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THE IMPACT OF THE TREATMENT WITH CÂMPENI RED PETROLEUM ON A XVIII-TH CENTURY ICON

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Abstract. This paper presents the study regarding the impact of the treatment with Câmpeni red petroleum on an XVIII-th Century icon made of wood, with the aim of active preservation and restoration. In accomplishing this endeavour, there were applied non-invasive techniques of analysis based on optical microscopy (OM), Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray analysis (EDX), micro-FTIR and colorimetry CIE*L*a*b**. A series of chemical, physical-structural and mechanical characteristics of the wood were traced, in order to assess the degree of preservation enhancement as a result of the applied treatment.

Keywords: old icon, conservation state, preservation, restoration.

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Introduction

Wood is a complex material, from morphological-structural point of view and physical-mechanical level. Regardless of its essence, the age of the tree and its antiquity, the structural characteristics of the wood are in a continuous dynamics, correlated with the environmental factors, which, depending on the difficult preservation or manipulation conditions, can determine active processes of alteration that are subsequently assisted by degradation processes, bringing the artefact up to the pre-breakdown stage, resulting in an aesthetic aspect [1-3].

The study regarding the behaviour of a number of active preservation and restoration of the polychrome wood shares the same endeavour and objectives with an impact study. The study follows the evolution in time of the chemical-, physical-structural and mechanical properties of wood by applying various old or new treatments. Thus, within this study the rate of alteration for these characteristics will be established, expressed in percentages, deviations or chromatic displacements, *etc.*, in order to assess the degree of preservation enhancement as a result of the applied treatment.

The impact studies or the supervision of the behaviour of active preservation interventions for an established period of time are prerequisites to any treatment applied to heritage objects, contributing to the optimization of operative system network and the application conditions. This stage of preservation implies the supervision of the applied treatment; the impact studies have at their core the alterations of the structural and functional characteristics of the object during the period of preservation or under the influence of high variations of the environmental factors.

Among the most relevant characteristics of old icons that suffer profound alterations and in time affect the preservation of the wood, we mention: the alteration of normal variation domain of the hydric equilibrium [4-8], reduction of porosity, density augmentation, contraction and extension, the chromatic deviation or displacement, *etc*. In addition to these, there are a number of characteristics that should be assessed

through instrumental methods, implying complementary techniques: SEM-EDX, micro-FTIR and FTIR coupled with ATR, reflectance colorimetry coupled with histochemical analysis, optical microscopy by reflection in UV and Vis, with crossed and paralleled Nicols, thermal derivatography, *etc*. These methods allow assessing the degree of penetration, the evolution of kinetic parameters (activation energy, reaction order, the degree of alteration, *etc.*), chromatic deviations and others [1,9-15].

In this paper we propose the study of the impact of treatment with Câmpeni red petroleum on an XVIIIth Century icon made of wood and affected by xylophagous insects. In the following analyses, a series of optical microscopy (OM) techniques were involved, Scanning Electron microscopy (SEM), coupled with Energy Dispersive X-ray analysis (EDX), micro-FTIR and colorimetry CIE*L*a*b**. The enhancement of the degree of preservation as a result of the applied treatment was assessed based on a series of chemical, physical-structural and mechanical characteristics of the wood.

Experimental

Materials

The subject of the study is an icon dating from the XVIIIth Century, and its theme is *"The Beheading of Saint John the Baptist"* (Figure 1), painted on linden wood *(Tillia sp*.), in *tempera grassa*, belonging to *„Precista Mică"* Church in Roman municipality, Neamţ district. This icon was created by an anonymous painter. The panel was made from a single worktop, with tangent section, which at both ends presents a beam - 280 mm long and 7 mm deep (Figure 2). The icon presents the following dimensions: length - 340 mm, width – 270 mm and depth – 250 mm.

The picture layer of the icon is impacted by multiple fissures and defective regions. The xylophagous attack is inactive, but the age and the complexity of this attack have been confirmed by the presence on the entire surface of the wood panel of the larval galleries and fly holes. The diameter of the fly holes is of approximately 1-2 mm, the fly holes are present on the front of the icon, also. On the reverse, on the lower side, the attrition due to the manipulation can be seen.

For development of this experiment, it was used, besides the icon itself, the following materials: a panel made of wood of the same nature with the support of the icon (linden) and the same type of xylophagous attack, Câmpeni red petroleum solution for the treatment, Japanese paper, rabbit glue, heat resisting polyester foil, filter paper, pallet knife, tweezers and syringes.

Figure 1. The icon *„The Beheading of Saint John the Baptist"*: *(a)* – front; *(b)* – reverse.

Figure 2. The edges of the icon *„The Beheading of Saint John the Baptist"*: *(a)* – lower side; *(b)* – upper side.

Methods

The species of xylophagous insects were established by sampling of some individuals from the wood bulk and analysis through OM and SEM. The OM analysis was performed using an optical microscope model CARL ZEISS AXIO IMAGER A1m equipped with a AXIOCAM camera and automated data processing through specialized software. SEM analysis was done using the scanning electron microscope model VEGA II LSH (TESCAN Co., Czech Republic), the resulted image were constituted by the secondary electrons (SE) at a magnification of 120X.

The impact of the treatment on wood composition was assessed based on the EDX spectrum obtained by means of a X-ray detector, type QUANTAX QX2 (BRUKER/ROENTEC Co., Germany), attached to the SEM, and based on the IR spectrum obtained with a FTIR spectrophotometer, coupled with a HYPERION 1000 microscope, both pieces of equipment from BRUKER Optic (Germany).

In order to determine the chromatic deviation subsequent to the treatment with Câmpeni red petroleum, we used the reflectance colorimetry, type CIE*L*a*b**, using a portable spectrophotometer - Lovibond RT 300. The colour difference was calculated using Eq.(1):

$$\Delta E* = [(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

In which:
ΔL^* = L^* sample – L^* standard
Δa^* = a^* sample – a^* standard
Δb^* = b^* sample – b^* standard

where, $-\Delta L^*$ indicates any difference luminosity i, and when: $\Delta L^*>0$ the sample is more luminous than the standard (lighter); $\Delta L^*<0$ the sample is darker than the standard.
$-\Delta a^*$ and Δb^* indicate the differences between the samples position (sample and standard) in the chromaticity diagram a^*b^*;
Δa^*- the difference red-green: $-\Delta a^*>0$, the sample is redder than the standard; $-\Delta a^*<0$, the sample is greener than the standard;
Δb^* - the difference yellow- blue: $-\Delta b^*>0$, the sample is yellower than the standard; $-\Delta b^*<0$, the sample is bluer than the standard.

The treatment solution

The red petroleum used in this study is a natural product from the old drills of the 1806's, in Câmpeni village, Pârjol commune, Bacău district, oil sector belonging to Modârzău-Moineşti lease. Together with a series of special characteristics, such as: very low density and viscosity, very high flammability and evaporation speed, low concentration in solid paraffin (colourless or white), high concentration in aromatic products and others, it exhibits a good capacity of extracting the active components from plants or other natural products by maceration at room temperature. Another characteristic that makes red petroleum special is the presence of iron in its structure. It has the consistence of kerosene or lamp oil, and in emission has a green luminous colour, and in absorption, varies from ruby red to brown [1].

Experimental protocol

Prior to experiments, all the solutions were tested for compatibility, because these possess no specificity regarding the wide range of the wood essences, preservation states, the age of the objects, the patina and the polychromatic layer's preservation, the environmental medium in which it is preserved, *etc*. [1,9].

From a linden panel with polychromy and affected by xylophagous activity (Figure 3*(a)*), two specimens of 40 mm long and 50 mm wide were cut; one was treated with Câmpeni red petroleum (Figure 3*(b)*), and the other one was used as a blank (Figure 3*(c)*). The treatment was made by applying the Câmpeni red petroleum with a brush and by injection. The prepared samples were microscopically analysed by means of optical microscopy (OM) and electronic microscopy (SEM) with the aim of establishing the degree of penetration of the treatment solution. Samples were analysed by CIE*L*a*b** colorimetry in order to establish the chromatic deviation as a result of the treatment. After assessing the impact of the treatment with Câmpeni red petroleum, we proceeded to the treatment of icon engaged into the study.

At the first stage of the treatment of the icon with Câmpeni red petroleum, this was covered with Manila Japanese paper (density 19 g/m^2 and pH=8) using rabbit glue (Masserini-Italy) with a concentration of 3% as an adhesive that was evenly applied using the brush (Figure 4). To ensure the adhesion, a warm spatula over a Bresciani Melinex polyester foil was used (23 μ-thick) together with the Bresciani filter paper (density 250 g/m^2 and pH=7) that absorbed the excess of glue. To eliminate the insects and their faeces, the support of the icon was vacuumed. In the next stage the reverse side was treated with Câmpeni red petroleum by brushing, and in the fly holes we introduced solution by injection.

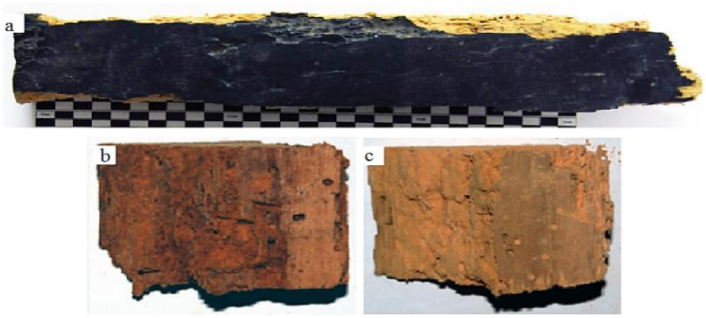

Figure 3. The samples used in the analysis: *(a)* – panel with polychromy; *(b)* – sample treated with red petroleum; *(c)* – blank sample.

Figure 4. Detail of covering with Japanese paper.

Results and discussion

In order to eliminate the xylophagous insects from the wood support of the icon, it is necessary to trace their morphological characteristics using the optical microscope (Figure 5) and the electronic microscope (Figure 6). The collected insect from the wood support was analysed on both sides (anterior and posterior), and we have been able to identify an adult from *Anobium punctatum* species [16,17].

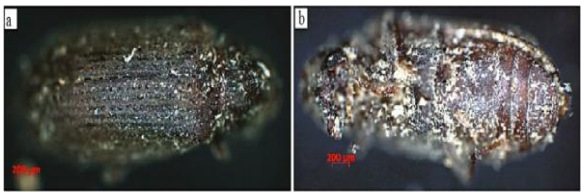

Figure 5. OM images of the insect at 50X magnification: *(a)* – anterior; *(b)* – posterior.

Figure 6. SEM images of the insect, at 120X magnification: *(a)* –anterior; *(b)* –posterior.

In order to preserve the wood, an ecological treatment with Câmpeni red petroleum was used that acts as a bolster for the frail wood. This substance was used on the sample cut from the panel, by brushing and injection with 20 mL of red petroleum, at different time intervals, until the total absorption Figure 7. Following the treatment, we noticed a lowering of the material porosity, due to the absorption of the red petroleum into the wooden fibre.

In Figures 8 and 9 we present the chemical composition assessed using SEM microphotogram of the cross-section and the EDX spectrum of the samples collected from the untreated old linden wood and treated with red petroleum, respectively, are presented. Following the treatment with red petroleum, the concentration of carbon increased because of the high weight of the organic compounds. Also, the presence of iron was identified indicating that Câmpeni red petroleum was retained by the wooden fibre.

Figure 10 presents the FTIR spectra of the untreated wood compared with the treated wood and the red petroleum. Because the old wood undergoes oxidative degradation processes (the alcoholic groups become carbonyl groups, and the later become carboxyl groups) and depolymerization resulting in 1,6-anhydro-*β*–D–glucopyranose, the first being affected the C=O groups (1738 cm^{-1}), and subsequently, the O-H groups (1647 cm^{-1}) and the C-O-C groups of the *β*-glycosidic type (1173 cm^{-1}), an aspect very well highlighted in the spectra.

It must be noted that in the registered spectra similar regions can be observed with significant alterations, in wood, as in the active principles of the preservation, we mention the domains: 2850-2960 cm^{-1}, 1400-1500 cm^{-1}, 1350-1400 cm^{-1} and the 950-600 cm^{-1}. The first set of peaks observed in the 2850-2960 cm^{-1} domain, with maximum at 2922 cm^{-1} and 2854 cm^{-1} correspond to the valence vibrations characteristic to C-H groups that undertake alterations due to, the processes of reduction-oxidation and to the interactions between the wood and the active principles.

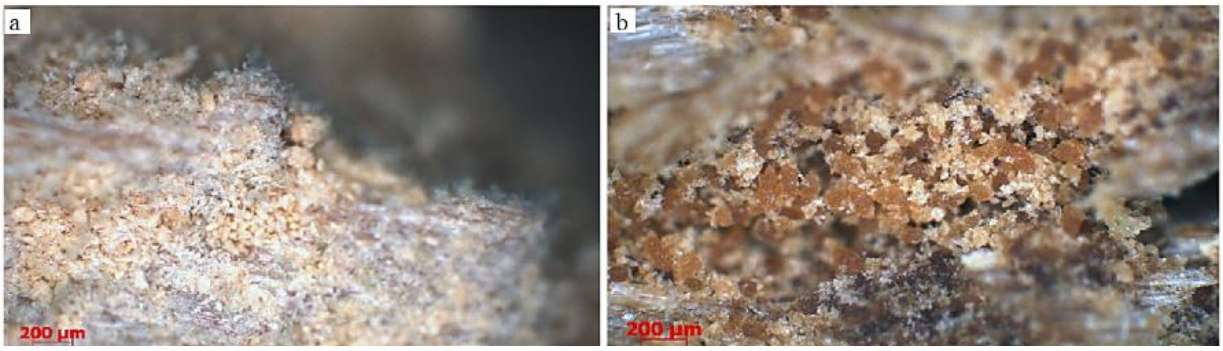

Figure 7. Optical microscopy: *(a)* – untreated sample; *(b)* – treated sample.

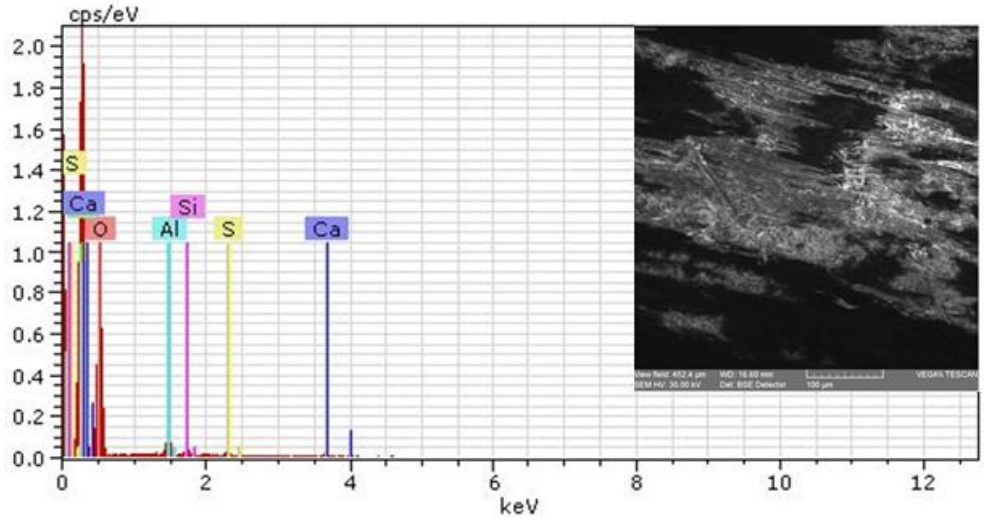

Figure 8. SEM microphotogram and EDX spectrum of the untreated old linden wood.

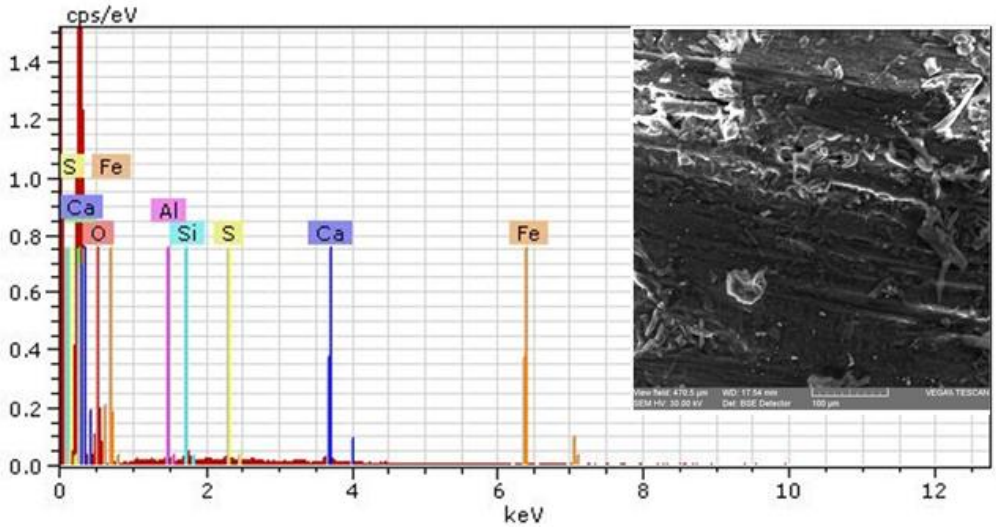

Figure 9. SEM microphotogram and EDX spectrum of the old linden wood treated with red petroleum.

The IR spectrum of the red petroleum presents vibration bands specific to a series of characteristic functional groups:

a. The C-H groups (from primary, secondary or tertiary carbon), with the three peaks from 2955.01 cm^{-1}, 2922.19 cm^{-1} and 2854.20 cm^{-1}, which are very well superimposed over the two peaks of the wood from 2922.02 cm^{-1} and 2854.20 cm^{-1} and because of the interaction with the wood, present a much attenuated absorbance. This group allows the assessment of the penetration degree of the red petroleum in wood.

b. The C-H groups of olefins and aromatic hydrocarbon, with peaks from 1459.78 cm^{-1} and 1375.80 cm^{-1}. These peaks can be used to evaluate

the penetration effect, especially the first peak, whose absorbance amplifies.

c. The olefin C-H groups, represented by the 724.72 cm^{-1} peak, are activated as a result of the interactions between the support and the petroleum, presenting a slightly higher absorbance, which very easily allows highlighting the penetration effect.

The variation of the absorbance for the active groups of the red petroleum demonstrates that most of the paraffinic compounds with a large number of carbon atoms concentrate towards the surface of the wood, at the exterior, and the interior pores, followed by the aromatic compounds and the inferior paraffins.

A very important aspect that should be underlined is that the shape of the obtained spectra, based on the intensity of the peaks, their position in the spectrum and the alteration resulted following the interactions wood-red petroleum, acknowledges the chemical compatibility of these two systems.

In Table 1, the values obtained based on the CIE*L*a*b** analysis are given, and in Figure 11 it is presented the chromatic deviation ΔE^* following the treatment with red petroleum. The negative values of ΔL^* demonstrate the darkening of the colour of the sample as a result of the treatment with red petroleum, aspect attested by the shape of the curve in Figure 11. The fact that ΔE^* has values under 5.00 signifies that the colour difference between the standard sample and the treated sample is not relevant for the observer's eye [19-22].

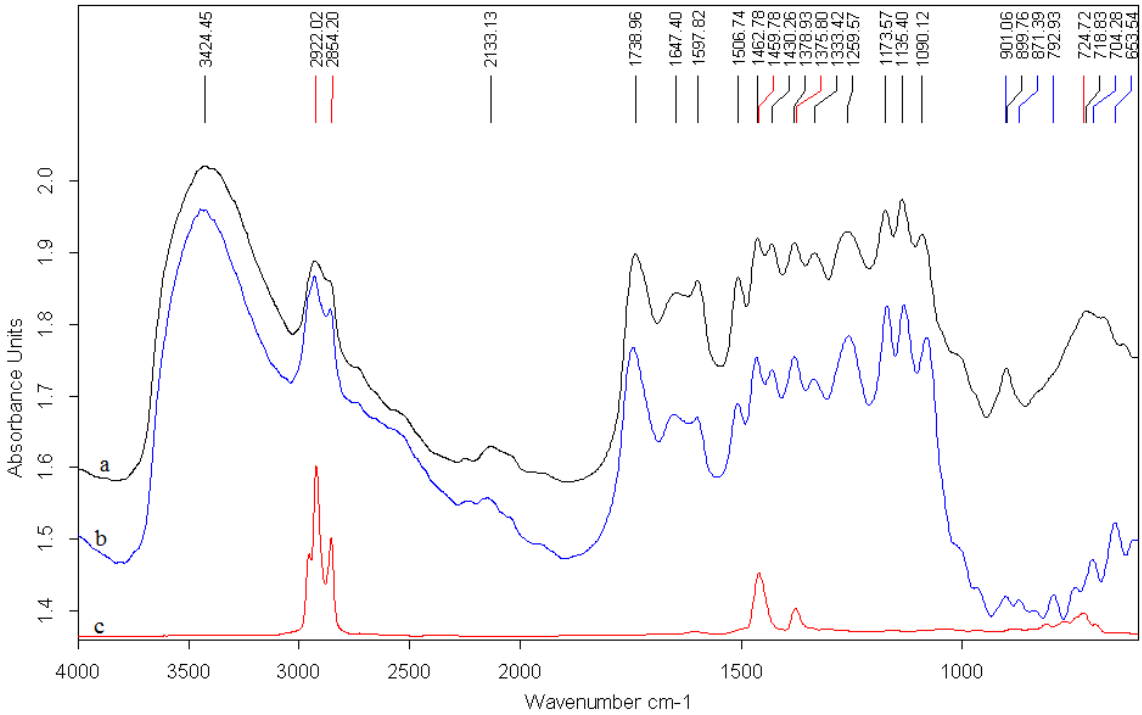

Figure 10. FTIR spectra of the analysed samples:
***(a)* – untreated linden wood, *(b)* – linden wood treated with red petroleum, *(c)* – red petroleum.**

Table 1

The values obtained based on the CIEL*a*b* analysis of the sample treated with red petroleum.

Time (h)	*L**	*a**	*b**	*ΔL**	*Δa**	*Δb**	$(\Delta L^*)^2$	$(\Delta a^*)^2$	$(\Delta b^*)^2$	*ΔE**
24	29.14	5.92	6.36	-1.3200	-0.3500	-2.4200	1.7424	0.1226	5.8564	2.7787
48	29.29	6.03	6.55	-1.1700	-0.2400	-2.2300	1.3689	0.0576	4.9729	2.5297
72	29.38	6.10	6.56	-1.0800	-0.1700	-2.2200	1.1664	0.0289	4.9284	2.4746
96	29.37	6.11	6.62	-1.0900	-0.1600	-2.1600	1.1881	0.0256	4.6656	2.4247
110	29.29	6.24	6.68	-1.1700	-0.0300	-2.1000	1.3689	0.0009	4.4100	2.4041
134	29.28	6.24	6.69	-1.1800	-0.0300	-2.0900	1.3924	0.0009	4.3681	2.4003
158	29.29	6.25	6.68	-1.1700	-0.0200	-2.1000	1.3689	0.0004	4.4100	2.4040

Standard values of L=30.46; a*=6.27; b*=8.78*

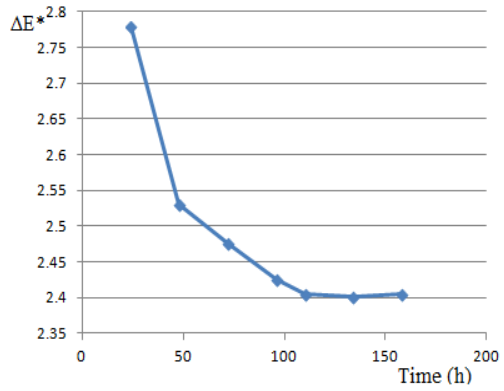

Figure 11. CIE*L*a*b- colour difference.**

Conclusions

Combining the techniques OM, SEM-EDX, micro-FTIR and CIE*L*a*b**, we have studied the impact of the treatment with red petroleum on the polychrome wood affected by the xylophagous attack. Using the OM and SEM analysis we have identified the species of the xylophagous insect that affected the support, and the lowering of the porosity of the wood as a result of the treatment. From the EDX analysis the retention of the petroleum in wood was highlighted based on the increase of the carbon and oxygen concentration and based on the presence of iron. The micro-FTIR analysis confirms the penetration of the active principles from the Câmpeni red petroleum through its characteristic peaks that can be found at the treated wood in the three domains: 2850-2960 cm^{-1}, 1350-1500 cm^{-1}, and 950-600 cm^{-1}. By means of the CIE*L*a*b** analysis, we have determined the chromatic deviation following the treatment, which proved to be insignificant for the human eye. Following the treatment we ascertained an improvement of the preservation of the wood through the amelioration if the wooden fibre and the slight alteration of the support's colour, bestowing it a patina appearance.

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