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STUDY ON THE IMPREGNATION OF LAROPAL A81 TO CONSOLIDATE THE WOOD SUPPORT IN EASEL PAINTINGS

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Abstract

The following work is focused on the study of the suitability of the urea-aldehyde resin, commercially known as Laropal® A81, for consolidation treatments on deteriorated wood from panel paintings. The physicochemical properties of this resin, such as the low molecular weight, low viscosity in solution and, interestingly, the possibility to be dissolved in low-toxicity solvents, suggest that Laropal® A81 could penetrate well into the wood microstructure thus offering an alternative option to other resins which require the use of more harmful solvents. The behaviour of Laropal® A81 for the consolidation of deteriorated wood was compared to that of other two resins widely used as consolidants – Regalrez® 1126 and Paraloid® B72. Laropal® A81 was dissolved in Mostanol and in Dowanol PM, the Paraloid® B72 in butyl ethanoate and the Regalrez® in cyclohexane. ATR-FTIR was used for the assessment of resin retention and penetration depth in the wood, whereas FESEM images allowed us to evaluate the morphological changes undergone by the wood as a consequence of the application of the consolidation treatments. The changes in the gloss of the wood were also evaluated, which complemented the results obtained by the other two tests. According to the results obtained in this study, we argue that urea-aldehyde resin has good specificities (good retention and penetration depth) in order to be used as a consolidant for deteriorated wood in easel paintings.

Keywords*: Wood consolidation; Panel paintings; Laropal A81; Low toxicity; Penetration*

Introduction

The wood support of panel paintings is prone to different types of deterioration, depending on the agent that causes it. The main cause of deterioration is biological attack, resulting in the substantial weakening of the wood. This loss of mechanical strength is mainly due to the excavation of galleries and holes left by the adult xylophagous insects when emerging from the wood. In order to strengthen the wood, a consolidation treatment can be applied [1].

In this study, the use of urea-aldehyde resin Laropal ® A81, commonly used in the field of conservation and restoration as a binder [2], or a varnish [3] is proposed, in this case, as a consolidation treatment for deteriorated wood of panel painting. This choice was based on the

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low molecular weight of the resin and the possibility of being used with low toxicity solvents. This last reason is particularly important, since other products widely used for this purpose, such as Paraloid® B72, require the use of high toxicity solvents, mainly toluene and xylene [4] to facilitate the wood impregnation. However, they have harmful effects on the environment and the conservator-restorer health.

In order to assess if Laropal® A81 has the required characteristics to be used as a consolidant treatment, several tests were done [5]. In this investigation the impregnation of this resin in deteriorated wood support is evaluated, an indispensable criterion for achieving suitable consolidation, and is compared with other resins normally used with this purpose.

Experimental part

Materials

Wood samples

Examination of the anatomy of the wood samples indicated they belonged to the genus *pinus sp*, either the species *Pinus Sylvestris* or *Pinus Negra Arnold* [6].

The samples showed deterioration caused by attack of xylophagous agents, mainly *Anobium punctatum* and white rot fungi. For that reason, the wood was first disinfected with a solution of Xylores Pronto® applied with a syringe and a brush. After that, the samples were cut in pieces of 3 × 3 × 4cm.

The samples were kept at controlled conditions of temperature and relative humidity (20±2ºC and 65±3% R.H), until they reached equilibrium which usually happens when the intern humidity reaches 12% [7]. Measurements made using a *xylohygrometer (TESTO 606-2)* indicated that wooden pieces reached a balance of 11.3 % of inter relative humidity after two weeks in these conditions.

The samples were classified in two levels of degradation caused by the xylophagous insects: level 1 corresponding to low deterioration woods, with a degradation average of 5.66% and level 2 corresponding to high deterioration woods, with a degradation average of 17.9% (Fig. 1). Level 2 is divided into samples with one application of consolidant (2.1) and two applications (2.2). This percentages of deterioration indicates the weight loss percentage by comparison with pieces of wood without xylophagous insect's attack.

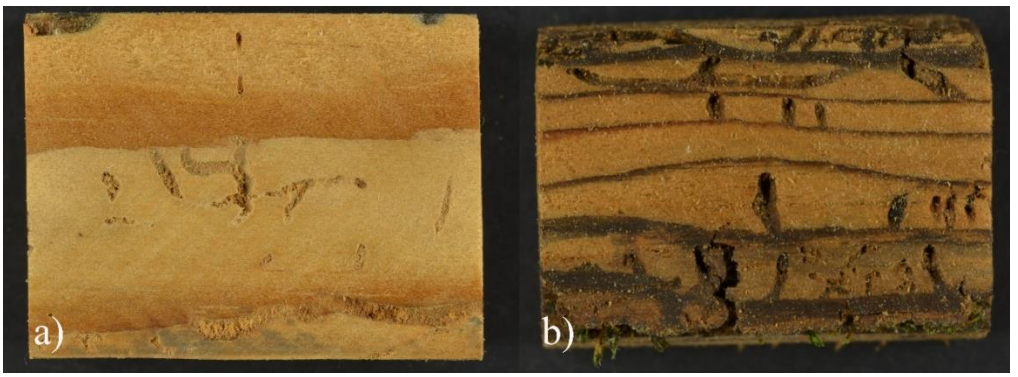

Fig. 1. Classification of degradation levels caused by the xylophagous insect's attack:
a. Level 1 wood samples in tangential section; b. Level 2 wood samples in radial section

Wood consolidants and their usage

The following resins were tested in order to compare their properties as consolidant agents for deteriorated wood:

- Laropal® A81, a urea-aldehyde resin (Kremer Pigmente brand)

- Paraloid® B72, an acrylic resin – the copolymer of ethyl methacrylate (EMA) and methyl acrylate (MA) (Rohm & Haas brand)
- Regalrez® 1126, a hydrogenated aliphatic resin (Kremer Pigmente brand)

Paraloid® B72 was selected because it is widely used in the field of conservation and restoration for a broad variety of applications [8-12]. The Regalrez®1126 was chosen because it presents some specificities that make them better than acrylic resin, such as its low molecular weight [13].

The solvents, were selected based on the low toxicity of the product, presented by Leonardo Borgioli in C.T.S. [14], the solubility of the chosen resins, and the viscosity and the volatility [15].

Bearing this in mind, Laropal® A81 was dissolved in Dowanol PM ($CH_3OCH_2CHOHCH_3$) and in Mostanol (a mixture of ethyl alcohol and isopropyl alcohol); Paraloid® B72 was dissolved into butyl ethanoate ($CH_2COO(CH_2)_3CH_3$) and Regalrez® 1126 in cyclohexane (C_6H_{12}).

All the solutions have a 10% (w/v) of concentration and were applied in all orientation on woods with a syringe and with a brush. On the level 1 test pieces, the consolidant solution was applied once, while on the level 2 test pieces of the solution was applied twice (assigned as level 2.1) and two applications (level 2.2) were made.

Methods

The methods used to perform this work was divided into 3 parts. First, wood samples and consolidant solutions were prepared. The solutions were applied to the test specimens. Finally, microscopic examinations using field emission scanning electron microscopy (FESEM) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) analysis, and gloss measurements were performed on the treated wood samples.

Optical Microscopy

A Leica DM750 microscope operating with transmitted light and equipped with a digital camera (MC170) (Leica Microsystems. Heidelberg, Germany) was used for the anatomical examination of the wood samples.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

This technique was used to evaluate the resin retention in the samples [16] and how far the consolidant impregnates the support, based on the ratio of the intensity of the absorbance bands characteristic for the wood and the resin [17].

In order to evaluate the retention and the penetration of the resins into the consolidated wood, these were analysed using ATR-FTIR spectroscopy. For that purpose, samples were taken from the surface in the radial section of the wood and at different depths, up to 5mm of depth on level 1 woods and up to 10mm depth on level 2. ATR-FTIR spectra were recorded using a Vertex 70 Fourier-transform infrared spectrometer with an FR-DTGS (fast recovery deuterated triglycine sulphate) temperature-stabilized coated detector and a MKII Golden Gate Attenuated Total Reflectance (ATR) accessory. A total of 32 scans were collected at a resolution of 4 cm^{-1} and the spectra were processed using the OPUS/IR software.

To obtain the infrared spectra of the pure resins tested, the solutions were brushed on a glass coverslip. After the solvent evaporated, a sample was scraped of a scalpel. Samples from the wooden pieces were taken with a scalpel in the radial section of the wood, at various depths.

Field Emission Scanning Electron Microscopy (FESEM)

Secondary electron images of the consolidated wood samples were obtained using a Zeiss model ULTRA 55 operating with an Oxford-X Max X-ray microanalysis system controlled by Inca software. The analytical conditions were: 3kV accelerating voltage and 800× magnification. The samples were previously carbon coated for eliminating charging effects.

For the microscopic examination small cubes of 2mm long by 2mm wide and 2mm depth of the deteriorated woods levels 1 and 2 were extracted.

Gloss meter

The changes in gloss of the treated wood samples were evaluated using a gloss meter Multi Gloss 268, supplied by MINOLTA (Germany). According to EN 13722 [18] measurements were carried out at an angle of 85°.

Results and discussion

FTIR spectroscopy

As shown in figure 2, the infrared spectra obtained revealed changes in the intensity of the absorption bands ascribed to the resins depending on the depth.

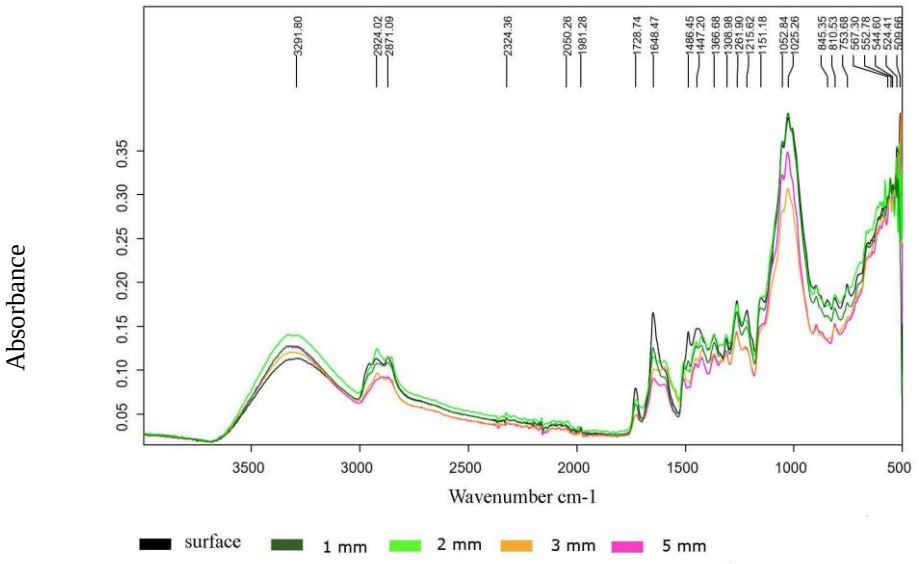

Fig. 2. Spectra of penetration of Laropal® A81 dissolved with Mostanol in level 1 wood, in the radial section of the wood

On the basis of these results, and with the aim of evaluating the variations in the relative proportion of the resins applied as consolidants, one of the more specific absorption bands for each product - Laropal® A81 (1645cm^{-1}), Paraloid® B72 (1719cm^{-1}) and Regalrez® 1126 (2918cm^{-1}), and for the wood (1025cm^{-1}) without any treatment, were selected for obtaining the retention index (I), as the result of calculating the ratio between the height of the chosen band for each resin and the height of the chosen band for the wood. For instance, for the consolidated wood with Paraloid® B72, the retention index was calculated using the height of the absorption bands at 1719cm^{-1} corresponding to the carbonyl group of the acrylic resin and at 1025cm^{-1} ascribed to the C-O stretching vibrations of the wood. In parallel, a reference value (I_0) was calculated as the ratio of the height of the same absorption bands but for the wooden sample without any treatment, and it was subtracted from the retention index of the resin at the different depths, in order to measurements of the absorption band heights were performed through the spectra processing by using the OPUS/IR software.

The graphic representation of these results versus the depth for the consolidated wood samples in level 1 are shown in figure 3. As can be seen, the highest retention indexes were obtained for the wood samples consolidated with Regalrez® 1126 dissolved in cyclohexane, although these values decrease significantly down to a minimum value, similar than for the other resins, at 5mm depth. The other two solutions with Laropal® A81 got similar results, showing slightly higher retention indexes when Laropal® A81 was dissolved with Mostanol.

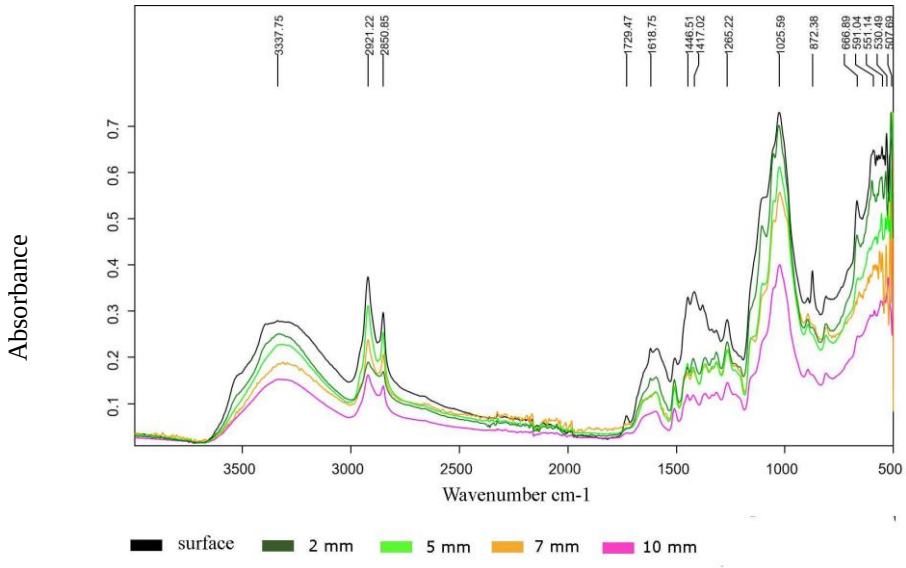

Fig. 3. Spectra of penetration of Regalrez® 1126 in level 2 wood with one layer, in the radial section of the wood.

Paraloid® B72 dissolved in butyl ethanoate showed a good retention index on surface, but its penetration was almost null.

Regarding the retention of all resins, they presented a retention index on the surface of approximately 0.2, except for the Paraloid® B72 solution applied on the level 2.2 wood, which raised at 0.5 (figure not shown). That reveals an accumulation of the acrylic resin on the surface. The level of retention on level 2.1 woods (figure not shown) was lower in depth than on the surface, except for the Regalrez® 1126 solution.

Table 1 shows the retention index for all the solutions used as consolidants for the different depths and deterioration levels. Analysing it, one can conclude that there was greater penetration and a higher retention index in the woods consolidated with Regalrez® 1126 and with Laropal® A81 dissolved in Mostanol. Paraloid® B72 had the lowest retention index and penetration depth.

Table 1. Penetration and retention index of Paraloid® B72 dissolved in butyl ethanoate (PB72), Regalrez® 1126 dissolved in cyclohexane (RG), Laropal® A81 dissolved in Mostanol (LP+MT), Laropal® A81 dissolved in Dowanol PM (LP+DW) in level 1 woods (depth up to 5 mm), level 2 with one or two layer (depth up to 10 m) in the radial section.

Level	PB72	LP+DW	LP+MT	RG	PB72	LP+DW	LP+MT	RG
1	0	2	3	5	0	0.05	0.15	0.15
2.1	5	5	5	10	0.05	0.1	0.05	0.2
2.2	7	7	10	5	0.1	0.15	0.2	0.15

Field emission scanning electron microscopy (FESEM)

Some representative images of the radial section of level 1 and level 2 woods were chosen. On level 1 woods, on figure 4a and b, it was revealed that the solution with Laropal® A81 dissolved in Mostanol is visible on the surface by the recovering of the cross-section and by the fissures done in result of the product drying.

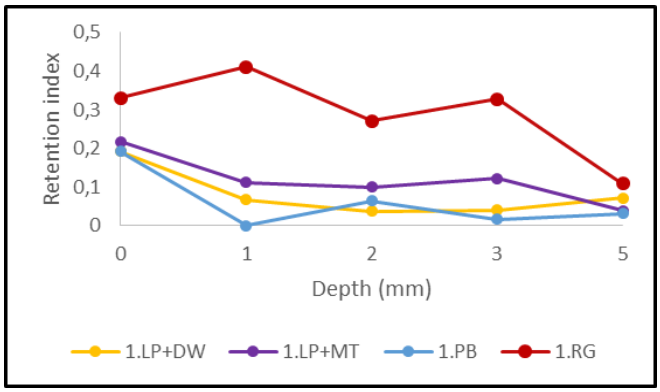

Fig. 4. Retention index of solutions in the radial section of level 1 woods.
Legend: LP+DW - Laropal® A81 dissolved in Dowanol PM; LP+MT - Laropal® A81 dissolved in Mostanol; PB - Paraloid® B72 dissolved in butyl ethanoate; RG - Regalrez® 1126 dissolved in cyclohexane.

At 2mm depth, the resin was also there. On wood treated with Regalrez® 1126 we could observe that the presence of the resin is most noticeable at greater depth (2mm), rather than at the surface (see figure 2c and d). This is easily visible on the left side of figure 2d.

About the level 2 woods, at 5mm depth, treated with a single application of Laropal® A81 dissolved in Dowanol PM and in Mostanol (Fig. 5a and c), put in evidence the deterioration of the material, as revealed by the irregular topography of the wood with abundant loose particles and delamination, while in the wood treated with two applications of the same consolidants (Fig. 5b and c) the wooden material showed a smoother topography and some of the radial section areas appeared partially coated by the resin.

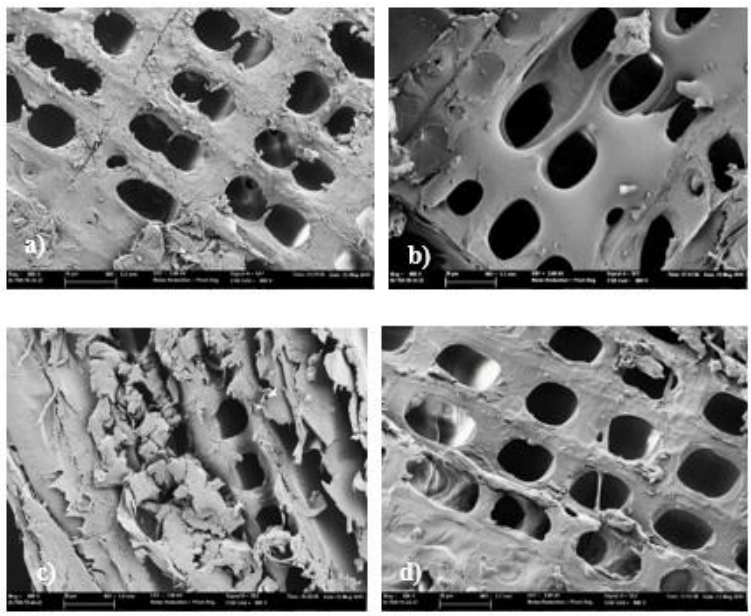

Fig. 5. FESEM images of level 1 consolidated wood: a. Wood sample with Laropal® A81 dissolved in Mostanol (LP+MT) on the surface; b. Wood sample with the LP+MT at a depth of 2mm;
c. Surface of wood sample treated with the Regalrez® 1126 (RG) dissolved in cyclohexane;
d. Wood sample with RG at a depth of 2 mm.

On the wood sample consolidated with Regalrez® 1126 dissolved in cyclohexane (Fig. 6) it is not clear if the image shows the resin or a thin layer of wood, in agreement with the results obtained by FTIR spectroscopy which showed a significant decrease in the retention index of this resin at this depth (5mm). On the other hand, in the sample treated with two applications of the resin the presence of a coating is clearly visible, which unequivocally covers almost the entire radial section area

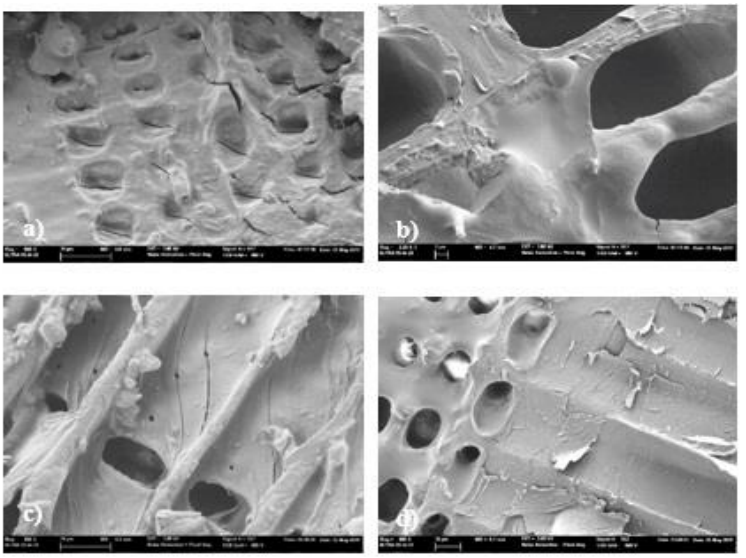

Fig. 6. FESEM images of level 2 consolidated wood at a depth of 5mm:
a. Wood sample with a single application of Laropal® A81 dissolved in Dowanol PM (LP+DW);
b. Wood sample with two applications of the solution of LP + DW;
c. Wood sample treated with a single application of Laropal® A81 dissolved in Mostanol (LP+MT);
d. Wood sample with two applications of the solution of LP + MT.

Finally, the level 2 wooden sample consolidated with one and two applications of Paraloid® B72 dissolved in butyl ethanoate (Figs. 7 and 8), showed similar behaviour to the sample consolidated with Regalrez® 1126 previously mentioned. Whereas in the sample with a single application of the resin, the wood shows a deteriorated microstructure, the treatment with two applications of the resin solution leads to a reinforced microstructure and a partial covering of the cross-section area.

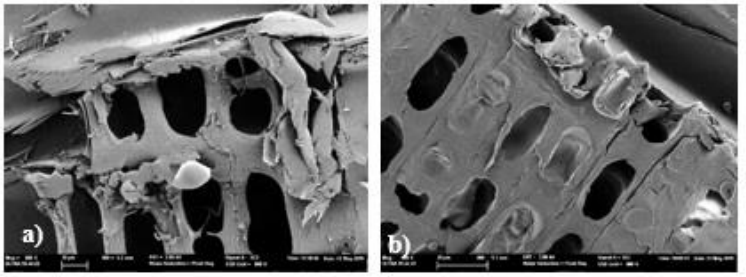

Fig. 7. FESEM images with 800× of level 2 wood with Regalrez® 1126 dissolved in cyclohexane at a depth of 5mm with a consolidant layer (a) and two layers (b).

Based on these observations, in the following table (Table 2) is reported an overview of the results obtained from the morphological examination of the consolidated wood samples, indicating the identification or not of the resins at different depths.

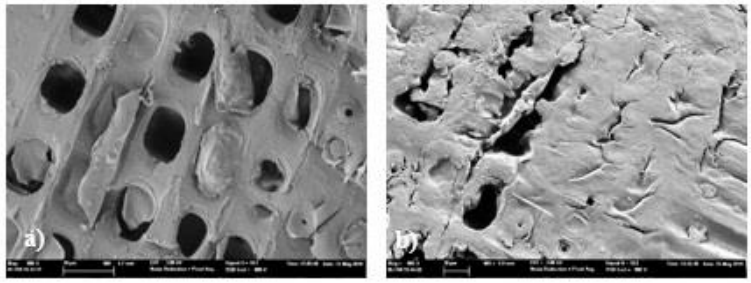

Fig. 8. FESEM images of level 2 woods treated with a single application of Paraloid® B72 dissolved in butyl ethanoate at a depth of 5mm (a) and with two applications (b).

Table 2 – Results of the identification of the resins in the consolidated wood samples through the morphological examination by using FESEM. Legend: LP+MT - Laropal® A81 dissolved in Mostanol; LP+DW - Laropal® A81 dissolved in Dowanol PM; PB72- Paraloid® B72 dissolved in butyl ethanoate; RG - Regalrez® 1126 dissolved in cyclohexane.

		LP+MT	LP+DW	PB72	RG
	Surf.	Yes	Yes	Yes	Yes
Level 1	**Depth 2 mm**	Yes	Yes	No	Yes
Level 2.1	**Depth**	Imperceptible	No	No	Imperceptible
Level 2.2	**5 mm**	Yes	Yes	Imperceptible	Yes

Gloss measurement

The data obtained from gloss measurement of the wood samples before and after the consolidation treatment revealed different behaviour of the tested resins.

For the evaluation of the changes in the gloss of the wood due to the application of the consolidation treatments, an average value of nine measurements (three in each specimen in the radial section of the woods) for each consolidant was calculated. The greatest increase in gloss in level 1 wood samples (low deterioration woods) was observed for the wood consolidated with Laropal® A81 dissolved in Mostanol, followed by Paraloid® B72 dissolved in butyl ethanoate, and Regalrez® 1126 in cyclohexane. The minimum variations in gloss were observed for the application of Laropal® A81 in Dowanol PM (results not shown).

However, these values vary widely for level 2 wood samples (high deterioration woods) (Fig. 9). The woods with one application of the products caused low increase in gloss except for Paraloid® B72 which obtained values similar to those of level 1 woods. Nevertheless, in woods with two applications, the one with higher gloss was consolidated with Paraloid® B72, slightly lower values were obtained for Laropal® A81 dissolved in Dowanol PM, and Laropal® A81 in Mostanol and finally the lowest variations in gloss were registered for the samples treated with Regalrez® 1126.

These gloss variations are related to the penetration of the resins into the wood samplesand are in line with the results obtained by FTIR spectroscopy and FESEM. Thus, Paraloid B72 which produces the highest gloss values has also shown the lowest penetration depth, creating a film on the surface of the wood.

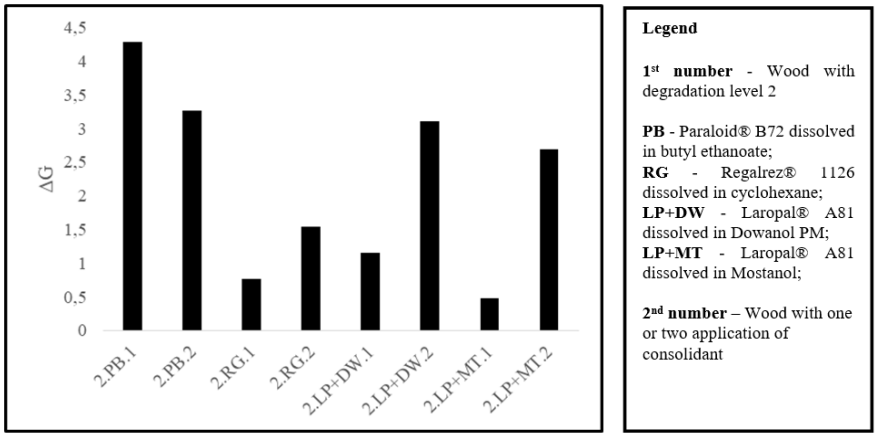

Fig. 9. Difference in gloss values (ΔG) before and after the application of the consolidant in samples with degradation level 2 with one or two applications.

On the other hand, Regalrez® 1126 and Laropal® A81 with Mostanol showed good penetration depth and lower gloss variations. In general, after consolidation, the woods increased their gloss from 1 to 4 gloss units to values between 4 and 10 gloss units (except for one of the woods with Paraloid® B72 that obtained approximately 13 units). Nevertheless, objects with values below 10 are considered of low gloss [18].

Conclusions

According to all the tests done, it is now concluded that the resin which showed the highest impregnation was Regalrez® 1126, followed by Laropal® A81 dissolved in Mostanol, Laropal® A81 diluted on Dowanol PM and, in last place, the Paraloid® B72.

Regalrez® 1126 and Laropal® A81 presented the best results according to the examinations by FESEM and FTIR spectroscopy analyses, although Regalrez® 1126 showed lower gloss variations. Still with ATR-FTIR it was perceived that Regalrez® 1126 had greater penetration and retention index in the specimens with a single application whereas Laropal® A81 showed better results in level 2 wood samples with two applications.

Based on this criterium, the impregnation, we can say that urea-aldehyde resin has good specificities in order to be used as a consolidant for deteriorated wood in easel paintingts. However, this study is a first approach to the assesment of the suitability of this resin as a consolidant, and additional tests are necessary in order to evaluate the mechanical properties of the consolidated wood and its stability across time through ageing and mechanical tests.

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