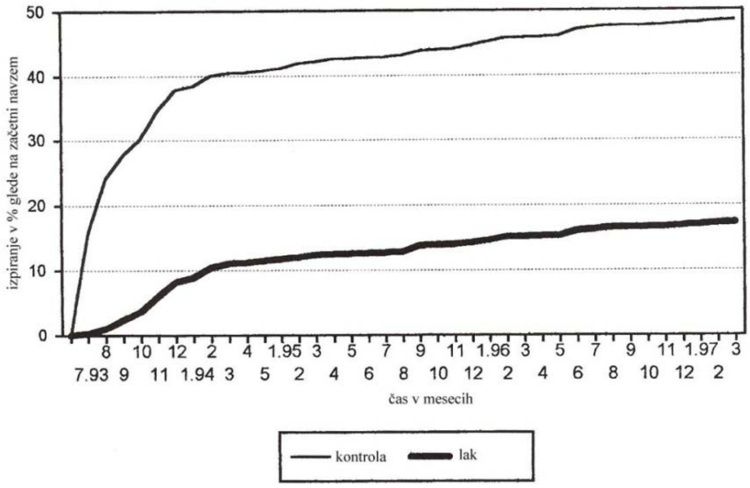


Slika 3: Primerjava izpiranja bora v laboratoriju (lab.) in na prostem. Površina vzorcev je bila zaščitena z lazurnim oziroma alkidnim premazom ali pa ni bila zaščitena ($^{\#}$Peylo, 1995).

Figure 3: Comparation of boron leaching in laboratory (lab.) and outdoor. Surfaces of samples were coated with a stain or an alkyd coating or were unprotected ($^{\#}$Peylo, 1995).

Peylo in Willeitner (1997) sta s terenskim testom (tretji razred izpostavitve) ugotavljala učinkovitost površinskih premazov pri omejevanju izpiranja bora iz lesa, impregniranega z 0,1-odstotno raztopino borove kisline. Glede na začetno količino bora v lesu se je iz vzorcev po treh letih in pol izpralo približno 47 % bora, medtem ko se je iz vzorcev, premazanih s premazom na osnovi naravnih smol (približno 80 g/m^2) izpralo približno 20 % bora. Ugotovila sta, da površinski premaz v začetni fazi močno zmanjša izpiranje. Po približno šestih mesecih poteka izpiranje iz kontrolnih in premazanih vzorcev enako hitro (slika 4). Po petih letih testiranja sta Peylo in Willeitner (1999) ugotovila, da izpiranje bora iz vzorcev z zaščiteno in nezaščiteno površino še vedno poteka vzporedno. Delež bora, izpranega iz vzorcev brez premaza, se je povečal na okoli 80 %, iz vzorcev s površinskim premazom pa na približno 50 %. Razlika, ki je nastala na začetku testa, ostane po petih letih približno enaka. Intenziteta izpiranja se manjša z zmanjševanjem koncentracijskega gradienta in se nadaljuje, vse dokler se ne izpere celotna količina vnesenega bora. S površinskim premazom torej ne moremo preprečiti izpiranja bora, ampak ga lahko le upočasnimo (Peylo in Willeitner, 1999).

Po do sedaj znanih podatkih iz literature strokovnjakom in industriji še ni uspelo razviti rešitve, s katero bi popolnoma preprečili ali zmanjšali izpiranje bora na raven pod 5 % (Obanda in sod., 2008). Za zmanjšanje izpiranja so uporabljali različna hidrofobna sredstva (Peylo in Willeitner, 1995; Peylo, 1995; Baysal in sod., 2006; Kartal in sod., 2007; Kartal in sod., 2004), površinske premaze (Peylo in Willeitner, 1995; Peylo, 1995; Peylo in Willeitner, 1997; Peylo in Willeitner, 1999), tanin (Pizzi in Baecker, 1996), borove estre (Mohareb in sod., 2004), kemično spojino s kombinacijo boratov in vodoodbojnim delovanjem (amonijev borat oleat) (Lyon in sod., 2007), »nano-bor« (Kartal in sod., 2009), termično modifikacijo (Kartal, 2006), vendar nobena od naštetih rešitev ni preprečila intenzivnega izpiranja bora iz lesa. To pomeni, da je uporaba lesa, zaščitenega le z borovimi spojinami (brez drugih fungicidov in insekticidov), kljub dodatkom za fiksacijo še vedno omejena. Uporablja se lahko v pokritih prostorih, kjer ni nevarnosti močenja oziroma zelo visoke vlage v prostoru.



Slika 4: Izpiranje bora na prostem iz lesa, impregniranega z 0,1-odstotno raztopino borove kisline, z nepremazano površino in z zaščiteno površino (dvakrat premazano z lakom iz naravnih smol (80 g/m^2)) (#Peylo in Willeitner, 1997)

Figure 4: Outdoor leaching of boron from wood impregnated with 0,1% solution of boric acid with uncoated surface and two times coated surface with natural resin varnish (80 g/m^2) (#Peylo in Willeitner, 1997)

2.2.8 Borovi pripravki za zaščito lesa

Borovi pripravki se v praksi lahko uporabljajo samostojno ali pa jih kombiniramo z drugimi biocidi. Ker so relativno slabo topni v vodi, jim topnost izboljšamo z različnimi dodatki, kot so amini, hidroksidi … V Sloveniji so na trgu trije samostojni borovi pripravki in sicer Belbor (Belinka), Borosol (Regeneracija) in Silvanol GB (Silvaprodukt). Za izboljšanje učinkovitosti proti modrenju nekateri proizvajalci borove spojine kombinirajo s fungicidi (kvartarne amonijeve spojine, azoli …). Poleg tega pa borove spojine v nekaterih pripravkih nastopajo le kot insekticidi ali sekundarni fungicidi. Najbolj je poznan klasični pripravek CCB. Borovo kislino najdemo tudi v novi generaciji pripravkov na osnovi bakra in etanolamina, kjer ima borova kislina predvsem vlogo insekticida in sekundarnega fungicida. V Sloveniji lahko kupimo dva takšna pripravka in sicer Kuproflorin (Regeneracija) in Silvanolin (Silvaprodukt). Ta pripravka lahko uporabljamo tudi za zaščito lesa v tretjem in četrtem razredu izpostavitve.

Poleg klasičnih pripravkov je na trgu na voljo tudi trimetilborat, ki ga v les vnesemo s posebnim, plinskim postopkom zaščite. Trimetilborat je v vakuumu hlapen in v les prodira kot plin, zato lahko dobro prodre tudi v slabo permeabilne lesne vrste. Ob stiku z vodo se pretvori v borovo kislino. Priporočljiva vlažnost lesa pred impregnacijo je 8-odstotna. Če je les prevlažen, ves trimetilborat reagira že na površini, pri preveč suhem lesu pa sploh ne pride do reakcije med trimetilboratom in vodo oziroma je ta prepočasna. Les je po zaščiti s plinskim postopkom suh in takoj primeren za obdelavo. Ker voda kot topilo ni potrebna, se les ne krči oziroma ne nabreka, kar je posebej pomembno za konstrukcijski les.

2.2.9 Zadrževanje gorenja

Že kmalu po prvi industrijski uporabi v zaščitnih pripravkih so se borove spojine začele uporabljati tudi v protipožarnih sredstvih. Za zadostno protipožarno zaščito mora les vsebovati vsaj 48 kg/m^3 borove kisline (Le Van in Tran, 1990). To pomeni približno 10-krat višjo vrednost borove kisline v lesu kot je potrebna za učinkovito zaščito pred glivami razkrojevalkami lesa. Okorn (1999) je ugotovil, da se zmanjša vnetljivost lesa, zaščitenega z biocidnimi borovimi pripravki, a njihovo delovanje ni dovolj učinkovito, da bi jih lahko prištevali med protipožarna sredstva. Kakor koli, vsako zmanjšanje gorljivosti je pomembno ob požaru, saj tako izboljša varnost objekta.

2.3 VOSKI IN NJIHOVA UPORABA V LESARSTVU

Voski so relativno stabilne netoksične spojine, ki jih človek uporablja za najrazličnejše namene že vse od prazgodovinskih časov dalje. Zdaj se voski v glavnem uporabljajo kot aditivi in aktivne učinkovine. V prihodnosti bo uporaba voskov najverjetneje še naraščala zaradi njihovih ugodnih toksikoloških in okoljskih lastnosti.

2.3.1 Kaj so voski in kako jih delimo

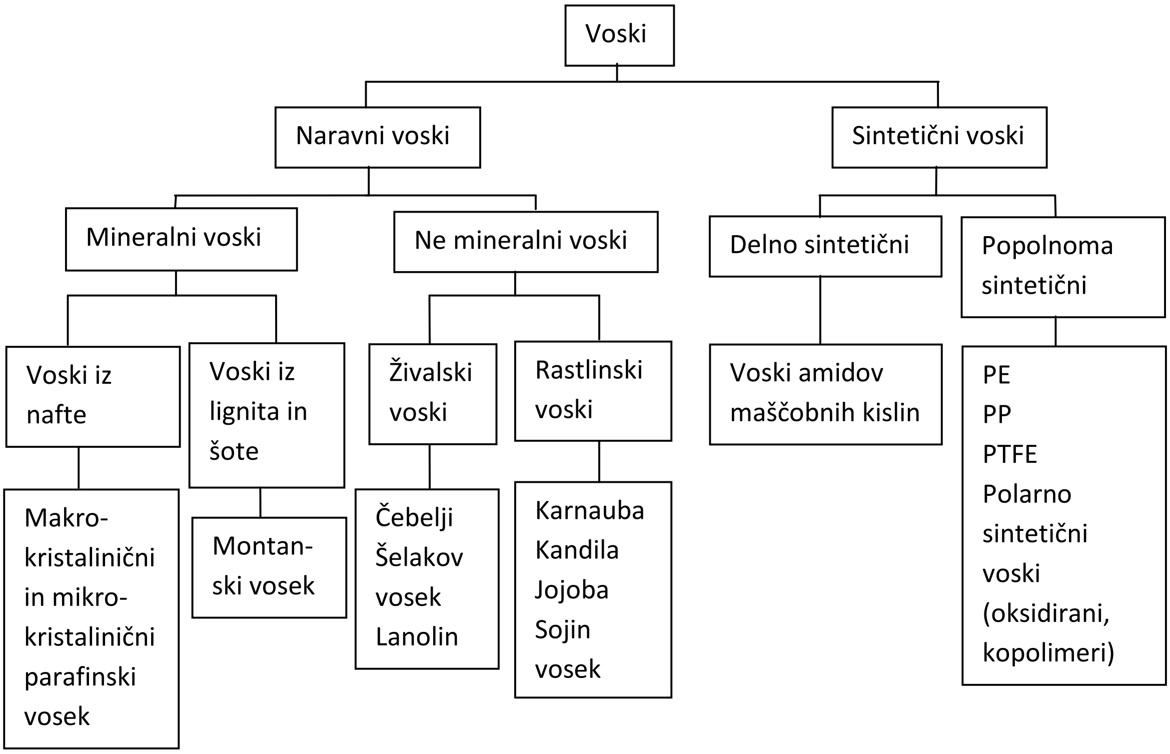
Pojem voski združuje široko skupino spojin, ki ne tvorijo kemijsko homogene skupine. Vsi voski so vodoodbojni materiali, sestavljeni iz različnih sestavin in sicer: ogljikovodikov (nerazvejeni ali razvejeni alkani in alkeni), ketonov, diketonov, primarnih in sekundarnih alkoholov, aldehidov, estrov, sterolov, alkanojskih kislin in terpenov (Wolfmeier, 2003).

Zgodovinski prototip za vse voske je čebelji vosek (Matthies, 2001; Wolfmeier, 2003). Glede na njegovo sestavo so znanstveno definirali voske. Voski so kemijsko gledano estri višjih karboksilnih kislin z višjimi alkoholi. Ta definicija je uporabna le za nekaj klasičnih voskov (npr. čebelji in karnauba vosek). Preostalih voskov, kot je na primer parafinski vosek, ta definicija zaradi drugačne kemijske sestave ne zajema (Wolfmeier, 2003). V zadnjem času se je bolj uveljavila definicija, ki določa voske na podlagi fizikalnih lastnosti.

Wolfmeier (2003) navaja, da so voski snovi, ki:

- se lahko polirajo pod majhnim tlakom in imajo gostoto in topnost močno odvisni od temperature,
- so pri 20 °C gnetljive ali nedrobljive, grobo do fino kristalne, transparentne do motne, toda neprozorne ali močno viskozne,
- se nad 40 °C talijo, ne da bi se pri tem razgradile,
- imajo viskoznost nad točko tališča v negativni odvisnosti od temperature,
- imajo v večini primerov točko tališča med 50 °C in 90 °C (v izjemnih primerih nad 200 °C),
- v splošnem gorijo s sajastim plamenom,
- lahko tvorijo paste ali gele in so slab prevodnik toplote in elektrike (toplotni in električni izolatorji).

Voske lahko razdelimo po različnih kriterijih glede na njihov izvor, kemične, fizikalne ali tehnične lastnosti ali glede na uporabo. Osnovna delitev voskov je glede na njihov izvor in sintezo (slika 5). Tako voske delimo v dve glavni skupini, na naravne in sintetične, vendar pri delitvi ni jasne meje. Naravni voski kažejo svoje voskaste lastnosti brez kemične obdelave. Sintetični voski navadno pridobijo lastnosti voskov v postopku sinteze (Wolfmeier, 2003). Drugo ime za sintetične in parafinske voske, ki ga zasledimo v literaturi, je Fischer-Tropsch. Ime izvira iz postopka pridobivanja voskov iz surove nafte.



Slika 5: Razvrstitev voskov (Wolfmeier, 2003; SpecialChem, 2008)

Figure 5: Classification of waxes (Wolfmeier, 2003; SpecialChem, 2008)

2.3.2 Osnovne lastnosti voskov

V lesarstvu se tradicionalno uporabljajo naravni voski (čebelji, karnauba, montanski …). Vedno bolj prodirajo tudi sintetični voski, ker so cenejši in imajo lastnosti, prilagojene za specifično uporabo.

2.3.2.1 Čebelji vosek

Je snov, ki jo izločajo medonosne čebele delavke iz voskovnih žlez. Glavna sestavina voska so estri nasičenih maščobnih kislin z enovalentnimi alifatskimi alkoholi. Poleg tega čebelji vosek vsebuje še proste maščobne kisline, alifatske ogljikovodike, barvila in aromatske snovi (Plut, 2008; Cyberlipid, 2008). Povprečne molekule vsebujejo med 40 in 47 ogljikovih atomov. Molekule alifatskih alkoholov v čebeljem vosku so veliko bolj razvejene kot tiste v sintetičnih voskih (Basson in Reynhardt, 1988a). Pri 32 °C do 35 °C je čebelji vosek plastičen in upogljiv ter se z lahkoto gnete, pri malo nižjih temperaturah (od 25 °C do 30 °C) pa je trši in se ga težje preoblikuje. Čebelji vosek v vodi ni topen. Nekaj njegovih sestavin lahko raztopimo v hladnem etanolu, veliko bolje pa se topi v toplem etanolu in v številnih drugih organskih topilih, kot na primer v etru, bencinu in terpentinu (Wolfmeier, 2003). Tališče ima med 62 °C in 64 °C. Navadno je rumene do rumeno rjave barve, odvisno od starosti in prehrane čebel (Wolfmeier, 2003; Plut, 2008). Vosek se zaradi vsebnosti prostih maščobnih kislin, diolov in hidroksi kislin enostavno umili ter emulgira (Cyberlipid, 2008). Ni toksičen za sesalce in je eden od najpomembnejših voskov za voskanje lesa v stavbah, pohištva, lesenih tal in lesenih igrač … (Petrič, 2000). Povoskana površina ščiti les pred nečistočami in tekočo vodo, medtem ko čebelji vosek ne zaščiti lesa pred glivami razkrojevalkami lesa in lesnimi insekti (Leiße, 1996; Weissenfeld, 1988).

Čebelji vosek se uporablja v čisti obliki ali v mešanicah z drugimi voski, olji, smolami in topili. Pripravimo ga lahko v trdni obliki in tudi v obliki paste ali tekočega pripravka. Razmerje med voskom, olji in topili določa trdoto končnega premaza (Weissenfeld, 1988).

2.3.2.2 Karnauba vosek

Karnauba vosek je rastlinskega izvora. Pridobivajo ga iz listov palme *Copernicia cerifera*, ki raste v severovzhodnem delu Brazilije. Vosek služi kot zaščita listov pred ekstremnimi klimatskimi razmerami. Je brez vonja in okusa, stabilen in nestrupen. Barva (zlato rumen do črn) je odvisna od čistosti in kvalitete voska ter starosti listov (Slika 6) (Foncepi, 2008). Sestavljen je iz mono- in dihidroksi maščobnih kislin, alkoholov z 28 do 34 ogljikovimi atomi, hidroksilnih kislin in njihovih estrov ter poliestrov. Karnauba vosek je najtrši naravni vosek in ima najvišjo točko tališča (med 80 °C in 86 °C) med naravnimi voski (Wolfmeier, 2003; Foncepi, 2008; Cyberlipid, 2008). Je kompatibilen s skoraj vsemi naravnimi in sintetičnimi voski ter številnimi naravnimi in sintetičnimi smolami. Dobro se topi v nepolarnih topilih in se nad točko tališča z njimi meša v vseh razmerjih, medtem ko je v polarnih topilih delno topen le med segrevanjem (Wolfmeier, 2003). Karnauba vosek se pogosto uporablja kot dodatek drugim voskom, na primer čebeljemu, za izboljšanje trdote, povišanje točke tališča oziroma zmanjšanje lepljivosti površine ter za povečanje sijaja (Leach 1993; Kregar, 1956). Uporablja se lahko tudi samostojno v trdni obliki, v obliki past ali emulzij.

Slika 6: Različno rafinirani karnauba voski ([#]Foncepi, 2008)

Figure 6: Differently refined carnauba waxes ([#]Foncepi, 2008)

2.3.2.3 Montanski vosek

Montanski vosek je fosiliziran rastlinski vosek, ekstrahiran iz lignita oziroma premoga. Najpomembnejše komercialno nahajališče je v centralni Nemčiji, vzhodno od reke Elbe, v rjavem premogu. Montanski vosek je mešanica voskov, smol in asfaltnih snovi. Kot ostali rastlinski voski je surov montanski vosek sestavljen iz estrov višjih karboksilnih kislin z višjimi alkoholi in prostih višjih kislin. Drugih sestavin, kot so prosti alkoholi ali ketoni, parafini in terpeni, je le v manjših količinah (Matthies, 2001). Rafinirani montanski vosek je bledo rumen, sestavljen v glavnem iz višjih karboksilnih kislin z dolžino verig med 22 in 34 ogljikovih atomov.

Takšen delno sintetičen produkt je izjemno trd, zelo dobro se polira in ni toksičen za sesalce (Basson in Reynhardt, 1988b; Matthies, 2001; Heinrichs, 2003). Ena od najbolj pomembnih lastnosti tega voska je tudi sposobnost tvorjenja tankega odpornega filma (Warth, 1959). Montanski vosek je topen v številnih organskih topilih, še posebno v aromatskih in kloriranih ogljikovodikih, celo pri nizkih temperaturah (Heinrichs, 2003). Tališče voska je pri temperaturi med 82 °C in 95 °C. Uporablja se kot polnovreden nadomestek za karnauba vosek (ChemCor, 2008). Montanski vosek se uporablja v lesarstvu, za polirne paste za avtomobile, čevlje, električne izolacije in maziva v proizvodnji plastike ter v papirni industriji (Cyberlipid, 2008).

2.3.2.4 Šelakov vosek

Šelakovo smolo pridobivamo iz izločka insektov (*Tachardia lacca*). Šelak vsebuje od 4 % do 5 % voska, ki ga lahko pridobimo z raztapljanjem izločka insektov v razredčeni raztopini natrijevega karbonata ali 90 do 95-odstotnem etanolu kot netopno komponento. Šelakov vosek je trd, rumen do rjav produkt (Wolfmeier, 2003). Glavna sestavina voska so estri maščobnih kislin (Cyberlipid, 2008). Topen je v vročem alkoholu in vsebuje 72 % do 83 % snovi, ki se ne dajo umiliti. To se izkorišča za pripravo past in raztopin za matiranje (Kregar, 1956). Uporablja se v proizvodnji lakov in politur in kot zamenjava za karnauba vosek (Cyberlipid, 2008).

2.3.2.5 Parafinski vosek

Kot že omenjeno, parafinski vosek kemijsko ne sodi med voske, vendar ga v to skupino snovi uvrščamo zaradi njegovih fizikalnih lastnosti. Je brezbarven, brez vonja, kemijsko inerten, tali pa se pri 48 °C do 66 °C (Wolfmeier, 2003). Njegove lastnosti močno variirajo glede na stopnjo čistosti. Vodoodbojna učinkovitost parafinskih voskov je močno odvisna od stereokemične konfiguracije ogljikovodikov in njihove strukture. Glavna sestavina parafinskega voska so nerazvejene alkanske verige, ki dajejo vosku najboljšo vodoodbojnost. Čim daljše so verige ogljikovodikov, tem boljša je vodoodbojnost (Garai in sod., 2005). Topen je v bencinu, terpentinu in raznih drugih organskih topilih (Wolfmeier, 2003). Parafinski vosek uporabljajo v industriji na različnih področjih. V lesarstvu se uporablja kot dodatek lepilu pri proizvodnji vodoodpornih ivernih plošč in ostalih lesnih kompozitov (Rice in Wang, 2002; Zhang in sod., 2007), kot dodatek zaščitnim sredstvom za povečevanje vodoodbojnosti (Evans in sod., 2003). Poleg tega se v mešanicah z drugimi voski, smolami itd. uporablja še pri proizvodnji barv in premazov za izboljšanje hidrofobnosti. Uporabljajo ga v trdnem stanju in v obliki emulzij. Ena izmed novejših aplikacij voska je tudi uporaba v mavčno-kartonskih ploščah za uravnavanje klime v prostoru (BASF, 2009).

2.3.2.6 Sintetični voski

Sintetične voske proizvajajo predvsem iz etilena. So predvsem polietilenski (PE), tudi PE visoke gostote (HDPE), polipropilenski (PP), kopolimerni etilenski in politetrafluoroetilenski (PTFE) voski (ChemCor, 2008). Sintetični voski so cenejši in imajo v primerjavi z naravnimi boljšo uporabnost in konstantno kakovost. Zaradi naštetih lastnosti pogosto zamenjujejo naravne, na primer karnauba in montanski vosek. Voskom med sintezo enostavno prilagodijo lastnosti glede na njihov namen uporabe. Lastnosti sintetičnih voskov določata molska masa polimera in razvejenost verig. Sintetični voski so brezbarvni, beli do prozorni in tvorijo čisto talino. Kot drugi voski so pri segrevanju topni v nepolarnih topilih (alifatskih, aromatskih in kloriranih ogljikovodikih), pri ohlajanju pa jih večina kristalizira v zelo fine delce. Odvisno od tipa in koncentracije voska tvorijo sintetični voski mobilne disperzije ali gele s tiksotropnimi lastnostmi (Wolfmeier, 2003). Točka tališča sintetičnih voskov je odvisna od vrste voska, lahko pa doseže tudi 130 °C ali več.

Sintetične voske je možno pridobivati tudi iz obnovljivih virov, kot je rastlinsko olje oljne repice. Petersson in sodelavci (2005) so tako z encimi proizvedli 4 različne estre voskov. Biokatalitična proizvodnja estrov voskov potrebuje manj energije kot konvencionalne kemične metode, toda pridelovanje repičnega semena je še vedno zelo obremenjujoče za okolje (Tufvesson in Borjesson, 2008). Analiza življenjskega cikla (LCA) različnih premazov za površinsko zaščito lesa je pokazala, da je okolju najprijaznejši 100-odstotni UV-lak, sledi vodni UV-lak in šele na tretjem mestu je vosek, proizveden iz obnovljivih virov. Kot zadnji, najbolj obremenjujoč za okolje, je parafinski vosek. Če bi uspeli zagotoviti daljšo življenjsko dobo premazov na osnovi voskov, bi bili okolju prijaznejši kot UV-premazi (Gustafsson in Borjesson, 2007).

2.3.3 Vodoodbojna učinkovitost voskov in njihova uporaba v lesarstvu

Voski se uporabljajo za najrazličnejše namene. Pogosto temelji uporaba voskov na posnemanju njihove naravne funkcije. To še posebno izkoriščamo v lesarstvu, kjer voske uporabljamo predvsem kot sredstva za preprečevanje navlaževanja lesa oziroma za povečevanje vodoodbojnosti površine. Tako voske uporabljamo samostojno za površinsko zaščito lesa ali kot dodatek premazom (laki, lazure) za površinsko obdelavo lesa ali kot dodatek lepilom za povečanje vodoodpornosti lesnih kompozitov. Voski se uporabljajo še v kemični, kozmetični, prehrambeni, , gumarski, letalski, farmacevtski industriji, elektroindustriji, v medicini, gradbeništvu in pri proizvodnji plastike (Wolfmeier, 2003; SpecialChem, 2008; ChemCor, 2008). Pri proizvodnji premaznih sredstev se voski uporabljajo predvsem v obliki vodnih emulzij. Voski so tipični dodatek, ki s spreminjanjem proste površinske energije pomembno vplivajo na lastnosti kakršnega koli površinskega premaza (SpecialChem, 2008; ChemCor, 2008). Vosek v premazih vpliva na boljšo vodoodbojnost, večjo odpornost proti razenju in zmanjšuje sijaj površine (povečuje motnost) (SpecialChem, 2008).

Obdelava lesa z vodoodbojnimi sredstvi je v praksi zelo pogosta in se uporablja za zaščito pred navzemom tekoče vode ter za preprečevanje razvoja in rasti gliv (Passialis in Voulgaridis, 1999). Največkrat uporabljene hidrofobne snovi so emulzije voskov (predvsem parafinskih) (Banks, 1973; Feist in Mraz, 1978; Passialis in Voulgaridis, 1999; Treu in sod., 2004; Schultz in sod., 2007b; Zhang in sod., 2007), sušeča olja (Sailer in sod., 1998; Treu in sod., 2004), ekstrakti naravnih smol (Passialis in Voulgaridis, 1999; Schultz in sod., 2007b) in silikonske emulzije (Ghosh in sod., 2008). Na učinkovitost vodoodbojnosti vplivajo vrsta, sestava in koncentracija uporabljenega sredstva. Čim višja je, tem večji je vodoodbojni učinek (Rice in Wang, 2002; Garai in sod., 2005; Zhang in sod., 2007) in boljša je zaščita pred modrivkami in plesnimi (Schultz in sod., 2007b; Ghosh in sod., 2008). Glavne sestavine vodoodbojnih pripravkov so hidrofobne snovi, fungicidi in smole (Feist in Mraz, 1978; Svensson in sod., 1987; Passialis in Voulgaridis, 1999; Schultz in sod., 2007b). Med fungicidi so najpogosteje zastopane bakrove (Schultz in sod., 2007b) in borove spojine (Placckett in Chittenden, 1986; Drysdale in Placckett, 1987). Smole se uporabljajo za povezovanje hidrofobnih sredstev z interfibrilarnimi prostori na površini celičnih sten. Tako kombinacija smole in parafinskega voska daje boljšo vodoodbojnost, kot če bi uporabili vsako komponento posebej (Rowell in Banks, 1985)

Vosek na površini lesa ne utrjuje kemijsko s premreženjem, temveč tvori tanko plast, ki dobro zapolni pore (Petrič, 2000). Z vodoodbojnimi sredstvi na lesu lahko preprečimo ali zmanjšamo kapilarni tok tekoče vode, medtem ko vodoodbojni pripravki ne preprečujejo parne difuzije ali difuzije vezane vode, razen če med impregnacijo ne pride do visoke stopnje zapolnitve por ali tvorjenja filma na celičnih stenah. Po daljšem namakanju lesa, zaščitenega s parafinskim voskom v vodi, se pojavi kapilarni tok, ki lahko povzroči navlaževanje lesa tudi nad točko nasičenja celičnih sten (Banks, 1973). Dejstvo, da vosek izgubi učinek odbojnega delovanja po ponavljajočem se navlaževanju, ugotavlja tudi Treu s sodelavci (2004), saj se odložene snovi počasi raztapljajo in z vodo izpirajo. Vzrok temu so poškodbe vezi med celično steno in depoziti (voski), ki so posledica degradacije površine lesa (Banks in Voulgaridis, 1980). Ena od možnih rešitev te težave je uporaba hidrofobnih sredstev, ki se kemijsko vežejo v celično steno (Banks, 1973; Rowell in Banks, 1985).

Idealizirani model lesa, zaščitenega z vodoodbojnim sredstvom, je površinski hidrofobni ovoj celic, ki obdaja nezaščiteno jedro. Površinske celice v zaščiteni coni so hidrofobne (kontaktni kot je večji od 90°), tekoča voda ne more prodreti v notranjost, razen če je zunanji tlak večji od kapilarnega (Rowell in Banks, 1985). Debelina zaščitnega plašča je odvisna od impregnabilnosti lesne vrste. Zadostno globino penetracije lahko dosežemo pri dobro impregnabilnih vrstah lesa. V slabo impregnabilne lesne vrste prodrejo voski v vzdolžni smeri le nekaj centimetrov in 1 mm do 2 mm v prečni smeri (Rowell in Banks, 1985). Scholz in sodelavci (2010) so ugotovili, da je globina penetracije voskov odvisna od vrste lesa, postopka impregnacije in deleža suhe snovi v emulziji. Staljeni vosek je v borovino prodrl v rani, kasni les in trakovne traheide, v bukovini pa je prodrl v traheje in vlakna, medtem ko ga je veliko manj v trakovnih in aksialnih traheidah. Boljša penetracija se doseže z uporabo sredstev na vodni osnovi v primerjavi s sredstvi na osnovi topil, ki ne povzročajo nabrekanja celičnih sten. Sredstva na vodni osnovi in na osnovi organskih topil dobro zapolnijo aksialne traheide in trakove, medtem ko je globlje v lesu vosek le v trakovih (Svensson in sod., 1987)

Lesene površine, obdelane z voskom, so zmerno odporne na različne tekočine ali reagente (voda, etanol, olivno olje, kava) in toploto. Učinkovitost je odvisna od vrste voska in dodatkov (topila, olja) (Mihevc in sod., 1994). Voskano plast je treba redno vzdrževati in obnavljati. Zelo pomembno je redno čiščenje. Prah in različne smeti namreč lahko hitro poškodujejo plast voska in poslabšajo videz voskanih površin (Petrič, 2002).

3 ZNANSTVENA DELA

3.1 PONOVNO VREDNOTENJE FUNGICIDNIH LASTNOSTI BOROVE KISLINE

RE-EVALUATION OF FUNGICIDAL PROPERTIES OF BORIC ACID

Boštjan Lesar in Miha Humar
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V raziskavi smo določali minimalno inhibitorno fungicidno koncentracijo borove kisline v hranilnem gojišču in v impregniranem lesu smreke. Testiranje smo izvajali na treh glivah rjave trohnobe (*Antrodia vaillantii, Gloeophyllum trabeum* in *Serpula lacrymans*), treh glivah bele trohnobe (*Pleurotus ostreatus, Trametes versicolor* in *Hypoxylon fragiforme*) in dveh glivah modrivkah (*Aureobasidium pullulans* in *Sclerophoma pythiophila*). Rezultati kažejo, da so glive rjave trohnobe bolj občutljive kot glive bele trohnobe. Za zaviranje rasti gliv razkrojevalk, uporabljenih v raziskavi, je potrebno 0,8 kg/m^3 BAE, medtem ko avtorji starejših raziskav poročajo, da je potrebni minimalni navzem za učinkovito zaščito pred omenjenimi glivami 1,92 kg/m^3 BAE.

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BRIEF ORIGINALS · KURZORIGINALIA

Re-evaluation of fungicidal properties of boric acid

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Subject Minimal inhibitory fungicidal concentrations of one of the most important biocides were determined in nutrient medium and on impregnated wood specimens. The results showed, that brown rot fungi are more sensitive to boric acid than white rot ones. To inhibit growth of wood decay fungi, lower minimal effective retentions have been determined than reported in previous publications.

1 Introduction

The field of chemical wood preservation has significantly changed over the past years, as several classical active ingredients were removed from the market after implementation of the biocidal products directive (BPD 98/8/EC). Boron compounds are one of the oldest active ingredients that still remained on the market. Most of the efficacy data of boron compounds against wood decay fungi are rather variable (Carr 1964, Becker 1959, Drysdale 1994) and are sometimes not inline with novel results (Humar and Lesar 2008). Therefore, minimal boron inhibitory concentrations against wood inhabiting fungi are re-considered.

2 Materials and methods

Minimal inhibitory concentration of boric acid (BA) against fungi was determined in nutrient medium and impregnated wooden blocks. For testing, three brown rot fungi (*Antrodia vaillantii, Gloeophyllum trabeum* and *Serpula lacrymans*), three white rot fungi (*Pleurotus ostreatus, Trametes versicolor* and *Hypoxylon fragiforme*) and two blue stain fungi (*Aureobasidium pullulans* and *Sclerophoma pythiophila*) were used. In the first part of the research, diluted BA solutions were added to 20 ml of sterilized cooling potato dextrose agar to achieve different final concentrations, as shown in Table 1. Media without addition of BA served as controls. Solidified growth media were inoculated with 0.7 cm diameter pieces of mycelium. Fungicidal properties of BA was calculated from the ratio between radial fungal growth at BA-supplement and control Petri dishes after 10 days of incubation and expressed as percentages of retardation. In the second part of the experiment, specimens ($1.0 \times 1.5 \times 4.0\,\text{cm}^3$) were vacuum impregnated with different aqueous solutions of BA (Table 2). Control specimens were left un-impregnated. Beech wood specimens were exposed to white rot fungi, and Norway spruce ones were exposed to brown rot fungi. Fungicidal properties were determined according to the modified EN 113 procedure. After 12 weeks of exposure mass loss of the decayed specimens was gravimetrically determined. Both experiments were performed in five parallels.

3 Results and discussion

As expected, boron exhibited good fungicidal efficacy against the tested wood decay fungi. However, lower concentrations (6.25–12.5 ppm) of B in certain cases did not retard fungal growth, but on the contrary promoted it. This was expected, as boron is a well known essential element. To inhibit growth of the fungi growing on nutrient medium, 200 ppm of boron was necessary at six of the eight fungal species tested. The most resistant white rot fungus *H. fragiforme* was inhib-

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Table 1 Influence of boron concentration in nutrient medium on retardation of fungal mycelia growth. Negative values indicate that growth of fungal mycelia in presence of boron was faster than on control nutrient media. Standard deviations are given in the parenthesis

Tabelle 1 Einfluss der Borkonzentration im Nährmedium auf die Hemmung von Pilzmyzelwachstum. Negative Werte geben an, dass das Wachstum von Pilzmyzel in Gegenwart von Bor schneller war als bei den Kontrollnährböden. Standardabweichungen in Klammern

Fungal species	Boron concentration (ppm)							
	0	6.25	12.5	25	50	100	200	400
	Retardation of fungal growth (%)							
Antrodia vaillantii	0 (0)	6 (2)	4 (1)	6 (2)	10 (0)	82 (9)	100 (0)	100 (0)
Gloeophyllum trabeum	0 (0)	−8 (4)	−1 (1)	0 (2)	32 (9)	73 (7)	100 (0)	100 (0)
Serpula lacrymans	0 (0)	−3 (1)	0 (0)	−2 (1)	4 (1)	91 (6)	100 (0)	100 (0)
Pleurotus ostreatus	0 (0)	−11 (1)	−10 (1)	−7 (0)	−1 (1)	−13 (1)	8 (1)	38 (2)
Trametes versicolor	0 (0)	−14 (2)	−14 (2)	3 (1)	22 (4)	38 (4)	100 (0)	100 (0)
Hypoxylon fragiforme	0 (0)	0 (1)	0 (0)	0 (2)	0 (3)	34 (3)	96 (3)	100 (0)
Aureobasidium pullulans	0 (0)	4 (1)	8 (3)	32 (4)	57 (8)	76 (6)	100 (0)	100 (0)
Sclerophoma pythiophila	0 (0)	−3 (1)	14 (2)	23 (3)	58 (8)	68 (4)	100 (0)	100 (0)

Table 2 Mass loss of the specimens impregnated with aqueous solutions of boric acid (BA) of various concentrations after 12 weeks of exposure to wood decay fungi. Standard deviations are given in the parenthesis

Tabelle 2 Masseverlust der mit einer wässrigen Borsäurelösung (BA) unterschiedlicher Konzentrationen imprägnierten Proben nach 12-wöchigem Befall mit Holz zerstörenden Pilzen. Standardabweichungen in Klammern

B conc. (ppm)	Targeted retention of BA (kg/m^3)	*G. trabeum*	*A. vaillantii*	*S. lacrymans*	*T. versicolor*	*H. fragiforme*	*P. ostreatus*
		Mass loss (%)					
0	0	44.0 (5.9)	30.3 (6.7)	40.5 (7.0)	27.8 (4.5)	46.3 (9.3)	30.4 (5.7)
22	0.1	17.4 (9.9)	13.2 (4.0)	12.9 (9.8)	17.5 (3.2)	41.5 (3.4)	21.1 (2.8)
44	0.2	0.0 (1.4)	16.1 (3.7)	17.6 (5.4)	15.5 (3.7)	37.6 (3.8)	22.3 (4.5)
88	0.4	0.3 (0.1)	0.0 (2.4)	0.4 (0.9)	0.5 (0.1)	32.3 (5.8)	10.4 (3.4)
176	0.8	0.7 (0.3)	0.0 (0.3)	0.0 (0.3)	0.5 (0.2)	2.0 (1.7)	2.7 (1.1)
220	1.0	0.3 (0.1)	0.0 (0.3)	0.0 (0.0)	0.4 (0.3)	0.9 (0.3)	1.1 (0.6)

ited at 400 ppm of B, while *P. ostreatus* was still growing at that high concentration. Experiments performed on nutrient medium showed, that white rot fungal species were slightly more resistant against boron than brown rot or blue stain fungi (Table 1). A similar relationship is evident from the experiments performed on wooden blocks. The most boron sensitive species was *G. trabeum*. This fungus was inhibited at a retention of 0.2 kg of BA/m^3. Furthermore, retention of 0.4 kg/m^3 was enough to inhibit growth of *A. vaillantii*, *S. lacrymans* and *T. versicolor*. However, white rot fungi *P. ostreatus* and *H. fragiforme* were found the most boron resistant fungal species in this part of experiments too (Table 2). Retention of 0.8 kg/m^3 of BA were required to preserve wood against the above mentioned fungi. From an application point of view, it is very important that BA is more effective against brown rot species that are more frequent in use class II applications, than white rots, as BA is predominately used for protection of wood in this use class. In use class III, higher retentions are required due to the prominent boron leaching. However, our results indicate that boric acid has higher efficacy against most of the tested wood decay fungi than reported in the cited literature. For example, Carr (1964), Becker (1959), Beachler and Roth (1956) reported, that retentions between 0.52 and 2.88 kg of BA/m^3 are required to prevent wood against *G. trabeum* in laboratory conditions. Similarly, cited references reported that up to 1.92 kg of BA/m^3 is necessary to stop decay processes of *T. versicolor*. However, efficacy of the boric acid against *S. lacrymans* was in the same range as reported by Becker (1959) considering biological variability of the fungal strains used and inhomogeneity of the wood specimens tested.

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3.2 MINIMALNE FUNGICIDNE IN FUNGISTATIČNE KONCENTRACIJE BOROVIH UČINKOVIN ZA KURATIVNO ZAŠČITO LESA

MINIMAL FUNGICIDAL AND FUNGISTATIC CONCENTRATIONS OF BORON COMPOUNDS FOR WOOD REMEDIATION

Boštjan Lesar in Miha Humar
Zbornik gozdarstva in lesarstva, 2009, 90: 79–83
Prejeto 5. 7. 2009, sprejeto 23. 12. 2009

V raziskavi smo določili minimalno fungicidno mejno vrednost borove kisline in bakrovega sulfata pentahidrata za tri glive rjave trohnobe (*Gloeophyllum trabeum, Serpula lacrymans in Antrodia vaillantii*) in tri glive bele trohnobe (*Trametes versicolor, Pleurotus ostreatus in Hypoxylon fragiforme*). Kurativno učinkovitost smo določali tako, da smo okužene smrekove in bukove lesne vzorce za 10 minut potopili v vodno raztopino bakrovih oziroma borovih učinkovin. Zatem smo jih postavili na sterilno hranilno gojišče in opazovali preraščanje. Rezultati kažejo, da je bil navzem zaščitnih raztopin veliko višji pri vzorcih bukovine kot pri vzorcih smrekovine. Razlog za to je v boljši impregnabilnosti bukovega lesa. Fungicidni testi kažejo, da so borove učinkovine boljši fungicidi kot bakrove spojine. Minimalna inhibitorna koncentracija borove kisline v lesu za kurativno zaščito znaša 11 kg/m^3 BAE in je približno petkrat višja od mejne inhibitorne koncentracije za preventivno zaščito.

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MINIMALNE FUNGICIDNE IN FUNGISTATIČNE KONCENTRACIJE BOROVIH UČINKOVIN ZA KURATIVNO ZAŠČITO LESA

Boštjan LESAR[1], Miha HUMAR[2]

Izvleček

V raziskavi smo določili minimalno fungicidno mejno vrednost borove kisline in bakrovega sulfata pentahidrata za tri glive rjave (*Gloeophyllum trabeum, Serpula lacrymans* in *Antrodia vaillantii*) in tri glive bele trohnobe (*Trametes versicolor, Pleurotus ostreatus* in *Hypoxylon fragiforme*). Kurativno učinkovitost smo določali tako, da smo okužene smrekove in bukove lesne vzorce za 10 min potopili v vodno raztopino bakrovih oziroma borovih učinkovin. Zatem smo jih postavili na sterilno hranilno gojišče in opazovali preraščanje. Rezultati kažejo, da so borove učinkovine boljši fungicidi kot bakrove spojine. Minimalna inhibitorna koncentracija borove kisline v lesu za kurativno zaščito je približno petkrat višja od mejne inhibitorne koncentracije za preventivno zaščito.

Ključne besede: bakrove spojine, borove spojine, glive razkrojevalke lesa, kurativna zaščita lesa

MINIMAL FUNGICIDAL AND FUNGISTATIC CONCENTRATIONS OF BORON COMPOUNDS FOR WOOD REMEDIATION

Abstract

Minimal remedial fungicidal concentrations of boric acid and copper sulphate pentahydrate for three brown (Gloeophyllum trabeum, Serpula lacrymans and Antrodia vaillantii) and three white rot (Trametes versicolor, Pleurotus ostreatus and Hypoxylon fragiforme) fungi were determined. Remedial efficacy was determined on infested spruce and beech wood specimens, which were immersed into selected copper- or boron-based preservative solutions for ten minutes. The treated specimens were transferred to nutrient medium and fungal growth was monitored. The results showed that boron compounds where better fungicides than the copper ones. Furthermore, minimal remedial boron fungicidal concentration is approximately five times higher, than the preventive minimal inhibitory concentration.

Key words: copper compounds, boron compounds, wood-decay fungi, remedial treatments of wood

INTRODUCTION
UVOD

Področje kemične zaščite lesa se v zadnjem času močno spreminja, saj je bilo kar nekaj klasičnih aktivnih učinkovin odstranjenih s trga po uvedbi direktive o biocidih (BPD 98/8/EC). Borove spojine so ene izmed najstarejših aktivnih učinkovin, ki so ostale na trgu. Večina znanih podatkov o učinkovitosti borovih spojin proti glivam razkrojevalkam lesa je le za preventivno zaščito lesa (BEACHLER / ROTH 1956; BECKER 1959; CARR 1964; DRYSDALE 1994; LESAR / HUMAR 2009). Kljub temu da se borove spojine množično uporabljajo tudi za kurativno zaščito lesa (RICHARDSON 1995), je malo znanih podatkov o mejnih vrednostih borovih učinkovin za takšen namen uporabe. Kurativno učinkovitost borovih spojin proti glivam razkrojevalkam smo primerjali z učinkovitostjo najpomembnejših komercialnih fungicidov-bakrovih pripravkov.

MATERIALI IN METODE
MATERIALS AND METHODS

Vzorce beljave smrekovine (*Picea abies*) in bukovine (*Fagus sylvatica*) (1 cm x 1,5 cm x 4 cm) smo označili, avtoklavirali in za šest tednov izpostavili šestim glivam razkrojevalkam lesa, kot zahteva standard SIST EN 113. Uporabili smo tri glive rjave trohnobe, in sicer navadno tramovko *Gloeophyllum trabeum*, sivo hišno gob *Serpula lacrymans* in belo hišno gobo *Antrodia vaillantii*, ter tri glive bele trohnobe, in sicer pisano ploskocevko *Trametes versicolor,* bukovega ostrigarja *Pleurotus ostreatus* in ogljeno kroglico *Hypoxylon fragiforme*. Vzorce bukovine smo izpostavili beli trohnobi,

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Preglednica 1: Vpliv potapljanja z glivami koloniziranih vzorcev v vodno raztopino borove kisline različnih koncentracij na rast gliv. Rast gliv je bila ocenjena vizualno, z ocenami med 0 (popolno zaviranje rasti gliv pri vseh vzorcih) in 3 (micelij gliv raste iz vseh okuženih vzorcev). V oklepajih so podane standardne deviacije.

Table 1: Influence of immersion of fungal colonised specimens into boron-based aqueous solutions of various concentrations on fungal growth. Fungal growth was estimated visually, with marks between 0 (complete retardation of fungal growth in all specimens) and 3 (fungal mycelia grew from all infested specimens). Standard deviations are given in the parentheses.

Vrsta glive *Fungal species*	Izguba mase *Mass loss* %	Mokri navzem *Uptake of solution* kg/m^3	Koncentracija bora v raztopini (ppm) *Boron concentration in a solution (ppm)*				
			0	1000	2500	5000	8700
			Rast gliv (0 – popolno zaviranje; 3 – ni zaviranja rasti) *Fungal growth (0 – complete retardation; 3 – no retardation)*				
Antrodia vaillantii	8,5 (2,9)	78,9 (46,4)	3	3	2	1	1
Gloeophyllum trabeum	24,3 (3,8)	49,8 (23,8)	3	3	0	0	0
Serpula lacrymans	11,5 (3,5)	128,6 (25,3)	3	3	1	1	0
Pleurotus ostreatus	9,2 (3,9)	89,8 (31,7)	3	3	2	0	0
Trametes versicolor	17,4 (3,5)	272,4 (62,1)	3	3	1	0	0
Hypoxylon fragiforme	15,1 (5,0)	401,0 (42,8)	3	3	2	0	0

vzorce smrekovine pa glivam rjave trohnobe. Po šestih tednih glivnega razkroja smo vzorcem v sterilnih razmerah odstranili površinski micelij in jih za 10 min potopili v vodne raztopine borove kisline (BA) in bakrovega sulfata različnih koncentracij (preglednici 1, 2). Kontrolne vzorce smo namočili le v sterilizirano destilirano vodo. Zatem smo vzorce položili v petrijevke s hranilnim gojiščem in jih postavili v rastno komoro (T = 25°C, RH = 85 %). Po enem tednu smo vizualno ocenili rast gliv iz zaščitenih in nezaščitenih vzorcev. Ocenjevali smo z ocenami od 0 – popolno zaviranje rasti do 3 – ni zaviranja rasti. Po ocenjevanju smo vzorcem gravimetrično določili izgubo mase in izračunali povprečje za vse vzorce, izpostavljene določeni glivi (skupaj za vse vzorce kontrolne in impregnirane). Povprečni navzem zaščitnih pripravkov smo ocenili iz primerjave s potapljanjem, glivam izpostavljenih vzorcev, v destilirano vodo za vsako glivo posebej. Gostota in viskoznost zaščitnih pripravkov sta bili primerljivi z destilirano vodo. Poleg tega smo v eni izmed naših starejših raziskav (neobjavljeni podatki) navzemov vode in zaščitnih pripravkov na osnovi borove kisline ter modre galice ugotovili, da so le-ti primerljivi. Zaradi zagotavljanja sterilnosti ga nismo mogli določati na vseh vzorcih, temveč le na izbranih, ki smo jih potem izločili. Določili smo ga gravimetrično in ga izračunali na podlagi petih vzporednih meritev.

Preglednica 2: Vpliv potapljanja z glivami koloniziranih vzorcev v vodno raztopino bakrovega sulfata različnih koncentracij na rast gliv. Rast gliv je bila ocenjena vizualno, z ocenami med 0 (popolno zaviranje rasti gliv pri vseh vzorcih) in 3 (micelij gliv raste iz vseh okuženih vzorcev). V oklepajih so podane standardne deviacije.

Table 2: Influence of immersion of fungal colonised specimens into copper-based aqueous solutions of various concentrations on fungal growth. Fungal growth was estimated visually, with marks between 0 (complete retardation of fungal growth in all specimens) and 3 (fungal mycelia grew from all infested specimens). Standard deviations are given in the parentheses.

Vrsta glive *Fungal species*	Izguba mase *Mass loss* %	Mokri navzem *Uptake of solution* kg/m^3	Koncentracija bakra v raztopini (ppm) *Cooper concentration in a solution (ppm)*				
			0	1000	2500	5000	10000
			Rast gliv (0 – popolno zaviranje; 3 – ni zaviranja rasti) *Fungal growth (0 – complete retardation; 3 – no retardation)*				
Antrodia vaillantii	8,5 (2,9)	78,9 (46,4)	3	3	3	3	3
Gloeophyllum trabeum	24,3 (3,8)	49,8 (23,8)	3	3	3	3	2
Serpula lacrymans	11,5 (3,5)	128,6 (25,3)	3	3	3	2	1
Pleurotus ostreatus	9,2 (3,9)	89,8 (31,7)	3	3	2	1	0
Trametes versicolor	17,4 (3,5)	272,4 (62,1)	3	3	3	2	1
Hypoxylon fragiforme	15,1 (5,0)	401,0 (42,8)	3	3	3	3	2

Preglednica 3: Izračunani suhi navzem borove kisline (BA) v vzorce smrekovine in bukovine, ki so bili pred zaščito 6 tednov izpostavljeni posamezni glivi.

Table 3: Calculated retention of boric acid (BA) into Norway spruce and beech specimens, exposed to wood-decaying fungi for 6 weeks.

Vrsta glive *Fungal species*	Vrsta lesa *Wood species*	Mokri navzem *Uptake of solution* kg/m³	Koncentracija bora (ppm) / *Boron concentration (ppm)*				
			0	1000	2500	5000	8700
			Navzem BA* *Retention of BA**	Navzem BA* *Retention of BA**	Navzem BA* *Retention of BA**	Navzem BA* *Retention of BA**	Navzem BA* *Retention of BA**
Antrodia vaillantii	smreka	78,9 (46,4)	0	0,45	1,13	2,26	3,92
Gloeophyllum trabeum		49,8 (23,8)	0	0,29	0,71	1,42	2,48
Serpula lacrymans		128,6 (25,3)	0	0,74	1,84	3,68	6,40
Pleurotus ostreatus	bukev	89,8 (31,7)	0	0,51	1,28	2,57	4,47
Trametes versicolor		272,4 (62,1)	0	1,56	3,89	7,79	13,55
Hypoxylon fragiforme		401,0 (42,8)	0	2,29	5,73	11,46	19,95

*Suhi navzem borove kisline (kg/m³)

**Retention of boric acid (kg/m³)*

REZULTATI IN RAZPRAVA
RESULTS AND DISCUSSIONS

Mokri navzem zaščitnih raztopin je odvisen od lesne vrste in vrste glive, ki so ji bili izpostavljeni vzorci. Višje povprečne navzeme zaščitnih raztopin smo dosegli pri bukovih vzorcih (254 kg/m³), medtem ko so smrekovi vzorci navzeli le 86 kg/m³ (preglednica 3). Menimo, da je vzrok za te razlike v boljši impregnabilnosti bukovine v primerjavi s smrekovino. Navzemi se močno razlikujejo tudi med vzorci, izpostavljeni posamezni glivi, vendar ne moremo potrditi neposredne povezave med izgubo mase, ki jo je povzročila posamezna gliva, in navzemom zaščitne raztopine.

Povprečne izgube mase kontrolnih in impregniranih vzorcev po sedmih tednih razkroja so znašale med 8,5 % (*A. vaillantii*) in 24,3 % (*G. trabeum*), kar kaže, da so bile vse glive aktivne. Vitalnost gliv potrjuje tudi dejstvo, da so glive iz vseh kontrolnih vzorcev, ki so bili 10 min potopljeni v vodi, po tednu dni povsem prerasle petrijevko, kamor smo jih položili po namakanju. Razlike med izgubo mase kontrolnih in impregniranih vzorcev s posamezno zaščitno raztopine niso statistično značilne. V nadaljevanju nas je zanimalo, kakšen kurativen vpliv imajo biocidi. Iz preglednice 1 je razvidno, da na glive ni delovalo desetminutno potapljanje v vodno raztopino borove kisline s 1000 ppm bora, medtem ko je potapljanje vzorcev v raztopine z višjo koncentracijo bora delno ali

Preglednica 4: Izračunani suhi navzem bakrovega sulfata (CuS) v vzorce smrekovine in bukovine, ki so bili pred zaščito 6 tednov izpostavljeni posamezni glivi.

Table 4: Calculated retention of copper sulphate (CuS) into Norway spruce and beech specimens, exposed to wood-decaying fungi for 6 weeks.

Vrsta glive *Fungal species*	Vrsta lesa *Wood species*	Mokri navzem *Uptake of solution* kg/m³	Koncentracija bakra v raztopini (ppm) *Copper concentration in a solution (ppm)*				
			0	1000	2500	5000	1000
			Navzem CuS* *Retention of CuS**	Navzem CuS* *Retention of CuS**	Navzem CuS* *Retention of CuS**	Navzem CuS* *Retention of CuS**	Navzem CuS* *Retention of CuS**
Antrodia vaillantii	smreka	78,9 (46,4)	0	0,31	0,77	1,55	2,69
Gloeophyllum trabeum		49,8 (23,8)	0	0,29	0,49	0,98	1,70
Serpula lacrymans		128,6 (25,3)	0	0,51	1,26	2,52	4,39
Pleurotus ostreatus	bukev	89,8 (31,7)	0	0,35	0,88	1,76	3,06
Trametes versicolor		272,4 (62,1)	0	1,07	2,67	5,34	9,29
Hypoxylon fragiforme		401,0 (42,8)	0	1,57	3,93	7,86	13,68

*Suhi navzem bakrovega sulfata pentahidrata (kg/m³)

**Retention of copper sulphate pentahydrate (kg/m³)* popolnoma zavrlo rast glivnega micelija. Nižje koncentracije bora torej ne zavirajo rasti, ampak jo v določenih razmerah celo pospešujejo, saj je bor poznan tudi kot eden izmed elementov, ki jih glive nujno potrebujejo za rast in razvoj (LLOYD 1998). Med testiranimi glivami je največjo odpornost izkazala ogljena kroglica. Rast micelija je popolnoma zavrlo komaj 11,5 kg borove kisline na m^3 (BAE) (preglednici 1, 3), medtem ko je tramovko zavrlo že 0,71 kg/m^3 BAE. Popolne zaustavitve rasti nismo mogli določiti pri beli hišni gobi, rasla je tudi še iz vzorcev, ki so bili potopljeni v nasičeno raztopino borove kisline (87000 ppm; navzem 3,92 kg/m^3 BAE). Iz dinamike zaviranja micelija pri različnih navzemih sklepamo, da je minimalna kurativna inhibitorna koncentracije borove kisline v lesu za zaustavitev rasti bele hišne gobe primerljiva z minimalno kurativno inhibitorno koncentracijo BA pri sivi hišni gobi (6,40 kg/m^3 BAE). Pri glivah bele trohnobe smo ugotovili popolno zaviranje rasti micelija pri vseh treh glivah po potapljanju okuženih vzorcev v pripravek s 5000 ppm bora. Vendar pa se količine borove kisline v lesu potrebne za zaviranje rasti močno razlikujejo. Rast bukovega ostrigarja zavre že 2,57 kg/m^3 BAE, medtem ko je za prekinitev rasti ogljene kroglice potrebnih kar 11,46 kg/m^3 BAE (preglednici 1, 3). Iz primerjave kurativne učinkovitosti borove kisline na lesne glive lahko zaključimo, da so glive bele trohnobe nekoliko bolj odporne proti borovi kislini kot pa glive rjave trohnobe. Ta rezultat je v skladu s prejšnjimi raziskavami preventivne učinkovitosti borovih spojin (CARR 1694; LESAR / HUMAR 2009). Za kurativno zaščito pred zgoraj omenjenimi glivami je zahtevan minimalni navzem 11 kg/m^3 BAE, kar je približno petkrat več kot za preventivno zaščito (BEACHLER / ROTH 1956; BECKER 1959; CARR 1964). Zanimivo je, da smo v novejših raziskavah ugotovili, da so borove učinkovine boljši fungicidi, kot so ugotovili v preteklosti (LESAR / HUMAR 2009). Tako starejše raziskave navajajo bistveno višje mejne vrednosti, potrebne za preventivno zaščito (2 kg/m^3 BAE), kot nakazujejo zadnje raziskave (0,8 kg/m^3 BAE).

V nasprotju z borovo kislino se je bakrov sulfat izkazal kot slabši fungicid za kurativno zaščito lesa. Prvo manjše zaviranje rasti smo opazili pri vzorcih, ki so bili izpostavljeni bukovemu ostrigarju in so potopljeni v raztopini z 2500 ppm Cu navzeli 0,88 kg modre galice na m^3, medtem ko smo po namakanju delno razkrojenih vzorcev v pripravek z najvišjo koncentracijo bakrovih učinkovin (c_{Cu} = 10000 ppm) popolno zaviranje rasti zaznali le pri vzorcih, izpostavljenih bukovemu ostrigarju (preglednici 2, 4). Močno zaviranje rasti (ocena 1) pa smo ugotovili pri sivi hišni gobi in pisani ploskocevki. Kljub temu da so bili pri vseh testnih glivah navzemi modre galice višji od navzema borove kisline, nismo mogli določiti minimalne količine modre galice za kurativno zaščito lesa za zaščito pred belo hišno gobo, tramovko, sivo hišno gobo, pisano ploskocevko in ogljeno kroglico (preglednici 2, 4). Rezultat za belo hišno gobo ni presenetljiv, saj je znana velika tolerantnost bele hišne gobe do bakrove učinkovine (HUMAR *et al.* 2005). Ob primerjavi navzema elementarnega bora in bakra ugotovimo, da za zaščito že okuženega lesa potrebujemo v lesu najmanj 2 kg bora (B) na m^3 in več kot 3,5 kg bakra (Cu), kar potrjuje večjo učinkovitost borovih učinkovin na lesne glive.

SUMMARY

In the present study, minimal remedial fungicidal concentrations of boric acid and copper sulphate for three brown rot fungi (*Gloeophyllum trabeum, Serpula lacrymans* and *Antrodia vaillantii*) and three white rot fungi (*Trametes versicolor, Pleurotus ostreatus* and *Hypoxylon fragiforme*) were determined. Remedial efficacy was determined on infested spruce and beech wood specimens, which were immersed into the selected copper- or boron-based preservative solutions for ten minutes. The treated specimens were transferred to a nutrient medium and fungal growth was monitored. Retention of preservative solution was gravimetrically determined on five parallel samples; each group of samples was exposed to a respective fungal species. The results showed that retention of preservative solution was much higher at beech samples compared to the spruce samples. The reason for such effect is intrinsically better treatability of beech wood. In our research, white rot fungi were more resistant to boron compounds than brown rot fungi, which is in line with published data. The results show that boron compounds are better remedial fungicides than copper compounds. Furthermore, minimal remedial boron fungicidal concentration is much higher than the preventive minimal inhibitory concentration.

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3.3 ZAŠČITNE LASTNOSTI SREDSTEV NA OSNOVI BOROVIH SPOJIN, ETANOLAMINA IN KVARTARNIH AMONIJEVIH SPOJIN PROTI IZPIRANJU, GLIVAM RAZKROJEVALKAM IN GLIVAM MODRIVKAM

PERFORMANCE OF BORON-ETHANOLAMINE-QUATERNARY AMMONIUM BASED WOOD PRESERVATIVES AGAINST LEACHING, WOOD DECAY AND BLUE STAIN FUNGI

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Pomen borovih spojin narašča zaradi majhnega vpliva na okolje, visoke učinkovitosti in dejstva, da je bilo po uveljavitvi Biocidne direktive veliko aktivnih učinkovin umaknjenih s trga. Borove spojine zelo učinkovito delujejo proti glivam razkrojevalkam, a se v vlažnem okolju izpirajo iz lesa. Da bi izboljšali njihovo vezavo, topnost in učinkovitost, smo raztopinam na osnovi boraksa in borove kisline dodali etanolamin in kvartarno amonijevo spojino. Zatem smo vzorce smrekovine (*Picea abies*) impregnirali z vodnimi raztopinami in jih po standardu EN 113 izpostavili trem glivam razkrojevalkam lesa *(Antrodia vaillantii, Gloeophyllum trabeum* in *Trametes versicolor*). Pred izpostavitvijo smo polovico vzorcev izpirali po standardu EN 84. Vezavo testnih pripravkov smo določali po navodilih standarda ENV 1250-2. Vzporedno smo po standardu EN 152 določali učinkovitost proti glivam modrivkam (*Aureobasidium pullulans* in *Sclerophoma pithyophila*). Za identifikacijo interakcij med zaščitnimi raztopinami in lesom smo uporabili spektroskopijo FT-IR. Rezultati analize FT-IR kažejo, da borove spojine in kvartarne amonijeve spojine ne vplivajo na les, opazen pa je vpliv etanolamina zaradi depolimerizacije hemiceluloze in lignina. Rezultati izpiranja nakazujejo izboljšano vezavo borovih spojin zaradi dodatka etanolamina. Les, impregniran z zaščitnimi raztopinami najnižje koncentracije ($c_B = c_{quat} = 0,1$ %), je bil odporen proti glivam razkrojevalkam, vendar je za učinkovito zaščito proti glivam modrivkam potrebna petkrat ali desetkrat višja koncentracija bora v zaščitni raztopini.

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ABSTRACT

Importance of boron compounds is increasing due to their low environmental impact, high efficacy and fact that many other active ingredients have been removed from the market after introduction of the Biocidal products directive. Borates are very effective against wood decay fungi; unfortunately they leach out of wood in wet environment. In order to improve their fixation, solubility and efficacy, borax and boric acid were combined with ethanolamine and quaternary ammonium compound. Afterwards, Norway spruce (*Picea abies*) specimens were impregnated with aqueous solutions and exposed to three wood decay fungi *(Antrodia vaillantii, Gloeophyllum trabeum* and *Trametes versicolor*) according to EN 113 procedure. Half of the specimens were leached prior exposure. Fixation of testing formulation in samples was determined as proposed by ENV 1250-2 standard. In parallel efficacy against blue stain fungi (*Aureobasidium pullulans* and *Sclerophoma pithyophila*) were determined as well according to 152 EN standard. The results showed, that addition of ethanolamine slightly improves boron fixation. Wood impregnated with preservative solutions of the lowest concentration ($c_B = c_{quat} = 0.1\%$) was resistant against wood decay fungi. However, to ensure efficacy against blue stain fungi five or ten times more concentrated solutions needs to be used.

KEY WORDS: boron, ethanolamine, quaternary ammonium compound, fixation, Norway spruce, wood preservation

INTRODUCTION

Field of chemical wood preservation changed drastically in past years. Several classical active ingredients were removed from the formulation due to increased environmental awareness, only two boron based fungicides are allowed according to the Biocidal Products Directive (1998). Less than 40% of the biocides those were on the market before September 2006 remained on the list of the approved active compounds. Therefore, industry and other users looked for wood preservatives with low environmental impact. One of the remaining, active ingredients are boron compounds. Boron is on the first place very effective fungicide and insecticide. On the other hand toxicity (LD_{50}) of the boric acid and borax is similar to the toxicity of the table salt (NaCl) (Lloyd 1998), what increases the usefulness of the boron compounds in the field of wood preservation. Even more, boron has some fire retardant effect as well, therefore is recommended for protection of construction wood (Ramos et al. 2006).

High water solubility and good diffusibility of borates resulted in fact that borates are easily leached from impregnated wood, when treated wood is exposed to precipitations. Because of their non-fixed characteristics, boron preservatives are normally recommended for use in protected environments and are not recommended for use in use class three (above ground) or use class four (ground contact) (Baysal et al. 2006). Another weak point of borates is insufficient effectiveness against some moulds (Petrič et al. 2000). Thus boron compounds are usually used for protection of wood in use classes I and II (above ground, cowered) or they are added as co-biocides to copper based wood preservatives (Humar et al. 2004). The aim of this work was to prepare boron based aqueous solution, with addition of quaternary ammonium compounds (to improve fungicidal properties) and ethanolamine (to improve boron solubility) and test it against the most important wood decay and staining fungi.

MATERIAL AND METHODS

Preservative solutions

For experimentation two types of boron based solutions of three different concentrations were prepared. They consist of boron, ethanolamine and quaternary ammonium compound. As boron source boric acid and borax were chosen. As quaternary ammonium compound (quat), alkyl diethyl benzyl ammonium chloride (C12-C16) (CAS - 68424-85-1, Merck) was chosen. Those two compounds were chosen, as they are allowed according to the Biocidal products directive. Concentration of boron equals to quat concentrations. Namely, concentrations of 1, 0.5 and 0.1 % were chosen. Ethanolamine concentration was 10 times higher than boron concentration. Such concentration enable us suitable solubility of all components.

Leaching test

For leaching tests specimens made of Norway spruce (*Picea abies*) sapwood (1.5 × 2.5 × 5 cm) were vacuum impregnated with six different preservative formulations according to the EN 113 (ECS 1996) procedure. Average retention of preservative solution was 515 kg/m^3. After impregnation specimens were conditioned for four weeks according to the requirements of this standard.

Leaching was performed according to the modified ENV 1250-2 (ECS 1994) method. In order to speed up experiment, following two modifications were done: instead of five three specimens were positioned in the same vessels. Water mixing was achieved with shaking on shaking device instead of magnetic stirrer. To have three parallel leaching procedures, nine specimens per solution/

concentration/treatment were put in three vessels (three specimens per vessel). Afterwards, samples in the vessel were positioned with a weight. 300 g of distilled water were added and the vessel with its content was shaking with the frequency of 60 min^{-1}. Water was replaced daily for seven times in ten subsequent days. Leachates from the same vessel were collected and mixed together. Boron in the leachates was determined using inductively coupled plasma mass spectrometer (ICP-MS).

The Agilent Technologies (Palo Alto, USA) HP 4500 quadrupole ICP-MS with Burgener Mira Mist nebuliser was used as a detection system for boron. The spray chamber temperature was 4°C. The plasma RF power was set to 1300 W. Plasma gas flow rate was 15 L min^{-1}, auxiliary gas flow rate 0.7 L min^{-1} and nebuliser gas flow rate 1.05 L min^{-1}. Sampler and skimmer cones were made of nickel.

Standard boron solutions for calibration curve were prepared by diluting a stock standard solution of boron (1000 mg L^{-1}) (Merck, Germany). Samples were diluted 50-fold with MQ water prior the analysis. The final standard and sample solutions contained 1% (v/v) of nitric acid. The memory effect (as a consequence of introduction of solutions with high boron concentration) was eliminated by washing the system with 20% (v/v) ammonia solution after each sample. The washout time was 60 seconds. Analytical grade nitric acid and ammonia solution (Merck, Germany) were used. NIST standard reference material 1643e (trace elements in water) was used to verify the accuracy of the measurements.

Percentages of leached boron were calculated from the amount of retained boron determined gravimetrically and amount of boron in collected leachates.

Wood decay test

The same specimens as prepared for leaching test were prepared for wood decay testing as well. This part of research was performed according to the EN 113 (ECS 1996) procedure. Following conditioning, the samples were leached according to the EN 84 procedure for 14 days (ECS 1994). Afterwards, the samples were oven dried (103°C), after which their masses were determined and then conditioned at 25°C, 65% RH. The samples were finally steam- sterilized prior to exposure to the fungi. Experiment was performed on five parallel specimens.

In order to determine resistance of impregnated wood against decay, two brown rot fungi (*Antrodia vaillantii* and *Gloeophyllum trabeum*) and one white rot fungus (*Trametes versicolor*) were used. Jars with PDA (Potato dextrose agar) medium were inoculated with small pieces of mycelium after which the wood samples (one each of treated and untreated) were placed on a plastic net in each inoculated jar. In parallel jars only control specimens were exposed in order to completely avoid influence of biocide on vitality of testing fungi. The samples were incubated in the growth chamber at 25°C, RH 75% for 16 weeks. After expose mycelia were carefully removed from the samples and mass losses were determined, and no correlation factors were considered. The experiment was replicated five times.

Blue stain testing

Blue stain test was done on pine (*Pinus sylvestris*) wood, because this wood is much more susceptible to staining than spruce wood. The experiment was performed according to the EN 152-1 standard (ECS 1996). The samples (1 × 4 × 11 cm) were brushed with all aqueous solutions to achieve final retention of approximately 300 g/m^2. After brushing, the samples were let to dry for three weeks, and afterwards were exposed to blue stain fungi (*Aureobasidium pullulans* and *Sclerophoma pithyophila*) for six weeks. After exposure the specimens were isolated and staining was visually evaluated. The samples were cut on three parts and penetration of hyphens from lower to upper (treated) part was measured, as well. Experiment was performed on five parallel specimens.

FTIR analysis

Fourier transform infra red (FTIR) analysis is perfect tool that enables us deeper understanding of fixation mechanism of biocides in wood. Therefore, FTIR spectra of control and impregnated specimens were measured. For this part of the research specimens were impregnated with the highest content of preservative solutions, only. A Perkin Elmer Spectrum One spectrometer was used for this study. IR spectra were measured using HATR (Horizontal Attenuated Total Reflection) technique. The HATR accessory ZnSe crystal (Perkin Elmer) was used. Specimens were positioned on the surface of the ZnSe crystal and 64 scans were performed at 1 cm^{-1}.

RESULTS AND DISCUSSION

Boron compounds have limited solubility in water (50 g/L for boric acid; 25.6 g/L for borax). Therefore, aqueous solutions with 1 % of boron can not be prepared. Addition of ethanolamine into the aqueous solution improves solubility of both boron compounds. Quaternary ammonium compound was added into this solution to improve fungicidal properties of this formulation. After mixing of these compounds, there were no precipitates observed. Formulations of boron, ethanolamine and quaternary ammonium compound were stable for at least six month.

Boron is extremely diffusible in wood. It is well known, that boron does not fixate in wood and therefore it is extremely prone to leaching in wet environments. Those properties reflect in rather extensive boron leaching. In laboratory conditions, in average between 60 and 70% of boron is leached from impregnated wood treated with boric acid (Peylo and Willeitner 1995). From specimens impregnated with our testing formulations, between 46.9 and 59.7% of boron was leached from wood. Boron fixation was influenced by concentration and composition of preservative. Aqueous solutions where boric acid was used as boron source performed better than the ones based on borax. In average, from wood treated with preservative formulation BxEQ 55.8% of boron was leached, while more than 10% lower leaching rates were determined from spruce impregnated with BaEQ (Tab. 1). However, if we compare leaching of tested preservative systems, particularly those based on boric acid, with literature data (Peylo and Willeitner 1995), it can be concluded that addition of ethanolamine into preservative formulation does not decrease boron fixation, but even slightly improves it (Tab. 1). Furthermore, the higher leaching rates were determined at wood block impregnated with solutions of the lowest boron concentration ($c_B = 0.1\%$). This is rather unusual observation, as in most of the other biocides like copper, leaching increases with increasing concentration (Zhang and Kamdem 2000, Humar et al. 2007).

Identification of interactions between preservative solutions and wood, FTIR spectroscopy were used. FTIR spectra of wood impregnated with boron-ethanolamine and ethanolamine based solutions only were comparable, indicating, that changes in wood appears as a result of interactions of ethanolamine with wood. Any influence of boron and quaternary ammonium compounds on wood can not be resolved from the FTIR spectra. Data shown in Fig. 1 confirms, that the most of the changes in impregnated wood can be seen on peaks assigned to hemicelluloses (1737, 1268, 1100, 1056 cm^{-1}) and lignin (1601, 1268 cm^{-1}) (Fig. 1) (Michell 1989). Those changes are result of the lignin and hemicelluloses depolymerisation induced by ethanolamine (Humar et al. 2007). This depolymerisation resulted in higher number of available active sites for boron absorption. At specimens impregnated with more concentrated solutions, more prominent depolymerisation appears. Therefore, there were more active sites formed, and consequently lower boron leaching was observed (Tab. 1). However, ethanolamine does not depolymerise cellulose (Claus et al. 2004), which is the most important absorption site for boron (Ramos et al. 2006), therefore it had no negative impact on boron fixation.

Tab. 1: Boron leaching from Norway spruce wood specimens impregnated with different boron (borax – Bx, Boric acid – Ba; ethanolamine – E; quat - Q) based aqueous solutions

Preservative solution	$c_B = c_{QUAT}$ [%]	Boron leaching [%]
BxEQ	0.1 0.5 1	59.7 53.0 54.6
BaEQ	0.1 0.5 1	50.8 50.6 46.9

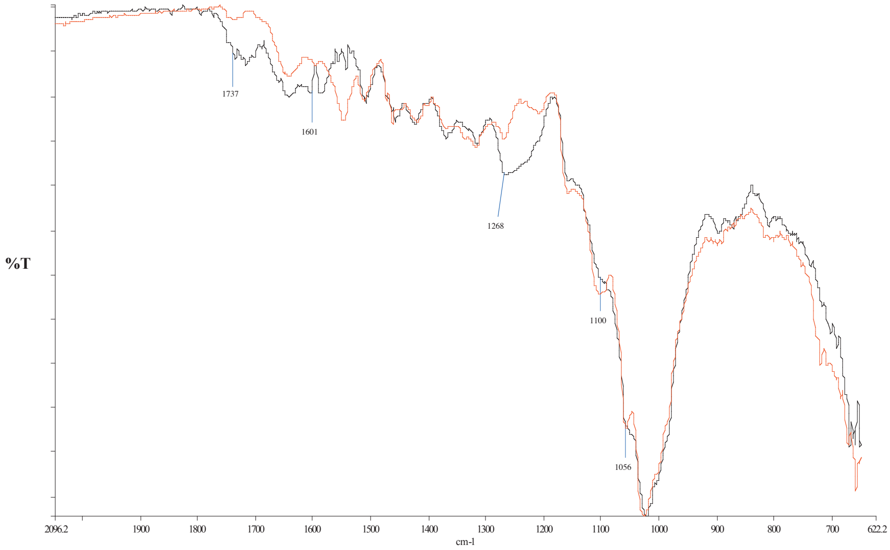

Fig. 1: FTIR spectra of unimpregnated Norway spruce wood (black) and of spruce wood impregnated with aqueous solution of boric acid, ethanolamine and quaternary ammonium compound ($c_B = c_{QUAT} = 1.0\%$)

However, the most important question related to tested preservative solution is their effectives against targeted wood decay fungi. All used fungi species were vital and control specimen's loss mass of 37.2% at *Gloeophyllum trabeum*, 26.6% at *Antrodia vaillantii* and 22.2% at *Trametes versicolor*, respectively (Tab. 2). All tested solutions even the ones of the lowest concentration successfully preserved wood against tested wood decay fungi. None of the impregnated wood specimen did lose more than 3% of their initial masses (Tab. 2). Therefore, we can conclude, all tested formulations completely fulfil requirements of the EN 113 standard (1996). Furthermore, even two weeks of leaching (artificial ageing) of the impregnated wood did not influence the resistance of impregnated wood against wood decay fungi. This confirms that remaining biocides (boron and quaternary ammonium compounds) are sufficient to protect wood against tested wood decay fungi. But, it should not be overlooked that even ethanolamine has some influence on the growth of the wood decay fungi, and contributes to the effectiveness of the tested preservative solutions (Humar and Lesar in press). Fortunately, nitrogen introduced into wood via impregnation (ethanolamine) does not stimulate fungal growth. On the basis of this data, we presume that tested preservative solutions could be used at lest for preservation of wood in use class 3 (above ground applications). Effectiveness of this preservative in such conditions will be confirmed in ongoing field testing. After two years of lap joint testing according to procedure described by Rapp and Augusta (2004), there are no signs of decay observed until now.

Tab. 2: Mass loss of control and impregnated Norway spruce (Picea abies) specimens exposed to wood decay fungi for 16 weeks according to EN 113 procedure. Half of the specimens were leached (EN 84) before fungal exposure. (borax - Bx, Boric acid – Ba; ethanolamine – E; quat - Q)

Preservative solution	Leached	$c_B = c_{QUAT}$ [%]	Wood decay fungi		
			G. trabeum	*A. vaillantii*	*T. versicolor*
			Mass loss [%]		
BxEQ	No	0.1	-0.6	0.8	0.5
		0.5	-0.1	0.3	0.5
		1	-0.1	0.7	0.9
	Yes	0.1	0.8	1.3	0.6
		0.5	0.6	1.2	0.9
		1	1.0	1.2	1.0
BaEQ	No	0.1	0.2	0.5	0.1
		0.5	0.3	0.0	0.1
		1	0.4	0.7	0.5
	Yes	0.1	0.3	0.6	0.5
		0.5	0.1	0.4	1.5
		1	0.0	0.3	1.4
Control	No	/	37.2	26.6	22.2

Tested preservative solutions are not effective only against wood decay but against blue stain fungi as well. After six weeks control specimens were completely covered by stains, and therefore marked with estimation 3. To ensure appropriate protection of pine sapwood against blue stain organisms, preservative solution of higher concentrations ($c_B = c_{QUAT} = 0.5 – 1.0\%$) should be used, than for protection against wood decay fungi. Specimens brushed with solution of the lowest concentration BxEQ, and exposed to blue stain fungi, were graded with mark 2.4 and effectiveness of solution BaEQ of the same concentration against blue staining were estimated with 1.2 (Tab. 3), what indicates that the surface of treated specimens were not as stained as of the control ones, but there was still considerable portion of surface discoloured. There are several reasons for lower effectiveness against blue stain fungi. Firstly specimens exposed to blue stain fungi were brushed only while specimens exposed to decay fungi were vacuum impregnated, and secondly boron is well known to be less effective against blue stains (Becker 1959), what reflects from our results as well.

Tab. 3: Influence of boron-ethanolamine-quat preservative solutions on blue staining of pine (Pinus sylvestris) wood

Preservative solution	$c_B = c_{QUAT}$ [%]	Visual estimation of surface	Depth of hyphen penetration (mm)
BxEQ	0.1	2.4	10
	0.5	0	1-2
	1	0	1-2
BaEQ	0.1	1.2	10
	0.5	0.2	2-3
	1	0	1-2
Control	/	3	10

CONCLUSIONS

Addition of quaternary ammonium compounds and ethanolamine into boron based aqueous solution significantly improves its solubility and slightly improves its fixation in wood. Norway spruce wood impregnated with these solutions is well protected against wood decay fungi even after artificial ageing (leaching). Boron, quaternary ammonium compounds and ethanolamine based aqueous solutions are effective against blue stain fungi as well. However, for protection of wood against blue stain fungi, higher concentrations of active ingredients should be used than for protection against wood decay strains.

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3.4 MIKROSKOPSKA ANALIZA LESA, IMPREGNIRANEGA Z VODNO EMULZIJO MONTANA VOSKA

MICROSCOPIC ANALYSIS OF WOOD IMPREGNATED WITH AQUEOUS MONTAN WAX EMULSION

Boštjan Lesar, Martin Zupančič in Miha Humar
Les, 2008, 60: 320–326
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Proučevali smo vpliv postopka impregnacije ter vrste emulzije montanskega voska na retencijo, globino penetracije in porazdelitev v lesu smreke (*Picea abies*). Uporabili smo tri postopke impregnacije: vakuumsko-tlačni, vakuumski in premazovanje. Navzem smo določili gravimetrično. Po impregnaciji smo iz vzorcev pripravili anatomske preparate, na katerih smo pod mikroskopom preučevali globino prodora in porazdelitev montanskega voska v vzorcih. Ugotovili smo, da je največ voska prodrlo v aksialni smeri, v prečni smeri pa je vosek prodrl le v prve poškodovane celice na površini. Z vakuumsko tlačnim postopkom impregnacije smo v aksialni smeri dosegli globlji prodor voska, ki je presegel dolžino traheid. Količina voska, ki je prodrla preko pikenj, je bila majhna, vzrok za to so aspirirane piknje. Delež voska v emulziji ni znatno vplival na globino prodora, je pa vplival na delež depozitov oziroma zapolnjenost celic z voskom. Sušenje vzorcev nad točko tališča ne vpliva na razporeditev voska po prerezu vzorcev.

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UDK: 630*841

MIKROSKOPSKA ANALIZA LESA, IMPREGNIRANEGA Z VODNO EMULZIJO MONTANA VOSKA

Povzetek: *V raziskavi smo preučevali vpliv postopka impregnacije ter vrste emulzije montana voska na retencijo, globino penetracije in porazdelitev v lesu smreke (Picea abies). Uporabili smo tri postopke impregnacije: vakuumsko-tlačni, vakuumski in premazovanje. Navzem smo določili gravimetrično. Po impregnaciji smo iz vzorcev pripravili anatomske preparate, na katerih smo pod mikroskopom, preučevali globino prodora in porazdelitev montana voska v vzorcih. Ugotovili smo, da je največ voska prodrlo v aksialni smeri, medtem ko je vosek v prečni smeri prodrl le v prve poškodovane celice na površini. Z vakuumsko tlačnim postopkom impregnacije smo v aksialni smeri dosegli globlji prodor voska, ki je presegel dolžino traheid. Delež voska v emulziji ni znatno vplival na globino prodora, medtem ko je vplival na količino oziroma zapolnjenost celic z voskom.*

Ključne besede: globina penetracije, montana vosek, smreka (Picea abies), zaščita lesa

Abstract: *Influence of impregnation procedure, type of montan wax emulsion on retention, penetration and distribution in Norway spruce (Picea abies) wood was elucidated. Three different procedures ware applied: vacuum-pressure, vacuum and brushing. After impregnation slices for microscopy observation were prepared for microscopically determination of penetration and distribution of montan wax in wood. The results showed that the most of the wax emulsion penetrated in wood in axial direction, while in radial or tangential direction wax emulsion penetrated trough the upper layer of cells only. Usage of vacuum pressure technique, wax penetrated dipper than the average tracheid length. Concentration of wax emulsions did not influence on depth of penetration, but it has considerable influence on fulfilling of cell lumen with wax.*

Key words: depth of penetration, montan wax, Norway spruce (Picea abies), wood preservation

Originalni znanstveni članek (original scientific paper)

Uvod

Zaradi vedno večjega poudarka na varovanju okolja, skrbi za zdravje ljudi ter administrativnih prepovedi se v zaščiti lesa vse bolj uporabljajo naravni in okoljsko neoporečni materiali. Mednje sodijo tudi voski. Voski se že od prazgodovinskih časov uporabljajo za najrazličnejše namene: barve, lake, lepila, polirne paste, sveče, kozmetiko itd. V lesarstvu čebelji vosek tradicionalno uporabljamo za površinsko obdelavo lesa. Voske delimo na naravne in sintetične. Naravni voski so lahko fosilini ali ne-fosilini. V skupino fosilnih voskov spadajo voski, pridobljeni iz nafte (parafinski vosek) in voski, pridobljeni iz lignita. Glavni predstavnik voskov, pridobljenih iz lignita, je montana vosek (Wolfmeier, 2003).

Neobdelan montana vosek spada v skupino naravnih rastlinskih voskov, kot sta carnauba vosek in candelilla vosek. Montana vosek je fosiliziran rastlinski vosek, ekstrahiran iz lignita. Najpomembnejše komercialno nahajališče je v centralni Nemčiji, vzhodno od reke Elbe, v rjavem premogu. Montana vosek je mešanica kemijskih spojin, ki jih lahko razdelimo v tri skupine: voske, smole in asfaltne snovi. Kot drugi rastlinski voski je sestavljen iz estrov višjih karboksilnih kislin z višjimi alkoholi in prostih višjih kislin. Druge sestavine, kot so prosti alkoholi voskov ali ketoni, parafini in terpeni, najdemo le v manjših količinah. Montana vosek je izjemno trd, svetle barve, zelo dobro se polira ter je izjemno odporen na oksidacijo (Matthies, 2001). Ena od najbolj pomembnih lastnosti montana voska je sposobnost tvorjenja tankega odpornega filma (Warth, 1959).

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Novejše tehnike zaščite lesa se osredotočajo predvsem na izdelke in procese, ki kemično, fizikalno ali biološko modificirajo celično strukturo lesa in tako preprečijo razkroj. Večina gliv, insektov in bakterij, ki razkrajajo les, potrebuje za rast in razvoj poleg lesa še kisik, idealno temperaturo in vodo. Razkroj lesa se prepreči, če manjka eden ali več teh dejavnikov. Ena od pogostih metod zaščite je uporaba vodoodbojnih sredstev, ki v določenem časovnem obdobju preprečujejo prekomerno navlaževanje celičnih sten. Najpogosteje se v ta namen uporabljajo voski, olja in alkidi (Svensson in sod., 1987), ki pa pogosto ne morejo prodreti v celično steno, ampak se odložijo na celično steno in na njej tvorijo vodno bariero. Vendar se učinek odbojnega delovanja izgubi po ponavljajočem se navlaževanju, saj se odložene snovi počasi raztapljajo in z vodo izpirajo (Treu in sod., 2004).

Učinkovita zaščita impregniranega lesa je funkcija mnogih dejavnikov, toda najpomembnejši so: učinkovitost zaščitnega sredstva, globina penetracije, navzem pripravka in enakomerna penetracija v različne celice in enakomerna mikro porazdelitev v celičnih lumnih in celičnih stenah (Morrell in Morris, 2002). Globina penetracije zaščitnega sredstva v les je odvisna predvsem od treh dejavnikov: lastnosti uporabljenega zaščitnega pripravka, anatomskih lastnosti lesa in parametrov postopka zaščite. Najbolj hitro in globoko penetracijo dosežemo s sredstvom, ki ima majhno viskoznost, majhen kontaktni kot ter visoko površinsko napetost (Richardson, 1993). Zelo pomemben dejavnik penetracije zaščitnega sredstva je uporabljena lesna vrsta. Smrekovino standard SIST EN 350-2 (1994) razvršča med težko do zelo težko impregnabilne lesne vrste. To v praksi pomeni, da sta navzem in globina penetracije pri tlačni impregnaciji majhna v prečni in vzdolžni smeri, saj tudi po treh do štirih urah impregnacije prodor ni večji kot 3 do 6 mm v prečni smeri (SIST EN 350-2, 1994; Morrell in Morris, 2002). Tlak med impregnacijo ima izrazit vpliv na globino penetracije pri lahko impregnabilnih lesnih vrstah, medtem ko ima tlak majhen vpliv na globino penetracije pri težko impregnabilnih lesnih vrstah (Richardson, 1993). Čas impregnacije ima primerljiv vpliv kot tlak, daljši kot je, bolj globoko prodre zaščitni pripravek v les, vendar je vpliv časa večji pri lahko impregnabilnih vrstah (Richardson, 1993). Namen naše raziskave je bil določiti globino penetracije vodne emulzije montana voska in njegovo porazdelitev v smrekovini, pri različnih postopkih impregnacije.

Materiali in metode

V raziskavi smo uporabili orientirane vzorce smrekovine (*Picea abies* (L.) Karst.) treh dimenzij: 20 × 20 x 20 mm (tangencialna × radialna × aksialna dimenzija, vzorci A), 15 × 15 x 15 mm (vzorci B) in 15 × 25 x 50 mm ((tangencialna × radialna × aksialna dimenzija, vzorci C). Osemnajstim vzorcem smo zaščitili čelne površine z epoksidnim premazom (Epolor HB, Helios). Nato smo vse vzorce stehtali in jih impregnirali po dveh različnih postopkih; prvič po vakuumsko-tlačnem postopku (30 min podtlak, 90 min nadtlak 10 bar in 5 min podtlak) in drugič po vakuumskem postopku (30 min podtlak ter 120 min namakanje pri normalnem tlaku). Dvanajst vzorcev smo le dvakrat premazali. Za zaščito lesa smo uporabili vodno emulzijo montanskega voska LGE (LGE) (Samson, Kamnik), dveh koncentracij LGE-A 12 % suhe snovi in LGE-B 6 % suhe snovi ter vodno emulzijo montanskega voska Poligen MW 1 (MW) (BASF, Nemčija), dveh koncentracij MW-A 40 % suhe snovi in MW-B 20 % suhe snovi. Po tretiranju smo vzorce en teden sušili pri normalnih pogojih, dvanajst vzorcev pa še 24 ur v sušilniku pri temperaturi 103±1°C.

Pred rezanjem tankih rezin lesa smo vzorce za en dan potopili v destilirano vodo. Sledilo je rezanje rezin prečne, radialne in tangencialne ksilotomske ravnine na drsnem mikrotomu Leica SM 2000R, debelina rezin je bila 25 μm. Rezine lesa smo obarvali z namenom, da bi dosegli čim boljši barvni kontrast med voskom in lesom, kar je omogočalo natančnejšo in lažjo detekcijo voska v posameznih plasteh lesa z mikroskopom. Barvanje je bilo diferencialno, s safraninom (rdeče barvilo) in nato še z astra modrim barvilom. Sledilo je izpiranje barvil in vklapljanje objektov v euparal. S tem smo pripravili trajne preparate za opazovanje in merjenje pod mikroskopom.

Pred merjenjem penetracije voska smo si preparate ogledali pod mikroskopom Nikon ECLIPSE E 800, nato smo na preučevanem vzorcu izbrali območje brez ekstremnih nepravilnosti (npr. velike razpoke ali smolni kanali). Na tem območju smo nato naključno izbrali površino z voskom za merjene penetracije. Z uporabo različnih optičnih filtrov, tehnik senčenja in kontrastov smo dobili sliko, kjer je bilo moč vosek brez težav vizualno ločiti od lesa.

Rezultati in razprava

Med impregnacijo smo gravimetrično spremljali navzem emulzij voskov na vzorcih z nezaščitenimi čeli. Vzorci so vpili od 135 do 841 kg/m^3 vodne emulzije. Najmanjši mokri navzem smo dosegli pri postopku premazovanja 135 kg/m^3 (LGE-A), največjega pa pri postopku vakuumsko-tlačnega impregniranja 841 kg/m^3 (LGE-B). Poleg postopka impregnacije na navzem vpliva še vrsta zaščitnega pripravka (Richardson, 1993) in velikost vzorcev oziroma delež čelnih površin. Pri vakuumsko-tlačni impregnaciji smo največji mokri navzem dosegli z emulzijo LGE-B, najmanjšega pa z emulzijo MW-A 485 kg/m^3. To kaže, da večji delež suhe snovi v emulziji zmanjšuje penetracijo in navzem voska v smrekovino. S povečevanjem deleža

■ Preglednica 1. Mokri in suhi navzem ter globina penetracije emulzij montana voskov (LGE-A, LGE-B, MW-A in MW-B) v smrekove vzorce, impregnirane po vakuumsko-tlačnem, vakuumskem postopku ter premazane vzorce.
Table 1. Uptake of preservative solution, retention and depth of penetration the montan wax emulsions (LGE-A, LGE-B, MW-A in MW-B) in Norway spruce samples, impregnated according to vacuum-pressure, vacuum process and brushed samples.

Emulzija montana voska	Postopek impregnacije*	Vzorci**	Čela***	Sušenje****	Suhi navzem	Mokri navzem	Globina penetracije
					kg/m^3	kg/m^3	mm
LGE-A	v+n+v	A	nezaščiteni	nesušeni	96,26	802,43	sredina
	v+n+v	B	nezaščiteni	nesušeni	100,40	836,63	sredina
	v+n+v	C	nezaščiteni	nesušeni	60,02	500,19	13,76
	v+n+v	A	zaščiteni	nesušeni	-	-	-
	v+n+v	B	zaščiteni	nesušeni	-	-	-
	v+n+v	A	nezaščiteni	sušeni	96,11	800,91	sredina
	v+n+v	B	nezaščiteni	sušeni	99,53	829,45	sredina
	v	B	nezaščiteni	nesušeni	-	-	5,81
	v	C	nezaščiteni	nesušeni	27,42	228,53	8,73
	p	B	nezaščiteni	nesušeni	16,29	135,77	2,25
LGE-B	v+n+v	A	nezaščiteni	nesušeni	48,87	814,49	sredina
	v+n+v	B	nezaščiteni	nesušeni	49,25	820,8	sredina
	v+n+v	A	zaščiteni	nesušeni	-	-	-
	v+n+v	B	zaščiteni	nesušeni	-	-	-
	v+n+v	A	nezaščiteni	sušeni	48,31	805,15	sredina
	v+n+v	B	nezaščiteni	sušeni	50,51	841,91	sredina
	v	B	nezaščiteni	nesušeni	-	-	4,22
	p	B	nezaščiteni	nesušeni	9,36	156,01	2,57
MW-A	v+n+v	A	nezaščiteni	nesušeni	194,00	485,73	sredina
	v+n+v	A	zaščiteni	nesušeni	-	-	-
	p	B	nezaščiteni	nesušeni	152,5*	381,24	1,75
MW-B	v+n+v	A	nezaščiteni	nesušeni	155,58	777,89	sredina
	v+n+v	A	zaščiteni	nesušeni	-	-	-
	p	B	nezaščiteni	nesušeni	19,02	168,62	2,39

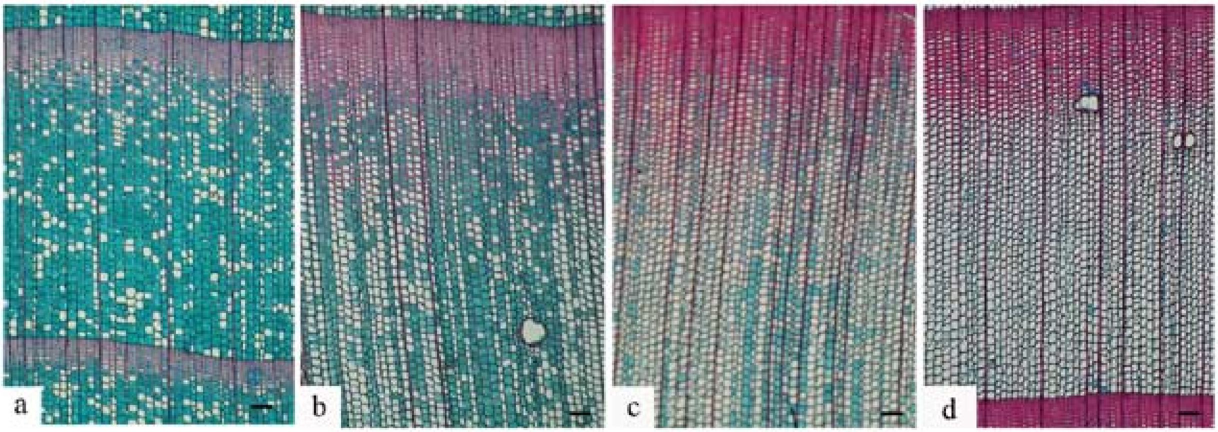
*v+n+v: impregnacija 30 min vakuum, 90 min nadtlak 10 bar in 5 min vakuum; v: impregnacija 30 min vakuum ter 120 min namakanje pri normalnem tlaku; p: premazovanje

**A: 20 × 20 x 20 mm; B: 15 × 15 x 15 mm; C: 15 × 25 x 50 mm, (T × R × A)

***Nezaščiteni.: nezaščitena čela vzorcev; zaščiteni: čela vzorcev zaščitena z epoksidnim premazom

****Sušeni: vzorci po kondicioniranju 24 ur sušeni na 103±1 °C; nesušeni: vzorci po kondicioniranju niso bili dodatno sušeni

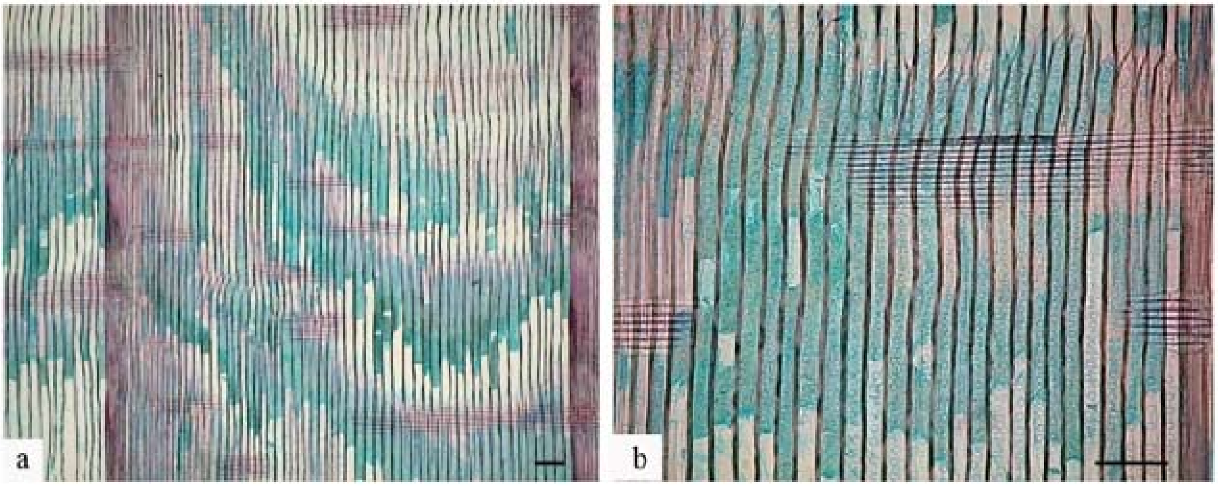
voska (suhe snovi) se povečuje tudi viskoznost emulzije, kar je vzrok, da smo pri postopku premazovanja dosegli največji mokri navzem z MW-A emulzijo (381 kg/m^3), najmanjšega pa z LGE-B emulzijo (156 kg/m^3). V vzorce je med premazovanjem prodrla le manjša količina emulzije, večji del emulzije je ostal na površni. Poleg mokrega navzema smo spremljali tudi suhi navzem, ki je v neposredni povezavi z mokrim navzemom in deležem suhe snovi posameznega pripravka (preglednica 1). Največji suhi navzem voska smo določili pri vakuumsko-



■ **Slika 1. Prečni prerez smrekovine impregnirane po vakuumsko-tlačnem postopku (30 min vakuum, 90 min 10 bar in 5 min vakuum) z emulzijami voskov a) MW-A, b) MW-B, c) LGE-A, d) LGE-B. Vosek v lumnih celic je zeleno obarvan. Merilne daljice = 100 µm**
Fig. 1. Cross section of Norway spruce samples impregnated according to vacuum-pressure process (30 min vacuum, 90 min 10 bars and 5 min vacuum) with wax emulsions a) MW-A, b) MW-B, c) LGE-A, d) LGE-B. Wax in cell lumina is green. Scale bars = 100 µm.

tlačno impregniranih vzorcih z MW-A emulzijo (194 kg/m^3), najmanjšega pa pri vzorcih, premazanih z LGE-B emulzijo (9,6 kg/m^3). Podobno kot za mokri navzem velja tudi za suhi navzem, da je le-ta odvisen od postopka impregnacije, tipa emulzije in vrste oziroma velikosti vzorcev.

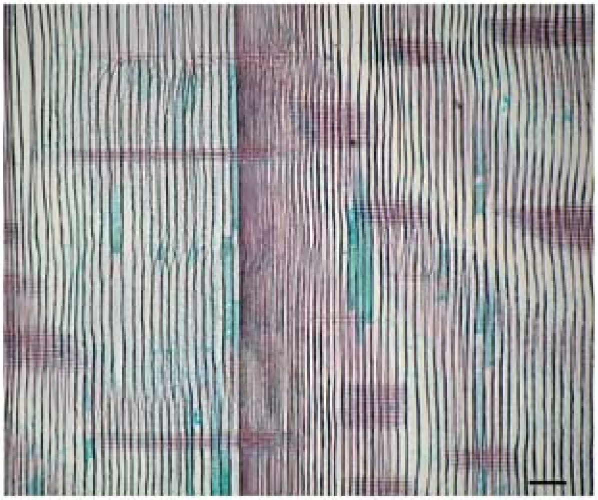
Glavni namen naše raziskave je bil ugotoviti, kako globoko in kam se je med impregnacijo odložil vosek. V ta namen smo si pod mikroskopom natančno ogledali prečne in radialne rezine vzorcev, impregniranih z različnimi voski. Na sliki 1 so prikazane prečne površine vzorcev, impregniranih v skladu z vakuumsko-tlačnim postopkom z različnimi emulzijami. Prečne rezine lesa, narejene iz vzorcev, prepojenih z MW-A, vsebujejo največ voska, najmanj pa prečne smrekove rezine iz vzorcev, zaščitenih z vodno emulzijo LGE-B. Podobne rezultate smo dobili tudi pri vakuumsko impregniranih in premazanih vzorcih. Rezultat je pričakovan, saj ima MW-A emulzija največji delež voska, LGE-B pa najmanjšega. Več voska je v lumnih ranega in prehodnega lesa, manj pa v lumnih kasnega lesa. Večji delež voska v ranem in prehodnem



■ **Slika 2. Montana vosek (MW-B) v vakuumsko-tlačno impregiranem lesu a) v traheidah tik pod površino vzorca, b) zgostitev montana voska v konicah traheid. Merilne daljice = 100 µm.**
Fig. 2. Montan wax (MW-B) at vacuum-pressure impregnated wood a) in tracheides close to surface of sample b) compression of montan wax in tracheides nibs. Scale bars = 100 µm.

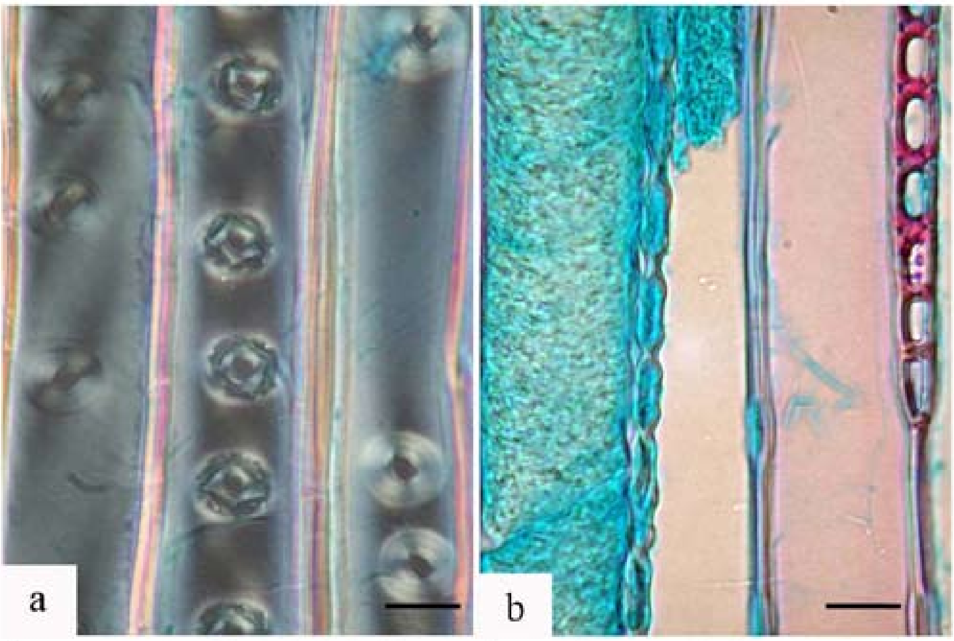
lesu je pričakovan, saj je penetracija odvisna predvsem od premera por (Richardson, 1993), v našem primeru od dimenzije lumna traheid. Proti pričakovanjem vosek ni prodrl v smolne kanale, kljub temu, da je njihov premer veliko večji od premera lumnov osnovnega tkiva. Najverjetneje je glavni vzrok v napolnjenosti smolnih kanalov z balzamom.

Na radialnih in tangencialnih rezinah vzorcev smo poleg razporeditve voska v branikah opazovali še globino prodora voska v aksialni in prečni smeri. Večji del voska je v vzorce penetriral v aksialni smeri. Pri vakuumsko-tlačnem postopku impregnacije so vsi štirje tipi voskov prodrli do sredine vzorcev A in B (10 oziroma 7,5 mm). Vendar je večina voska prodrla le približno 5 mm od čela, oziroma do koncev prerezanih traheid (slika 2), globlje, v sredini vzorca je voska veliko manj. Vosek najdemo le v posameznih celicah (slika 3). V vakuumsko-tlačne impregnirane vzorce C je LGE-A emulzija prodrla največ 13,76 mm globoko. Pričakovano, smo pri vzorcih, ki so bili impregnirani le z vakuumskim postopkom, brez nadtlaka, opazili bistveno slabšo penetracijo. LGE-A in LGE-B voska med vakuumskim postopkom impregnacije nista prodrla v sredino vzorcev. Največja globina penetracije emulzije LGE-A iz čelne strani v vzorce C je znašala 8,73 mm. Ta podatek potrjuje, da uporaba vakuumskih postopkov ni zadosti, če želimo učinkovito prepojiti smrekovino z vodnimi emulzijami montanskih voskov.



■ **Slika 3. Montana vosek (LGE-A) v sredini vzorca A (20 × 20 x 20 mm). Merilna daljica = 100 µm.**
Fig. 3: Montan wax (LGE-A) in the middle of sample A (20 × 20 x 20 mm). Scale bar = 100 µm.

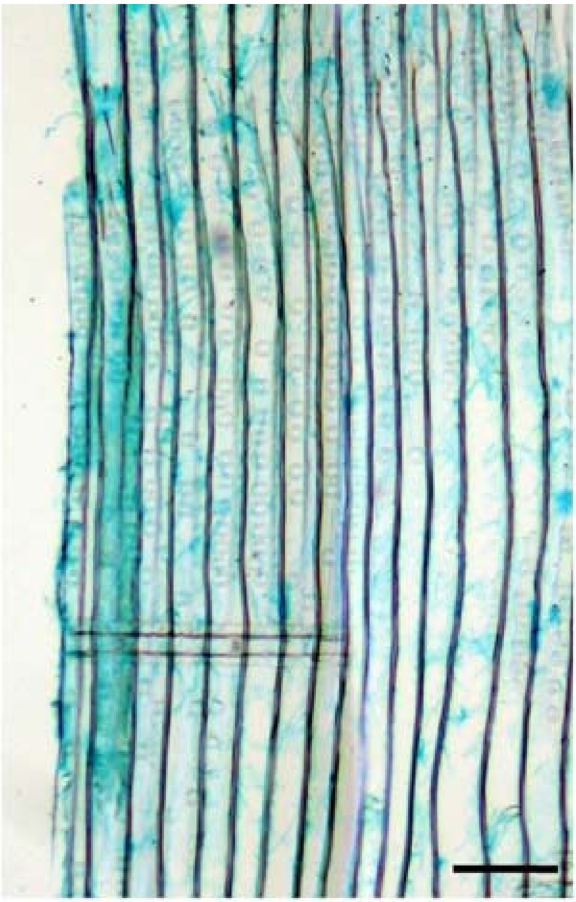
Povsem razumljivo je, da smo najmanjšo globino penetracije dosegli s premazovanjem. Voski so prodrli od 1,75 mm MW-A do 2,57 mm LGE-B globoko v aksialni smeri (preglednica 1), kar je več kot so določili pri baker-etanolaminskih pripravkih, v prečni smeri (Humar in Žlindra, 2007). Vzrokov za relativno majhno penetracijo voska v vzorce smrekovine je več. Prvi je slaba impregnabilnost smrekovine (Morrell in Morris, 2002; Wang in DeGroot, 1996). Impregnabilnost lesa je v veliki meri odvisna od strukture pikenj, saj je premer pikenjskih odprtin veliko manjši od lumnov traheid (Wang in DeGroot, 1996). Poleg tega so piknje med sušenjem aspirirale in tako preprečile



■ **Slika 4. Montana vosek v obokanih piknjah a) radialni prerez, b) tangencialni prerez. Merilne daljice = 10 µm.**
Fig. 4. Montan wax bordered pits a) radial section, b) tangential section. Scale bars = 10 µm.

prehod emulziji globlje v les. Dokaz za to so zgostitve voska na koncu traheid, kjer je največ pikenj (slika 2b). Zelo majhne količine voska smo kljub temu našli tudi globlje, kot je dolžina traheid (1,2 do 7,4 mm) (Čufar, 2006). Predvidevamo, da je emulzija prešla preko pikenj, ki niso bile aspirirane, ali pa so se med impregnacijo deaspirirale. To nakazuje tudi vosek v obokanih piknjah (slika 4). Pod določenimi pogoji je aspiracija pikenj v beljavi delno reverzibilna. Za deaspiracijo sta potrebna ustrezen tlak in omočitev z vodo (Thomas in Nicholas, 1966). Drugi vzrok za majhno penetracijo je relativno velika viskoznost emulzij voskov in velike molekule, ki sestavljajo montana vosek (Matthies, 2001).

Na vzorcih s čelnimi površinami, zaščitenimi z epoksidnim premazom, smo ugotavljali penetracijo emulzij v prečni smeri (radialni in tangencialni). Ugotovili smo, da vosek ni penetriral skozi celične stene. Na preparatih smo našli vosek le v lumnih poškodovanih traheid, ki smo jih med pripravo vzorcev (žaganjem in/ali skobljanjem) prerezali (slika 5). Podobno smo ugotovili za trakovno tkivo. Vosek smo našli le v prerezanih parenhimskih celicah na površini vzorca. Glavna smer transporta vode v lesu je aksialna (Čufar, 2006), kar je vzrok za manjšo penetracijo emulzij v prečni smeri. Vzrok za slabo impregnabilnost smrekovine v prečni smeri je tudi v majhnem deležu trakovnih traheid, saj so te v splošnem bolj učinkovite pri radialnem prevajanju kot trakovne parenhimske celice (Liese in Bauch, 1967). Nekaj voska smo našli v celicah na čelnih površinah, ki so bile pred impregnacijo predhodno premazane z epoksidnim premazom, kljub temu, da velja epoksidni premaz za enega najmanj prepustnih. Po natančnem pregledu vzorca pod lupo smo ugotovili, da ima epoksidni premaz manjše napake (razpoke in kraterje), skozi katere je emulzija voska lahko prodrla v les. Nepoškodovan premaz ni prepuščal emulzije, saj je bil vosek le v celicah, ki so direktno pod poškodbo premaza.



■ **Slika 5. Vosek je v prečni smeri prodrl le v prve poškodovane celice. Merilna daljica = 100 µm.**
Fig. 5. Wax break through the first damaged cells in cross section only. Scale bar = 100 µm.

Del vzorcev, impregniranih po vakuumsko tlačnem postopku, smo po tednu dni kondicioniranja še dodatno sušili na 103 °C. Sušenje je potekalo nad točko tališča voska, ki za montana vosek znaša 85 °C (Heinrichs, 2003). Po pregledu preparatov smo ugotovili, da sušenje pri temperaturi nad tališčem voska ne vpliva na razporeditev voska po prerezu vzorca. Porazdelitev je bila povsem primerljiva kot pri nesušenih vzorcih, impregniranih po istem postopku. Razlike so opazne le na površini, kjer vosek odteče s površine vzorca. Po sušenju smo pod vzorci opazili madeže. Do spremembe v globini penetracije in razporeditvi najverjetneje ne pride zaradi visoke viskoznosti staljenega voska, ki brez nadtlaka ne more prodreti skozi piknje.

Sklepi

Navzem in globina penetracije vodnih emulzij montana voskov sta odvisni od deleža suhe snovi v emulzijah. Vodne emulzije z večjim deležem suhe snovi, težje prodirajo v les. Po drugi strani pa pri vzorcih, impregniranih z emulzijami z večjim deležem suhe snovi, opazimo višje suhe navzeme. Edino vakuumsko-tlačni postopki impregnacije zagotavljajo ustrezno globino penetracije v aksialni smeri, ki presega dolžino traheid. Za prehod emulzij voskov preko pikenj je potreben zadosten nadtlak. V prečni t.j. radialni in tangencialni smeri emulzije montana voska niso penetrirale v les.

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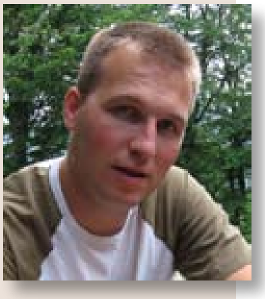
O AVTORJU PRISPEVKA BOŠTJAN LESAR



Boštjan Lesar, univ. dipl. inž. les., (rojen 1980) je leta 2005 diplomiral na Oddelku za lesarstvo, Biotehniška fakulteta, Univerza v Ljubljani. V začetku leta 2006 je opravljal trimesečno prakso v podjetju Haas Fertigbau GmbH v Avstriji in nato še pol leta v slovenski podružnici istega podjetja Haas Dom v Hočah pri Mariboru. Jeseni istega leta se je na Biotehnični fakulteti Univerze v Ljubljani vpisal na podiplomski študij bioloških in biotehnoloških znanosti – lesarstvo. Sedaj je zaposlen kot mladi raziskovalec na Oddelku za lesarstvo. Njegovo znanstveno raziskovalno delo je usmerjeno k zmanjševanju izpiranja bora iz impregniranega lesa in razvoju ter izdelavi okolju prijaznih zaščitnih sredstev na osnovi bora in vodnih emulzij voskov. V bibliografiji Boštjana Lesarja je med drugim znanstveni prispevek na konferenci, dva pregledna znanstvena članka, kratek znanstveni prispevek in dva izvirna znanstvena članka.

3.5 UPORABA EMULZIJ VOSKOV ZA IZBOLJŠANJE ODPORNOSTI LESA IN SORPCIJSKIH LASTNOSTI

USE OF WAX EMULSIONS FOR IMPROVEMENT OF WOOD DURABILITY AND SORPTION PROPERTIES

Boštjan Lesar in Miha Humar

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Voski se v lesarstvu uporabljajo že nekaj desetletij, predvsem za obdelavo lesenih površin zaradi slabe penetracije v les. Da bi se izognili temu problemu, smo v testu uporabili vodne emulzije voskov. Uporabili smo pet emulzij različnih koncentracij: dve emulziji montanskega voska in po eno emulzijo polietilenskega, etilen kopolimernega ter oksidiranega polietilenskega voska. Testirali smo učinkovitost zaščite z voski impregnirane bukovine (*Fagus sylvatica*) in smrekovine (*Picea abies*) proti glivam bele trohnobe (*Trametes versicolor, Pleurotus ostreatus* in *Hypoxylon fragiforme*), glivam rjave trohnobe (*Antrodia vaillantii, Serpula lacrymans* in *Gloeophyllum trabeum*), glivam modrivkam (*Aureobasidium pullulans* in *Sclerophoma pithyophila*) in plesnim (*Fusarium solani, Gliocladium viride, Penicillium expynsum* in *Penicillium janthinellum*). Vzporedno smo določali dinamiko navlaževanja smrekovine, impregnirane z emulzijo montanskega voska, izpostavljene v komori z visoko zračno vlažnostjo, dinamiko navzemanja vode med namakanjem in dinamiko navzemanja vode na tenziometru. Impregnirani vzorci smrekovine so bolj odporni na delovanje gliv razkrojevalk lesa kot nezaščiteni kontrolni vzorci. Posebej učinkovita sta bila polietilenski (WE1) in oksidirani polietilenski (WE6) vosek. Po drugi strani pa voski niso zaščitili lesa pred delovanjem gliv modrivk in plesni. Smrekovina, impregnirana z montanskim voskom, se je počasneje navlaževala kot nezaščiteni kontrolni vzorci. Kontrolni vzorci so dosegli ravnovesno vlažnost že po osemnajstih dneh navlaževanja, impregnirani vzorci pa niso dosegli ravnovesnega stanja niti po triinpetdesetih dneh. Na koncu navlaževanja na zraku in namakanja v vodi je bila vlažnost impregniranih vzorcev za približno 15 % nižja od vlažnosti kontrolnih vzorcev smrekovine. Še veliko večji vodoodbojni učinek montanskega voska pa se je pokazal pri kratkotrajnem namakanju na tenziometru.

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ORIGINALS ORIGINALARBEITEN

Use of wax emulsions for improvement of wood durability and sorption properties

Boštjan Lesar · Miha Humar

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Abstract Waxes are used for treatment of wood surfaces for several decades predominately as surface treatments because they weakly penetrate into the wood. In order to overcome this issue, water emulsions were applied in the present experiment. Five water emulsions of various concentrations were used, namely montan wax, polyethylene, ethylene copolymer and oxidized polyethylene wax. Performance of wax treated beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*) against white rot, brown rot and blue stain fungi was tested. In parallel, sorption properties of wax treated wood were determined. The treated specimens were more resistant to wood decay fungi. Polyethylene and oxidized polyethylene wax were found to be particularly efficient. Although this treatment does not improve resistance to blue stain fungi, it reduces the sorption of water.

Die Verwendung von Wachsemulsionen zur Verbesserung der Dauerhaftigkeit und der Sorptionseigenschaften von Holz

Zusammenfassung Seit Jahrzehnten werden Wachse fast ausschließlich zur Oberflächenbehandlung von Holz verwendet, weil sie nur schwach in das Holz eindringen. Um das Eindringverhalten zu verbessern, wurden in dieser Studie fünf verschiedene Wasseremulsionen in unterschiedlichen Konzentrationen verwendet, und zwar zwei Montanwachse, Polyethylen, Ethylen-Copolymer und oxidiertes Polyethylenwachs. Die Resistenz von wachsbehandeltem Buchenholz (*Fagus sylvatica*) und Fichtenholz (*Picea abies*) gegen Weißfäule-, Braunfäule- und Bläuepilze wurde untersucht. Daneben wurden die Sorptionseigenschaften von wachsbehandeltem Holz bestimmt. Die behandelten Prüfkörper waren gegen Holz zerstörende Pilze resistenter, wobei sich Polyethylen und oxidiertes Polyethylenwachs als besonders wirksam erwiesen. Zwar wird mit dieser Behandlung die Resistenz gegen Bläue nicht verbessert, jedoch wird die Wasseraufnahme reduziert.

1 Introduction

Despite the fact that wood has been used for construction applications for thousands of years, it remains one of the most important building materials. The first users of wood faced the same problem that people face nowadays. Wood is not durable in outdoors applications; therefore, it has to be protected in some way if used in such environment. In the pa st, most preservative solutions had biocidal properties and therefore, inhibited pest growth and development (Richardson 1993). Future solutions for the improvement of the durability of wood preservatives are designed differently. They change the structure of wood so that wood pests do not recognize it as food source (Tjeerdsma et al. 1998); or, wood moisture content is kept so low that decay processes are no longer possible (Goethals and Stevens 1994). It is believed that wax emulsions can be used in such manner as well. Treatment of wood with resin/wax water-repellent formulations greatly reduces the rate of water flow in the capillaries and significantly increases the dimensional stability of specimens exposed to wet conditions (Berninghausen et al. 2006; Kurt et al. 2008). The most important applications of waxes in wood industry are found in particleboard production.

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Paraffin emulsions are introduced to the particleboards reducing water uptake and improving dimensional stability (Amthor 1972; Deppe and Ernst 1996). Nowadays, wax emulsions are added to OSB boards for the same reason (Neimsuwan et al. 2008). However, there are reports that paraffin treatment can reduce water capillary uptake in wood as well (Scholz et al. 2009). Furthermore, wax treated wood exhibited increased compression strength and hardness (Rapp et al. 2005). In addition, wax and oil emulsion additives are incorporated into aqueous wood preservatives to reduce checking and improve the appearance of treated wood exposed outdoors as well (Evans et al. 2009).

Montan and carnauba waxes are some of the possible water repellent agents to be applied in order to improve wood durability as they are among the most resistant waxes that form thin films. Montan and carnauba wax as well as other waxes are almost non-toxic and are used for a variety of applications like for instance cosmetics (Anonymus 2005). Crude montan wax belongs to the group of naturally occurring waxes of vegetable origin such as carnauba wax or candelilla wax. Montan wax is fossilized vegetable wax extracted from lignites, principally from central German brown coal reserves west of the Elbe River. It is a mixture of chemical compounds that can be divided into three substance groups: waxes, resins, and asphaltic substances. Just like existing vegetable hard waxes such as carnauba wax, the pure wax substance in montan wax consists mainly of esters of long-chain acids with long-chain alcohols and free long-chain acids. Other components such as free wax alcohols or ketones, paraffins or terpenes are usually present in small quantities (Matthies 2001). Wax is soluble in many organic solvents, particularly aromatic or chlorinated hydrocarbons, even under moderate heating. Montan wax is used in the form of flakes, powders, pastes with solvents, or aqueous emulsions (Heinrichs 2003). One of the most important advantages of montan wax is its capability to form thin-layer resistant films (Warth 1959). One of the objects of this study was to show that this thin film could limit water penetration and as such improve performance against wood decay fungi. There are also other waxes—beside montan wax—used for the protection of concrete against stains, particularly polyethylene, ethylene copolymer and oxidized polyethylene wax. Some of those waxes are already being used for car and plastic polishing (Erhuai 2008), as they protect the surface against salt, dust and other pollutants. Another important application is the protection of concrete walls and facades against weathering, staining etc. It is believed that they can form a film on the wood surface as well as cell lumen. This enables faster water removal and decreases water sorption and desorption which results in an improved dimensional stability of wood. Dry wood will be less susceptible to fungal decay. Until now, wax (bee and paraffin waxes) has predominately been used for surface coatings (Burger 2006). It was dissolved in an organic solvent or melted prior use. However, melted waxes are only of minor importance as they do not penetrate deeper into the wood and remain on the surface of the treated material for most of the treatments. A second treatment of wood with melted waxes requires special equipment, it is expensive and there is an increased risk of fire (Scholz et al. 2009). On the other hand, organic solvents are becoming less and less desired due to environmental issues. The authors' intention is to prepare wax emulsions which will penetrate deeper into the wood and, therefore, protect it against fungal decay. To the authors' knowledge nothing has been reported on wax use in the field of wood protection.

2 Material and methods

2.1 Treatment solutions used

For impregnation, five types of wax emulsions of various concentrations were used, namely two emulsions of montan wax (LGE, MW1), one emulsion of polyethylene (WE1), one emulsion of ethylene copolymer (WE3) and one emulsion of oxidized polyethylene (WE6) wax. The solutions are commercially available and produced by Samson (Slovenia) and BASF (Germany). Concentrations (dry content) and basic properties of the wax emulsions can be seen in Table 1. In order to elucidate the penetration of wax emulsions to wooden specimens, the uptake of emulsions and the retention of waxes were determined gravimetrically. For retention measurements, samples were dried at 103°C for 24 hours, and their masses were determined before and after impregnation, and then the retention was calculated. This gravimetrically determined retention of wax was compared to the theoretical retention calculated from the uptake of solution and the concentration of wax in the emulsion.

2.2 Wood decay test

Resistance of wood impregnated with various wax emulsions against wood decay fungi was determined according to EN 113 procedure (EN 113:1989). Specimens were treated with various wax emulsions prior fungal exposure (vacuum—70 mbar; 20 min; pressure—9.5 bar; 60 min; vacuum—70 mbar; 10 min), as can be seen in Table 1. Wax treated specimens were air dried for four weeks. Steam sterilized, impregnated and unimpregnated wood specimens were exposed to three brown rot (*Antrodia vaillantii, Serpula lacrymans* and *Gloeophyllum trabeum*) and three white rot fungi (*Trametes versicolor, Pleurotus ostreatus* and *Hypoxylon fragiforme*). Beech wood (*Fagus sylvatica*) specimens were exposed to white rot and Norway spruce (*Picea* abies) specimens to brown rot fungi. After 16 weeks of fungal exposure, specimens were isolated and mass losses were gravimetrically determined and expressed in percentages.

Table 1 Selected properties of the undiluted/commercial wax emulsions used
Tab. 1 Verschiedene Eigenschaften der verwendeten unverdünnten/handelsüblichen Wachsemulsionen

Preservative solution	Dry content (%)	pH	Emulsion viscosity (4 mm 23°C) ISO 2431 (s)	Density (g/m^3)	Melting point of solids (°C)	Average particle size (nm)	Emulsifier system
LGE	11.4	5.5	13	1.00	76–80	100	n.a.
MW1	46.2	4.6	25	1.01	78	100	Nonionic
WE1	36.4	9.9	20–36	1.00	130–135	100	Nonionic/anionic
WE3	28.4	9.7	85	1.00	85	100	n.a.
WE6	38.2	8.9	20–60	1.00	126–133	100	Nonionic/anionic

Table 2 Uptake of wax emulsions during impregnation process with regard to concentration, wood species and composition of solution. In addition, there are gravimetrically determined retention and differences between theoretically calculated and actual retention
Tab. 2 Aufnahme von Wachsemulsionen während der Imprägnierung in Abhängigkeit von der Konzentration, der Holzart und der Zusammensetzung der Lösung. Zusätzlich sind die gravimetrisch bestimmte Einbringmenge sowie die Unterschiede zwischen theoretisch berechneter und tatsächlicher Einbringmenge angegeben

Wax emulsion	Conc. (%)	Dry cont. (%)	Spruce wood			Beech wood		
			Uptake of wax emulsion (kg/m^3)	Retention of wax (kg/m^3)	Difference between theoretical and actual wax retention (%)	Uptake of wax emulsion (kg/m^3)	Retention of wax (kg/m^3)	Difference between theoretical and actual wax retention (%)
LGE	50	5.3	555	26	12	644	34	2
	100	11.4	386	32	27	647	67	10
MW1	25	10.9	441	41	16	639	58	17
	50	23.1	347	53	34	662	126	18
WE1	25	9.4	500	39	16	641	56	6
	50	18.2	370	52	24	668	113	7
WE3	25	7.3	569	30	29	659	40	17
	50	14.2	494	18	74	663	72	23
WE6	25	9.4	462	35	19	655	56	9
	50	19.1	340	45	31	670	110	14

2.3 Blue stain and moulds test

Scots pine (*Pinus sylvestris*) wood specimens were surface brushed with various wax emulsions (Table 2). Their resistance was determined according to EN 152-1 procedure (EN 152-1:1996). The uptake of wax emulsions was approximately 200 g/m^2. After brushing, samples were left to dry for 3 weeks. Half of the samples were exposed to blue stain fungi, while the other half was exposed to moulds for 6 weeks according to the requirements of EN 152-1:1996. *Aureobasidium pullulans* and *Sclerophoma pithyophila* were used to test blue stain organisms. *Fusarium solani*, *Gliocladium viride*, *Penicillium expynsum*, and *Penicillium janthinellum* were used for testing mould organisms. Resistance against disfiguring fungi was estimated visually according to EN 152-1:1996. Additionally, color change was determined as well and expressed in the CIELab color system.

2.4 Sorption properties

Only LGE emulsion was used for the determination of sorption properties. There were two types of tests performed to determine sorption properties. In the first one, impregnated specimens were conditioned in water container or in a high humidity chamber, and their masses were monitored. In the the second set of experiments, a tensiometer was used.

The first set of sorption experiments were performed on Norway spruce wood specimens (1.5 × 2.5 × 5.0 cm^3) with end sealed (epoxy coating) axial surfaces. They were impregnated (vacuum—70 mbar; 20 min; pressure—9.5 bar; 60 min; vacuum—70 mbar; 10 min) with LGE emulsions of two different concentrations, LGE 50 and LGE 100. After four weeks of air drying, specimens were oven dried (40°C) for three days. Afterwards, half of the specimens were transferred to the chamber with a relative air humidity of 82%. The masses of the specimens were monitored daily for six weeks. The second half of the specimens were immersed in distilled water. The masses of the specimens were monitored for three weeks after predetermined periods shown in Fig. 2. All moisture contents given are based on dry mass with wax.

In the second part of experiments, Norway spruce wood specimens of the following size 2.0 × 3.0 × 4.0 cm^3 (T × R × A) were utilized. The measurements were carried out at room temperature (20°C) at a RH of 40–50% on a Krüss Processor Tensiometer K100. Axial surfaces of the specimens were positioned such that in contact with water, and afterwards their masses were measured continuously for 200 s. Each curve in Fig. 3 is an average value of 10 measurements.

3 Results and discussion

Wax emulsions used for impregnation in this experiment had different dry contents. They varied between 5.3% (LGE 50) and 23.1% (MW1 50) (Table 2). The influence of dry content on the properties of the emulsions, predominately viscosity, is significant. However, viscosity is also influenced by other parameters. The highest viscosity was observed for the WE3 emulsion, where a considerably higher viscosity is reported compared to the other waxes with a similar or even higher dry content. All emulsions applied, with the exemption of LGE, have a rather high viscosity. Their penetration is presumably more limited compared to the penetration of aqueous solutions. In general, no difference was observed between the uptakes of preservative solution for beech wood specimens. Those specimens in average retained 650 kg/m^3 of wax emulsions. However, considerably higher variations in retentions were observed for spruce wood specimens. Specimens impregnated with LGE 50 wax emulsion retained 570 kg/m^3 of emulsion, while parallel specimens that were treated with the WE6 50 emulsion up to 340 kg/m^3 of wax emulsion was retained (Table 2). It is presumed that the main reason for the observed effect could be a better impregnability of beech wood compared to spruce wood. It seems that the ability to penetrate into spruce wood specimens is in tight correlation with the dry content of wax emulsions applied. For specimens that were impregnated with emulsions of higher concentration, lower uptakes of preservative solutions were determined than for parallel specimens preserved with emulsions with a lower dry content (Fig. 1). Although the emulsion particles (disperse phase) are rather small (100 nm), they are too big to penetrate into the cell wall. Lignified wood cell walls contain a nanocapillary network that is 1–10 nm in size (Fujino and Itoh 1998). Therefore, wax is deposited in the cell lumen only (Lesar et al. 2008).

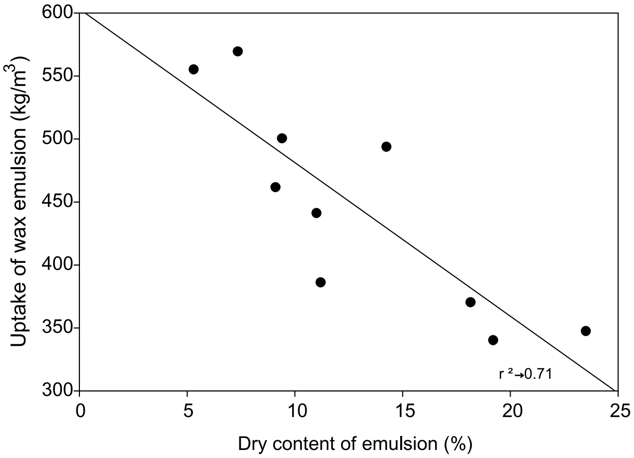

Fig. 1 Correlation between dry contents of the emulsion and uptake of preservative solutions in spruce wood specimens
Abb. 1 Korrelation zwischen Trockengehalt der Emulsion und Schutzmittelaufnahme in Fichtenholzprüfkörpern

The fact that particles in the emulsion are too big to penetrate into the cell wall is reflected in the differences between gravimetrically determined wax retentions and theoretical wax retentions calculated from the solution uptake and dry content (Table 2). These differences varied between 2% and 23% in beech wood specimens and between 12% and 74% in spruce specimens. This result shows a better impregnability of beech wood. However, differences in retention are most evident in spruce specimens impregnated with the WE3 emulsion, where 73% less wax was determined than was presumed from the uptake of solutions. It is presumed that during the impregnation process, water penetrated deeper into the specimens while wax remained on the surface.

A more important object of this research was to determine the effect of wax treatment on performance against wood decay fungi. All wood decay fungi used in this experiment were vital, as mass losses of control specimens were higher than 20%, with the exception of *A. vaillantii*

Table 3 Mass loss of the wax treated spruce and beech wood specimens exposed to various wood decay fungi according to EN 113 procedure
Tab. 3 Masseverluste der wachsbehandelten Fichten- und Buchenholzprüfkörper nach Befall mit verschiedenen Holz zerstörenden Pilzen gemäß EN 113

Wax emulsion	Conc. (%)	Wood decay fungi					
		G. trabeum	*A. vaillantii*	*S. lacrymans* Mass loss (%)	*P. ostreatus* Mass loss (%)	*T. versicolor*	*H. fragiforme*
LGE	50	26.1	11.2	18.8	15.2	24.6	28.5
	100	24.7	14.8	17.8	11.4	20.4	23.7
MW1	25	22.2	10.4	17.2	13.2	21.4	24.4
	50	15.8	11.7	13.1	7.3	13.9	20.7
WE1	25	6.0	7.3	12.2	14.8	20.8	30.9
	50	3.8	10.9	5.7	8.4	3.9	18.3
WE3	25	21.2	16.1	27.4	13.7	30.6	27.6
	50	13.6	16.2	30.0	20.4	22.3	32.4
WE6	25	23.0	11.3	7.1	10.0	17.9	22.4
	50	7.7	7.8	3.2	8.9	1.6	21.7
Control	/	35.7	16.9	40.2	23.0	32.0	32.7

where control specimens only lost 16.9%. This fungal strain is known as a less aggressive, but on the other hand very effective degrader of impregnated and modified wood (Table 3).

Mass losses of specimens impregnated with different wax emulsions varied from 2% (WE6 50; *T. versicolor*) up to 32% (WE3 50; *H. fragiforme*). As seen in Table 1, it can be concluded that applied wax emulsions can slow down wood fungi to grow. Among the treatments the WE3 wax emulsion (emulsion of ethylene copolymer wax) was found to be least effective. This emulsion was the most viscose one among the emulsions tested, and its penetration into the wooden specimens was the worst. It should be considered that most of the wax remained on the surface of the treated specimens and therefore did not have prominent influence on the performance of the impregnated wood (Table 2). Additionally, specimens impregnated with montan wax emulsions (LGE and MW) were decayed less than the control ones. Among the fungi tested, montan wax emulsions were found to be the least effective ones against *G. trabeum*. During the 16 weeks of exposure to the fungi mentioned above, the control specimens lost 35.7% while the specimens impregnated with montan wax emulsions lost between 26.1% and 15.8% depending on the concentration of montan wax in emulsions. Specimens impregnated with emulsions of higher concentrations were better protected against wood decay fungi than specimens impregnated with lower concentrations of montan wax (Table 3). Among the tested wax emulsions, emulsions WE1 (emulsion of polyethylene wax) and WE6 (emulsion of oxidized polyethylene wax) proved to be the most effective agents for the protection of wood against wood rotting fungi. For example, after 16 weeks of exposure to *G. trabeum*, mass losses of spruce wood specimens impregnated with the WE1 50 emulsion were only 3.8% and 5.7% after exposure to *S. lacrymans*. This treatment was effective against white rot species as well. *P. ostreatus* caused mass loss of 8.4%, while *T. versicolor* decayed only 3.9% of impregnated specimens (Table 3). Unfortunately, WE1 and WE6 emulsions were not that effective against *A. vaillantii* and *H. fragiforme*. A comparison of the dry content data and mass losses after fungal decay revealed that there is no statistically significant correlation between those two parameters. This indicates that fungicidal properties of impregnated wood depend more on the properties of wax than those of dry content. pH is one of the mechanisms which could explain the efficacy of the wax treated wood. Wood treated with wax emulsions WE1 and WE6 with pH around 9 exhibited a better performance against wood decay fungi than montan wax treated wood. It is well known that fungi prefer slightly acidic substrates rather than alkaline ones (Schmidt 2006). However, resistance of wax treated wood to wood decay fungi cannot be explained by pH dependent mechanisms, as wax emulsion WE3 has alkaline pH, but fungi can degrade WE3 treated wood to similar extent to the LGE ones. The other mechanism that potentially improves the performance of the wax treated wood against wood de-

Table 4 Resistance of pine wood specimens to blue stain and mould fungi determined according to EN 152-1 procedure

Tab. 4 Resistenz der Kiefernholzprüfkörper gegen Bläue und Schimmelpilze gemäß EN 152-1 bestimmt

Wax emulsion	Conc. (%)	Visual estimation – moulds	Visual estimation – blue stain	ΔE – Color change after exposure to moulds	ΔE – Color change after exposure to blue stain fungi
LGE	50	2.8	3	13.1	40.2
	100	2.4	2.8	12.0	39.8
MW A	25	2.3	3	8.3	32.9
	50	2.4	3	8.3	39.2
WE1 A	25	2.4	3	11.1	29.2
	50	2.9	2.6	12.2	21.1
WE3 A	25	3	2.8	18.1	27.7
	50	3	3	18.6	41.6
WE6 A	25	2.6	2.6	12.0	32.9
	50	2.25	3	27.2	32.3
Control	/	3	3	9.1	25.9

cay fungi is film/barrier formed in the cell lumina and on the surface of the specimens. This barrier slows down moisturizing, the diffusion of enzymes and degradation products between hyphen and wood. It is presumed that this mechanism only slows down the degradation processes and does not stop them. Therefore it is suggested that the EN 113 test should be prolonged to overcome the influence of a slow down diffusion. This experimental issue is overcome in long lasting field tests. The preliminary results of the double layer field trial showed that after two and a half years of natural exposure there is considerable decay at the control unimpregnated spruce wood specimens. After eight months of exposure, the first fruiting bodies of the *Gloeophyllum sp.* were noticed. On the other hand, there were no signs of decay on the parallel spruce wood treated with LGE, WE1 or WE6 emulsions. This is additional evidence that wax treated wood exhibits a better performance against wood decay fungi than untreated wood. As already explained, the authors believe that the most important reason for improved performance of wax treated wood in double layers is due to moisture relating effects. Moisture content of wax treated wood was lower. Therefore they are les susceptible to decay.

Unfortunately, wax emulsions do not improve the resistance of wax treated wood against blue stain and mould fungi. Both control and impregnated specimens were completely stained after blue stain exposure as well as after exposure to moulds. The surface of the specimens was covered with stains that covered more than 60% of the surface (Table 4). Despite the fact that both specimens exposed to blue stains and moulds were estimated with the same mark (3), the color change (ΔE) that can be seen in Table 4 clearly shows that control specimens exposed to the blue stain fungi were considerably darker than the ones exposed to mould fungi. A similar effect can be observed for impregnated specimens as well. Unfortunately, none of the wax emulsions improved the resistance of the treated wood against staining organisms. A visual estimation showed some traces of inhibitory properties. All wax emulsions, with the exception of WE3, slightly inhibit moulding. This effect was not expressed for all specimens but only for some of them. The effect of waxes against blue staining was even less prominent. The color analysis of the wax treated specimens exposed to staining fungi showed an even more negative influence of waxes on the resistance against staining. This analysis showed that there might be fewer individual stains on the surface of the specimens, and there was less surface covered with stains, but those stains were darker than the stains on control specimens. There might be a better resistance of wax treated wood observed if the specimens had been impregnated instead of surface treated.

The impregnation of spruce wood with waxes has an effect on sorption properties of impregnated wood as well. An increase of the moisture content of the LGE impregnated specimens was slower compared to the specimens conditioned in humid air as well as the ones immersed in water. The moisture content (MC) of wood impregnated with the LGE emulsion after 60 days of conditioning was also lower than the MC of control specimens. It can be seen from Fig. 2a that the MC of LGE 100 impregnated specimens at RH of 80% was 12.1%, while an 15% higher moisture content was observed for the control specimens after 60 days of conditioning. The MC mentioned above was even reached after 18 days for control specimens. It can be seen in Fig. 2a that even after 60 days of conditioning of specimens impregnated with the LGE 100 emulsion, they did not reach their equilibrium moisture content. The MC of LGE treated specimens was still slightly increasing even after two months of conditioning. This indicates that the LGE wax can form a film on wood that is able to significantly slow down the adsorption. A similar effect was observed during the wetting of

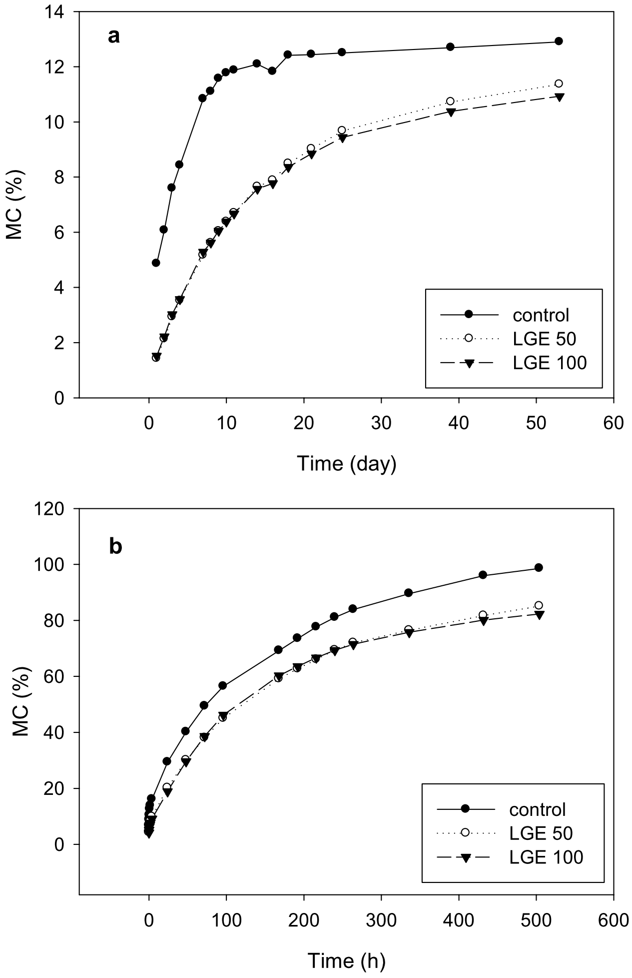

Fig. 2 Changes in moisture contents (MC) of the control specimens and specimens treated with LGE wax emulsions in atmosphere with RH of 82% (**a**) or during immersion in water (**b**)

Abb. 2 Änderung der Holzfeuchte (MC) der Kontrollproben und der mit LGE Wachsemulsionen behandelten Prüfkörper (**a**) in einer Umgebung von 82% rel.Lf. oder (**b**) bei Wasserlagerung

wooden specimens (Fig. 2b). The uptake of water of specimens impregnated with LGE emulsions was slower than that of control specimens. The final MC of control specimens was 96%, while LGE impregnated specimens absorbed approximately 17% less water. It is presumed that there are three reasons for this. Firstly, waxing makes the surface of the specimens more hydrophobic. Secondly, the cell lumina were at least partly filled with waxes and this physically prevents moisturizing. Finally, there were thin film-barriers formed on the surface of the wooden specimens, which slow down water movement.

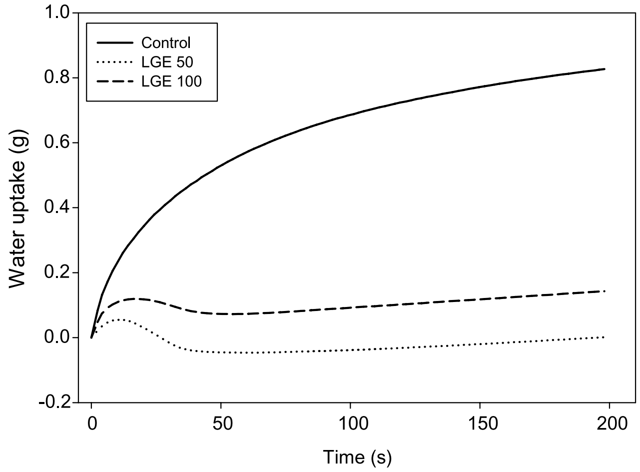

Fig. 3 Water uptake of axial surfaces of the montan wax (LGE) and control specimens expressed in grams. Uptake was determined with tensiometer

Abb. 3 Wasseraufnahme über die Hirnholzflächen von mit Montanwachs (LGE) behandelten sowie Kontrollproben, in Gramm. Die Wasseraufnahme wurde mit einem Tensiometer gemessen

This hydrophobic effect of the montan wax can also be seen from the measurement of the water uptake using tensiometer (Fig. 3). During this test, axial surfaces of wooden specimens were positioned such that in contact with water. Afterwards, the water uptake was gravimetrically measured. The uptake of water in control spruce wood specimens was relatively fast. Within 200 s, specimens from axial surfaces (6 cm^2) retained more than 0.8 g of water. The shape of the uptake is clearly logarithmical. The uptake of water is faster in the beginning and then slows down. Approximately half of the water was absorbed after 30 s (Fig. 3). The water uptake in the montan wax impregnated specimens was considerably lower for both specimens impregnated with pure LGE emulsion (LGE 100) and for the ones impregnated with the same emulsion of a lower concentration (LGE 50). The shape of the water uptake curve for LGE treated specimens significantly differs from the curve observed for control specimens. The water uptake decreased during the initial stage. It reached its maximum after 12 s (LGE 100) or 16 s (LGE 50), and then appeared to decrease rapidly before it started increasing again after 50 s (Fig. 3). This pattern is characteristic for hydrophobic surfaces (Rowell and Banks 1985). There was no decrease in the water uptake, but this pattern is a result of the hydrophobic properties and the lifting power of the water in contact with the surface where contact angles are higher than 90 degrees. However, after 200 s the LGE 50 treated spruce specimens took eight times less water up than the control ones, while the uptake in LGE 100 treated wood was even lower. This is an additional proof that montan wax treatment improves the sorption properties of wax treated wood.

4 Conclusion

The uptake of wax emulsion based solutions in spruce wood specimens was influenced by dry content and viscosity of the wax emulsions applied. Some of the wax emulsions tested do considerably slow down fungal degradation, but do not stop it. Emulsions of oxidized polyethylene wax (WE6) were found to be particularly effective. Unfortunately, treatment of wood with waxes does not prevent staining. One of the positive properties of treated wood is that the impregnation of wood with emulsion of montan wax reduces water uptake of the wax treated wood. It is believed that wax emulsions have the potential to be used for wood protection in less hazardous outdoor applications.

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3.6 MONTANSKI VOSEK IZBOLJŠUJE LASTNOSTI ZAŠČITNIH SREDSTEV ZA LES NA OSNOVI BORA

MONTAN WAX IMPROVES PERFORMANCE OF BORON-BASED WOOD PRESERVATIVES

Boštjan Lesar, Polona Kralj in Miha Humar

International Biodeterioration & Biodegradation, 2009, 63: 306–310
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Borove spojine se za zaščito lesa uporabljajo že zelo dolgo, vendar ves ta čas ostaja problem njihovega izpiranja iz lesa v vlažnem okolju. Za izboljšanje vezave in delovanje proti glivam razkrojevalkam lesa smo pripravili zaščitno sredstvo, sestavljeno iz borove kisline (BA) in emulzije montanskega voska. Možne sinergistične učinke borove kisline in montanskega voska smo določali po modificiranem standardu EN 113. Smrekove in bukove vzorce smo za 12 tednov izpostavili trem glivam bele trohnobe (*Trametes versicolor, Pleurotus ostreatus* in *Hypoxylon fragiforme*) in trem glivam rjave trohnobe (*Gloeophyllum trabeum, Antrodia vaillantii* in *Serpula lacrymans*). Izpiranje bora smo določali s kontinuirnimi (EN 84 in ENV 1250-2) ter nekontinuirnimi (OECD in prCEN/TS 15119-1) postopki izpiranja. V zbranih izpirkih smo bor določali z ICP masno spektroskopijo. Rezultati kažejo na sinergistično delovanje emulzije montanskega voska in borove kisline proti glivam razkrojevalkam. Približno za polovico manjši navzem borove kisline je potreben v kombinaciji z montanskim voskom, da se doseže zadostna zaščita pred glivami razkrojevalkami. Za učinkovito zaščito zadostuje 0,8 kg/m^3 BAE, v kombinaciji z montanskim voskom pa zadostuje že 0,4 kg/m^3 BAE. Te vrednosti veljajo le za glive bele trohnobe, saj so glive rjave trohnobe še bolj občutljive. Rezultati izpiranja so pokazali, da je izpiranje bora večje pri kontinuiranem kot pri nekontinuiranem izpiranju, tako iz vzorcev, zaščitenih samo z borovo kislino, kot tudi iz vzorcev, impregniranih z borovo kislino in montanskim vokom. Pri vseh testih izpiranja je dodatek montanskega voska zmanjšal izpiranje bora iz impregniranega lesa za 20 % do 50 %.

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Montan wax improves performance of boron-based wood preservatives

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ABSTRACT

Importance of boron compounds in wood preservation is increasing due to their low environmental impact, high efficacy and the fact that many other active ingredients have been removed from the market after the introduction of the Biocidal Products Directive. The most important drawback of boron is prominent leaching in wet environment. In order to improve their fixation, and performance against wood decay fungi, boric acid was combined with montan wax emulsion. Possible synergistic effects of boric acid and montan wax were determined according to modified EN 113 procedure. Norway spruce and beech wood specimens were exposed to three white rot (*Trametes versicolor*, *Pleurotus ostreatus* and *Hypoxylon fragiforme*) and brown rot wood decay fungi (*Gloeophyllum trabeum*, *Antrodia vaillantii* and *Serpula lacrymans*) for 12 weeks. Boron leaching from vacuum/pressure treated Norway spruce wood was determined according to the continuous (EN 84 and ENV 1250-2) and non-continuous (OECD and prCEN/TS 15119-1) procedures. Boron was determined with ICP mass spectrometry in collected leachates. The results of the fungicidal tests clearly showed that montan wax emulsion and boric acid act synergistically against tested wood decay fungi. Approximately 50% lower boric acid retentions are required in combination with montan wax emulsions to achieve sufficient protection against wood rotting fungi. However, it is even more important that all leaching tests performed proved that the addition of montan wax decreased boron leaching from impregnated specimens for 20% up to 50%.

1. Introduction

Boron compounds are one of the longest-used active ingredients that are still in use for wood preservation. After implementation of Biocidal product directive in 2006, several classical active ingredients have been removed from the market, and boron-based formulations have turned out as one of the strongest alternative in the field of wood preservation (Ramos et al., 2006). Thus their importance increased significantly. Boron compounds have low mammalian toxicity but, they are very effective against most of wood pests. Their use is limited due to its diffusibility and susceptibility to leaching (Lloyd, 1998). This is the main reason why boron cannot be applied for outdoor applications without additives or surface coatings that reduce boron leaching (Obanda et al., 2008).

To increase the use of boron compounds as environmentally benign wood preservatives, several fixation systems have been developed to limit or decrease boron leaching. Some attempts have relied on limiting the water penetration of treated wood using water repellents, monomer and polymer systems (Kartal et al., 2004, 2007). The most important solutions for limiting boron leaching are: combination of boron with glycerol/glyoxal (Toussaint-Davergne et al., 2000), vinyl monomers (Yalinkilic et al., 1999), silanes (Kartal et al., 2007), alkydes (Peylo and Willeitner, 1995), and tall oil derivates (Temiz et al., 2008). Similarly, Pavlič et al. (2005) applied surface coatings to impregnated wood in order to limit boron emissions. Despite extensive research, there is no commercial solution available that could limit boron leaching below 5% (Obandan et al., 2008). However, most of the water repellents decrease boron leaching in the initial stages, but they become ineffective after a few months of weathering. Peylo and Willeitner (1995) concluded that water repellent treatments do not prevent boron leaching, but only slow it down.

To improve its performance against fungi and to decrease leaching boron was combined with montan wax in this investigation. Treatment of wood with resin/wax water repellent formulations greatly reduces the rate of water flow in the capillaries and significantly increases the dimensional stability of specimens exposed to wet conditions (Kurt et al., 2008). Crude montan wax belongs to the group of naturally occurring waxes of vegetable origin such as carnauba wax or candelilla wax. Montan wax is fossilized vegetable wax extracted from lignites, principally from the central German brown coal reserves west of the Elbe river. It is

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a mixture of chemical compounds that can be divided into three substance groups: waxes, resins and asphaltic substances. Like existing vegetable hard waxes such as carnauba wax, the pure wax substance in montan wax mainly consists of esters of long-chain acids with long-chain alcohols and free long-chain acids. Other components such as free wax alcohols or ketones, paraffins or terpenes are usually present in small quantities (Matthies, 2001). The wax is soluble in many organic solvents, particularly aromatic or chlorinated hydrocarbons, even on moderate heating. Montan wax is used in the form of flakes, powders, pastes with solvents, or aqueous emulsions (Heinrichs, 2003). One of the most important advantages of montan wax is capability of forming thin-layer resistant films (Warth, 1959). Therefore the premise of this study was that this thin film could limit water penetration and limit boron emissions from impregnated wood.

2. Material and methods

There were two different sets of specimens prepared for testing. Bigger blocks (1.5 × 2.5 × 5 cm) were used for leaching tests, and the smaller ones (1.0 × 1.5 × 4.0 cm) for biological tests. Leaching tests were performed on specimens made of Norway spruce (*Picea abies*) only, while fungicidal tests were performed on spruce and beech (*Fagus sylvatica*) sapwood.

Two sets of preservative solutions were used for impregnation. The first one was aqueous solution of boric acid of various concentrations, and the second set contained boric acid and montan wax emulsion of two different ratios (LGE – emulsion, Samson d.o.o., Slovenia) of 12% or 6% of montan wax, respectively. Composition of preservative solutions is resolved from Table 2. Specimens were vacuum/pressure impregnated. Impregnated specimens were conditioned first two weeks after treatment in closed chambers, the third week in half-closed and the fourth week in open ones, according to the requirements of the standard (ENV 1250-2, 1994). Control specimens exposed to wood decay fungi were left un-impregnated.

Fungicidal properties were determined according to the modified EN 113 (1989) procedure. Beech wood specimens were exposed to white rot fungi (*Trametes versicolor*, *Pleurotus ostreatus* and *Hypoxylon fragiforme*) and spruce wood specimens were exposed to brown rot ones (*Gloeophyllum trabeum*, *Antrodia vaillantii* and *Serpula lacrymans*). Three specimens were exposed in the same incubation jar ($V = 500$ mL). The surface of the inoculated nutrient medium was approximately 115 cm^2. After 12 weeks of exposure mass loss of the decayed specimens was gravimetrically determined. Biological part of the investigation was performed on five replicate specimens.

For leaching test only one combination of boron and montan wax was chosen. Aqueous solution contained 0.1% of boron. Specimens leached according to the OECD, ENV 1250-2 and prCEN/TS 15119-1 procedure, had end-sealed axial surfaces before impregnation, while axial surfaces of the specimens planned for EN 84 leaching testing remained unsealed.

Leaching was performed according to four different procedures: EN 84 (1994), ENV 1250-2 (1994), OECD procedure (2006) and prCEN/TS 15119-1 (2007). ENV 1250-2 (1994) procedure requires the shortest leaching time; it is completed in only four days. In order to further speed up the experiment, following two modifications were done: instead of five, three specimens were positioned in the same vessels and water mixing was achieved with shaking on device non-rotatory shaker (Kambič) instead of magnetic stirrer. To obtain three parallel leaching procedures, nine specimens per solution/concentration/treatment were put in three vessels (three specimens per vessel). Afterwards, samples in the vessel were positioned with a weight. 300 g of deionized water was added and the vessel with its content was shaken with the frequency of 60 min^{-1}. Water was replaced for six times in four subsequent days, as prescribed by the standard. Leachates from the same vessel were collected and compiled. The concentration of boron in leachates was determined after first and fourth day of leaching.

EN 84 standard requires vacuum pre-treatment of the specimens with water as the first step of leaching; specimens thusly take up as much water as possible. Three samples, impregnated by the same treatment were positioned in the vessel and immersed into 300 g of deionized water. There was no water stirring during leaching. Water (300 g) was exchanged ten times in 14 subsequent days. Boron content in leachates was determined after first and second week of leaching.

In contrast to ENV 1250-2 and EN 84, OECD (2006) and prCEN/TS 15119-1 (2007) methods are based on non-continuous leaching. OECD prescribes that specimens should be exposed to water for relatively short period of time within three weeks. In order to have comparable results, three specimens with end-sealed axial surfaces were immersed to 300 g of deionized water for 1 h, and afterwards air dried for 4 h and than again immersed into the same solution for additional 1 h. This cycle was repeated after two days, in total for nine times in three weeks lasting experiment. Boron content was determined at the end of each week. For each treatment nine specimens leached in three parallel vessels were utilised. In contrast to OECD method prCEN/TS 15119-1 procedure prescribes even shorter immersion periods. Specimens of the same shape and number are soaked in 300 mL of water for 1 min only, and afterwards dried for 2 h and afterwards leached again for 1 min and again dried and leached. This cycle of three leaching sets is repeated for 9 times as described at OECD protocol.

The Agilent Technologies (Palo Alto, USA) HP 4500 quadrupole ICP-MS with Burgener Mira Mist nebuliser was used as a detection system for boron. The spray chamber temperature was 4 °C. The plasma RF power was set to 1300 W. Plasma gas flow rate was 15 L min^{-1}, auxiliary gas flow rate 0.7 L min^{-1} and nebuliser gas flow rate 1.05 L min^{-1}. Sampler and skimmer cones were made of nickel. Standard boron solutions for calibration curve were prepared by diluting a stock standard solution of boron (1000 mg L^{-1}) (Merck, Germany). Samples were diluted 50-fold with MQ water prior to the analysis. The final standard and sample solutions contained 1% (v/v) of nitric acid. The memory effect (as a consequence of introduction of solutions with high boron concentration) was eliminated by washing the system with 20% (v/v) ammonia solution after each sample (Al-Ammar et al., 1999). The washout time was 60 s. Analytical grade nitric acid and ammonia solution (Merck, Germany) were used. NIST standard reference material 1643e (trace elements in water) was used to verify the accuracy of the measurements.

3. Results and discussion

Composition of preservative solutions has considerable influence on its retention. This study showed that the influence was more prominent at specimens with end-sealed axial surfaces. Specimens with end-sealed surfaces had an average uptake of 211 kg/m^3 of preservative solutions, while three times higher loadings were determined at specimens that were not sealed. Spruce wood specimens (unsealed) retained on average 652 kg/m^3 of preservative while beech wood retained 612 kg/m^3 of boron-based solutions (Table 1). However, spruce wood specimens with unsealed surfaces in average retained 726 kg/m^3 of solution without montan wax, and 578 kg/m^3 of solution with 12% of montan wax. This clearly indicates that molecules (particles) of montan wax reduce the penetration of preservative solution into the wood. Previous research by this group confirmed that montan wax emulsion can penetrate through bordered pits in wood if

Table 1
Retentions of the preservative solutions, montan wax and boric acid to vacuum/pressure treated into spruce and beech wood specimens, impregnated with aqueous solution of boric acid (B) and aqueous solution of boric acid and montan wax emulsion (B + montan wax) ($c_B = 0.1\%$; $c_{\text{montan wax}} = 12\%$). Standard deviations are given in the parentheses.

Preservative solution	Axial planes sealed	Wood species	Retention (kg/m^3)		
			Preservative solution	Wax	Boric acid
B	No	Spruce	726 (26)	/	4.4 (0.2)
		Beech	609 (13)	/	3.3 (0.1)
	Yes	Spruce	231 (4)	/	1.3 (0.1)
B + montan wax	No	Spruce	578 (97)	69.6 (14.3)	2.9 (0.8)
		Beech	615 (14)	73.8 (1.7)	3.3 (0.1)
	Yes	Spruce	191 (4)	22.29 (0.5)	1.1 (0.1)

vacuum and pressure are applied during impregnation procedure (Lesar et al., 2008). On the other hand, influence of montan wax on preservatives' loadings was insignificant at beech wood specimens. Specimens impregnated with aqueous solution without wax retained 609 kg/m^3, and at the ones impregnated with 12% of montan wax, uptake of 615 kg/m^3 was determined (Table 1). This reflects the fact that voids (pits) between cells in beech wood are bigger than in spruce wood, therefore montan wax emulsion can penetrate wood easier than at spruce wood. Beech wood is known to be more permeable than spruce wood (EN 350-2, 2005), therefore composition of preservative solution did not have that prominent influence on loadings as reported for spruce wood.

Fungicidal properties of the boron-impregnated wood were tested according to the modified EN 113 procedure. Mass loss of the control specimens was higher than 25% required by standard, which proves that all the strains used were vital. The highest mass losses of spruce wood specimens, caused by brown rot fungi, were observed at *G. trabeum* (44.0%), followed by *S. lacrymans* (40.5%) and *A. vaillantii* (30.3%). White rot fungi decayed considerable portion of beech wood as well. The most effective was *H. fragiforme* (46.3%), followed by *Picea ostreatus* (30.4%) and *T. versicolor* (27.8%) (Table 2).

The main object of this part of research was to determine possible synergistic effects between montan wax and boron compounds. Montan wax itself exerts influence on the fungicidal properties of impregnated wood. The most important mode of fungicidal action is hydrophobation of wooden surfaces (Kurt et al., 2008). Although water repellence improves performance of wood in outdoor applications, it has to be considered that this mechanism is usually insufficient to protect wood against wood decay fungi, particularly in use class III and class IV applications.

Data presented in Table 2 clearly indicates that emulsion of montan wax itself improves resistance of impregnated wood against wood decay fungi. However, impregnation with montan wax emulsion itself was not enough to fulfil requirements of the standards. Specimens impregnated with montan wax emulsion of the highest concentration (12%), exposed to *P. ostreatus* and *G. trabeum* lost approximately 20% less initial mass than control specimens. Influence of montan wax emulsion was even more prominent at montan wax-impregnated specimens exposed to *A. vaillantii* and *S. lacrymans*. At those two fungi, 50% lower mass loss of montan wax-impregnated specimens was observed than of control ones. As those results were relatively good, we were interested in the mode of action of montan wax emulsion. There are two possibilities for improved performance of the wax/boron preservative system: it may have a direct fungicidal effect or there is some physical effect as an underlying mechanism of improved performance. In order to briefly elucidate this issue, montan wax emulsion was introduced to nutrient medium. Growth of the fungal cultures on medium with and without montan wax was compared. The results showed that fungal mycelia were able to grow on the medium containing 0.25% of montan wax without retardation. This indicates that montan wax emulsion does not have fungicidal properties, but there must be some other mechanisms involved. One of the possible explanations is that there is a thin film formed in the interior of the cell wall, which delays water and enzymes diffusion and therefore slows down decay processes as well. This presumption is further supported by sorption observation of montan wax-impregnated wood. Previous publications (Warth, 1959) support this presumption. Furthermore, Melanšek (2008) proved that moisture content of montan wax-treated wood soaked in water is significantly lower compared to control-untreated specimens.

Results of the boron testing confirmed prominent fungicidal efficacy of boron compounds (Freitag and Morrell, 2005). Similar to the report by Carr (1964), *G. trabeum* was found the most boron sensitive species among six fungal species tested in this investigation. The results showed that retention of 0.2 kg/m^3 of boric acid

Table 2
Mass loss of the specimens impregnated with aqueous solutions of boric acid in several concentrations (B conc.) and montan wax emulsions in two concentrations (montan wax conc.) after 12 weeks of exposure to wood decay fungi. Standard deviations are given in the parentheses.

B conc. (ppm)	Montan wax conc. (%)	*G. trabeum*	*A. vaillantii*	*S. lacrymans*	*T. versicolor*	*H. fragiforme*	*P. ostreatus*
		Mass loss (%)					
0	0	44.0 (5.9)	30.3 (6.7)	40.5 (7.0)	27.8 (4.5)	46.3 (9.3)	30.4 (5.7)
	6	34.4 (4.2)	15.1 (4.8)	21.2 (6.0)	20.7 (2.1)	30.5 (3.6)	24.2 (3.3)
	12	29.2 (4.8)	18.0 (3.6)	16.4 (1.7)	13.4 (2.0)	19.7 (7.1)	18.3 (4.9)
22 (0.1[a])	0	17.4 (9.9)	13.2 (4.0)	12.9 (9.8)	17.5 (3.2)	41.5 (3.4)	21.1 (2.8)
	6	0.8 (0.2)	2.0 (2.1)	8.2 (2.1)	2.7 (1.5)	25.2 (6.2)	14.8 (3.1)
	12	7.9 (7.4)	10.9 (1.5)	10.1 (2.0)	7.2 (3.5)	25.3 (1.9)	13.8 (2.2)
44 (0.2[a])	0	0.0 (1.4)	16.1 (3.7)	17.6 (5.4)	15.5 (3.7)	37.6 (3.8)	22.3 (4.5)
	6	2.8 (1.7)	1.8 (2.2)	9.6 (4.3)	10.4 (2.4)	32.6 (4.8)	20.2 (4.1)
	12	0.4 (0.0)	11.8 (2.3)	12.6 (1.3)	10.7 (4.1)	21.3 (4.0)	15.3 (1.8)
88 (0.4[a])	0	0.3 (0.1)	0.0 (2.4)	0.4 (0.9)	0.5 (0.1)	32.3 (5.8)	10.4 (3.4)
	6	1.4 (0.5)	0.0 (0.5)	0.0 (0.4)	1.0 (0.3)	21.0 (5.1)	9.5 (2.9)
	12	0.8 (0.6)	0.0 (0.5)	3.4 (1.6)	0.8 (0.3)	20.8 (2.4)	9.3 (1.5)
176 (0.8[a])	0	0.7 (0.3)	0.0 (0.3)	0.0 (0.3)	0.5 (0.2)	2.0 (1.7)	2.7 (1.1)
	6	0.2 (1.1)	0.0 (0.3)	0.4 (0.5)	0.7 (0.2)	1.2 (0.8)	2.1 (1.4)
	12	1.5 (1.0)	0.2 (0.2)	0.7 (0.4)	1.1 (0.4)	3.8 (2.5)	2.5 (1.1)

[a] Targeted retention of boric acid in the impregnated samples expressed in kg/m^3.

(BA) was enough to inhibit the growth of this fungus. Furthermore, the retention of 0.4 kg BA/m^3 was required to prevent decay caused by *A. vaillantii*, *S. lacrymans* and *T. versicolor*. *H. fragiforme* and *P. ostreatus* proved to be the most boron resistant species in the experiment. Approximately 0.8 kg BA/m^3 was required to inhibit those two fungi (Table 2). The data showed that tested fungi were slightly more sensitive to boron than reported in the literature. It is evident from cited references that between 0.4 and 1.4 of BA kg/m^3 is required to fulfil requirements of the agar blocks testing (Becker, 1959). For soil block test, slightly higher loadings are required (Beachler and Roth, 1956), as diffusion of boron, and consequent boron losses, at solid block test are more prominent than at agar block tests.

Addition of montan wax emulsion into boron-based preservative solutions considerably improves fungicidal properties of the system. Synergistic effect of combination of boron and montan wax emulsion is well resolved from Table 2. However, combination of boric acid and montan wax emulsion of lower concentration was in most of the cases more effective than combination of boric acid and montan wax emulsion of higher concentration. It is believed that the main reason of lower efficacy of preservative solution on the basis of montan wax emulsion of the higher concentration resulted in lower retention of those solutions as reported above.

Minimal inhibitory concentration of boron decreased considerably in the presence of montan wax. Approximately 50% lower boric acid retentions (concentrations) are required in the presence of montan wax. For example, in tests with *G. trabeum* and *A. vaillantii* only 22 ppm of boron in preservative solution is enough in combination with montan wax ($c_{\text{montan wax}} = 6\%$), to prevent decay. In order to avoid damage caused by *S. lacrymans* approximately 88 ppm of boron had to be introduced into montan wax emulsion of the lowest concentration. Slightly less significant, but still prominent, effect of montan wax on efficacy of boron is observed at the species most resistant to boron, *H. fragiforme* and *P. ostreatus* (Table 2). Therefore, the presented data are clear evidence that efficacy of boron compounds can be significantly improved with addition of montan wax emulsion. As boron compounds are predominately used for applications in use class II and class III, where brown rot species are more frequent decay factors (Unger et al., 2001), it is particularly important that synergistic effect of montan wax on boron compounds is more prominent at brown rot fungi than at white rot ones.

Leaching tests were performed with one concentration of boron in preservative solutions only ($c_B = 0.1\%$). This concentration was chosen, as it was proven in our experiment, that is sufficient to inhibit growth of all fungi tested and on the other hand it is frequently used in commercial preservative solutions as well (Freitag and Morrell, 2005). In order to determine effect of montan wax on boron fixation, four different leaching procedures were applied. Two of them are continuous (EN 84 and ENV 1250-2) and two are non-continuous ones (OECD and prCEN/TS 15119-1). EN 84 method is considered as the most severe, as axial surfaces of the specimens are not sealed, and as specimens are vacuum treated with water before leaching. Potential surface hydrophobic effect cannot therefore be expressed. This method was initially designed for preconditioning of the specimens prior to biological testing. Indeed, during two weeks of leaching of specimens, treated with boron without montan wax, all boron has emitted from the specimens. Furthermore, from the data presented in Table 3 it can be resolved that approximately 85% of retained boron has emitted from wood during first week of leaching (Table 3).

Despite of the fact that leaching performed according to ENV 1250-2 method is considered less severe (Hughes, 1999), results of the boron leaching from specimens impregnated with aqueous solution of the boric acid do not prove that presumption. In both cases comparable ratios of boron emitted from wood (Table 3). It is interesting that the major part, approximately 60% of the total leached boron, emitted from wood during first 7 h of leaching according to the ENV 1250-2 protocol (Table 3). This indicates that even the short period of leaching resulted in considerable boron loss. This finding is in line with the observation on boron leaching determined with non-continuous leaching according to the OECD recommendation. From the data presented in Table 3 it is evident, that 36% of the retained boron is leached from wood during the first week of leaching. However, after three weeks of non-continuous leaching, in average 73.5% of boron has leached from specimens impregnated with the boric acid-based solution without montan wax. The least severe method was prCEN/TS 15119-1 one, where only 38.8% of boron was leached from impregnated wood. Comparison of both non-continuous leaching protocols is influenced by the ratio between soaking and drying. This ratio between soaking and drying time at prCEN/TS 15119-1 is around 1:1400. In contrary at OECD this ratio is significantly lower 1:36.

It was expected that addition of montan wax emulsion into aqueous solution of boric acid would reduce boron leaching from impregnated specimens. From the data presented in Table 3 it can be evident, that addition of montan wax into boron-based aqueous solutions reduced leaching of boron from impregnated wood. At specimens leached according to the EN 84, 20% less boron was leached from wood, while from the parallel specimens, leached according to the ENV 1250-2 procedure, even higher reduction in boron leaching was observed. Addition of montan wax into the preservative solution reduced boron leaching for prominent 44% as determined by ENV 1250-2 (Table 3).

Table 3

Portion of boron determined in leachates from spruce wood specimens, impregnated with aqueous solution of boric acid (B) and aqueous solution of boric acid and montan wax emulsion (B + montan wax) ($c_B = 0.1\%$; $c_{\text{montan wax}} = 12\%$), regarding to leaching procedure used. Standard deviations are given in the parentheses.

Preservative solution	Leaching procedure	Leaching period[a]			Σ (%)
		1	2	3	
		Leached boron (%)			
B	ENV 1250-2	19.1 (2.5)	29.5 (1.8)	/	48.6 (2.9)
	EN 84	85.0 (4.5)	14.8 (5.7)	/	99.8 (6.2)
	OECD	36.6 (2.8)	22.6 (1.4)	14.2 (0.7)	73.5 (3.1)
	prCEN/TS 15119-1	13.0 (1.5)	16.4 (1.3)	9.3 (0.3)	38.8 (1.4)
B + montan wax	ENV 1250-2	22.4 (6.0)	33.2 (0.3)	/	55.6 (5.9)
	EN 84	63.8 (5.2)	12.8 (3.1)	/	76.6 (8.3)
	OECD	23.2 (0.3)	15.6 (3.0)	9.4 (1.8)	48.2 (3.8)
	prCEN/TS 15119-1	15.6 (1.7)	13.6 (1.0)	7.0 (2.1)	36.2 (1.9)

[a] EN 84: leaching period 1 – first week, leaching period 2 – second week; ENV 1250-2: leaching period 1 – first day, leaching period 2 – second, third and fourth day; OECD: leaching period 1 – first week, leaching period 2 – second week, leaching period 3 – third week; prCEN/TS 15119-1 leaching period 1 – first week, leaching period 2 – second week, leaching period 3 – third week.

OECD leaching procedure leads us to similar conclusions. Addition of montan wax into aqueous solution of boric acid reduces leaching for 50%. From specimens impregnated with pure boric acid solution, 73.5% of boron was leached, while only 48.2% of boron emitted from wood preserved with combination of boric acid and montan wax (Table 3). Positive effect of montan wax emulsion was notable during the first, second and third leaching period. In contrast to other leaching procedures, prCEN/TS 15119-1 method does not indicate that prominent influence of montan wax on boron leaching as observed at specimens leached according to other procedures. The results in Table 3 show, that addition of montan wax reduces leaching for 6% only.

However, even after the most severe leaching (EN 84), approximately 25% of boron that was introduced into wood by impregnation remained in wood. Our results of fungicidal testing showed that remained boric acid content in wood (0.73 kg/m^3) in synergism with montan wax exhibits sufficient protection at least against the most important wood decay fungi (Table 2). Boron compounds are predominately used in use class II and class III applications, where brown rot fungi are more frequent than white rot ones. From the data presented in Table 2, it is well resolved that brown rot fungal species are more susceptible to boron than white rot ones, what furthermore indicates that remaining boron is sufficient to limit possibility of fungal decay.

Analysis of the leaching results showed that surface hydrophobation is not the only mode of wood preservation by montan wax. This phenomenon is important and probably reduces boron leaching particularly at OECD protocol and slightly less at ENV 1250-2 procedure. However, presume stipulation could be made that hydrophobation is surpassed during EN 84 leaching. Therefore, one of the reasons for this reduced boron leaching in the presence of montan wax could originate in the formation of a thin film in the wood cell lumina. Such occurrence delayed and diminished boron leaching. Formation of barriers on wax-impregnated wood was supported by microscopy observation (Lesar et al., 2008).

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3.7 VPLIV EMULZIJE PVA NA IZPIRANJE BORA IN BAKRA TER NA UČINKOVITOST DELOVANJA PROTI GLIVAM RAZKROJEVALKAM LESA

INFLUENCE OF PVA EMULSION ON LEACHING OF BORON AND COPPER AND EFFICACY ON WOOD DECAY FUNGI

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Z namenom doseči čim boljšo vezavo v les smo v raziskavi borovo kislino, boraks in bakrov(II) sulfat pentahidrat kombinirali s polivinil acetatno (PVA) emulzijo. Z izbranimi pripravki smo impregnirali vzorce smreke (*Picea abies*) in jih izpostavili trem različnim glivam razkrojevalkam lesa (*Antrodia vaillantii, Gloeophyllum trabeum* in *Trametes versicolor*) po postopku mini blok. Del impregniranih vzorcev smo izpirali v skladu s standardom ENV 1250-2. Ugotovili smo, da dodatek PVA rahlo izboljša vezavo borovih in bakrovih učinkovin v les. Smrekovina, impregnirana s pripravki z najnižjo koncentracijo borovih učinkovin (c_B = 0,1 %), je odporna na vse testne glive, medtem ko je les, zaščiten z raztopinami na osnovi bakra, dobro zaščiten le pred glivama *Gloeophyllum trabeum* in *Trametes versicolor* in neustrezno zaščiten pred glivo *Antrodia vaillantii.* Dodatek emulzije PVA že sam po sebi nekoliko zavre delovanje gliv in izboljša delovanje bakrovih in borovih učinkovin.

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Vpliv emulzije PVA na izpiranje bora in bakra iz lesa ter na učinkovitost delovanja proti glivam razkrojevalkam lesa

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Izvleček

Borove spojine učinkovito delujejo proti glivam razkrojevalkam, a se na žalost v vlažnem okolju izpirajo iz lesa. Z namenom doseči čim boljšo vezavo v les, smo borovo kislino, boraks in bakrov(II) sulfat pentahidrat kombinirali s polivinil acetatno (PVA) emulzijo. Z izbranimi pripravki smo impregnirali vzorce smreke (*Picea abies*) in jih izpostavili trem različnim glivam razkrojevalkam lesa (*Antrodia vaillantii, Gloeophyllum trabeum* in *Trametes versicolor*) po postopku mini blok. Del impregniranih vzorcev smo izpirali v skladu s standardom SIST EN 1250-2. Ugotovili smo, da dodatek PVA-emulzije rahlo izboljša vezavo borovih in bakrovih ionov v les. Smrekovina, impregnirana s pripravki z najnižjo koncentracijo borovih učinkovin (c_B = 0,1 %), je odporna na vse testne glive, medtem ko je les, zaščiten z raztopinami na osnovi bakra, dobro zaščiten pred glivama *Gloeophyllum trabeum* in *Trametes versicolor* in neustrezno zaščiten pred glivo *Antrodia vaillantii.* Dodatek emulzije PVA že sam po sebi nekoliko zavre delovanje gliv in izboljša delovanje bakrovih in borovih učinkovin.

Ključne besede: baker, bor, PVA emulzija, smreka, vezava, zaščita lesa

Influence of PVA emulsion on leaching of boron and copper from wood and efficacy on wood decay fungi

Abstract

*Boron compounds are very effective fungicides, but they leach from wood in wet environments, unfortunately. In order to improve boron fixation, boric acid, borax and copper(II) sulphate were combined with polyvinyl acetate emulsion (PVA). Selected preservative solutions were chosen for impregnation of Norway spruce wood specimens (*Picea abies*). Wood blocks were exposed to three wood decay fungi* Antrodia vaillantii, Gloeophyllum trabeum *and* Trametes versicolor *according to the mini block procedure. Part of impregnated specimens was leached according to the EN 1250-2 procedure. The results showed that addition of PVA emulsion slightly improves copper and boron fixation. Spruce wood impregnated with the lowest concentration of boron based solutions (c_B = 0.1%) was found resistant against tested fungi. In contrast, wood blocks impregnated with copper were sufficiently protected against* G. trabeum *and* T. versicolor *but not against* A. vaillantii. *Furthermore, PVA itself has a negative impact on fungal growth, and it improves performance of boron and copper based aqueous solutions.*

Keywords: *boron, copper, fixation, Norway spruce, PVA emulsion, wood preservation*

1 Uvod

1 Introduction

Borove spojine so ene izmed najstarejših aktivnih učinkovin, ki se še vedno uporabljajo za zaščito lesa. Njihova uporaba je dovoljena tudi po uvedbi direktive o biocidih (Biocidal Products Directive) (BPD 98/8EC; HUMAR, 2004). Glavne lastnosti borovih spojin so širok spekter delovanja proti insektom in glivam, dobra difuzivnost, ki omogoča kakovostno prepojitev slabo permeabilnih lesnih vrst in nizka toksičnost za ljudi in okolje. Akutna toksičnost (LD_{50}) borove kisline in boraksa za sesalce je podobna strupenosti kuhinjske soli (NaCl) (LLOYD 1998). Poleg že naštetega pa imajo borove spojine tudi zaviralni učinek na gorenje, kar je še posebej pomembno za konstrukcijski les (RICHARDSON 1993).

Slaba stran dobre difuzivnosti in topnosti boratov je, da se borove spojine iz impregniranega lesa izpirajo. Zato je uporaba borovih spojin za zaščito lesa omejena na uporabo v prvem in drugem razredu izpostavitve (uporaba v suhih razmerah z občasnim zvišanjem lesne

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vlažnosti nad 18 %). V tretjem razredu izpostavitve se les, impregniran z borovimi spojinami, lahko uporablja v kombinaciji s površinskimi premazi, a izpiranja bora ne moremo preprečiti (ORSLER / HOLLAND 1993), ampak ga lahko le upočasnimo (PEYLO / WILLEITNER 1999). Ena izmed možnosti za zmanjšanje izpiranja bora je uporaba okolju prijaznih hidrofobnih sredstev (PEYLO / WILLEITNER 1995). Hidrofobna sredstva v celičnih lumnih ne vplivajo na zmanjšanje izpiranja bora, zato morajo biti molekule hidrofobnih sredstev tako majhne, da lahko prodrejo v celično steno (PEYLO / WILLEITNER 1995).

Namen našega dela je bil določiti vpliv polivinil acetatne emulzije (PVA) na izpiranje aktivnih učinkovin spojin iz lesa in njihov vpliv na glive razkrojevalke. Emulzija PVA je cenovno ugodna in okoljsko sprejemljiva kemikalija, za katero domnevamo, da bi lahko zmanjšala izpiranje aktivnih učinkovin iz lesa. Glavni cilj raziskave je bilo določiti vpliv emulzije na izpiranje borovih spojin (borova kislina in boraks), za primerjavo pa smo pripravili še vodno raztopino bakrovega(II) sulfata z dodatkom PVA.

2 Materiali in metode

2 Materials and methods

2.1 Zaščitni pripravki

2.1 Preservative solutions

V raziskavi smo uporabili dva tipa vodnih raztopin. Prve so kot aktivno učinkovino vsebovale borove, druge pa bakrove ione. Kot vir bora smo uporabili borovo kislino (Ba) ali boraks (Bx), kot vir bakra pa bakrov(II) sulfat pentahidrat (Cu). Vodne raztopine so vsebovale 0,1 ali 0,5 % bora oziroma bakra. Za zmanjšanje izpiranja aktivnih učinkovin iz lesa smo raztopini dodali PVA-emulzijo (Mekol D3, Mitol Sežana). Zaščitni pripravki so vsebovali dve koncentraciji PVA; 1 in 5 %. Suha snov komercialne PVA-emulzije je znašala 50 %.

2.2 Izpiranje aktivnih učinkovin iz lesa

2.2 Leaching of active ingredients from wood

Vzorce beljave smrekovine (*Picea abies*) (1,5 × 2,5 × 5 cm) smo vakuumsko impregnirani s šestimi različnimi zaščitnimi pripravki po standardu SIST EN 1250-2 (1994). Po impregnaciji smo vzorce štiri tedne sušili, kot to zahteva omenjeni standard.

Izpiranje je potekalo po nekoliko modificiranem protokolu SIST EN 1250-2 (1994). Zaradi poenostavitve in hitrejšega poteka dela smo naredili dve spremembi, v čašo smo vstavili po tri vzorce namesto po pet in mešanje je potekalo na stresalniku (65 hodov/min), medtem ko standard zahteva mešanje z magnetnim mešalom. Izpiranje je potekalo v treh paralelnih čašah, v katere smo vstavili po tri vzorce, skupaj po devet vzorcev na posamezno raztopino/koncentracijo. Zatem smo vzorce obtežili in jih prelili s 300 g destilirane vode. Vodo smo menjavali v intervalih, kot jih zahteva standard. Izpirke iz iste čaše smo zbirali in zlivali v isto posodo.

Za določitve koncentracij bora v izpirkih smo uporabili kvadrupolni masni spektrometer z induktivno sklopljeno plazmo proizvajalca Agilent Technologies, Palo Alto, ZDA (HP 4500). Raztopine smo v sistem vnašali z razpršilnikom (Burgener Mira Mist). Moč plazme je bila 1300 W. Pretok plazemskega plina je bil 15 L min^{-1}, pomožnega plina 0,7 L min^{-1} in nosilnega plina 1,05 L min^{-1}. Temperatura razpršilne komore je bila 4 °C. Oba stožca (vzorčevalni in posnemovalni) sta bila nikljeva.

Standardne raztopine bora za umeritveno krivuljo smo pripravili z razredčevanjem standardne raztopine bora s koncentracijo 1000 mg L^{-1} proizvajalca Merck (Darmstadt, Nemčija). Vzorce smo pred meritvijo 50-krat razredčili z MQ prečiščeno vodo. Končne standardne raztopine bora in raztopine vzorcev (pripravljene za meritev) so vsebovale 1 % (v/v) dušikove(V) kisline. Spominski efekt, ki se pojavi kot posledica vnosa raztopin z visokimi koncentracijami bora, smo preprečili tako, da smo po vsaki meritvi sistem spirali z 20 % (v/v) raztopino amoniaka. Čas izpiranja je bil 60 sekund. Dušikova(V) kislina in raztopina amoniaka (oba proizvajalca Merck) sta bila kvalitete p.a. Za preverjanje točnosti meritev koncentracij bora smo uporabili standardni referenčni material NIST 1643e (kovine v sledovih v vodi).

Delež izpranega bora smo izračunali iz gravimetrično določene količine vnesenega bora v vzorce in količine bora v zbranih izpirkih.

2.3 Test mini blok

2.3 Mini block test

Vzorce beljave smrekovine (*Picea abies*) (0,5 × 10 × 25 mm) smo vakuumsko impregnirali z zaščitnimi raztopinami, kot zahteva standard SIST EN 113 (1996). Po štirih tednih sušenja vzorcev na sobni temperaturi smo jih sušili še 24 ur na 103 °C. Nato smo jim določili absolutno suho maso in jih pred izpostavitvijo glivam 30 min sterilizirali s paro pri tlaku 1,5 bara.

Vzorce smo izpostavili trem različnim glivam razkrojevalkam lesa, dvema izolatoma gliv rjave trohnobe *Gloeophyllum trabeum* – tramovka (Gt2) (ZIM L017) in *Antrodia vaillantii* – bela hišna goba (Pv2) (ZIM L037) ter izolatu, ki povzroča belo trohnobo *Trametes versicolor* – pisana ploskocevka (ZIM pred kratkim izoliran sev). Petrijevke s sterilnim hranilnim gojiščem (krompirjev glukozni agar, PDA – Difco) smo inokulirali z majhnim kosom micelija. V sterilizirano plastično petrijevko z micelijem smo vstavili tri impregnirane in en nezaščiten vzorec (kontrola). Po osmih tednih izpostavitve lesa glivam v rastni komori (T = 25 °C, RH = 85 %) smo vzorcem površinsko odstranili micelij ter jim določili absolutno suho maso in izračunali izgubo mase. Eksperiment smo napravili s petimi ponovitvami.

3 Rezultati in razprava

3 Results and discussion

Borove spojine imajo omejeno topnost v vodi borova kislina (50,0 g/L = 8,7 g B/L) in boraks (51,4 g/L = 5,8 g B/L) pri 20 °C (MERCK 2007). Ob dodajanju PVA-emulzije pa se topnost še poslabša. Maksimalna možna koncentracija emulzije PVA v raztopini z borovo kislino oziroma boraksom je 10 %. Pri pripravi raztopin je pomembno upoštevati vrstni red dodajanja posameznih komponent. PVA-emulzijo je treba najprej razredčiti na želeno koncentracijo (največ 10 %) in nato dodati ustrezno količino borove kisline oziroma boraksa. Enako velja za pripravo raztopin z bakrovim(II) sulfatom pentahidratom.

3.1 Izpiranje

3.1 Leaching

Bor v lesu ni trdno vezan, temveč v primeru višje lesne vlažnosti dobro prehaja z mest z višjo koncentracijo na mesta z nižjo. To je razvidno tudi iz primerjave vezave borovih in bakrovih ionov iz lesa. Na primer, iz smrekovine, zaščitene s pripravkom na osnovi borove kisline (Ba) nizke koncentracije (c_B = 0,1 %), se je izpralo 40 % več aktivnih učinkovin (67,2 %) kot iz smrekovine, prepojene s pripravki na osnovi bakra iste koncentracije (38,9 %). Nekoliko manjša razlika je opazna pri pripravkih z višjo koncentracijo biocidov. Dobra difuzivnost bora je vzrok za močno izpiranje iz lesa v vlažnih razmerah.

Iz kontrolnih vzorcev, impregniranih z borovo kislino (Ba) oziroma boraksom (Bx), se je izpralo med 49,7 in 67,2 % bora (preglednica 1). Podobne vrednosti smo zasledili tudi v literaturi (PEYLO / WILLEITNER 1995; GEZER / MICHAEL / MORRELL 1999). Citirani avtorji poročajo, da se je iz lesa, impregniranega z borovo kislino v laboratorijskih razmerah, v povprečju izlužilo med 50 in 75 % borovih učinkovin. Dobra izpirljivost borovih učinkovin je razlog, da teh biocidov ne uporabljamo samostojno v tretjem oziroma četrtem razredu izpostavitve. Pripravki, kjer smo kot vir bora uporabili boraks, so se v les vezali rahlo bolje kot pripravki na osnovi borove kisline. Pri obeh pripravkih pa smo opazili, da so se pripravki z višjo koncentracijo borovih ionov v les vezali bolje kot tisti, kjer je bilo bora manj (preglednica 1), kar se ujema z ugotovitvami iz literature (GEZER / MICHAEL / MORRELL 1999).

Dodatek emulzije PVA je v večini primerov zmanjšal izpiranje aktivnih učinkovin iz lesa. Količina izpranega bora iz vzorcev, impregniranih s pripravki borovih spojin in PVA-emulzije, variira med 25,9 in 78,7 % (preglednica 1). Vezava bora je odvisna od koncentracije in sestave zaščitnega pripravka. Dodatek emulzije PVA zaščitenim pripravkom na osnovi borovih spojin izboljša vezavo pripravkov z višjo koncentracije bora, medtem ko na vezavo bora v les, impregniran s pripravki nizke koncentracije, nima vpliva, ali pa je vpliv celo negativen (preglednica 1). Pripravek na osnovi boraksa (c_B = 0,5 %) in 1 % emulzije PVA se je izkazal za najbolj odpornega proti izpiranju, saj se je iz lesa izločilo le 25,9 % borovih spojin. V primeru, ko smo les prepojili s pripravkom na osnovi boraksa (c_B = 0,5 %) in 5 % emulzije PVA, je dodatek emulzije vplival negativno na vezavo borovih spojin v les. Negativen, vendar ne tako izrazit, vpliv višjih koncentracij emulzije PVA smo opazili tudi pri primerljivem pripravku na osnovi borove kisline. Razlogov za to razliko si ne znamo v celoti pojasniti, možen vzrok za to razliko pa je viskoznost. Morda so bile raztopine s 5 % emulzijo PVA preveč viskozne in zaradi prevelikih monomerov niso prodrle dovolj globoko v celično steno in zato niso imele tako izrazitega vpliva na vezavo kot pripravki z nižjo koncentracijo emulzije. Zato je večina pripravka ostala v lumnih celic, kjer so se borove spojine oborile in bile tako bistveno bolj izpostavljene izpiranju kot tiste borove spojine, ki so prodrle v celično steno. Na splošno lahko zaključimo, da je bil vpliv emulzije PVA na vezavo bora pozitiven, vendar ne v zadostni meri, da bi tako prepojeni les lahko uporabili v tretjem oziroma četrtem razredu izpostavitve. Naši rezultati se ujemajo z ugotovitvami GEZER / MICHAEL / MORRELL (1999), ki so skušali izboljšati vezavo borovih spojin v les z dodatkom polietilenglikola. Ugotovili so, da polietilenglikol v zaščitnem pripravku z borovo kislino oziroma boraksom nima učinka na vezavo bora, ker večina polietilen glikola ostane v celičnem lumnu in ne prodre v celično steno. Drugi razlog za večje izpiranje lesa, impregniranega s pripravki na osnovi PVA, je nasproten. Če so vodne emulzije PVA prodrle v celično steno, se impregnirani les med sušenjem zaradi fizičnih ovir ni toliko skrčil kot neimpregnirani les. Ker so celične fibrile ostale razmaknjene, je voda laže in hitreje prodrla v les, kar se kaže v večjem izpiranju borovih spojin iz lesa.

Preglednica 1: Izpiranje borovih in bakrovih učinkovin iz impregniranega lesa, določeno v skladu z metodo SIST EN 1250-2

Table 1: *Leaching of boron and copper ingredients from impregnated specimens determined according to the standard procedure (SIST EN 1250-2)*

Zaščitni pripravek *Preservative solution*	c_{pva} [%]	$c_B = c_{Cu}$ [%]	Izpiranje bora [%] *Boron/copper leaching* [%]
Ba	-	0,1	67,2
		0,5	50,0
Bx	-	0,1	60,7
		0,5	49,7
Cu	-	0,1	38,9
		0,5	37,2
PVABa	1	0,1	70,9
		0,5	38,7
	5	0,1	50,8
		0,5	44,1
PVABx	1	0,1	68,2
		0,5	25,9
	5	0,1	78,7
		0,5	55,4
PVACu	5	0,1	54,6
		0,5	24,2

Za primerjavo smo primerjali tudi les, impregniran z vodno raztopino bakrovega(II) sulfata in emulzijo PVA. Podobno kot pri borovih pripravkih smo ugotovili, da dodatek emulzije PVA poslabša vezavo pripravkov z nizko koncentracijo učinkovin in izboljša vezavo pripravkov z visoko koncentracijo Cu (preglednica 1). Kakorkoli že, PVA ni bistveno izboljšala vezave bakrovih spojin v les. Izpiranje Cu iz lesa je še vedno previsoko, da bi to rešitev lahko uporabili za zaščito lesa na prostem. Bistveno boljšo vezavo bakrovih učinkovin v les lahko dosežemo že z dodajanjem etanolamina (HUMAR / ŽLINDRA / POHLEVEN 2007). Menimo, da bi morali za boljšo vezavo borovih spojin v les uporabiti spojine, ki omogočajo tvorbo tankih, za vodo slabo prepustnih filmov, kot so na primer vodne emulzije voskov.

3.2 Fungicidne lastnosti impregniranega lesa

3.2 Fungicidal properties of impregnated wood

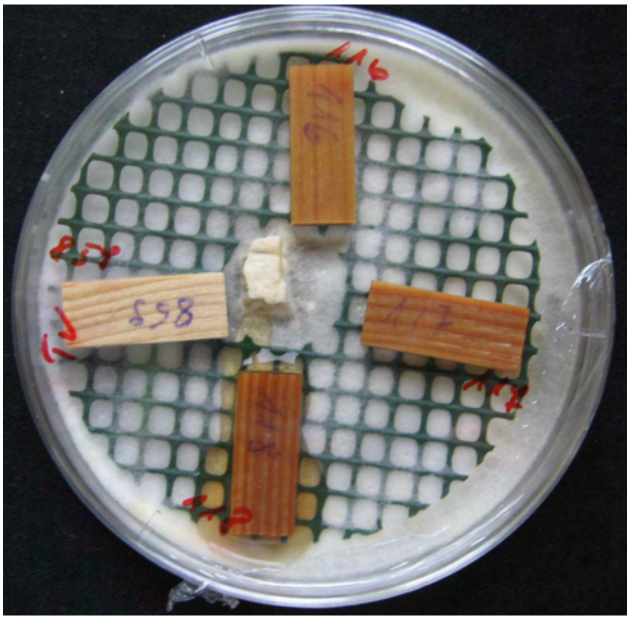
Za praktično uporabo zaščitenega lesa je poleg zadostne vezave aktivnih učinkovin v les pomembno, da je zaščiten les v zadostni meri odporen proti lesnim glivam. Zato smo v drugem delu eksperimenta preverjali učinkovitost delovanja testnih zaščitnih pripravkov na glive razkrojevalke lesa. Vse uporabljene glive so bile vitalne. Izguba mase kontrolnih vzorcev je bila pri vseh glivah pričakovana in je znašala 35,1 % pri tramovki (*Gloeophyllum trabeum*), 23,4 % pri beli hišni gobi (*Antrodia vaillantii*) in 11,0 % pri pisani ploskocevki (*Trametes versicolor*) (preglednica 2). Vzrok za tako nizko izgubo mase kontrolnih vzorcev, izpostavljenih glivi *T. versicolor*, je v uporabljeni lesni vrsti vzorcev. *T. versicolor* je gliva bele trohnobe, ki v naravi bolje razkraja les listavcev kot pa les iglavcev, mi pa smo za eksperiment uporabili smrekovino.

Preglednica 2: Izguba mase kontrolnih in impregniranih vzorcev smrekovine (*Picea abies*) po osmih tednih izpostavitve glivam razkrojevalkam lesa.

Table 2: *Mass loss of control and impregnated Norway spruce (Picea abies) specimens after eight weeks of their exposure to wood decay fungi.*

Zaščitni pripravek *Preservative solution*	c_{pva} [%]	$c_B = c_{Cu}$ [%]	Izguba mase [%] *Mass loss* [%]		
			G. trabeum	*A. vaillantii*	*T. versicolor*
Ba	-	0,1	0,1	-0,9	0,3
		0,5	1,5	0,9	1,6
Bx	-	0,1	0,6	-0,3	0,8
		0,5	3,7	1,7	3,8
Cu	-	0,1	2,9	8,5	3,8
PVA	1	-	16,6	10,3	1,2
	5	-	2,9	11,1	1,0
PVABa	1	0,1	0,7	0,1	1,0
		0,5	1,0	0,6	1,0
	5	0,1	0,6	0,1	0,6
		0,5	1,3	0,9	1,5
PVABx	1	0,1	0,6	-0,4	0,9
		0,5	2,4	1,8	3,5
	5	0,1	0,6	0,1	0,8
		0,5	2,7	2,5	2,6
PVACu	5	0,1	2,7	6,3	2,6
kontrola *control*	-	-	35,1	23,4	11,0

Izguba mase vseh vzorcev, impregniranih z zaščitnimi pripravki na osnovi borove kisline in boraksa nizke koncentracije ($c_B = 0,1$ %), tistih z dodano emulzijo in tistih brez emulzije, je bila nižja od treh odstotkov (preglednica 2), medtem pa je bila izguba mase vzorcev, zaščitenih s sredstvi na osnovi 0,5 % boraksa (Bx, PVABx), med 1,7 in 3,8 %. Menimo, da ta izguba mase ni posledica delovanja gliv, ampak izpiranja zaščitnega sredstva, saj vzorci z višjo koncentracijo boraksa niso bili preraščeni z micelijem, bili pa so zelo vlažni. Okoli vzorcev so stale lužice rumeno obarvane tekočine (slika 1). Zato predvidevamo, da je med izpostavitvijo glivam prišlo do izpiranja borovih učinkovin iz lesa (ORSLER / HOLLAND 1993). Vzrok za visoko vlažnost lesa je velika higroskopnost borovih spojin (WHITE / DIETENBERGER 1999).



Slika 1: Izcedek pod impregniranimi vzorci med izpostavitvijo glivi *T. versicolor*

Fig. 1: Water spots beneath impregnated specimens exposed to fungus *T. versicolor*

Kakorkoli, pozitivno nas je presenetilo dejstvo, da so dobršno mero odpornosti proti lesnim glivam izkazali tudi vzorci, impregnirani le z vodno emulzijo PVA brez dodanih biocidov. Smrekovina, prepojena z najnižjo koncentracijo PVA, je bila popolnoma odporna proti glivi bele trohnobe *T. versicolor*, medtem ko je bilo treba za zaščito pred glivo tramovko uporabiti petkrat višjo koncentracijo emulzije PVA. Žal pa emulzija sama po sebi ne zaščiti lesa pred glivo *A. vaillantii.* Možnih razlogov za te razlike je več. Glivi *G. trabeum* in *T. versicolor* razkrajata les pretežno z encimatskimi mehanizmi (GREEN III / HIGHLEY 1997).

Verjetno film, ki ga tvori PVA na celičnih stenah, omejuje dostop encimov do celične stene, kar se kaže v nižjih izgubah mase glivam izpostavljenega lesa. Po drugi strani razkroj lesa z glivo *A. vaillantii* temelji predvsem na neencimatskem razkroju lesa, pri čemer igra glavno vlogo oksalna kislina (GREEN III / HIGHLEY 1997). Molekula oksalne kisline je manjša, in zato lahko prodre globlje v les, kar se kaže tudi v večjih izgubah mase (preglednica 2). Rezultati nakazujejo, da bi bilo smiselno preveriti uporabnost emulzije PVA za zaščito lesa tudi v eni izmed prihodnjih raziskav.

Tudi kombinacija bakrovega sulfata in emulzije PVA je dobro zaščitila les pred delovanjem tramovke in pisane ploskocevke (preglednica 2). Žal pa ta koncentracija Cu ni bila zadosti, da bi zaščitila les pred glivo *A. vaillantii*, za katero je dobro znano, da je tolerantna na bakrove pripravke (HUMAR *et al.* 2005). Za zaščito lesa pred to glivo bi morali kombinirati bakrove in borove učinkovine.

4 Zaključki

4 Conclusions

PVA-emulzija nekoliko zmanjša izpiranje borovih učinkovin iz lesa, vendar ne v tolikšni meri, da bi tako prepojeni les lahko uporabili v tretjem oziroma četrtem razredu izpostavitve. Podoben učinek PVA smo opazili tudi pri zaščitnih pripravkih na osnovi bakra. PVA-emulzija tudi bistveno ne izboljša vezave bakra v les. Po drugi strani pa smo opazili, da impregnacija lesa z vodno emulzijo PVA zavre delovanje gliv *G. trabeum*, *A. vaillantii* in *T. versicolor.* Razkrojne procese gliv *G. trabeum, T. versicolor* učinkovito preprečuje že PVA-emulzija (5 %) brez dodanih biocidov, medtem ko proti glivi *A. vaillantii* sama emulzija ni učinkovita. Fungicidno delovanje emulzije PVA lahko izboljšamo z dodajanjem borovih ali bakrovih učinkovin.

5 Povzetek

Les je izpostavljen biotskim in abiotskim dejavnikom razkroja. Glive razkrojevalke lesa so najpomembnejši dejavnik v našem klimatskem prostoru. Da bi preprečili glivni razkroj lesa za zunanjo uporabo, ga moramo zaščititi. Kemična zaščita se danes uporablja samo za namene, kjer razkroja ne moremo preprečiti na kak drug način. Med klasičnimi biocidi so v uporabi ostale samo še borove spojine. Večina drugih biocidov je bila umaknjena s trga po uvedbi direktive o biocidih. Borove spojine so zelo učinkovit fungicid, a se žal v vlažnih razmerah izpirajo iz lesa.

Za zmanjšanje izpiranja bora, borove kisline, boraksa in bakrovega(II) sulfata smo te učinkovine kombinirali s polivinil acetatno emulzijo (PVA). Koncentracija bora ali bakra v zaščitni raztopini je bila 0,1 in 0,5 %, koncentracija PVA pa 1 ali 5 %. Z izbranimi zaščitnimi raztopinami smo impregnirali vzorce smreke (*Picea abies*). Les smo izpostavili trem glivam razkrojevalkam lesa, *Antrodia vaillantii, Gloeophyllum trabeum* in *Trametes versicolor*, kot zahteva postopek mini blok. Del impregniranih vzorcev smo izpirali po standardu EN 1250-2.

Rezultati kažejo da dodatek PVA-emulzije rahlo izboljša vezavo bakra in bora v les, toda ne dovolj za zaščito lesa v stiku z zemljo. Vzorci smrekovine, impregnirani z raztopino na osnovi najnižje koncentracije bora ($c_B = 0{,}1$ %), so bili odporni proti testiranim glivam. Po drugi strani pa je bil les, impregniran z bakrom, zaščiten pred glivama *G. trabeum* and *T. versicolor*, a ne pred baker tolerantno *A. vaillantii.* Zelo pomembna pa je ugotovitev, da ima že sama emulzija PVA zaviralni učinek na rast gliv in izboljša učinek vodnih raztopin na osnovi bora in bakra. Rezultati so pomembni s praktičnega vidika in kažejo na možnost uporabe lesa, zaščitenega s kombinacijo PVA-emulzije in biocidov v zunanjih razmerah, če vlaženje ni prepogosto.

6 Summary

Wood is exposed to biotic and abiotic factors of decay. Wood decay fungi are the most important decay factors in our climate region. In order to prevent fungal decay of wood used outdoors we have to preserve it. Chemical preservation is nowadays utilized only for purposes where decay cannot be prevented by other means of protection. Among classical biocides, only boron compounds are still being used use. Most of the other biocides were removed from the market after the implementation of biocidal products directive. Boron compounds are very effective fungicides, but they frequently leach from wood in wet environment, unfortunately.

In order to reduce boron leaching, boric acid, borax and copper(II) sulphate were combined with polyvinyl acetate emulsion (PVA). Concentration of boron or copper in preservative solutions was 0.1 and 0.5%, respectively. The concentration of PVA in aqueous solutions was 1 or 5%. Selected preservative solutions were chosen for impregnation of Norway spruce wood specimens (*Picea abies*). Wood blocks were exposed to three wood decay fungi *Antrodia vaillantii, Gloeophyllum trabeum* and *Trametes versicolor* according to the mini block procedure. Part of impregnated specimens was leached according to the EN 1250-2 procedure.

The results showed that addition of PVA emulsion slightly improves copper and boron fixation, but not enough to be applied for wood in ground contact. Spruce wood impregnated with the lowest concentration of boron based solutions ($c_B = 0.1\%$) was found resistant against tested fungi. In contrast, wood blocks impregnated with copper were sufficiently protected against *G. trabeum* and *T. versicolor* but not against copper tolerant *A. vaillantii.* Furthermore, PVA itself has inhibitory influence on fungal growth, and it improves performance of boron and copper based aqueous solutions. This result is important from practical point of view, and indicates that combination of PVA emulsion and biocides can be used for protection of wood in outdoor applications, if wetting is not too frequent.

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3.8 VPLIV EMULZIJE MONTANSKEGA VOSKA NA DINAMIKO IZPIRANJA BOROVE KISLINE IZ IMPREGNIRANEGA LESA

INFLUENCE OF MONTAN WAX EMULSIONS ON LEACHING DYNAMICS OF BORIC ACID FROM IMPREGNATED WOOD

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Izpiranje aktivnih učinkovin iz impregniranega lesa je eden izmed najpomembnejših kriterijev za presojanje uporabnosti zaščitnih pripravkov za zaščito lesa na prostem. Z namenom zmanjšati izpiranje borovih učinkovin iz lesa smo vzorce smreke (*Picea abies*) vakuumsko impregnirali s pripravki na osnovi borove kisline in dodatkom emulzije montanskega voska (LGE). Del vzorcev smo impregnirali samo z vodno raztopino borove kisline in jih po impregnaciji in sušenju premazali z emulzijo montanskega voska. Za določanje izpiranja smo uporabili dve nekontinuirni metodi, nestandardna priporočila OECD in standardno prCEN/TS 15119-1. Obe metodi se uporabljata za oceno izpiranja borovih učinkovin iz lesa v drugem in tretjem razredu uporabe. Rezultati kažejo, da dodatek emulzije montanskega voska bistveno ne zmanjša izpiranja borove kisline oziroma ga v nekaterih primerih celo poveča. Vzrok za to je visoka viskoznost montanskega voska, ki ne prodre globoko v les in skupaj z borovo kilsino ostane na površini, od koder se bor brez težav hitro izpere. To so pokazali tudi rezultati izpiranja po metodi OECD, kjer se je že v prvem dnevu testiranja izpralo tudi do 60 % navzete borove kisline. V naslednjih dneh se je količina izpranega bora močno zmanjšala. Izpiranje borove kisline iz vzorcev, ki smo jih najprej impregnirali le z borovo kislino in jih kasneje zaščitili z montanskim voskom, je bilo do 20 % manjše. Obe uporabljeni metodi sta nekontinuirni in obe vodita do podobnih zaključkov, s tem da je metoda OECD veliko bolj agresivna kot prCEN/TS 15119-1.

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INFLUENCE OF MONTAN WAX EMULSIONS ON LEACHING DYNAMICS OF BORIC ACID FROM IMPREGNATED WOOD

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ABSTRACT

Boron biocides are one of the most frequently used components of commercial wood preservatives. They are very effective fungicides and insecticides, but they do not react with wood and thus leach from it in wet applications. In order to reduce leaching of boric acid, montan wax emulsion was introduced to the preservative solution. Spruce wood specimens were vacuum impregnated and afterwards leached according to the novel OECD and prCEN/TS 15119-1 procedures. Those two methods are non-continuous and are used for estimations of boron leaching from use class II and III applications. The results showed that addition of LGE emulsion does not reduce boron leaching significantly. Despite of the fact that both methods applied are non-continuous, it can be evident, that OECD procedure is much more severe than prCEN/TS 15119-1 one.

KEY WORDS: boric acid, leaching, montan wax emulsion, Norway spruce, wood preservation

INTRODUCTION

Boron based compounds are one of the most important classical biocides, that remained on the market even after implementation of European Biocidal Product Directive (BPD 98/8/EC, 1998). Due to their broad spectrum of fungicidal and insecticidal properties, borates are considered more effective preservatives than copper and zinc ones, with the later two performing better only because of their fixation in wood, not their inherent fungicidal activity (Obanda et al. 2008). To inhibit growth of the fungi growing on nutrient medium, between 200 and 400 ppm of boron is necessary. In contrary, to inhibit growth of copper sensitive species 650 ppm and to inhibit growth of copper tolerant up to 1500 ppm of copper is required (Lesar and Humar 2009). Use of borates is limited due to their high mobility and good water solubility what results in insufficient fixation. The solubility and mobility of borates allows them to treat wood species that are difficult to treat with copper-based preservatives. Even when not applied on the whole cross-section, they redistribute by diffusion if sufficient moisture is available in wood to provide one of the most effective preservation systems available today (Peylo and Willeitner 1999).

To increase the use of boron compounds as environmentally benign wood preservatives, several fixation systems have been developed to limit or decrease boron leaching. Some attempts have relied on limiting the water penetration of treated wood using water repellents, monomer and polymer systems (Kartal et. al. 2007). The most important solutions for limiting boron leaching are: combination of boron with glycerol/glyoxal (Taussaint-Davergne et al. 2000), vinyl monomers (Yalinkilic et al. 1999), silanes (Kartal et. al. 2007), alkydes (Peylo and Willeitner 1995), tall oil derivates (Temiz et al. 2008). Despite numerous researches, there is no commercially solution available that could limit boron leaching below 25 %).

In our investigation boron was combined with montan wax. Our previous results showed, that montan wax acts synergistically with boric acid and improve its performance against fungi (Lesar et al. 2008). Crude montan wax belongs to the group of naturally occurring waxes of vegetable origin such as carnauba wax or candelilla wax. It is a mixture of chemical compounds that can be divided into three substance groups: waxes, resins and asphaltic substances. Like existing vegetable hard waxes such as carnauba wax, the pure wax substance in montan wax mainly consists of esters of long-chain acids with long-chain alcohols and free long chains acids. Other components such as free wax alcohols or ketones, paraffins or terpenes are usually present in small quantities (Matthies 2001). Montan wax is used in the form of flakes, powders, pastes with solvents, or aqueous emulsions (Heinrichs 2003). One of the most important advantages of montan wax is capability of forming thin-layer resistant films (Warth 1959). Therefore we anticipated that this thin film could limit water penetration and limit boron emissions from impregnated wood.

There are several standard methods developed to evaluate biocides emissions from impregnated wood. The oldest ones DIN 52172-2 (1972), EN 84 (1994) and ENV 1250-2 (1994) were based on continuous leaching, where specimens were in contact with water within the majority of the leaching procedure. Those standards were designed for testing of wood preservatives in ground contact like CCA or CCB. Boron based biocides are not used in such wet environments as copper based preservatives. Thus novel leaching procedures were developed in past years, as in most of the cases hydrophobic properties of wood can not be expressed if leached according to the continuous methods. The newly designed methods like OECD (2006) and prCEN/TS 15119-1 (2007) are designed for estimation of biocidal emissions from wood in use class III applications (above ground). Those standards are significantly less severe, as specimens are in water contact minor part of the leaching experiment. In present research, boron emissions from impregnated wood were evaluated using non-continuous methods to prove or reject hydrophobic effect of montan waxes.

MATERIAL AND METHODS

Samples (1.5 × 2.5 × 5 cm) made of Norway spruce (*Picea abies*) were vacuum impregnated with different preservative solutions according to the EN 113 (1996) procedure. Preservative solutions consists of montan wax water emulsions (LGE – emulsion, Samson d.o.o., Slovenia) and boric acid (c_B = 0.1 % or 0.5 %). For testing, two types of LGE emulsions were purchased. Emulsion LGE-A contain 6 % and emulsion LGE-B 12 % of montan wax. Specimens used for leaching have end sealed axial surfaces before impregnation(Tab. 1).

Tab. 1: Retention of wax and boron at vacuum impregnated and surface treated specimens. Axial surfaces of specimens were sealed before impregnation. Standard deviations are given in the parentheses

Wax type	c_B	Retention kg.m^{-3}	
		Wax	Boron
Without	0.1	0	0.19 (0.10)
	0.5	0	0.53 (0.29)
LGE-A	0.1	4.78 (1.84)	0.08 (0.03)
	0.5	5.10 (1.57)	0.43 (0.13)
LGE-B	0.1	7.71 (1.13)	0.06 (0.01)
	0.5	8.42 (2.26)	0.35 (0.09)
Surface treated with LGA-B	0.1	4.51 (0.58)	0.15 (0.05)
	0.5	4.74 (0.41)	0.63 (0.40)

Some specimens were impregnated with aqueous solution of boric acid, and afterwards brushed with montan wax type LGE-B. For leaching according to OECD procedure, all combinations of wax emulsions and boric acid were applied, while reduced quantity of preservative solutions were applied for protection of specimens leached in line with prCEN/TS 15119-1 (2007) standard (Tab. 2 and 4).

Tab. 2: Percentages of boron determined in leachates from boron impregnated wood determined according to the OECD (2006) procedure regarding the concentration of montan wax and boron. Standard deviations are given in the parentheses

Wax type	Leaching day										Σ
	c_B	1	2	3	4	5	6	7	8	9	
	Leached boron (%)										
Without	0.1	38 (2)	10 (2)	6 (1)	4 (1)	3 (0)	2 (0)	2 (0)	2 (0)	2 (0)	67 (4)
	0.5	46 (2)	12 (2)	5 (1)	4 (0)	2 (0)	1 (0)	1 (0)	1 (0)	1 (0)	75 (3)
LGE-A	0.1	57 (3)	14 (5)	5 (22)	4 (1)	3 (0)	2 (0)	2 (0)	1 (0)	1 (0)	89 (5)
	0.5	47 (3)	11 (1)	5 (1)	4 (1)	2 (0)	1 (0)	1 (0)	1 (0)	1 (0)	75 (4)
LGE-B	0.1	60 (3)	12 (1)	4 (1)	3 (0)	3 (1)	2 (0)	2 (1)	1 (1)	0 (0)	86 (3)
	0.5	46 (6)	11 (1)	4 (1)	3 (0)	2 (0)	1 (0)	1 (0)	1 (0)	1 (0)	71 (7)
Surface treated with LGA-B	0.1	35 (4)	11 (2)	6 (2)	4 (0)	3 (0)	2 (0)	2 (0)	2 (0)	2 (0)	66 (6)
	0.5	26 (5)	11 (2)	6 (1)	3 (1)	2 (1)	2 (0)	2 (0)	2 (0)	1 (1)	55 (6)

Tab. 3: Moisture content of impregnated wood leached according to the OECD (2006) procedure at the end of each leaching cycle. Standard deviations are given in the parentheses

Wax type	Leaching day									
	cB	1	2	3	4	5	6	7	8	9
	Moisture content (%)									
Without	0.1	17 (3)	19 (3)	18 (3)	20 (3)	20 (2)	20 (2)	20 (2)	21 (2)	22 (2)
	0.5	14 (2)	16 (2)	16 (2)	17 (2)	18 (2)	19 (2)	18 (1)	19 (1)	21 (1)
LGE-A	0.1	14 (4)	17 (4)	17 (3)	19 (4)	20 (3)	19 (3)	19 (3)	20 (3)	23 (3)
	0.5	14 (4)	18 (4)	17 (3)	19 (4)	20 (3)	20 (3)	20 (3)	22 (3)	23 (3)
LGE-B	0.1	12 (1)	15 (2)	14 (2)	16 (2)	17 (2)	17 (2)	17 (3)	18 (2)	19 (2)
	0.5	13 (3)	16 (4)	15 (3)	17 (4)	18 (4)	19 (3)	18 (2)	20 (2)	21 (2)
Surface treated with LGA-B	0.1	14 (2)	18 (3)	17 (3)	19 (3)	20 (3)	21 (3)	20 (3)	22 (3)	23 (3)
	0.5	13 (3)	15 (2)	15 (2)	17 (3)	18 (3)	18 (2)	18 (2)	19 (3)	19 (2)

Tab. 4: Percentages of boron determined in leachates from boron impregnated wood determined according to the prCEN/TS 15119-1 (2007) procedure regarding the concentration of montan wax and boron. Standard deviations are given in the parentheses

Wax type	Leaching day										Σ
	cB	1	2	3	4	5	6	7	8	9	
	Leached boron (%)										
Without	0.1	3 (0)	6 (2)	4 (1)	5 (1)	6 (1)	6 (1)	4 (0)	3 (1)	2 (0)	39 (3)
	0.5	7 (1)	7 (1)	6 (3)	4 (2)	4 (0)	4 (0)	2 (0)	2 (1)	2 (0)	38 (4)
LGE-B	0.1	5 (2)	7 (3)	4 (0)	4 (2)	3 (2)	6 (0)	3 (0)	2 (0)	2 (0)	36 (2)
	0.5	8 (1)	7 (1)	6 (0)	5 (1)	4 (0)	4 (1)	2 (0)	1 (0)	1 (0)	39 (3)

Leaching was performed according to the OECD (2006) and prCEN/TS 15119-1 (2007) procedure. Those methods are non-continuous, thus the specimens were not immersed to water all the time during the leaching, but there are extensive drying periods included as well.

Both methods applied are relatively similar. In order to have comparable results, at both methods three specimens with end sealed axial surfaces were immersed to 300 mL of deionised water. Specimens leached according to OECD method were immersed to water for 1 hour, and air dried for 4 hours and afterwards immersed again for additional 1 hour. This cycle was repeated after two days, in total for nine times in three weeks lasting experiment. Similarly, prCEN/TS 15119-1 protocol prescribes shorter leaching cycles. Specimens are immersed to deionised water for 1 minute, and air dried for 2 hours and afterwards immersed again for 1 min and than dried (2 h) and immersed again (1 min). Leaching protocol prCEN/TS 15119-1 consists of nine above mentioned leaching cycles in three weeks in total. Water was collected after each set of cycle and boron content was determined using inductively coupled plasma mass spectrometer (ICP-MS). For each treatment, nine specimens leached in three parallel vessels was used. Moisture content of wooden specimens leached according to the OECD protocol was determined at the end of each leaching cycle.

The Agilent Technologies (Palo Alto, USA) HP 4500 quadrupole ICP-MS with Burgener Mira Mist nebuliser was used as a detection system for boron. The spray chamber temperature was 4 °C. The plasma RF power was set to 1300 W. Plasma gas flow rate was 15 L min^{-1}, auxiliary gas flow rate 0.7 L min^{-1} and nebuliser gas flow rate 1.05 L min^{-1}. Sampler and skimmer cones were made of nickel. Standard boron solutions for calibration curve were prepared by diluting a stock standard solution of boron (1000 mg L^{-1}) (Merck, Germany). Samples were diluted 50-fold with MQ water prior the analysis. The final standard and sample solutions contained 1 % (v/v) of nitric acid. The memory effect (as a consequence of introduction of solutions with high boron concentration) was eliminated by washing the system with 20 % (v/v) ammonia solution after each sample (Al-Ammar et al. 1999). The washout time was 60 seconds. Analytical grade nitric acid and ammonia solution (Merck, Germany) were used. NIST standard reference material 1643e (trace elements in water) was used to verify the accuracy of the measurements.

RESULTS AND DISCUSSION

As a result of impregnation process, specimens retained between 64 and 193 kg.m^{-3} of preservative solutions. Those values are rather low but it has to be considered, that axial surfaces of the specimens were sealed with epoxy coating. Secondly Norway spruce (*Picea abies*) wood is difficult to impregnate (Morrell and Morris 2002). The highest loadings were observed at specimens impregnated with aqueous solution without addition of wax (193 kg.m^{-3}) and the lowest one at specimens that was impregnated with LGA-B solution with 0.1 % of boron. This clearly indicates that addition of montan wax emulsions reduces penetration of preservative solution to the spruce wood specimens. In dry specimens, between 0.06 and 0.63 kg.m^{-3} of boron (equivalent 0.34 and 3.60 of H_3BO_3 kg.m^{-3}) remained in wood after impregnation (Tab. 1). Those retentions are sufficient to protect wood against most common basidiomycetes in use class II or III (Freitag and Morrell 2005, Lesar and Humar 2009).

Our results proved that boron, does not react with wood, and therefore leaches form wood considerably. From the data presented in Tab. 2 is evident, that between 38 % and 46 % of retained boron is leached from wood during the first leaching cycle of OECD protocol, consisting of two one hours' immersion phases. However, after three weeks of non-continuous OECD leaching, in average 67 % of boron leached from specimens impregnated with the lowest and 75 % of boron was released from the spruce wood specimens impregnated with the boric acid based solution of the highest concentration. However, leaching performed according to the prCEN/TS 15119-1 was les severe (Tab. 4). During first leaching cycle, consisting of three one minutes' immersion phases, between 3 % and 8 % of retained boron was leached, only. This is 5 to 10 times les than observed during first OECD leaching cycle. Furthermore, at the end of leaching prCEN/TS 15119-1 procedure, between 36% and 39% of boron emitted from impregnated wood (Tab. 4). This final value was approximately two times lower than observed at the end of OECD procedure. If those values are compared to other, continuous leaching procedures, it can be seen, that those methods are less severe than continuous leaching protocols. Literature data revealed (Lesar et al. 2008), that from the specimens leached in line with EN 84 (1984) and ENV 1250 guidelines, considerably higher portion of boron was leached. Namely, from specimens impregnated with aqueous solution containing 0.1 % of B, all boron released from the specimens.

It was expected, that addition of montan wax into aqueous solution of boric acid will reduce boron leaching from impregnated specimens. From the data presented in Tab. 2 and 4 it can be evident, that in certain conditions addition of montan wax into boron based aqueous solutions does not reduces leaching of boron from impregnated wood. Even more in the first stages of leaching, addition of montan wax have even negative effect on boron leaching. We presume that the reason for this occurrence resulted in the fact, that more viscose LGE based aqueous solutions did not penetrate that depth as less viscose boric acid based solutions without LGE emulsion. Boron on the surface of LGE/boric acid based aqueous solutions was therefore more exposed to leaching than boron in the centre of the spruce wood specimens impregnated with aqueous solution of boric acid, only. It was even more surprising, that in certain cases addition of LGE emulsion to boron based aqueous solutions have even considerably negative influence on release of boron from impregnated wood. If we compare leaching data with moisture content of wooden specimens after each leaching cycle (OECD procedure only), it can be seen that specimens impregnated with aqueous solutions containing waxes have slightly lower moisture content (Tab. 3). Another interesting observation is that very prominent diffusion appeared at relatively dry specimens. From specimens with average moisture content between 13 % and 14 %, during first day of leaching, between 46 % and 60 % of boron was leached. Perhaps the reason for this originates in fact, that surface of the specimens, where the majority of the boron was present, has considerably higher moisture content than interior of the specimens. However, we were not able to determine the moisture content of the outer part, but of the whole specimens only. Another reason for prominent emissions of boron from leached specimens is fact that the surface of specimens was drying after each leaching cycle, what resulted in mass flow of the water with dissolved boron from interior to the surface of leached specimens.

Part of the specimens, were after impregnation with boron based aqueous solutions surface treated with montan wax. Those specimens were leached according to the OECD procedure only. Retention of wax applied with surface treatment is comparable to the specimens treated with preservative solutions based on montan wax emulsion LGE-A. However, there was considerable difference between those two treatments. At surface treated specimens, the major part of the wax was present on the surface of the specimens, while at vacuum treated specimens dipper penetration of wax was achieved. It seems like that wax introduced into the surface of spruce wood specimens formed a barrier that limit boron leaching. Surface treatment with montan wax reduced emissions from specimens treated with the highest concentration of boron for more than 25 % (Tab. 3). Similar effect of surface applied water repellents is reported by (Peylo and Willeitner 1995) as well.

CONCLUSIONS

Despite of the fact that prCEN/TS 15119-1 leaching procedure is less severe than OECD method, both methods lead us to similar conclusion. Considerable portions of boron are leached from wood in the first leaching cycles, already. The addition of montan wax emulsion to boric acid aqueous solution does not reduce leaching of boron compounds from spruce wood, unfortunately.

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3.9 VPLIV EMULZIJE POLIETILENSKEGA IN OKSIDIRANEGA POLIETILENSKEGA VOSKA NA DINAMIKO IZPIRANJA BOROVE KISLINE IZ IMPREGNIRANE SMREKOVINE

INFLUENCE OF POLYETHYLENE AND OXIDIZED POLYETHYLENE WAX EMULSIONS ON LEACHING DYNAMICS OF BORIC ACID FROM IMPREGNATED SPRUCE WOOD

Boštjan Lesar, Polonca Kralj in Miha Humar

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Borove spojine so ene od največkrat uporabljenih biocidov v komercialnih pripravkih za zaščito lesa. Vendar je uporaba tako zaščitenega lesa v vlažnem okolju omejena, ker se bor zelo izpira iz lesa. Za zmanjšanje izpiranje bora smo pripravili zaščitne raztopine na osnovi borove kisline (c_B = 0,1% ali 0,5 % bora) z dodatkom emulzije polietilenskega (WE1) in emulzije oksidiranega polietilenskega voska (WE6). S pripravljenimi sredstvi smo z vakuumsko tlačnim postopkom impregnirali vzorce smreke in jih nato izpirali po standardih prCEN/TS 15119-1, ENV 1250-2 in EN 84. Izpiranje bora smo določali v izpirkih, ki smo jih zbirali po vnaprej določenih obdobjih. Na koncu vsakega obdobja smo gravimetrično določali vlažnost vzorcev med izpiranjem. Ugotavljamo, da na izpiranje bora prevladujoče vpliva vlažnost lesa med postopkom izpiranja in dodatno še koncentracijski gradient (pogostost menjavanja vode). Dejstvo, da je metoda prCEN/TS 15119-1 manj stroga kot preostali dve metodi, se odraža tudi v rezultatih. Rezultati postopkov izpiranja EN 84 in ENV 125-2 so primerljivi, medtem ko rezultati prCEN/TS 15119-1 testiranja niso v skladu z preostalima metodama. Velik delež bora se je iz lesa izpral že v prvih obdobjih izpiranja. Emulzija oksidiranega polietilenskega voska v kombinaciji s segrevanjem nad točko tališča voska v določeni meri zmanjša izpiranje borovih ionov. Impregnacija lesa z WE1 (emulzijo polietilenskega voska) pa ne zmanjša, ampak celo povečuje izpiranje.

Boštjan Lesar[1], Polonca Kralj[2], Miha Humar[1]

Influence of Polyethylene and Oxidized Polyethylene Wax Emulsions on Leaching Dynamics of Boric Acid from Impregnated Spruce Wood

Utjecaj polietilenske i oksidirane polietilenske voštane emulzije na dinamiku ispiranja borne kiseline iz impregnirane smrekovine

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ABSTRACT • *Boron biocides belong to the most frequently used ingredients of commercial wood preservatives. They are very effective fungicides and insecticides, but they do not react with wood and thus leach from it in wet applications. This fact significantly limits use of boron compounds in the field of wood preservation. In order to reduce leaching of boric acid, the emulsion of polyethylene (WE1) and an emulsion of oxidized polyethylene (WE6) wax were combined with boric acid (c_B = 0.1 % or 0.5 % of boron). Spruce wood specimens were vacuum impregnated and afterwards leached according to the prCEN/TS 15119-1, EN 1250-2 and EN 84 procedures. The results showed that the boron leaching is predominantly influenced by moisture content of wood during leaching, and furthermore by the concentration gradient (frequency of water replacement). The fact that the prCEN/TS 15119-1 leaching procedure is less severe than other two methods is also reflected in the results. The results of the EN 84 and ENV 1250 test are comparable, while the results of the prCEN/TS 15119-1 testing are not in line with the other two methods. Considerable portions of boron are leached from wood in the first leaching cycles, already. WE6 wax emulsion (oxidized polyethylene wax emulsion) in combination with heat treatment reduces boron leaching to a certain extent. On the other hand, impregnation of wood with WE1 (polyethylene wax emulsion) does not reduce it and it even enhances it.*

Key words: *boric acid, leaching, wax emulsion, Norway spruce, wood preservation*

SAŽETAK • *Biocidi bora pripadaju najčešće upotrebljavanim sastojcima komercijalnih zaštitinih sredstava za drvo. Vrlo su učinkovita zaštita od gljiva i insekata, no ne vežu se s drvom i stoga su skloni ispiranju iz drva, posebno kada se takvo drvo primjenjuje u vlažnim uvjetima. Ta činjenica znatno ograničava upotrebu spojeva bora na području zaštite drva. U nastojanju da se smanji ispiranje borne kiseline, polietilenska emulzija (WE1) i oksidirana polietilenska voštana emulzija (WE6) kombinirane su s bornom kiselinom (c_B = 0,1 ili 0,5 % bora). Uzorci smrekovine vakuumski su impregnirani i nakon toga ispirani prema procedurama opisanim u prCEN/TS 15119-1, EN 1250-2 i EN 84. Rezultati su pokazali da na ispiranje bora najviše utječe sadržaj vode u drvu tijekom*

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ispiranja, a zatim gradijent koncentracije (frekvencija zamjene vode). Činjenica da je testiranje ispiranja prema proceduri prCEN/TS 15119-1 manje strogo od druge dvije metode odražava se i na rezultate ispitivanja. Rezultati ispitivanja prema procedurama EN 84 i ENV 1250 usporedivi su, dok se rezultati prema proceduri testiranja prCEN/TS 15119-1 ne mogu usporediti s rezultatima dobivenim drugim dvjema metodama. Znatan dio bora iz impregniranog drva ispire se već u prvom ciklusu ispiranja. WE6 emulzija (oksidirana polietilenska voštana emulzija) u kombinaciji s termičkom obradom donekle smanjuje ispiranje bora. Nasuprot tome, impregnacija drva s WE1 (polietilenskom emulzijom) ne smanjuje već, naprotiv, pojačava ispiranje bora.

***Ključne riječi**: borna kiselina, ispiranje, voštana emulzija, smrekovina, zaštita drva*

1 INTRODUCTION
1. UVOD

Wood preservation in Europe has changed significantly in the past 20 years. There were more changes in the past two decades than in the past 200 years (Connell, 2004). The most important factors that lead to these changes are: increased environmental awareness of the consumers and introduction of the Biocidal Products Directive (BPD 98/8/EC, 1998). It should be considered that there were 89 active ingredients available for wood preservation before introduction of the BPD, and there are only 40 that remained in the list of the approved active ingredients nowadays in the EU. It is forecasted that the number of the approved biocides for wood preservation will decrease further on (Suttie and Englund, 2008).

Boron-based compounds are one of the most important classical biocides that remained in the market after the implementation of the European Biocidal Product Directive (BPD 98/8/EC, 1998). Due to their broad spectrum of fungicidal and insecticidal properties, borates are considered to be more effective preservatives than copper- and zinc-based preservatives, the latter two performing better only because of their fixation in wood, and not because of their inherent fungicidal activity (Obanda *et al*., 2008). Between 200 ppm and 400 ppm of boron is necessary to inhibit the growth of fungi on nutrient medium. On the other hand, 650 ppm is required to inhibit the growth of copper sensitive species, and up to 1500 ppm of copper is required to inhibit the growth of copper tolerant species (Lesar and Humar, 2009). The use of borates is limited due to their high mobility and good water solubility, which results in insufficient fixation. The solubility and mobility of borates allows them to treat wood species that are difficult to treat with copper-based preservatives. Even when not applied on the whole cross-section, they redistribute by diffusion if sufficient moisture is available in wood to provide one of the most effective preservation systems available today (Peylo and Willeitner, 1999).

However, boron compounds have been classified as substances of very high concern due to potential teratogenic effect according to the GHS (Globally Harmonized System). Therefore, the use of boron compound in “do it yourself” is only allowed, if the concentration of boric acid is not more than 5.5 %.

To increase the use of boron compounds as environmentally benign wood preservatives, several fixation systems have been developed to limit or decrease boron leaching. Some attempts have relied on limiting water penetration of treated wood using water repellents, monomer and polymer systems (Kartal *et. al.,* 2007). The most important solutions for limiting boron leaching are: combination of boron with glycerol/glyoxal (Taussaint-Davergne *et al*., 2000), vinyl monomers (Yalinkilic *et al*., 1999), silanes (Kartal *et. al*., 2007), alkydes (Peylo and Willeitner, 1995), tall oil derivates (Temiz *et al*., 2008), and montan wax emulsions (Lesar *et al*., 2009). Despite numerous researches, there is no commercial solution available that could limit boron leaching below 25 % determined according to the standard ENV 1250-2 (2004).

In our investigation boron was combined with polyethylene and oxidized polyethylene wax emulsions. Our previous results showed that these waxes act synergistically with boric acid and improve its performance against fungi (Lesar *et al*., 2009; Lesar and Humar 2010). The treatment of wood with resin/wax water-repellent formulations greatly reduces the rate of water flow in the capillaries and significantly increases the dimensional stability of specimens exposed to wet conditions (Berninghausen *et al*., 2006, Kurt *et al*., 2008). The most important applications of waxes in wood industry are found in particleboard production. Paraffin emulsions are introduced to particleboards, thus reducing the water uptake and improving dimensional stability (Amthor, 1972). Nowadays, wax emulsions are added to the OSB boards for the same reason (Neimsuwan *et al*., 2008). However, there are reports that wax treatment can reduce the water capillary uptake in wood as well (Scholz et al. 2009). Furthermore, wax treated wood exhibited increased compression strength and hardness (Rapp *et al*., 2005). In addition, wax and oil emulsion additives are incorporated into aqueous wood preservatives to reduce checking and improve the appearance of treated wood exposed outdoors (Evans *et al*., 2009). However, up to our best knowledge, this is the first report on the use of polyethylene wax emulsions for improvement of performance of boron-based preservatives.

There are several standard methods developed to evaluate biocides emissions from impregnated wood. The oldest ones DIN 52172-2 (1972), EN 84 (2002) and ENV 1250-2 (2004) were based on continuous leaching, where specimens were in contact with water within the majority of the leaching procedure. These standards were designed for testing wood preservatives in ground contact such as CCA (wood preservative based on Cu, Cr and As compounds) or CCB (wood preservative based on Cu, Cr and B compounds). Boron-based biocides are not used in such wet environments as copper-based preservatives. Thus novel leaching procedures were developed in past years, as in most of the cases hydrophobic properties of wood cannot be expressed if leached according to the continuous methods. The newly designed methods like prCEN/TS

Table 1 Selected properties of undiluted/commercial wax emulsions used
Tablica 1. Određena svojstva upotrijebljenih nerazrijeđenih/komercijalnih voštanih emulzija

Wax emulsion *Voštana emulzija*	**Dry content** *Sadržaj suhe tvari* %	**pH**	**Emulsion viscosity (4 mm 23 °C) ISO 2431** *Viskoznost emulzije* s	**Density** *Gustoća* g/m^3	**Melting point of solids** *Točka topljenja krute tvari* °C	**Average particle size** *Prosječna veličina čestice* nm	**Emulsifier system** *Sustav emulgatora*
WE1	36.4	9.9	20 – 36	1.00	130 – 135	100	Nonionic/anionic
WE6	38.2	8.9	20 – 60	1.00	126 – 133	100	Nonionic/anionic

15119-1 (2007) are designed for estimation of biocidal emissions from wood in use class III (above ground). These standards are significantly less severe, as specimens are in water contact only for the minor part of the leaching experiment. In the present research, boron emissions from impregnated wood were evaluated using continuous and non-continuous methods to prove or reject hydrophobic effect of montan waxes.

2 MATERIAL AND METHODS
2. MATERIJAL I METODE

2.1 Specimens preparation and impregnation
2.1. Priprema uzoraka i impregnacija

Samples (1.5 × 2.5 × 5 cm) made of Norway spruce (*Picea abies*) were vacuum/pressure impregnated with different preservative solutions according to the full cell process (20 min vacuum (0.05 bar), 3 hours pressure (8 bar), 10 min vacuum (0.1 bar). After impregnation, retentions of preservative solutions were determined gravimetrically. Preservative solutions used consist of emulsion of polyethylene (WE1) and an emulsion of oxidized polyethylene (WE6) wax and boric acid (c_B = 0.1 % or 0.5 % of boron). Wax emulsions were purchased from BASF (Germany). Concentrations (dry content) and basic properties of wax emulsions can be obtained from Table 1. Impregnation wax emulsions of two different concentrations were used. Namely, the emulsions WE1 25 and WE 6 25 contain 25 % of the original emulsions, while the emulsions WE1 50 and WE 6 50 contain 50 % of the original emulsions. Control specimens were impregnated with aqueous solutions of boric acid, only. Half of the specimens were dried above melting point of the waxes used (140 °C) prior to leaching. Specimens were dried for 3 hours, which ensured that even the centre of the specimens was heated above 135 °C for one hour as determined with temperature sensor EL-USB-TC Lascar electronics (United Kingdom). Specimens used for leaching according ENV 1250-2 (2004) and EN prCEN/TS 15119-1 (2007) had end sealed axial surfaces prior to leaching, while with specimens that were used for leaching according EN 84 (2002) method, axial surfaces remained unsealed during leaching.

2.2 Leaching procedures
2.2. Procedure ispiranja

Leaching was performed according to three different procedures: EN 84 (2002), ENV 1250-2 (2004), and prCEN/TS 15119-1 (2007). ENV 1250-2 (2004) procedure requires the shortest leaching time; it was completed in only four days. In order to further speed up the experiment, the following two modifications were made: instead of five, three specimens were positioned in the same vessels and water mixing was achieved with shaking on non-rotatory shaker (Kambič) instead of magnetic stirrer. To obtain three parallel leaching procedures, nine specimens per solution/concentration/treatment were put in three vessels (three specimens per vessel). Afterwards, samples in the vessel were positioned with a weight. 300 g of deionized water were added and the vessel with its content was shaken at the frequency of 60 min^{-1}. Water was replaced for six times in four subsequent days, as prescribed by the standard. Leachates from the same vessel were collected and compiled. The concentration of boron in leachates was determined after the first and fourth day of leaching.

EN 84 (2002) protocol requires vacuum pre-treatment of the specimens with water as the first step of leaching; specimens thus take up as much water as possible. Three samples, impregnated by the same treatment were positioned in the vessel and immersed into 300 g of deionized water. There was no water stirring during leaching. Water (300 g) was exchanged ten times in 14 subsequent days. Boron content in leachates was determined after the first day, the first and second week of leaching.

In contrast to ENV 1250-2 (2004) and EN 84 (2002), the prCEN/TS 15119-1 (2007) method is based on non-continuous leaching. The standard prescribes that specimens should be exposed to water for a relatively short period of time within three weeks. Specimens of the same shape and number were soaked in 300 mL of water for one minute only, and afterwards dried for two hours and then leached again for one minute and again dried and leached. This cycle was repeated after two days, in total for nine times in a three-week experiment. Boron content in leachates was determined at the end of each week.

2.3 Detection of boron
2.3. Detekcija bora

The Agilent Technologies (Palo Alto, USA) HP 4500 quadrupole ICP-MS with Burgener Mira Mist nebuliser was used as a detection system for boron. The spray chamber temperature was 4 °C. The plasma RF power was set to 1300 W. Plasma gas flow rate was 15 L·min^{-1}, auxiliary gas flow rate 0.7 L·min^{-1} and nebuliser gas flow rate 1.05 L·min^{-1}. Sampler and skimmer cones were made of nickel. Standard boron solutions for calibration curve were prepared by diluting a stock standard solution of boron (1000 mg·L^{-1}) (Merck, Germany). Samples were diluted 50-fold with MQ water before the analysis. The final standard and sample solutions contained 1 % (v/v) of nitric acid. The memory effect (as a consequence of introduction of solutions with high boron concentration) was eliminated by washing the system with 20 % (v/v) ammonia solution after each sample (Al-Ammar *et al.* 1999). The washout time was 60 seconds. Analytical grade nitric acid and ammonia solution (Merck, Germany) were used. NIST standard reference material 1643e (trace elements in water) was used to verify the accuracy of the measurements.

2.4 Moisture content
2.4. Sadržaj vode

In order to understand leaching mechanisms more precisely, moisture content of leached specimens were gravimetrically determined as well. It is believed that moisture content is a suitable indicator for boron diffusion processes. If wood moisture content is kept low, boron diffusion does not appear. Initial mass was derived from the mass of the oven dried wax treated samples considering (subtracting) mass of the epoxy sealer and wax. Mass of the wax and epoxy sealer was calculated from uptakes of impregnation solution/wax sealer considering dry content. Mass of the wax and epoxy sealer in wood cannot be determined by any other method, as some samples were heated above 140 °C, resulting in degradation of wood and epoxy sealer.

3 RESULTS AND DISCUSSION
3. REZULTATI I DISKUSIJA

As a result of impregnation process, specimens retained between 252 kg/m^3 and 555 kg/m^3 of preservative solutions (Table 2). These values are rather high, but it should be considered that specimens were made of sapwood, and that a rather severe impregnation process was applied. The highest loadings were observed with specimens impregnated with aqueous solution of boric acid ($c_B = 0.5$ %) without wax (555 kg/m^3) and the lowest with specimens that were impregnated with WE1 50 emulsion with 0.5 % of boron. This clearly indicates that the addition of wax emulsions reduces the penetration of preservative solution to spruce wood specimens. The emulsion particles are too big to penetrate the cell wall completely. With dry specimens, between 0.25 kg/m^3 and 2.77 kg/m^3 of boron (equivalent 1.43 and 15.84 of H_3BO_3 kg/m^3) remained in wood after impregnation (Table 2). These retentions are sufficient to protect wood against most common basidiomycetes in use class 2 or 3 (Freitag and Morrell 2005; Lesar and Humar, 2009). As there were considerably higher concentrations of wax in treatment solutions, it can be reasonably expected that there were higher retentions of wax determined in wood. The highest retentions of 49.9 kg/m^3 were determined with wood treated with preservative WE 1 50 with 0.1 % of boron (Table 2).

Our results reconfirmed that boron does not react with wood, and therefore leaches from wood considerably. The data presented in Tables 3, 4 and 5 clearly show the leach of 10 % to 100 % of retained boron from wood, depending on the methods applied. In line with our expectations, the standard procedure EN 84 is the most severe one, while the prCEN/TS 15119-1 method is the least rigorous. One of the factors that influence the intensity of boron leaching is moisture content. The highest average moisture content of the specimens was measured at the end of the EN 84 procedure (87 %), followed by ENV 1250-2 method (54 %) and prCEN/TS 15119-1 protocol (29 %). Moisture content and boron leaching are tightly correlated, which indicates that migration of boron in wood with higher moisture content is more distinctive (Figure 1). Concentration of the boron in preservative solutions without wax does not influence the fixation determined according to the prCEN/TS 15119-1 and ENV 1250-2 procedure. On the other hand, with specimens leached according EN 84 procedure, more prominent leaching was determined with specimens impregnated with lower concentration of aqueous solutions of boric acid (78 %) compared to the specimens treated with the one of the highest concentration (89 %). Additionally, comparison of the boron leaching according to the ENV 1250-2 and according to the EN 84 revealed that concentration gradient influences boron leaching as well. Despite of the fact that EN 84 leached specimens were vacuum impregnated with water at the beginning of the leaching, higher boron emission are determined with ENV 1250-2 leached specimens, where water was re-

Table 2 Uptake of treatment solutions, retention of wax and boron at vacuum/pressure of impregnated Norway spruce wood specimens (standard deviations are given in the parentheses)

Tablica 2. Unos otopine za impregnaciju, zadržanje voska i bora u impregniranim uzorcima smrekovine (u zagradi su dane standardne devijacije)

Emulsion *Emulzija*	c_{wax}* %	c_B** %	**Solution uptake** *Unos otopine* kg/m^3	**Retention** / *Zadržanje* kg/m^3	
				Wax / *vosak*	**Boron** / *bor*
/	0	0.1	493 (111)	0	0.49 (0.14)
		0.5	555 (88)	0	2.77 (0.44)
WE 1	25	0.1	329 (75)	30.9 (7.1)	0.33 (0.08)
		0.5	351 (89)	33.0 (8.4)	1.75 (0.44)
	50	0.1	274 (105)	49.9 (21.0)	0.27 (0.12)
		0.5	252 (54)	45.9 (9.9)	1.26 (0.27)
WE 6	25	0.1	339 (86)	31.9 (8.1)	0.34 (0.09)
		0.5	307 (72)	28.9 (6.8)	1.54 (0.36)
	50	0.1	249 (43)	47.5 (8.3)	0.25 (0.04)
		0.5	257 (50)	49.2 (9.6)	29.29 (0.25)

* Concentration of the original emulsion in the respective solution / *koncentracija izvorne emulzije u odgovarajućoj otopini*

** Concentration of boron in the respective solution / *koncentracija bora u dogovarajućoj otopini* placed for three times during the first day of leaching, than with EN 84 leached specimens where specimens are soaked in the same water for the whole period (Tables 4 and 5). This clearly indicates the influence of concentration gradient on boron leaching. Half of the specimens were heated prior to leaching. Heat treatment itself does not have considerable influence on boron leaching with specimens impregnated with boron-based aqueous solutions without wax emulsions. It was expected that a film of melted wax would be formed on the surface of the samples and on the surface of the cell walls. It was presumed that this film would be a barrier that would limit water as well as boron diffusion. However, our presumptions were not confirmed.

During the first week of leaching according to the prCEN/TS 15119-1 protocol, consisting of nine one-minute immersion phases, between 5 % and 11 % of boron was leached from impregnated specimens. The differences between various treatments are not significant. Furthermore, leaching rates decrease within the second and third week. This result is reasonable, as during the first week, particularly, boron deposited on the surface layer is leached from wood. However, analyses of wood moisture contents revealed that moisture content of respective wooden specimens during the whole process of leaching were comparable (Table 3). It was expected that the addition of wax emulsions into aqueous solution of boric acid would reduce boron leaching from impregnated specimens. From the results presented in Table 3 it can be seen that there was some reduction in boron leaching in certain treatments observed, but it was not as distinctive as expected. In general, from specimens that were impregnated with preservatives based on wax emulsions and boric acid, and not heated prior to leaching, no reduction of boron leaching was observed. Between 11 % and 16 % of boron leached from all impregnated, unheated specimens. On the other hand, with specimens that were heated up to 140 °C, some reduction of leaching was observed. This difference was the most notable with specimens impregnated with preservatives based on emulsion WE1 25. For example, from heated Norway spruce specimens impregnated with WE1 25 (c_B = 0.1 %) 10 % of the retained boron compounds was leached, while 50 % higher leaching rates were determined at parallel specimens that were not heated prior to leaching (Table 3). It seems like that heat treatment causes redistribution and more uniform formation of film than air drying of wood treated with wax emulsions. From the results presented in Table 3 it becomes obvious that preservatives based on aqueous solution of the lowest wax concentration were more effective than the ones of the highest wax concentration. It can be presumed that the preservatives with the highest wax emulsion concentration were too viscose to achieve good penetration in wood.

Leaching of the boron according to the ENV 1250-2 was more distinctive. It should be considered that specimens leached according to the ENV 1250-2

Table 3 Percentages of boron (B) leached from impregnated wood, determined according to the prCEN/TS 15119-1 procedure and moisture content (MC) of the specimens after respective leaching period (Standard deviations to the averages of triplicates are given in the parentheses)

Table 3. Postotak ispranog bora (B) iz impregniranog drva određen prema proceduri prCEN/TS 15119-1i sadržaj vode (MC) u uzorcima nakon odgovarajućeg vremena ispiranja (u zagradama su dane standardne devijacije srednjih vrijednosti triju mjerenja)

Wax type *Tip voska*	c_{wax} %	c_B %	**Heated** *Grijano*	**Leached B during 1st week** *Isprani bor B tijekom prvog tjedna* %	**Leached B during 2nd week** *Isprani bor B tijekom drugog tjedna* %	**Leached B during 3rd week** *Isprani bor B tijekom trećeg tjedna* %	**Sum of leached B** *Zbroj ispranog bora B* %	**MC after 1st week** *Sadržaj vode nakon prvog tjedna* %	**MC after 2nd week** *Sadržaj vode nakon drugog tjedna* %	**MC after 3rd week** *Sadržaj vode nakon trećeg tjedna* %
/	0	0.1	Yes	8 (3)	4 (0)	3 (0)	15 (3)	30 (1)	33 (1)	33 (1)
			No	8 (2)	4 (1)	3 (1)	15 (4)	35 (3)	38 (3)	37 (4)
		0.5	Yes	7 (1)	4 (1)	3 (1)	14 (3)	33 (5)	35 (4)	36 (4)
			No	7 (0)	4 (0)	3 (0)	14 (0)	33 (2)	34 (2)	35 (2)
WE 1	25	0.1	Yes	6 (3)	3 (1)	1 (1)	10 (2)	26 (1)	28 (1)	28 (1)
			No	7 (1)	4 (0)	5 (3)	16 (3)	27 (1)	32 (1)	31 (1)
		0.5	Yes	5 (2)	2 (3)	3 (1)	10 (4)	26 (1)	28 (1)	28 (1)
			No	7 (2)	4 (0)	3 (1)	14 (3)	27 (1)	31 (1)	30 (1)
	50	0.1	Yes	6 (0)	2 (1)	3 (2)	11 (1)	22 (1)	24 (1)	24 (5)
			No	8 (3)	3 (2)	2 (0)	13 (1)	26 (1)	28 (2)	30 (2)
		0.5	Yes	8 (3)	4 (0)	3 (1)	14 (4)	24 (1)	26 (1)	27 (1)
			No	8 (1)	4 (1)	3 (1)	15 (1)	26 (1)	30 (1)	28 (1)
WE 6	25	0.1	Yes	7 (0)	4 (0)	3 (2)	14 (2)	24 (2)	27 (4)	28 (1)
			No	8 (1)	2 (0)	1 (0)	11 (1)	27 (1)	29 (1)	29 (1)
		0.5	Yes	5 (0)	4 (0)	3 (0)	12 (4)	27 (1)	29 (1)	25 (4)
			No	8 (3)	4 (0)	3 (1)	15 (4)	28 (1)	31 (1)	29 (1)
	50	0.1	Yes	7 (1)	4 (1)	2 (0)	12 (1)	23 (1)	26 (7)	25 (2)
			No	11 (3)	3 (1)	2 (0)	16 (4)	26 (1)	27 (1)	27 (1)
		0.5	Yes	8 (0)	4 (2)	2 (1)	14 (3)	24 (2)	25 (4)	25 (1)
			No	7 (3)	3 (1)	3 (0)	13 (4)	27 (1)	29 (1)	28 (1)

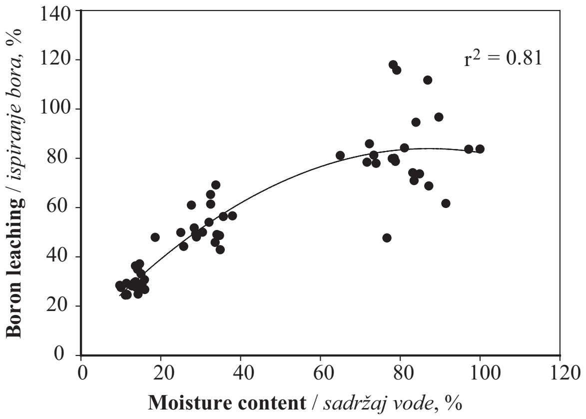

Figure 1 Correlation between wood moisture content and boron leaching
Slika 1. Korelacija između sadržaja vode u drvu i ispiranja bora

procedure were in water contact for almost 80 hours, while specimens leached according to the considerably longer period than specimens leached according to the prCEN/TS 15119-1 protocol (27 min). This reflects in the MC of wood and leached boron. MC of wood at the end varied between 43 % and 69 %, which is considerably higher than MC values measured during prCEN/TS 15119-1 procedure (Tables 3 and 4). In contrast to prCEN/TS 15119-1 method, the difference in boron leaching was firstly evident during the first leaching day (7 hours of leaching). Boron leaching rates varied between 1 % (WE6 50 c_B = 0.5 %) and 69 % (WE1 50 c_B = 0.1 %) (Table 4). It was surprising that the highest leaching was not determined with control specimens (12.5 %), but on the contrary, with specimens impregnated with a combination of WE1 50 wax emulsion and boron of the lowest concentration. From these specimens in average 66 % of boron was leached during the first day. Heat treatment does not influence the leaching results in this case. This result is somehow surprising, but on the other hand in line with previous results (Grof, 2009). Our previous data clearly indicate that the surface of wood impregnated with this wax is not hydrophobic, as it supposed to be, but quite the opposite - hydrophilic. Therefore, these samples took up more water, predominately in the first leaching periods, which results in more prominent leaching of boron from wood. The reason for hydrophilic properties originates in the morphology of the wax surface on the wood. With WE1 treated wood there were small cracks on the surfaces of the wax impregnated wood samples (Lesar *et al.*, in press). The cracks acted as capillaries, which took up water and reduced the contact angles of the surfaces (de Meijer and Militz, 2000). The contact angle of water on vacuum dried WE6 treated wood was about 10°. This makes penetration of water into the wood considerably faster. However, polyethylene wax formed a compact thin film after curing above the melting point, which repelled water. Hydrophilic influence is not evident for WE6 impregnated wood, and therefore the lowest leaching rates were determined in the first hours of leaching (Table 4). After 4 days of leaching, differences between various treatments were less distinctive. The FTIR analysis of the waxes and boric acid showed that there are no chemical interactions between these two ingredients (Lesar *et al.*, in press). However, this issue will be addressed in the future studies. With specimens impregnated with WE1 50 emulsion of the lowest boron concentration, the highest boron leaching rates were determined (84 %). If moisture content and boron leaching are correlated (Figure 1) it is evident that with specimens of lower moisture content less boron was leached from wood. Therefore, with specimens with the one of the lowest MC (WE6 50 c_B = 0.5 %), the lowest leaching rates were determined as well.

However, during the third leaching protocol (EN 84), the most pronounced leaching rates were determined. This was expected, as EN 84 procedure is known as one of the most severe standard leaching procedures. Moisture contents of all specimens were very high. The highest one was determined with control specimens (113 %). Moisture content of all other specimens were lower, as the cell lumina was at least partly filled up with wax, which resulted in lower water uptake compared to control specimens. However, moisture contents of wax treated wood were still two to three times above fibre saturation point, which enables efficient diffusion (Morell and Freitag, 1995). EN 84 method was found less sensitive for determination of boron leaching from wood impregnated with hydrophobic treatments, as all specimens were vacuum treated with water prior to leaching, which diminished the hydrophobic effect. This can also be seen from our results. For example, from control specimens in average 83 % of boron was leached, while from the specimens impregnated with WE1 50 emulsion of the lowest boron concentration, the highest boron leaching rates were determined (98 %), similarly as observed at ENV1250-2 leaching (Tables 4 and 5). One of the reasons for low difference in boron leaching among different treatments is related to MC. As can be obtained from Figure 1, moisture content has more significant influence on boron leaching at lower MC, while at MC higher than 60 % this influence is not significant any more.

Comparison of the methods can be obtained from Figure 2. It can be clearly seen that there is a rather good correlation between moisture content of the specimens after leaching according to various procedures. The correlation varied between 0.68 and 0.38 (Figure 2A, B and C). On the other hand, there is less correlation between boron leaching determined according to various procedures. Although there is some correlation between B leaching ratios determined according to the EN 84 and ENV 1250-2, there is actually no correlation between prCEN/TS 15119-1 method and the other two continuous methods (Figure 2D, E and F). This is predominately due to different approaches. PrCEN/TS 15119-1 method is no-continuous, while the other two methods are the continuous ones.

4 CONCLUSIONS
4. ZAKLJUČCI

The results of the boron leaching studies indicate that boron leaching is predominantly influenced by moisture content of wood during leaching. If wood moisture content is kept low, boron leaching can be slowed down considerably. Considerable portions of boron are leached from wood in the first leaching cycles, already. WE6 wax emulsion (oxidized polyethylene wax emul-

Table 4 Percentages of boron (B) leached from impregnated wood determined according to the ENV 1250-2 procedure and moisture content (MC) of the specimens after respective leaching period. Standard deviations to the averages of triplicates are given in the parentheses.
Tablica 4. Postotak ispranog bora (B) iz impregniranog drva određen prema proceduri ENV 1250-2 i sadržaj vode (MC) u uzorcima nakon odgovarajućeg vremena ispiranja (u zagradama su dane standardne devijacije srednjih vrijednosti triju mjerenja)

Wax type *Tip voska*	c_{wax} %	c_B %	**Heated** *Grijano*	**Leached B during 1st day** *Isprani bor B tijekom prvog dana* %	**Leached B during 2nd, 3rd and 4th day** *Isprani bor B tijekom drugog, trećeg i četvrtog dana* %	**Sum of leached B** *Zbroj ispranog bora B* %	**MC after 1st day** *Sadržaj vode nakon prvog dana* %	**MC at the end** *Sadržaj vode na kraju* %
/	0	0.1	Yes	12 (6)	21 (2)	33 (4)	42 (9)	61 (9)
			No	10 (3)	24 (8)	34 (5)	38 (9)	69 (9)
		0.5	Yes	15 (1)	18 (3)	34 (2)	41 (7)	66 (6)
			No	13 (3)	19 (9)	33 (5)	43 (5)	65 (9)
WE 1	25	0.1	Yes	10 (4)	24 (3)	34 (5)	34 (9)	49 (9)
			No	8 (2)	20 (9)	28 (5)	36 (9)	61 (9)
		0.5	Yes	11 (4)	25 (9)	36 (6)	30 (3)	56 (4)
			No	12 (1)	17 (0)	28 (6)	33 (5)	52 (9)
	50	0.1	Yes	69 (7)	22 (2)	91 (2)	31 (4)	62 (9)
			No	64 (7)	13 (5)	77 (6)	29 (9)	48 (6)
		0.5	Yes	10 (1)	22 (4)	32 (3)	24 (4)	54 (3)
			No	12 (1)	22 (4)	35 (3)	25 (8)	49 (1)
WE 6	25	0.1	Yes	10 (0)	25 (4)	35 (0)	18 (4)	43 (5)
			No	9 (1)	16 (2)	26 (4)	30 (4)	44 (9)
		0.5	Yes	11 (1)	27 (3)	38 (2)	41 (9)	57 (2)
			No	8 (1)	17 (1)	25 (3)	30 (7)	50 (2)
	50	0.1	Yes	8 (1)	20 (3)	29 (2)	24 (7)	49 (3)
			No	10 (1)	21 (1)	30 (3)	34 (9)	50 (9)
		0.5	Yes	1 (1)	28 (1)	29 (1)	26 (9)	48 (2)
			No	1 (1)	17 (1)	19 (1)	27 (5)	48 (2)

Table 5 Percentages of boron (B) leached from impregnated wood determined according to the EN 84 procedure and moisture content (MC) of the specimens after respective leaching period (Standard deviations to the averages of triplicates are given in the parentheses)
Tablica 5. Postotak ispranog bora (B) iz impregniranog drva, određen prema proceduri EN 84 i sadržaj vode (MC) u uzorcima nakon odgovarajućeg vremena ispiranja (u zagradama su dane standardne devijacije srednjih vrijednosti triju mjerenja)

Wax type *Tip voska*	c_{wax} %	c_B %	**Heated** *Grijano*	**Leached B during 1st day** *Isprani bor B tijekom prvog dana* %	**Leached B during 1st week** *Isprani bor B tijekom prvog tjedna* %	**Leached B during 2nd** week / *Isprani bor B tijekom drugog tjedna* %	**Sum of leached B** *Zbroj ispranog bora B* %	**MC after 1st day** *Sadržaj vode nakon prvog dana* %	**MC after 2nd week** *Sadržaj vode nakon drugog tjedna* %
/	0	0.1	Yes	12 (2)	34 (3)	32 (1)	78 (3)	82 (12)	118 (12)
			No	10 (2)	37 (1)	32 (3)	79 (4)	71 (15)	116 (10)
		0.5	Yes	9 (1)	38 (2)	43 (1)	90 (1)	69 (10)	107 (9)
			No	8 (1)	37 (2)	41 (1)	87 (2)	74 (9)	112 (11)
WE 1	25	0.1	Yes	13 (2)	36 (4)	24 (1)	74 (4)	38 (2)	78 (5)
			No	14 (4)	39 (3)	26 (5)	79 (1)	27 (3)	80 (9)
		0.5	Yes	10 (1)	30 (2)	32 (4)	72 (6)	54 (12)	86 (11)
			No	13 (3)	35 (5)	36 (2)	84 (2)	61 (13)	95 (13)
	50	0.1	Yes	17 (2)	36 (5)	45 (2)	97 (7)	46 (11)	84 (10)
			No	16 (3)	39 (4)	45 (5)	100 (8)	38 (10)	84 (12)
		0.5	Yes	12 (1)	38 (3)	34 (1)	83 (4)	33 (5)	71 (5)
			No	14 (4)	35 (2)	29 (4)	78 (5)	36 (7)	80 (13)
WE 6	25	0.1	Yes	19 (2)	29 (4)	23 (1)	72 (7)	38 (9)	78 (14)
			No	16 (1)	32 (2)	26 (4)	73 (7)	33 (11)	81 (8)
		0.5	Yes	9 (1)	36 (4)	37 (2)	81 (1)	49 (11)	84 (7)
			No	12 (3)	33 (4)	34 (1)	79 (6)	38 (13)	79 (8)
	50	0.1	Yes	23 (2)	42 (3)	21 (4)	85 (6)	40 (7)	74 (9)
			No	17 (1)	32 (2)	17 (4)	65 (5)	35 (8)	81 (12)
		0.5	Yes	11 (4)	37 (3)	35 (3)	83 (1)	42 (10)	74 (7)
			No	12 (1)	38 (3)	38 (2)	87 (5)	24 (4)	69 (9)

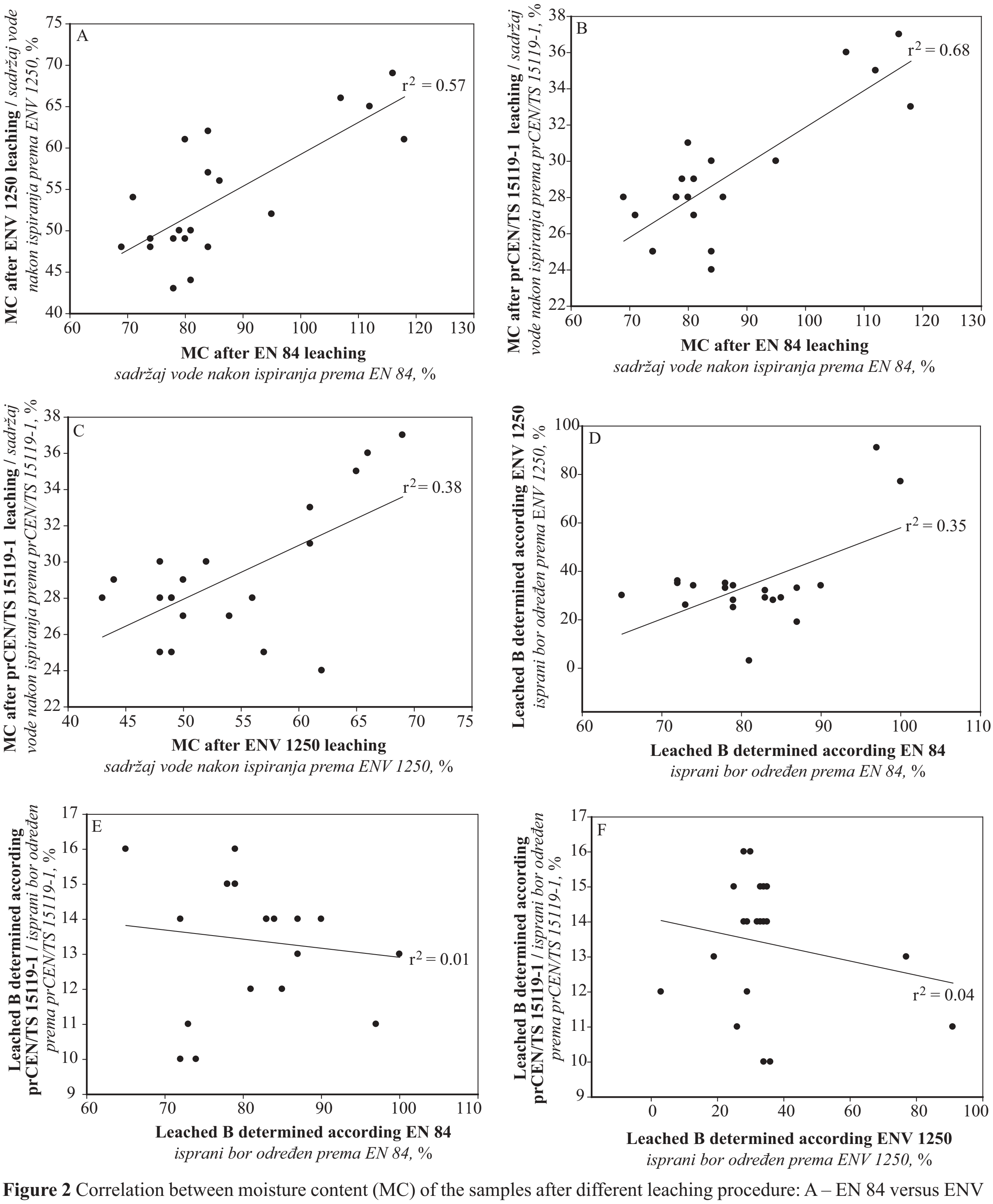

Figure 2 Correlation between moisture content (MC) of the samples after different leaching procedure: A – EN 84 versus ENV 1250-2; B – EN 84 versus prCEN/TS 15119-1; C – ENV 1250-2 versus prCEN/TS 15119-1. Correlation between boron leaching determined according various procedures is shown as well D – EN 84 versus ENV 1250-2; E – EN 84 versus prCEN/TS 15119-1; F – ENV 1250-2 versus prCEN/TS 15119-1.

Slika 2. Korelacija između sadržaja vode (MC) u uzorcima nakon različitih testova ispiranja: A – EN 84 i ENV 1250-2; B – EN 84 i prCEN/TS 15119-1; C – ENV 1250-2 i prCEN/TS 15119-1. Korelacija između vrijednosti ispranog bora određenih različitim metodama testiranja: D – EN 84 i ENV 1250-2; E – EN 84 i prCEN/TS 15119-1; F – ENV 1250-2 i prCEN/TS 15119-1.

sion) in combination with heat treatment reduced boron leaching to a certain extent. On the other hand, impregnation of wood with WE1 (polyethylene wax emulsion) did not reduce it and it even enhanced it.

The fact that prCEN/TS 15119-1 leaching procedure is less severe than other methods is reflected in the results. There is no correlation between boron leaching obtained according to this method and other two methods (EN 84 and ENV 1250-2). From the practical point of view, the method ENV 1250-2 is the most suitable one, as it is rather short and simple. On the other hand, prCEN/TS 15119-1 is the most suitable method for the estimation of the emissions in above ground applications. It provides information regarding leaching dynamics, but this method is rather long lasting and more expensive. In order to further improve the predictability of the applied methods, laboratory methods will be compared to field test results in future.

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3.10 IZPIRANJE BORA IZ LESA, IMPREGNIRANEGA Z ZAŠČITNIM SREDSTVOM NA OSNOVI BOROVE KISLINE IN UTEKOČINJENEGA LESA

LEACHING OF BORON FROM WOOD IMPREGNATED WITH PRESERVATIVES SOLUTION BASED ON BORIC ACID AND LIQUEFIED WOOD

Boštjan Lesar, Franc Budija, Polonca Kralj, Marko Petrič in Miha Humar

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Da bi zmanjšali izpiranja bora iz lesa smo pripravili vodne raztopine borove kisline (c_B = 0,1 % ali 0,5 % bora) v kombinaciji z utekočinjenim lesom (c_{lw} = 11 % ali 33 %) smreke, s katerimi smo po vakuumsko tlačnem postopku impregnirali vzorce smrekovine in bukovine in jih nato izpirali po standardu ENV 1250-2. Rezultati kažejo, da ima utekočinjen les pozitiven učinek na vezavo bora. Ta učinek je bil večji na vzorcih iz smrekovine kot na vzorcih iz bukovine. Najmanj intenzivno izpiranje (15,9 %) borovih spojin je bilo na impregniranih vzorcih smrekovine z vodno raztopino borove kisline (c_B = 0,1 %) in najvišjim deležem utekočinjenega lesa (c_{lw} = 33 %). Izpiranje bora iz impregniranih vzorcev smrekovine samo z borovo kislino, je bilo kar šestkrat višje. Pri omenjeni kobinaciji smo določili najmanj intenzivno izpiranje borovih učinkovin med vsemi testiraniranimi pripravki v naših raziskavah.

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BRIEF ORIGINALS KURZORIGINALIA

Leaching of boron from wood impregnated with preservative solutions based on boric acid and liquefied wood

**Boštjan Lesar · Franc Budija · Polonca Kralj ·
Marko Petrič · Miha Humar**

Received: 2 November 2010

Abstract Reducing boron leaching from impregnated wood has been one of the most challenging tasks for at least 50 years. In order to slow down the leaching of boron, aqueous solutions of boric acid were combined with liquefied spruce wood. The results clearly showed that leaching of boron from spruce wood impregnated with preservative solutions based on boric acid and liquefied wood was significantly reduced.

Auswaschung von Bor aus Holz, das mit Schutzmittellösungen auf Basis von Borsäure und verflüssigtem Holz imprägniert wurde

1 Introduction

Boron based compounds are one of the most important classical biocides that remained on the market after implementation of the European Biocidal Product Directive (1998). Due to their broad spectrum of fungicidal and insecticidal properties, boron based compounds are considered as more effective preservatives than copper and zinc based ones, with the latter two performing better only because of their fixation in wood and not due to their inherent fungicidal activity (Obanda et al. 2008). In order to increase the use of boron compounds as environmentally benign wood preservatives, a variety of fixation systems have been developed: a combination of boron with glycerol/glyoxal, vinyl monomers, silanes, alkydes, tall oil derivates, and montan wax emulsions (Obanda et al. 2008; Lesar et al. 2009). Despite numerous investigations, there is no commercial solution available able to limit boron leaching below 25%, determined according to standard ENV 1250-2 (2004). In order to enable better fixation, boron compounds were combined with liquefied wood and the results of this study are presented herein. Liquefied wood is one of the novel biomaterials derived from wood. It can be used for a variety of applications, such as surface coatings, adhesives etc. (Budija 2010). It is believed that liquefied wood also has potential in wood preservation.

2 Material and methods

The liquefaction of Norway spruce (*Picea abies*) sawdust (0.24 mm fraction) was carried out in a 1 L three-neck glass reactor, equipped with a condenser and a stirring system. The reaction mixture was prepared with 150 g of wood, 450 g of ethylene glycol and 13.5 g of sulfuric acid. The reaction parameters, time (90 min) and temperature (180°C) had been optimized in previous experiments (Budija 2010). Liquefied spruce wood was used for impregnation without any purification or modification, with the exception of dilution with water and subsequent homogenization. Norway spruce and beech (*Fagus sylvatica*) specimens (1.5 cm × 2.5 cm × 5.0 cm) were vacuum/pressure impregnated (20 min vacuum −0.09 MPa; 2 h 0.9 MPa, 10 min vacuum −0.08 MPa) with six preservative solutions based on boric acid and liquefied wood, as can be seen from Table 1. Impregnated specimens were dried for 3 weeks, as proposed by the standard procedure (ENV 1250-2 2004) and then oven dried (103°C; 24 h). In order to speed up leaching protocol ENV 1250-2, the following two modifications were made: water

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Table 1 Influence of boron and liquefied wood concentration in a preservative solution on boron leaching from impregnated wood

Tab. 1 Einfluss der Konzentration von Bor und verflüssigtem Holz in der Schutzmittellösung auf die Auswaschung von Bor aus imprägniertem Holz

Concentration of liquefied wood (%)	Boron concentration (%)	Wood species	Leached B (%)
33	0.1	Beech	39.1
		Spruce	15.9
	0.5	Beech	37.5
		Spruce	29.2
11	0.1	Beech	53.5
		Spruce	27.3
	0.5	Beech	49.8
		Spruce	37.4
0	0.1	Beech	92.1
		Spruce	90.1
	0.5	Beech	46.2
		Spruce	48.6

mixing was achieved with shaking on a shaking device instead of a magnetic stirrer and nine specimens per solution were put into three vessels (three specimens per vessel) in order to have three parallel leaching procedures. Specimens were positioned in the vessel with a ballasting device. Distilled water (300 g) was added and the vessel with its contents was shaken at a frequency of 55 min^{-1}. The water was replaced six times, as proposed by the standard. Leachates from similar samples were collected and mixed together. An Agilent Technologies (Palo Alto, USA) HP 4500 quadrupole ICP-MS with Burgener Mira Mist nebuliser was used as a detection system for boron. The percentages of leached boron were calculated from the amount of retained boron determined gravimetrically and the amount of boron in the collected leachates.

3 Results

The impregnation process resulted in fairly high uptakes of preservative solutions. Specimens retained on average 650 kg/m^3 of liquid. The wood species and composition of the preservative solutions did not have a significant influence on the uptake, for two main reasons. Firstly, the specimens were relatively small, with a high proportion of axial surfaces and secondly, the liquefied wood contained ethylene glycol, which causes wood swelling (Mantanis et al. 1994) and thus also enables penetration of larger molecules of the constituents of liquefied wood into the wood.

Between 46.2% and 92.1% of boron was leached from wood impregnated only with an aqueous solution of boric acid (Fig. 1). Considerably higher leaching rates were determined with specimens impregnated with aqueous solutions of a lower concentration ($c_B = 0.1\%$) compared to parallel specimens impregnated with preservatives of a five times higher boron concentration. This result is in line with previous observations by the authors (Lesar et al. 2009). There was no influence of wood species on the leaching of boron from wood impregnated with a pure boric acid solution. However, the main purpose of this work was to determine the possible influence of liquefied wood on boron fixation. The results (Table 1) clearly showed that the addition of liquefied wood has a positive effect on boron fixation in wood. This effect was more prominent with spruce than with beech. The lowest boron leaching was determined with spruce impregnated with an aqueous solution of boric acid ($c_B = 0.1\%$) and liquefied wood ($c_{lw} = 33\%$). Only 15.9% of retained boron was leached from these specimens. This is almost six times lower than determined with control specimens impregnated with a pure boric acid solution. With specimens impregnated with preservative solutions based on liquefied wood and boric acid of the highest concentration ($c_B = 0.5\%$) fixation was not very high. It seems that the ratio between the boric acid and liquefied wood was too high to achieve better fixation. This presumption is further supported by the leaching results with spruce specimens impregnated with aqueous solutions that contained lower concentrations of liquefied wood ($c_{lw} = 11\%$). A possible explanation for reduced boron leaching is that, during oven drying of the impregnated specimens, self cross-linking of the liquefied wood could occur, as has already been demonstrated. In contrast, supplementation of preservative solutions with liquefied wood did not reduce boron leaching from beech specimens to such an extent as with spruce ones. This might be related to the fact that the liquefied wood was made from spruce. This presumption needs to be addressed in future studies, since the results of this study show that the right combination of liquefied spruce wood and boric acid can have a promising positive effect on reducing boron leaching.

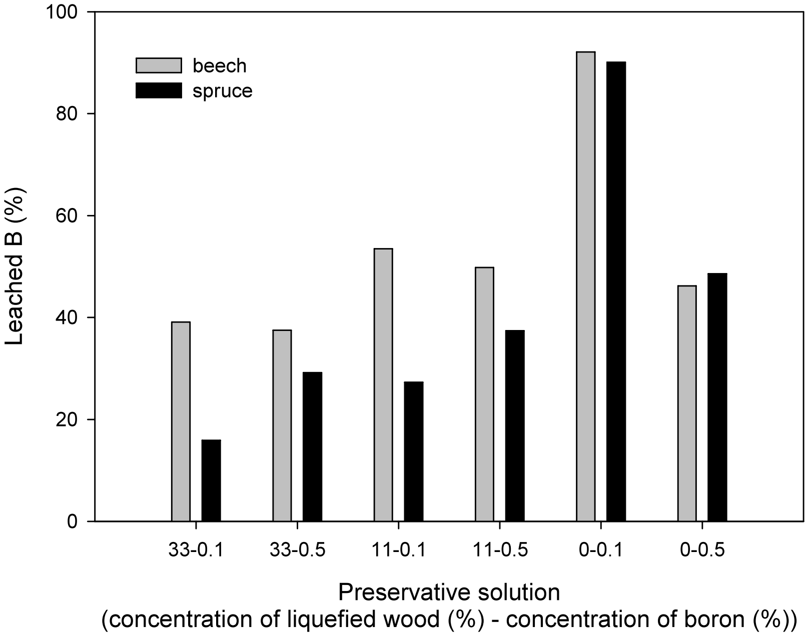

Fig. 1 Comparison of boron leaching from spruce and beech wood with regard to concentration of liquefied wood and boron in preservative solution

Abb. 1 Vergleich der Auswaschung von Bor aus Fichte und Buche in Abhängigkeit der Konzentration von verflüssigtem Holz und Bor in der Schutzmittellösung

4 Conclusion

Addition of liquefied wood to boron based aqueous solution considerably reduces boron leaching from impregnated Norway spruce wood. This effect is less prominent for beech wood.

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3.11 SORPCIJSKE LASTNOSTI LESA, IMPREGNIRANEGA Z BOROVIMI SPOJINAMI, NATRIJEVIM KLORIDOM IN GLUKOZO

SORPTION PROPERTIES OF WOOD IMPREGNATED WITH BORON COMPOUNDS, SODIUM CHLORIDE AND GLUCOSE

Boštjan Lesar, Željko Gorišek in Miha Humar
Drying Technology, 2009, 27: 94–102
Prejeto 25. 5. 2008, sprejeto 19. 8. 2008

Na sorpcijske lastnosti lesa vplivajo tudi različni postopki obdelave lesa, med katerimi je kemična zaščita lesa. Ugotavljali smo vpliv impregnacijskih sredstev in njihove koncentracije na sorpcijske karakteristike impregnirane smrekovine (*Picea abies*) z borovo kislino, boraksom, natrijevim kloridom in glukozo. Spremljali smo ravnovesna stanja v postopkih adsorpcije in desorpcije pri petih stopnjah relativne zračne vlažnosti (φ_1 = 20 %, φ_2 = 33 %, φ_3 = 65 %, φ_4 = 88% in φ_5 = 98 %). Ugotovili smo, da impregnacija bistveno ne vpliva na ravnovesno vlažnost lesa, izpostavljenega nižjim relativnim zračnim vlažnostim. V zgornjem higroskopskem območju na ravnovesne vlažnosti značilno vpliva delež in vrsta impregnacijskega sredstva. Pri posameznih sredstvih se ravnovesna vlažnost sorazmerno povečuje z deležem sredstva v lesu. Najmanjši vpliv na ravnovesne vlažnosti lesa ima borova kislina, največjega pa natrijev klorid. Eksperimentalne podatke smo prilagodili Guggenheim-Andersen-deBoerovemu (GAB) in Dent matematičnemu modelu za natančno razlago sorpcijskega mehanizma impregniranega lesa. Sorpcijske izoterme po modelu GAB kažejo najboljše prilagajanje eksperimentalnim podatkom v spodnjem delu in na sredini higroskopskega območja. Nekoliko večje odstopanje se pojavi pri zračnih vlažnostih nad 65 %. Rezultati kažejo, da je model GAB primeren za napovedovanje vlažnosti impregniranega lesa z borovimi spojinami v spodnjem delu in na sredini higroskopskega območja.

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Sorption Properties of Wood Impregnated with Boron Compounds, Sodium Chloride and Glucose

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Chemical protection is one of the possible treatment processes that influence the sorption characteristics of wood. In the present research we have investigated the influence of biocides (boric acid, borax) and their concentrations on the sorption characteristic of impregnated wood. For comparison, two other chemicals were included in the research as well (NaCl and glucose). The equilibrium moisture content during the adsorption and desorption process at five levels of relative humidity ($\varphi_1 = 20\%$, $\varphi_2 = 33\%$, $\varphi_3 = 65\%$, $\varphi_4 = 88\%$, and $\varphi_5 = 98\%$) was monitored. The results showed that impregnation does not influence the wood moisture content of specimens conditioned at low relative air humidity. In the upper hygroscopic region, moisture content is significantly influenced by the concentration and properties of impregnation chemicals. The Guggenheim-Andersen-deBoer (GAB) and Dent models of sorption isotherms was fitted to experimental data to explain the sorption mechanisms in detail.

Keywords Boron compounds; GAB parameters; Moisture content; Sorption; Wood protection

INTRODUCTION

Wood is hygroscopic due to its specific chemical composition and a large inner surface. Therefore, the moisture content of wood oscillates regarding to oscillating climatic conditions. At stable conditions, wood reaches the hygroscopic equilibrium or the equilibrium moisture content (EMC). The amount of hygroscopic or bonding water depends on the number of hydroxyl groups that can be occupied by water molecules and on the microcapillary structure of cell walls as well.[1] The relationship between the equilibrium moisture content and relative air humidity (RH) is expressed with sorption isotherms, which are obtained by progressive equilibration in the adsorption or desorption process. Differences in hygroscopic and sorption isotherms are the result of the chemical composition of wood, the portion of microcracks in cell walls, density, possible hydrothermal and chemical treatment, and stress conditions.

Sorption isotherms can be divided into three regions. The first region represents the equilibrium moisture contents (EMC) from an absolutely dry condition to the equilibrium state reached at RH between 20 and 30%. In this interval, the absorption of water molecules continues progressively until the complete constitution of a monolayer, which covers the external surface of the cell wall. The wood moisture content (MC) changes are faster at the upper part of the hygroscopic region, but when coming closer to a dry state they slow down.[2] The second region starts when the first layer has been saturated. The absorption of water molecules on the first layer and consequential forming of additional layers is a characteristic of this region. The isotherms in this region are quasi-linear.[3] In the third region, capillary condensations of water in microcapillaries occur. Water molecules form large groups, whereas the bonds between hydroxyl groups and the first layer of water molecules weaken. Therefore, water molecules may move in clusters.[4] The water concentration in this region is sufficient for liquid water to be formed in pores via capillary condensation. Thus, microcapillary water forms a continuous phase.[2] In the third hygroscopic region, sorption properties are influenced by low-molecular secondary heartwood compounds such as polyphenols (flavonoides, lignans, tannins) as well. They are encrusted in the cell wall, limiting the space for bonded water.[5]

There are several reasons for differences in the equilibrium wood moisture content obtained in the adsorption and desorption process (e.g., relaxation times, energy loss because of plastic transformations,[6] the moisture angle is higher during adsorption than during desorption,[7] formation of hydrogen bonds, stress conditions). Hysteresis can be explained with the desorption of water from active sorption places of moist wood, resulting in the closing up of cellulose chains until they come closer and crosslink with hydrogen bonds. For the interruption of these bonds and re-adsorption of water in these active places, more energy

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or a larger partial water pressure is needed. At a higher temperature (70°C or more), hysteresis is not so obvious any more due to a higher kinetic energy of water molecules and a larger oscillation of cellulose crystal structure.[8]

As already mentioned, hygroscopic properties of wood can be influenced by different treatment processes, one of which is the chemical preservation of wood. After the implementation of the Biocidal product directive in 2006, most inorganic wood preservatives were removed from the market. Among the few that have remained in use are boron active ingredients. Boron compounds have already been used in wood protection for a long time. Their use is still increasing nowadays, particularly because boron compounds have a lot of advantages, namely, low toxicity to environment, effectiveness at low concentration toward wood decay fungi, insects, and, particularly, termites.[9] Furthermore, they have very good diffusibility in the cell walls,[10] which provides sufficient preservation even of nonimpregnable wood species. Boron compounds are also used as flame retardants. Boric acid readily forms complexes with 1-methoxy-2-hydroxy benzene and 1,2-dimethoxy benzene groups in lignin.[11] Such monoskeletal tetrahedral complexes are easily soluble in aqueous solution, as boron is not chemically bonded to the wood structure, but it seems to be a physical adsorption with weak forces acting like the Van der Waals and hydrogen bonds.[12] Due to insufficient fixation of boron compounds in wood, boron-based wood preservatives are normally not recommended for outdoor applications. It is important to consider that boron in impregnated wood is not bonded at all and it tends to diffuse if a concentration gradient and moist conditions are present.[10] Because of only physical adsorption of boron compounds in wood there is no influence on the availability of hydrophilic hydroxyl groups in wood.[11]

Wood impregnated with different inorganic salts is usually more hygroscopic than untreated wood, particularly in high relative air humidity. The increase of EMC of such wood depends on the type of wood preservative used, retention, and wood species.[13] The equilibrium moisture content of impregnated wood and the influence of preservative retention on the equilibrium point is still unknown. A high EMC is problematic because of more prominent leaching of active ingredients, creating favorable conditions for the growth of fungi and particularly molds and due to difficulties related to surface treatment and gluing of moist wood.

The sorption properties of wood impregnated with aqueous solutions of boric acid, borax, sodium chloride, and glucose in the whole hygroscopic region during the adsorption and desorption process were investigated in this research. The influence of retention of the above-mentioned chemicals on the equilibrium moisture content was elucidated as well. A regression analysis was applied to fit the experimentally obtained data with the Guggenheim-Andersen-deBoer (GAB) and Dent sorption models.

MATERIALS AND METHODS

Norway spruce (*Picea abies* (L.) Karst.) samples of 20 mm × 20 mm × 10 mm dimensions were used in this experiment. Prior to vacuum impregnation (30 min vacuum, and 2 h immersion at normal pressure) specimens were oven dried (103±1°C) and their masses were determined. For impregnation, four aqueous solutions of boric acid (Ba, H_3BO_3), borax (Bx, $Na_2B_4O_7 \times 10H_2O$), sodium chloride (NaCl), and glucose (G, $C_6H_{12}O_6$) of three different concentrations (1, 2, and 5%) were used. After impregnation, specimens were conditioned for two weeks at 25°C, 65% RH, and afterwards oven dried (103 ± 1°C) and then retention was gravimetrically determined. Retentions were expressed in grams of the remaining ingredient per kilogram of treated wood and in $\mathrm{kg/m^3}$.

After drying, samples were conditioned at 20 ± 0.5°C at five different levels of relative air humility (RH), which were obtained with saturated salt solutions (CH_3COOK; $\varphi = 20 \pm 1\%$ (only desorption), $MgCl_2 \times 6H_2O$; $\varphi = 33 \pm 1\%$, $NaNo_2$; $\varphi = 65 \pm 1\%$. $ZnSO_4 \times 6H_2O$; $\varphi = 88 \pm 1\%$, H_2O; $\varphi = 98 \pm 1\%$), first in the adsorption and then in the desorption process. In parallel, the influence of various RH on moisture content of pure chemicals was elucidated as well.

The equilibrium moisture content was fitted to the GAB model (Eqs. (1), (2), and (3)).[14]

$$\frac{u}{u_0} = \frac{CKh}{(1 - Kh)(1 - Kh + CKh)} \quad \text{or} \qquad (1)$$

$$\frac{h}{u} = \frac{1}{u_0 CK} + \frac{C - 2}{u_0 C} \cdot h - \frac{K(1 - C)}{u_0 C} \cdot h^2 \qquad (2)$$

Equation (2) is recognized as square where coefficients are expressed:

$$a = \frac{1}{u_0 CK}, \quad b = \frac{C - 2}{u_0 C}, \quad c = \frac{K(1 - C)}{u_0 C} \qquad (3a, b, c)$$

The parameters of model are expressed by the regression analysis of experimentally defined points.

$$aK^2 + bK + c = 0 \qquad (4a)$$

$$C = \frac{b}{aK} + 2 \qquad (4b)$$

$$u_0 = \frac{1}{b + 2Ka} \qquad (4c)$$

In these equations, a, b, and c are the coefficients of square equations of the GAB model; u_0, C, and K are the constants of the GAB model; u is the wood moisture content; and h is the water activity or the relative air humidity.

For comparison and evaluation of the hygroscopy of impregnated samples, the ratio of sorption was determined:

$$s = \frac{\Delta u}{\Delta \varphi} = \frac{u_2 - u_1}{\varphi_2 - \varphi_1} \quad (5)$$

Δu is the change in the wood moisture content between equilibrium states u_1 and u_2, and $\Delta\varphi$ is the difference between the relative air humidity levels φ_1 and φ_2.

RESULTS AND DISCUSSION

During the impregnation, samples on average absorbed 721 kg/m3 preservative solution. The samples were relatively small with a high portion of axial planes, and as there was a relatively severe process of impregnation utilized, they were completely soaked with the preservative solution. There were insignificant differences in the retention of impregnating solution between particular samples impregnated with different solutions. However, more prominent differences were observed after drying. The retention depends on the type of preservative solution used and its concentration. As expected, retentions increase with an increasing concentration (Table 1). The lowest retention was observed at samples impregnated with 1% boric acid solution (6.3 g Ba/kg wood) and the highest retention was observed at samples impregnated with 5% sodium chloride solution (93.0 g NaCl/kg wood).

Sorption isotherms of all specimens impregnated with various aqueous solutions have a characteristically sigmoid shape with clearly resolved hysteresis (Figs. 1 and 2). Isotherm sorption regions of impregnated wood are significantly influenced by the type of preservative solution on the one hand and the concentration on the other hand (Fig. 3). However, differences in moisture content of impregnated and control wood are less visible at lower RH and differences in moisture contents increases with an increasing RH.

Treated wood had a narrower linear part of the sorption curve (region two) than untreated wood. The main reason for this difference originates in the fact that the EMC of impregnated wood increases faster in the third hygroscopic region. In this region, the effect of capillary condensation is particularly important, and this phenomenon is the most important reason for higher moisture contents of treated wood as well. This somehow indicates that there are some new voids formed between crystals as sites for capillary condensation.

Boric acid– and borax-impregnated specimens conditioned at 20% RH in the desorption process have similar moisture content than the control ones. The conditioning of boron-impregnated wood specimens at a higher RH resulted in considerably higher equilibrium moisture content in both the adsorption and desorption process. The equilibrium moisture content increases with increasing amounts of boron in wood (Fig. 1). These data are in contradiction with the data of Choong and Achmadi,[5] who claimed that deposits in cell walls reduce the moisture content at a higher relative humidity. Despite the fact that boron occupies some space in cell walls, this fact is not reflected in a lower MC. On the contrary, even higher MCs were observed. We presume that the reason for this phenomenon originates in the fact that boron compounds are slightly hygroscopic[12] and, secondly, there are several voids formed, where capillary condensation can occur. Both effects somehow cover the effect of occupation of spaces in cell walls. However, boron compounds are considerably less hygroscopic than NaCl or glucose (Table 2), which is reflected in lower MC of boron-impregnated wood in comparison to the specimens impregnated with glucose or NaCl.

The moisture content of samples, impregnated with the highest concentration of boric acid (5%) after two weeks of conditioning at 98% RH, had a 20% higher moisture content (30.3%) than control (25.3%), while the moisture content of samples treated with a 5% water solution of borax had a two times higher EMC (56.3%) than the control, unimpregnated samples. The boric acid solution had a pH of 5.2, which is very similar to the pH of wood,[15] enhancing the absorption of the neutral species of H_3BO_3. The pH value of the borax solution is around 9.2; therefore, a negatively charged wood surface repels negative borate ions,[12] resulting in a weaker physical binding of borax in wood. This can partly explain the higher equilibrium moisture contents of borax-treated wood in the lower hygroscopic region. The experimental data showed that boric acid and borax do not have any important influence on the equilibrium state of wood conditioned at 20% RH, as the impregnation of wood specimens with boron compounds does not influence the number and availability of hydroxyl groups.[11] At specimens exposed to 20% RH, the equilibrium moisture content of boric acid–impregnated wood was even lower than control due to a weak physical absorption of boric acid to hydroxyl groups.[12] One possible reason for a higher moisture content of borax-treated wood is the pH value of the borax aqueous solution. The moisture content of boric acid–impregnated wood was considerably lower at a higher RH in comparison to borax-impregnated wood. At the highest RH (98%) the equilibrium moisture content of borax-impregnated wood is more than 50% higher than that of boric acid–treated wood. However, from comparison of sorption properties of borax and boric acid itself and boron-impregnated wood, it is evident that hygroscopic properties of boron are not the main (only) reason for higher MC at higher RH, but there are other factors that result in high MC of impregnated wood as well. We presume that formation of small crystals, with several voids suitable for capillary condensation, are formed as well,[16] which partly explains the higher MC of impregnated wood at higher RH. However, there is one issue related to this

TABLE 1

Retention, ratio of sorption (s), and the GAB sorption model constants (K, C, U_0) of wood impregnated with boric acid, borax, sodium chloride, and glucose aqueous solutions of three different concentrations conditioned in five hygroscopic regions in the adsorption (A) and desorption (D) process

						Sorption quotient(s)							
		Retention				Hygroscopic region					GAB model		
Chemical	Conc. (%)	(g/kg)	Std.	(kg/m^3)	Sorption	33–20	65–20	65–33	88–65	88–33	K	C	U_0%
Control	0	0	0	0	A	—	—	0.15	0.23	0.19	0.00796	10.574	5.5
					D	0.20	0.20	0.20	0.26	0.22	0.00619	6.616	10.9
Boric acid	1	6.3	2.70	2.4	A	—	—	0.17	0.24	0.20	0.00781	10.771	6.2
					D	0.21	0.20	0.20	0.30	0.24	0.00666	6.721	10.1
	2	14.3	3.68	5.4	A	—	—	0.17	0.24	0.20	0.00794	16.085	6.1
					D	0.23	0.21	0.20	0.30	0.24	0.00672	5.904	10.5
	5	38.1	3.74	14.4	A	—	—	0.17	0.25	0.20	0.00786	20.838	6.6
					D	0.25	0.21	0.20	0.32	0.25	0.00681	5.737	10.8
Borax	1	7.9	1.82	3.1	A	—	—	0.18	0.25	0.21	0.00831	13.421	5.7
					D	0.21	0.21	0.20	0.33	0.26	0.00748	8.275	8.9
	2	16.9	3.27	6.8	A	—	—	0.19	0.27	0.22	0.00859	15.622	5.4
					D	0.21	0.21	0.21	0.35	0.27	0.00798	9.975	8.1
	5	53.6	6.38	20.4	A	—	—	0.18	0.29	0.23	0.00909	23.203	5.0
					D	0.26	0.22	0.21	0.35	0.27	0.00848	19.222	8.1
Sodium chloride	1	19.7	4.26	7.7	A	—	—	0.19	0.29	0.23	0.00908	17.532	4.9
					D	0.19	0.22	0.23	0.5	0.28	0.00864	12.258	7.1
	2	39.6	5.67	15.1	A	—	—	0.20	0.41	0.29	0.00951	18.498	4.7
					D	0.21	0.24	0.25	0.42	0.31	0.00914	14.745	6.9
	5	93.0	10.38	35.1	A	—	—	0.22	0.98	0.53	0.00989	19.372	5.5
					D	0.23	0.31	0.34	1.11	0.65	0.00964	7.097	8.7
Glucose	1	18.1	1.39	6.8	A	—	—	0.17	0.23	0.20	0.00822	9.117	5.5
					D	0.20	0.20	0.20	0.26	0.23	0.00713	6.723	9.2
	2	34.9	5.06	13.3	A	—	—	0.17	0.25	0.20	0.00871	12.608	4.9
					D	0.18	0.19	0.19	0.31	0.24	0.00808	9.910	7.2
	5	67.3	3.06	25.2	A	—	—	0.18	0.26	0.21	0.00895	9.869	4.8
					D	0.16	0.18	0.19	0.31	0.24	0.00862	11.785	6.2

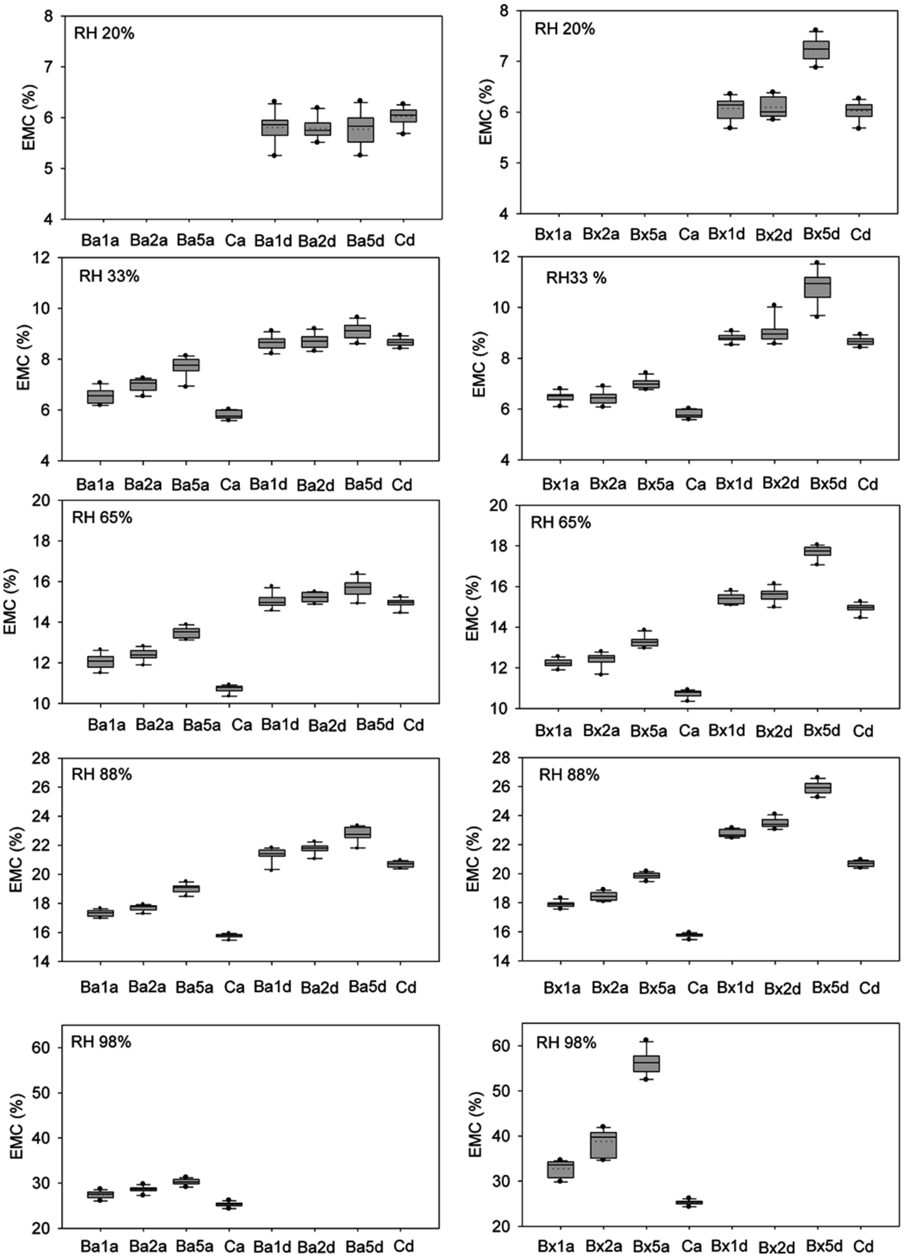

FIG. 1. The equilibrium moisture content (EMC) of wood specimens conditioned at five relative air humidity levels (RH) in the adsorption (a) and desorption (d) process. Specimens were impregnated with aqueous solutions of boric acid (Ba) and Borax (Bx) of three different concentrations (1, 2, and 5%) and control, unimpregnated samples (C).

phenomenon. At this high MC, boron diffusion is relatively fast, which may result in unwanted leaching.[17] On the basis of our data we conclude that boric acid is more suitable for the protection of wood in humid environments than borax. If the wood moisture content is lower, the loss of boron due to leaching is lower and the conditions for mold growth are less favourable as well.

However, the simulation of monomolecular sorption according to the GAB model showed that the monomolecular moisture content in impregnated samples increases with an increasing concentration of boric acid (Table 1). The monomolecular moisture content of boric acid–treated samples is also higher than the monomolecular moisture content in the control samples. This difference is insignificant and is probably a consequence of a lower number of equilibrium states. The monomolecular sorption of borax in the impregnated samples is lower than in control and decreases with an increasing borax concentration in wood (Table 1).

The treatment of wood specimens with sodium chloride (NaCl) had an even more prominent influence on the EMC

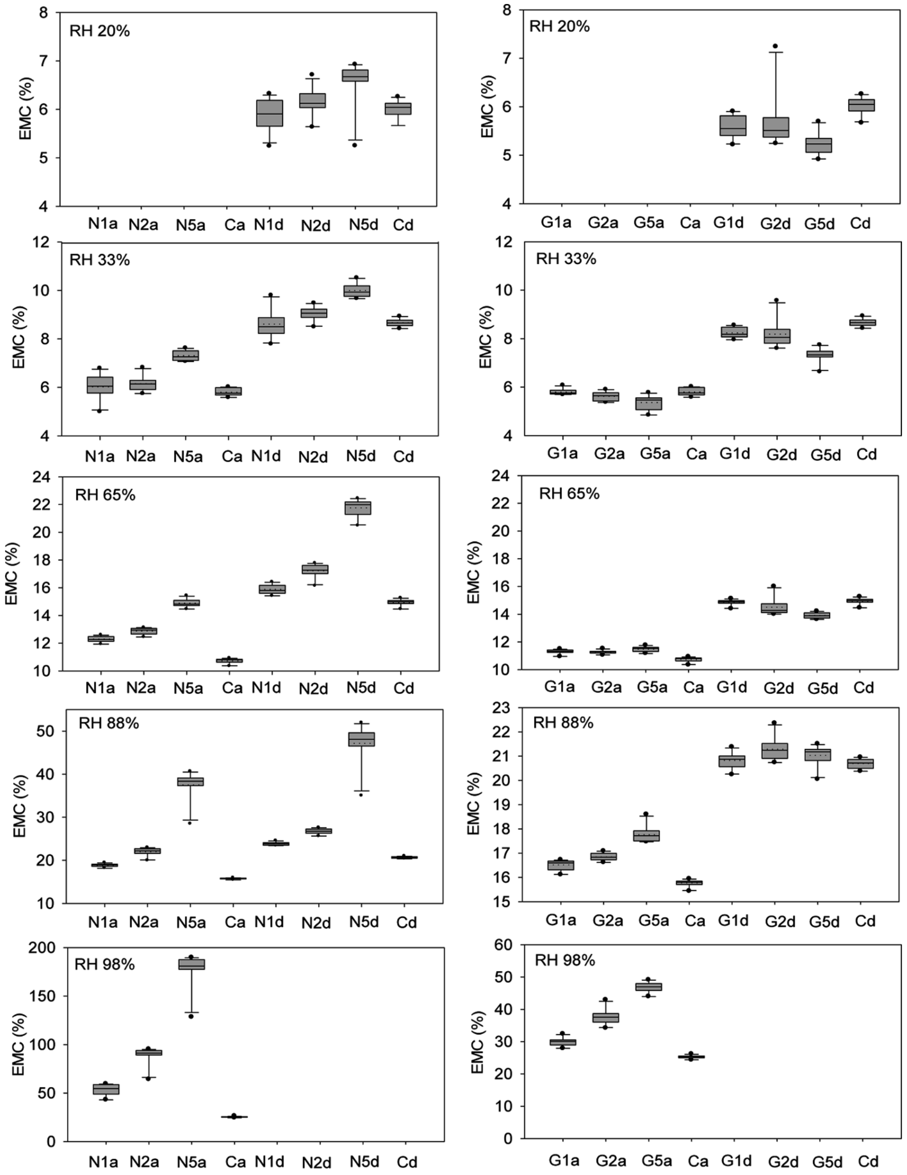

FIG. 2. The equilibrium moisture content (EMC) of wood specimens conditioned at five relative air humidity levels (RH) in the adsorption (a) and desorption (d) process. Specimens were impregnated with aqueous solutions of sodium chloride (NaCl) and glucose (G) of three different concentrations (1, 2, and 5%) and control, unimpregnated samples (C).

of wood than borax. Similarly as for borax-treated specimens, the equilibrium moisture content of wood increases with an increasing concentration of NaCl in wood (Fig. 2). The reasons for this occurrence are the well-known hydroscopic properties of table salt (Table 2).

An increasing glucose concentration in impregnated wood results in a decrease of moisture content at specimens conditioned in the first hygroscopic region (Fig. 2). A calculation of monomolecular sorption according to the GAB model and the ratio of sorption calculated in the region between 20 and 33% RH led us to the same conclusion (Table 1). The reason for a lower moisture content of glucose-impregnated wood presumably originates in the hydrogen bonds between glucose and free hydroxyl groups. This presumption is further supported by the fact that in parallel with an increasing glucose concentration in wood, less free sorption places are available, preventing water molecules from binding. However, this phenomenon is present only in the lower hydroscopic region. In contrast, in the second hygroscopic region (at 65% RH) the equilibrium moisture content increases with an increasing glucose concentration in wood. At higher RH the EMC increases even more prominently (Fig. 2). At higher RH glucose offers some new absorption sites for water molecules,

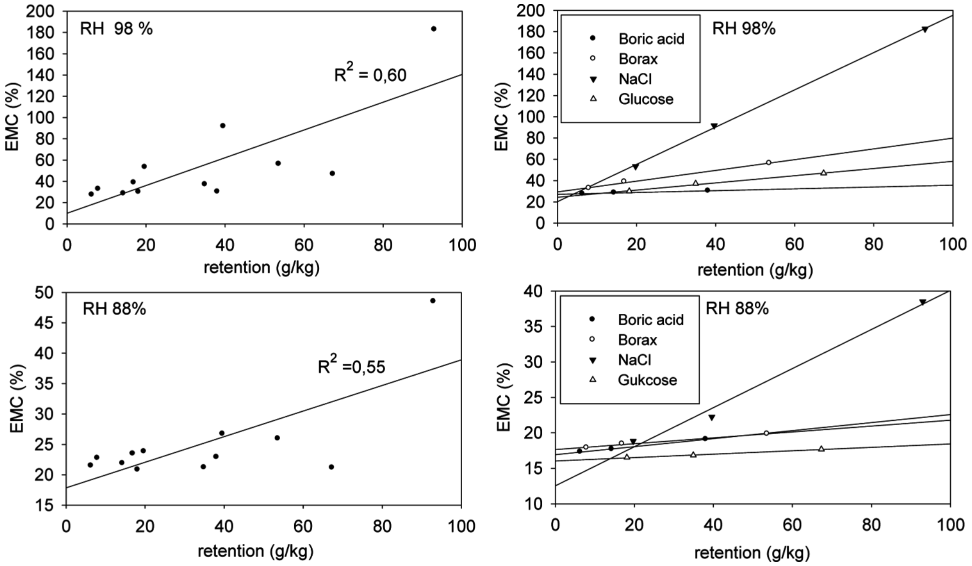

FIG. 3. The correlation between the equilibrium moisture content (EMC) of Norway spruce impregnated wood specimens and retention for all treatments used (left) and for individual impregnation chemicals (right) at two relative humidity levels (98% above and 88% below).

which is reflected in significantly higher wood moisture contents.

Boric acid, borax, sodium chloride, and glucose have crystal structures. Ramos and coworkers[12] reported that boric acid and borax are bonded in wood only physically. Therefore, we suppose that an impregnation of wood with those compounds does not cause any change in wood structure, which means that boric acid, borax, and glucose in wood are in smaller or larger crystals, deposited into cell walls and cell lumina. Crystals dissolve in extremely moist environments and recrystallize when the air humidity decreases, because the absorbed and free water in wood acts as a solvent. The process is reversible as dissolution and crystallization follow different paths, depending on the wood moisture content.[18] In specimens impregnated with more concentrated solutions, there are more crystals formed in wood, which is reflected in a higher MC.[16] There are numerous pores between crystals where capillary water condenses at humidity above 90%.[18] Our results clearly show that chemicals introduced to wood with impregnation have an opposite effect than the heartwood substance, which reduces moisture content in the upper hygroscopic region.[5] Furthermore, it is evident from MC of pure chemicals presented in Table 2 that increase of MC of impregnated wood at higher RH cannot be explained with hydroscopic properties of chemicals introduced into wood with impregnation, but there must be other factors that influences that high moisture content as well.

Variation in chemical composition of wood can influence sorption properties.[19,20] In general, hemicellulose is the most hygroscopic, followed by cellulose and lignin. On average, spruce wood contains around 30% of lignin, but its contribution to the sorption is between 10 and 15%.[21] However, all our specimens were prepared from the same part of the board; therefore, we believe that in our experiment chemical composition of wood did not have a statistically significant influence on the sorption properties.

The equilibrium moisture content in the upper hygroscopic region is influenced by hygroscopic properties of individual chemicals as well. Increased concentrations of hygroscopic chemicals in wood result in an increased moisture content of impregnated wood (Fig. 3). Hygroscopicity and therefore

TABLE 2

Moisture content (MC) of boric acid, borax, NaCl, and glucose regarding relative air humidity in the adsorption (A) and desorption (D) process. Moisture content of the tested chemicals below 65% RH is insignificant

		Relative air humidity		
		65%	87%	98%
Chemical	Sorption	MC (%)	MC (%)	MC (%)
Boric acid	A	1.2	1.2	1.1
	D	1.1	1.1	—
Borax	A	0.2	0.3	2.8
	D	2.3	2.3	—
Sodium chloride	A	0.0	42.5	123.4
	D	0.0	49.4	—
Glucose	A	0.0	0.3	16.8
	D	0.0	3.9	—

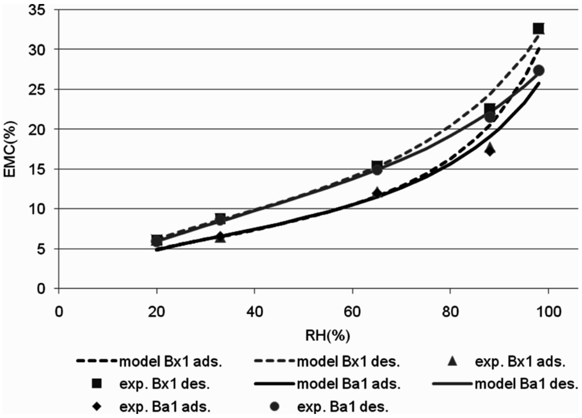

FIG. 4. The average equilibrium moisture content of wood impregnated with 1% water solution of boric acid (Ba) and borax (Bx) and fit curve with sorption isotherms according to the GAB model for the adsorption and desorption process.

the influence of borax is higher than that of boric acid. The hygroscopic properties of boron compounds included in this experiment are described in the cited literature.[12]

We presume that one of the reasons for large differences in the equilibrium moisture content of impregnated wood at 98% RH is the consequence of the different saturation pressures of the chemicals used. Chemicals in impregnated wood lower the saturation pressure. The critical relative air humidity for NaCl at 20°C is 75.3%. Our results presented in Table 2 indicate that the critical relative humidity of borax is higher than the critical relative humidity of sodium chloride and glucose. From these data it is evident that MC of boric acid did not increase notably with increasing RH. Slightly higher influence of RH on MC was measured for borax. However, more than five times higher MC at 98% RH was observed for glucose and almost 50 times higher MC of pure NaCl was observed compared to borax.

Sorption isotherms, according to the GAB model, exhibited the best fitting of experimental data in the lower and the middle part of the hygroscopic region. However, more prominent deviations appear at RH above 65%. Above this level, the influence of sorption characteristics of individual chemicals on the equilibrium state of impregnated wood increases significantly, which is evident from the comparison of sorption isotherms (Fig. 4). On the basis of these results it can be concluded that the GAB model is suitable for the prediction of the MC in wood impregnated with boron compounds in the lower and the medium part of the sorption curve.

CONCLUSION

The equilibrium moisture content of impregnated wood depends on the chemicals used for impregnation and their concentration (retention). This influence is the most prominent at high air humidity. For individual chemicals, the equilibrium moisture content of impregnated wood proportionally increases with an increasing concentration in wood. Among the tested chemicals the least prominent influence on the equilibrium moisture contents of impregnated wood was found for specimens impregnated with boric acid and the most prominent one was determined for sodium chloride. A higher equilibrium moisture content of treated wood is particularly important from the practical point of view. Moist wood represents suitable conditions for mold and fungal growth and decreases the resistance of such wood.

NOMENCLATURE

a	Constant parameter in the quadratic polynomial expression of the h/u ratio (Eqs. (3), and (4)); generally, constant parameter in the polynominal expression of a higher order for the h/u ratio
b	Parameter at linear member in the quadratic polynomial expression of the h/u ratio (Eqs. (3), and (4)); generally, constant parameter in linear member in the polynomial expression of a higher order for the h/u ratio
c	Parameter at quadratic member in the quadratic polynomial expression of the h/u ratio (Eqs. (3), and (4)); generally, a parameter at quadratic member in the polynomial expression of a higher order for the h/u ratio
C	Parameter of GAB equation; see Eqs. (1) and (2)
h	Water activity
K	Parameter of GAB equation; see Eqs. (1) and (2)
s	Ratio of sorption
u	Moisture content (water content) dry basis
u_0	Moisture content in monomolecular layer, parameter of GAB equation; see Eqs. (1) and (2)
Δu	Change in wood moisture content between equilibrium states

Greek Letters

φ	Relative air humidity
$\Delta\varphi$	Difference between relative air humidity levels

Acronyms

Ba	Boric acid
Bx	Borax
EMC	Equilibrium moisture content
G	Glucose
MC	Moisture content
N	Sodium chloride
RH	Relative humidity

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3.12 SORPCIJSKE LASTNOSTI LESA, IMPREGNIRANEGA Z VODNO RAZTOPINO BOROVE KISLINE IN EMULZIJO MONTANSKEGA VOSKA

SORPTION PROPERTIES OF WOOD IMPREGNATED WITH AQUEOUS SOLUTION OF BORIC ACID AND MONTAN WAX EMULSION

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V zadnjih letih postajajo nebiocidne tehnike zaščite lesa vedno bolj pomembne. Eden od možnih postopkov zaščite je uporaba vodoodbojnih sredstev. V lesarstvu se za zagotavljanje vodoodbojnosti največkrat uporabljajo voski. Preučevali smo vpliv emulzije montanskega voska na navlaževanje in sorpcijske značilnosti impregniranega lesa. Za boljšo zaščito impregniranega lesa pred delovanjem gliv razkrojevalk smo les impregnirali z emulzijo montanskega voska in borovo kislino. Ravnovesne vlažnosti lesa smo določali med postopkom adsorpcije in desorpcije pri petih relativnih zračnih vlažnostih (φ_1 = 20 %, φ_2 = 33 %, φ_3 = 65 %, φ_4 = 88% in φ_5 = 98 %). Prepustnost za paro smo določali v komori z visoko zračno vlažnostjo (87 %) in vodoodbojnost med potapljanjem v vodi. Med petmesečno izpostavitvijo impregniranih vzorcev zunanjim razmeram (2. razred izpostavitve) smo ugotavljali spreminjanje vlažnosti lesa glede na spremembo zunanje temperature in relativne vlažnosti zraka. Rezultati kažejo, da so sorpcijske lastnosti impregniranega lesa močno povezane z navzemom zaščitnih raztopin med impregnacijo in njihovo sestavo. Montanski vosek zmanjša ravnovesno vlažnost impregniranega lesa do 25 % (relativno). Po drugi strani je bila vlažnost vzorcev, impregniranih samo z borovo kislino, višja od kontrolnih vzorcev, vlažnost lesa, impregniranega s kombinacijo borove kisline in emulzije montanskega voska po kondicioniranju v visoki zračni vlažnosti, namakanju v vodi in zunanji izpostavitvi pa je bila nižja od vlažnosti neimpregniranih vzorcev. Eksperimentalne podatke smo prilagodili Guggenheim-Andersen-deBoerovemu (GAB) matematičnemu modelu za razlago sorpcijskega mehanizma impregniranega lesa. Rezultati kažejo, da je model GAB primeren za napovedovanje vlažnosti lesa, impregniranega z emulzijo montanskega voska in lesa, impregniranega s kombinacijo emulzije montanskega voska in borove kisline.

Sorption Properties of Wood Impregnated with Aqueous Solution of Boric Acid and Montan Wax Emulsion

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ABSTRACT: Nonbiocidal techniques for wood protection have become more and more important in the last few years. One of the possible treatments to enhance wood durability is use of water repellents. In this research, the influence of one of the possible water repellents, the montan wax emulsion, on the moisturizing and the sorption characteristics of impregnated wood was investigated. To achieve a better protection against wood decay fungi, wood was impregnated with montan wax emulsion enriched with boric acid. The equilibrium moisture content (MC) was monitored during the adsorption and the desorption processes at five levels of relative air humidity ($RH_1 = 20\%$, $RH_2 = 33\%$, $RH_3 = 65\%$, $RH_4 = 88\%$, and $RH_5 = 98\%$). Water repellence efficiency was monitored in the chamber with high RH (87%) and during dipping in the water. Impregnated samples were also exposed outdoors in a covered position for 5 months to determine MC changes according to changes in outdoor humidity and temperature. The results showed that the sorption properties of the impregnated wood are strongly related to retention of preservative solutions after impregnation and its composition. Montan wax reduced equilibrium MC of the impregnated wood up to 25% (relatively), whereas specimens impregnated with combination of montan wax and boric acid resulted in decreased MC in some cases and in increased MC in some cases. The Guggenheim–Andersen–deBoer model of sorption isotherms was fitted to experimental data to explain the sorption mechanisms. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1337–1345, 2011

Key words: boron compounds; moisture content; montan wax; sorption; wood protection; adsorption; surfaces; coatings

INTRODUCTION

Wood is the most important biopolymer in the world. It is the most important natural material used for construction applications, but it is exposed to weathering and biotic decay. To slow down these processes, wood is frequently treated with polymers like surface coatings, waxes, oils, etc. Treatment of the wood with water repellents can influence the long-term properties of this material. Rain and dew water are causing surface erosion and leaching of wood components. Second, the moisture content (MC) of repellent-treated wood in service is reduced, and thus the risk of crack formation and biological degradation is lowered as well. It is well known that water repellent treatment lowers the MC of treated wood in water submersion tests considerably.[1] Furthermore, combinations of active ingredients such as fire retardants, biocides, or ultraviolet light protectants with water repellents prevented or at least limited their leaching.[2–5] The most important water repellents used in the wood preservation are waxes, particularly paraffin waxes.[6,7] Paraffin waxes find their second most important applications in wood industry after candle industry. The importance of use of waxes in wood industry is increasing in Europe in particular because consumers, due to increased environmental awareness, avoid biocidal-treated wood and wood from tropical forest. Therefore, industry is interested in development of alternatives, like treatment with waxes. There is at least one commercially operated treatment of wood with paraffin (Dauerholz in Germany).[8] However, our experimental results clearly indicate that montan wax perform better than paraffin wax.[9]

Montan and carnauba waxes are one of the possible water repellent agents to be applied in the field of wood preservation, as well. Those waxes are among the most resistant waxes, and it should not be overseen that they have the ability of thin film formation. Montan and carnauba wax, as well as other waxes, are almost nontoxic and are used for variety of applications like fruit treatment to slow down fruit drying.[10] Crude montan wax belongs to the group of the naturally occurring waxes of vegetable origin such as carnauba wax or candelilla wax. Montan wax is fossilized vegetable wax extracted

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from lignites, principally from the central German brown coal reserves west of the Elbe River. It is a mixture of chemical compounds that can be divided into three substance groups: waxes, resins, and asphaltic substances. Like existing vegetable hard waxes such as carnauba wax, the pure wax substance in montan wax mainly consists of esters of long-chain acids with long-chain alcohols and free long-chain acids. Other components such as free wax alcohols or ketones, paraffins, and terpenes are usually present in small quantities.[11] The wax is soluble in many organic solvents, particularly aromatic or chlorinated hydrocarbons, even on moderate heating. Montan wax is used in the form of flakes, powders, pastes with solvents, and aqueous emulsions.[12] One of the most important advantages of montan wax is its capability of forming thin-layer resistant films.[13] Montan wax improves performance against wood decay fungi, but not sufficiently to be used for in-ground applications.[14] However, wood impregnated with the preservative solutions, based on the montan wax and the boron compounds, is well protected against wood decay fungi in above-ground applications. Combinations of boron and montan wax have synergistic effect against the wood inhabiting fungi, and montan wax additionally reduces the leaching of boron compounds from impregnated wood.[14]

However, neither montan wax nor paraffin or synthetic waxes react with wood. They either form thin films on the surface of wood or on the surface of cell walls, or filled cell lumina with waxes, thus limiting water penetration to wood. Because they are insoluble in water, they do not leach from wood.[15] However, it is reported that paraffin treatment in most of the cases does not prevent degradation processes, but only slows them down.

Boron compounds are one of the oldest active ingredients for wood preservation that still remains on the market, even after introduction of biocidal products directive in the European Union. Their importance increased significantly. Boron compounds have low mammalian toxicity, but they are very effective against most of the wood pests. Their use is limited because their diffusibility and susceptibility to leaching. This is especially important when boron-impregnated wood is used for outdoor applications. It is important to consider that boron in impregnated wood is not bound at all; therefore, it tends to diffuse if concentration gradient and moist conditions are present.[16] Because of only physical adsorption of boron compounds in wood, boron treatment does not influence the availability of hydrophilic hydroxyl groups in wood.[17] Wood impregnated with boron compounds (boric acid [Ba]or borax) is more hygroscopic than untreated wood, particularly in high relative air humidity (RH). The increase in equilibrium moisture content (EMC) of such wood depends on the type of wood preservative used, retention, and wood species.[18,19] An EMC is problematic because of the more prominent leaching of active ingredients, creating favorable conditions for the growth of fungi, particularly molds, and because there are difficulties related to surface treatment and gluing of the moist wood.

To lower the EMC of the boron-treated wood, Ba-based aqueous solution was combined with the montan wax emulsion. To determine the effectiveness of preservative solution, three different tests were performed; conditioning in water or in a chamber with high RH, conditioning in chambers in the whole hygroscopic region during the adsorption and desorption processes, and monitoring of MC during outdoor exposure.

MATERIALS AND METHODS

Treatment solutions used

For impregnation of wood, the montan wax emulsion (LGE) (Samson, Slovenia) of two different concentrations 6% (LGE-A) and 12% (LGE-B), respectively, were used. Some solutions contained Ba as well ($c_B = 0.5\%$). The composition and the concentrations (dry content) of wax emulsions and boron compounds are shown in Table I.

Sorption properties

To determine the sorption properties, three types of tests were performed. In the first one, small impregnated wood specimens (SP) were conditioned in chambers with different RH. In the second set of experiments, slightly bigger specimens (EN 113) were submerged in water or conditioned in a chamber with high humidity, and their masses were monitored. In the third set of experiments, wood specimens were exposed outside, under a roof. MC of wood was determined gravimetrically based on the mass of impregnated specimens.

The first set of sorption experiment was performed on Norway spruce (*Picea abies*) specimens. Samples of 2.0 × 2.0 × 1.0 cm (SP) dimensions were used in this experiment. Before vacuum impregnation (vacuum, 20 min; pressure, 90 min; and vacuum, 10 min) specimens (10 per preservative solution) were oven dried (40°C ± 1°C for 3 days) and their masses were determined. In parallel, control specimens were dried according to the same procedure. For impregnation, two preservative solutions, montan wax emulsion (LGE-A) and montan wax emulsion with Ba ($c_B = 0.5\%$), were used. After impregnation, specimens were conditioned for 3 weeks at 25°C, 65% RH, and afterward oven dried (40°C ± 1°C for

TABLE I
Retentions ($n = 10$) of the Preservative Solutions, Montan Wax, and Boric Acid in Vacuum/Pressure Treated Specimens and in Wood Specimens Impregnated with Various Aqueous Emulsions of Montan Wax (LGE-A, LGE-B, LGE-A-Ba, and LGE-B-Ba)

						Retention (kg/m^3)		
Preservative solution	Wax content (%)	Boron concentration (%)	Axial planes sealed	Type of samples[a]	Wood species	Preservative solution	Wax	Boric acid
LGE-A	6	0	Yes	EN 113	Spruce	138 (21)	16.5 (2.5)	0.0
LGE-A		0	No	EN 113	Spruce	696 (119)	83.5 (14.3)	0.0
LGE-A-Ba		0.5				598 (135)	71.8 (16.2)	2.99 (0.68)
LGE-B	12	0	No	EN 113	Spruce	555 (162)	66.7 (19.4)	0.0
LGE-B-Ba		0.5				595 (129)	71.4 (15.5)	2.97 (0.63)
LGE-B		0	Yes	EN 113	Spruce	159 (26)	19.1 (3.1)	0.0
LGE-B-Ba		0.5				154 (25)	18.5 (3.0)	0.77 (0.13)
Ba	0	0.5	No	EN 113	Spruce	776 (69)		3.88 (0.35)
Control	0	0	No	EN 113	Spruce	0	0	0
Control	0	0	Yes	EN 113	Spruce	0	0	0
LGE-A	6	0	No	EN 252	Spruce	178 (42)	10.7 (2.5)	0.0
LGE-B	12	0				83 (26)	10.0 (3.0)	0.0
LGE-B-Ba	12	0.5				121 (13)	14.5 (1.6)	0.61 (0.06)
Control	0	0				0	0.0	0.0
LGE-A	6	0	No	EN 252	Beech	402 (58)	24.1 (3.5)	0.0
LGE-B	12	0				236 (15)	28.3 (1.8)	0.0
LGE-B-Ba	12	0.5				264 (26)	31.7 (3.1)	1.3 (0.13)
Control	0	0				0	0	0
LGE-B	12	0	No	SP	Spruce	699 (30.4)	83.8 (3.6)	0.0
LGE-B-Ba		0.5				677 (56.4)	81.2 (6.8)	3.4 (0.28)
Control		0				0	0	0

Standard deviation shown in parentheses.
[a] Size of the specimens: EN 113, 1.5 × 2.5 × 5.0 cm; EN 252, 2.5 × 5.0 × 50 cm; and SP, 2.0 × 2.0 × 1.0 cm.

3 days), and, then, the retention was gravimetrically determined. Retentions were expressed in kg/m^3.

After drying, samples were conditioned at 20°C ± 0.5°C at five different levels of RH, which were obtained with saturated salt solutions (CH_3COOK, RH = 20% ± 1%; $MgCl_2{\cdot}6H_2O$, RH = 33% ± 1%; $NaNO_2$, RH = 65% ± 1%; $ZnSO_4{\cdot}6H_2O$, RH = 88% ± 1%; H_2O, RH = 98% ± 1%), first in the adsorption and then in the desorption processes. A regression analysis was applied to fit the experimentally obtained data with the Guggenheim–Andersen–deBoer (GAB) sorption model.[19,20] Sorption isotherms, according to the GAB model, exhibited good fitting of experimental data of various kinds of wood in the water activity range (h) 0.0–0.9.[21] This model was used to predict MC of control and impregnated wood.

$$\frac{u}{u_0} = \frac{CKh}{(1-Kh)(1-Kh+CKh)} \tag{1}$$

In the above equation, u_0, C, and K are the three free sorption parameters characterizing sorption properties of the material, u is wood MC, and h is water activity or RH fraction. The u_0 denotes MC corresponding to the monomolecular layer on the whole free surface of the material (on every free hydroxyl groups of wood one molecule of water is bonded). It is known that monolayer values decrease with increasing temperature.[21] K constant is the measure of the difference of free enthalpy (standard chemical potential) of the sorbate (water) molecules in two states, the pure liquid and second sorption stage, the layers above the monolayer. It is always found that $K < 1$.[22] Other GAB energy constant C measures the difference of the chemical potentials of the sorbate (water) molecule in the upper sorption layers and in the monolayer.[22]

For comparison and evaluation of hygroscopy of impregnated samples sorption quotient [eq. (2)] was determined:

$$s = \frac{\Delta u}{\Delta RH} = \frac{u_2 - u_1}{RH_2 - RH_1} \tag{2}$$

where, Δu is the change in wood MC between equilibrium states u_1 and u_2 and ΔRH is the difference between RH_1 and RH_2, where samples were conditioned.

The second set of sorption experiments was performed on Norway spruce (*P. abies*) wood specimens (1.5 × 2.5 × 5.0 cm [EN 113]), with end-sealed (epoxy coating) axial surfaces. Approximately 43% of the samples were unsealed before impregnation as evident from Table I. They were impregnated (vacuum, 20 min; pressure, 90 min; and vacuum, 10 min) with LGE-A, LGB-B, and LGE-A-Ba solutions (Table I).

After 4 weeks of air drying (25°C; 65%), the impregnated and control specimens were oven dried (40°C) for 3 days. Before drying, axial surfaces of unsealed specimens were sealed. Specimens dedicated to sorption monitoring were afterward transferred to the chamber with RH of 87%. The mass of the specimens was monitored daily for 6 weeks. On the other hand, specimens dedicated to water uptake analysis were immersed into distilled water. Masses of the specimens were monitored after predetermined periods, as shown in Figure 3(c,d,f), for 3 weeks.

Norway spruce and beech (*Fagus sylvatica*) specimens of 2.5 × 5.0 × 50 cm (EN 252) dimensions were used in the third part of the experiment. After drying (103°C ± 2°C for 24 h), samples were vacuum impregnated (vacuum, 30 min; pressure, 150 min; and vacuum, 10 min) with three different preservative solutions; LGE-A; LGE-B, and LGE-B-Ba (Table I). After 4 weeks of conditioning (25°C, 65% RH), samples were oven dried (103°C ± 2°C for 24 h) and then retention of active ingredients was gravimetrically determined. Those specimens were oven dried because they are considerably larger than other samples used. This reflects in slower drying rates compared with smaller specimens. Second, one of the objectives was to determine the dry content of retained wax because it is well known that chromatographic effect could take place, and, thus, there is less retained wax as it can be assumed from the quantities of retained solution. Control specimens were dried in parallel as well. Samples were exposed outside, under a roof (use class II). Masses of the specimens were monitored after predetermined periods for 5 months from February until June 2009. Outdoor temperature and RH were measured with EL-USB-2 data logger (Lascar Electronics, Whiteparish Salisbury, UK). This part of the investigation was also performed on 10 replicate specimens per solution/wood species.

RESULTS AND DISCUSSION

Composition of the preservative solution, wood species, and type of samples influence the retention of the preservative solutions considerably. In general, addition of montan wax negatively influences the uptake of aqueous solutions used (Table I).

Size of the specimens had a considerable influence on the retention of the preservative solutions as well. As expected, the highest average uptakes of preservative solutions was determined at SP specimens (688 kg/m^3), followed by EN 113 specimens with unsealed surfaces (642 kg/m^3), followed by EN 252 specimens (214 kg/m^3), and the lowest retention was observed for EN 113 with end-sealed surfaces (150 kg/m^3). Specific surface of the specimens was the most important factor that can explain the above-mentioned results. The highest uptake of preservative solution (776 kg/m^3) among all specimens was observed for EN 113 specimens made of Norway spruce, impregnated with Ba aqueous solution only. Ba in this solution are small enough to penetrate into the cell wall.[23] In contrary, for EN 252 samples treated with montan wax emulsion (12% dry content), 10 times lower uptake (83 kg/m^3) was observed. Two times higher loadings was measured at parallel specimens impregnated with montan wax emulsion containing 6% dry content (LGE-A) (178 kg/m^3) (Table I). The main reason for lower penetration of aqueous solutions that contained LGE emulsion was because particles in the emulsion are too big to penetrate into the cell wall, and, even more, they form a barrier on the surface of the cell wall and reduce penetration of the water into the cell wall. Similar results were obtained in previous research.[14] The addition of Ba to LGE emulsions did not influence the loadings of the preservative solutions during impregnation process. On the other hand, influence of the wood species on the retention was the most prominent at the biggest EN 252 specimens. Uptakes of preservative solutions at beech specimens (EN 252) are two times higher than those at Norway spruce specimens. For example, beech specimens impregnated with LGE-A retained 402 kg/m^3, and spruce wood specimens treated with the same solution only retained 178 kg/m^3 (Table I). Described differences are a consequence of better impregnability of the beech wood because pits between cells in beech wood are bigger, and they are not aspirated as at spruce wood. Thus, montan wax emulsion can easily penetrate into the beech wood than into the spruce wood. However, beech wood is known to be more permeable than spruce wood.[24] Therefore, composition of preservative solution did not have that prominent influence on loadings at beech wood specimens, as reported for spruce ones.

Furthermore, prominent differences between end-sealed and unsealed EN 113 samples were noticed. There is no significant difference in loadings of the preservative solutions between EN 113 specimens with end-sealed axial surfaces and bigger EN 252 samples impregnated with the same preservative solution because both specimen types had approximately the same specific surface ratio. However, it is well known that wood is more permeable in axial than in transverse direction.[25] Therefore, at specimens with end-sealed axial planes, preservative solution had to penetrate through 15–100 less permeable radial and tangential planes.[26,27] Our previously published experimental data[28] clearly indicate that the smallest SP samples and unsealed EN 113 samples are completely preserved with tested aqueous emulsions and solutions, whereas for EN 113 with end-sealed surfaces and for EN 252 samples, only

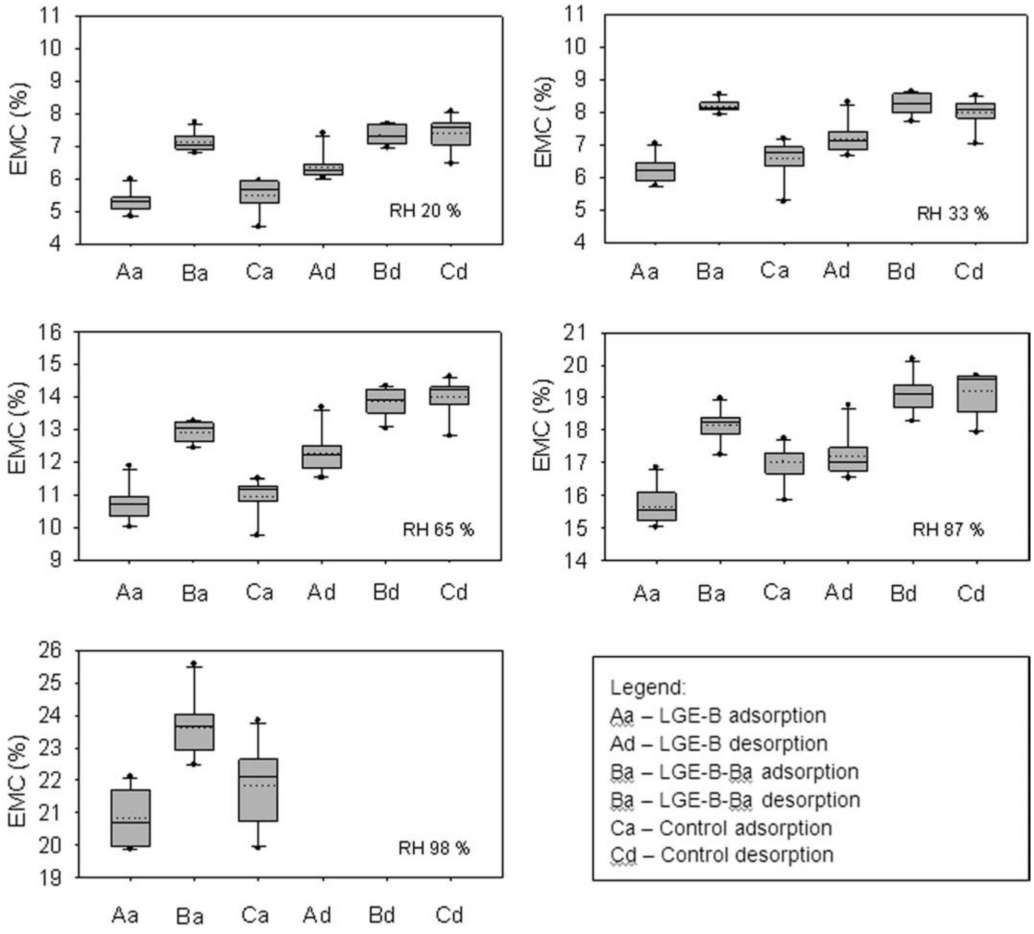

Figure 1 Box-and-whisker plots of the equilibrium moisture content (EMC) of control and impregnated Norway spruces specimens conditioned at five relative air humidity (RH) levels in the adsorption and desorption. Solid line is median, and dotted line is mean value.

the outer part of the specimens is treated, whereas the core remained almost unimpregnated.

However, the most important topic of our research was to elucidate how impregnation of wood with different combinations of montan wax emulsion and Ba influences sorption properties of impregnated wood. First set of sorption experiments was performed in chambers with different RH where Norway spruce specimens impregnated with LGE-B and LGE-B-Ba solution were exposed. Sorption isotherms of all impregnated and control samples have a characteristically sigmoid shape with hysteresis (Figs. 1 and 2). The graphs clearly show that the EMC in desorption process is always higher than that during adsorption at whole hygroscopic region. Hysteresis effect is greater for the control samples than for the impregnated ones. EMC of the samples impregnated with LGE-B was lower than EMC of control samples at all RH stages, for adsorption and desorption processes. For example, MC of montan wax (LGE-A)-treated specimens was lowered by 3–9% in adsorption and by more than 10% in desorption process. It is presumed that the main reason for the reduced MC of LGE-A-treated specimens originates in the hydrophobic effect of thin layer of montan wax on the wood surface and on the surface of the cell walls.[2,6] Second reason for lower EMC was deposits

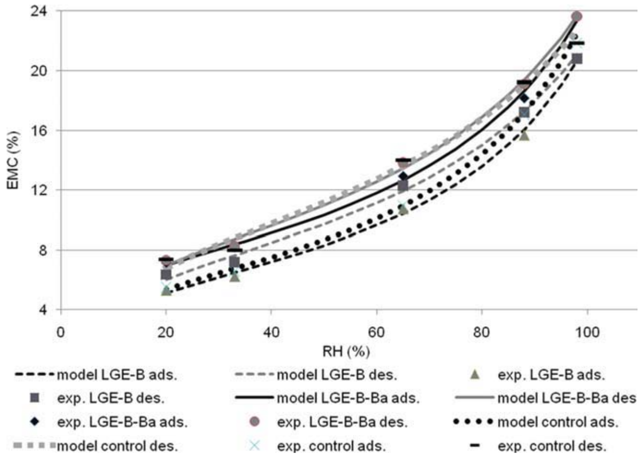

Figure 2 The average EMC of wood impregnated with aqueous emulsion of montan wax (LGE-B) and montan wax emulsion with boric acid (LGE-B-Ba) and control specimens ($n = 10$). GAB model fit curves are shown as well. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Sorption Quotient (s) and the GAB Sorption Model Constants (K, C, and u_0) of Control Wood and Wood Impregnated with Emulsion of Montan Wax (LGE-B) and with Montan Wax Emulsion with Boric Acid (LGE-B-Ba) Conditioned in Five Hygroscopic Regions in the Adsorption (A) and Desorption (D) Process

		Sorption quotient (s), hygroscopic region–RH (%)					GAB model		
Preservative solution	Sorption	33–20	65–20	65–33	88–65	88–33	K	C	u_0 (%)
Control	A	0.08	0.12	0.14	0.26	0.19	0.007604	19.94835	5.8
	D	0.05	0.15	0.19	0.23	0.20	0.006469	14.81227	8.6
LGE-B	A	0.07	0.12	0.14	0.21	0.17	0.00745	18.73971	5.7
	D	0.06	0.13	0.16	0.21	0.18	0.006863	17.13259	7.1
LGE-B-Ba	A	0.08	0.13	0.15	0.23	0.18	0.007201	37.19465	6.9
	D	0.07	0.15	0.18	0.23	0.20	0.006886	20.26673	7.9

of montan wax in cell lumina and cell walls; wood cells were completely filled because of small dimension of samples and high retention.[28] On the other hand, EMC of specimens impregnated with LGE-B-Ba solution was higher than that of control ones, in average for 1.6% points (Fig. 1). The difference between LGE-B-Ba and control samples was approximately the same in the whole hygroscopic region. This is not in line with our previous research,[19] where EMC's of Ba-impregnated wood were higher than the control ones only above 65% RH. However, the differences in EMC at desorption process of LGE-B-Ba-treated and control wood were not significant. It is supposed that higher adsorption EMC's of LGE-B-Ba-impregnated samples originates in hygroscopic properties of Ba[19] and in formation of small crystals with several voids suitable for capillary condensation.[29,30] Sorption quotient shows higher hygroscopicity of LGE-B-Ba-treated wood also (Table II).

Sorption isotherms of the wood treated with montan wax emulsions and of the control unimpregnated wood, obtained according to the GAB model, exhibited good fitting of experimental data in the whole hygroscopic region (Fig. 2). Similar results were obtained also in the previous research.[31] Examination of the GAB parameters in adsorption shows that the values of the monolayer MC u_0 are lower and those of the Guggenheim constant C are higher than for desorption (Table II). In terms of the sorption phenomenon, this means that during adsorption, although there are less sorption sites, they have a greater binding energy, with the multilayer molecules deviating from the free bulk water.[25] Comparison between treatments shows that at adsorption and desorption processes the highest monolayer MC (u_0) was that of samples treated with montan wax and Ba solution (LGE-B-Ba). This indicates that these samples have more available sorption sides, and that they have a greater binding energy, which is shown by a higher constant C at control and only montan-wax-treated samples.[25] For drying samples with higher C constant, more energy is needed, and, at wetting of these samples, more energy is loosen than at samples with lower Guggenheim constant C. Third, constant of GAB model K is just the measure of the difference of free enthalpy of the sorbate (water) molecules in two states and does not give any important information about material. On the basis of the reported results (Fig. 2), it can be concluded that the GAB model is suitable for the prediction of the MC of wood impregnated with montan wax and of wood treated with aqueous solution of montan wax emulsion and Ba.

Results of the moisture changes during dipping in water and during conditioning at high RH (87%) showed that the composition of preservative solutions and their retention have considerable influence on the sorption properties of the treated wood. Moisturizing of wax (LGE-A, LGE-B, LGE-A-Ba, and LGE-B-Ba)-impregnated unsealed specimens was slower compared with control specimens conditioned in the humid air and at the ones immersed in water. On the other hand, moisturizing of Ba-treated specimens was faster, and MC of Ba-treated wood was higher than MC of control specimens [Fig. 3(a–d)]. The samples impregnated with montan wax had lower MC than the control specimens [Fig. 3(a–d)]. Final MC of unsealed specimens impregnated with LGE-A solution, conditioned in chamber with 87% RH, was 11.4%, whereas approximately considerably higher MC was observed at control specimens (12.9%), and the highest MC was measured at Ba-treated samples (14.5%) [Fig. 3(a)]. Moreover, MC of LGE-B- and LGE-B-Ba-impregnated unsealed wood was around 11%, which is considerably lower than MC of control specimens (12.9%) [Fig. 3(b)]. Even more, EMC of control samples was reached at the 18th day, whereas the MC of LGE-B and LGE-B-Ba increased for 53 days, when the experiment was finished. Similar effect was observed for LGE-A-impregnated samples. However, rising of MC of LGE-A-Ba-impregnated wood was faster and reached the same MC than control samples at the end of the conditioning in the humid atmosphere [Fig. 3(a)]. During dipping experiment, similar effect of moisturizing of control and impregnated samples to the effect during conditioning in humid environment was observed

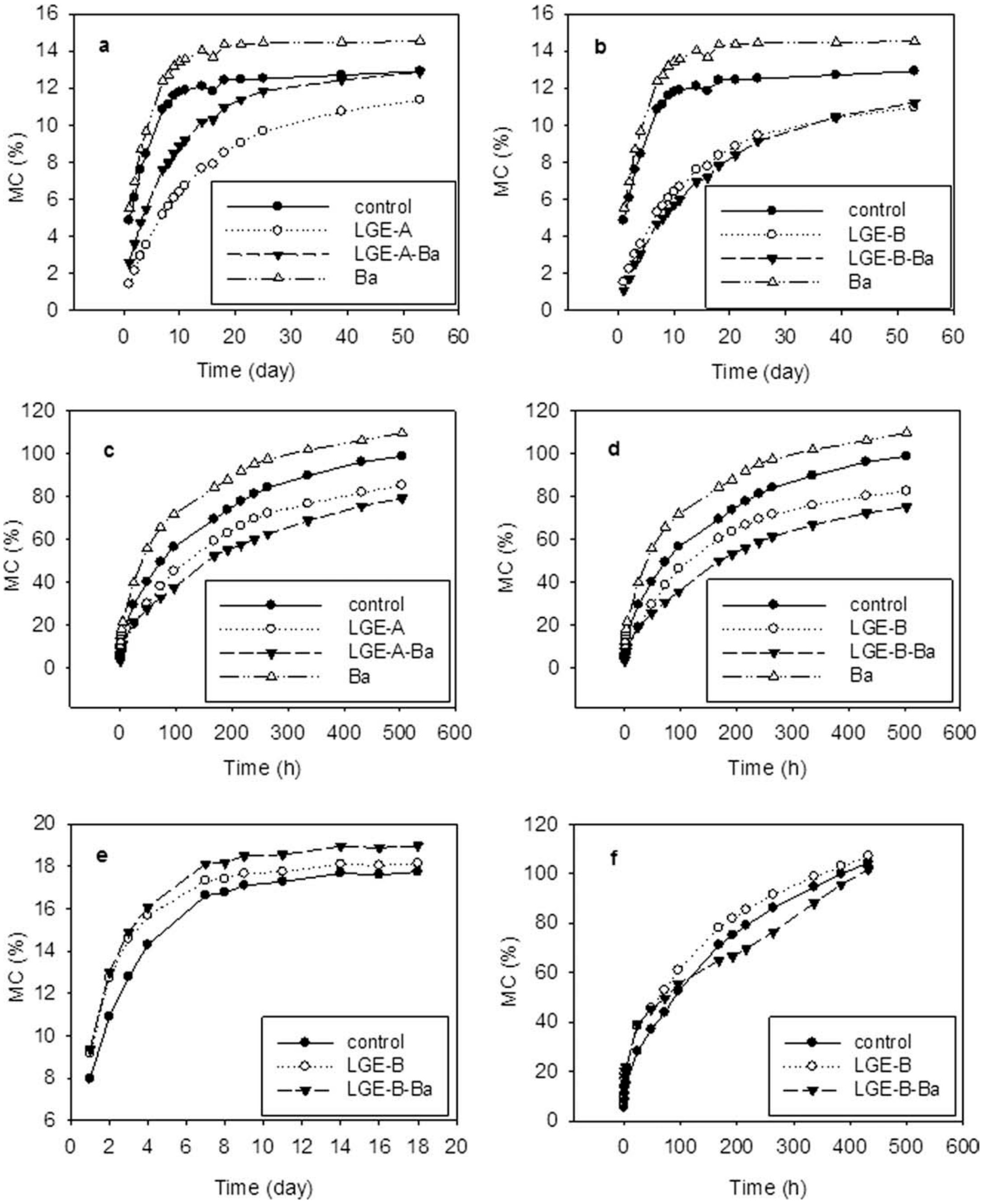

Figure 3 Changes in moisture contents (MC) of the EN 113 Norway spruce control specimens and specimens impregnated with preservative solutions based on montan wax emulsion with (LGE-B-Ba) or without (LGE-B) boric acid, or boric acid alone (Ba) in atmosphere with RH of 82% (a, b, and e) or during immersion in water (c, d, and f). The graphs a, b, c, and d show moisture contents of unsealed specimens and graphs e and f showed MC of sealed specimens.

[Fig. 3(c,d)]. With one exception, MC of LGE-A-Ba- and LGE-B-Ba-impregnated wood was lower than MC of specimens impregnated only with montan wax (LGE-A and LGE-B), but the differences were not significant. After 500 h of dipping in water, LGE-B-Ba-impregnated specimens reached MC of 75%, LGE-B specimens reached MC of 82%, and even higher MC was determined for control samples (99%). The highest MC (109%) was determined for Ba-impregnated specimens [Fig. 3(c,d)].

The results of this study clearly show that the addition of LGE emulsion lowers MC and EMC of impregnated wood. Even more, montan wax emulsion retains positive influence on the MC even in the presence of Ba. MC of wood treated with montan wax emulsion and Ba is lower than that of wood treated with Ba only [Fig. 3(a–d)]. MC of wood treated with Ba is generally higher than control or than LGE-treated wood. The reasons for higher MC of Ba-treated wood were explained in the previous paragraphs. Additionally, possible explanations for lower MC of montan wax-treated wood are similar to those stated before. Namely, wood surface of wax-treated wood is more hydrophobic, which particularly slowed down moisturizing in the first hours of exposure. Second, montan wax forms thin-layer resistant film[13] on the wood surface and acts as barrier. Third, deposits of montan wax and Ba form in the cell lumina, which physically reduce space for water accumulation.[2] All above-mentioned facts are valid for specimens with unsealed axial surfaces, where high retention of wax emulsions were achieved. Conversely, specimens with end-sealed axial surfaces retained approximately three to four times less LGE-based emulsions. It can be clearly seen from Figure 3(e,f) that low quantity of retained wax had no significant influence on MC of impregnated wood. It seems that montan wax, which remained on the surface of the test specimens, was not sufficient to form a barrier that would limit water penetration to the treated wood. It is presumed that wax treatment is suitable for impregnation of more permeable wood species than Norway spruce like Scots pine, radiata pine, beech, etc.

Similar effect as for spruce wood specimens with sealed axial surfaces was evident for bigger (EN 252) Norway spruce specimens, too. As mentioned previously, retention of wax emulsions at EN 113 samples with sealed axial surfaces and EN 252 ones was comparably low. It is supposed that low loadings of emulsion had no influence on MC of Norway spruce specimens exposed in outdoor application. (However, it has to be considered that those specimens were not exposed to the rain.) All wax-treated spruce specimens had MC comparable to the MC of control specimens. This is clear evidence that loadings of wax need to be sufficient to reduce the MC of impregnated wood. On the other hand, two times higher retentions of LGE emulsion and Ba were achieved at beech wood EN 252 specimens; thus, it was presumed that there will be more considerable influence of wax treatment on MC of impregnated beech wood. It can be seen from Figure 4 that MC of treated and untreated control wood was related to RH. At the beginning of the experiment, MC of all impregnated samples was around 3%, whereas MC of control samples was 4.3%. This difference in MC increased during the experiment. After 5 months, MC of impregnated samples with LGE-A and LGE-B was 9.5%, MC of LGE-B-Ba was 20% higher, and MC of control specimens was 35% higher (Fig. 4). It is believed that the main reason for this difference originates in the wax treatment of wood. Montan wax can influence the MC of wood, if it is applied in sufficient loadings. Detailed mode of action is described in the previous sections. Furthermore, it should be considered that those bigger specimens were dried at 103°C before outdoor exposure. Drying of wood at this temperature causes some depolymerization of hemicellulose, which results in lower MCs compared with nondried wood.[32]

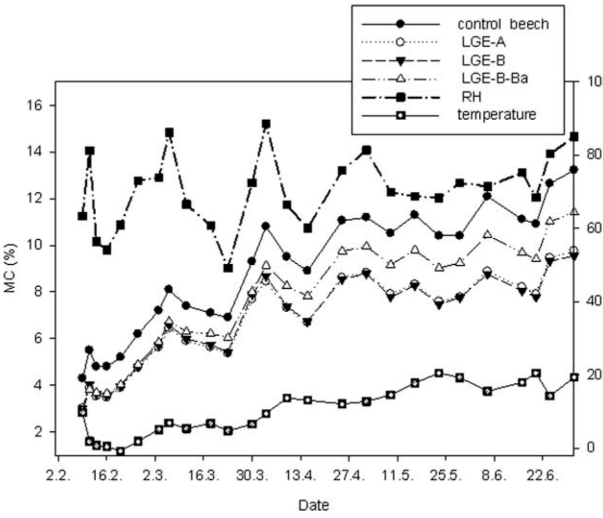

Figure 4 The monitored RH and MC changes of the control and impregnated beach wood EN 252 specimens exposed outdoors, covered application for 5 months, between February and June 2009.

CONCLUSIONS

Retention of preservative solutions was influenced by concentration (viscosity) of the preservative solution, the wood species used, and type (specific surface) of the samples. However, concentration of montan wax in the solution had minor effect on the total amount of retained wax. Specimens impregnated with the lower concentration of montan wax retained approximately the same amount of wax as specimens impregnated with the higher concentration. The amount of retained montan wax determined the hydrophobic effect and sorption properties. The more wax was introduced into the wood specimens, the lower was EMC. To the contrary, the MC of Ba-treated wood was higher than that of the control wood, and MC of wood impregnated with combination of Ba and montan wax, after conditioning at chamber with 87% RH, dipping experiment, and outside exposition, was lower than that of the control wood. In some cases, the MC content of wood treated with montan wax and Ba was even lower than the MC of only montan wax treated wood. The lower MC of treated wood is particularly important from the practical point of view. Leaching of boron compounds from the wood with lower MC is considerably reduced. Second, lower MC of treated wood offers less suitable conditions for mold and fungal growth and increases the performance of such wood.

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3.13 VPLIV SUŠENJA LESA NA SORPCIJSKE LASTNOSTI IMPREGNIRANEGA LESA S POLIETILENSKIMI VOSKI

INFLUENCE OF DRYING ON SORPTION PROPERTIES OF POLYETHYLENE WAX TREATED WOOD

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Drewno
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Pomen voskov v lesni industriji narašča, še posebej v Evropi, odkar se potrošniki zaradi vse večje okoljske ozaveščenosti izogibajo lesu, zaščitenemu z biocidi, in lesu iz tropskih gozdov. Uporabili smo dve vodoodbojni emulziji različnih koncentracij in sicer emulziji polietilenskega (WE1) in oksidiranega polietilenskega (WE6) voska. Lastnosti impregnirane smrekovine (*Picea abies*) in bukovine (*Fagus sylvatica*) smo testirali v dveh sorpcijskih eksperimentih: kondicioniranje pri visoki zračni vlažnosti (87 %) (difuzija vodne pare) in nekontinuirano potapljanje v vodi (kapilarni tok). Sorpcijske lastnosti smo določali na impregniranih vzorcih, sušenih nad točko tališča voska (140 °C), in sušenih v vakuumu (60 °C). Rezultati kažejo, da so sorpcijske lastnosti lesa, impregniranega s polietilenskim (WE1) in oksidiranim polietilenskim (WE6) voskom, odvisne od njihovega navzema. Manjši navzem voska pri smrekovini v primerjavi z bukovino vodi k manjšim razlikam v vlažnosti lesa med impregniranimi in kontrolnimi vzorci tako med kondicioniranjem v vlažnem okolju kot tudi med navlaževanjem med nekontinuiranim namakanjem. Pri kondicioniranju v vlažni klimi smo ugotovili pozitivni učinek impregnacije le pri vakuumsko sušenih vzorcih bukovine. Za zmanjšanje penetracije vode v impregnirane vzorce med nekontinuiranem namakanjem je potrebno vzorce posušiti nad točko tališča voska. Poleg tega rezultati kažejo, da impregnacija vzorcev bukovine in smrekovine s polietilenskim voskom, ki so bili sušeni nad točko tališča, upočasni sušenje med dvema potapljanjema.

Influence of drying on the sorption properties of polyethylene wax treated wood

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Summary

The importance of the use of waxes in the wood industry is increasing, in Europe in particular, since consumers the use of biocidally treated wood and wood from tropical forests due to their increased environmental awareness. In our research, two water repellent emulsions in various concentrations were used: polyethylene and oxidized polyethylene wax emulsion. The performance of wax treated Norway spruce (*Picea abies*) and beech (*Fagus sylvatica*) wood was tested in two sorption experiments: conditioning in high relative air humidity (vapour diffusion) and non-continuous dipping (liquid flow). The sorption properties of oven and vacuum dried impregnated specimens were determined. During conditioning, wax treated Norway spruce vacuum and oven dried specimens had the same moisture content as control ones, while treated vacuum dried beech had up to 25% lower moisture content than parallel control specimens. An even higher difference was evident in volume changes of vacuum and oven dried beech specimens during the sorption test.

Keywords: beech, Norway spruce, polyethylene wax, sorption, wood preservation, water repellents

Introduction

Wood is the most important biopolymer in the world. It is also the most important natural material used for construction applications. As a natural material, it is exposed to weathering and biotic decay. In order to use wood in outdoor applications, it has to be protected somehow. In the past, most preservative solutions had biocidal properties and therefore inhibited pest growth and development [Richardson 1993]. Future solutions for improving the durability of wood preservatives are designed differently. They change the structure of the wood so that wood pests do not recognize it as a food source [Tjeerdsma et al. 1998]; alternatively, the wood moisture content is kept so low that decay processes are no longer possible [Goethals and Stevens 1994]. The treatment of wood with water repellents can affect the long-term properties of this material. Impregnation of wood with resins, waxes, silicones, coatings and other water-repellent formulations greatly reduces the rate of water flow in the capillaries and significantly increases the dimensional stability of specimens exposed to wet conditions [Berninghausen et al. 2006, Kurt et al. 2008]. The most important applications of waxes in the wood industry are therefore found in particleboard production. Paraffin emulsions are introduced to the particleboards in order to reduce the water uptake and improve the dimensional stability [Amthor 1972]. However, there are reports that paraffin treatment can also reduce the water capillary uptake in wood [Scholz et al. 2009]. Furthermore, wax treated wood exhibits increased compression strength and hardness [Rapp et al. 2005]. In addition, wax and oil emulsion additives are incorporated into aqueous wood preservatives to reduce checking and improve the appearance of treated wood exposed outdoors [Evans et al. 2009]. However, paraffin, montan wax or synthetic waxes does not reacts with wood. They either form thin films on the surface of the wood or on the surface of the cell walls, or they fill the cell lumina with waxes and thus limit water penetration into the wood. Since they are insoluble in water, they do not leach from the wood [Berninghausen et al. 2006].

The importance of the use of waxes in the wood protection industry is increasing in Europe in particular, since consumers are avoiding biocidally treated wood and wood from non-sustainable tropical forest due to increased environmental awareness. The industry is therefore interested in the development of alternatives, such as treatment with waxes. There are at least two commercially used wax treatments of wood (Dauerholz in Germany and Natwood in Austria). Nowadays, synthetic waxes, which are used in various coatings, are becoming more and more important in the wood industry. They have some advantages compared to natural waxes: they are cheaper and their properties (melting point) can be set during production [Wolfmeier 2003]. Among the most promising waxes for potential applications in the field of wood protection are polyethylene waxes, which considerably slow down fungal degradation of impregnated Norway spruce or beech wood [Lesar and Humar 2010]. They can also be used as water repellents, since they decrease the water uptake up to 5 times in a short submersion test. However, it was indicated in previous preliminary research that heating or curing wax treated wood affected the wood sorption properties. The present research was performed in order to elucidate the effect of heating wax emulsion treated wood above melting point on the sorption properties of the treated wood.

Material and Methods

Samples (2.0 cm × 2.0 cm × 5 cm) made of Norway spruce (*Picea abies*) and beech (*Fagus sylvatica*) were vacuum/pressure impregnated with various preservative solutions according to the full cell process (20 min -0.9 bar vacuum, 1.5 hour pressure 8 bar, 10 min -0.8 bar vacuum). All specimens had end-sealed (Epoxy coating, EPOLOR, Color) axial surfaces before impregnation. However, sealing needed to be reapplied after the treatment, since some cracks formed. After impregnation, the retention of the preservative solution was determined gravimetrically. The preservative solutions used consisted of aqueous emulsion of polyethylene (WE1) and aqueous emulsion of oxidized polyethylene (WE6) wax. Wax emulsions were purchased from BASF (Germany). The concentrations (dry content) of the wax emulsions can be seen from Table 1. Wax emulsions of two different concentrations were used for impregnation: WE1-A and WE6-A emulsions contained 25% of the original emulsions, while WE1-B and WE6-B emulsions contained 50% of the original emulsions. Control specimens were left un-impregnated and also had end sealed axial surfaces. After three weeks of conditioning at room temperature, half of the impregnated and half of the un-impregnated specimens were oven dried for 21 hours at 103 ± 2

°C and 3 hours above the melting point of the waxes used (140 ± 2°C) [Anonymous 2004a; Anonymous 2004b]. Specimens were cured for 3 hours, which ensured that even the centre of the specimens was heated above 135°C for one hour, as determined by a temperature sensor (EL-USB-TC Lascar Electronics, United Kingdom). The other half of the specimens were vacuum (-0.75 bar) dried at 60°C in a vacuum chamber (Kambič, Slovenia) for 24 hours. The samples were then conditioned in room conditions (21°C and 65% RH) for two weeks.

In order to determine the sorption properties, two types of tests were performed: a vapour diffusion test and a liquid penetration test. In order to elucidate vapour diffusion, half of the oven dried and half of the vacuum dried specimens were transferred to a chamber with a relative air humidity (RH) of 87%. The mass and dimensions of the specimens were monitored for 41 days according to predetermined periods (Figures 1 and 2). In the second part of the experiment, we were interested in liquid penetration and drying of impregnated wood. The other half of the specimens planned for water uptake analysis were immersed in distilled water for 10 minutes on the 1st, 2nd, 3th, 4th, 7th, 9th, 10th, 11th, 14th, 16th, 17th and 18th day. The masses and dimensions of the specimens were monitored before and after immersion (Figures 3, 4 and 5). Dimensions were measured with laser equipment (Department of Wood Science and Technology, Slovenia). Both sorption experiments were performed on ten replicate specimens per emulsion/wood species/drying.

A SEM microscope (JEOL 5500 LV, Japan) was used for surface observation. Wax impregnated and control specimens were coated with a highly conductive film of gold (Sputter Coater SCD 005, Baltec, Germany). Specimens were scanned in high vacuum and an accelerating voltage of 20 kV was used.

Results and discussion

As a result of the impregnation process, Norway spruce specimens retained between 135 kg/m^3 and 197 kg/m^3. In contrast, beech specimens retained considerably higher amounts of the emulsions. In general, they retained between 641 kg/m^3 and 689 kg/m^3 of wax emulsions (Table 1). This result is reasonable as beech wood is significantly more permeable than spruce. It is clearly evident that retention in Norway spruce wood was influenced by the emulsion type and the dry content of the wax. The main reason for this is that the particles in the emulsions are too big (100 nm) [Anonymous 2004a; Anonymous 2004b] to penetrate the cell walls; they even form a barrier on the surface of the cell wall and reduce the penetration of the solvent (water) into the cell walls.

However, the most important focus of our research was to elucidate how polyethylene wax emulsions influences the sorption properties of the impregnated wood. The first set of sorption experiments was performed in a chamber with 87% RH, in which impregnated specimens were conditioned. Half of the specimens were oven dried (140 °C) and the other half were vacuum dried (60 °C). The moisture content (MC) of various control specimens reached equilibrium moisture content (EMC) at approximately 15% after 17 days of conditioning (Fig. 1a, 1b, 1c and 1d). Surprisingly, there are no significant differences in the process of moisturizing and final MC after 41 days of conditioning of vacuum and oven dried control and impregnated Norway spruce specimens (Fig. 1a and 1b). It is presumed that the reason for this is the low retention of wax emulsions in spruce wood [Lesar and Humar 2010; Lesar et al 2010]. Furthermore, there were also almost no differences in the MC of oven dried control and wax treated beech (Fig. 1d). On the other hand, the most prominent vapour barrier was formed with wax treated, vacuum dried beech. Those specimens exhibited lower MC than control ones. The lowest final MC was determined with WE6-B impregnated, vacuum dried beech specimens, the MC of which was 25 % lower than the MC of control ones (Fig. 1c). These results are not in line with our expectations. It was expected that vacuum dried control and wax treated specimens would have a higher MC than oven dried ones. Our finding is in contradiction with two things; first, the thermal decomposition of wood begins at temperatures above 100°C [LeVan 1989; Esteves and Pereira 2009], resulting in decomposition of hemicelluloses [Fengel and Wegener 1989; Orfao and Figueiredo 2001], which are the most hygroscopic wood component [Skaar 1972]. Heat treated wood thus in general has a lower MC in the process of conditioning than non-heated wood. Secondly, curing above melting point led to the formation of a compact film of wax on the wood surface, as can be clearly seen from Fig. 2. There must therefore be some voids in this wax film to enable the diffusion of water vapour. However, it must be taken into account that wax itself is not hydroscopic, since the moisture content of the wax at 98% relative air humidity varied between 1.1% and 1.3%, so it is the sorption properties of the wood that determine the sorption properties of the wax-wood complex.

Table 1: Dry content of waxes used and their retention in Norway spruce and beech wood after vacuum pressure impregnation

Wax emulsion	Conc. (%)	Dry content %	Wood	Retention kg/m^3
WE1-A	25	8.2	Spruce	197 (67)
WE1-B	50	16.5		138 (56)
WE6-A	25	8.3		189 (35)
WE6-B	50	17.8		135 (27)
WE1-A	25	8.2	Beech	689 (24)
WE1-B	50	16.5		641 (78)
WE6-A	25	8.3		683 (31)
WE6-B	50	17.8		679 (40)

The difference in volume changes of wax treated and control specimens were very notable. Fig. 3 shows the volume changes during exposure of the control and wax treated specimens in a chamber with RH of 87%. The shape of the volume change curve during moisturizing is similar to the curve of moisture changes. The differences in volume changes of vacuum and oven dried control and wax treated Norway spruce specimens were not significant, with the exception of vacuum dried WE6-A impregnated specimens, in which swelling was considerably more prominent than the swelling of control specimens (Fig. 3a and 3b). In contrast, all wax treated beech specimens, regardless of the type of drying applied, had up to 40% improved dimensional stability in comparison to control ones. Furthermore, a difference was observed in the dimension changes of vacuum dried and oven dried specimens. The volume changes of impregnated oven dried beech specimens are, surprisingly, lower than the dimensional changes of control ones in terms of the moisture content during the test (Fig. 1d and 2d). These results indicate that polyethylene wax was to some extent bound in the cell walls of the wood [Banks 1973], which prevented swelling of the treated wood. Our results are in contradiction to those of Rowell and Banks [1985], who reported that water repellents cannot interfere to any significant extent with the movement of water into wood by vapour-phase or bound water mechanisms.

In the second set of sorption experiments, control and treated specimens were dipped in and out of distilled water for a period of 10 minutes in order to simulate the occasional wetting that occurs in service life. The moisture content of vacuum dried control spruce specimens before immersion varied between 5.4% and 8.5%. The MC of vacuum dried control beech specimens was between 4.8% and 10.8% (Fig. 4a and 4c). The MC of wood specimens before immersion depended mostly on the drying time between immersion events. The MC of oven dried Norway spruce and beech control specimens before immersion, increased from 1.0% to 7.0% (Fig. 4a, 4b, 4c and 4d). Surprisingly, wax treated Norway spruce and beech specimens exhibited higher MC than control ones. The type of wax emulsions used for the impregnation of spruce did not have a significant influence on the moisture content of the impregnated wood before immersion. The shape of the curve of MC changes before impregnation with wax treated vacuum dried beech specimens is similar to that of vacuum dried Norway spruce specimens, but in general the MC of wax treated beech specimens was higher (Fig. 4a and 4c). Oven dried control and wax treated specimens had similar MC at the beginning of the immersion test in all cases.

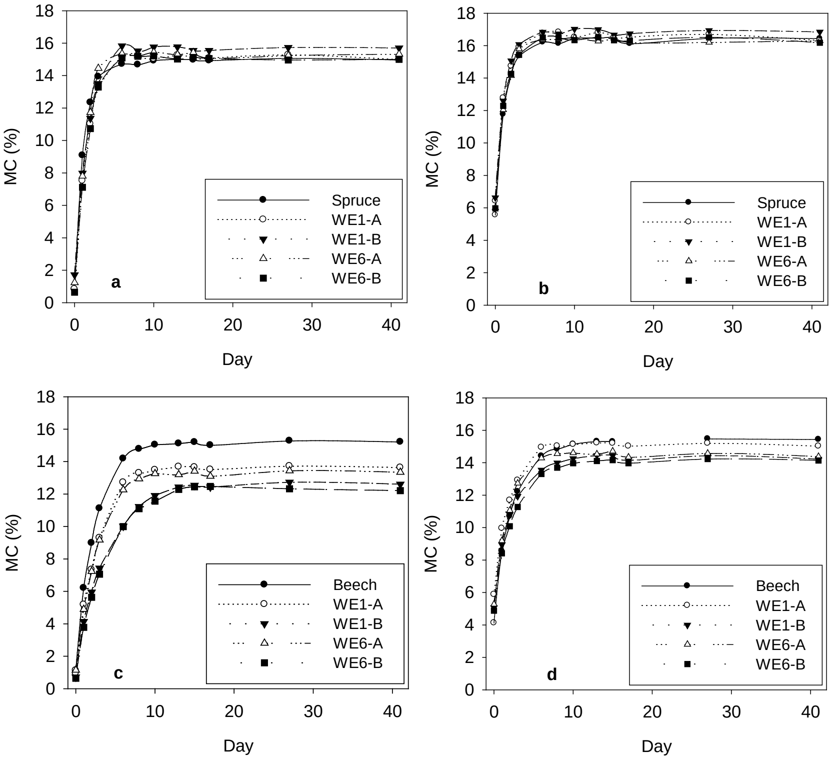

Figure 1: Moisture content during moisturizing in 87 % humidity environment, of polyethylene wax emulsion treated vacuum dried spruce (a), cured spruce at 140 °C (b), vacuum dried beech (c) and cured beech at 140°C (d).

After the immersion events, the MC of all specimens oscillated similarly as reported in the previous chapter, although all values were considerably higher. The MC of vacuum dried Norway spruce control specimens increased on average by approximately 5 percent after immersion. The moisture content of the specimens increased during the tests. For example, the MC of vacuum dried beech control specimens was 9.3% after the first immersion and increased up to 20.5% after the last immersion. Surprisingly, impregnation of spruce wood with waxes did not improve the water repellence but, on the contrary, in certain cases even made the wood hydrophilic. The MC of wax treated vacuum dried Norway spruce specimens was nearly 150% higher than that of control ones. The influence of wax treatment on water uptake during immersion was even more prominent with beech specimens (Fig. 5a and 5c). A comparison of the oven dried and vacuum dried wax treated beech specimens clearly indicates that polyethylene waxes (WE1 and WE6 of both concentrations) must be cured (heated) above the wax melting point in order for the surfaces of the treated specimens to become hydrophobic. We presume that the main reason for this is the morphology of the wax surface on the wood. With vacuum dried specimens, there were small cracks on the surfaces of polyethylene wax impregnated wood samples (Fig. 2a). The cracks acted as capillaries, which took up water and reduced the contact angles of the surfaces [de Meijer and Militz, 2000]. The contact angle of water on vacuum dried WE6 treated wood was about 10°. This makes penetration of water into the wood considerably faster. However, polyethylene wax formed a compact thin film after curing above melting point, which repelled water. This can be clearly seen from the SEM figure (Fig. 2b). However, it must be taken into account that oven drying at 140°C has some effect on the material. The MC of oven dried Norway spruce and beech control specimens increased during the experiment and were approximately 4 percent higher than before immersion. After the last immersion, the MC of spruce specimens was 12.5% and that of beech specimens 12.0%. This is reasonable, since heat treatment is a well-established technology for wood modification [Esteves and Pereira 2009]. However, a combination of wax treatment and oven drying was even more effective. WE1-A, WE1-B, WE6-A treated oven dried Norway spruce specimens had lower MC than control ones (WE6-A up to 15%) (Fig. 5b). WE6-B treated specimens had the lowest MC among oven dried beech specimens; MC was on average 18% lower than determined with parallel control specimens (Fig. 5d). The weak hydrophobic efficacy of polyethylene waxes did not reduce the shrinking or swelling of wood. Differences between vacuum dried control and wax treated spruce and beech specimens were not significant (Fig. 5a, 5b, 5c, and 5d).

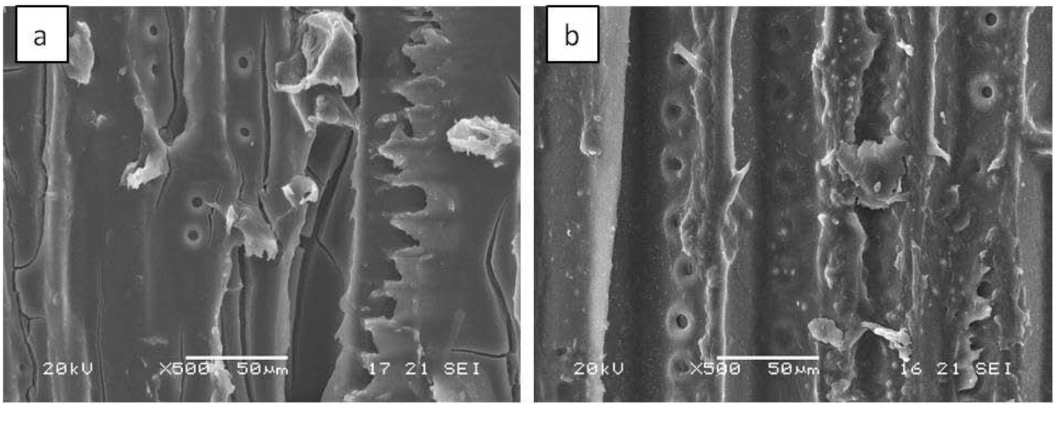

Figure 2: SEM images of surface of un-cured WE6-B (a) and of cured WE6-B (b) impregnated Norway spruce specimens.

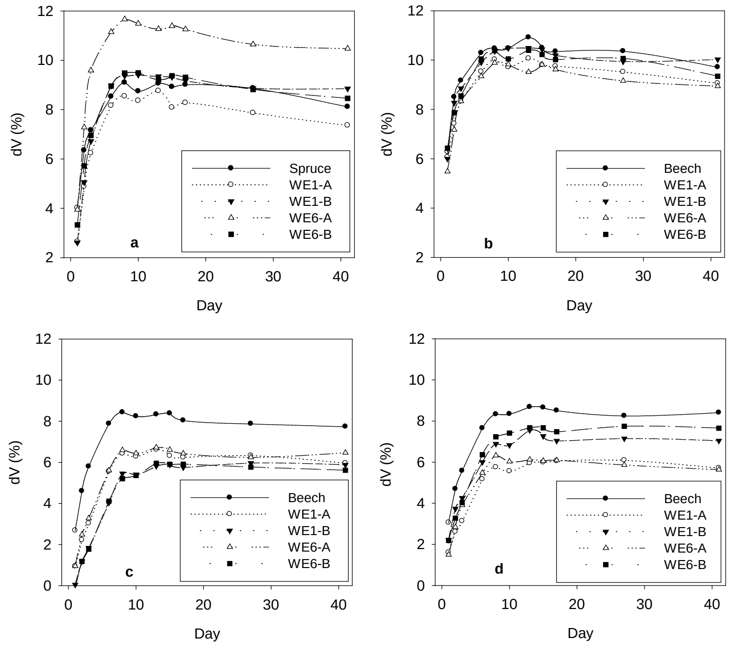

Figure 3: Volume changes during moisturizing in 87% humidity environment, of polyethylene wax emulsion treated vacuum dried spruce (a), cured spruce at 140 °C (b), vacuum dried beech (c) and cured beech at 140°C (d).

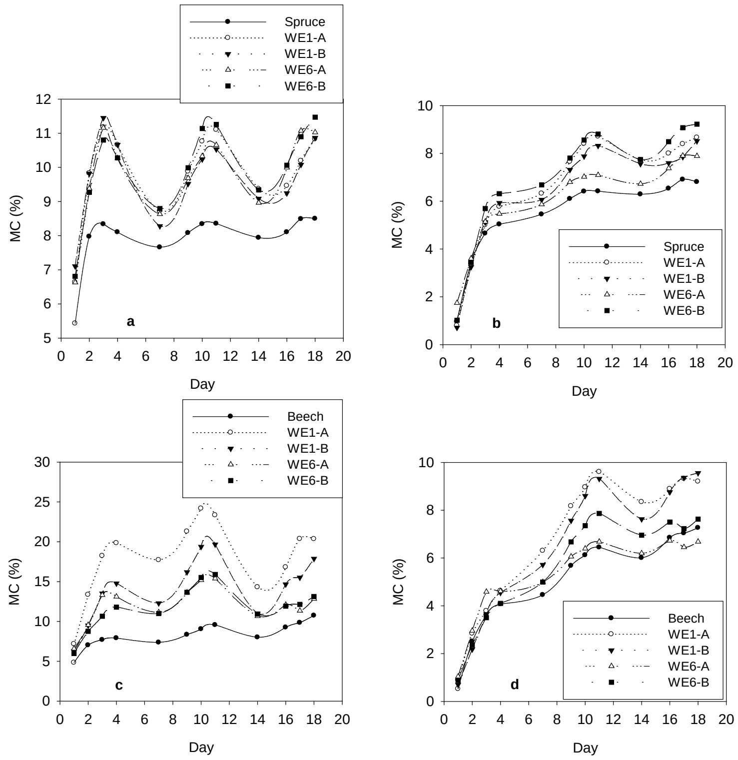

Figure 4: Moisture content of polyethylene wax emulsion treated vacuum dried spruce (a), cured spruce at 140 °C (b), vacuum dried beech (c) and cured beech at 140°C (d) before 10 min non-continuous dipping in water.

From the results presented in this research, it can be seen that vacuum drying of wax treated wood was not as effective a hydrophobic treatment as oven drying of wax treated wood. As already mentioned, the main reason for a higher MC of vacuum dried specimens is the small cracks visible on the surface of WE6 and WE1 treated wood. The small cracks on the surface of vacuum dried treated wood form capillaries, which increase the water flow (de Meijer and Militz 2000). It is also known that some liquid water flow may occur in water repellent treated specimens due to the phenomenon of preferential wetting of wood surfaces by water [Banks 1973]. A reduction of the MC of polyethylene wax treated Norway spruce and beech specimens was only achieved with oven drying at temperatures above the melting point of waxes. After drying the wax treated wood above melting point, polyethylene (WE1) and oxidized polyethylene (WE6) wax formed a film, which prevented fast water penetration into the treated wood and also enabled fast drying of this material after dipping (Fig. 2b). The lower moisture content of treated oven dried wax treated Norway spruce and beech specimens during dipping in water did not result in improved dimensional stability. Rowell and Banks [1985] reported that water repellent treated wood exposed to liquid water for a prolonged period will not only swell to the same extent as similar untreated wood but will also accumulate free water in the cell lumens and therefore eventually attain an MC in excess of fibre saturation. This is in line with our findings.

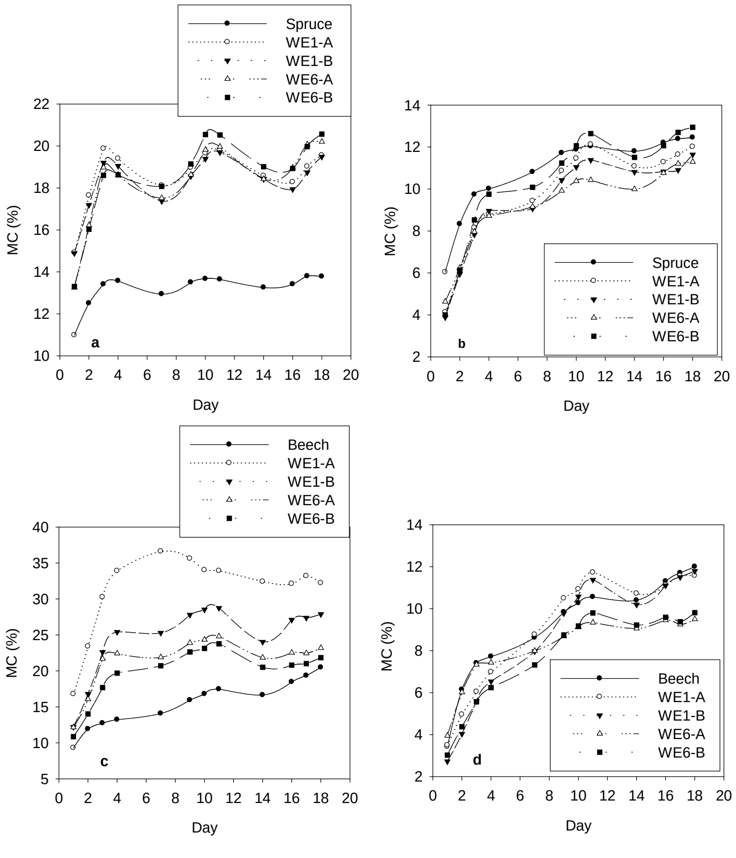

Figure 5: Moisture content of polyethylene wax emulsion treated vacuum dried spruce (a), cured spruce at 140 °C (b), vacuum dried beech (c) and cured beech at 140°C (d) after 10 min non-continuous dipping in water.

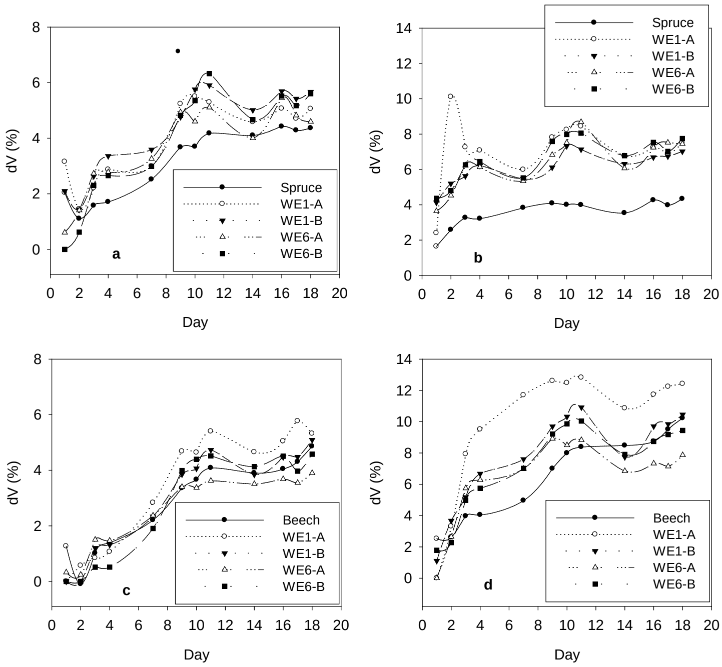

Figure 6: Volume changes of polyethylene wax emulsion treated vacuum dried spruce (a), cured spruce at 140 °C (b), vacuum dried beech (c) and cured beech at 140°C (d) during non-continuous dipping in water.

Conclusions

The sorption properties of polyethylene (WE1) and oxidized polyethylene wax (WE6) are influenced by its retention. Lower retention of wax by Norway spruce compared to beech specimens led to smaller differences between the MC of treated and control specimens during conditioning in humid air and moisturizing during non-continuous dipping in water. During conditioning in humid air, a positive effect of wax treatment was observed on vacuum dried treated beech specimens only. There was improved dimensional stability found with oven dried beech only. In order to achieve slower water penetration into wax treated wood during dipping in water, the wax treated material must be oven dried above the melting point of the wax used. Furthermore, our results clearly showed that polyethylene wax treatment slows down the drying of oven dried Norway spruce and beech specimens.

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3.14 OBDELAVA LESA Z VOSKI UPOČASNI PROCES FOTODEGRADACIJE

WAX TREATMENT OF WOOD SLOWS DOWN PHOTODEGRADATION PROCESSES

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V prispevku smo preučevali vpliv umetnega pospešenega staranja na površinske lastnosti impregnirane smrekovine s tremi tipi emulzij voskov, dveh različnih koncentracij. Za impregnacijo smo uporabili emulzijo montanskega voska (LGE), emulzijo polietilenskega voska (WE1) in emulzijo oksidiranega polietilenskega (WE6) voska. Impregnirane in kontrolne vzorce smo za 500 ciklov izpostavili umetnemu pospešenemu staranju. Pred staranjem in po njem smo določali barvo, kontaktni kot vode in vlažnost izpostavljenih vzorcev. Kemične spremembe izpostavljenih površin smo spremljali z FT-IR spektroskopijo in vrstičnim elektronskim mikroskopom (SEM). Vzporedno smo s tenziometrom določali navzem emulzij voskov in vode s prečne površine vzorcev. Meritve vlažnosti lesa kažejo, da imajo najboljši hidrofobni učinek vzorci, impregnirani z montanskim voskom. Nadalje FT-IR analiza umetno staranih površin lesa kaže, da LGE emulzija upočasni kemično degradacijo in barvne spremembe lesenih površin. Meritve na tenziometru kažejo, da je navzem vode v impregnirane vzorce do devetkrat nižji kot v kontrolne neimpregnirane vzorce.

Wax treatment of wood slows down photodegradation processes

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Abstract

Waxes and wax emulsions are one of the most important solutions for non biocidal wood protection. Wax treated wood is designed for outdoor use, therefore it is of considerable importance to elucidate the influence of weathering on the photo-degradation processes. It is presumed, that wax treatment will reduce water uptake and thus reduce or slow down photo-degradation processes. In order to test this hypothesis, three types of wax emulsions at two different concentrations were vacuum impregnated into Norway spruce wood specimens: an emulsion of montan wax (LGE), an emulsion of polyethylene (WE1) and an emulsion of oxidized polyethylene (WE6) wax. The samples were exposed to artificial accelerated weathering (AAW) for 500 cycles. Before and after AAW colour, the contact angle of water and moisture content were determined. Chemical and morphological changes at exposed surfaces were also investigated with FTIR spectroscopy and SEM. In parallel, the uptake of wax emulsions and water into the axial surfaces of samples was determined with a tensiometer. The moisture content measurements showed that the best hydrophobic effect was achieved with LGE treated wood, where the lowest colour and FTIR changes were observed as well. These results were supported by tensiometer measurements as well. Presented data clearly showed that high loadings of waxes reduce or at least slow down weathering. Among tested waxes, montan wax was found the most effective.

Keywords: contact angle, CIELAB-system, FTIR, wax emulsion, water repellent, weathering

Introduction

Wood is one of the most important materials used for construction. When wood is used outdoors in above ground applications, a variety of different environmental factors degrade its main chemical constituents. These processes, caused by diverse physico-chemical factors are described as weathering [1]. Photochemical degradation is manifested by an initial colour change followed by loss of gloss, roughening and checking. The change of wood colour is thought to be due mainly to the UV light component of sunlight. UV light acts in combination with moisture, heat, environmental pollutants and oxidative agents such as oxygen and/or ozone to depolymerise lignin and cellulose in the wood cell wall [2-4]. Wood contains several chromophoric functional groups and an aromatic skeleton, which make it a good light absorber. Lignin is the most sensitive wood constituent to weathering. Among different wood components, lignin absorbs between

80% and 95% of total UV irradiation due to its various reactive groups and sites, such as primary and secondary hydroxyl groups, carboxyl groups, aromatic and phenolic groups, carbonyl groups, which interact with UV light to form free radicals [5]. This is evident from experiments with lignin models as well. These experiments indicate that destruction of wood polymers is driven predominately by self-sustaining free radical reactions, leading to preferential depolymerisation of lignin, leaving behind a week disorganised surface of cellulose fibres, appearing white to grey in colour [5-7]. Changes in wood colour are therefore a direct indication of chemical or biological changes [1]. However, it should be considered that weathering is surface phenomenon. Weathering reduces service life of wood and increases maintenance cost. For example, permanent failure and replacement of preservative treated pine poles and decking are often caused by checking [5]. Therefore there is increasing interest in the solutions that reduce weathering of wood.

Environmental concerns in the last few years have resulted in renewed interest in non-biocidal solutions for wood protection, such as water repellents. The most important water repellents used in wood preservation are waxes, particularly paraffin waxes [8]. When wax emulsions are applied to wood by vacuum/pressure treatment, waxes penetrates beyond the zone affected by UV degradation, and the wax is expected to perform throughout the life of the treated wood [9]. This has been proved during extensive field trials [7, 10]. Water repellents influence the rate of water uptake and thus reduce dimensional changes of wood during exterior exposure. It is well known that water repellent treatments lower the moisture content of treated wood in water submersion tests [11]. However, laboratory and field tests clearly indicate, that the main reason for failure of hydrophobic treatments is interaction between wood and water, which causes displacement of waxy deposits in the cell wall by a process of preferentid wetting [12]. The inclusion of water repellent additives into preservative treatments, and use of the water repellent alone, improves physical performance of treated wood and minimizes checking and splitting of treated wood in service [7, 9, 13, 14], but on the other hand they do not affect colour change significantly. Long lasting field trials of wood impregnated with solutions containing 1% of water repellent, clearly showed, that water repellent treatment greatly reduce water uptake and imparted a significant degree of long-term dimensional stability to treated wood in service [10]. However field trials of wax treated wood showed, that checking and colour changes were not strongly correlated [7]. Lower-melting point waxes provided better protection against checking, than higher-melting point waxes in the short term, but the latter waxes performed better during long-lasting tests [7]. Furthermore, high-melting point waxes provided better protection against colour changes than low-melting point waxes, as they formed thicker film on the surface reducing penetration of the UV light. In order to increase the ability of hydrophobes (waxes and oils) to limit the colour changes due to water and UV light, it has been suggested that they should contain photoprotective additives [3] or pigments [7]. However, it should be noted that some waxes may be able to photostabilize cellulose, as one of the roles of natural waxes in nature is photo-protection. This is particularly evident at the thin wax layer on the epicuticula. For example, a wax, on the needles of conifers contains nonacosan-10-ol, which is a known photo-stabiliser [15].

Waxes are nowadays used more and more to prolong the service life of wood. In the past, waxes were predominately uses as additives in water-repellent finishes and wood preservatives [5, 10]. Today there are several commercial treatments based on the wax alone without biocides [16], nowadays. This wax treated wood is designed for outdoor use. Therefore it important to understand how waxes influence the weathering of the wood. The objective of this study was to evaluate colour and chemical changes, contact angle of water, of wood treated with montan wax and two polyethylene waxes during artificial accelerated weathering (AAW). It is presumed, that high loadings of waxes applied in the form of emulsion, will reduce water uptake during weathering. It is well known that moisture content and photo-degradation are related [17, 18], thus we presume that wax treatment will slow down photo-degradation processes compared to untreated wood. This effect should be more prominent at the wood treated with waxes that exhibited better water repellence.

Material and Methods

Treatment solutions

Three different types of water based wax emulsions, at two concentrations, were impregnated into wood as follows: an emulsion of montan wax (LGE), an emulsion of polyethylene (WE1) and an emulsion of oxidized polyethylene (WE6) wax. These emulsions are commercially available. The concentrations (dry content) and basic properties of the water based wax emulsions can be seen in Table 1. Emulsifier system used was nonionic/anionic, APEO-free. The density was measured with 100 mL pycnometer at 23 °C according to standard EN ISO 2811-1 (2002) [19]. The viscosity of the wax emulsions was measured with a 4 mm ISO 2431 [20] cup. The surface tension was determined by the Du Noüy Ring method on a Processor Tensiometer K100MK2 Krüss (Germany). A Methrom 827 pH Lab (Switzerland) was used to determine the pH of emulsions. The producers of the emulsions provided data about the melting point of solids and the average particle size.

Table 1: Basic properties of the wax emulsions used. Standard deviations are given in parenthesis.

Wax emulsion	Wax content (%)	Density (g/cm^3)	Surface tension (mN/m)	Viscosity (4 mm, 23 °C) ISO 2431 (s)	pH	Melting point of solids (°C)	Average particle size (nm)
LGE-A	4.9	0.9987	22.1 (0.2)	13	5.5	76-80	100
LGE-B	11.7	0.9976	21.8 (0.2)	12	5.5		
WE1-A	8.2	0.9969	36.6 (0.01)	12.8	9.8	130-135	100
WE1-B	16.5	0.9967	35.9 (0.05)	11.8	9.8		
WE6-A	8.3	0.9967	37.8 (0.01)	12.6	9.1	126-133	100
WE6-B	17.8	0.9966	37.3 (0.02)	12	9.2		
tap water	0	1.0000	67.4 (0.15)	12	-	-	

Artificially accelerated weathering (AAW) and arrangement for accompanying measurements

Norway spruce (*Picea abies* Karst.) wood samples (20_T mm × 100_R mm × 150_A mm) were treated with various wax emulsions prior to AAW (vacuum – 30 min; pressure – 180 min; vacuum – 10 min) (Table 2). The uptake of emulsions and the retention of waxes in wood specimens were determined gravimetrically. Six samples were used for each treatment and six non-treated ones were used as a control. After three weeks of conditioning at 25 °C and 65% relative air humidity (RH) five of each of the impregnated and control samples were exposed to AAW for 500 cycles and one of each was placed in a dark and dry room for 6 weeks. One cycle of AAW lasted for 60 min and was composed of water spray (22 min), UV and IR radiation (27 min) and rest (11 min). Examination of the surface by FTIR spectroscopy and measurements of colour, contact angle of water and moisture content by gravimetrical determination were performed before and after AAW. Furthermore, FTIR analysis and gravimetrical determination of moisture content were also performed after every 100 cycles of AAW. Only measurements of the contact angle of water and FTIR analyses were performed on the unexposed controls.

FTIR analysis

Diffuse reflectance infrared fourier transform DRIFT spectra of wood samples were recorded between 4000 cm^{-1} and 450 cm^{-1} with a Perkin Elmer FTIR Spectrum One Spectrometer using Abrasive Pad 600 Grit-Coated, PK/100 (Perkin Elmer) paper. Spectra were collected at 4 cm^{-1} resolution by co-adding 16 scans. Spectra were displayed in transmittance and limited to the region of interest: 2000 cm^{-1} – 600 cm^{-1}.

Uptake of water (Tensiometer)

Samples for determination of the uptake of wax emulsions and water were prepared from ten radial battens of Norway spruce (*Picea abies* Karst.), measuring 20_T mm × 30_R mm × 800_A mm. The battens were first conditioned for one week at a temperature of 23 ± 2 °C and relative humidity of 50 ± 5 %. The battens were then cut into 21 successive samples measuring 20_T mm × 30_R mm × 40_A mm. From each batten, six sets of three samples were treated with the six different wax emulsions (Table 1) and one set was not treated, and was later used for determination of water uptake of untreated wood. Two samples from the set of three were impregnated (vacuum – 20 min; pressure – 90 min; vacuum – 10 min) with wax emulsion and one was not treated at all. Furthermore, one of them was oven dried (24 h, 135 °C) in order to melt the wax in the wood. These two samples were then used for determination of water uptake to see the effects of treatment on water uptake of wax treated wood. The samples were conditioned for an additional week prior to determination of wax impregnation and water uptake. The measurements were carried out at room temperature 20 °C at an RH of (50 ± 5) % on a Krüss Processor Tensiometer K100MK2. Axial surfaces of the specimens were positioned to be in contact with the test liquid and their masses were subsequently measured continuously every 2 s for 200 s. Other parameters used were: velocity before contact 6 mm/min, sensitivity of contact 0.005 g and depth of immersion 0.5 mm.

Contact angle of water

The sessile drop method was to determine contact angle [21-23]. Contact angle was measured 1 s after the first contact of the liquid with the substrate. Samples were conditioned for one week at (23 ± 2) °C and relative humidity (50% ± 5%). On each sample, five drops (around 5 µL) of deionized water (23 °C) were injected on the radial surface.

The drop of water was filmed for ten seconds with a digital camera mounted on an Olympus SZH stereomicroscope. The camera has the ability to produce 12 pictures per second. Images of the drop in contact with the substrate were continuously captured at full video speed during the first second. From the binary image, the drop profile was evaluated and transferred to a computer. From this profile, the diameter of the contact area and the drop height was measured and the contact angle was calculated.

Colour measurements

A SP62 spectrophotometer produced by X-Rite GmbH - OPTRONIK™ was used to measure the color of treated wood and controls before and after AAW. Ten colour measurements were taken per specimen. On the basis of the measurements before and after AAW, the differences in colour were calculated according to the CIELAB-system [24].

Scanning electron microscopy (SEM)

A SEM microscope (JEOL 5500 LV, Japan) was used to examine the surface of treated wood and controls. Wax impregnated and control specimens were coated with a highly conductive film of gold (Sputter Coater SCD 005, Baltec, Germany). Specimens were scanned in a high vacuum and an accelerating voltage of 20 kV was used.

Results and discussion

Retention of wax emulsions during impregnation

The wax emulsions used in this experiment had different dry contents. They varied between 4.9% (LGE-A) and 17.8% (WE6-B) (Table 1). The densities and viscosities, however, were almost the same for all emulsions used. Specifically, the densities were approximately 1 gm^{-3} and viscosities between 11.8 s and 13.0 s (4 mm) (Table 1). The retention of preservative solutions varied between 151 kgm^{-3} (WE1-B) and 261 kgm^{-3} (LGE-A) for larger samples (20_T mm × 100_R mm × 150_A mm) and between 302 gm^{-3} (WE1-B) and 555 kgm^{-3} (LGE-A) for smaller ones (20_T mm × 30_R mm × 40_A mm). It is clear that retention was influenced by the emulsion type and the dry content of the wax. The main reason for a lower retention of emulsions with a higher dry content is that particles in the emulsions are too big (100 nm) to penetrate the cell walls and, even more, they form a barrier on the surface of the cell wall and also reduce the penetration of the solvent (water) into the cell walls. Similar results have been obtained in previous research [25].

FTIR analysis

The most characteristic bands for the FTIR spectra of WE1, WE6 and LGE waxes are in the regions of 1725 cm^{-1} – 1700 cm^{-1}, 1485 cm^{-1} – 1445 cm^{-1} and 730 cm^{-1} – 710 cm^{-1}. The band between 1485 cm^{-1} and 1445 cm^{-1} is assigned to bending vibrations of -CH_3 and -CH_2- groups, while the bands between 750 cm^{-1} and 720 cm^{-1} represent -CH_2- rocking vibrations. Strong methylene/methyl bands are indicative of a long-chain linear aliphatic structure [26]. The spectra of LGE wax had an additional characteristic peak between 1200 cm^{-1} and 1150 cm^{-1}, which is assigned to ester groups. The FTIR spectra of impregnated wood samples reflect the wax treatment. Characteristic bands for waxes also appear on the spectra of wax impregnated wood. The characteristic bands for wood remain the same as determined for the spectra of untreated wood.

Weathering of wood causes degradation of wood components. Photo-induced degradation of untreated wood led mainly to changes in the absorption intensity at 1740 cm-1 – 1720 cm-1, 1600 cm-1, 1510 cm-1 and 1261 cm-1 (Fig. 2). The assignment of these characteristic IR absorption peaks in wood is shown in Table 2. The same pattern of degradation is also reported in the literature [3, 27-29]. The intensities and changes in these bands are related to changes in the chemical composition of the wood components. The spectra of weathered control samples exhibited reduced absorption at the peaks assigned to lignin. The most significant change as a result of AAW appeared at the peak at 1510 cm-1. This peak almost disappeared within a few hours of AAW [27, 28]. A similar effect is also reported for naturally weathered wood [3]. The absorption peak at 1510 cm-1 is a characteristic peak for lignin C=C stretching vibrations of the aromatic rings present. This peak usually appears at 1515 cm-1 – 1500 cm-1, depending on the ring constituents [29].

Table 2: Characteristic bands of the infrared spectra of the wood samples studied [32]

Wave number(cm^{-1})	Assignment
1740	C=O stretching of acetyl or carboxylic acid
1610 - 1595	C=C stretching of aromatic ring (lignin)
1510	C=C stretching of aromatic ring (lignin)
1465	asymmetric bending in CH_3
1426	CH_2 bending (cellulose)
1335	OH in plane bending (cellulose)
1316	CH_2 wagging
1158 – 1162	asymmetric bridge C-O-C stretching (cellulose)
898	asymmetric out of phase ring stretching (cellulose)

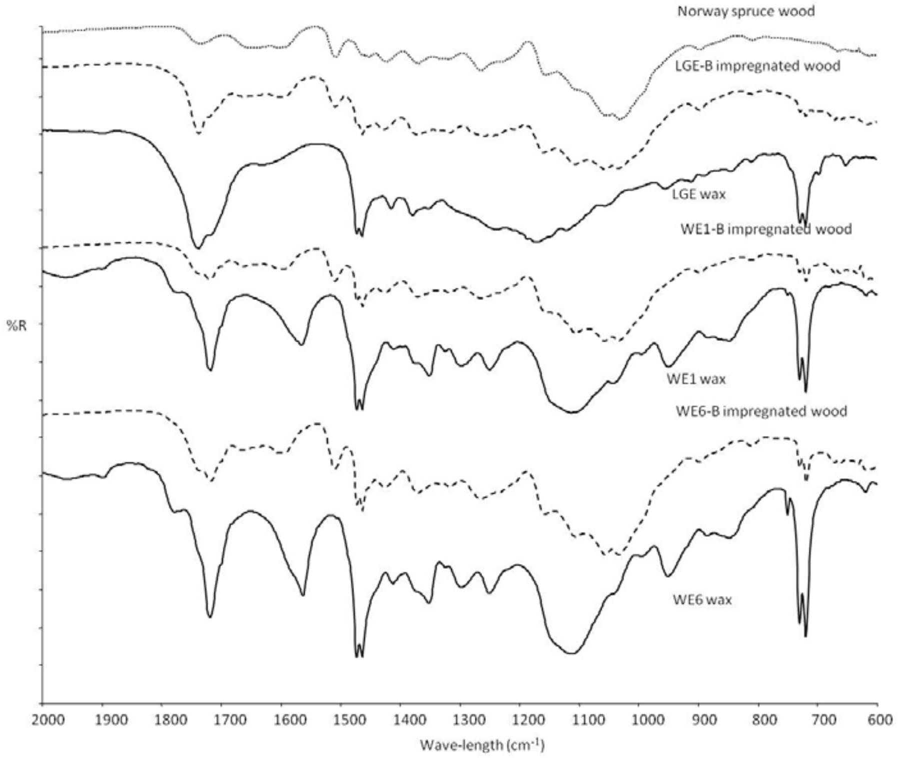

Figure 1: FTIR spectra of montan (LGE) and polyethylene waxes (WE1, WE6) and spectra of wood treated with these wax emulsions.

With all spectra of weathered, wax treated samples, the peak at 1510 cm^{-1} shifted to 1540 cm^{-1} (Fig. 3). Degradation of lignin was slightly reduced due to impregnation with the polyethylene waxes WE1-A, WE1-B, WE6-A and WE6-B. It can be presumed, that the reason for slower photodegradation originates in lower moisture content of wax treated wood (Table 3) and secondly wax forms a layer on the surface of the wood that absorbs certain portion of UV irradiation as well. However, the least prominent changes of the FTIR spectra were found with wood impregnated with the montan wax LGE A and LGE B. With those spectra, the absorption peak at 1510 cm^{-1} remained approximately the same during AAW. This shows that degradation of lignin with LGE-A and LGE-B impregnated wood samples was reduced, which is also in line with colour measurements (below). However, the peaks at 1600 cm^{-1} and 1261 cm^{-1} completely disappeared after 500 cycles of weathering with all impregnated samples. From practical aspects, it is very important that the bands related to waxes in the ranges of 1725 cm^{-1} – 1700 cm^{-1}, 1485 cm^{-1} – 1445 cm^{-1} and 730 cm^{-1} – 710 cm^{-1} remained even after weathering. This clearly indicated that the waxes had remained on the wood surface and had not been washed out during AAW and that they had not been chemically changed. It should also be noted that the spectra of treated and control wood samples stored in a dark room did not exhibit any chemical changes (at least as shown by the FTIR spectra not shown). This indicates that all chemical changes on the control and treated wood samples were the consequence of weathering.

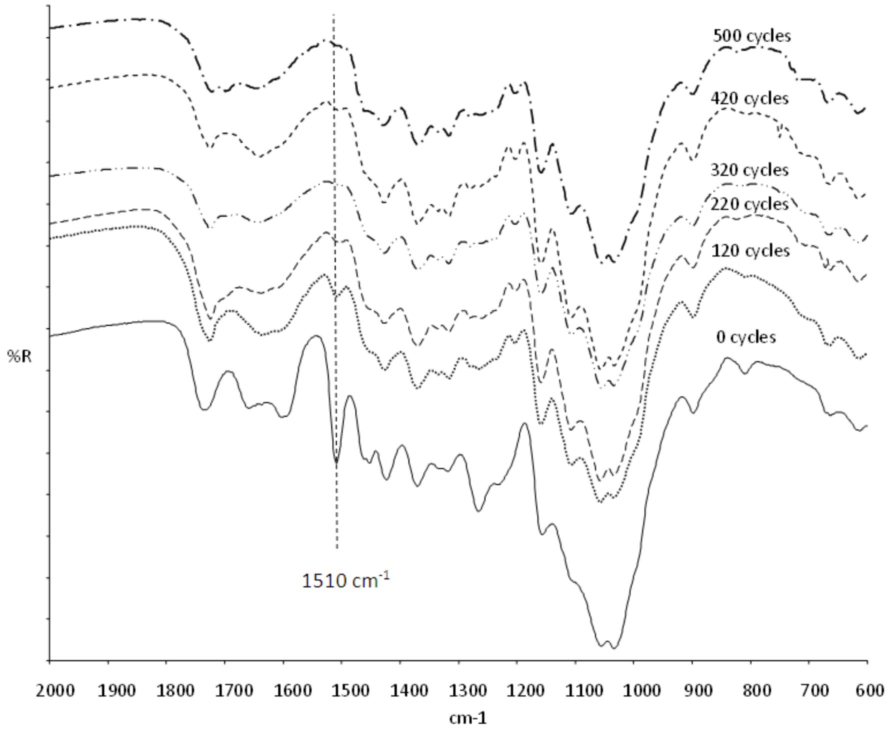

Figure 2: FTIR spectra of artificially accelerated weathered non-impregnated Norway spruce samples.

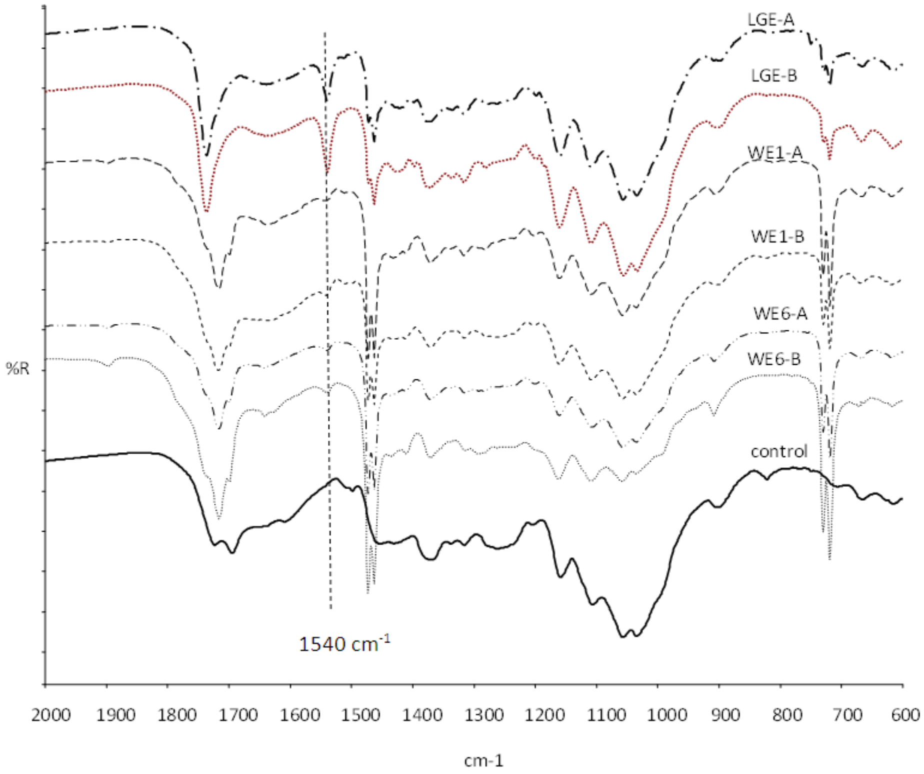

Figure 3: FTIR spectra of non-impregnated and wax treated samples after 500 cycles of artificially accelerated weathering.

Colour measurement

Impregnation of Norway spruce wood specimens with wax emulsions before wethering did not have a significant influence on the colour of treated specimens (Table 4). Colour observations of weathered specimens are in line with the FTIR measurements to the same extent. For specimens where there was little change in FTIR spectra, less prominent colour changes were observed. Nevertheless, the colour of specimens exposed to AAW changed considerably. Colour changes of wax treated wood after 500 cycles of AAW were less prominent than the colour changes of the control specimens (ΔE^{*}= 21.6). The most prominent colour changes appeared after the first 120 cycles of AAW; thereafter, the colour did not change so much (data not shown). Similar results were also observed on melted wax impregnated specimens exposed outside, in which the biggest changes in colour were observed in the first three months of exposure [30]. The lowest ΔE^{*} after AAW was observed with LGE-B treated specimens (16.5) (Table 4). It should be noted that the same samples also had the lowest moisture content during AAW (Table 3). There is a fairly good correlation between the moisture content and the observed colour changes (r^2 = 0.84). Specimens that were less moist during AAW were less discoloured.

However, among colour parameters monitored, the lightness of the specimens (L^{*}) was the most sensitive parameter. All specimens become darker as a result of weathering. Among the tested specimens, the control specimens became the darkest. Changes in the a^{*} and b^{*} components were similar with treated and with control spruce wood specimens. The positive values of Δa^{*} show a tendency of the wood surface to turn reddish, while the negative values of Δb^{*} indicate an increase of blue tones of weathered wood surfaces (Table 4). Colour changes of the weathered surfaces are indicators of chemical changes due to photodegradation [1, 18, 31, 32]. In order to reduce the photodegradation of lignin and to limit the development of visible checks on wood, water repellents should be supplemented with photoprotective additives [3] such as UV absorbers or radical scavengers [33].

Moisture content measurements

The moisture content (MC) of treated and control samples during artificial accelerated weathering was more or less constant during all weathering cycles, with the exception of the first one. The initial moisture content of the treated samples was between 2.7% (WE6-B) and 3.3% (LGE-A). The moisture content of the control samples was a bit higher (4.1%). After 120 cycles of AAW, LGE-B treated samples had the lowest moisture content (29.3%) and control samples the highest (45.8%) (Table 3). Similar differences were noticed during additional cycles of AAW. The moisture content of the weathered control specimens was relatively higher, by approximately 25%, than those of wax treated wood specimens. There was no correlation between the contact angles of water on the surface of the wax treated wood and the moisture content during AAW (Table 3 and 5). However, it is believed that the lower moisture content of impregnated specimens can be summarized in two main reasons. Firstly, the cell lumina in the outer part of the samples were at least partly filled with waxes and this physically prevents moisture uptake. Secondly, there were thin films formed on the surface of the wood specimens, which slowed down water uptake [25, 34]. Slower uptake of water into montan wax (LGE) treated specimens were demonstrated in our previous research [34]. This effect was in particularly evident here with montan wax treated specimens. During conditioning in a wet atmosphere (RH 82%, T 22 °C), they did not reach equilibrium moisture content even after 53 days, while the control specimens reached this point after 21 days [34].

Table 3: Moisture content of control and wax treated samples during artificially accelerated weathering.

Wax emulsion	Moisture content (%)					
	0 cycle	120 cycles	220 cycles	320 cycles	420 cycles	500 cycles
LGE-A	3.3 (0.2)	32.9 (3.4)	33.4 (4.8)	31.5 (2.2)	34.6 (6.7)	33.6 (2.8)
LGE-B	3.2 (0.2)	29.3 (3.7)	28.7 (2.7)	29.6 (2.7)	32.1 (3.4)	31.0 (2.1)
WE1-A	3.1 (0.4)	38.0 (7.2)	38.9 (7.3)	32.9 (3.3)	35.5 (7.0)	32.3 (4.9)
WE1-B	3.0 (0.1)	33.4 (2.4)	34.8 (5.3)	33.6 (3.9)	32.3 (3.6)	33.9 (3.8)
WE6-A	3.2 (0.4)	35.6 (2.4)	32.6 (3.3)	34.7 (2.0)	34.1 (4.6)	31.5 (2.9)
WE6-B	2.7 (0.2)	34.0 (3.6)	33.4 (3.9)	34.2 (2.8)	35.4 (4.5)	34.1 (3.2)
control	4.1 (0.2)	45.8 (4.8)	42.8 (3.0)	41.6 2.8)	45.3 (4.6)	43.9 (2.4)

The hydrophobic effect of the waxes used is evident from the measurement of the water uptake using a tensiometer (Fig. 4). The uptake of water into control spruce wood specimens exceeded 0.8 g. The highest uptake of water was measured with WE1-A treated, uncured specimens (0.86 g), which was a bit higher than that of control samples (0.84 g). The lowest uptake was observed with LGE-B treated specimens (0.05 g) (Fig. 4). The water uptake was faster at the beginning and the speed of uptake then decreased. The curves of the uptake are clearly logarithmic. With control specimens, approximately half of the water was absorbed after 30 s. The curve of the uptake in impregnated specimens was similar to control specimens, but the absorption rate was lower. After 200 s, the LGE-B treated wood took up nine times less water than the control. These results show the hydrophobic effect of the waxes used [13]. The surface of the specimens was also exposed to IR radiation during AAW. The surface of the specimens, probably affected high surface temperatures. It is therefore of considerable interest to determine how heating (curing) of wax impregnated specimens influences water uptake. The results showed that there was a significant difference in cured and uncured wax treated specimens. In general, uptake of water was higher in uncured specimens than in cured ones, with the exception of LGE-B treated specimens. Polyethylene waxes (WE1 and WE6 of both concentrations) must be cured above their melting points for the surfaces of treated specimens to become hydrophobic. Before curing, there were small cracks on the surfaces of the polyethylene wax treated wood samples (Fig. 5a). Cracks formed capillaries, with capillary pressure driving water uptake and reducing the contact angles; the penetration of water into the wood was thus faster. Particles of polyethylene wax formed a compact thin film after curing above the melting point, which repelled water (Fig. 5c). A wax film was found inside both earlywood and latewood tracheids, as well as in ray cells. Similar results were observed with the impregnation of wood with melted waxes [35]. On the other hand, a compact film of wax was already formed on LGE treated specimens after impregnation and air drying. Curing of LGE treated specimens above the melting point of the waxes led to a more uniform distribution of the wax (Fig. 5b and 5d).

Table 4: Colour of the control and wax treated wood before weathering and colour differences after weathering, expressed in the CIELAB-system.

Wax emulsion	*L**	*a**	*b**	*ΔL**	*Δa**	*Δb**	*ΔE**
LGE-A	83.2	3.9	23.7	-18.3	2.3	-4.2	18.9
LGE-B	81.7	4.4	25.1	-15.7	1.6	-4.6	16.5
WE1-A	82.8	3.0	23.3	-17.4	1.2	-5.2	18.2
WE1-B	82.5	2.8	22.8	-16.6	1.3	-5.2	17.5
WE6-A	83.1	3.5	22.2	-17.6	1.1	-4.1	18.1
WE6-B	84.0	3.1	21.1	-18.1	2.5	-2.9	18.5
control	82.6	4.2	22.9	-21.4	1.5	-2.5	21.6

Contact angles of water on the wood surface

The contact angles of water were measured before and after AAW. The highest initial contact angle of water was determined on the control, non-treated specimens (126°), followed by WE1-A (96°) and WE1-B (94°) impregnated samples. This result is rather surprising, since the impregnation of wood with waxes did not result in higher but in lower contact angles of water. The contact angles of water on unweathered Norway spruce controls were slightly higher than those reported in the literature [36-38], but this is not surprising since the wood surface was planed approximately one month before contact angle measurements and oven drying [6]. The lowest contact angle was determined for WE6-A treated samples (3.5°) (Table 5). There could be several reasons for such low contact angles. One is the presence of hydrophilic emulsifiers in wax emulsions. Secondly, polyethylene (WE1) and oxidized polyethylene (WE6) waxes in particular do not form a clear film as LGE wax does. On the contrary, there were visible small cracks in the wax observed on the surface of the treated wood, which prevented the formation of clearly shaped droplets on the surface (Fig. 5a and 5b). The cracks in the wax on the wood surface formed capillaries, with capillary pressure as the driving force for increased water uptake. Secondly, cracks on the surface may have also reduce the contact angle of the water droplets.

Artificial weathering resulted in changes in the contact angles of water in the control and wax treated wood. Specifically, samples with hydrophobic surfaces (contact angle > 90° [13]) (WE1 and control) became hydrophilic after AAW. On the other hand, contact angles of LGE-A and LGE-B impregnated wood increased after AAW. The contact angles of impregnated and control wood specimens did not change significantly during storage, with the exception of the WE1-B treated samples (Table 5).

Results here indicate that high loadings of waxes can slow down photodegradation processes. Among the various waxes tested the montan wax was the most effective. Spruce wood impregnated with montan wax had the lowest changes in FTIR spectra as well as colour changes. There are several explanations for this findings. The most important reason is fact that montan wax reduces the moisture content during weathering more efficiently than other waxes. This is clearly evident from observations during weathering (Table 3) and results for water uptake during immersion (Fig. 4). Previous research has shown that wood moisture content and photodegradation are related [17]. Water molecules swell wood, thereby opening up inaccessible regions of the cell wall to photodegradation. Furthermore, water itself can hydrolyse hemicelluloses in the wood cell wall as well [39]. It follows therefore that high loadings of wax which can restrict moisture uptake by wood could reduce the photodegradation and weathering of wood [18].

Table 5: Retentions of wax emulsions and influence of artificial accelerated weathering (AAW) on contact angles of water on control and wax treated wood. The contact angles of water on wood stored in the dark were monitored in parallel. Standard deviations are given in parenthesis.

Wax emulsion	Retention (kg/m^3)		Contact angle (°)		Contact angle (°)	
	samples 1*	samples 2**	before AAW	after AAW	before storage	after storage
LGE-A	261 (47)	555 (13)	33 (8)	88 (12)	33 (9)	35 (9)
LGE-B	259 (35)	364 (19)	19 (6)	81 (15)	20 (4)	21 (5)
WE1-A	243 (19)	499 (16)	96 (5)	59 (12)	107 (3)	97 (8)
WE1-B	151 (20)	302 (5)	94 (9)	57 (14)	93 (11)	66 (12)
WE6-A	229 (41)	497 (11)	4 (1)	54 (14)	4 (1)	7 (1)
WE6-B	189 (5)	322 (22)	8 (3)	54 (15)	7 (1)	7 (1)
control	0,0	0	126(5)	85 (25)	122 (6)	115 (5)

* samples 1 20_T mm × 100_R mm × 150_A mm, samples for artificially accelerated weathering

** samples 2 20_T mm × 30_R mm × 40_A mm, samples for uptake of water on tensiometer

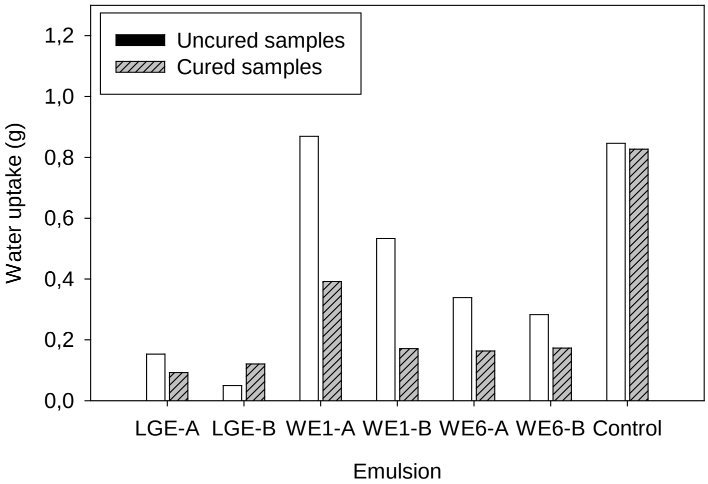

Figure 4: Uptake of water, determined by a tensiometer, into treated cured (135 °C) and uncured Norway spruce samples.

Secondly, montan wax is known as one of the waxes that forms thin and resistant films on the applied surface. This film is more compact and durable than films formed by polyethylene waxes (Fig. 5) and thus performs better. Thirdly, montan wax is produced from lignite and therefore contains aliphatic and aromatic components. Those aromatic compounds presumably absorb UV light possibly protecting wood from photodegradation.

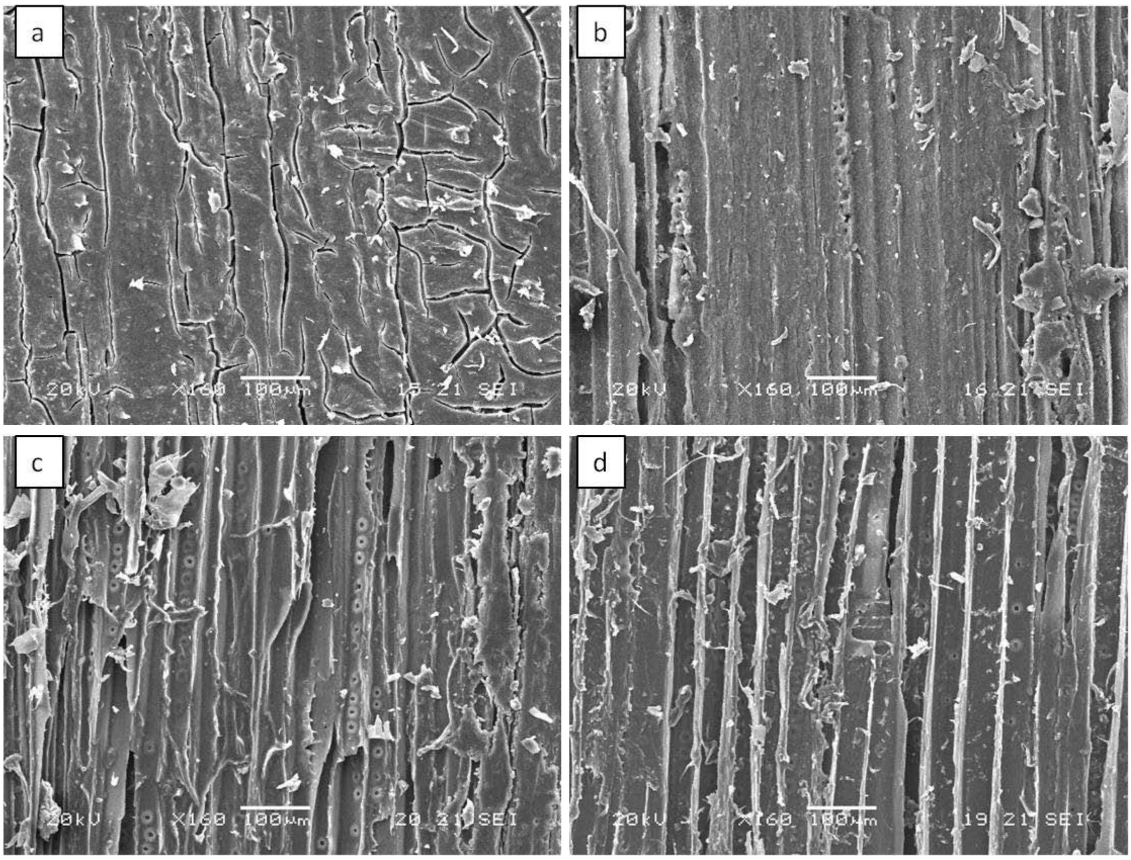

Figure 5: SEM images of surface of uncured WE1-B (a), of uncured LGE-B (b), of cured WE1-B (c) and cured LGE-A (d) impregnated Norway spruce specimens.

Conclusions

Impregnation of wood with waxes influences the performance of wood during artificial accelerated weathering. Treatment of wood with high loadings of wax reduces moisture absorption by wood subjected to accelerated weathering and restricts photodegradation of wood. Among selected waxes, montan wax was the most effective at restricting photodegradation. However, wax treatments reduce the photodegradation only to certain extent; therefore it is of considerable scientific and commercial importance to improve performance of this treatment. One of the ideas for improvement is heating of wax treated wood above wax melting point.

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3.15 VREDNOTENJE ŽIVLJENJSKE DOBE LESA, ZAŠČITENEGA Z EMULZIJAMI VOSKOV IN BAKER-ETANOLAMINSKIMI PRIPRAVKI V TRETJEM RAZREDU IZPOSTAVITVE

SERVICE LIFE PREDICTION OF WOOD TREATED WITH WAX EMULSIONS AND COPPER AMINE BASED SOLUTIONS EXPOSED IN THIRD USED CLASS

Boštjan Lesar in Miha Humar
Zbornik gozdarstva in lesarstva, 2010, 93: 23–36
Prejeto, 7. 9. 2010, sprejeto 19. 11. 2010

Raziskovali smo življenjsko dobo lesa, izpostavljenega na prostem, v tretjem razredu izpostavitve, z dvoslojnim (double layer) testom. V prvem delu raziskave smo naravnim razmeram izpostavili vzorce smrekovine, impregnirane z vodnimi emulzijami montanskih in polietilenskih voskov v kombinaciji z borovimi spojinami. V drugem delu testa pa smo testirali vzorce, zaščitene z baker-etanolaminskim pripravkom na vodni osnovi (Silvanolin) in posameznimi sestavinami tega pripravka. Za primerjavo smo izpostavili še nezaščitene vzorce smrekovine, macesnovine, bukovine in hrastovine. Skozi celotno obdobje izpostavitve smo spremljali klimatske podatke pod vzorci in na vremenski postaji. Rezultati kažejo, da impregnacija z emulzijami voskov in pripravki na osnovi bakra podaljšuje življenjsko dobo lesa, a je zaščita s pripravki na osnovi bakrovih spojin boljša. Odpornost lesa, zaščitenega z emulzijami voskov in baker etanolaminskimi pripravki je odvisna od koncentracije emulzije / raztopine in kvalitete lesa. Na podlagi spremljanja vlažnosti in temperature lesa smo ugotovili, da les nudi ustreznejše vlažnostne pogoje za razvoj gliv, kot bi sklepali iz meritev temperature in vlažnosti zraka.

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Vrednotenje življenjske dobe lesa, zaščitenega z emulzijami voskov in baker-etanolaminskimi pripravki v tretjem razredu izpostavitve

Boštjan LESAR[1], Miha HUMAR[2]

Izvleček

V raziskavi smo preučevali življenjsko dobo lesa, izpostavljenega na prostem, v tretjem razredu izpostavitve, z dvoslojnim testom. V prvem delu raziskave smo naravnim razmeram izpostavili vzorce smrekovine, impregnirane z vodnimi emulzijami montana in polietilenskih voskov v kombinaciji z borovimi spojinami. V drugem delu testa pa smo testirali vzorce, zaščitene z baker-etanolaminskim pripravkom na vodni osnovi (Silvanolin) in posameznimi sestavinami tega pripravka. Za primerjavo smo izpostavili tudi nezaščitene vzorce smrekovine, macesnovine, bukovine in hrastovine. Skozi celotno obdobje izpostavitve smo spremljali klimatske podatke pod vzorci in na vremenski postaji. Rezultati kažejo, da impregnacija z emulzijami voskov in pripravki na osnovi bakra podaljšuje življenjsko dobo lesa, a je zaščita s pripravki na osnovi bakrovih spojin boljša. Odpornost lesa, zaščitenega z emulzijami voskov in baker etanolaminskimi pripravki, je odvisna od koncentracije emulzije / raztopine in kakovosti lesa. Na podlagi spremljanja vlažnosti in temperature lesa smo ugotovili, da se v lesu ustvarjajo ustreznejše vlažnostne razmere za razvoj gliv, kot bi sklepali iz meritev temperature in vlažnosti zraka.

Ključne besede: borove spojine, bakrove spojine, napovedovanje življenjske dobe, naravna odpornost, vlažnost lesa

Service life prediction of wood treated with wax emulsions and copper amine based solutions exposed in third use class

Abstract

In our research, service life of wood exposed outdoor in the third use class, determined with double layer test, was investigated. In the first part of the investigation, Norway spruce wood specimens were impregnated with montan and polyethylene water based wax emulsion in combination with boron compounds. In the second part of the research, Norway spruce wood samples were impregnated with a copper-ethanolamine (Silvanolin) water based solution and aqueous solutions of individual components. For comparison, untreated Norway spruce, larch, beech and oak wood specimens were exposed as well. During exposition time, climate data under specimens and at weather station were recorded. The results showed that impregnation with wax emulsions and copper based solutions prolongs service life of wood, but protection with copper-ethanolamine solutions is considerably better. Resistance of wood, preserved with wax emulsions and copper-ethanolamine solutions, was influenced by concentration of emulsions/solutions and wood quality. The parallel measurements of wood moisture content and wood temperature clearly showed that there were more suitable conditions in wood for development and growth of fungi than indicated by air temperature and relative air humidity measurements.

Key words: *boron compounds, copper compounds, service life prediction, natural durability, wood moisture content*

1 Uvod

1 Introduction

Napovedovanje življenjske dobe lesa na prostem postaja vedno bolj pomembno. Zahtevajo ga različni gradbeni predpisi po vsem svetu. Za Slovenijo je najpomembnejša evropska direktiva o gradbenih proizvodih (European Construction Products Directive, CPD 89/106/EEC), ki v aneksu I podaja zahteve za mehansko odpornost, trdnost in varnost med uporabo.

Na začetku moramo pojasniti tri osnovne pojme, ki so ključni za razumevaje prispevka: naravno odpornost, trajnost in življenjsko dobo lesa. Naravna odpornost lesa je lastnost, ki jo ima les v naravnem zdravem stanju in označuje dovzetnost za škodljivce (SIST EN 350-1 1994). Izraz naravna odpornost se uporablja zgolj za nezaščiten les, medtem ko se za zaščiten ali modificiran les uporablja izraz odpornost lesa. Življenjska doba lesa je obdobje, v katerem les ohrani trdnost in stabilnost, ki sta zahtevani za določen proizvod. Ko so te lastnosti manjše oziroma slabše od zahtevanih, je treba proizvod zamenjati, tako

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da se zagotovi varnost uporabnikov skozi celotno dobo uporabe (BRISCHKE / BAYERBACH / RAPP 2006). V slovenščini se poleg življenjske dobe uporablja še drug podoben izraz: trajnost lesa, ki je definirana kot obdobje, v katerem les obdrži vse svoje naravne lastnosti in je odvisna od (naravne) odpornosti lesa ter mesta in načina vgradnje oziroma konstrukcije ter mesta uporabe (POHLEVEN 2008). Naravne lastnosti lesa so trdnost, odpornost, barva itd., ki se lahko s časom uporabe spreminjajo, na primer barva, a ne vplivajo na zmanjšanje mehanskih lastnosti in odpornosti, ki sta ključni za zagotavljanje varnosti skozi celotno obdobje uporabe lesa. Zato se nam zdi življenjska doba bolj primeren izraz in ga bomo uporabljali v nadaljevanju prispevka.

Življenjsko dobo lesa določa njegova odpornost, ki je posledica kemijske in fizikalne sestave nezaščitenega, modificiranega ali z biocidnimi pripravki obdelanega lesa. Poleg omenjenega na življenjsko dobo vplivajo še dejavniki okolja, ki so bolj ali manj ugodni za razkrojne organizme (glive, bakterije). Zato ima klima pomembno vlogo, vendar je treba razlikovati različne klimatske nivoje: makro klima - določajo jo vremenski podatki določenega kraja, lokalna klima, ki jo določajo lokalne razmere (na primer senca, vetrovna lega…), in mikro klima, kjer se razmere kažejo v konstrukciji. Klima v materialu ima neposreden vpliv na razkroj lesa (BRISCHKE / BAYERBACH / RAPP 2006). S »klimo materiala«, ki jo določajo vlažnost in temperatura lesa ter njuna dinamika, je možno oceniti tveganje za začetek razkroja (BRISCHKE / RAPP 2008b).

Ti dejavniki so ključni za rast in razvoj gliv. Minimalna vlažnost lesa mora biti nad točko nasičenja celičnih sten, optimalna vlažnost lesa za najpomembnejše prostotrosnice znaša med 40 % in 70 % (SCHMIDT 2006). Glive rastejo v temperaturnem območju med 0 °C in 45 °C. Optimalna temperatura je odvisna od vrste gliv in se giblje med 20 °C in 35 °C (HUCKFELDT / SCHMIDT / QUADER 2005). Študije vpliva temperature lesa na življenjsko dobo lesa so redke, vendar se kaže tendenca, da ima les v krajih s povprečno višjo temperaturo zraka krajšo življenjsko dobo (GRINDA / CAREY 2004; BRISCHKE / RAPP 2008a). BRISCHKE in RAPP (2008a) sta preučevala življenjsko dobo lesa v 27 krajih po Evropi in ugotovila, da se je rjava trohnoba pojavila le na borovih vzorcih, izpostavljenih v Ljubljani, medtem ko sta na vseh drugih 26 krajih prevladovali bela in mehka (soft rot) trohnoba.

V preteklosti se je že izkazalo, da so lahko rezultati laboratorijskih testiranj odpornosti zaščitenega lesa zavajajoči. V laboratoriju namreč ni možno v celoti simulirati naravnih razmer za delovanje vseh organizmov, ki povzročajo razkroj lesa (RAPP / AUGUSTA / BRANDT 2006). Namen naše raziskave je bil določiti življenjsko dobo lesa, impregniranega z vodnimi emulzijami voskov, lesa, zaščitnega s sredstvi na osnovi bakra in etanolamina, ter nezaščitenega lesa v tretjem razredu izpostavitve. Vsem omenjenim kombinacijam zaščite lesa, ki smo jih terensko testirali, smo z laboratorijskimi testi že določili njihovo odpornost (HUMAR / LESAR 2008; LESAR / KRALJ / HUMAR 2009; LESAR / HUMAR 2009; LESAR / HUMAR 2010). Zaradi velikega vpliva klimatskih dejavnikov smo celoten čas raziskave spremljali izbrane klimatske podatke (makroklima, mikroklima in »klimo materiala«), ki v največji meri vplivajo na razkroj lesa.

2 Materiali in metode

2 Materials and methods

2.1 Zaščitni pripravki

2.1 Preservative solutions

Raziskavo smo razdelili na dva dela: v prvem delu smo naravnim razmeram izpostavili vzorce, zaščitene z emulzijami voskov, v drugem delu testa pa smo uporabili vzorce, zaščitene z baker etanolaminskimi pripravki in posameznimi sestavinami teh pripravkov. Uporabili smo emulzije montanskega voska (LGE) (Samson Kamnik), emulzijo polietilenskega voska (WE1) BASF (Nemčija) in emulzijo oksidiranega polietilenskega voska (WE6) BASF (Nemčija), različnih koncentracij, razvidnih v preglednici 1. Za primerjavo smo del vzorcev impregnirali z vodno raztopino borove kisline (Ba) (cB = 0,5 %) ter mešanico borove kisline in emulzije montanskega voska dveh koncentracij (LGE-C-Ba in LGE-E-Ba) (Preglednica 1).

Osnovni baker etanolaminski zaščitni pripravek (CuEaQO), ki je dostopen tudi kot komercialni pripravek Silvanolin (Silvaprodukt d.o.o.), smo pripravili z bakrovim(II) sulfatom, kvartarnimi amonijevimi spojinami (alkil dimetil benzil amonijev klorid (ADBAC)) in topborom ($Na_2B_8O_{13} \times 4H_2O$). Etanolamin in oktanojska kislina sta bila dodana za izboljšanje vezave (HUMAR / POHLEVEN 2008). Poleg osnovnega smo pripravili še štiri zaščitna sredstva, ki smo jih zmešali brez ene ali več sestavin osnovnega zaščitnega sredstva. Prva je bila pripravljena z bakrovim(II) sulfatom, etanolaminom in oktanojsko kislino (CuEaO), druga samo z bakrovim(II) sulfatom (CuS), tretja z bakrovim(II) sulfatom in etanolaminom (CuEa) in četrta z etanolaminom, topborom in kvartarnimi amonijevimi spojinami (EaBQ) (Preglednica 2). Kot referenčni biocidni pripravek smo uporabili komercialni pripravek Silvanol GBP (Silvaprodukt d.o.o.) na osnovi bakrovih, kromovih in borovih spojin (CCB), ki se fiksira v les in se že več desetletij uporablja za zaščito lesa na prostem. Vse zaščitne raztopine smo uporabili v dveh različnih koncentracijah, tako da smo po impregnaciji dosegli ciljni navzem zaščitnih raztopin (Preglednica 3). Ciljne navzeme smo izbrali na osnovi laboratorijskih testiranj (ATELŠEK 2007) in priporočil mejnih vrednosti iz literature (WILLEITNER 2001).

Preglednica 1: Mokri navzem zaščitnih pripravkov, suhi navzem voskov, ocena razkroja in globina prodora Pilodyna v vzorce smrekovine in izbranih lesnih vrst.

Table 1: Uptake of preservative solutions, retention of waxes, decay ratings and depth of Pilodyn striker pin into Norway spruce samples and selected wood specimens.

Zaščitni pripravek / *Preservative solution*	Delež voska v emulziji / *Dry content of wax* (%)	Mokri navzem / *Uptake of preservative solution* (kg/m^3)	Suhi navzem / *Dry content*		Datum izposta-vitve / *Beginning of exposure*	Ocena / *Rating*			Pilodyn 3. leto 2010 / *Pilodyn 3rdyear* (mm)
			Vosek / *Wax* (kg/m^3)	Ba / *Ba* (kg/m^3)		2008	2009	2010	
LGE-A	0,12	580	0,7	0	28.5.07	0,4	1,9	2,8	-
LGE-B	0,59	557	3,2	0	28.5.07	0,1	0,7	2,0	-
LGE-C	1,17	546	3,1	0	28.5.07	0,2	2,1	3,0	-
LGE-D	5,90	149	8,5	0	19.6.08	-	0	0,1	14
LGE-E	11,70	118	13,8	0	19.6.08	-	0	0	11,3
LGE-C-Ba	1,17	488	5,6	13,7	28.5.07	0	0,2	1,5	20,8
LGE-E-Ba	11,70	119	13,9	3,3	19.6.08	-	0	0	15,7
LGE-P	1,17	17	0,2	0	28.5.07	0	0,1	1	20,3
WE1	16,50	100	16,5	0	19.6.08	-	0	0	-
WE6	17,00	106	18,2	0	19.6.08	-	0	0	-
Ba	0	661	0	18,8	28.5.07	0	0	0,7	22,3
Smreka 07**	0	0	0	0	28.5.07	1,4	2,5	3,7	*25+
Smreka 08**	0	0	0	0	19.6.08	-	0	0,2	19,3
Macesnovina	0	0	0	0	19.6.08	-	0	0	13,3
Bukovina	0	0	0	0	28.5.07	1,2	2,5	3,0	*25+
Hrastovina	0	0	0	0	28.5.07	0,3	0,1	0,1	-

*25+ - igla je prodrla skozi celotno debelino vzorca
Smreka 07** - kontrolni vzorci smrekovine izpostavljeni 28. 5. 2007
Smreka 08** - kontrolni vzorci smrekovine izpostavljeni 19. 6. 2008

Preglednica 2: Sestava zaščitnih pripravkov na osnovi bakra in etanolamina. Pred uporabo smo pripravke ustrezno razredčili, da smo dosegli zastavljeni ciljni navzem.

Table 2: Composition of preservative solutions based on copper and ethanolamine. Prior to use, the preservative solutions were diluted in order to achieve targeted retentions.

Zaščitni pripravek / *Preservative solution*	Masa posamezne sestavine v 1000 g zaščitnega pripravka / *Mass of selected ingredient in the 1000 g of the respective preservative solution*				
	Bakrov(II) sulfat penta hidrat (CuS) / *Copper(II) sulphate pentahidrate (CuS)*	Etanolamin (EA) / *Ethanolamine (Ea)*	Oktanojska kislina (O) / *Octanoic acid (O)*	ADBAC*	Topbor (B) / *Topbor (B)*
	(g)	(g)	(g)	(g)	(g)
CuS	39,3	-	-	-	-
CuEa	39,3	57,7	-	-	-
CuEaO	39,3	57,7	8,1	-	-
CuEaQO	39,3	57,7	8,1	10	22,7
EABQ	-	57,7	8,1	10	22,7

* alkil dimetil benzil amonijev klorid

Preglednica 3: Navzem baker etanolaminskih pripravkov, ocena razkroja in globina prodora Pilodyna v vzorce smrekovine. Vzorci so bili izpostavljeni terenskemu testiranju od 7. 4. 2006 do 15. 6. 2010.

Table 3: Retention of copper ethanolamine preservative solutions, decay ratings and depth of Pilodyn striker pin into Norway spruce specimens. Specimens were exposed outdoors from 7. 4. 2006 to 16. 6. 2010.

Zaščitno Sredstvo /*Preservative solution*	Ciljni navzem / *Expected dry content* (kg/m^3)	Mokri navzem / *Uptake of preservative solutions* (kg/m^3)	Suhi navzem / *Dry content* (kg/m^3)	Ocena / *Rating*				Pilodyn 4. leto / *Pilodyn* 4th*year* (mm)
				2007	2008	2009	2010	
CuEaQO	4,9	397	4,0	0	0	0	0	11,3
	19,6	368	18,1	0	0	0	0	11,7
CuEaO	1,2	276	1,3	0	0	0	0,1	14,7
	5,6	301	5,6	0	0	0	0	12,0
	14,9	340	12,7	0	0	0	0	10,3
CuS	1,4	305	1,1	0	0	0	0,1	14,3
	5,6	461	6,5	0	0	0	0	11,0
CuEa	3,4	210	2,1	0	0	0	0,3	12,8
	13,8	316	10,9	0	0	0	0	10,3
EaBQ	3,5	339	3,4	0	0	0,1	0,4	19,0
	14,0	254	8,9	0	0	0,5	0,5	12,5
CCB	4	409	4,1	0	0	0	0	12,3
Smreka 06*	0	0	0	0,2	0,8	1,8	2,8	15

Smreka 06*- kontrolni vzorci smrekovine izpostavljeni 7. 4. 2006

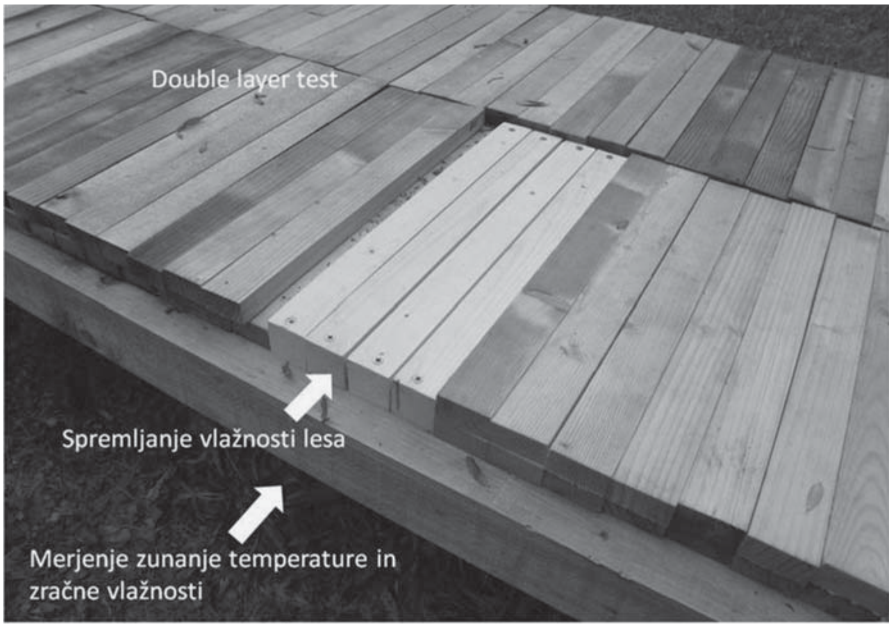
2.2 Impregnacija in izpostavitev vzorcev

2.2 Impregnation and exposure of wood samples

V raziskavi smo uporabili vzorce smrekovine (*Picea abies* Karst.), dimenzij 25 mm × 50 mm × 500 mm. Vzorci so bili pol-radialni, branike so z vzdolžno površino tvorile kot 45±15°. Vzorce smo po treh tednih uravnovešanja pri 20 °C in 65-odstotni relativni zračni vlažnosti (RH) impregnirali z emulzijami voskov po vakuumsko tlačnem postopku (30 min -0,9 bar vakuum, 3 h nadtlak 8 bar, 10 min -0,8 bar vakuum). Z baker etanolaminskimi pripravki smo vzorce impregnirali po nekoliko spremenjenem postopku; 1 h -0,9 bar vakuum, 2 h 6 bar in 15 min pri normalnem tlaku. Po impregnaciji smo vzorcem gravimetrično določili mokri navzem posameznih zaščitnih sredstev. Za vsako/vsakega od uporabljenih emulzij/raztopin/kontrolnih vzorcev smo uporabili po 10 vzporednih vzorcev.

Po štirih tednih sušenja v sobnih razmerah smo impregnirane in kontrolne vzorce terensko testirali. Poleg kontrolnih smrekovih vzorcev smo za primerjavo uporabili neodporne vzorce bukovine (*Fagus sylvatica* L.) in odporne vzorce jedrovine macesna (*Larix* sp.) in jedrovine hrasta (*Quercus* sp.). Ves les je izviral iz osrednje Slovenije. Vzorce smo izpostavili terenskemu testiranju v različnih časovnih obdobjih, in sicer: 7. 4. 2006, 28. 5. 2007 in 19. 6. 2008 (Preglednica 1 in Preglednica 3). Izpostavili smo jih na Oddelku za lesarstvo v Rožni dolini v Ljubljani na pretežno senčno in zatišno lego (310 m n.m.). Izpostavljeni so bili v tretjem razredu izpostavitve (nepokrito na prostem, pogosto močenje) (SIST EN 335-1/2 1992). Za določanje trajnosti lesa smo v naši raziskavi uporabili dvoslojni test (ang. double layer test) (RAPP / AUGUSTA 2004; SIST EN 252 2004). Pet enako obdelanih vzorcev smo zložili v spodnjo in pet v zgornjo vrsto. Vzorci v zgornji vrsti so bili za polovico vzorca zamaknjeni. Med različno obdelanimi vzorci so bili slepi vzorci (nezaščiteni smrekovi vzorci slabše kvalitete) (Slika 1).

Skozi celotno obdobje trajanja raziskave smo vsako uro spremljali temperaturo in zračno vlažnost z vremensko postajo Davis, ki je bila postavljena na Gozdarskem inštitutu (cca. 300 metrov oddaljena od testnega polja). Podatke o dnevni količini padavin smo pridobili od Agencije Republike Slovenije za okolje s klimatološke postaje Ljubljana Bežigrad. Klimatski podatki so prikazani kot povprečja tedenskih meritev.



Slika 1: Dvoslojni test in spremljanje vlažnosti kontrolnih in zaščitenih vzorcev smrekovine na Biotehniški Fakulteti Oddelku za lesarstvo v Ljubljani.

Figure 1: Double layer test and moisture content measurements of control and treated samples at the Biotechnical Faculty Department for Wood Science and Technology.

Ocenjevanje vzorcev je potekalo vsako leto med petnajstim majem in petnajstim junijem. Vsak vzorec smo si natančno ogledali in ocenili stopnjo razkroja po standardu (SIST EN 252 2004; SIST-TS CEN/TS 12037 2005; RAPP / AUGUSTA 2004) (Preglednica 4). V letu 2010 smo vizualno oceno podkrepili še z meritvijo prodora udarne igle v vzorec. V ta namen smo uporabili Pilodyn 6J proizvajalca Fuji Teck K.K (Japonska). Naprava deluje tako, da s konstantno udarno močjo (6 J) udari iglo s premerom 2,5 mm in dolžino 60,2 mm v les.

Preglednica 4: Ocene razkroja vzorcev (RAPP / AUGUSTA 2004; SIST EN 252 2004).

Table 4: Decay ratings of samples (RAPP / AUGUSTA 2004; SIST EN 252 2004).

Ocena / *Rating*	Razvrstitev / *Classification*	Opis preizkušanca / *Definition of condition*
0	Ni znakov razkroja	Na preizkušancu ni zaznavnih sprememb
1	Neznaten razkroj	Na vzorcu so vidni znaki razkroja, vendar razkroj ni intenziven in je zelo prostorsko omejen: - Spremembe, ki se pokažejo predvsem kot sprememba barve ali zelo površinski razkroj, mehčanje lesa je najpogostejši kazalec, razkroj sega do 1 mm v globino.
2	Zmeren razkroj	Jasne spremembe v zmernem obsegu: - Spremembe, ki se kažejo kot mehčanje lesa 1 mm do 3 mm globoko na 1 cm^2 ali večjem delu vzorca.
3	Močen razkroj	Velike spremembe: - Izrazit razkroj lesa 3 mm do 5 mm globoko na velikem delu površine (večje od 20 cm^2), ali mehčanje lesa globlje kot 10 mm na površini, večji od 1 cm^2.
4	Propadanje	Preizkušanec je močno razkrojen: - Ob padcu z višine 0,5 m se zlomi.

Nato na merilcu odčitamo globino prodora igle. Meritve prodora igle smo opravljali na treh vzporednih vzorcih za posamezno serijo.

2.3 Spremljanje vlažnosti lesa

2.3 Moisture content measurements

Vzporedno smo na impregniranih in kontrolnih vzorcih smrekovine (45 mm × 45 mm × 500 mm) spremljali vlažnost lesa (Slika 1). V obdobju od 3. 7. 2007 do 26. 8. 2008 smo spremljali vlažnost lesa na dveh kontrolnih in dveh vzorcih, impregniranih z 10-odstotno vodno emulzijo voska montana (LGE). V obdobju od 27. 8. 2008 do 15. 6. 2010 pa smo spremljali vlažnost dveh kontrolnih in dveh vzorcev, zaščitenih z oksidiranim polietilenskim voskom (WE6). Impregnacija vzorcev in uravnovešanje sta potekala po enakem postopku kot pri vzorcih za dvoslojni test. Po uravnovešanju smo v sredini vzorca do polovice globine izvrtali luknjo premera 20 mm in vanjo vstavili H-gumbek 23 (Thermo Track, ProgresPlus). Luknjo smo zatesnili z lesenim čepom, zavitim v PVC folijo (Slika 2).

Slika 2: H-gumbek 23 za merjenje temperature in zračne vlažnosti ter njegova namestitev v vzorec.

Figure 2: H-button 23 for temperature and relative humidity measurement and its installation into wood samples.

H-gumbek 23 omogoča merjenje in beleženje temperature v območju od -20 °C do + 85 °C ± 0,5 °C in zračne vlažnosti od 0 % do 100 % ± 0,1 %. Temperaturo in zračno vlažnost v vzorcu smo zabeležili vsako uro. Ko smo podatke prenesli v računalnik, smo s pomočjo enačbe 1 izračunali vlažnost lesa (EVANS 2004) in jih podali kot povprečne tedenske vlažnosti lesa.

$$MC=(5RH^3-(589,1-0,76T)RH^2+100(370,1-0,7T)RH-100(564,9-6,8T))10^{-5} \tag{1}$$

MC = vlažnost lesa v %, RH = relativna zračna vlažnost v %, in T = temperatura v °C

Vzporedno smo s H-gumbkom merili zunanjo zračno vlažnost in temperaturo. Gumbek je bil nameščen na gredici pod vzorci, ki smo jim merili vlažnost (Slika 1). Tako smo zagotovili popolno senčenje gumbka. Meritve smo beležili vsako uro in jih podali kot povprečne tedenske temperature oziroma zračne vlažnosti.

3 Rezultati in razprava

3 Results and discussion

V prvem delu smo preučevali življenjsko dobo vzorcev, impregniranih z emulzijami voskov in raztopino borove kisline. Mokri navzem zaščitnih sredstev na osnovi emulzij voskov je znašal za premazane vzorce 17,3 kg/m^3, za vakuumsko-tlačno impregnirane vzorce je bil po pričakovanju precej višji, in sicer med 100 kg/m^3 (WE1) do 580 kg/m^3 (LGE-A), najvišji navzem pa so imeli vzorci, impregnirani z raztopino borove kisline (c_B = 0,5 %) 661 kg/m^3 (Preglednica 1). Iz rezultatov je razvidno, da na mokri navzem vpliva delež suhe snovi (voska) v emulziji. Glavni razlog za manjšo penetracijo emulzij z višjim deležem suhe snovi je, da so delci emulzije po informacijah proizvajalcev (ANONYMUS 2005) preveliki (100 µm), da bi prodrli v celično steno. Voski na površini celičnih sten tvorijo oviro in tako zmanjšujejo tudi prodiranje vode v celične stene med impregnacijo. Podobne rezultate smo dobili tudi v eni izmed naših prejšnjih raziskav (LESAR / ZUPANČIČ / HUMAR 2008). Dodatek borove kisline k emulziji ni vplival na mokri navzem. Poleg mokrega navzema smo spremljali tudi suhi navzem, ki je v neposredni povezavi z mokrim navzemom in deležem suhe snovi posameznega pripravka. Najnižji suhi navzem voska je bil pri premazanih vzorcih (LGE P) (0,2 kg/m^3), najvišji pa pri vzorcih impregniranih, z emulzijo oksidiranega polietilenskega voska (WE6) (18,2 kg/m^3). Suhi navzem borove kisline je znašal med 3,3 kg/m^3 (LGE-E-Ba) in 18,8 kg/m^3 (Ba) (Preglednica 1). Visoki navzem borove kisline v vzorce, impregnirane le z raztopino borove kisline, je pričakovan, saj v pripravku ni bilo emulzije, ki bi ovirala prodiranje borove kisline v les. Kakorkoli, koncentracija borove kisline v lesu je zadostna za zaščito lesa pred najpomembnejšimi glivami razkrojevalkami. Predhodni eksperimentalni podatki so namreč potrdili, da je za zaščito lesa pred lesnimi glivami dovolj 0,8 kg borove kisline / m^3 (LESAR / HUMAR 2009). Po drugi strani pa je treba upoštevati, da se borova kislina iz lesa izpira in s tem slabi tudi kakovost zaščite.

V drugem delu raziskave smo uporabili različne kombinacije biocidnih pripravkov na osnovi bakra, za vsak pripravek smo izbrali po dva ciljna suha navzema. Dobljeni navzemi so se od ciljnih razlikovali za približno ± 25 %, razen pri vzorcih, impregniranih z EaBQ, ker je bil dejanski navzem manjši za 37 %. Razlike v pričakovanih in doseženih suhih navzemih so večinoma posledica nehomogene zgradbe lesa. Do podobnih nihanj prihaja tudi v praksi (RICHARDSON 1993).

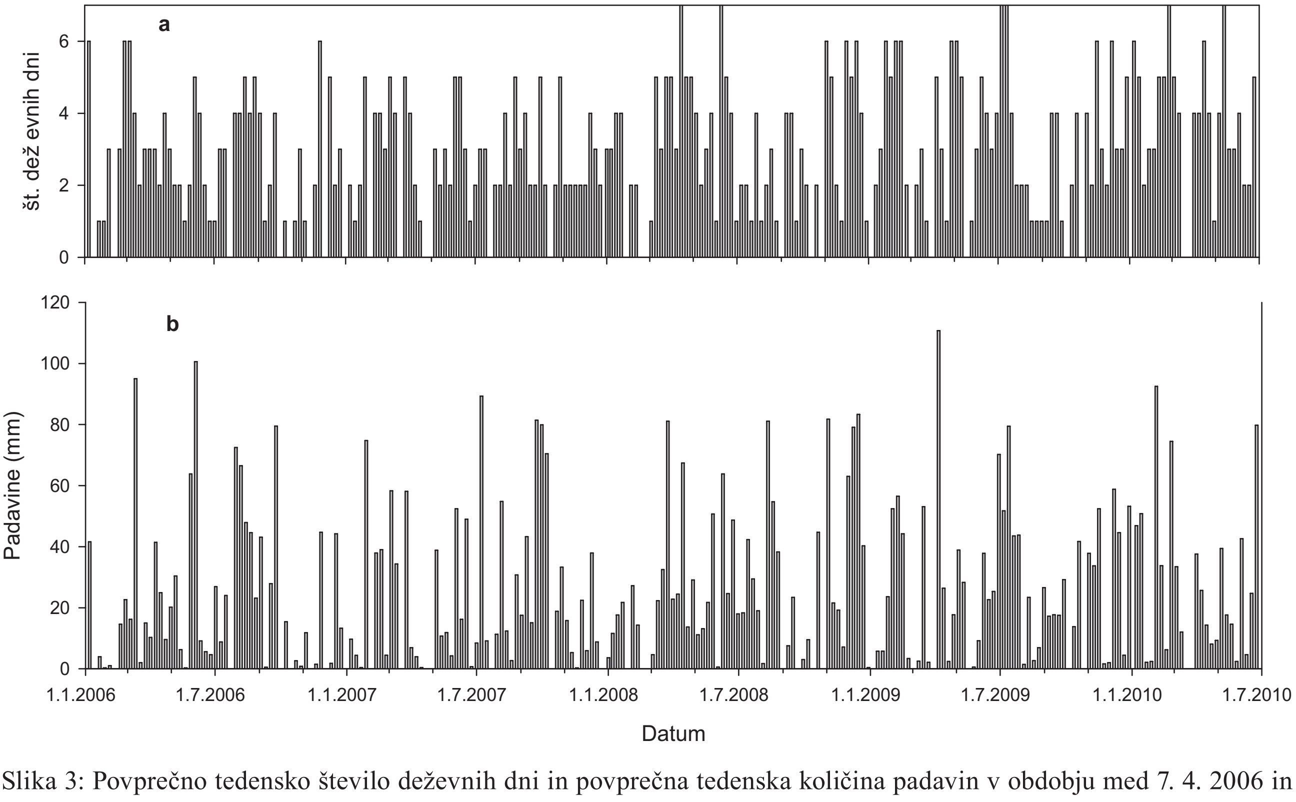
V celotnem obdobju izpostavitve vzorcev smo spremljali makro, lokalno in mikro klimatske podatke, ki vplivajo na pogoje za razkroj lesa (preglednica 5). Povprečna letna temperatura je bila med 10,5 °C (2006) in 11,1 °C (2007, 2009), povprečna relativna zračna vlažnost pa med 50,8 (2009) % in 72 % (2006). V letu 2010 so povprečna temperatura (8,5 °C), relativna zračna vlažnost (47 %) in količina padavin nekoliko nižje, ker je v povprečje zajeta le prva (hladnejša in bolj suha) polovica leta. Letna količina padavin znaša za preiskovano obdobje med 1195 mm in 1440 mm (Preglednica 5). Na življenjsko dobo lesa zunaj veliko bolj vpliva število deževnih dni kot količina padavin (BRISCHKE / BAYERBACH / RAPP 2006). Opazili smo, da zadnja leta število deževnih dni narašča, in sicer je bilo v letu 2006 takšnih 113 dni, v letu 2009 že 166, v prvi polovici leta 2010 pa kar 94 (Preglednica 5, Slika 3). V štirih letih in pol so bila samo tri suha obdobja daljša od dveh tednov (Slika 3). Les se v takšnih razmerah

Preglednica 5: Povprečna letna temperatura, zračna vlažnost, letna količina padavin in število deževnih dni v posameznih letih izpostavitve vzorcev.

Table 5: Average year temperature, relative air humidity, sum of year precipitation and number of rainy days in the years of samples exposure.

Leto / *Year*	Povprečna temperatura / *Average temperature* (°C)	Povprečna relativna zračna vlažnost / *Average relative air humidity* (%)	Letna količina padavin / *Sum of precipitation* (mm)	Število deževnih dni / *No. of rainy days*
2006	10,5	72,0	1440	113
2007	11,1	69,5	1195	136
2008	10,7	58,9	1411	153
2009	11,1	50,8	1405	166
2010*	8,5	47,0	675	94

*1. 1. do 30. 6. 2010



Slika 3: Povprečno tedensko število deževnih dni in povprečna tedenska količina padavin v obdobju med 7. 4. 2006 in 15. 6. 2010.

Figure 3: Average weekly number of rainy days and average weekly sum of precipitation in the period between 7. 4. 2006 and 15. 6. 2010.

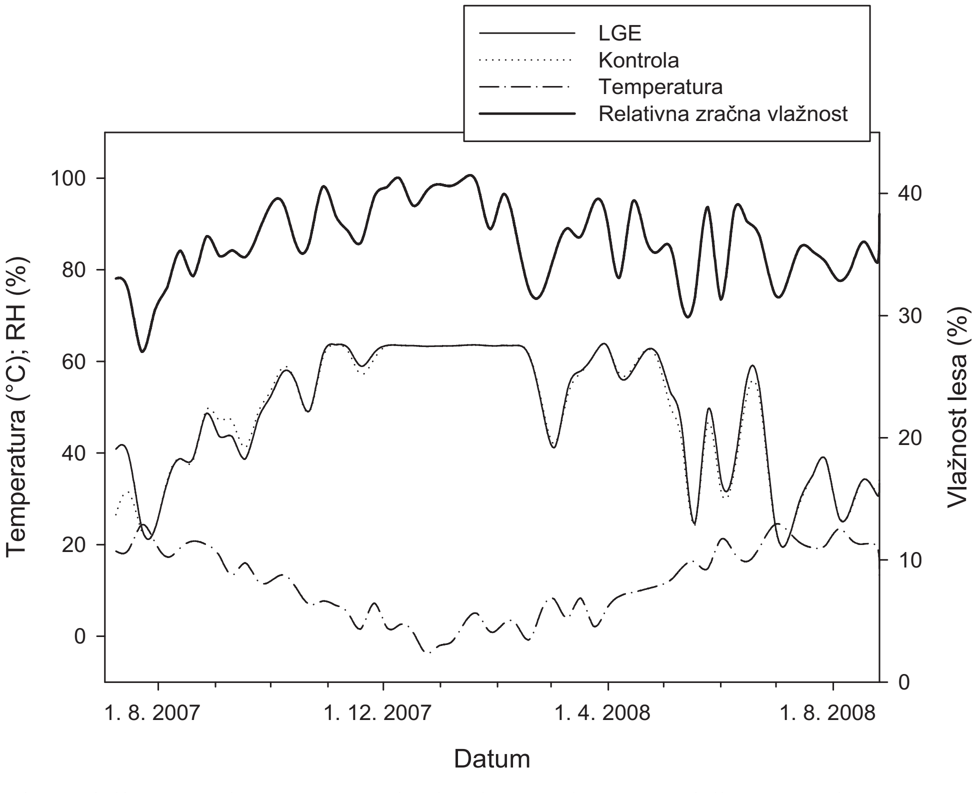
ne osuši in ima stalno vlažnost, ki jo glive potrebujejo za razkroj. Velik pomen imajo tudi lokalne klimatske razmere, kot je na primer izpostavljenost na soncu oziroma v senci. Večja količina padavin in večje število deževnih/snežnih dni pozimi imata manjši vpliv na razkroj kot spomladi, poleti in jeseni oziroma v obdobju, ko so temperature ugodne za razkroj (BRISCHKE et al. 2010).

Primerjava meritev temperature in zračne vlažnosti pod dvoslojnim testom z meritvami na merilni postaji je pokazala, da se lokalna temperatura pod vzorci statistično ne razlikuje od temperature, izmerjene z vremensko postajo na Gozdarskem inštitutu. Manjše razlike se kažejo pri ekstremnih temperaturah, le-te so nekoliko manjše pod vzorci. Povprečna vlažnost zraka, izmerjena na merilnem mestu, je bila 59 %, pod vzorci pa kar 87 %. Znano je, da so v senci temperaturni ekstremi manjši, poleg tega se les počasneje suši, kar po drugi strani vodi k bolj intenzivnemu razkroju lesa (BRISCHKE / RAPP 2008b). Ugotovili smo, da so tudi temperature lesa manj ekstremne, vendar se le-te statistično ne razlikujejo od temperature zraka, izmerjene s H-gumbkom pod vzorci. Relativna zračna vlažnost, izmerjena v lesu, počasneje sledi vlažnosti zraka pod vzorci. Vzrok za to je počasno navlaževanje in sušenje lesa. To je razvidno iz izračunanih vlažnosti lesa, prikazanih na slikah 4 in 5. Vlažnost kontrolnih in impregniranih vzorcev smrekovine je v obdobju od julija 2007 do sredine junija 2010 znašala med 10 % in 28 % in je sledila zračni vlažnosti. Najvišja vlažnost (28 %) LGE, WE6 impregniranih in kontrolnih vzorcev je bila v vseh treh letih izpostavitve v zimskem obdobju približno od začetka novembra do začetka marca. V tem obdobju je bila zračna vlažnost najvišja in najbolj konstantna, povprečna temperatura je bila stalno pod 10 °C, v januarju in februarju vsa tri leta, nekaj tednov celo pod 0 °C. Izkazalo se je, da je vlažnost lesa v zimskem času nekoliko precenjena, saj pri vzporednem testu, kjer smo vlažnost lesa spremljali gravimetrično, nismo zaznali tako visoke vlažnosti lesa prek zime (HAFNER 2009). Spomladi, poleti in jeseni je vlažnost lesa bolj nihala. Nihanje je bilo posledica nihanja zračne vlažnosti in količine padavin. Vlažnost vzorcev, impregniranih z LGE emulzijo, je bila približno enaka vlažnosti kontrolnih vzorcev (Slika 4), medtem ko je pri vzorcih, impregniranih z WE6 emulzijo, opazen hidrofobni učinek. Impregnirani vzorci so dosegli za približno 2 odstotni točki nižjo vlažnost v določenem obdobju, medtem ko je bila dinamika navlaževanja in sušenja primerljiva tako za impregnirane kot tudi za kontrolne vzorce (Slika 5). Manjšo učinkovitost LGE emulzije v primerjavi z WE6 emulzijo pripisujemo nižjemu deležu suhe snovi v LGE emulziji in posledično manjšemu navzemu voska LGE (LESAR / HUMAR 2010). Pri impregnaciji s 50-odstotno emulzijo WE6 oksidiranega polietilenskega voska je prišlo do delne zapolnitve celičnih lumnov, medtem ko tega učinka z emulzijo LGE voska montana zaradi prenizkega deleža suhe snovi nismo dosegli (LESAR / ZUPANČIČ / HUMAR 2008).

Glavni namen naše raziskave je bil določiti življenjsko dobo zaščitenega lesa, izpostavljenega v tretjem razredu izpostavitve. Vzorci, zloženi v spodnji vrsti, so bili ne glede na tip impregnacije bolj vlažni in bolj razkrojeni kot vzorci v zgornji vrsti. Poleg tega se je pri vzorcih v spodnjem sloju razkroj pojavil prej. Na vseh vzorcih v zgornji vrsti je bila zgornja površina bolj ali manj degradirana zaradi delovanja UV-svetlobe ne glede na tip impregnacije. Površina je postala siva in vlaknasta zaradi razgradnje osnovnih komponent lesa (CHANG / HON / FEIST 1982; GRELIER / CASTELLAN / KAMDEM 2000; ZHANG / KAMDEM / TEMIZ 2009). Nobena izmed emulzij voskov ali bakrovih pripravkov ni preprečila ali upočasnila foto-degradacije lesa. Med ocenjevanjem nismo opazili, da bi bila foto- degradacija površine vzrok za razkroj. Veliko hitreje se je razkroj pojavil na mestih, kjer je zastajala voda oziroma so se vzorci težko sušili. Najbolj degradirano površino smo opazili pri pripravkih, impregniranih z vodno raztopino bakrovega(II) sulfata. Na površini je bilo opaziti več razpok, ki so potekale po letnicah. Očitno je kisla raztopina bakrovega(II) sulfata (pH 3,5) pospešila degradacijo površine.

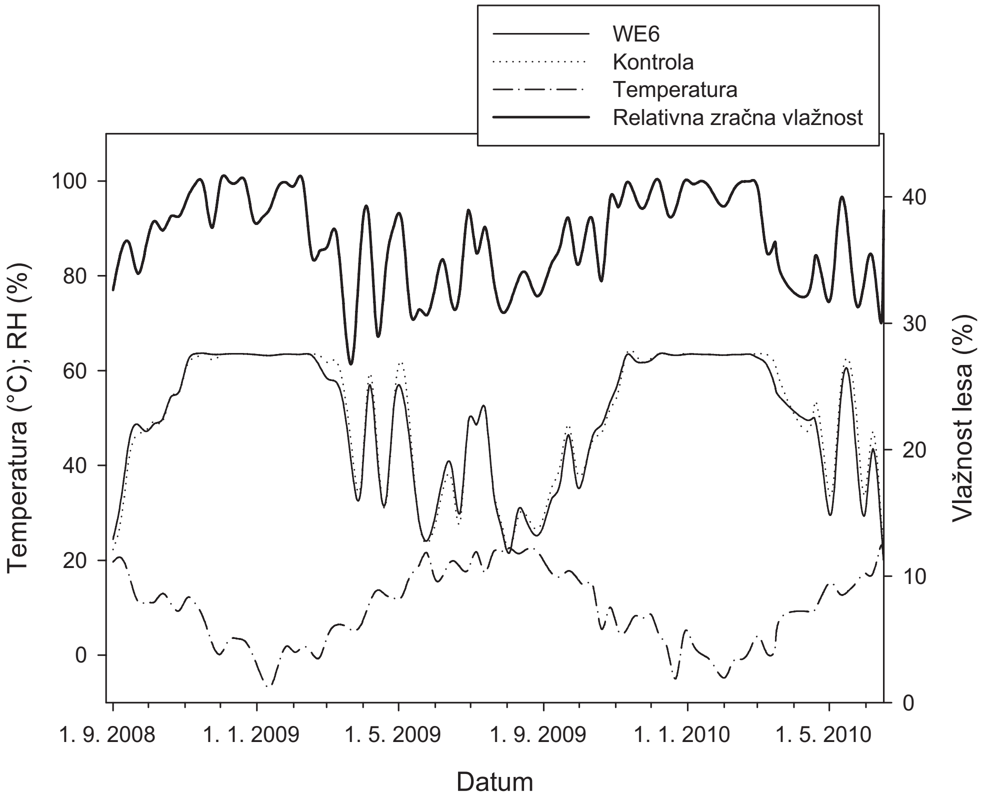
Po prvem, drugem in tretjem letu izpostavitve so bili najbolj razkrojeni kontrolni vzorci smrekovine 07 (kontrolni vzorci smrekovine, začetek izpostavitve 28. 5. 2007) in bukovine. Že po prvem letu izpostavitve smo na smrekovini 07 in bukovini na majhnem delu površine opazili prve znake razkroja (Preglednica 1). Skoraj na vseh vzorcih je bil viden micelij, na bukovini pa so bila poleg micelija še plodišča glive bele trohnobe pahljačice (*Schizophyllum commune*). V drugem in tretjem letu se je stopnja razkroja še povečevala. Tako so bili nekateri smrekovi 07 in bukovi vzorci že zelo močno razkrojeni (ocena 4) in so se zlomili že ob padcu z višine 0,5 m. Veliko bolj odporni so bili kontrolni vzorci smrekovine 06 (kontrolni vzorci smrekovine, začetek izpostavitve 7. 4. 2006). Po štirih letih so imeli povprečno oceno 2,8, kar je ena ocena nižje, kot je bila zabeležena pri vzorcih smrekovine 07. Vzorce smrekovine 08 (kontrolni vzorci smrekovine, začetek izpostavitve 19. 6. 2008), ki smo jih testirali leta 2008, so imeli po dveh letih veliko nižjo oceno (0,2) kot pa smrekovina 07 po enem letu testiranja (1,4). Vzorci hrastovine tudi po treh letih niso kazali znakov razkroja, razen enega vzorca, ki je dobil oceno 1. Omenjeni vzorec je bil poleg slepih vzorcev (vzorci smrekovine slabše kakovosti , ki smo jih namestili med vzorce posameznih obdelav oziroma druge vrste lesa), ki so bili že po prvem letu močno razkrojeni. Vzorci macesnovine po dveh letih ne kažejo nikakršnega razkroja. Omenjene rezultate podpirajo tudi rezultati merjenja prodora igle Pilodyna v letu 2010. Igla Pilodyna je po treh letih testiranja prodrla skozi celotno debelino (25 mm) vzorcev smrekovine 07 in bukovine, medtem ko je v vzorce smrekovina 08 prodrla 19,3 mm, v vzorce macesnovine pa le 13,3 mm (Preglednica 1). Tako majhna globina prodora igle v macesnovino ni presenetljiva, saj na globino prodora vplivajo gostota lesa in smer prodora igle (tangencialna ali radialna) ter stopnja razkroja lesa. Vpliv razkroja je veliko večji, kot je vpliv gostote ali orientacije lesnih vlaken. Iz rezultatov je razvidno, da so vzorci smrekovine 07 v našem podnebnem pasu slabše odporni od bukovine, čeprav standard SIST EN 350-2 (1994) navaja ravno obratno. Slabše odporni so bili tudi od smrekovine 06 in smrekovine 08. Predvidevamo, da je vzrok za slabšo odpornost vzorcev smrekovine 07 tudi slabša kakovost lesa. Omenjeni vzorci so imeli zelo široke branike z velikim deležem ranega lesa in povprečno gostoto 477 kg/m^3 (u = 10 %), medtem ko je bila gostota vzorcev z začetkom izpostavitve leta 2006 493 kg/m^3. Iz literature ni znanih podatkov o vplivu gostote na naravno odpornost smrekovine. Za macesen poročajo, da gostota nima vpliva na odpornost (VIITANEN et al. 1997), za hrastovino pa velja, da višja gostota pomeni bolj odporen les (HUMAR et al. 2008).

V letu 2007 in 2008 smo izpostavili naravnemu staranju vzorce, zaščitene z različnimi emulzijami voskov. Ti vzorci so bili nekoliko manj razkrojeni kot kontrolni vzorci. Po prvem letu so imeli vzorci povprečne ocene od 0 (LGE-P) do 0,4 (LGE-A), v drugem letu so bile razlike večje od 0,1 (LGE-P) do 2,1 (LGE-C) in v tretjem letu od 1 (LGE-P) do 3 (LGE-C) (Preglednica 1). Rezultati kažejo, da vakuumsko tlačna impregnacija z emulzijami voska montana (LGE) koncentracij od 0,12 % do 1,17 % ne izboljšuje odpornosti oziroma ne vpliva na življenjsko dobo vzorcev. Premazovanje z emulzijo (LGE-P) povečuje odpornost, saj se šele po drugem letu kažejo prvi znaki razkroja. Vzorci, impregnirani z višjimi koncentracijami voskov (LGE-D, LGE-E, WE1 in WE6), ki smo jih izpostavili leto kasneje (2008), kažejo nekoliko večjo odpornost. Pri teh vzorcih po drugem letu še ni vidnih znakov razkroja razen na enem vzorcu LGE-D. Vendar pa so bili ti vzorci naravnim dejavnikom izpostavljeni premalo časa, da bi lahko zaključili oziroma napovedali življenjsko dobo tako obdelanega lesa. Vzorci, impregnirani z raztopino borove kisline (Ba), kažejo prve znake razkroja po treh letih izpostavitve. Njena učinkovitost je v kombinaciji z emulzijo LGE manjša. Po treh letih razkroja so bile na polovici vzorcev manjše poškodbe do globine 1 mm, na drugi polovici vzorcev pa so poškodbe bile že večje od 1 cm^2 in globoke od 1 mm do 3 mm. Vzorci LGE-D-Ba, ki so bili izpostavljeni testiranju samo dve leti, še ne kažejo nikakršnih poškodb. Rezultate te raziskave potrjujejo tudi laboratorijski testi fungicidnih lastnosti emulzij voskov (LESAR / KRALJ / HUMAR 2009). Ugotovili smo, da borova kislina povečuje odpornost, vendar se njen učinek skozi leta zmanjšuje. Glavni vzrok za to je izpiranje bora iz lesa (LLOYD 1998; OBANDA / SHUPE / BARNES 2008; HUMAR / LESAR 2008). Zaradi slabše odpornosti predvidevamo, da je bilo največje izpiranje bora pri vzorcih, impregniranih z emulzijo LGE-C-Ba, kljub temu da je bilo v laboratoriju izpiranje bora manjše v kombinaciji z voskom montana kot brez voska (LESAR / KRALJ / HUMAR 2009). Predvidevamo, da je vzrok za to film voska montana na površini vzorca, skozi katerega je bor med impregnacijo veliko težje prodiral v les in ga je tako veliko ostalo pod površino, od koder se je zato hitreje izpral.



Slika 4: Vlažnost kontrolnih vzorcev in vzorcev smrekovine, impregnirane z emulzijo LGE voska montana, izpostavljenih terenskemu testiranju od 9. 7. 2007 do 26. 8. 2008.

Figure 4: Moisture content of control and LGE montan wax treated samples exposed outdoor from 9. 7. 2007 to 26. 8. 2008.



Slika 5: Vlažnost kontrolnih vzorcev in vzorcev smrekovine, impregnirane z emulzijo WE6 oksidiranega polietilenskega voska, izpostavljenih terenskemu testiranju od 26. 8. 2008 do 15. 6. 2010.

Figure 5: Moisture content of control and WE6 wax polyethylene wax emulsion treated samples exposed outdoor from 26. 8. 2008 to 15. 6. 2010.

V primerjavi z vzorci, impregniranimi z emulzijami voskov, vzorci iz serije, zaščitene s sredstvi na osnovi etanolamina in/ali bakrovih spojin, kažejo na veliko boljšo odpornost. Po treh letih testiranja so se pokazali prvi znaki razkroja le na vzorcih, impregniranih z raztopino EaBQ obeh ciljnih navzemov (0,1 oziroma 0,5). Omeniti pa velja, da ta pripravek ni vseboval bakrovih spojin, temveč le bor in kvartarno amonijevo spojino. Po štirih letih pa smo prve šibkejše znake razkroja zaznali še na vzorcih, impregniranih z nižjo koncentracijo CuEaO (0,1), CuS (0,1) in CuEa (0,3) (Preglednica 1). Razkroj je bil opažen le na površini, manjši od 1 cm^2, in v globini do 1 mm, na vseh drugih vzorcih pa ni bilo vidnih znakov razkroja. Skupna značilnost teh vzorcev je, da smo uporabili relativno nizek navzem. Poleg tega pa so vsi omenjeni biocidni pripravki vsebovali le eno biocidno učinkovino – baker. Ti podatki jasno potrjujejo laboratorijske podatke (HUMAR / LESAR 2008), da biocidni pripravki, ki vsebujejo le bakrove učinkovine, ne zagotavljajo popolne zaščite pred glivami rjave trohnobe, zato jih moramo kombinirati z drugimi biocidi (kvartarno amonijevo spojino, borom, triazoli…), če želimo doseči zadostno zaščito lesa. Po štirih letih izpostavitve vzorcev ni statistično značilnih razlik v globini prodora igle Pylodina med posameznimi zaščitnimi sredstvi in njihovimi koncentracijami. Razlikujejo se le vzorci EaBQ, impregnirani s pripravkom brez bakrovih spojin s ciljnim navzemom 3,5 kg/m^3, v katere je igla prodrla povprečno 19,0 mm, saj je bila globina prodora pri drugih vzorcih med 10,3 mm in 14,3 mm. Rezultati nakazujejo trend povečevanja globine prodora igle pri vzorcih, na katerih se pojavlja razkroj, glede na vzorce brez znakov razkroja (preglednica 3).

4 Zaključki

4 Conclusions

Primerjava rezultatov razkroja vzorcev, zaščitenih z emulzijami voskov in vzorcev, zaščitenih s sredstvi na osnovi bakrovih spojin, pokaže, da so slednji bolje zaščitili les. Rezultat je pričakovan, saj je baker biocid, ki se s pomočjo etanolamina veže v les in tako zagotavlja dolgotrajno zaščito (JIANG / RUDDICK 1999; HUMAR / LESAR 2008; LEE / COOPER 2010).

Emulzije voska montana (LGE) niso vsebovale biocidov, ampak so lesu le povečale hidrofobnost. V primeru, da je bila koncentracija le-teh dovolj visoka, izboljšajo odpornost lesa.

Poleg tega je na končni rezultat vplivala kakovost vzorcev. Vzorci, ki so bili izpostavljeni naravnim razmeram v letu 2007, so bil izdelani iz lesa slabše kvalitete, s širokimi branikami, kar se kaže v slabši odpornosti in večji dovzetnosti za glivni razkroj.

5 Summary

Service life prediction is becoming more and more important. In our research, service life of wood exposed in Use Class 3 was tested. Untreated wood and wood impregnated with water based wax emulsions and copper-ethanolamine based preservative solution was used. In the first part, Norway spruce wood was impregnated with three different wax emulsions: montan wax, polyethylene and oxidised polyethylene wax emulsion of different concentrations in combination with boron compounds. In the second part of the research, wood specimens were impregnated with copper-ethanolamine preservative solution (Silvanolin) and individual components of the original solution. CCB preservative, consisting of copper compounds, chromium compounds and boron compounds) was used as a reference solution. For comparison, untreated Norway spruce, larch, beech and oak wood specimens were used. Wood specimens were exposed outdoor in double layer test on the field test site at the Department of Wood Science and Technology in Ljubljana for three and four years. During exposure, temperature and relative humidity were measured under specimens with H-button and at weather station (Davis) 300 m away from the test field. Visual estimation according to SIST EN 252 standard was performed every year between fifteenth of May and fifteenth of June. In parallel, wood temperature and air humidity were measured in untreated Norway spruce control and wood impregnated with montan and polyethylene wax emulsions. Afterwards, wood moisture content was calculated.

Retention of wax emulsion was influenced by dry content and impregnation process. Emulsions with higher dry content had lower retention. For copper-ethanolamine based solutions target retention before impregnation was chosen based on literature and experimental data. After impregnation, the retention differed for ± 25%, and was influenced by inhomogeneous wood structure. The average year temperature during exposure was around 11°C and average relative air humidity was around 60%. Yearly amount of rainfall was approximately the same during exposure years (1400 mm), but numbers of rainy days increased from 113 in the year 2006 up to 166 days in the year 2009. The temperature under the specimens and the temperature measured at the weather station were almost the same; however, extreme temperatures measured under the specimens were slightly lower. The average relative air humidity under the specimens was by approximately 30% points higher. Temperature of wood was less extreme than air temperature, but the difference was not significant. Wood moisture content was almost constant (28%) during the winter season from November to March. From March to November, wood moisture content was lower and oscillating with relative air humidity. However, it should be considered that moisture content was measured indirectly.

Specimens exposed in the lower layer had higher moisture content and consequently decay started earlier. All specimens in the upper layer were UV degraded, but this degradation did not result in decay. After the first, the second and the third exposure years, the control specimens were the most decayed, Norway spruce 07 and beech specimens in particular. There were no signs of decay at larch and oak specimens after three years of exposure. Resistance of specimens impregnated with wax emulsion was influenced by retention of wax emulsion. Higher decay resistance was evident at specimens impregnated with wax emulsion and boric acid. But after three years of exposure, the first signs of decay become evident. It is supposed that leaching of boron compounds is the main reason for this phenomenon. As expected, resistance of copper-amine treated wood was higher than resistance of wax emulsion treated specimens. The first signs of decay became evident after the third and/or the fourth years of exposure of the specimens impregnated with lower retention of preservative solutions. In these solutions, copper was the only biocidal component. Furthermore, results showed that wood quality had considerable influence on resistance of treated and untreated wood. For more exact service life prediction of treated wood exposure, time has to be longer (five or more years).

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3.16 VPLIV BOROVIH SPOJIN V LEPILNEM SPOJU NA KVALITETO LEPLJENJA IN FUNGICIDNE LASTNOSTI LEPLJENEGA LESA

INFLUENCE OF BORON COMPOUNDS IN ADHESIVES ON THE BONDING QUALITY AND FUNGICIDAL PROPERTIES OF WOOD

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Les je eden od najpomembnejših konstrukcijskih materialov. Vendar njegovo uporabo omejujeta neustrezna trajnost in omejene dimenzije. Te omejitve rešujemo z lepljenjem in zaščito lesa. Preučevali smo možnosti zaščite lepljenega lesa z dodatkom biocida v lepilo. V ta namen smo melaminsko formaldehidnemu in poliuretanskemu lepilu dodali borovo kislino in tako skušali izboljšati odpornost lepljenega lesa smrekovine. Rezultati mehanskih testiranj (strižni in delaminacijski test) kažejo, da dodatek borove kisline v lepilu ni negativno učinkoval na mehanske lastnosti lepljenega lesa oziroma so se nekatere lastnosti celo izboljšale. Vendar dodatek borove kisline v lepilni mešanici ni izboljšal odpornosti lepljene smrekovine proti glivam rjave trohnobe.

Influence of boron compounds in adhesives on the bonding quality and fungicidal properties of wood

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Abstract:

Wood is one of the most important construction materials. However, users of wood face two issues: limited dimensions and insufficient durability. These issues have been overcome with the development of bonding and wood preservation. The preservation of glued wood is elucidated in this paper. Through the addition of boric acid to adhesives, we tried to improve the fungicidal properties of glued wood. The results of mechanical testing (shear strength and delamination) showed that the addition of boric acid to glue did not have a negative impact on the performance of the glued wood. On the contrary, some properties were even improved. Unfortunately, the addition of boric acid to impregnated wood does not improve the resistance of the glued wood to brown rot fungi.

Keywords: adhesive, boric acid, delamination, diffusion, shear strength, wood

Introduction

Wood has been one of the most important building materials for centuries. It has several advantages, but its use is frequently limited for two reasons: durability and limited dimensions. Issues relating to inadequate durability can be overcome using proper preservation treatment. Furthermore, problems related to the limited dimensions of wood were solved when engineered wood composites were developed. However, there are not many solutions available for improving the durability of engineered wood composites. Insufficient durability therefore limits the use of such products made of wood mainly to indoor use.

There have been several attempts to improve the durability of glued wood. The easiest and the most frequently applied procedure is surface treatment, such as brushing or spraying the glued composites. The surface treatment of glued wood is not sufficient, since only the outside layer of the wood is protected, and the major part of the wood remains untreated (Walker et al. 1993). Unfortunately, impregnation procedures are not feasible for glued wood, since glued woods are difficult to impregnate, and impregnation can also result in shrinking, swelling and unwanted cracking of the wood or adhesive bond lines. One of the most promising techniques for the treatment of glued wood, particularly glued laminated beams is supercritical impregnation (Morrell et al. 2005). Under supercritical conditions, substances can diffuse through solids like a gas, and dissolve materials like a liquid. Additionally, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties to be "tuned". Supercritical fluids are very suitable as a substitute for organic solvents. Of various chemicals, carbon dioxide is the most commonly used supercritical fluid for the impregnation of wood. Unfortunately, there is only one supercritical plant operating, since this process is currently fairly expensive compared to traditional treatments (Kjellow and Henriksen 2009).

There have also been parallel attempts to impregnate wood before bonding with adhesives (Janowiak et al. 1992). However, there is a technical problem, since most glued laminated wood production processes require the lamellas to be planed prior to bonding in order to achieve good contact between the lamellas in the process of bonding. It does not therefore make sense to impregnate lamellas and then remove a significant portion of the protective layer with planning. It was thus decided in our research to include biocides in the adhesive and merge the two phases: bonding and preservation. Boric acid was chosen as a model biocide, since it is one of the few remaining diffusible biocides since implementation of the Biocidal Products Directive (Kose et al. 2009). Boron compounds are prone to diffuse from places with a higher concentration to those with lower concentrations, if the moisture content of wood exceeds 22% (Morell et al. 1992). Secondly, boric acid is a very effective fungicide and insecticide, even at relative low concentrations. An important advantage of boric acid is its water solubility and general environmental sensitivity (Drysdale 1994; Baysal et al. 2006). However, some boron compounds have recently been classified as toxic for reproduction in Europe (Directive 2008/58/EC; 2008), which will presumably influence their use in wood preservation.

Material and methods

Material

The experiments were performed on Norway spruce (*Picea abies* L. Karst.) wood of an average density of 450 ± 100 kg/m^3. This material was chosen because Norway spruce is the most important wood for construction in our region. The dimensions of the lamellas were 105 mm(t) × 35 mm (r) × 900 mm(l). The lamellas were conditioned at a relative humidity (RH) of 65 % and a temperature (T) of 20 °C for one month.

Two types of adhesives were used for bonding: melamine-urea formaldehyde (MUF) (Akzo Nobel) and polyurethane (PUR) (H.B. Fuller, ICEMA R 145/12). Boric acid (Merck) was added to the adhesive mixture to achieve two different final concentrations of boron: 0.5% and 0.1%.

Bonding of the wood

Prior to bonding two lamellas together, the surface layer of each lamella was removed by planning. The adhesive mixture was applied uniformly to the surface of one lamella using a roller at an application rate of 200 ± 50 g/m^2. Pressing was carried out at room temperature (20 ± 2 °C) for 2 hours at a specific pressure of about 0.5 MPa. After pressing, two layered samples were conditioned in a standard climate (RH = 65 %, T = 20 °C) until testing.

Shear test of the bond line

The shear test of the bond line was performed according to the EN 392 standard (1995) on specimens with a nominal size of 40 mm (t) × 70 mm (r) × 40 mm (l), which were cut out of the bonded assemblies. Twenty-four specimens for each adhesive mixture were tested. The specimens were tested "dry" (conditioned in the standard climate). Shear strength (f_v) was determined from the equation:

$$f_v = k\frac{F_v}{A}$$

where k is the modification factor (k = 0,78 + 0,0044 t), t is the specimen thickness (mm), F_v is the shear force applied (N), and A is the cross sectional area (mm^2). The shear test was carried out with a ZWICK/Z100 universal testing machine.

Delamination of the bond line

The delamination test of the bond line was conducted according to the EN 391 standard (2001) on specimens with a nominal size of 80 mm (t) × 70 mm (r) × 7 5mm (l). Four specimens for each adhesive mixture were tested. The delamination test cycle used method B, subsection 6.4.4 of the EN 391 standard (2001).

Determination of diffusion

Two types of specimens were prepared from the bonded assemblies, 10mm (t) × 70mm (r) × 20mm (l) (type A) and 3 mm (t) × 50 mm (r) × 25 mm (l) (type B), for the diffusion test. These specimens were conditioned in a chamber with RH = 100% and T = 25 °C, since preliminary experiments showed that the diffusion of boron is fairly slow with wood conditioned at a lower relative humidity. The boron diffusion was monitored occasionally over the course of a 14-week period. In order to visualize the boron in the wood, a color spot reagent was used. Comprising of two components: a saturated solution of salicylic acid in an ethanol (70%) and HCl (30%) mixture. The second component was ethanol extract of curcuma (*Curcuma sp.)*. In the presence of boron, the wood is colored red, while the untreated part remained yellow (Theden and Kottlors, 1965).

In the second part, type B specimens were used. They were conditioned for 0, 7 and 14 days in a chamber with a relative humidity of 100% and temperature of 25 °C. The diffusion of the boron from the adhesive bond line was determined by means of laser ablation sampling (solid-state Nd:YAG laser, model UP 213 A/F, New Wave Research) in conjunction with inductively coupled plasma–mass spectrometric detection (octopole reaction system ICP–MS 7500 ce&cs, Agilent Technologies). Since wood is a fairly inhomogeneous material, it is difficult to prepare a calibration curve. The concentration of boron was therefore expressed in arbitrary units.

A 213 nm laser was operated at 20 Hz with a typical fluence of 2.5 J/cm^2 and spot size of 100 µm. A scan speed of 500 µm/s was used. A 0.9 L/min flow of helium carrier gas was used to entrain sample aerosols from the ablation cell to the plasma torch. The optimal operation conditions for ICP-MS, determined by the NIST 612 glass standard, were a plasma gas flow rate of 13 L/min, auxiliary gas flow rate of 0.85 L/min and RF power of 1500 W. Ion intensities of $^{11}B^+$ were acquired in the time resolved analysis (TRA) mode. An ablation line at the middle of the specimens was chosen. It started 2 mm below and stopped 25 mm above the adhesive bond line. Prior to ablation, the surface of the specimens was cleaned with pre-ablation.

Fungicidal properties

Fungicidal properties were determined according to a modified EN 113 (2002) procedure. Specimens of 10 mm (t) × 30 mm (r) × 40 mm (l) (the adhesive bond line was in the middle of the specimens 15 mm from the tangential plane) were exposed to three brown rot fungi: *Gloeophyllum trabeum* (ZIM L017), *Antrodia vaillantii* (ZIM L037)and *Serpula lacrymans* (ZIM L057). Brown rot fungi were chosen since they predominately degrade softwoods and glued wood in indoor applications. Steam sterilized specimens were placed in jars with overgrown nutrient medium above a plastic net for 16 weeks, according to the EN 113 (2002) protocol. After the period of exposure, the specimens were isolated and weight loss was determined gravimetrically.

Results and discussion

The shear strength, percentage of wood failure and delamination of the wood specimens bonded with the MUF and PUR adhesive mixtures are shown in Table 1. The shear strength was highest for pure MUF adhesive (8.65 N/mm^2) and dropped slightly in specimens that were bonded with MUF adhesives containing boron compounds, but this reduction was not significant. On the other hand, the percentage of wood failure increased from 83% (MUF) to 95% for both MUF adhesives containing boron. Delamination was 0% for all MUF adhesive mixtures. It can be concluded that the inclusion of boric acid compounds in the MUF adhesive did not significantly affect the bonding quality. In terms of performance requirements for glued laminated timber (EN 386 2001), all the specimens bonded with MUF adhesive mixtures fulfilled the requirements.

Specimens bonded with PUR adhesive exhibited shear strength of 7.37 N/mm^2 and 74% of wood failure. The inclusion of boron in the PUR adhesive increased both the shear strength and the percentage of wood failure, but the difference was not significant. Total delamination was high for specimens bonded with pure PUR adhesive (9.8%) but was significantly reduced for specimens bonded with PUR adhesive containing boron. The improvement of the bonding quality of PUR adhesives containing boron can be ascribed to crystal water in the boron acid, which promotes curing. It is known that PUR adhesives react with water molecules (particularly with OH groups) during the curing process (Marra 1992). In terms of performance requirements for glued laminated timber (EN 386 2001), the specimens bonded with pure PUR adhesive did not fulfil the requirements, whereas both PUR adhesive mixtures containing boron were satisfactory.

Table 1. Shear strength, amount of wood failure, and delamination of adhesive bond lines

Adhesive mixture	Shear strength (N/mm^2)	Wood failure (%)	Total delamination (%)	Maximum delamination (%)
MUF	8.65	83	0	0
MUF c_B = 0.5 %	8.07	95	0	0
MUF c_B = 0.1 %	7.71	95	0	0
PUR	7.37	74	9.8	13.1
PUR c_B = 0.5 %	7.54	80	2.4	4.8
PUR c_B = 0.1 %	7.93	75	1.2	2.4

The object of the second part of the research was to investigate whether boron remained in the adhesive bond line or whether it diffused from the adhesive bond line to the wood. In order to elucidate this issue, two sets of experiments were performed. In the first, the boron concentration was determined using a color spot reagent. This is a very sensitive and reliable technique (Grell et al. 1994). The results showed that there is virtually no boron diffusion with wood conditioned in a chamber with a relative humidity of 88%. The moisture content of the wood was obviously too low. This is in line with statements in the literature that boron diffusion starts when the wood moisture content exceeds 20% (Morell et al. 1990). Considerably more prominent diffusion from the adhesive bond line was observed with specimens conditioned in a chamber with a relative humidity of 100%. However, the concentration of boron in lamellas prepared with adhesives in which 0.1% of boron was added to the adhesive mixture was too low to be monitored with color reagents (Figure 1 A). On the other hand, the concentration of boron in wooden lamellas bonded with adhesives with the highest concentration of boron was sufficient to be monitored using color spot reagent. The first signs of diffusion were observed after the second day of observation. The boron had diffused approximately 1 mm from the adhesive bond line. The boron diffusion increases fairly fast during the process of conditioning. After 13 days of conditioning, the boron diffused approximately 4 mm from the adhesive bond line (Figure 1 A). However, it must be taken into account that boron diffusion was monitored on the surface of the wooden specimens. The surface has a higher moisture content in the process of conditioning than the inner part of the specimens, so it can be assumed that the moisture content in the center of the specimens was lower, and consequently the boron diffusion was also slower. Furthermore, visual observation showed that the pattern of boron diffusion was also influenced by other parameters, one of which is growth rings. Annual rings form a barrier that slows down boron diffusion in wood. Darker/denser late wood slows down boron diffusion more than lighter/light late wood.

In the second step, diffusion was additionally monitored with a more accurate technique. The surface layer was laser-ablated and analyzed with ICP-MS. From the results presented in Figure 1 B, it is clearly evident that the boron concentration in the control wood was fairly low. The most interesting concentration gradient was observed in specimens that had not been conditioned in a chamber with high humidity. It is clear that the concentration of boron in the adhesive bond line or close to the adhesive bond line is considerably higher than in untreated specimens. Secondly, from the concentration gradient in the unconditioned specimens it can be seen that the boron diffuses from the adhesive bond line in the process of bonding. However, after 12 days of conditioning the specimens in a chamber with RH of 100%, there was almost equal distribution of boron determined in the area 10 mm from the adhesive bond line. The boron concentration thereafter decreased and almost reached the background level 25 mm from the glue line. Comparable results were observed in spruce wood bonded with MUF and PUR based adhesives. This is clear evidence for increased boron diffusion with high moisture contents. It can be concluded that none of the adhesives used immobilized the boron in the adhesive bond line. The boron remained mobile and began diffusing from the adhesive bond line during the process of bonding, but boron diffusion became particularly notable in a moist environment.

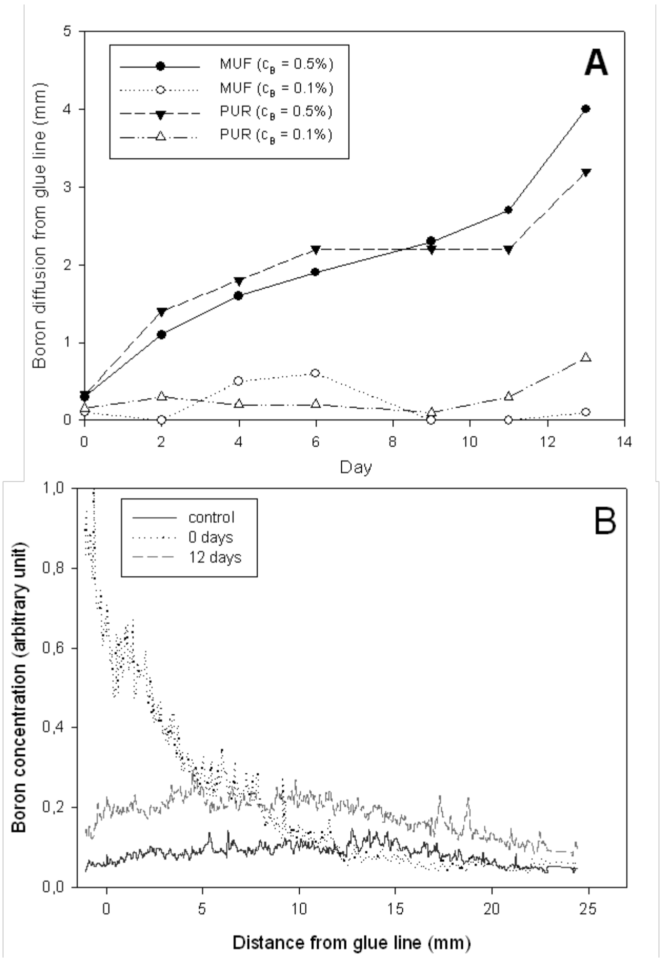

Figure 1: Influence of time on boron diffusion from glue line to wooden lamellas (A), concentration gradient of boron in wooden lamellas at the beginning and after 12 days of conditioning in a humid environment (B).

The last question related to the addition of boron to the adhesives was how the addition of boron influences wood decay fungi. Mass losses of the control specimens, bonded with adhesives without biocides, varied between 25% (*A. vaillantii,* PUR)and 54% (*S. lacrymans*, MUF). This clearly showed that the fungal strains were vital and that the wood used was susceptible to fungal decay. The adhesive itself has an insignificant influence on decay fungi. However, as can be seen from Figure 2, the concentration of boron added to the adhesive was not sufficient to protect the wood against fungal decay. Mass losses of the wooden lamellas bonded with adhesive enriched with boron were comparable to the control ones. It seems that the wood volume to adhesive bond line ratio was too high to achieve sufficient protection against fungal decay. It is therefore believed that the proposed technique is not suitable for protection of glued laminated beams but for the production of plywood or OSB, for example. This issue needs to be addressed in future studies.

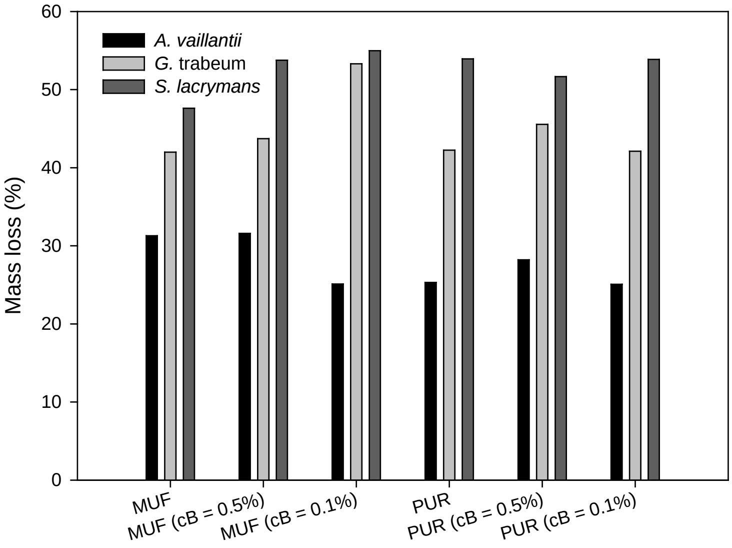

Figure 2: Mass loss of glued wooden specimens after 16 weeks of exposure to wood decay fungi in terms of type of glue used

Conclusion

The inclusion of boron compounds in the MUF adhesive did not significantly affect the bonding quality. In terms of performance requirements for glued laminated timber, all the specimens bonded with MUF adhesive mixtures fulfilled the standard requirements. The inclusion of boron in PUR adhesive increased both the shear strength and the percentage of wood failure but the difference was not significant. The total delamination was high for specimens bonded with pure PUR adhesive but was significantly reduced for specimens bonded with PUR adhesive containing boron. The specimens bonded with pure PUR adhesive did not fulfil the standard requirements, whereas both PUR adhesive mixtures containing boron were satisfactory. The concentration of boron in the adhesive bond line was not sufficient to protect spruce wood against wood decay fungi. The mass loss of specimens made of bonded wood in which the adhesive was supplemented with boron was comparable to the mass loss of the control specimens. It is assumed that a considerably better effect would be achieved with thinner lamellas or veneers.

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4 RAZPRAVA IN SKLEPI

4.1 RAZPRAVA

Raziskovalno delo za doktorsko disertacijo je sestavljeno iz treh sklopov: fungicidnih lastnosti borovih spojin in emulzij voskov, zmanjševanju izpiranja bora iz lesa z dodajanjem vodoodbojnih sredstev in določanju sorpcijskih lastnosti lesa, impregniranega z borovimi spojinami in emulzijami voskov.

V prvem delu smo preučevali fungicidne lastnosti borovih spojin in vodoodbojnih sredstev, s katerimi smo kasneje skušali zmanjšati izpiranje bora iz lesa. Prvi preliminarni testi so pokazali, da so mejne fungicidne vrednosti borovih spojin nižje, kot jih navaja literatura (Beachler in Roth, 1956; Becker, 1959; Carr, 1964). Zato smo na novo določili mejne fungicidne vrednosti borove kisline (BA) za glive rjave in bele trohnobe v hranilnem gojišču in v lesu. Mejne vrednosti smo določali za preventivno (poglavje 3.1) in kurativno zaščito (poglavje 3.2) lesa. Ugotovili smo, da mejna vrednost za preventivno zaščito smrekovine znaša 0,8 kg/m^3 BAE (boric acid equivalent), medtem ko je mejna vrednost za kurativno zaščito približno petkrat višja. V obeh primerih smo ugotovili, da je minimalna inhibitorna koncentracija za borovo kislino višja za glive bele trohnobe kot za glive rjave trohnobe. Za najbolj odporni sta se izkazali ogljena kroglica (*H. fragiforme*) in bukov ostrigar (*P. ostreatus*), tramovka (*G. trabeum)* pa za najbolj občutljivo. Rast in razvoj tramovke zavre že 0,2 kg/m^3 BAE. Iz praktičnega vidika je zelo pomembno, da je borova kislina bolj učinkovita proti glivam rjave trohnobe, ki se pogosteje pojavljajo v drugem in tretjem razredu izpostavitve, kot proti glivam bele trohnobe (Unger in sod. 2001), saj se borova kislina pogosteje uporablja v tem razredu izpostavitve. Za uporabo borove kisline v tretjem razredu izpostavitve so sicer zaradi močnega izpiranja bora potrebne višje koncentracije.

Pri fungicidnih testih smo ugotovili, da zelo nizke koncentracije borovih spojin ne zavirajo rasti gliv, ampak jo v določenih primerih celo pospešujejo, bor je namreč eden od elementov, ki jih glive nujno potrebujejo za rast in razvoj (Lloyd, 1998; Lehto in sod. 2010). Minimalne inhibitorne koncentracije za boraks neposredno nismo določali, vendar pa smo ugotovili, da delež 0,1 % bora v zaščitni raztopini, ne glede na uporabljeni vir bora (borova kislina ali boraks), učinkovito zaščiti les pred glivami rjave trohnobe. Pri vzorcih, impregniranih z boraksom z višjo koncentracijo bora (0,5 %), smo ugotovili celo višje izgube mase kot pri vzorcih, impregniranih z nižjo koncentracijo. Menimo, da ta izguba mase ni posledica delovanja gliv, ampak izpiranja boraksa iz lesa, saj vzorci z višjo koncentracijo boraksa niso bili preraščeni z micelijem, bili pa so zelo vlažni (poglavje 3.7). Predvidevamo, da je med izpostavitvijo prišlo do izpiranja borovih učinkovin. Vzrok za visoko vlažnost vzorcev, izpostavljenih glivam, je v veliki higroskopnosti boraksa, kar smo podrobneje opisali v poglavju 3.11.

Delovanje borovih učinkovin proti glivam modrivkam in plesnim je nekoliko slabše kot proti glivam razkrojevalkam. Za učinkovito zaščito lesa pred modrenjem je potrebna približno pet- do desetkrat višja koncentracija bora v zaščitni raztopini kot za zaščito pred glivami razkrojevalkami (poglavje 3.3). Naši rezultati potrjujejo navedbe avtorjev starejših raziskav, da je za preprečitev razvoja in rasti gliv modrivk potreben višji navzem borovih spojin kot za delovanje proti glivam razkrojevalkam (Becker, 1959).

Fungicidne lastnosti smo določali tako lesu, impregniranemu z borovimi spojinami, kot tudi lesu, prepojenemu z vodoodbojnim pripravki, s katerimi smo skušali zmanjšati izpiranje bora iz lesa. Uporabili smo utekočinjen les in različna hidrofobna sredstva, in sicer dve emulziji montanskega voska, tri emulzije različnih polietilenskih voskov in emulzijo PVA (polivinil acetat). Čeprav ta sredstva ne vsebujejo biocidov, so vsa bolj ali manj zavrla rast gliv. Vendar odpornost impregniranega lesa samo z emulzijami voskov ni bila dovolj visoka, da bi zadostila zahtevam standarda EN 113. Učinkovitost delovanja je odvisna od uporabljenega voska oziroma emulzije in navzema posameznega sredstva. Za najmanj učinkovito med impregnacijskimi sredstvi se je izkazala emulzija etilen kopolimernega voska (WE3). Ta emulzija je bila najbolj viskozna, zaradi česar ni penetrirala globoko v les, ampak je večina voska ostala na površini in tako ni učinkaučinkovala na fungicidne niti na druge lastnosti impregniranega lesa. Po drugi strani sta se emulzija oksidiranega polietilenskega voska (WE6) in emulzija PVA izkazali za najbolj učinkoviti. Emulzija WE6 je popolnoma zavrla delovanje pisane ploskocevke (*T. versicolor*) in sive hišne gobe (*S. lacrymans*), medtem ko je emulzija PVA popolnoma zavrla delovanje pisane ploskocevke in tramovke. Za zelo učinkovito se je izkazala tudi emulzija polietilenskega voska (WE1), glivam *G. trabeum*, *S. lacrymans*, *P. ostreatus* in *T. versicolor* izpostavljeni vzorci, impregnirani z višjo koncentracijo te emulzije, so po 16 tednih izgubili le med 4 % in 10 % mase. Slabšo odpornost so kazali vzporedni impregnirani vzorci, izpostavljeni glivama *H. fragiforme* in *A. vaillantii*, kjer je bila izguba mase 18,3 % oziroma 10,9 % (poglavje 3.5). Omenjeni glivi sta se izkazali za najbolj učinkoviti razkrojevalki lesa, impregniranega z ostalimi kombinacijami emulzij voskov in emulzij PVA. Zelo učinkovito je les pred glivami zaščitila tudi emulzija montanskega voska. Pri lesu, prepojenem s to emulzijo, je bila izguba mase v primerjavi s kontrolnimi vzorci manjša za 20 % do 50 % (poglavji 3.5 in 3.6). Vzrokov za manjše izgube mase impregniranega lesa z emulzijami voskov in emulzijo PVA je več. Predvidevamo, da emulzije na glive niso neposredno biocidno delovale, ampak le s fizikalnim zaviralnim učinkom. Da emulzije voskov ne delujejo biocidno, kažejo rezultati testa rasti gliv na hranilnem gojišču. Rezultati tega testa so pokazali, da glive normalno rastejo tudi na hranilnem gojišču z dodatkom 0,25 % emulzije montanskega voska. To kaže, da ta emulzija in predvidoma tudi vse ostale uporabljene emulzije v naši raziskavi nimajo fungicidnega učinka, ampak obstajajo drugi vzroki za manjšo izgubo mase impregniranih vzorcev. Ena od možnih razlag je tvorba tankega filma/ovire na površini lesa in celičnih lumnih lesa (Warth, 1959) (poglavje 3.4). Ta bariera upočasni navlaževanje in difuzijo encimov ter razkrojnih produktov med hifo in lesom. Domnevamo, da mehanizem zgolj upočasni razkroj in ga ne zavre popolnoma. Te domneve podpirajo tudi rezultati sorpcijskih testiranj impregniranega lesa z emulzijami montanskega in polietilenskih voskov (poglavji 3.12 do 3.14) in rezultati terenskega testiranja (poglavje 3.15). Kontrolni vzorci smrekovine, izpostavljeni double layer terenskemu testiranju, so kazali prve znake razkroja že v prvem letu izpostavitve, po osmih mesecih so se namreč na teh vzorcih že pojavila plodišča glive *G. trabeum*. Prvi znaki razkroja na impregniranih vzorcih z emulzijami montanskega (LGE) in emulzijami polietilenskih voskov (WE1 in WE6) pa se niso pojavili niti po drugem letu izpostavitve. Izjema so bili le impregnirani vzorci s suhim navzemom voska, manjšim od 8,5 kg/m^3. To je dodaten dokaz, da imajo vzorci, impregnirani z emulzijami voskov, boljšo odpornost na glive kot kontrolni neimpregnirani vzorci. Vendar so bili ti vzorci naravnim dejavnikom izpostavljeni prekratek čas, da bi lahko zaključili oziroma napovedali življenjsko dobo tako obdelanega lesa. Kot smo že omenili, predvidevamo, da je najpomembnejši vzrok za izboljšanje odpornosti impregniranega lesa vodoodbojni učinek. Menimo, da je eden od vzrokov za boljšo odpornost lesa, impregniranega z emulzijo polietilenskega (WE1) in emulzijo oksidiranega polietilenskega (WE6) voska, v primerjavi z montanskim voskom, višja vrednost pH polietilenskih voskov. Emulziji WE1 in WE6 sta bazični in imata vrednost pH približno 9. Poleg tega imata zaradi sestave visoko pufrsko kapaciteteto. Splošno je znano, da glive bolje uspevajo v rahlo kislem okolju, kot v bazičnem (Huckfeldt in sod., 2005).

Emulzije voskov so učinkovite pri izboljšanju odpornosti lesa proti glivam razkrojevalkam, niso pa izboljšale odpornosti lesa proti glivam modrivkam in plesnim, ne glede na postopek obdelave vzorcev. Preizkušali smo namreč delovanje emulzij proti modrivkam in plesnim po standardni metodi EN 152, na premazanih (poglavje 3.5) in impregniranih vzorcih (podatkov nismo objavili). V obeh primerih smo dobili primerljive rezultate. Kontrolni, premazani in impregnirani vzorci so bili obarvani na več kot 60 % površine. Večje barvne spremembe so na obdelanih in kontrolnih vzorcih povzročile glive modrivke v primerjavi z vzorci, izpostavljenimi plesnim. Za zaščito pred glivami modrivkami in plesnimi je treba emulzijam voskov dodati biocidna sredstva. Avguštinčič (2010) je ugotovil, da dodatek borove kisline (c_B = 0,5 %) učinkovito prepreči obarvanje vzorcev, izpostavljenih glivam modrivkam, po drugi strani dodatek enake koncentracije borove kisline ne prepreči obarvanja površine vzorcev s plesnimi.

V nadaljevanju nas je zanimal možni sinergistični učinek borovih spojin in emulzij montanskega voska, emulzije PVA in etanolamina na glive razkrojevalke. Dodatek emulzije montanskega voska v raztopini na osnovi borovih učinkovin pomembno izboljša fungicidne lastnosti sistema. Vendar je bila kombinacija borove kisline in emulzije montanskega voska nižje koncentracije bolj učinkovita kot kombinacija borove kisline in emulzije montanskega voska visoke koncentracije (poglavje 3.6). Predvidevamo, da je vzrok nižje učinkovitosti zaščitnega pripravka na osnovi višje koncentracije emulzije montanskega voska manjši navzem le-tega. V nekoliko manjši meri se podoben učinek kaže tudi pri pripravkih na osnovi borove kisline in emulzije PVA. Minimalna inhibitorna koncentracija borove kisline je za glive rjave trohnobe *G. trabeum* in *A. vaillantii* v kombinaciji z montanskim voskom približno za polovico nižja. Nekoliko manj značilen, a še vedno pomemben sinergistični učinek montanskega voska je na glive bele trohnobe *H. fragiforme* in *P. ostreatus*, ki so najbolj odporne na borove spojine. Kot smo že omenili, se borove spojine največ uporabljajo v drugem in tretjem izpostavitvenem razredu (Unger in sod. 2001), zato je posebej pomembno, da je sinergistični učinek montanskega voska na borove spojine večji pri glivah rjave trohnobe, kot pri glivah bele trohnobe. Zaščitni pripravki na osnovi borove kisline oziroma boraksa v kombinaciji s kvartarnimi amonijevimi spojinami in etanolaminom so popolnoma zaščitili les pred glivami razkrojevalkami. Zaščita impregniranega lesa je bila učinkovita tudi še po dvotedenskem izpiranju (EN 84) vzorcev. To pomeni, da je preostanek biocidov (bor in kvartarne amonijeve spojine) v lesu učinkovito zaščitil pred uporabljenimi glivami razkrojevalkami lesa (*G. trabeum*, *A. vaillantii* in *T. versicolor*). Poleg tega ne smemo spregledati dejstva, da tudi etanolamin vpliva na zaviranje rasti gliv in tako prispeva k večji učinkovitosti celotnega zaščitnega pripravka (Humar in Lesar, 2008).

Sinergistični učinek med montanskim voskom in borovo kislino smo dokazali tudi s terenskim testiranjem. Les, impregniran s pripravkom na osnovi 10 % emulzije montanskega voska in borove kisline (c_B = 0,5 %) je bil bistveno bolj odporen kot les, impregniran samo z enako koncentracijo montanskega voska, in nekoliko bolj odporen kot les, impregniran le z borovo kislino. Odpornost lesa, impregniranega s pripravki na osnovi borove kisline, na prostem s časom izpostavitve pada zaradi izpiranja bora. Vzorci, impregnirani z montanskim voskom najvišje koncentracije in borovo kislino, so bili izpostavljeni le dve leti in v tem času ne kažejo še nikakršnih znakov razkroja, po drugi strani pa je na kontrolnih vzorcih zaslediti intenziven razkroj. Za natančnejšo določitev odpornosti bo potreben daljši čas izpostavitve (poglavje 3.15).

V drugem delu smo preučevali izpiranje borovih učinkovin iz lesa. Splošno znano je, da bor zelo dobro difundira in se ne veže v les ter je zato v vlažnih razmerah močno izpostavljen izpiranju (Peylo in Willeitner, 1995; Gezer in sod., 1999; Obanda in sod., 2008). V laboratorijskih testih izpiranja se je iz lesa, impregniranega samo z borovo kislino, izpralo med 33 % in 100 % borovih učinkovin, kar potrjuje podatke iz literature (Peylo 1995; Peylo in Willeitner, 1995). Delež izpranega bora je odvisen od koncentracije borovih učinkovin v lesu, vira bora in vlažnosti lesa oziroma uporabljene metode izpiranja. Pripravki, pri katerih smo kot vir bora uporabili boraks, so se v les vezali nekoliko bolje kot pripravki na osnovi borove kisline. Pri nekaterih testiranjih smo opazili, da so se pripravki z višjo koncentracijo bora v les vezali nekoliko bolje kot tisti, v katerih je bilo bora manj (poglavji 3.7 in 3.10), kar se ujema s podatki iz literature (Gezer in sod., 1999). Vendar tega pri nekontinuirnih metodah izpiranja nismo ugotovili, pri teh testih smo ugotovili, da na količino izpranega bora ne vpliva koncentracija borove kisline v lesu (poglavji 3.8 in 3.9). Med izpiranjem po zelo strogem standardu EN 84 se je izpralo več bora iz lesa, impregniranega z višjo koncentracijo borove kisline (poglavje 3.9), vendar razlika ni bila statistično značilna. Drugi dejavnik, ki vpliva na izpiranje bora, je vlažnost lesa. Vlažnost lesa in izpiranje bora sta tesno povezana, čim višja je vlažnost lesa, tem več bora se izpere. Do podobnih ugotovitev so prišli tudi drugi raziskovalci (Peylo, 1995; Peylo in Willeitner, 1995; Kartal in sod., 2004; Baysal in sod., 2006). Vlažnost lesa je močno odvisna od postopka izpiranja. Z izpiranjem po standardni metodi EN 84 smo dosegli najvišje vlažnosti lesa (100 %) in najbolj intenzivno izpiranje borovih spojin. Iz lesa, izpranega v skladu s to metodo, se je izpralo do 95 % med impregnacijo vnesenega bora. Pri ostalih testih smo ugotovili manjše deleže izpiranih borovih spojin in nižje vlažnosti lesa. Pričakovano najnižje izpiranje smo dosegli s postopkom po standardu prCEN/TS 15119-1, saj standard predvideva zelo kratke čase potapljanja in sicer dvakrat na dan po 1 minuto. Postopek se ponavlja vsak drugi dan tri tedne. Naši rezultati se skladajo s podatki iz literature, da je izpiranje borovih spojin iz impregniranega lesa pri nekontinuirnih postopkih približno za četrtino manjše kot pri kontinuirnih postopkih, kljub enakemu času namakanja (Peylo 1995; Peylo in Willeitner, 1995). Poleg vlažnosti na izpiranje vpliva tudi koncentracijski gradient. Čeprav so bili vzorci, ki smo jih izpirali po standardu EN 84, na začetku vakuumsko impregnirani z vodo, smo v nekaterih primerih ugotovili večji delež izpranega bora iz vzorcev, izpranih po standardu ENV 1250-2, kjer smo vodo prvi dan zamenjali trikrat, medtem ko so bili vzorci pri EN 84 ves čas potopljeni v isti vodi. Pri postopkih izpiranja je potrebno opozoriti na slabo ponovljivost rezultatov izpiranja. Pri enakem postopku izpiranja vzorcev, impregniranih samo z vodno raztopino borove kisline, delež izpranega bora ni bil vedno enak. Predvidevamo, da so vzrok temu številni dejavniki, na katere nismo mogli vplivati: variabilnost lesa (širina branik, orientacija), predpriprava lesa za vzorce, na primer sušenje (naravno oziroma tehnično) in starost tega lesa. Zato absolutne vrednosti izpiranja lahko primerjamo samo z vzorci iz iste serije, relativne vrednosti med posameznimi serijami pa so primerljive med seboj.

Glede na to, da vlažnost lesa tako zelo vpliva na izpiranje bora, smo ga skušali zmanjšati z uporabo različnih vodoodbojnih sredstev. Uporabili smo emulzijo montanskega voska, emulzije polietilenskih voskov, emulzijo PVA, etanolamin in utekočinjeni les. Ugotovili smo, da je učinkovitost zmanjšanja izpiranja borovih spojin odvisna od vrste vodoodbojnega sredstva, njegove koncentracije, deleža borovih učinkovin v zaščitnem pripravku in postopka izpiranja. Tako kot pri vzorcih, impregniranih samo z borovimi učinkovinami, smo opazili največje izpiranje borovih spojin iz vzorcev, izpranih po standardu EN 84. Izpiranje bora iz vzorcev, impregniranih z emulzijo montanskega voska in borovo kislino, je bilo za 20 % manjše kot iz vzorcev, impregniranih samo z borovo kislino. Približno enak učinek smo ugotovili tudi pri vzorcih, impregniranih s polietilenskimi voski (WE1 c_{wax} = 25 %, c_B = 0,5 %). Iz teh vzorcev se je izpralo med 75 % in 85 % vnesenega bora, kar je bilo približno 10-odstotno zmanjšanje glede na kontrolne vzorce, impregnirane le z borovo kislino. Pri izpiranju v skladu s standardom ENV 1250-2 se je najmanj bora (15,9 %) izločilo iz lesa, impregniranega s pripravkom na osnovi utekočinjenega lesa (c_{lW} = 33 %) in borove kisline (c_B = 0,1 %), kar je bilo kar 5,5-krat manj, kot smo ugotovili pri vzorcih, impregniranih le z vodno raztopino borove kisline (poglavje 3.10). Z emulzijo montanskega voska (c_{mw} = 12 %) nam je uspelo zmanjšati izpiranje približno za polovico. Enak učinek smo dosegli tudi na vzorcih, impregniranih z emulzijo PVA (c_{PVA} = 1 %) in borovo kislino (c_B = 0,1 %) (poglavje 3.7), s polietilenskimi voski WE1 in WE6 pa smo dosegli do 25 % manjše izpiranje, določeno po standardu ENV 1250-2 v primerjavi z vzorci, impregniranimi le z borovo kislino (poglavje 3.7). Dodatek etanolamina ni vplival na vezavo borovih spojin. Z nekontinuirnima metodama (OECD in prCEN/TS 1511-1) smo preverjali učinkovitost zaščite pred izpiranjem bora le za emulzije montanskega in polietilenskih (WE1 in WE6) voskov. Izpiranje se je najbolj (30 %) zmanjšalo pri vzorcih, impregniranih z emulzijo polietilenskega voska WE1 nižje koncentracije in borove kisline obeh koncentracij (c_B = 0,1 % in 0,5%), ki so bili po impregnaciji segrevani nad točko tališča voska in izprani po prCEN/TS 1511-1. Izpiranje borovih spojin iz vzorcev, impregniranih z montanskim voskom in borovo kislino, je bilo okrog 10 % manjše kot iz vzorcev, impregniranih le z borovo kislino. Pri omenjenem standardu je bilo izpiranje bora tudi iz kontrolnih vzorcev manjše, izpralo se je okrog 40 % vnesenega bora. Nekoliko močnejše izpiranje (65 %) je bilo pri drugi nekontinuirni metodi OECD. Rezultat je pričakovan, saj je razmerje med potapljanjem in sušenjem veliko manjše pri metodi OECD (1 : 36), medtem ko znaša to razmerje pri prCEN/TS 15119-1 kar 1: 1400. Analiza rezultatov kaže, da hidrofobnost površin lesa, impregniranega z montanskim in polietilenskimi voski ter emulzijo PVA ni edini dejavnik za manjše izpiranje bora. Vpliv tega dejavnika je značilen in najverjetneje pozitivno deluje pri metodi prCEN/TS 15119-1,OECD in standardu ENV 1250-2. Vendar hidrofobnost površin ne pride do izraza med izpiranjem po EN 84. Zato predvidevamo, da na zmanjševanje izpiranja bora vplivajo še drugi dejavniki. Eden med njimi je tvorba tankega filma na površini celičnih lumnov in depoziti voskov oziroma PVA v lumnih celic, ki preprečujejo navzemanje vode. Tvorba filma in depoziti v lumnih upočasnjujejo navlaževanje in s tem izpiranje bora. Tvorbo filma in depozitov voskov v lumnih celic impregniranega lesa smo dokazali z mikroskopsko analizo (poglavje 3.4).

V raziskavi smo ugotovili, da impregnacija z emulzijami voskov in emulzijo PVA ne vodi vedno do zmanjšanega izpiranja bora, ampak ga lahko celo poveča. Povečano izpiranje smo ugotovili pri vzorcih, impregniranih z velikim deležem suhe snovi (emulzije montanskega voska in emulzije PVA). Predvidevamo, da so bile emulzije z velikim deležem suhe snovi preveč viskozne in niso prodrle tako globoko kot pripravki z nižjo koncentracijo emulzije. Na površini lesa, impregniranega s pripravki z velikim deležem suhe snovi (voska), so bile borove učinkovine bolj izpostavljene izpiranju kot tiste v sredini vzorcev, impregniranih samo z vodno raztopino borove kisline ali s pripravki z manjšo vsebnostjo voskov in emulzije PVA ter borovo kislino. Slabšo penetracijo emulzije montanskega voska visoke koncentracije smo potrdili z mikroskopsko analizo. Ugotovili smo, da so bili depoziti v sredini vzorcev, impregniranih z emulzijo z velikim deležem montanskega voska, zelo redki oziroma vosek sploh ni prodrl skozi piknje. Na visoko stopnjo izpostavljenosti bora na površini kažejo tudi testi dinamike izpiranja, saj se je v prvih obdobjih izpralo največ bora, ne glede na postopek izpiranja. Iz vzorcev, impregniranih z najvišjo koncentracijo (c_v = 12 %) montanskega voska in borovo kislino (c_B = 0,1%) ter izpranih po priporočilih OECD, se je v treh tednih izpralo 86 % vnesenega bora, od tega v prvem dnevu kar 60 % (poglavje 3.8). Zelo podobno dinamiko izpiranja borovih spojin smo opazili tudi pri vzorcih, impregniranih le z vodno raztopino borove kisline in kasneje premazanih z najvišjo koncentracijo montanskega voska (c_v = 12 %), a je bilo končno izpiranje za 25 % manjše kot iz vzorcev, ki so bili impregnirani le z borovo kislino. Ta rezultat nakazuje, da film montanskega voska na površini lesa upočasni izpiranje bora, ki je globlje v lesu. Montanski vosek na površini deluje hidrofobno in tako znižuje vlažnost lesa.

Kljub intenzivnemu izpiranju borovih spojin je med izpiranjem po standardu ENV 1250-2, prCEN/TS 15119-1 in priporočilih OECD v lesu ostalo vsaj 25 % vnesenega bora. To pomeni, da je ob najslabšem navzemu zaščitnih pripravkov med impregnacijo (okrog 200 kg/m^3), ki smo ga dosegli z impregnacijo smrekovine z zaščitenimi čeli in najvišjim deležem montanskega voska (c_v = 12 %), v lesu ostalo 0,25 kg/m^3 borove kisline. S fungicidnimi testi smo ugotovili, da ima borova kislina v kombinaciji z montanskim voskom sinergističen učinek in da takšna količina borove kisline učinkovito zaščiti les pred najpomembnejšimi glivami razkrojevalkami lesa (poglavje 3.6). Enako predvidevamo tudi za kombinacijo borove kisline in polietilenskih voskov. Borove učinkovine se v glavnem uporabljajo v drugem in tretjem izpostavitvenem razredu, kjer les veliko pogosteje razkrajajo glive rjave trohnobe kot glive bele trohnobe. S fungicidnimi testi smo določili nižje inhibitorne koncentracije borove kisline in emulzij voskov za glive rjave trohnobe, kot za glive bele trohnobe (poglavja 3.1, 3.5, 3.6 in 3.7). Z izpiranjem po standardu EN 84 se izpere iz lesa več bora kot pri ostalih postopkih izpiranja. Toda ta standard je namenjen za uporabo lesa v četrtem razredu izpostavitve v stiku z zemljo, kjer se borove učinkovine za zaščito lesa zelo redko uporabljajo, kadar pa se, se poleg borovih spojin uporabljajo še drugi biocidi, na primer bakrove spojine.

V tretjem delu raziskav smo se osredotočili na sorpcijske lastnosti lesa, zaščitenega z borovimi učinkovinami, montanskim voskom (LGE), polietilenskim (WE1) in oksidiranim polietilenskim (WE6) voskom. Najprej smo preverili sorpcijske lastnosti lesa, impregniranega z borovo kislino in boraksom. Za testiranje smo se odločili, ker smo med izpostavitvijo glivam opazili zelo visoko vlažnost lesa, impregniranega z borovo kislino in boraksom. Med uravnovešanjem pri petih relativnih zračnih vlažnostih (RH = 20 %, 33 %, 65 %, 88 % in 98 %) smo ugotovili, da je ravnovesna vlažnost odvisna od tipa zaščitnega pripravka in njegove koncentracije. Vendar so razlike med vlažnostjo nezaščitenega in impregniranega lesa pri nizkih relativnih zračnih vlažnostih minimalne in naraščajo z vlažnostjo zraka. V tretjem higroskopskem območju nad 65 % RH, ravnovesna vlažnost impregniranega lesa narašča hitreje od ravnovesne vlažnosti neimpregniranega lesa (poglavje 3.11). V tem območju je posebej pomembna kapilarna kondenzacija, kar je glavni vzrok za višjo vlažnost impregniranega lesa. Borova kislina in boraks se v les ne vežeta s kemijskimi vezmi, ampak le fizikalno z Van der Waalsovimi vezmi (Ramos in sod., 2006). Zato sklepamo, da ni prišlo do spremembe v zgradbi lesa, kar pomeni, da se borova kislina in boraks v lesu nahajata v obliki manjših ali večjih kristalov, ki so se odložili v celični steni in lumnih celic. Kristali se ob spremembi vlažnosti raztapljajo in ponovno kristalizirajo, saj absorbirana voda v impregniranih vzorcih deluje kot topilo. Med kristali so številne pore, kjer se pri vlažnosti nad 90 % kondenzira kapilarna voda (Mangel, 2000). V zgornjem higroskopskem območju vplivajo na vlažnost impregniranega les tudi impregnacijska sredstva. Les, impregniran z borovo kislino, je imel pri višjih zračnih vlažnostih v primerjavi z boraksom znatno nižje ravnovesne vlažnosti. Pri najvišjih zračnih vlažnosti je ravnovesna vlažnost z boraksom impregniranega lesa znašala celo okrog 50 %, pri teh vlažnostih lesa je difuzija bora najhitrejša (Morrell in Freitag, 1995). Rezultat kaže, da je borova kislina primernejša predvsem za zaščito bolj ogroženih izdelkov. Difuzija bora v lesu je zaradi nižje vlažnosti počasnejša (Lloyd, 1998), kar pomeni, da se bor počasneje izpira in tako ostane les dlje časa in bolje zaščiten pred delovanjem gliv in insektov. Prav tako so pogoji za rast gliv in plesni manj ugodni. Zaradi omenjenih razlogov smo v večini raziskav kot vir bora uporabljali borovo kislino.

Z namenom zmanjšati ravnovesno vlažnost lesa, impregniranega z borovo kislino, smo pripravili vodne raztopine borove kisline v kombinaciji z emulzijo montanskega voska (poglavje 3.12). Z uravnovešanjem pri konstantnih zračnih vlažnostih smo ugotovili, da so ravnovesne vlažnosti lesa, impregniranega s kombinacijo borove kisline in emulzijo montanskega voska, v celotnem higroskopskem območju višje kot vlažnost lesa neimpregniranih kontrolnih vzorcev. Še nižje pa so bile vlažnosti vzorcev, impregniranih le z emulzijo montanskega voska. Rezultati spremembe vlažnosti med potapljanjem v vodi in kondicioniranjem pri visoki zračni vlažnosti (87 %) kažejo, da imajo vzorci, impregnirani le z borovo kislino, višjo stopnjo vlažnosti med uravnovešanjem kot kontrolni vzorci. Vzorci, impregnirani z emulzijo montanskega voska in s kombinacijo borove kisline in montanskega voska, se uravnovešajo počasneje in imajo do 10 % nižje končne vlažnosti od kontrolnih vzorcev. Tudi vzorci, impregnirani le z montanskim voskom višje in nižje koncentracije, se uravnovešajo počasneje kot kontrolni vzorci. Kontrolni in vzorci, impregnirani samo z vodno raztopino borove kisline, so se uravnovesili že po 18 dneh testiranja, medtem ko se vzorci, impregnirani z dodatkom emulzije montanskega voska, niso uravnovesili niti po 53 dneh, ko smo zaključili poskus (poglavje 3.12). Med potapljanjem v destilirani vodi smo ugotovili podoben učinek kot med uravnovešanjem v visoki zračni vlažnosti. Z eno izjemo je bila vlažnost lesa, impregniranega z montanskim voskom in borovo kislino, celo nižja od vlažnosti vzorcev, impregniranih le z emulzijo montanskega voska.

Hidrofobni učinek montanskega voska smo opazili tudi z meritvami navzema vode s tenziometrom. Vzorci, impregnirani z emulzijo montanskega voska, so v aksialni smeri po 200 sekundah navzeli približno štirikrat manj vode kot kontrolni vzorci (poglavji 3.5 in 3.14). Za nižjo vlažnost lesa, impregniranega z emulzijo montanskega voska, je več vzrokov. Prvi med njimi je, da je les, impregniran z emulzijo montanskega voska, hidrofoben, kar v prvih urah izpostavitve upočasni navlaževanje. Drugi razlog je, da montanski vosek na površini tvori tanek odporen film (Warth, 1959), ki deluje kot bariera. Tretji razlog pa so depoziti montanskega voska v lumnih celic, ki fizično zmanjšajo prostor za akumulacijo vode (Rowell in Banks, 1985).

Vsa dejstva veljajo za vzorce z visokim navzemom emulzije voska. Izkazalo se je namreč, da majhen delež voska v lesu nima pomembnega vpliva na vlažnost impregniranega lesa. Vzorci, ki smo jim pred impregnacijo zaščitili čela z epoksidnim premazom, so navzeli približno 3- do 4-krat manj emulzije kot vzorci z nezaščitenimi čeli. Enako se je izkazalo tudi pri večjih smrekovih vzorcih (2,5 cm × 5 cm × 50 cm (EN 252), impregniranih z emulzijo montanskega voska, ki smo jih izpostavili na prostem. Impregnirani in neimpregnirani vzorci, izpostavljeni pod streho, so imeli med polletno izpostavitvijo zunaj skozi celotno obdobje primerljivo vlažnost. Tudi v vlažnostih kontrolnih in impregniranih vzorcev smrekovine, ki smo jo merili kontinuirano s H-gumbki (poglavje 3.15), nismo opazili statistično značilne razlike. Omenjeni vzorci so bili izpostavljeni v tretjem razredu izpostavitve. Pri impregnaciji bukovih vzorcev EN 252 smo dosegli dvakrat večji navzem emulzije LGE kot pri smrekovini. Takšna količina voska v lesu je občutno vplivala na znižanje vlažnosti impregnirane bukovine, ki je s časom naraščala. Po petih mesecih izpostavitve je bila vlažnost impregniranih vzorcev z montanskim voskom in emulzijo LGE za 20 % nižja, vlažnost vzorcev, impregniranih samo z emulzijo LGE, pa kar za 35 % nižja od vlažnosti kontrolnih vzorcev. Menimo, da so vzroki za manjšo vlažnost lesa, impregniranega z emulzijo montanskega voska, enaki, kot smo jih navedli že zgoraj.

Rezultati sorpcijskih testov lesa, impregniranega s polietilenskimi (WE1) in oksidiranimi polietilenskimi (WE6) voski, so zelo podobni tistim, ki so bili narejeni na lesu, impregniranem z montanskim voskom. Razlika je v tem, da je treba les, impregniran s polietilenskimi voski, za doseganje hidrofobnosti segreti nad točko tališča voska. Polietilenski voski namreč šele po segrevanju nad točko tališča tvorijo tanek kompakten film. Pred tem je na površini plast voska, ki je drobno razpokana (poglavje 3.13). Ko takšen les pride v stik z vodo, se v drobnih razpokah voska na površini pojavi kapilarni vlek (de Meijer in Militz, 2000), ki zvišuje navzem vode, kar nam kažejo rezultati navzemanja vode na tenziometru (poglavje 3.13 in 3.14). Drugače je pri impregnaciji z montanskim voskom, ki že takoj po impregnaciji tvori kompakten tanek film (Warth, 1959), s segrevanjem pa se še bolj enakomerno porazdeli po površini in v notranjosti lesa, čeprav v prečni smeri ne prodre globlje, kot je prodrl med impregnacijo. Test navzemanja vode na tenziometru je pokazal, da je hidrofobni učinek segrevanih polietilenskih voskov in montanskega voska skoraj enak. To ugotovitev potrjuje tudi nižja stopnja vlažnosti impregniranega lesa med izpostavitvijo umetnemu pospešenemu staranju. Na znižanje vlažnosti lesa, impregniranega s polietilenskimi voski, v primerjavi z vlažnostjo neimpregniranega lesa, vplivajo enaki dejavniki kot pri lesu, impregniranem z montanskim voskom.

Med umetnim pospešenim staranjem smo poleg že omenjene vlažnosti spremljali še barvne in kemijske spremembe. Tako kot številni raziskovalci pred nami, smo ugotovili, da so barvne spremembe na površini staranega lesa kazalnik kemičnih sprememb zaradi fotodegradacije (Feist, 1983; Feist in Hon, 1984; Grelier in sod., 2000; Petric in sod., 2004; George in sod., 2005). Najmanjše spremembe barve in kemijske spremembe smo opazili na lesu, impregniranem z emulzijo montanskega voska (c_v = 12 %). Rezultati analize FT-IR so pokazali, da je bila degradacija lignina pri vzorcih, impregniranih z montanskim voskom, manjša kot pri vzorcih, impregniranih s polietilenskimi voski ali pri kontrolnih vzorcih. Za praktično uporabo je zelo pomembno, da so v FT-IR spektrih trakovi, ki jih prisojamo voskom vrhovi spektrov FT-IR povezani z vezmi voskov, vidni na lesu še po 500 ciklih umetnega pospešenega staranja. To jasno kaže, da so voski ostali na površini in da se med staranjem niso izprali ali kemijsko spremenili.

Pokazali smo že, da bor v lesu dobro difundira, zato smo skušali v eni od raziskav to lastnost izkoristiti za zaščito lameliranega lepljenega lesa. Borovo kislino smo dodali lepilu in simulirali izdelavo lepljenih nosilcev. Na zlepljenih vzorcih smo preverili vpliv bora na mehanske lastnosti lepilnega spoja, difuzijo borovih spojin iz lepilnega spoja in fungicidne lastnosti. Ugotovili smo, da borova kislina ni vplivala na mehanske lastnosti lepljencev, zlepljenih z melaminskoformaldehidnim lepilom (MUF), vzorci, zlepljeni s poliuretanskim lepilom (PUR), pa niso zadostili kriterijem standarda (EN 386, 2001). Ugotovili smo tudi, da nobeno lepilo ne imobilizira borovih učinkovin v lepilnem spoju, bor skupaj z lepilom iz lepilnega spoja difundira v les že med postopkom lepljenja. Bor v lesu difundira, če je vlažnost lesa višja od 20 % (Morell in sod. 1990). Po dvanajstih dneh uravnovešanja vzorcev pri relativni zračni vlažnosti 100 %, je bor difundiral približno 10 mm iz lepilnega spoja. Bil je bolj enakomerno porazdeljen po vzorcu, koncentracija ob lepilnem spoju je padala in se izenačevala po celotni površini. Vendar je bila koncentracija bora v lesu prenizka, da bi preprečila rast in razvoj gliv. Predvidevamo, da bi bila predlagana tehnika zaščite primerna za zaščito vezanih plošč ali plošč OSB, kar pa bi bilo treba preveriti v nadaljnjih raziskavah.

4.2 SKLEPI

V raziskavi smo ugotovili, da med obdelavo lesa z borovimi spojinami, montanskim in polietilenskimi voski pride do interakcij z lesom in lesnimi glivami. Na podlagi dobljenih rezultatov smo potrdili naslednji hipotezi:

- Les, zaščiten z voski, je imel nižje ravnovesne vlažnosti od nezaščitenega lesa ali zaščitenega z borovimi spojinami in se je počasneje uravnovešal.
- Dodatek voskov borovim spojinam za zaščito lesa je zmanjšal izpiranje bora iz lesa.

Delno smo potrdili hipotezi:

- Voski z borovimi spojinami delujejo proti glivam razkrojevalkam in glivam modrivkam sinergistično. Hipotezo smo potrdili za glive razkrojevalke in zavrnili za glive modrivke. Borove spojine in emulzije voskov niso delovale sinergistično proti glivam, ki povzročajo obarvanje lesa (modrivkam in plesnim).
- Dodatek borove kisline lepilu ne zmanjša trdnosti lepilnega spoja, ko se les navlaži, bor difundira iz lepilnega spoja in zaščiti les. Potrdili smo, da bor ne zmanjša trdnosti lepilnega spoja in da bor difundira iz lepilnega spoja, ko se les navlaži. Količina bora, ki smo ga dodali lepilu, je bila premajhna, da bi les zaščitili pred glivami razkrojevalkami.

Poleg omenjenih, smo z raziskavami prišli še do naslednjih sklepov:

Minimalna inhibitorna koncentracija borove kisline v lesu za preventivno zaščito znaša 0,8 kg/m^3 BAE, mejna vrednost za kurativno zaščito pa je približno petkrat višja. Veliko bolj tolerantne kot glive razkrojevalke so se izkazale glive modrivke, kjer je potrebna koncentracija borove kisline v lesu za učinkovito zaščito desetkrat višja kot za glive razkrojevalke lesa. Med glivami razkrojevalkami so se za bolj tolerantne na borove učinkovine izkazale glive bele trohnobe.

Navzem emulzij voskov v smrekovino je odvisen od deleža suhe snovi in viskoznosti uporabljenega voska. Vodne emulzije z večjim deležem suhe snovi težje prodrejo v les. Samo z vakuumsko-tlačnim postopkom impregnacije lahko dosežemo v aksialni smeri globino penetracije, ki je večja od dolžine aksialnih traheid. V prečni (radialni in tangencialni) smeri emulzije voskov v smrekovino niso penetrirale.

Emulziji polietilenskega (WE1) in oksidiranega polietilenskega (WE6) voska sta močno upočasnili razgradnjo lesa, vendar je nista preprečili. Glive bele trohnobe so bolj odporne na voske kot glive rjave trohnobe. Obdelava lesa z emulzijami voskov ne prepreči obarvanja lesa z modrivkami in plesnimi.

Izpiranje borovih učinkovin iz lesa, impregniranega s pripravki na osnovi borove kisline in vodoodbojnih sredstev, je odvisno od vrste vodoodbojnega sredstva, njegove koncentracije, deleža borovih učinkovin v zaščitnem pripravku in postopka izpiranja ter vlažnosti lesa. S standardno metodo EN 84 smo iz lesa, pri katerem so bile vlažnosti najvišje, izprali največ bora, najmanjše izpiranje pa smo ugotovili pri standardni nekontinuirani metodi izpiranja prCEN/TS

15119-1. Najmanjše izpiranje borovih spojin je bilo ugotovljeno pri vzorcih smrekovine, impregniranih s pripravkom na osnovi utekočinjenega smrekovega lesa in borove kisline.

Med emulzijami voskov se je za najbolj učinkovito pri preprečevanju izpiranja izkazala emulzija montanskega voska, vendar delež izpranega bora v nobenem primeru ni bil manjši od 15 %. Emulzije z visokim deležem suhe snovi in visoko viskoznostjo lahko zaradi slabe penetracije povzročijo večje izpiranje borovih spojin, kot je izpiranje borovih spojin iz lesa, impregniranega le z borovo kislino.

Les, impregniran z borovimi spojinami, ima višje ravnovesne vlažnosti kot neimpregniran les. Dodatek emulzije montanskega voska upočasni parno difuzijo med uravnovešanjem pri visoki zračni vlažnosti in navzemanje vode med namakanjem ter zniža vlažnost takšnega lesa. Les, impregniran s polietilenskimi voski, je treba za dosego hidrofobnosti segreti nad točko tališča voskov.

Najmanjšo spremembo barve in najmanjše kemijske spremembe zaradi fotodegradacije med umetno pospešenim staranjem kažejo vzorci smrekovine, impregnirane z montanskim voskom. Impregnacija lesa z emulzijami montanskega in polietilenskih voskov izboljša njegovo odpornost na prostem pod pogojem, da je koncentracija voska v lesu dovolj visoka. Življenjska doba smrekovine, zaščitene z borovo kislino in emulzijami voskov, je daljša od nezaščitene. Vendar je bil les izpostavljen terenskemu testiranju prekratek čas, da bi lahko zaključili, koliko daljša je življenjska doba impregniranega lesa. Zato bomo s terenskimi testi nadaljevali, dokler ne propadejo vsi zaščiteni vzorci.

Emulzije voskov v kombinaciji z borovo kislino so obetavna sredstva za zaščito lesa v tretjem razredu izpostavitve. Vendar so za komercialno uporabo potrebne dodatne raziskave. Raziskati bi bilo treba možnosti uporabe sintetičnih voskov z nizkim tališčem in možnosti nehidrofilnih emulgatorjev za pripravo emulzij. Poleg borovih spojin bi bilo treba za izboljšanje fungicidnih lastnosti emulzij voskov raziskati možnosti uporabe še drugih okoljsko in zakonsko sprejemljivih biocidov, kot so na primer kvartarne amonijeve spojine, triazoli, IPBC …

5 POVZETEK

5.1 POVZETEK

Na področju zaščite lesa se zaradi vedno večje okoljske ozaveščenosti ljudi in pritiskov zakonodaje dogajajo številne spremembe. Direktiva o biocidih (Biocidal Products Directive, 98/8/EC), ki je stopila v veljavo leta 2006, prepoveduje ali pa močno omejuje uporabo klasičnih biocidov. Ene od redkih spojin, ki so še dovoljene, so borove spojine. Vendar je njihova značilnost poleg dobrih fungicidnih lastnosti tudi močno izpiranje iz lesa. V naših raziskavah smo borove spojine kombinirali s hidrofobnimi pripravki in tako skušali zmanjšati izpiranje borovih spojin. Hidrofobni pripravki in nebiocidna zaščita lesa so tudi ena od alternativ klasičnim pripravkom na osnovi težkih kovin. Predvsem za les, obdelan s hidrofobnimi sredstvi, nimamo na voljo dovolj podatkov, kako se ta rešitev obnese v praksi ter kateri so mehanizmi fungicidnega ter fungistatičnega delovanja. V ta namen smo v doktorski disertaciji preučevali fungicidne in sorpcijske lastnosti montanskega in polietilenskih voskov ter emulzije PVA.

V prvem delu smo preučevali fungicidne lastnosti borovih spojin in vodoodbojnih sredstev (emulzije montanskega, polietilenskega, oksidiranega polietilenskega, etilen kopolimernega voska in emulzije PVA), s katerimi smo kasneje skušali zmanjšati izpiranje bora iz lesa. Minimalne preventivne inhibitorne koncentracije borove kisline smo določali v hranilnem gojišču in v impregniranem lesu smreke. Uporabili smo standardne (EN 113) in nestandardne (mini blok, test rasti na hranilnem gojišču) metode določanja fungicidnih lastnosti. Minimalna inhibitorna koncentracija za preventivno zaščito pred glivami razkrojevalkami znaša 0,8 kg/m^3 BAE. Ugotovili smo, da so glive rjave trohnobe bolj občutljive na borove učinkovine kot glive bele trohnobe. Minimalna kurativna inhibitorna koncentracija borove kisline, ki smo jo prav tako ugotavljali na smrekovini, pa je 5,5-krat višja. Za preprečitev razvoja in rasti gliv modrivk je potrebna približno desetkrat višja koncentracija kot za glive razkrojevalke. Enako se je izkazalo tudi za les, impregniran z emulzijami voskov. Najbolj tolerantna gliva na borove učinkovine in emulzije voskov je bila ogljena kroglica (*Hypoxylon fragiforme*).

Vzorci smrekovine, impregnirani z emulzijami voskov, so bolj odporni na delovanje gliv razkrojevalk lesa kot nezaščiteni kontrolni vzorci. Posebej učinkovita sta bila polietilenski (WE1) in oksidirani polietilenski (WE6) vosek. Po drugi strani pa voski niso zaščitili lesa pred delovanjem gliv modrivk in plesni. S standardnim testom EN 113 smo ugotovili, da je potrebenpotrebni navzem borove kisline približno za polovico manjši v kombinaciji z montanskim voskom za dosego zadostne zaščite pred glivami razkrojevalkami, kot če je les impregniran le z borovo kislino.

V drugem delu doktorske disertacije so bile naše raziskave posvečene zmanjševanju izpiranja bora iz lesa. V ta namen smo les impregnirali z borovo kislino oziroma boraksom in vodoodbojnimi sredstvi. Sredstva, ki smo jih dodali borovim spojinam, so bile emulzije montanskega, polietilenskega in oksidiranega polietilenskega voska, emulzija PVA, etanolamin ter utekočinjen les. Impregnirane vzorce smo izpirali po dveh kontinuirnih (EN 84 in ENV 1250-2) in dveh nekontinuirnih (OECD in prCEN/TS 15119-1) metodah. Ugotovili smo, da je delež izpranega bora odvisen od koncentracije borovih učinkovin v lesu, vira bora, vrste in koncentracije vodoodbojnega sredstva ter vlažnosti lesa oziroma uporabljene metode izpiranja. Med posameznimi postopki izpiranja so se vzorci različno navlažili. Vlažnost vzorcev je bil najpomembnejši dejavnik, ki je vplival na končni delež izpranega bora. Ne glede na velike razlike v deležu izpranega bora iz vzorcev, impregniranih z istimi pripravki in izpranimi po različnih postopkih, so nas vsi postopki izpiranja privedli do podobnih zaključkov. Velik delež borovih spojin se izpere že v prvih ciklih izpiranja. Iz vzorcev, ki so bili impregnirani z manjšim deležem borove kisline, se izpere več borovih spojin kot iz vzorcev, impregniranih z večjim deležem borove kisline. Emulzije voskov z manjšim deležem suhe snovi so med impregnacijo prodrle globlje v les in so bile bolj učinkovite pri zmanjševanju izpiranja kot tiste z večjim deležem suhe snovi, ki so zaradi visoke stopnje viskoznosti ostale bolj na površini. V nekaterih primerih se je zaradi tega iz vzorcev, impregniranih z borovo kislino in emulzijami z večjim deležem suhe snovi izpralo več bora kot iz vzorcev, impregniranih le z borovo kislino.

V tretjem delu raziskav smo preučevali sorpcijske lastnosti borovih spojin in že omenjenih vodoodbojnih sredstev. Spremljali smo ravnovesna stanja lesa, impregniranega z borovo kislino, boraksom in montanskim voskom pri petih relativnih zračnih vlažnostih v procesu adsorpcije in desorpcije. Vodoodbojno učinkovitost in prepustnost za paro emulzij montanskega in polietilenskih voskov smo ugotavljali v komori z visoko zračno vlažnostjo (87 %), med potapljanjem v vodi in s testiranjem navzemanja vode v čelne površine impregniranih in neimpregniranih vzorcev s tenziometrom. Med petmesečno izpostavitvijo impregniranih vzorcev zunanjim razmeram (pod streho) smo spremljali spreminjanje vlažnosti glede na spremembo zunanje temperature in vlažnosti zraka.

Rezultati sorpcijskih testov kažejo, da borove spojine v zgornjem higroskopskem območju zvišujejo ravnovesno vlažnost impregniranega lesa. Vpliv je odvisen od uporabljene spojine in njene koncentracije. Čim višja je koncentracija borovih spojin v lesu, tem višja je ravnovesna vlažnost. Nasprotno velja za montanski vosek. Čim večji je delež voska v lesu, tem nižja je ravnovesna vlažnost impregniranega lesa. Vlažnost lesa, impregniranega s kombinacijo borove kisline in montanskega voska, je bila po kondicioniranju v komori z visoko zračno vlažnostjo in po potapljanju v vodi ter izpostavitvi na prostem nižja kot vlažnost kontrolnih vzorcev. Dobro hidrofobno učinkovitost montanskega voska kažejo tudi rezultati testiranja navzemanja vode s tenziometrom, kjer je navzem vode v impregnirane vzorce približno štirikrat manjši kot v kontrolne vzorce. Nasprotno, se les, impregniran s polietilenskimi emulzijami voskov, navzame več vode kot kontrolni vzorci. Hidrofobno delovanje polietilenskega in oksidiranega polietilenskega voska dosežemo šele po segrevanju nad točko tališča voska, ko se na površini tvori film voska. Pred tem so namreč na površini lesa drobne razpoke, ki povzročajo kapilarni vlek vode in s tem večji navzem.

Med umetnim pospešenim staranjem smo spremljali barvo, kemijske spremembe, kontaktne kote in vlažnost smrekovine, impregnirane z montanskimi in polietilenskimi voski. Rezultati spremljanja vlažnosti so pokazali, da ima les, impregniran z montanskim voskom, največji hidrofobni učinek. Še več, analiza FT-IR umetno pospešeno staranega lesa kaže, da emulzija montanskega voska upočasni barvne spremembe in kemično degradacijo lesa.

Večjo odpornost smrekovine, impregnirane z emulzijami voskov, v primerjavi z nezaščitenim lesom, kažejo tudi rezultati terenskega (double layer) testiranja. Vzorci so bili tri leta izpostavljeni v tretjem izpostavitvenem razredu na Oddelku za lesarstvo Univerze v Ljubljani. Ugotovili smo, da je odpornost lesa, zaščitenega z emulzijami voskov, odvisna od koncentracije emulzije in kvalitete lesa. Na podlagi spremljanja vlažnosti in temperature med terenskim testiranjem smo ugotovili, da les nudi ustreznejše vlažnostne pogoje za razvoj gliv, kot bi sklepali iz meritev temperature in vlažnosti zraka.

Rezultati laboratorijskih in terenskih testiranj kažejo, da impregnacija z emulzijami voskov in kombinacijo emulzij voskov z borovimi spojinami povečuje odpornost lesa. Vendar življenjske dobe lesu še ne moremo določiti, ker terenski testi trajajo premalo časa in na vzorcih ni opaziti še niti prvih znakov razkroja.

5.2 SUMMARY

There have been a number of changes in the field of the wood protection as a result of increasing environmental awareness and new legal requirements. The Biocidal Products Directive (98/8/EC), which was introduced in 2006, prohibits or significantly restricts the use of conventional biocides. Boron compounds are among the few compounds that are still allowed. However,in addition to good fungicidal properties, they are also characterised by severe leaching from wood. In our research, we combined boron compounds with hydrophobic agents and thus attempted to reduce the leaching of boron compounds. A combination of hydrophobic substances and non-biocidal wood protection is also one of the alternatives to conventional wood preservatives based on heavy metals. Especially for wood, treated with hydrophobic substances, we do not have enough data on how these substances work in practical applications and on the mechanisms of fungicidal and fungistatic activity. We therefore studied the fungicidal and sorption properties of montan and polyethylene wax emulsions and a PVA emulsion.

In the first part, the fungicidal properties of boron compounds and water-repellent products (montan, polyethylene, oxidized polyethylene, ethylene copolymer wax water based emulsions and PVA emulsion) were investigated. They were later used to reduce leaching of the boron from the impregnated wood. The minimum inhibitory concentrations of boric acid in the nutrient medium and the impregnated spruce wood were determined. Standard (EN 113) and non-standard (mini-block test growth in the nutrient medium) methods were used for determining the fungicidal properties. The minimum inhibitory concentration for the preventive protection of the wood against fungal decay was 0.8 kg/m^3 BAE. We discovered that brown rot fungi were more sensitive to boron compounds than white rot fungi. The minimum fungicidal and fungistatic concentrations of boric acid for wood remediation of Norway spruce wood were also determined and were 5.5 times higher. In order to prevent the development and growth of blue stain fungi and moulds, approximately ten times higher concentrations than for wood decay fungi were required. This was also demonstrated for wood impregnated with wax emulsions. The most tolerant fungus to boron compounds and wax emulsions was *Hypoxylon fragiforme*.

Specimens of Norway spruce wood impregnated with wax emulsions were more resistant to fungal decay than the untreated controls. Polyethylene (WE1) and oxidized polyethylene (WE6) wax were especially effective. However, treatment of the wood with waxes does not prevent the growth of blue stain fungi and moulds. We discovered with the EN 113 standard test that, in order to achieve sufficient protection against fungal decay,the required uptake of boric acid in combination with montan wax was approximately half of the amount that was needed in wood impregnated only with boric acid.

The second part of my PhD thesis research was dedicated to study of reducing boron leaching from impregnated wood. For this purpose, we impregnated the wood with boric acid or borax and water repellents. The agents that were added to water solutions of boron compounds were: montan, polyethylene and oxidized polyethylene wax water emulsions, PVA emulsion, ethanolamine and liquefied wood. The impregnated specimens were leached according to two continuous (EN 84 and ENV 1250-2) and two discontinuous (OECD and prCEN / TS 15119-1)

leaching procedures. The proportion of leached boron compounds depends on the concentration of boron in the wood, the boron source, the type and concentration of water repellents, the wood moisture content and the leaching procedure used. There were differences in the moisture contents of specimens among the various leaching procedures. The moisture content of the wood samples was a key factor affecting the final proportion of leached boron.Despite the considerable differences in the proportion of leached boron from wood impregnated with the same preparations and leached according to the various procedures, all leaching methods led to similar conclusions. A large proportion of the boron compounds were leached out in the first few cycles of leaching. More boron ions were leached from specimens impregnated with a lower share of boric acid than samples impregnated with a higher share of boric acid. Wax emulsions with a lower proportion of dry content penetrated deeper into the wood during impregnation and were more effective in reducing leaching than those with a higher proportion of dry content. Due to the high viscosity, they remained more on the wood surface. In some cases, the result was that more boron ions were leached in specimens impregnated with boric acid and emulsions with a higher proportion of dry content than from samples impregnated only with boric acid.

In the third part of the research we studied the sorption properties of boron compounds and the aforementioned water-repellent products. The equilibrium state of wood impregnated with boric acid, borax and montan wax at five levels of relative humidity in the adsorption and desorption process were monitored. The water repellent performance of montan and polyethylene wax emulsions was determined in a chamber with high air humidity (87%) during immersion in water and with sorption tests using a tensiometer. Over the course of five months exposure of the impregnated specimens to outdoor conditions (under a roof), changes in the moisture content according to outside temperature and humidity were monitored.

The results of the sorption tests show that boron compounds in the upper hygroscopic area increase the equilibrium moisture of the impregnated wood. The influence was dependent on the type of compound and its concentration. The higher the concentration of boron compounds in the wood the higher the equilibrium moisture content. The reverse was true for montan wax; the higher the proportion of wax in the wood, the lower the equilibrium moisture content of the impregnated wood. The moisture content of wood impregnated with a combination of boric acid and montan wax emulsion after conditioning in a chamber with high relative air humidity and after immersion in water and exposed outdoors, was lower than the moisture content of the control specimens. The good hydrophobic performance of montan wax was also shown in water uptake tests on the tensiometer, whereby water uptake into the impregnated specimens was approximately four times lower than in the control specimens. In contrast, wood impregnated with polyethylene wax emulsions absorbed more water than the untreated control specimens. The hydrophobic effect of polyethylene and oxidized polyethylene wax is achieved only after curing above the melting point of the wax, when the wax forms a film on the surface. Before curing, there were small cracks on the surface of the polyethylene wax treated wood, which formed capillaries, with capillary pressure taking up water.

During artificially accelerated weathering, the colour, chemical changes, contact angles and moisture content of the montan and polyethylene waxes impregnated Norway spruce were monitored. The results of moisture content measurements showed that wood impregnated with montan wax showed the largest hydrophobic effect. Moreover, FT-IR analysis of the artificially accelerated weathered wood showed that montan wax emulsion slows down the colour changes and chemical degradation of the treated wood.

The results of field testing (double layer) also demonstrated the greater resistance of Norway spruce wood impregnated with wax emulsions compared to untreated wood. The specimens were exposed for three years in the third use class at the Department of Wood Science and Technology, University of Ljubljana. We found that the resistance of the wax emulsion treated wood depended on the concentration of the emulsion and the wood quality. On the basis of the moisture content and temperature measurements during the field testing, it was concluded that the wood moisture content provides appropriate conditions for fungal growth.

The results of the laboratory and field tests show that impregnation with wax emulsions and with a combination of wax emulsions and boron compounds increases the resistance of the wood. However, the service life of the treated wood could not be determined because the field tests did not last long enough for the specimens to show even the first signs of decay.

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DOKTORSKA DISERTACIJA

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