ECOLOGICAL MATERIALS USED IN PRESERVATION AND RESTORATION ON NEW WOOD

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Abstract:
The paper presents the effects of ecological treatments on different wood species. Tests are made on lime tree and oak, which are immersed in red oil and propolis in alcohol solution dispersed in red oil. The subject of analysis is observing these substances effect on dimensional stability and hydric modification on new wood. Also, is highlighted the behavior of the wood species after the immersion in the two solutions, compared with untreated wood of the same species, hydric stabilised. Is presented a new preservation procedure safer for the curator.

Key words: old wood; lime tree; oak; hydric modification; dimensional stability.
INTRODUCTION

Old wood from artefacts, used either as panel (base), or as an ornament, suffers in time a series of degradations and deteriorations under the influence of the environment factors, which can be lead to precolaps depending on their aggression. Being an organic material with heterogenic porous structure, the effects of the deterioration and degradation processes act quickly in the absence of some adequate measures of passive (air conditioning) and active preservation (the treatment which stops the degradation and deterioration in their evolution). Some of the worst effects, very common in wood art work are: wood fragilisation and decay due to viruses, bacteria, yeasts, fungi, lichens etc., cracking and erosion due to the wood boring insects, all of them amplified by the aggression of the moisture and high temperature, and last but not the least carbonization due to combustion. Along with these, the fading effect of the wood is met and is seen on the panel paintings or at items with spatial configuration: the bending, twisting, cracking, fracturing and others (Hayashi 2008, 2009, 2010a, b, Sandu 2002, 2008, Unger et al. 2001, Vasilache et al. 2008, Walker 2006).

From this point of view, wood is the subject of some meticulous research regarding the implication of the optimal processes of hydric and dimensional stabilization, of protection against microbiological agents and boring insects, fireproofing, waterproofing, and everything that imply climatic and mechanical protection. The ideal situation would be that this treatments, with very good retention, are applied immediately after the artistic work is done, so that no later intervention would harm it (Ciocan et al. 2009, Hayashi et al. 2008, 2009, Hunter 1995, Sandu et al. 2007, 2008a, b, c and d, 2009a, b, 2010, Siau 1995).

The treatments needed for the occurrence of deterioration or degradation processes, in most cases with a complex mechanism induced by multiple factors from the time of the exhibition or utilization, are necessary to be applied on as few steps as possible, using materials with minimal influence over the wood (Sandu 2002, 2008, Unger et al. 2001, Walker 2006).

There are known a series of modern procedures for old wood protection through the use of synergistic organic systems (Sandu et al. 2009c, d, 2010b, 2011b), with various functions for blocking the cumulative effects of deterioration and degradation, with high permeability in the volume faze by forming an uniform nanolayer, compatible with the persistent retention. Lately attention turns to natural organinc products or of semisynthesis, ecological as: liquid paraffin and petroleum derivatives, wax products, tannins, lignin sulphonates, alkaloilds, terpenes, flavones and others (Sandu 2002, 2008, 2011a, Unger et al. 2001, Walker 2006).

It was developed a method of determination of the normal range of variation for the moisture content in new wood (Sandu et al. 2009e, 2010a, 2011c, Siau 1995, Vasilache et al. 2009), located between the limits in which the wood gives microstructural destructions on fiber and cell level: minimum moisture content (0,5…1,5%) and the saturation point of the moisture content in fibre (32…36%), depending on the specie, tree age, state of conservation etc. (Hayashi et al. 2010a, b). This method has wide applications in archaeometry, (for establishing some temporal occurrence characteristics) and in the impact studies of some active preservation treatments.

This work analyses the variation in longitudinal, radial and tangential shrinkage together with the variation in density and porosity for two wood species (lime and oak), when treated with red oil and alcoholic propolis solution in red oil compared with untreated samples, at different relative humidities (100%, 85%, 65% and 25%). The two natural treatments allow the hydric and dimensional stabilization, as well as protection against microbiological agents and boring insects. For waterproofing and everything that implies climatic and mechanical protection, it was necessary to study the effect of the large variations in the relative air humidity on the treated wood.

OBJECTIVE

The purpose of this paper is to present a study regarding the influence of two natural, organic products (propolis and red oil) used in a synergistic system, compatible with two species of new wood (lime tree and oak), over some physical and structural characteristics.

EXPERIMENTAL PART

Two species of new wood were taken for this study, the most common in Romanina’s art work: lime tree (Tilia sp.) and oak (Quercus petraes L.). For each type, as a reference it was used new wood hydric stabilized and untreated against treated new wood and hydric stabilized. The samples were made within the dimensions: longitudinal L (40mm), Tangential T (20mm) and Radial (10mm).

The hydric stabilization was made by holding the sample in the oven at 103±5 °C, until it a constant weight. A set of three samples from each specie was used as a reference and other sets of three samples were treated with red oil and alcoholic propolis solution 20% dispersed in red oil, by immersion for 60minutes, according to a new method (Sandu et al. 2009b, c, 2010b, 2011b). After the immersion, filter paper was used to absorb the excess solution and then the samples were weighed to a constant weight, for
6 days in normal atmospheric conditions (22°C and 55%RH) and afterwards measured over the three dimensions: radial, tangential and longitudinal. Afterwards the samples underwent a process of hydration in a climate controlled chamber type Aer concept (FIRLABO), with constant temperature of 20°C and a maximum of 100% humidity, until reaching a constant weight when the measures were taken again. Then, the samples underwent a gradual process of dehydration in the same climate controlled chamber at different humidity values (100%, 85%, 65% and 25%). At each dehydration step, the shrinkage of the samples was measured. Based on the wood shrinkage at each step of dehydration (100%→85%, 85%→65%, 65%→25% and 25%→0%) the volume change was measured, the specific mass and porosity. Porosity (P) was calculated with following formula:

\[ P = \frac{1 - \rho_0 / 1530}{100} \text{ (%)} \]  

Where: \( \rho_0 \) represents the oven dry density calculated with the formula:

\[ \rho_0 = \frac{W_0}{V_0} \text{ (kg/m}^3) \]  

For studying the variation in porosity, two levels of relative humidity were considered, “before treatment” and “after treatment”, respectively at 85% before treatment and 25% after the treatment.

RESULTS AND DISCUSSIONS

LIME TREE: variations recorded

In Fig. 1 it is presented the longitudinal shrinkage variation for the lime tree, treated with propolis in red oil solution, under the influence of atmospheric moisture, by comparison with new, untreated wood (absent) and the one treated with red oil.

![Fig. 1](image1.png)

**Fig. 1**

Variation of longitudinal shrinkage for lime tree:

Relative humidity (RH), with specifications: a - 100%, b - 85%, c - 65%, d - 25%

Treatment type with the specifications: i - reference (absent); ii - treated with red oil;

iii - treated with alcoholic propolis solution 30% dispersed in red oil.

In Fig. 2 it is presented the radial shrinkage variation for the lime tree, treated with propolis in red oil solution, under the influence of atmospheric moisture, by comparison with new, untreated wood (absent) and the one treated with red oil.

![Fig. 2](image2.png)

**Fig. 2**

Variation of the radial shrinkage for lime tree:

Relative humidity (RH), with specifications: a - 100%, b - 85%, c - 65%, d - 25%

Treatment type with the specifications: i - reference (absent); ii - treated with red oil;

iii - treated with alcoholic propolis solution 30% dispersed in red oil.
In Fig. 3 it is presented the tangential shrinkage variation for the lime tree, treated with propolis in red oil solution, under the influence of atmospheric moisture, by comparison with new, untreated wood (absent) and the one treated with red oil.

![Fig. 3 Variation of the tangential shrinkage for lime tree:](image)

Relative humidity (RH), with specifications: a - 100%, b - 85%, c - 65%, d - 25%

Treatment type with the specifications: i - reference (absent); ii - treated with red oil;

iii - treated with alcoholic propolis solution 30% dispersed in red oil.

In Fig. 4 it is presented the volume shrinkage variation for the lime tree, treated with propolis in red oil solution, under the influence of atmospheric moisture, by comparison with new, untreated wood (absent) and the one treated with red oil.

![Fig. 4 Variation of the volume shrinkage for lime tree:](image)

Relative humidity (RH), with specifications: a - 100%, b - 85%, c - 65%, d - 25%

Treatment type with the specifications: i - reference (absent); ii - treated with red oil;

iii - treated with alcoholic propolis solution 30% dispersed in red oil.
In Fig. 5 it is presented the density variation for the lime tree, treated with propolis in red oil solution, under the influence of atmospheric moisture, by comparison with new, untreated wood (absent) and the one treated with red oil.

**Fig. 5**
Variation of the density for lime tree:
- Relative humidity (RH), with specifications: a - 100%, b - 85%, c - 65%, d - 25%
- Treatment type with the specifications: i - reference (absent); ii - treated with red oil; iii - treated with alcoholic propolis solution 30% dispersed in red oil.

In Fig. 6 it is presented the porosity variation for the lime tree, treated with propolis in red oil solution, under the influence of atmospheric moisture, by comparison with new, untreated wood (absent) and the one treated with red oil.

**Fig. 6**
Variation of the porosity for lime tree:
- Relative humidity (RH), with specifications: a - before treatment 85%; b – after treatment 25%
- Treatment type with the specifications: i - reference (absent); ii - treated with red oil; iii - treated with alcoholic propolis solution 30% dispersed in red oil.
OAK: variations recorded

In Fig. 7 it is presented the longitudinal shrinkage variation for the oak, treated with propolis in red oil solution, under the influence of atmospheric moisture, by comparison with new, untreated wood (absent) and the one treated with red oil.

![Longitudinal shrinkage variation for oak](image)

**Fig. 7**

Variation of the longitudinal shrinkage for oak:

Relative humidity (RH), with specifications: a - 100%; b - 85%; c - 65%; d - 25%

Treatment type with the specifications: i - reference (absent); ii - treated with red oil;
   iii - treated with alcoholic propolis solution 30% dispersed in red oil.

In Fig. 8 it is presented the radial shrinkage variation for the oak, treated with propolis in red oil solution, under the influence of atmospheric moisture, by comparison with new, untreated wood (absent) and the one treated with red oil.

![Radial shrinkage variation for oak](image)

**Fig. 8**

Variation of the radial shrinkage for oak:

Relative humidity (RH), with specifications: a - 100%; b - 85%; c - 65%; d - 25%

Treatment type with the specifications: i - reference (absent); ii - treated with red oil;
   iii - treated with alcoholic propolis solution 30% dispersed in red oil.
In Fig. 9 it is presented the Tangential shrinkage variation for the oak, treated with propolis in red oil solution, under the influence of atmospheric moisture, by comparison with new, untreated wood (absent) and the one treated with red oil.

Fig. 9
Variation of the Tangential shrinkage for oak:
Relative humidity (RH), with specifications: a - 100%; b - 85%; c - 65%; d - 25%
Treatment type with the specifications: i - reference (absent); ii - treated with red oil; iii - treated with alcoholic propolis solution 30% dispersed in red oil.

In Fig. 10 it is presented the Volume variation for the oak, treated with propolis in red oil solution, under the influence of atmospheric moisture, by comparison with new, untreated wood (absent) and the one treated with red oil.

Fig. 10
Variation of the Volume for oak:
Relative humidity (RH), with specifications: a - 100%; b - 85%; c - 65%; d - 25%
Treatment type with the specifications: i - reference (absent); ii - treated with red oil; iii - treated with alcoholic propolis solution 30% dispersed in red oil.

In Fig. 11 it is presented the density variation for the oak, treated with propolis in red oil solution, under the influence of atmospheric moisture, by comparison with new, untreated wood (absent) and the one treated with red oil.

Fig. 11
Variation of the density for oak:
Relative humidity (RH), with specifications: a - 100%; b - 85%; c - 65%; d - 25%
Treatment type with the specifications: i - reference (absent); ii - treated with red oil; iii - treated with alcoholic propolis solution 30% dispersed in red oil.
Fig. 11

Variation of the Density for oak:
Relative humidity (RH), with specifications: a - 100%; b - 85%; c - 65%; d - 25%
Treatment type with the specifications: i - reference (absent); ii - treated with red oil;
iii - treated with alcoholic propolis solution 30% dispersed in red oil.

In Fig. 12 it is presented the porosity variation for the oak, treated with propolis in red oil solution, under the influence of atmospheric moisture, by comparison with new, untreated wood (absent) and the one treated with red oil.

Fig. 12

Variation of the Porosity for oak:
Relative humidity (RH), with specifications: a - before treatment 85%; b – after treatment 25%;
Treatment type with the specifications: i - reference (absent); ii - treated with red oil;
iii - treated with alcoholic propolis solution 30% dispersed in red oil.

Although lime wood is a hardwood, it should interact strongly with the propolis treatment, but the data obtained demonstrate the opposite. The oak samples which have high density, have interacted better with the organic solutions used in the experiment, their dimensional characteristics varying in much higher limits.

The shrinkage values on the three axes of both wood species, as expected, varied so: T > R > L.
The lime wood sample, untreated: T (5.5%) > R (3.5%) > L (0.26%), treated with red oil: T (6.7%) > R (4.8%) > L (0.27%), and treated with propolis in alcohol solution dispersed in red oil: T (6.0%) > R (4.0%) > L (0.32%). The oak wood sample, untreated: T (7.0%) > R (4.8%) > L (0.12%), treated with red oil: T (7.5%) > R (4.8%) > L (0.42) and treated with propolis in alcohol solution dispersed in red oil: T (6.8%) > R (4.6%) > L (0.17%).

In the same order the volume and density, vary as follows: for lime, according to the treatment type (i, ii, iii), ii > iii > i, while for oak, ii > i ≥ iii. However, the porosity, as function of the treatment, varies for lime i > iii > ii, while for oak i > ii ≥ iii.
In order to assess the influence of the treatment and of the relative humidity on the specimens dimensional shrinkage for both species investigated, are given in Fig. 13. This compares the variation of ratios $T/R$, $T/L$, $R/L$. Three cases are considered: i – untreated wood, ii – wood treated with red oil and iii – wood treated with alcoholic solution of propolis dispersed in red oil.

The variations of ratios $T/R$, $T/L$, $R/L$ when treating wood with red oil (ii), with alcoholic solution of propolis in red oil (iii) compared with untreated wood (i).

The three shrinkage ratios vary differently for the two species, which was to be expected because lime is lower in density than the oak, for which the process of organic solutions penetration takes place at a different speed. There is a good correlation between the penetration speed of the solution and species density.

According to the graphs, the differences in the ratio $T/R$ between lime and oak is greater for treatment with red oil than for untreated wood and decreases very much when treating wood with propolis dispersion solution in red oil. For the other ratios, the differences seem to increase for untreated and wood treated with propolis dispersion in red oil, but decrease for treatment with red oil. This behaviour can be explained by the fact that following the treatment, a great part of the red oil components with hydrophobic activity, leave the wood, while propolis makes a membrane system at the wood cell surface, which is permeable for reversible water. The deep penetration in the volume faze in the lime tree sample, of the propolis organic solution, led to the partial obstruction of the vessels and ducts, which are more reachable than the ones in oak. Instead at the oak samples the solution makes only a superficial layer, the anatomic elements quickly reacting to the atmospheric moisture.

In Fig. 14 it is illustrated the comparative variation of volume, density and porosity for the two wood species in all three situations considered: i – untreated wood, ii – wood treated with red oil and iii – wood treated with alcoholic solution of propolis dispersed in red oil.

Comparative variation of volume, density and porosity for the two wood species (lime and oak) when treating with red oil (ii), with alcoholic solution of propolis dispersed in red oil (iii) compared with untreated wood (i).
Compared with variation in ratios T/R, T/L si R/L, the variations in volume, density, porosity differ very much in the three situations i, ii and iii. The variations in volume seem to have similar trends, but the situation is not the same for density and porosity. Oak has an ascendant trend for the variation in density and descendent for porosity. This may be because of the retention of some volatile components of red oil and of the propolis solution, compared to lime, which permits the elimination with a higher rate of the same volatile components of the two treatments.

Fig. 13 and 14 illustrate the way in which the two organic solutions influence the wood shrinkage for the two species, whose values fall within the normal range of variation till the limit situation is reached (precollaps), when fissures and bows begin to occur.

This study enables the optimization of various organic solutions used for preservation and prevents the wood from fungal or borer insects attack, and waterproofing.

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<td></td>
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CONCLUSIONS

By applying the preservation method using propolis in red oil solution, which is the subject of a recent patented invention, the lime wood behaved differently from the oak sample. For both wood species, the shrinkage values varied so: T > R > L, as it was expected. This demonstrates that the treatments with the two organic solutions do not influence strongly the dimensional characteristics.

The differences in ratio T/R values for lime and oak are greater when red oil is used compared to untreated wood and they reduce substantially when treating wood with propolis dispersed in red oil. For the other ratios, T/L and R/L, the differences seem to increase for untreated and wood treated with propolis dispersion in red oil, but decrease for treatment with red oil. This behaviour can be explained by the fact that following the treatment, a great part of the red oil components with hydrophobic activity, leave the wood, while propolis makes a membrane system at the wood cell surface, which is permeable for reversible water. The deep penetration in the volume faze in the lime tree sample, of the propolis organic solution, led to the partial obstruction of the vessels and ducts, which are more reachable than the ones in oak. Instead at the oak samples the solution makes only a superficial layer, the anatomic elements quickly reacting to the atmospheric moisture.

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