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# Previous Preservation of Veneers Promotes Higher Preservative Retention and More Effective Protection in CCA-Preserved Plywood

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## Abstract

Plywood panel has a promising market in Wood Frame Construction System. Like any wood-based product, it can suffer deterioration, and preservative treatment is imperative. The preservative treatment can be done directly on a pressed panel - a conventional method that supposedly causes a decrease in physical-mechanical performance - or incorporated into the production process, by the previous treatment of veneers to develop panels with durability and quality. We compared the performance of these two processes. Panels were produced with *Pinus taeda* L., using 360 g m$^{-2}$ of phenolic adhesive in a double line, a pre-pressing and hot pressing for 20 minutes under 1.2 MPa pressure and 130°C and treatement on veneers and panels with CCA-C. Tests followed Brazilian standards. Panels with previous treatment had lower water absorption and swelling. Preservation of the veneers also promoted higher retention levels and better penetration of preservatives. Both treatments did not affect the mechanical performance.

**Keywords:** Physical-mechanical properties, phenolic resin, preservative treatment, production process, plywood pressing.

## 1. INTRODUCTION

Plywood panels have a potentially growing application, as structural and closing components of the Wood Frame Construction System. This system appears in Brazil as a faster and easier execution option, with competitive costs and environmental appeal (SOTSEK; SANTOS, 2018). In housing constructions, as well as in the use for floors in trains, buses, and trucks, these panels have persisting contact with humidity, favoring attacks by deteriorating agents that considerably decrease their durability (TUFOLO NETTO, 2010). Due to market demands for products of high quality, with resistance against water and xylophagous organisms (SPOSTO, 2005; RICHTER, 2007; MOLINA; CALIL JR., 2010; WERNWR; BURROWS, 2014, VASQUES, 2014; TECVERDE, 2015), several preservative treatments can be carried out, to avoid early deterioration and increase the useful life of the wood by up to 10 times (BARILLARI, 2002).

The type of treatment most used in the world - about 84% of preserved wood - is pressure treatment (FERRARINI et al., 2010; SILVA, 2008), with products such as CCA, a water-soluble preservative composed of chromium, copper, and arsenic. The use of this product would raise additional concerns about toxicity; however, research has shown that copper and arsenic are strongly linked to wood by the fixing effect of chromium, minimizing the danger of environmental contamination (FREITAS, 2002). During the fixation of the active ingredients that are soluble in water, there is the formation of a complex that becomes insoluble in the wood through the reduction of chromium – gaining and fixing electrons from copper and arsenic - which makes them resistant to leaching and adds moisture protection to the wood (BROWN; EATON, 2000). The fixation of the products is effective even when the temperature of the treated elements has risen to 280ºC, with only 6% by weight of the arsenic content being volatilized (CUYPERS et al., 2009).

Despite the benefits of preservative treatment of wood and its by-products, the active ingredients of preservative products, such as chromium, copper and arsenic, react with wood during fixation, causing significant reductions in mechanical properties, especially if the drying processes are not controlled (TSOUMIS, 1991; VICK; KUSTER, 1992; ACKER; STEVENS, 1993, BARNES et al., 1996; PINHEIRO, 2001; IBACH, 2010; MENDES et al., 2013; FERREIRA, 2017; SEGUNDINHO et al, 2017). Other research suggests that the vacuum-pressure system and not the preservative itself would be the cause of the drop in physical-mechanical properties (TAŞÇIOĞLU; TSUNODA, 2010; MENDES et al., 2013; TAŞÇIOĞLU et al., 2014). The treatment of wooden panels would cause excessive swelling, in some cases irreversible, damaging the other properties.

An alternative to avoid the reduction in mechanical properties of the plywood panels, in these cases, would be the conduction of the preservative treatment in the veneers, incorporated into the production process in a stage before the pressing, avoiding the rehumidification of the ready-made panel during the treatment under pressure and, therefore, reducing the warping of the panel, normally observed in industries. In addition, the treatment carried out on veneers could benefit the penetration and retention of the preservative in all layers of the plywood subsequently produced. This method has been little studied and, when done, it was performed only on samples on a laboratory scale. The results obtained so far have shown that these panels did not show a drop in flexural strength compared to untreated panels, however, the treatment was responsible for decreasing the surface wettability and, therefore, the bonding quality (DO MARCO et al., 2015; FERREIRA; CAMPOS; SILVA, 2016; LARA PALMA et al., 2017; FERREIRA, 2017).

In order to produce high quality and durable plywood panels – that could guide future applications in Wood Frame Construction System – we evaluated the effectiveness of preservative treatment and the physical-mechanical performance of the plywood panels promoted by two different processes: preservation of the veneers, in a stage before the pressing of the panel and preservation after pressing the panel. The study presents the use of panels of commercial dimensions as a differential, which may show the potential dimensional distortions already observed in previous studies.

## 2. MATERIALS AND METHODS

### *2.1. Plywood production*

Plywood was produced with *Pinus taeda* L. wood from commercial plantations. The panels were made up of seven veneers nominal thickness of 2.5 mm each –and commercial dimensions (2440 mm long and 1200 mm wide) (Figure 1) using phenol-formaldehyde resin (FF) CASCOPHEN HL-7090 HS from CASCO® - Hexion® with an application of 360 g $m^{-2}$ in a double line and variables of the usual manufacturing process in the industry (Table 1). Four situations of plywood panels production (treatments) were evaluated with five repetitions (panels) per situation (Table 2).

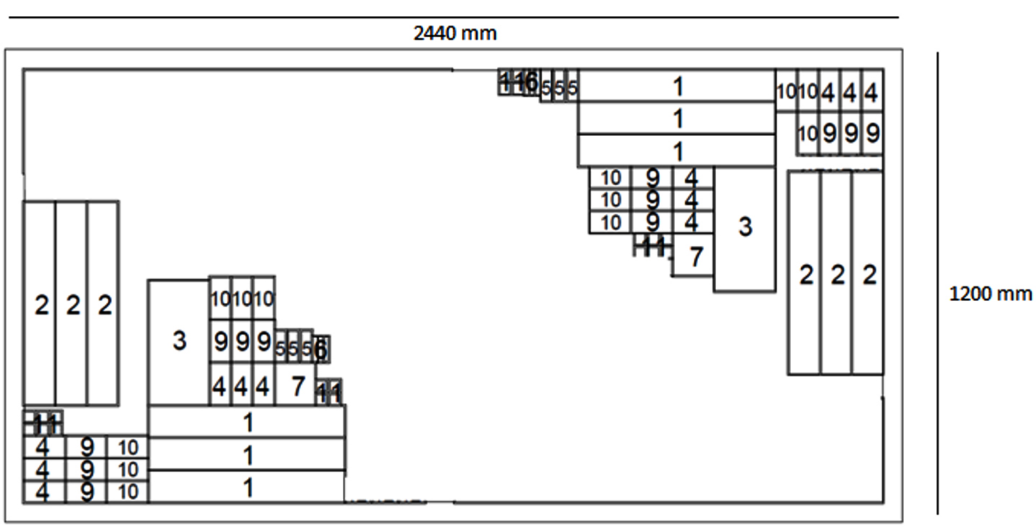


**Figure 1.** Cutting plane and plywood panels dimensions.

**Table 1.** Manufacturing process variables.

| Variables | | | |
|---|---|---|---|
| Stage | **Pressure (MPa)** | **Temperature (°C)** | **Duration (min)** |
| Cold pressing | 6 | room temperature | 10 |
| Hot Pressing | 12 | 130 | 20 |

**Table 2.** Experimental program situations.

| Situation | Reference | Productive process | Product used in the treatment |
|---|---|---|---|
| 1 | Untreated | without treatment | - |
| 2 | Panel - $H_2O$ | treatment on the panel (post-pressing) | water |
| 3 | Panel - CCA-C | | CCA-C |
| 4 | Veneers - CCA-C | treatment on the veneer (pre-pressing) | CCA-C |

## *2.2. Preservative treatment of veneers and panels*

The veneers and panels were treated at Usina Araucária (Cunha-SP-Brazil) with CCA-C (Montana Química Ltda, Brazil) and with water to evaluate the effect of the active ingredients (i.a.) of the preservative product and the vacuum-pressure process on the properties of the panels. A concentration of active ingredients of 0.018 kg per liter (1.8%) was used in a filled cell method (initial vacuum of 500 mmHg - 0.066 MPa - for 30 minutes; introduction of the diluted preservative product at a pressure of 1.0 MPa for 60 minutes; a final vacuum of 500 mmHg for 15 minutes). The panels were piled and tied during preservative treatment and drying, to minimize warping.

## *2.3. Preparation of specimens and tests*

The evaluation of the performance of the plywood panels was conducted with physical and mechanical tests according to international and Brazilian standards (Table 3).

Mechanical tests were performed with a servo-controlled testing machine (DL 30000, EMIC, Brazil) with 300 kN capacity. Wettability was evaluated by measuring the contact angle between the veneer and distilled water dripped onto its surface, photographed (Dino-lite Digital Microscope, Pro equipment, Taiwan) after 10 seconds, and processed on the scale of approximation 43 (Dino Capture v. 3.3.0.0 software, Taiwan) The penetration of preservative was visually assessed after application of a chromoazurol-S solution. The retention of the preservative was evaluated in a 2.5 cm diameter disk removed from samples and oven-dried. Specimens were heated and grounded in a Willey mill in a 30 mesh size for hot extraction in a water bath with a mixture of hydrogen peroxide and sulfuric acid. The concentrations of the elements (copper, chromium and arsenic)) were assessed by atomic absorption spectrophotometry according to NBR 6232 (ABNT, 2013).

Test results grouped by each panel - considered the sample unit - were analyzed in Exstat in Box-plot type graphs, to eliminate possible outliers, that is, discrepant results from the others. The average of the results obtained for each panel after eliminating outliers was used in the statistical analysis. The comparison between the situations studied (Table 1) was made using the Bonferroni method ($p < 0.05$).

**Table 3.** Tests and standards for wood plywood panels.

| Tests | Standards / methodologies | Repetitions per panel |
|---|---|---|
| Static bending (longitudinal and transverse - $E_{M,l}$; $E_{M,t}$; $f_{M,l}$; $f_{M,t}$) | NBR 9533 (ABNT, 2012a) | 5 |
| Bonding quality / shear on the glue line ($f_v$)* | NBR ISO 12466-1 (ABNT, 2012b)<br>NBR ISO 12466-2 (ABNT, 2012c) | 6 |
| Density | NBR 9485 (ABNT, 2011c) | 6 |
| Moisture content | NBR 9484 (ABNT, 2011d) | 6 |
| Swelling and absorption (dimensional stability) | NBR 9535 (ABNT, 2011e) and 9486 (ABNT, 2011f) | 6 |
| Warp | ISO 9709 (ISO,2005) | 1 |
| Wettability | Ferreira, 2017 | 12 |
| Penetration and Retention | NBR 6232 (ABNT, 2013) e IPT 2930, revisão 11 | 5 |

Notes: $E_{M,l}$ - modulus of elasticity at longitudinal bending; $E_{M,t}$ - modulus of elasticity at transversal bending; $f_{M,l}$ - strength at longitudinal bending; $f_{M,t}$ - strength at transverse bending; $f_v$ - shear. * Conditioning of specimens: 24-h immersion in freshwater and BDB - boiling, drying, boiling (NBR ISO 12466-1; ABNT, 2012).

## 3. RESULTS

Tables 4 to 6 present the results obtained. There was no statistically significant difference between treatments for physical properties, except absorption, recovery in thickness, and wettability, which were all higher for untreated panels.

Mechanical properties were generally better for untreated or water-treated panels. The retention and balance of CCA-C active ingredients were better for panels treated in veneers.

**Table 4.** Physical properties (mean ± standard deviation) of the plywood panels.

| Treatment | Warp (%) | Curling (%) | Density-r (kg m$^{-3}$) | Humidity (%) | Absorption (%) | Recovery in thickness (%) | Swelling (%) | Swelling + Recovery in thickness (%) | Veneers wettability (degrees) |
|---|---|---|---|---|---|---|---|---|---|
| Untreated | 0.46 ± 0.29 a | 0.78 ± 0.61 a | 493 ± 36 a | 8.18 ± 0.48 a | 55.54 ± 1.17 b | 3.59 ± 1.22 b | 6.11 ± 0.75 a | 9.70 ± 1.58 b | 87.48 ± 14.56 b |
| Panel - CCA-C | 0.44 ± 0.14 a | 0.92 ± 0.77 a | 464 ± 23 a | 12.41 ± 0.11 b | 49.80 ± 1.65 a | 0.82 ± 0.45 a | 6.84 ± 0.49 a | 7.66 ± 0.77 ab | - |
| Veneers - CCA-C | 0.58 ± 0.28 a | 0.23 ± 0.30 a | 496 ± 13 a | 8.11 ± 0.51 a | 50.00 ± 4.03 ab | 1.13 ± 0.67 a | 6.02 ± 0.79 a | 7.15 ± 0.73 a | 118.23 ± 6.54 a |

Note: In the same column, averages followed by, at least one equal letter, do not differ significantly (p> 0.05).

**Table 5.** Mechanical properties (mean ± standard deviation) of the plywood panels.

| Treatment | Shear strength (MPa) | | Static bending | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Longitudinal | | | Transversal | | |
| | Specimen conditioning | | | | | | | |
| | 24-h immersion in water | BDB | Modulus of rupture - MOR (MPa) | 100×MOR/r | Modulus of elasticity - MOE (MPa) | Modulus of rupture - MOR (MPa) | 100×MOR/ρ | Modulus of elasticity - MOE (MPa) |
| Untreated | 1.49 ± 0.22 a | 1.19 ± 0.16 a | 40.77 ± 2.31 ab | 8.21 ± 0.28 b | 4541 ± 419 a | 24.01± 2.97 a | 4.85 ± 0.74 a | 2241 ± 524 a |
| Panel - Water | 1.43 ± 0.47 a | 1.03 ± 0.14 a | 44.49 ± 1.22 a | 9.09 ± 0.28 a | 5141 ± 512 a | 26.29 ± 3.90 a | 5.37 ± 0.79 a | 2016 ± 366 a |
| Panel - CCA-C | 1.28 ± 0.24 a | 1.09 ± 0.32 a | 36.96 ± 4.91 ab | 7.97 ± 0.99 b | 3955 ±1126 a | 23.98 ± 4.24 a | 5.18 ± 0.96 a | 1861 ± 339 a |
| Veneers - CCA-C | 1.50 ± 0.36 a | 1.32 ± 0.21 a | 34.07 ± 5.61 b | 6.94 ± 1.10 b | 4475 ± 733 a | 21.00 ± 3.24 a | 4.28 ± 0.69 a | 2201 ± 149 a |

Notes: In the same column, averages followed by, at least one equal letter, do not differ significantly (p> 0.05). BDB – successive cycles of boiling, drying, boiling (NBR ISO 12466-1; ABNT, 2012). 100×MOR/ρ is the relative strength.

**Table 6.** Retentions and balancing of the active ingredients of the plywood panels and limits established by standards (mean ± standard deviation).

| Treatment | CuO | | $CrO_3$ | | $As_2O_5$ | | Total | |
|---|---|---|---|---|---|---|---|---|
| | Retention | Balancing | Retention | Balancing | Retention | Balancing | Retention | Balancing |
| | (kg m$^{-3}$) | (%) | (kg m$^{-3}$) | (%) | (kg m$^{-3}$) | (%) | (kg m$^{-3}$) | (%) |
| **Plywood-CCA-C** | 1.74 ± 0.27a | 18.22 ± 0.87 | 4.40 ± 0.51b | 46.26 ± 0.85 | 3.38 ± 0.39b | 35.54 ± 0.49 | 9.52 ± 1.16b | 100 |
| **Veneers-CCA-C** | 2.10 ± 0.32a | 16.36 ± 0.55 | 6.18 ± 0.68a | 48.42 ± 0.78 | 4.50 ± 0.58a | 35.20 ± 0.46 | 12.78 ± 1.58a | 100 |
| **IPT 32306 limits** | | 15.20 – 22.80 | | 41.80 – 53.20 | | 27.30 – 40.70 | | |
| **NBR 16202 limits** | | 17.00 – 21.00 | | 44.50 – 50.50 | | 30.00 – 38.00 | | |

Note: In the same column, for retention values, averages followed by, at least one equal letter, do not differ significantly (p> 0.05).

## 4. DISCUSSION

### *4.1. Warp*

Unlike expected, the pressure treatment on ready-made panels (panel-CCA-C) did not increased their warp and curling. The careful pile-stocking and tying during the treatment under pressure and the drying may have reduced the dimensional variation of the products (Table 4).

### *4.2. Density and humidity*

There was no statistically significant difference between panel densities of the studied situations. All panels were produced with raw material from the same source, in the same industrial process. In addition, the different humidity levels between treatments were not sufficient to promote significant differences in densities (Table 4). The humidity was statistically lower and equal for untreated panels and panels pressed with veneers previously treated with CCA-C. The post-pressing treated panels (panel-CCA-C) had higher humidity as they were the only ones to undergo complete immersion in a preservative solution inside the autoclave after pressing.

### *4.3. Absorption and swelling*

The lowest absorption values were observed in panels treated under pressure with CCA-C, especially when they were done after pressing (panel – CCA-C), while panels without treatment had absorption statistically superior to the others (Table 4). This lower absorption can be partially explained by the smaller amount of empty spaces in the wood since these panels had higher initial humidity, i.e., they had their hygroscopic sites filled with water or components of the preservative product before being subjected to the test of absorption (MENDES et al., 2013). Indeed, according to Kollmann and Côte (1984), the higher the humidity of the veneer, the lower the water absorption by the wood. In addition, CCA-C salts decrease the wettability of the wood surface and, consequently, also decrease its water absorption capacity and swelling (FERREIRA, 2017).

The same pattern observed in the absorption tests was found in the thickness recovery test, with worse values for the untreated panels. This behavior was expected because the smaller the amount of water absorbed, the smaller the variation in the thickness of the panel (Table 4). When pressing the veneers together to form the plywood panel, density and internal stresses increase. The increase in stresses affects the dimensional stability of the panel in the pressing direction (perpendicular to the panel plane). In contact with water, plywood panel experiments swelling in thickness caused by two components: water absorption and release of the pressing stresses.

Thickness recovery is a measure of the panel's ability to return to its initial dimensions after contact with water. Thickness recovery values close to zero indicate that, after immersion in water and drying, the thickness of the specimen remained practically the same as the thickness of the control specimen (which did not suffer immersion or, therefore, stress relief), i.e., the material did not have many internal stresses or the bonding was effective, revealing good performance.

Among the pressing variables, the time under pressure significantly affects the thickness recovery, with longer values corresponding to greater thickness recovery times. According to Wellons et al. (1983), longer pressing times increase the compression and, as a consequence, the internal stresses in the plywood panels increase, promoting greater values of thickness recovery.

Panels treated under pressure with CCA-C (pre- and post-pressing) had a recovery in thickness statistically equal to and less than the thickness recovery of the untreated panels. This superior performance may have been caused by lower internal stresses generated during pressing, but they would not be related to the pressing time or pressure levels since they were identical to those of the untreated panels.

Ferreira (2017) tested the previous treatment of veneers with CCA-C in lab-scaled plywood panels and also obtained lower values of swelling for panels with treatment carried out on the veneer. Our results, statistically equal to each other (Table 4) were also close to the values obtained by Ferreira: 6.87% for panels with previous treatment of the veneers and 7.84% for post-pressing treated panels. All these values were lower than those obtained by Mendes et al. (2013) who observed swelling in treated plywood between 7.84% and 8.37%.

### *4.4. Veneers wettability*

Corroborating the results obtained in the absorption tests, the veneer wetting test also showed that the preservative product reduces the access of water and, consequently, of adhesives to the interior of the wooden veneers (Table 4 and Figure 2). According to Ferreira (2017), chromium, responsible for fixing the preservative's active ingredients in wood, is mainly distributed on the surface of the veneer, preventing water from infiltrating. The angle measured between the drop and the veneer treated with CCA-C was very close to the 113.12° angle measured by Ferreira, Campos and Silva (2016). Veneer treated with CCA-C also had a greater contact angle, indicating less wettability caused by the accumulation of As, Cu and Cr oxides in the cell walls (ZHANG et al., 1997; MALDAS; KAMDEM, 1998 a and b; TAŞÇIOĞLU, 2007).

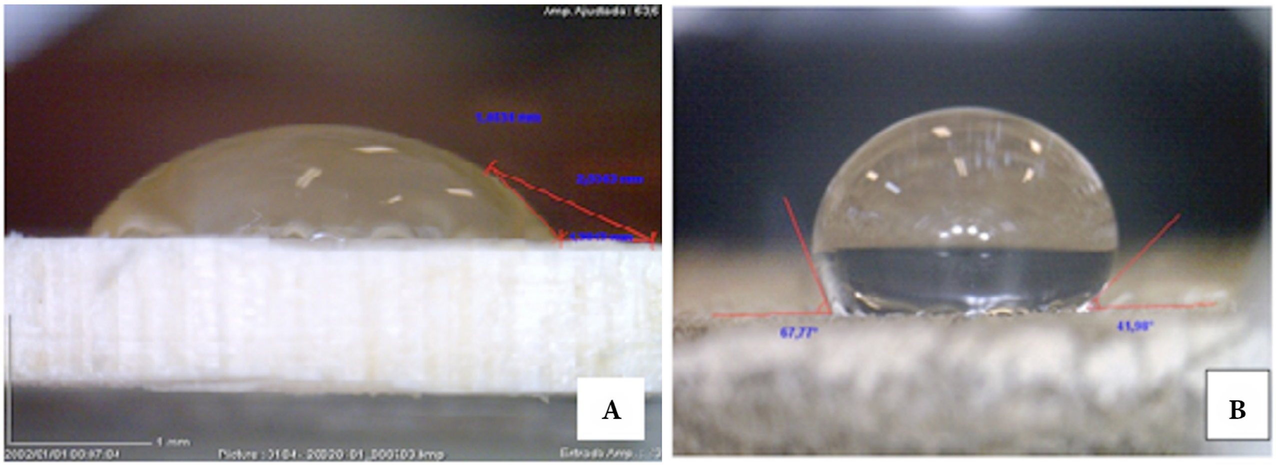


**Figure 2.** Contact angle between the water drop and the veneer surface in the wettability test. A - Untreated; B - CCA-C treated.

## *4.5. Bonding quality*

The panels, in all the situations studied (untreated, panel treated – CCA-C or water and veneer treated) showed no statistical difference in shear strength for either the two conditionings used – 24-hour immersion or two boiling cycles (Table 5). According to the standard NBR ISO 12466-1 (ABNT, 2012), as the strengths were superior to 1 MPa, it was not necessary to evaluate the percentage of wood failure. Preservative products reduced blade wettability and water absorption, demonstrating an increase in hygroscopic quality. Still, a possible harmful effect on the bonding quality, which was expected when the plywood sheets were pre-treated and which could harm the bonding quality, was not observed. The bonding capacity was not impaired by changing the treatment method.

Even without statistically significant differences in strengths, the panels pressed with treated veneers had better results for the two types of conditioning, followed by the panels without treatment, demonstrating that the treatment of ready-made panels under pressure, either with water or with CCA-C can, to a certain extent, negatively impact the mechanical properties of plywood (TSOUMIS, 1991; BARNES et al., 1996; PINHEIRO, 2001; MENDES et al., 2013).

## *4.6. Static bending*

In the longitudinal direction, although the situations with preservative treatment (pre- and post-pressing) revealed lower average strength; a statistical difference only was observed between panels with treated veneers and panels "treated" with water, which had, respectively, the lowest and highest results (Table 5). When the relative static bending (100 times bending strength divided by density) is analyzed, it is observed that the treatments with CCA-C (pre- and post-pressing) have lower strengths than the panels that received exclusively water in the autoclave. This association of occurrences suggests a probable harmful action of the active ingredients of the preservative product CCA-C on the mechanical performance of the plywood panel, as attributed by the Wood Handbook (IBACH, 2010) and by Acker and Stevens (1993), Vick and Kuster (1992) and Pinheiro (2001). This finding is contrary to that reported in the literature by Taşçioğlu *et al.* (2014) and by Mendes *et al.* (2013) who attributed the drop in properties to pressure treatment.

The modulus of elasticity in the longitudinal direction and all the results of static bending in the transverse direction did not reveal a statistically significant difference between the situations studied, demonstrating that the previous treatment of the veneers, despite improving the water repellent capacity of the plywood, does not impact its mechanical properties.

## *4.7. Penetration*

The conventional preservative treatment, done in the ready-made plywood panel, did not allow complete penetration of the product in all veneers, leaving the outer veneers of the plywood protected - in blue color – and the internal veneers unprotected - without coloring (Figure 3-B). When used as a component of housing constructions supposed to be sawn in many situations, the untreated parts will be exposed and susceptible to the action of xylophagous organisms and moisture. Tascioglu and Tsunoda (2012) also found a gradient of preservative retention between the surface sections and the cores of the pressure-treated plywood panels.

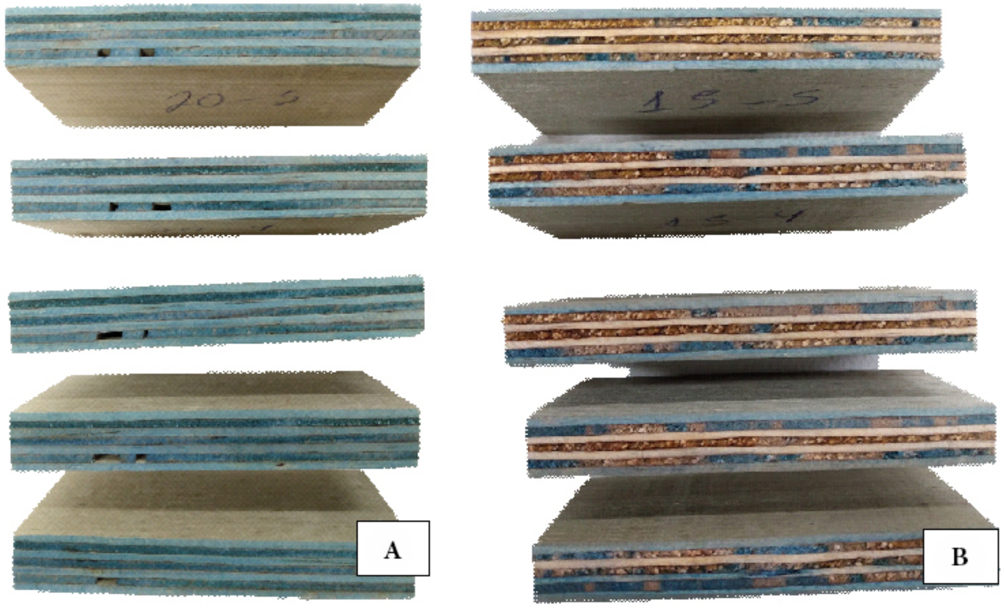


**Figure 3.** Penetration of the CCA-C preservative product into the treated plywood panels: A – pre- and B - post-pressing.

### *4.8. Retention*

The concentration of active ingredients of 0.018 kg per liter (1.8%) was used to achieve minimum retention of 6.5 kg $m^{-3}$, which would allow outdoor use, in Category 4 – elements out of contact with the soil and subject to weather, resistant to xylophagous organisms such as dry wood termite, wood borer, underground termite, tree termite, moldy or fungus (ABNT, 2013b).

Total retentions were higher than 9.5 kg $m^{-3}$ for both treatments (Table 6), allowing differentiated use of products in Category 5 - subcategories "c" - structural components that are difficult to maintain and buried in the soil or "e" – components in contact with freshwater subject to deterioration by xylophagous organisms (ABNT, 2013b).

Total retention of preservatives was 34% higher for the panels pressed with treated veneers (12.78 kg $m^{-3}$ against 9.52 kg $m^{-3}$), showing that this method is advantageous in comparison to the treatment on the ready-made panel, which blocks total penetration and greater retention, especially of chromium and arsenic (Table 6). Panels with post-pressing treatment had average retentions superior to the expected one, despite their external veneers creating a barrier to the penetration of the preservative product in the core of the panels. The retention in external veneers was, therefore, greater than the average retention (9.52 kg $m^{-3}$).

The retention of active ingredients in the plywood (Table 6), although different for treatment on the panel (greater copper retention) and treatment on the veneers (greater chromium retention), remained, in general, within the limits established by both standards NBR 16202 (ABNT, 2013) and IPT 32306 (1994) for wood retention, with the exception to treatment with CCA-C on veneers, which presented a proportion of copper lower than the minimum established by ABNT (ABNT, 2013b) as reported by Dahlgren and Hartford (1972) who observed a small imbalance of copper, chromium and arsenic during the mechanism of fixing the active ingredients in the wood attributed to the difference in the fixing time of each of the individual components of the CCA-C.

## 5. CONCLUSION

The preservative treatment applied on veneers, in a stage before the pressing of the panels, promoted higher retention and a more homogeneous penetration of the products (inner and outer veneers), checking out, by consequence, more effective protection and advantage over the treatment done directly on the panels. In addition, the treatment of the veneers before pressing did not impair the bonding quality of the panels, despite increasing the protection of the panel against moisture, since it presented lower levels of wettability, absorption and recovery in thickness. There was also no reduction in the mechanical performance of the panels when the treatment was done in veneers although, in both situations, panels' strengths were affected by the chemical interaction between wood and preservative product. No significant warping was observed in the panels treated post-pressing, possibly due to their careful pile-stocking and tying during the preservative treatment under pressure and the drying.

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Gisleine da Silva: Data curation (Equal); Formal analysis (Equal); Methodology (Equal); Resources (Equal); Supervision (Equal); Writing – review & editing (Equal).

Hernando Alfonso Palma: Conceptualization (Equal); Supervision (Equal); Writing – review & editing (Equal).

Gabriel D'Elaqua-Santos: Formal analysis (Supporting).

Adriano Ballarin: Conceptualization (Equal); Methodology (Equal); Project administration (Equal); Resources (Equal); Writing – review & editing (Equal).

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