Multi-analytical Study of an Ancient Icon on Wooden Panel

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This paper presents a physico-chemical study of the wooden support of the icon “Saint Nicholas” from the nineteenth century. The icon is crafted from linden wood panel, consisting of two boards glued together and the back being reinforced by two crossbeams. Due to intense Xylophagous insects attack and of the wood movements, the conservation status of the icon is precarious, the wooden support being heavily damaged. It became powdery and spongy filled with insect tunnels, thereby losing a lot of its density. Moreover the two panels were separated in time by wood movement under the influence of atmospheric moisture, remaining in place due to the crossbeams. Nail insertion through one of the beams has led to profound gaps in the panel and to paint layer cracking. Also there are present traces of wood burn by direct heat source, which led to a forced contraction of the wood. Due to environmental factors (relative humidity, temperature oscillation, borer insects attack) and anthropogenic factors (mechanical damage during handling and nails insertion) the icon underwent major damage and degradation of the support. Besides the characterization of materials and techniques, the purpose of this paper is to identify the environmental factors and make a physico-chemical analysis of the degradation and damage they produce, in order to create an optimal microclimate. In order to analyse the degradation and deterioration of wood, modern investigation techniques were involved, like Optical Microscopy (OM), Scanning Electron Microscope (SEM) and Micro-Fourier Transform Infrared Spectroscopy (Micro-FTIR). Thus, by Optical Microscopy the wood was identified to be Tilia Cordata, and with the SEM microphotographs of the cellular structure on three different directions of the fibre were made. Analysis of chemical alteration of wood was performed using the Micro-FTIR and gave us information on wood composition, the degradation degree of cellulose and lignin. With the help of the Optical Microscopy two wood samples and insect droppings were analyzed to identify their family as Anobiidae.

Keywords: panel painting, icon, OM, Micro-FTIR, SEM, wood degradation and deterioration

The cultural heritage, both the one from the museum collections and the one from the private collections, requires an increased amount of care in order to preserve it in optimal storage and display conditions. The purpose of all the preservation and restoration interventions is to help them have a life as long as possible. In order to control and minimize the effects of aging on the objects in the collection, the environmental, anthropogenic and biological factors need to be monitored and dealt with should the situation require it.

It has to be said that the deterioration of the artifacts can be detected by studying the modification of the physical state, leading to changes in the support’s smoothness, cracks, fractures, displacements, loss of resistance, cracking, detachments, exfoliation, abrasion, holes, bulges, etc. The degradation occurs at a molecular level, it is the result of several physico-chemical, microbiological or biochemical processes and it is irreversible [1-4]. Under the effect of light, temperature, humidity and pollutants, the materials oxidize and decompose, eventually leading to visible changes which damage the appearance of a work of art.

The most important consequences are produced by the environmental factors, especially by the relative humidity (RH). When the RH increases, the wood locks the water molecules to the cellulosic fibrils level with the help of hydrogen connections. The fibrils are changing their volume but longitudinally less so, leading to dimensional changes perpendicular to the fibre [5]. The hydration of the fibrils and the cellular dilation take place in the superficial layers but in depth, the un-hydrated cells lock the ones in the superior layers (they do not allow them to move sideways) and so tension appears. The dilated cells, with no room to move, are compressed (they become oval instead of round).

When the RH drops, the wood contracts, the ground gets compressed (they become oval instead of round). The temperature variations are just as important but they do not influence the dimensions of the wooden painting as much as the RH variations. However, an increase in temperature followed by a drop in RH can lead to the dehydration of the materials (the support). The differences in temperature inside the paint layer but also on the surface of the painting (caused by the uneven incandescent lighting) lead to the straining of the paint layer which eventually leads to cracks and detachments.

The microclimate in which the artifact is stored is what allows a biological attack to occur. The Xylophagous insects are encouraged by the fungi attack (Xestobium rufovillosum prefer the fungi infested wood) [10, 11]. The females lay their eggs on the cracked, fungi attacked...
surfaces where the humidity and temperature are higher. The larvae penetrate the wood and consume it, forming many tunnels which, if the attack is strong enough, lead to a drop in wood resistance and mass losses. Moreover, they can emerge to the painting’s surface and the holes damage the appearance of the painting. The amount of wood moisture must be between 10 and 30% (at a RH of 60-90% and a temperature of 12-29°C) for the Anobiidae larvae to hatch [12].

In this case, we speak of the effects of biodeterioration from Xylophagous insects attack, followed in time by enzymatic biodegradation. The influence of the other external factors (the microclimate and pollution), including anthropogenic (use, handling and inappropriate display, unauthorized preservation - restoration interventions, etc.) lead to deteriorations by physical-structural modification and degradations by changing or altering of the chemical nature of the used materials [2, 12].

This paper aims a differential identification of the effects due to microclimatic factors, chemical (pollution), biological and anthropogenic factors that degraded and deteriorated the studied icon, together with the assessment of the conservation state of a panel painting icon from XIXth century, with high patrimonial value. In this regard are proposed the optimal microclimate conditions used to display and keeping old icons.

**Experimental part**

**Observation of the icon**

For this study the icon of Saint Nicholas was taken into account. It comes from a private collection in Tecuci, Romania and is painted in Russian style with a reduced color palette, on silver leaf and linden wood panel. According to the characteristics of the technique and materials used by the painter, the icon was painted in the nineteenth century [13]. The artefact was painted on a wooden panel with two crossbeams on which a layer of cardboard was attached. On these the ground was added, in which various models have been sculpted (with small chippers of various shapes) after it had been drawn. After finishing the embroidery, the silver foil was attached, the painting was made and finally, the background and parts of the Saints garment was covered with yellow varnish to resemble gold.

The icon illustrates Saint Nicholas, centred, holding the Gospel in his left hand and blessing with his right. Close to the head to the right, there is a medallion in which Jesus Christ is painted and to the left the Virgin Mary. The scene is firstly framed by a sculpted embroidery and then by the canonical red one. Also, the Saint’s raiment and halo have various patterns sculpted in the ground. The entire front of the icon is covered with a silver foil except for the Saint’s face and a stole on his shoulders. From a chromatic point of view, the icon belongs to the Russian iconography with just a small range of natural pigments having been used, like ochre, red ochre (red iron oxide) and carbon black. The icon’s support is made of two main panels and a secondary narrower one, stuck together with rabbit skin glue and fixed with two parallel dovetail crossbeams. One of the original cross-pieces has been replaced with a copy made of a different type of wood which was nailed to the back.

**Conservation state assessment**

The preservation state of the icon is not a very good one. Because of the effects of the environmental and human factors, the panel and the paint layer have suffered various types of degradation and deterioration. Thus, the two main plates of the panel have drifted away, causing the entire painting to crack (fig. 2a). The paint layer has, on relative small surfaces, age-related crackles, enhanced by the roof detachments. These are vertical, along the wood fibre. Along the main fissure which separates the two plates, there are deep and semi-deep gaps. In the lower part of the icon, pieces of ground are missing measuring approximately 10 cm in length and 5 cm in width (fig. 2a and e). Beside this ground gap, where the panel is most deteriorated, traces of a burn can be noticed on the wood surface (fig. 2e). In the upper part of the icon, right beside the nose, halo and frame, the tips of the nails from the back have broken the preparation layer, emerging to the surface (fig. 2d). The entire painting, the borders and the back show the traces of a strong Xylophagous attack (fig. 2c). Also, the structure of the wooden panel has been severely damaged, having lost a lot of its density and elasticity and having become powdery and fragile when handling. A few breaks of the wooden support have taken place in the lower part of the icon, especially near the corners and the crack (fig. 2b). The instability, the replacement and the poor attachment of the crossbeams have led to the slight curvature and cracking of the panel.

**Analytical techniques**

For this study optical and scanning electron microscopy along with spectroscopic techniques were used to study the surface microstructures a light microscope CARL ZEISS AXIO IMAGER A1m, with attached camera AXIOCAM, images being enhanced between 50X and 500X and observed by reflexion. A scanning electron microscope was used, SEM VEGA II LSH model, manufactured by TESCAN Czech Republic, together with an EDX detector type QUANTAX QX2, manufactured by BRUKER/ROENTEC.
Germany have been used to highlight the elemental composition and the arrangement of the surface microstructures. The analysis of samples was performed at a magnification of 1000X and 2000X. A FT-IR spectrometer together with HYPERION 1000 microscope, both from Bruker Optic Equipment, Germany, have been used to record the FT-IR spectra.

To make the necessary analysis, several samples of wood have been taken. More precisely, out of the large fracture of the lower part of the support, a partially detached chip of wood has been extracted. From its surface, three wooden samples, each representing a section of the fibre (transversal, tangential and radial), have been cut with the help of a fine blade.

Using the same techniques that other authors have used [14-17], the wooden samples were put on a glass slide and analysed through Optical Microscopy by reflection, using magnifications ranging between 50X and 500X through transmission and reflection. With the help of the electronic microscopy SEM, the samples were photographed and magnified between 100X and 300X so that the cellular structure of the wood and its degree of deterioration could be studied with an increased amount of clarity.

In order to identify the wood species, the photos acquired using OM and SEM were compared with identification atlases [18].

**Results and discussions**

To indentify the wood species of the panel, the photographs obtained by OM and SEM (fig. 3) were used, along with a reference picture of *Tilia cordata Mill* (fig. 3b) [18].

The xylem within the genus *Tilia* is very homogenous and species cannot be distinguished. Ring boundaries are diffuse to semi-ring-porous and have distinct rings. Vessels occur in short radial multiples and/or in radial groups. Vessels walls have simple perforations, distinct helical thickenings and inter-vessel pits are arranged in alternating position. Fibres are mostly thin-walled, but are occasionally thin to thick-walled. The distribution of axial parenchyma in aprotachael diffuses in aggregates. Rays are normally 2-3- rarely up to 4 seriate. Rays are larger in slightly bent parts of stems. Rays of all species are either homocellular with procumbent cells or heterocellular with one row of square or upright marginal cells. Crystals are absent. Multi cellular, tangential, un-lignified sieve tube/ parenchyma bands alternate with a unicellular band of very thin-walled square parenchyma cells and a multicellular band of thick-walled fibres. Ray dilatations are very distinct. Crystal druses occur in the cortex. Some ray cells produce mucilage. Normal and mucilage-producing ray cells are non-distinguishable [19].

From the image analysis the following conclusion can be drawn: for transversal section, the identified ligneous species is from the hardwoods family, with diffuse pores dispersion with no pronounced difference between pores size from earlywood compared to latewood. Pores are numerous, have no tiles and appear thick-walled or grouped 2-3 in radial rows. Similar pores distribution and size is visible on the reference picture which describes the lime (*Tilia cordata Mill*). Radial section: here can be seen simple perforation plates and spiral thickenings in the vessels. Generally homogeneous rays are present, occasionally also with a row of square marginal cells. Ray-vessel pits are numerous and small. Tangential section: rays are generally bi- to 4-seriate, rarely 5- to 6-seriate. Ray height is very variable, often up to 10 cells, sometimes up to 50 or more cells. Ray cells are small, axial-oval.

The oval-shaped particles seen in the wooden fiber are the Xylophagous insects droppings mixed with wooden powder (Fig. 4a and b). Although during the preservation stages of the icon no insects have been found, dead or
alive, the shape of the excrements, along with a few other signs of the attack, give us the possibility to make a distinction concerning the specie and family of the insects that attacked the object. In our case, it is believed that Xylophagous attack was caused by *Anobium punctatum*, a common species in Romania and the main troublemaker for the cultural heritage. According to the literature [12, 20], this species attack is recognized by looking at the hatching holes which have a 1-2 mm diameter. In the case of hardwood, the galleries have irregular shape, with the same diameter and they are practically filled with feces mixed with wood powder. The *Anobium punctatum* feces are ovoid shaped, narrow on both sides and do not exceed 1 mm in length. In the case of hardwood, the insects attack from sapwood to heartwood and the tunnels are dug at the surface of the wood, going towards the interior as the attack becomes more intense. As the insects advance in consuming the wood, they only leave the rigid cell walls of the late wood [12, 21].

Using the Micro-FTIR, the chemical state of the wood was analyzed in order to see the wood level of degradation.

All wood types exhibit common features in the 3500 - 2500 cm\(^{-1}\) range: a band at 3300 cm\(^{-1}\), for the water molecules absorbed in the wood lumen cells. In the 1800 - 600 cm\(^{-1}\) fingerprint area, specific and common bands appear, assigned to cellulose, hemicelluloses and lignin moieties, as follows 1510 - 1501 cm\(^{-1}\) - a band specific to aromatic skeletal vibrations (this band depends on the wood species and is assigned to the total content of the lignin components); 1450-1456 cm\(^{-1}\) and 1417 - 1424 cm\(^{-1}\) - the bands of \(\delta_{\text{C}–\text{H}}\) in lignin; 1363 - 1370 cm\(^{-1}\) - of \(\delta_{\text{C}–\text{H}}\) in cellulose and hemicelluloses; 1320-1328 cm\(^{-1}\) - the band of \(\nu_{\text{C}–\text{H}}\) in cellulose; 1150-1156 cm\(^{-1}\) - \(\nu_{\text{C}–\text{O}}\) in lignin and xylan; 1166 cm\(^{-1}\) - \(\nu_{\text{C}–\text{O}_2}\) in cellulose and hemicelluloses, 1024-1039 cm\(^{-1}\) - \(\nu_{\text{C}–\text{O}_2}\) in cellulose and hemicelluloses, and 885-900 cm\(^{-1}\) - \(\delta_{\text{C}–\text{H}}\) in cellulose (fig. 5). The 1724-1736 cm\(^{-1}\) band remains very weak in softwoods, but well-defined in hardwoods. The water content in wood can be assessed from the 1660-1590 cm\(^{-1}\) region. In fresh lime samples, a large and more intense band lies in the 1650-1600 cm\(^{-1}\) domain. In the dried lime samples, this band decreases in intensity and splits into a band at 1594 cm\(^{-1}\) [22-26].

By comparing the spectrums of the icon panel with the reference [23-27], the degradation degree can be observed. Aside from the biological attack which leads to a deterioration of the support, high humidity, as well as its alternation with a very low humidity, leads to a chemical degradation of the wood which manifests itself through bending, fissures, panel detachments, surface shrinking, and others. The high water content is represented by the 3500 - 2500 cm\(^{-1}\) sharp peaks, with the same aspect as reference spectrum of linden wood, externally damaged. In the case of the “Saint Nicholas” icon, it went through periods of very low humidity in the microclimate, instead the 1735 cm\(^{-1}\) peak certifies that the panel is a hardwood. A humid microclimate with a high temperature created an ambience for Xylophagous attack. Peaks at 146 cm\(^{-1}\), 1427 cm\(^{-1}\), 1273 cm\(^{-1}\) and 1329 cm\(^{-1}\) are representative for lignin, hemicellulose and cellulose. They are well defined, but equal in intensity, which indicates their low content as an internally damaged and degraded wood, as the reference spectrum. Hemicelluloses and lignin decreased content results from the flattened peak of 1085 cm\(^{-1}\) and is due to the intense Xylophagous insects attack.

**Conclusions**

This paper presents a physico-chemical study of the wooden support of the icon “Saint Nicholas” from the nineteenth century. The artwork is very damaged by biological, anthropic and environmental factors, raising a lot of problems for its conservation and further analysis.

With the help of the OM and SEM, the wood species was identified as *Tilia cordata Mill*. Due to the heavily attack of the woodborer insects, the wood panel became spongy (full of tunnels), with very low resistance to handling, causing it to brake. Although no insect has been found, neither adult nor larvae, by studying the feces and the characteristics of the attack, we have reached the conclusion that the massive deterioration of the support was caused by the *Anobium punctatum*.

Because of a very low relative humidity and because of the main source of heat was in direct contact with the wood, the two main boards of the panel have separated, curved, causing the painting to crack. In consequence, the lower part of the panel, traces of slow and superficial burning can be seen.

In an attempt to secure the panel boards, the crossbeams were nailed, causing great damage to the painting and to the wood itself. Because of the continuous movement of the wood by its dehydration, weakening and contraction, the inserted nails have broken the paint layer causing major damage.

The Micro-FTIR revealed a low quantity of cellulose and hemicellulose, mostly because of the strong Xylophagous attack and a high moisture content from the current microclimate.

An optimal microclimate suitable for keeping a panel painting icon, involves maintaining constant levels of temperature and RH. For the icon not to be affected by high temperature, it should be kept between 18 and 24°C, without having contact with any heat source. The RH has a much greater impact and it has to be maintained around...
65% not to favor the appearance of mold or xylophages attack. Also, to avoid degradation of pigments and varnish, the icon should be kept in an area where direct light, natural or artificial, has low intensity. In terms of chemical degradation and deterioration, the icon should be kept away from sources of direct vent that could bring in the atmosphere smoke and emissions.

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