Chemical and Application Properties of Some Solvent and Water Based Coatings on Wooden Substrate

Kemijska svojstva i primjena premaznih materijala na bazi vode i organskih otapala na drvu

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ABSTRACT • Wood finishes are used extensively to improve the aesthetic value and protect wood products from moisture. These organic coatings generally contain volatile organic compounds (VOC) as solvents that evaporate when the coatings cure over the surface. Due to strict legislations against these hazardous VOCs, the buyers across the globe are shifting towards products finished with water borne coats. Two of the most commonly used wood coatings in India are polyurethane and nitrocellulose (NC) lacquer. This paper aims at comparing these two wood coatings with their water borne counterparts. The study was conducted on the wood substrate of Melia dubia. Chemical characterization of the cured coats was attempted through FTIR spectroscopy. Physical appearances in terms of gloss and film thickness were also studied. Bands of urethane, urea and nitric groups were identified, which helped in understanding the changes in chemical structure of the finishes after curing. The thickness of the organic coatings was significantly higher than that of their water-borne counterparts. Gloss of water based coatings was observed to be lesser than that of their organic solvent based counterparts in either coating material. In case of lacquer, the reduction was up-to 33 %, whereas in case of PU, gloss dropped down by about 54 %.

Keywords: organic coatings, water borne coatings, NC lacquer, polyurethane, Melia dubia, film thickness, FTIR, gloss

SAŽETAK • Premazni se materijali primjenjuju na drvu kako bi se očuvao njegov estetski izgled i drvni proizvodi zaštitili od vlage. Organski premazni materijali u osnovi sadržavaju hlapljive organske spojeve (HOS) kao otapala koja isparavaju dok premazni materijal otvrdnjava na površini drva. Zbog strogih propisa o tim opasnim hlapljivim organskim spojevima kupci diljem svijeta prelaze na vodene premazne materijale. Dva najčešće upotrebljavana premazna materijala za drvo u Indiji jesu poliuretanski i nitrocelulozni (NC) lak. Cilj rada bio je usporediti ta dva premazna materijala s istim premaznim materijalima na bazi vode. Istraživanje je provedeno na drvu Melia dubia. Kemijska karakterizacija otvrdnutih premaza provedena je primjenom FTIR spektroskopiije. Također su proučavani sjaj i debljina filma. Identificirane su skupine uretana, ureje i nitratne skupine koje su pridonijele razumijevanju promjena u kemijskoj strukturi premaza nakon otvrdnjavanja. Debljina premaza na bazi organskih otapala bila je znatno veća od debljine premaza na bazi vode. Uočeno je da je sjaj premaza na bazi vode manji od sjaja premaza na bazi organskih otapala. Za NC lak to je smanjenje bilo do 33 %, a sjaj PU laka smanjio se za oko 54 %.

Ključne riječi: premazi na bazi organskih otapala, premazi na bazi vode, NC lak, poliuretan, Melia dubia, debljina filma, FTIR, sjaj

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1 INTRODUCTION
1. UVOD

Wood has always been a much appreciated material for its structural and aesthetic properties. It represents a renewable resource and is widely used in many applications for exterior and interior purposes. Being an organic compound, wood is subject to degradation due to the weathering process. Organic coatings are used to protect the wood surface and to improve its aesthetics. The required properties and formulation of wood coatings depend on their end-use application: indoors or outdoors. In the case of interior products, more emphasis is placed on appearance with different aesthetic requirements. Finishing adds beauty by enhancing the aesthetic value of wood and improving its luster, also known as gloss. It is an attribute of finished surfaces that gives them shiny or lustrous metallic or matte appearance. Gloss is based on the ability of a surface to reflect directed light (Živković, 2004). This property of finishes is used widely as a parameter to evaluate and compare the quality of finishes.

Polyurethane (PU) is a hard, abrasion-resistant and durable wood coating, and is known to act as a good moisture barrier for wood based products (Poaty et al., 2013). It has been reported by Carter (2012) that PU-based varnishes possess good mechanical strength, adhesion to the surface as well as ease of applying multiple coats. In spite of the above advantages, PU based finishes are not very much favored for outdoor uses since they are prone to UV degradation (Kurtoğlu, 2000). Nitrocellulose lacquers are widely used by the solid wood industry in India. They are prevalent in this sector as they result in low lacquers are widely used by the solid wood industry moisture barrier for wood based products (Poaty et al., 2004). Studies on mechanical gluing and bonding properties showed that this species is a good candidate for the plywood industry as well (Saravanan et al. 2014; Uday et al. 2012). Some studies on finishing properties using common coating materials have generated data showing value added to solid wood products made of this wood (Gupta et al., 2016b, c).

Against this background, a study was conducted on physical appearance and chemical characterization of solvent borne and water borne commercial coatings on Melia dubia. Two of the most commonly used wood coatings, polyurethane (PU) and nitrocellulose lacquer, were chosen for the study. The aim was to observe the changes that take place in the chemical structure and physical appearance of the coatings by changing their solvents from organic volatile compounds to water.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

Planks of 3.2 cm thickness were sawn from a freshly felled log of Melia dubia and they were kilndried to 12 % moisture contents. These planks were further planed with a surface planer to make the surface level flat. From a defect free plank, 48 samples of size 15 cm×10 cm×2.5 cm (Axial × Tangential × Radial) were cut and then sanded with 80, 100, 120 grit sized sandpapers progressively to prepare smooth surfaces for coating. Samples were then kept in a humidity controlled chamber for conditioning at 300 °C temperature and 35 % RH. This conditioning was continued until the weights of the samples became constant.

The two coating polymers - Polyurethane and NC Lacquer with different solvents (organic and water) were procured from Plantag Coatings India Ltd. The procured coatings had the following physical and chemical specifications.

Organic Solvent based PU: One coat system with hardener addition 5 % wt
Solubility (water): Insoluble
Viscosity at 250 °C: 25 – 27 sec (4 mm)
Solid content: 21.39 % Wt.

Water based PU: One coat system
Solubility (water): Easily soluble at 200 °C
Viscosity at 250 °C: 90 – 110 sec (4 mm)
Solid content: 29.46 % Wt.

Organic solvent based NC Lacquer: Single pack system
Solubility (Water): Insoluble
Viscosity at 250 °C: 50 – 55 sec (4 mm)
Solid content: 24.56 % Wt.

Water based NC lacquer: Single pack system
Solubility (water): Easily soluble at 200 °C
Viscosity at 250 °C: 100 – 105 sec (4 mm)
Solid content: 32 % wt.

The above solid contents were estimated in the laboratory following the method by Zhu et al., (2018). Three coats of each combination were applied on the samples and were allowed to cure completely for 2 hrs.
between successive coats. 12 samples were each prepared with four coatings. Coatings were applied with painting brush to observe the ease of application of different coating combinations.

For chemical characterization of cured coatings, FTIR spectroscopy was adopted by using a FTIR Spectrometer (Bruker Germany, Tensor 27 model) equipped with an ATR probe. The spectral resolution was 4 cm\(^{-1}\) and the rate of scans/measurement was 64. Spectra were recorded for all the samples after 7 days of coating and were averaged for each combination. To study the luster of coats, gloss was measured at 5 random places on the tangential coated surface of each sample with the help of a gloss meter with 60 degrees gloss head angle. Thickness of the coating material was measured with the help of film thickness measuring unit in microns. A DeFelsko PosiTector 200, which conforms to ASTM D6132 and ISO 2808, was used for this purpose. This instrument uses ultrasonic technology to measure the coating thickness non-destructively (Gupta et al., 2016). The thickness was also measured at five random places on the surfaces of the coated samples. Thus, there were 60 random readings for both gloss and thickness for each coating.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Characterization of the coatings used
3.1. Karakterizacija premaznih materijala

FTIR spectra obtained for the coated samples were examined to identify the known absorption bands.

Polyurethane wood coatings cure to form urethane polymer film. It consists of an activator pack and a paint pack, whose active ingredients include isocyanates (-N=C=O) and hydroxyl groups (-O-H), respectively. Reaction of isocyanates and hydroxyl results in formation of urethane (H-N=C=O). From the FTIR spectra, the bands of (-N=C=O), (-O-H) and (H-N=C=O) could be identified.

\[
\text{R-N=C=O } + \text{ R’-OH } \rightarrow \text{ R-NH-C=O-R’}
\]

Figure 1 gives the FTIR spectrum of the PU coated wood surface, while the identified absorption bands are presented in Table 1.

The most important bands to take note are those at 2270 to 2280 cm\(^{-1}\) (–NCO vibration), 3360 to 3380 cm\(^{-1}\) (–NH vibration) and the shoulder around 3530 to 3550 cm\(^{-1}\) (–OH vibration). Other bands normally given a lot of importance are 1720 to 1730 cm\(^{-1}\) (urethane C=O vibration), 1680 to 1690 cm\(^{-1}\) (urea –C=O vibration) and 1600 cm\(^{-1}\) (aromatic v(C=C) vibration). The strong band in the range of 1720 to 1730 cm\(^{-1}\) in Figure 1 clearly indicates the formation of urethane in cured coatings. Bands of OH and NCO on the lower side give a clear indication that they have reacted together to form urethane. The band at 1460 cm\(^{-1}\) indicates the C-H bond in the polymeric chain. C-O-C molecular vibrations in the chain structure of PU are well indicated by vibration bands at 1230 cm\(^{-1}\) (Yang et al., 2001). Figure 2 shows the FTIR spectrum of the cured water-based PU used in the study.

Table 1. Identified bands in the FTIR spectrum of cured PU
Tablica 1. Identificirane vrpce na FTIR spektru otvrdnutog PU premaza

<table>
<thead>
<tr>
<th>Wavenumber / Valni broj</th>
<th>Assignments / Pripisane vrpce</th>
<th>Wavenumber / Valni broj</th>
<th>Assignments / Pripisane vrpce</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600 cm(^{-1})</td>
<td>Aromatic v(C=C) vibration</td>
<td>2270-2280 cm(^{-1})</td>
<td>–NCO vibration</td>
</tr>
<tr>
<td>1680-1690 cm(^{-1})</td>
<td>Urea –C=O vibration</td>
<td>3360-3380 cm(^{-1})</td>
<td>–NH vibration</td>
</tr>
<tr>
<td>1720-1730 cm(^{-1})</td>
<td>Urethane –C=O vibration</td>
<td>3530-3550 cm(^{-1})</td>
<td>–OH vibration</td>
</tr>
</tbody>
</table>

Figure 1 FTIR spectrum of cured PU wood coating
Slika 1. FTIR spektar otvrdnutog PU premaza
An examination of Figure 2 reveals that the wide and strong –OH absorptions between 3444 cm\(^{-1}\) and 3533 cm\(^{-1}\) have reduced. The NCO absorption band at 2275 cm\(^{-1}\) is not seen indicating that the –NCO group has reacted completely with OH of water solvent. The sharp band at 1700 cm\(^{-1}\) is attributed to C=O stretch vibration, which indicates that a reaction between water and –NCO has taken place resulting in formation of urethane. The sharp and strong band at 761 cm\(^{-1}\) is due to C–N bond vibration. All these indicate the presence of urethane bond and urea bond formation. A new band appearing at 1168 cm\(^{-1}\) is attributed to the C–N–C stretch vibration in the isocyanurate ring in the hydrophilic-modified curing agent (Zhang et al., 2007). Figure 3 shows the IR spectrum of organic solvent based NC lacquer coated surface.

Nitrocellulose lacquers contain nitrocellulose with oils as plasticizers and spreading agents. In Figure 3, nitrocellulose is identified by the nitric group at 1652, 1275 and 843 cm\(^{-1}\). The main bands reported for nitro-
cellulose are around 1660, 1280 and 840 cm\(^{-1}\). Lopez et al. (2010) attributed these to be antisymmetric and symmetric stretching of NO\(_2\) and valence stretching of NO. Cakic et al. (2007) also had earlier reported valence vibrations of the nitric group specifically occurring at the wave numbers of 1660 cm\(^{-1}\) (asymmetric valence vibration) and at 1280 cm\(^{-1}\) (symmetric valence vibration). The oil is verified with a carbonyl band at 1732 cm\(^{-1}\) and in the fingerprint regions at 1240, 1168, 1009 and 725 cm\(^{-1}\) (Dredge et al., 2014). Kovalenko et al. (1994) have also reported bands in the 950 – 1200 cm\(^{-1}\) region due to vibrations of CO group. Figure 4 represents the FTIR spectrum of water-based lacquer coated surface.

Water based lacquers contain oils as well as water as solvent medium. In order to reduce the emissions from organic VOC (Volatile Organic Compounds), coating particles are dispersed in the medium with more water and a lower amount of organic solvent. They are tiny dispersions, or droplets, of a cured reactive finish (cross-linked within the droplets) emulsified in water. Water serves as a thinner. A very slow evaporating solvent (usually glycol ether) is added to the coating so that droplets can cure as a film. When the solvent evaporates, droplets coalesce together to form a film. The main difference that can be noted in Figure 4 with respect to Figure 3 is that the intensities of nitric group bands have considerably reduced (843, 1275 and 1652 cm\(^{-1}\)). Larson (2015) argues that the nitric group bands show up intensely only when enough concentration of nitrocellulose is present in the emulsion and sometimes the low intensity bands get hidden in other intense bands of other groups. According to Ossa et al. (2012), nitrocellulose is often applied in paints, lacquers, varnishes, inks, etc. in lower concentrations than in explosives. Low concentration (< 35 %) of nitrocellulose in water based formulations of nitrocellulose lacquer has also been patented (Quinlan 1989). Figure 4 confirms the existence of stretching absorption of –C-C(O)-C- in the range of 1260 – 1230 cm\(^{-1}\) for acetate esters, which could be the binders. Many other esters result in bands in the 1210 – 1160 cm\(^{-1}\) range as seen in Figure 4.

3.2 Physical characteristics of coated surfaces

3.2. Fizička svojstva premazanih površina

Primary observations on physical appearance of the four types of coatings on the common wood substrate of Melia dubia revealed interesting results. Comparing two widely used wood coatings (Lacquer and Polyurethane) with their water borne counterparts on the grounds of ease of application, curing time and physical appearance was the main objective of this study.

During application by brush, it was observed that organic solvent based finishes were easy to apply on the surface in comparison to the water based ones. The wood of Melia dubia is reported to be of diffuse porous structure (Saravanan et al., 2013a). Diffuse porous hardwoods are reported to have high water uptake (Michalec and Niklasova, 2006). The wood fibers on the surface absorbing the solvent (water) of these finishes and making them too tacky to be spread properly might also be causing the application of such finishes a bit tedious. Torn grains causing fuzziness and roughness are common defects found with hardwoods unless sanded with high grit sizes (Laina et al., 2017; Varanda...
et al., 2010). The drying (curing) time of water based coatings was found to be much less compared to that of organic solvent based coatings. They were almost dry to touch after applying, whereas organic based coatings started to become tacky after 15 min from the time of application and cured properly after about 2 hours. Such low dry to touch (15 min) and tack (1.5 h) times for PU has been reported on Eucalyptus and teak surfaces (Pandey et al., 2007). The surface coated with organic solvent based coatings was smooth to touch while the surfaces coated with water based coatings became quite rough to touch. This was due to rising up of wood fibers after absorption of water from the coatings.

3.3 Characteristics of coated films

Having looked at the physical characteristics of the coated surfaces, a look at their lustre would be interesting. Table 2 gives the gloss values measured for four types of coatings.

Table 2 presents two facts: the gloss of PU seems to be consistently greater compared to that of lacquer, while the gloss of water based coating seems to be less than that of its organic solvent based counterpart in both coating materials. The water based lacquer has resulted in 32.6% less gloss compared to its organic based coating. In the case of PU, this reduction in gloss is 53.9%. Gloss is the result of specular reflection, where the reflecting surface is expected to be very smooth and mirror-like (Nadal et al., 2006). The presence of torn grains, raised grains or any such imperfections can interfere with the extent of smoothness of the coated surface. As already explained above, the water based coats had caused a certain amount of defects on the surface. Hence, the reduction in gloss with water based coats is in expected lines. The natural grains of wood influenced the aspect of the coating and gloss features of Tanganyika wood substrate when coated with water based PU (Scrinzi et al., 2011).

To ascertain the differences between the glosses of water-based and organic-solvent based coatings of both PU and lacquer, individual readings were analyzed through One-way ANOVA and the results are given in Table 3.

Table 3 clearly indicates that the gloss values of water based coatings in either case are significantly lower compared to gloss values of the corresponding organic solvent based coatings. A gloss value of 90.3 GU on Melia dubia substrate was reported with four consecutive coatings of PU (Gupta et al., 2016b). However, the value for lacquer is much less than that reported for nitrocellulose lacquer. The coating thickness achieved must have affected the gloss value achieved in the present study. However, the gloss values of lacquer in the present study are similar to those reported for two bamboo species (Bambusa polymorpha and Dendrocalamus giganteus), where two coats of lacquer were applied on their surfaces (Shukla et al., 2015). The values of water based lacquer coatings in the present case classify them into the category of gloss level 3 (Egg shell like finish), whereas those of organic solvent based lacquer coating give “satin like” finish, i.e. the gloss level 4 (MPI Architectural standards: mpi.arcomone.com). The measured gloss values of water based PU coating are categorized as a semi-gloss finish at gloss level 5 and those of organic solvent based PU coating are high gloss wood finish at gloss level 7.

It would now be interesting to see the thicknesses of the four coatings with an equal number of coats. Table 4 gives the results of the film thickness measurements carried out for all the four coatings on the wood substrate.

Table 2 Gloss values for organic solvent based and water based coatings

<table>
<thead>
<tr>
<th>Coating / Premaz</th>
<th>Number of readings</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Lacquer</td>
<td>60</td>
<td>20.7</td>
<td>36.5</td>
<td>27.6</td>
<td>4.0</td>
</tr>
<tr>
<td>Water based Lacquer</td>
<td>60</td>
<td>14.6</td>
<td>23.6</td>
<td>18.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Organic Polyurethane</td>
<td>60</td>
<td>73.6</td>
<td>114.9</td>
<td>92.4</td>
<td>11.3</td>
</tr>
<tr>
<td>Water based Polyurethane</td>
<td>60</td>
<td>33.3</td>
<td>56.3</td>
<td>42.6</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Table 3 ANOVA of gloss values of PU and Lacquer with the two solvents

<table>
<thead>
<tr>
<th>Source of Variation / Izvor varijacije</th>
<th>Df</th>
<th>Ms</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between two lacquer coatings između dva nitroceluloznih premaza</td>
<td>1</td>
<td>2408.45</td>
<td>216.20</td>
<td>&lt;0.001</td>
<td>3.92</td>
</tr>
<tr>
<td>Error / pogreška</td>
<td>118</td>
<td>11.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total / ukupno</td>
<td>119</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Between two PU coatings između dva PU premaza</td>
<td>1</td>
<td>74431.08</td>
<td>885.45</td>
<td>&lt;0.001</td>
<td>3.92</td>
</tr>
<tr>
<td>Error / pogreška</td>
<td>118</td>
<td>84.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total / ukupno</td>
<td>119</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4 Film thickness (μm) of organic solvent and water based coatings

<table>
<thead>
<tr>
<th>Coating / Premaz</th>
<th>Number of readings</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Lacquer nitrocelulozni premaz na bazi organskih otapala</td>
<td>60</td>
<td>30</td>
<td>50</td>
<td>38</td>
<td>5.1</td>
</tr>
<tr>
<td>Water based Lacquer nitrocelulozni premaz na bazi vode</td>
<td>60</td>
<td>27</td>
<td>41</td>
<td>34</td>
<td>3.2</td>
</tr>
<tr>
<td>Organic Polyurethane poliuretanski premaz na bazi organskih otapala</td>
<td>60</td>
<td>29</td>
<td>51</td>
<td>35</td>
<td>6.5</td>
</tr>
<tr>
<td>Water based Polyurethane poliuretanski premaz na bazi vode</td>
<td>60</td>
<td>28</td>
<td>37</td>
<td>32</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Table 5 ANOVA of film thickness values of PU and Lacquer with two solvents

<table>
<thead>
<tr>
<th>Source of Variation / Izvor varijacije</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between two lacquer coatings / između dva nitrocelulozna premaza</td>
<td>1</td>
<td>418.13</td>
<td>22.89</td>
<td>&lt;0.001</td>
<td>3.92</td>
</tr>
<tr>
<td>Error / pogreška</td>
<td>118</td>
<td>18.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total / ukupno</td>
<td>119</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Between two PU coatings / između dva PU premaza</td>
<td>1</td>
<td>330.01</td>
<td>13.31</td>
<td>&lt;0.001</td>
<td>3.92</td>
</tr>
<tr>
<td>Error / pogreška</td>
<td>118</td>
<td>24.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total / ukupno</td>
<td>119</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4 shows that the thicknesses of water based coats are slightly on the lower side than those of their organic counterparts. To ascertain the differences between the thicknesses of water-based and organic-solvent based coatings of both PU and lacquer, individual readings were analyzed through one way ANOVA and the results are given in Table 5.

Table 5 clearly indicates that the film thickness of organic solvent based lacquer and PU coats are indeed significantly higher than that of their water based counterparts. This reduction is due to the absorption of water based coatings by the wood fibers as discussed earlier instead of resulting in a clean film on the substrate. The important observation is that the thickness (35 μm) of three coats of PU achieved on Melia dubia is far less than the value (57.5 μm) reported for Dalbergia sissoo (Gupta et al., 2016a). The thickness obtained with two coats of an acrylic varnish containing PU on the surface of pine was 66.5 μm, which was attributed to the greater volume of voids in pine (Fernandez et al., 2013). It is interesting to see that the water based coatings resulted in significantly lower coating thicknesses than their organic counterparts in spite of having higher solid contents. This observation also supports the fact that the two water based formulations used in this study might have penetrated easily into the substrate.

4 CONCLUSIONS

The characteristic IR absorption band around 2270-2280 cm⁻¹ due to –NCO vibrations seen in organic solvent based PU is absent in its water borne counterpart indicating faster curing of water based PU. The water based lacquer band used in the study gave low intensity bands for the nitric group indicating lower nitrocellulose concentration in the coating formulation. It was observed that organic solvent based coatings were easy to apply and waterborne coatings resulted in less smoother surfaces. The film thickness was significantly lower for water borne coatings as compared to that of organic solvent borne coatings despite the fact that the former ones had higher solid contents. Water borne coatings resulted in gloss reductions of 32.6 % for lacquer and 53.9 % for PU compared to their organic solvent borne counterparts.

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5 REFERENCES
