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Scientific Paper
ISSN 0351-9465, E-ISSN 2466-2585
https://doi.org/10.62638/ZasMat1167

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(2024)

Antifungal Coating for Wood Protection

ABSTRACT

Antifungal hydro-repellent coatings were formulated for Pinus ponderosa panels' protection. The fomulated coatings were based on a hydroxylated acrylic resin chemically modified with n-octyltrieth-oxysilane (R8), n-octadecyltriethoxysilane (R18), and some mixtures of them as hybrid film-forming material. Diatomaceous silica was used as a pigment. The share of silane was 20% higher than the stoichiometric ratio to allow its interaction with cellulose hydroxyl groups (-OH).

Results indicated that the best antifungal efficiency was reached with coating formulated with 70R8/30R18 ratio due to the chemical reaction of cellulose hydroxyl groups (causing its blocking) and the physical barrier created by the degree of compaction of the film itself. Moreover, Biodeterioration of the film caused by the specific fungi was not observed, whit confirms the durability effect of the treat-ment. The protection mechanism is related to the water repellency and the blocking of the substrate.

Keywords: *Antifungal coating, Wood, Chemically modified acrylic resin, Silane, Water repellence, Decay resistance*

1. INTRODUCTION

The protective treatments of wood (impregnation and/or application of coatings) are applied, in many cases, to prevent its decay by water repellency of wood; however, solely the water repellency is not sufficient to prevent biodeterioration of wood.

An efficiency protective method that is being used against biodeterioration is wood chemical modification. This is based on the reaction between the cellulose hydroxyl groups with active protective products to improve dimensional stability, decay resistance, flame retardance and UV deterioration. The mentioned modification prevents biodeterioration because with only a random inclusion of a substituent in a hydroxyl group of any glycosidic ring prevents its enzymatic attack by the non-formation of the enzyme-substrate complex [1-6].

It is known that curing of the silanes involves hydrolysis and condensation reactions of the metal-organic precursors. When wood is treated with silanes, the chemical modification takes place which involves condensation reaction of the hydroxyl groups of cellulose (C-OH) with hydrolyzed silanes (≡Si-OH) forming ≡Si-O-C≡ bonds [7-16].

The aim of this paper was to formulate reactive hybrid coatings based on a hydroxylated acrylic resin and silanes mixture for the *Pinus ponderosa* panels protection, by proper combination of the main properties of wood in service: decay resistance, water repellency and water vapor permeability.

EXPERIMENTAL

Pigmented coatings were formulated with a hydroxylated acrylic resin chemically modified with n-octyltriethoxysilane, n-octadecyltriethoxysilane and some mixtures of them. The amount of silane was 20% upper to the stoichiometric ratio to allow its interaction with cellulose hydroxyl groups (-OH). As extender was used diatomaceous silica to improve the hardness and adhesion of the films and to give opacity to coatings.

Diatomaceous silica was dispersed in the film-forming material in form of the solution of hydroxylated acrylic resin to achieve a concentration

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Paper received: 20.05.2024.
Paper accepted: 9.06.2024.
Papir is available on the website: www.idk.org.rs/journal

of approximately 20% v/v of the dry film; the process was conducted in a high-speed disperser for 25-30 minutes (7-8 NS of Hegman Scale). Silanes and silanes mixtures were used in its original liquid state. The solvent mixture was formulated with ethanol / ethylene glycol acetate, 1/2 v/v and was used to adjust the solids content of all coatings to 70% v/v.

Solid wood panels made of *Pinus ponderosa*, kept in laboratory environment (25 ºC y 40%RH) were coated with brush; the dry film thickness (measured by ultrasound PosiTector 200B) ranged from 74-81µm. In all cases, and to ensure the total drying and curing of the films (hydrolysis and condensation reactions involved in the sol-gel process), the specimens were kept in the controlled laboratory conditions for ten days before start laboratory tests.

LABORATORY TESTS

The following tests were conducted after curing of the coatings:

***- Contact angle** (Ø).* Ø was measured by the sessile drop technique, using a microscope and a suitable source of illumination, with a CCD camera coupled to ocular (in triplicate). Drop Shape Analysis was made using the ImageJ software (NIH). Contact angle measurements were conducted on uncoated and coated wood panel samples.

- Water Repellency Effectiveness (WRE)**.** The size of the panels was 50x100x300mm; efficiency was determined under guidelines of ASTM D5401-03 (2014). The WRE values were evaluated by eight immersion cycles (in triplicate).

- Capillary water absorption (w)**.** The specimen sizes were 80x80x40mm (radial x tangential x axial). The test was carried out according to guidelines of ISO15148:2002 (in triplicate).

- Water vapor permeability. This test was performed on free films of coatings, under the guidelines of DIN52615:1987-11 (until the constant weight of samples in 24 hour intervals). DIN18558:1985-01 considered coating as water vapor permeable when Sd value is lower than 2m; for higher quality level should be Sd lower than 0.10m. Firstly, it was calculated the flux density of water vapor diffusion (DDV) in $g.m^{-2}.day^{-1}$ and then, the air thickness equivalent to the diffusion of water vapor (Sd, air layer that has the same resistance to the water vapor diffusion that the paint film thickness considered). For this purpose, it was used the expression Sd = 20/DDV.

- Fungal resistance. The specimen sizes were 20x20x20mm. The coated specimens of *Pinus ponderosa* were exposed, under laboratory conditions, to the action of *Trametes versicolor* and *Chaetomium globosum*, following general guidelines of ASTM D2017-05 (2014) and to *Aspergillus niger,* following guidelines of ASTM D4300-01 (2021).

RESULTS AND DISCUSION

- Contact angle. All coated panels had higher contact angle than untreated wood (ø = 50°), Table 1. Furthermore, Ø increased proportionally to the increase of R18 in coating composition. This would be based on presence of long hydrocarbon chain in R18 linked to the –OH of cellulose and acrylic resin giving hydrophobicity to the system. These findings are consistent with those reported by Chae Eun Pyo and Jeong Ho Chang [17], who reported a fourfold increase in contact angles for surfaces modified with C18 compared to unmodified surfaces.

Table 1. Contact angle

Alkoxide		Contact angle	Hidrofobicity
n-octyltriethoxysilane (R8)		60 ± 3	Low
n-octadecyltriethoxysilane (R18)		142 ± 2	Excellent
R8/R18, ratio v/v	90/10	70 ± 3	Low
	80/20	81 ± 5	Low
	70/30	91 ± 4	Regular
	60/40	95 ± 4	Regular
	50/50	98 ± 2	Regular
	40/60	100 ± 6	Regular
	30/70	108 ± 3	Regular
	20/80	113 ± 3	Satisfactory
	10/90	130 ± 5	Excellent
Reference		50 ± 2	Low

- Water repellent efficiency. Water repellent efficiency of the coated panels was analyzed by the coefficient WRE, Figure 1. The WRE values for coated wood were similar for all immersion cycles; this could be on the consequence of the high stability that the coatings have when are exposed to moisture-drying cycles.

The results show that the coating modified only with R8, although would form a compact dense coating, would not prevent the ingress of liquid water because the lack of high water repellency; the improved performance in terms of water repellence, in comparison to the untreated wood, can be explained by the chemical modification of the wood cell walls.

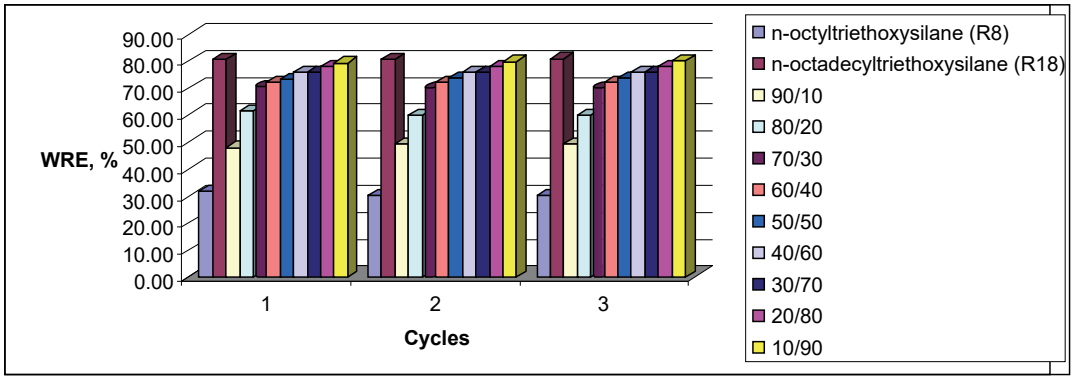

Figure 1. Water Repellence, WRE %

Meanwhile, the coating modified only with R18 also formed a reactive coating but hydrophobic and discontinuous because of the steric hindrance; this gives the best water repellency (WRE = 80.75 ± 0.16%) compared to the untreated wood and even to the treated only with R8 (WRE = 30.71 ± 0, 34%).

Regarding coatings formulated with mixtures of silanes, the results indicate that the increased level of R18 led to increased WRE, Figure 1; WRE values increase strongly with the increasing of R18 up to 60/40 R8/R18 ratio. This can be explained by the fact that while the packing density is lower (steric effect between R8 and R18 groups) the hydrophobicity of system is optimal. This aligns with the findings of Chen et al. [18], who emphasized the significance of alkyl chain length in establishing a hydrophobic network.

- Capillary water absorption. W coefficient decreased with increasing of R18 in binder, Figure 2; this probably the consequence of the film packing density and the chemical modification of wood. The coating that includes only R8 as cobinder forms a dense and compact film, but it was not sufficient to prevent the ingress of water; despite, the ingress of water was lower than for the untreated wood (2.30 ± 0.13 and 2.41 ± 0.12 respectively), due to the physical barrier which prevent capillary uptake.

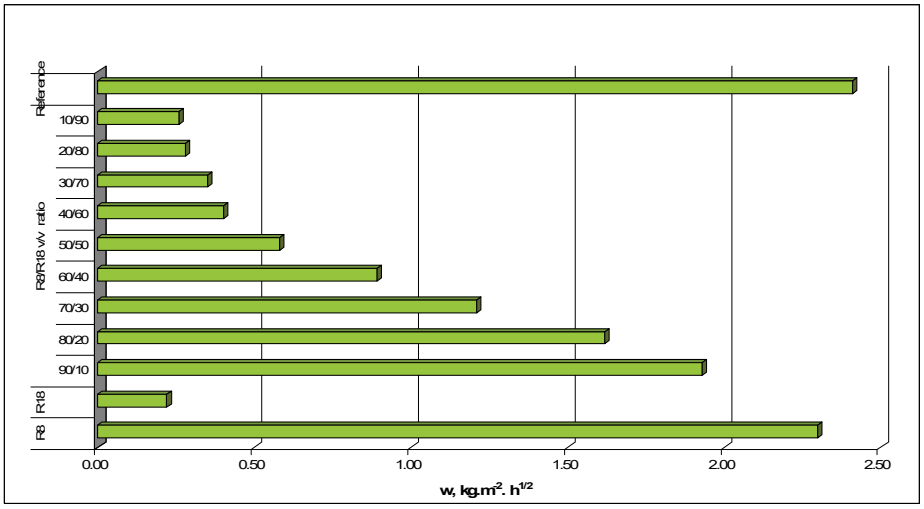

Figure 2. Water Repellence, w coefficient

Meanwhile, wood protected with coating that includes only R18 as cobinder also form physical barrier but with strongly hydrophobic characteristics; based on the best value of w (0.22 ± 0 01) [18].

For intermediate values of R8/R18, acceptable w values were obtained between 50/50 and 0/100 R8/R18 ratios (0.58 and 0.22 respectively). This is due to the achieved balance between water repellency and loss of fibers capillarity, resulting from the shutter of the -OH with the silanes employed.

- Water vapor permeability. The recorded Sd values were between 0.07 and 0.14 m; values that exceed 0.10 m correspond to R8 and to 90/10 R8/R18 ratio, Figure 3. What could have happened is that the long chains of R18, as their ratio increases, made the coating film more porous, decreasing the Sd up to the film with 60/40 ratio; after which water repellence begun to have more preponderance, and the Sd increased progressively. This agrees with Josip Miklečić, Vlatka Jirouš-Rajković [19] who reported that for non-porous materials, there is no theoretical difference between the penetration of liquids and water vapor, but due to the porous structure of the coating, water can also move by capillary flow, which can affect the differences in water and water vapor permeability [20]. It is known that uptake of moisture in liquid form occurs both by capillary sorption and moisture diffusion and consequently is strongly dependent on the structure of the wood [21].

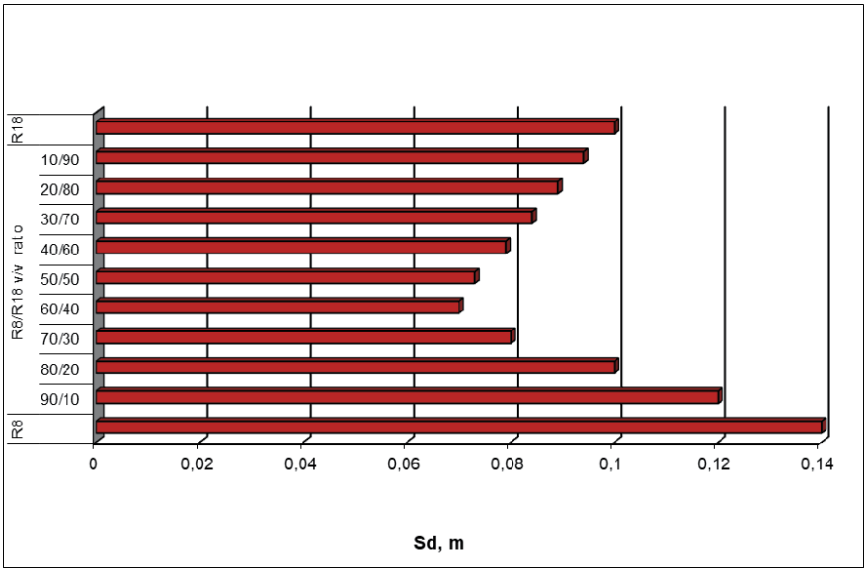

Figure 3. Water vapor permeability, Sd

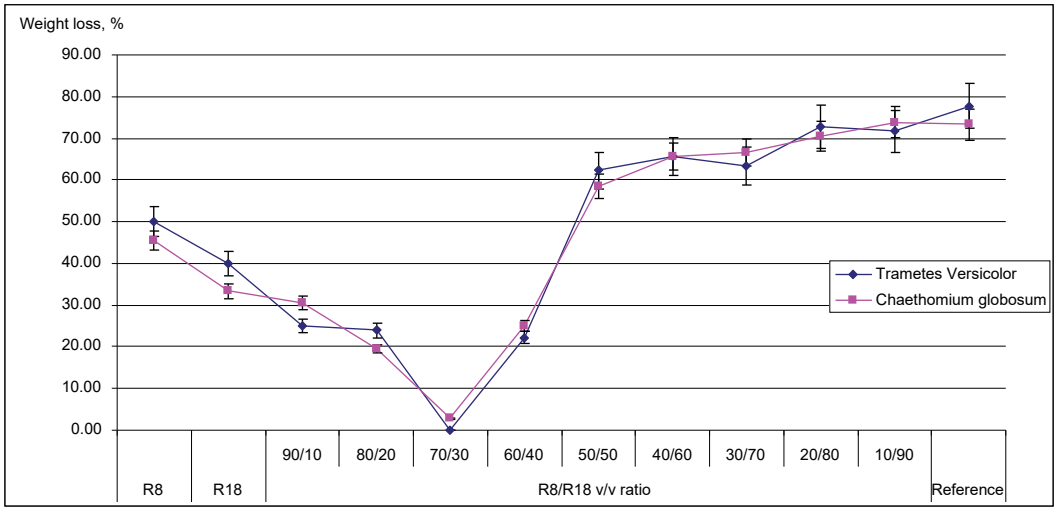

Figure 4. Decay resistance, Weight loss of specimens exposed to fungi

After analyzing the steric effect, it can be concluded that all films enabled water vapor permeability and natural wood movement, thus preventing loss of film adhesion [22].

- Fungal resistance. The analysis of results indicates that for the coating film with only R8 in its composition two effects occurred: high mass loss, but fungal vegetative body growth was not observed, Figure 4.

Moreover, in films with R8/R18 mixtures the following was observed: (i) reduced mass loss, with maximum for 70/30 R8/R18 ratio, where the mass loss becomes zero; (ii) no growth of fungal vegetative body; (iii) increased mass loss with the growth of the fungal vegetative body on the surface.

Finally, for the coating film wit only R18 it was observed: (i) high mass loss and (ii) growth of the fungal vegetative body.

The best antifungal efficiency was achieved with the coating formulated with 70/30 R8/R18 ratio, which can be explained by the achieved suitable degree of compatibility between the blocking of the cellulose (by chemical reaction with OH groups of coating), the physical barrier of film created by the compaction of the film (mainly conferred by R8 silane) and the hydrophobicity (primarily provided by the R18 silane). The protection mechanism based on the water repellency and the blocking of the substrate bonds was reported in previous works by many authors: In García et al. [23], the antifungal efficacy of acrylic varnishes on pine wood was studied, revealing that acrylic coatings form a protective film that prevents the entry of moisture and oxygen, both necessary for fungal growth. Miklečić and Jirouš-Rajković [19] also highlight the effectiveness of finishes in protecting wood against liquid water and water vapor. Finishes create an impermeable barrier that prevents moisture absorption, crucial for preventing fungal growth.

Regarding exposure to *Aspergillus niger*, there was no growth recorded on any film surface or in the surrounding encirclement, Figure 5. This result confirmes the durability of the treatment.

In summary, comparing findings in the literature, it could be observe that whether Hybrid (Cutz et al. [24]), Commercial (Jusic et al. [25]), Natural (Arminger et al. [26]), Acrylics (García et al. [23]), or Water-based Acrylics (Custódio et al. [27]) coatings, the aim is to achieve an Impermeable finish coat (Miklečić and Jirouš-Rajković [19]) and the excellent adhesion (Kúdela and Liptáková [28]), leading to an efficient physical and hydrophobic barrier that prevents the ingress and development of wood-degrading microorganisms. Each of these studies highlights different aspects and mechanisms contributing to the antifungal protection of coatings, from the incorporation of active agents like titanium dioxide, the use of chemical biocides, to the formation of physical barriers preventing moisture penetration.

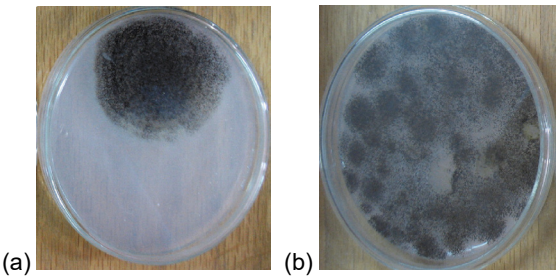

Figure 5. Decay resistance, Inhibition of Aspergillus níger growth (a) respect to control (b)

CONCLUSIONS

- The best antifungal efficiency was achieved with the coating formulated for the 70/30 R8/R18 ratio, which can be explained by achieved compatibility between the blocking of the cellulose (by chemical reaction of its -OH groups with coating components), the physical barrier created by the compaction of the film (mainly confirmed by R8 silane) and the hydrophobicity (primarily provided by R18 silane). This means that this treatment blocks all possible mechanisms of fungal attack.

- The values of Sd showed that the adhesion of the coating films to wood panels was very good in the range of 70/30 R8/R18 to 40/60 R8/R18 ratios. In this case the antifungal performance was ensured by physical blocking of the coating film.

- The water repellence, another important factor of biodeterioration prevention, increased with the level of R18 in binder. This shows that the water repellency of film is affected by the hydrophobicity of the co-binder employed, with positive impact of the long hydrocarbon chains in the composition to the water repellence.

- The results of eexposure of films to *Aspergillus niger,* allow us to conclude that formulated coatings resists to common environmental fungi action. This conclusion is important knowing that these fungi regulate the humidity of the colonized material.

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IZVOD

ANTIFUGALNI LAK ZA ZAŠTITU DRVETA

Antifungalni hidro-repelentni premazi su formulisani za zaštitu panela Pinus ponderosa. Formulisani premazi su zasnovani na hidroksilovanoj akrilnoj smoli hemijski modifikovanoj sa n-oktiltrietoksisilanom (R8), n-oktadeciltrietoksisilanom (R18) i nekim njihovim smešama kao hibridnim materijalom za formiranje filma. Kao pigment je korišćen dijatomejski silicijum. Udeo silana je bio 20% veći od stehiometrijskog odnosa da bi se omogućila njegova interakcija sa hidroksilnim grupama celuloze (-OH).

Rezultati su pokazali da je najbolja antifungalna efikasnost postignuta sa premazom formulisanim u odnosu 70R8/30R18 usled hemijske reakcije celuloznih hidroksilnih grupa (koje izaziva njeno blokiranje) i fizičke barijere stvorene stepenom zbijenosti samog filma. Takođe, nije primećeno biopropadanje filma izazvano specifičnim gljivama, što potvrđuje efekat dugotrajnosti tretmana. Mehanizam zaštite je vezan za vodoodbojnost i blokiranje podloge.

Ključne reči: *premaz protiv gljivica, drvo, hemijski modifikovana akrilna smola, silan, vodoodbojnost, otpornost na propadanje*

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Naučni rad

Rad primljen: 20.05.2024.

Rad prihvaćen: 9.06.2024.