Influence of Organic Solvents and Dispersions on Wooden Supports of Paintings

IRINA CRINA ANCA SANDU[1], MIKIKO HAYASHI[2], VIORICA VASILACHE[3], DANUT-GABRIEL COZMA[4], SILVEA PRUTEANU[3], MARIA URMA[5], ION SANDU[3,6*]

[1] Universidade de Évora, Laboratório HERCULES, Palácio do Vimioso, Largo Marquês de Marialva, 8, 7000-809, Évora, Portugal

[2] Center of Conservation Science and Restoration Techniques, National Research Institute of Cultural Properties, 13-43 Ueno Park, Taito-ku, 110-8713, Tokyo, Japan

[3] Alexandru Ioan Cuza University of Iasi, ARHEOINVEST Platform, 22 Carol I Blvd., 700506, Iasi, Romania

[4] Alexandru Ioan Cuza University of Iasi, Faculty of Chemistry, 11 Carol I Blvd., 700506, Iasi, Romania

[5] George Enescu University of Artes, 29 Cuza Vodă St., 700040, Iasi, Romania

[6] Romanian Inventors Forum, 3 Sf. Petru Movila St., Bloc L11, III/3, 700089, Iasi, Romania

This study presents the data regarding the influence of two organic solvents (ethylic alcohol and Red Petroleum from Campeni), mixed with bee propolis, on different wood essences. The impact of these systems was evaluated by studying several physical-structural dynamic characteristics of the treated samples. The shrinkage of lime, poplar, fir and oak wood was studied on three sections (longitude – L, tangential – T and radial – R), for four different variations of atmospheric humidity (100, 85, 65, 25% RH), by gradually lowering the value (100%→85%, 85%→65%, 65%→25% and 25%→0%). In order to evaluate the impact of the treatment, two chemometric characteristics were taken into consideration: difference of shrinkage (ΔL, ΔR and ΔT) and the ratio of those differences (ΔT/ΔL, ΔT/ΔR and ΔR/ΔL). At the end of the paper, the volumetric shrinkage vas studied, alongside with the density and porosity variations of the wood. In order to evaluate the impact of these systems several chemometric characteristics were used: ΔV, Δρ and Δp. The obtained results have shown that poplar tree is virtually unaffected by the two treatments, the lime tree is slightly influenced, while the fir tree and oak tree are the most affected, because the used solutions easily dissolve their organic components. These components leave the resinous channels and pores of the oak tree, thus changing the specific weight and porosity. After the dissolution of the organic components present in natural wood, these solutions create a nano-coating on the surface of the anatomical elements, which confer detectable behaviours only to the wood species containing volatile components that are not compatible with the studied organic solutions. The behaviours can be detected during the interactions of the above mentioned wood species with the hygroscopic moisture in the atmosphere.

Keywords: wood supports, moisture content, atmospheric humidity, propolis, Red Petroleum from Campeni, ethylic alcohol, dimensional shrinkage, chemometric characteristics.

Wood is an organic material which changes continuously under the influence of atmospheric temperature and humidity. Moreover, after the wood is put into place it undergoes a series of regular cleaning interventions, active preservation and/or restoration using liquid dispersions. These operations may cause the wood to behave differently in the presence of hygroscopic water in the atmosphere [1-4].

Cleaning old paintings by washing, strengthening by bonding with aqueous or organic solutions and preservation by immersion, injection or brushing with liquid fungal insecticide dispersions, affects both the wooden support and the pictorial layer [2, 4, 5]. In case of easel paintings, in relation to flexible supports, wood panels have a number of limitations: they are rigid and require a rigorous processing prior to use. Wood is a cellulose, hygroscopic material sensitive to micro-climatic parameter variations, suffering dimensional changes (“*wood expansion/contraction*”) that lead to damage; wood is susceptible to biological or chemical attacks. It can be altered very easily by rotting, embrittlement, charring etc. [2, 4, 6-8] .

Furniture, large painting panels are composed of multiple boards and need frames, feathers or beams, usually of the same wood, applied as structural elements on rear or ends. They counter dismemberment and the bending tendency of panels or boards. Wood-backed canvas is used to prevent longitudinal cracking of board jointing or plugs [9-13].

Thus, as wood is hygroscopic, it contains a certain percentage of humidity that could be reversed depending on air humidity, ranging from *the fibre saturation point* (30-36% depending on wood species) and *minimum hygroscopic water content* 0.5% (value limit which may give rise to micro fibrils expansions, macroscopically translated as longitudinal cracks). The introduction of various organic materials, often hydrophobic, will change the normal fluid balance and will irreversibly affect the anatomical structures by clogging the wood fibre [4, 14-22].

The specialized literature explains how the ageing of painting woodwork has a significant effect on the normal range of fluid balance variation and hence on the structural or mechanical characteristics [23, 24].These characteristics are modified due to the decrease in the adsorption capacity of crystalline cellulose caused by conversion into hemicellulose and amorphous cellulose [25, 26]. These changes are caused by a slow thermo-oxidative process. This process is caused by the oxygen in the air, leading to a decrease in wood strength and hardness. This observation can be explained through the

* *email: ion.sandu@uaic.ro*

reduced content of crystalline cellulose. Lignin becomes the main component especially resistant to compression.

An accurate knowledge of the mechanical properties of a painting's wood components is a fundamental requirement for the use of such components as competitive structural materials. This objective remains an open question for research due to *natural variability* (essence, tree age, wood age, state of preservation, the cut trunk area, the geographical area of origin, harvesting period, etc.), *heterogeneity* and *anisotropy*. Thus, wood behaves differently in three sections: *longitudinal* (**L**) - Along the fibre, *radial* (**R**) - Parallel to the growth rings and *tangential* (**T**) - Growth rings [27-32].

In this regard, the most important feature in the conservation of wood-backed paintings is the hydro mechanical behaviour of wood. Reversible or equilibrium moisture content continuously varies depending on the atmospheric humidity and the materials with which it comes into contact during cleaning, preservation treatments and restorative interventions (especially liquid or gaseous materials which produce condensate). The mechanical behaviour of a wooden element is well and fully characterized by stress-strain relations, mechanical testing being the only way to determine the response to various stress the wood samples are subject to (tensile, shear, torsion, compression and bending) [13, 33-36]. The mechanical behaviour of a wooden element is well and fully characterized by stress-strain relations [37-41].

Several authors using modern non-invasive and real-time determination have studied the distribution and dynamics of wood hygroscopic water and its influence on preservation [23, 33, 42-44].

It is also know that various authors [45-49] studied fluid balance changes under the influence of natural and artificial ageing by means of hydrothermal treatment and ultraviolet photochemical or visible light irradiation of both cellulose and lignin structures.

Starting from these premises, based on specialised literature data and the experience of our team, in recent years an experimental protocol was proposed. This protocol was meant to assess the impact of new or old wood treatments with various organic systems used in cleaning, consolidation, active preservation and patina restoration on morphological and structural characteristic modifications involving different chemometric sizes of wooden supports [3, 4, 50-53].

When assessing the influence of solvents and solutions used in washing operations or active preservation (e.g. insectofungicide treatments) on the chemometric characteristics of wood, the only study method remains the micrometer measuring of the three sections [54]. It is a known fact that most wood swells towards annual growth rings (tangentially). Approximately half of the radial sectional and a small part of the longitudinal section get swollen [30-32, 50-53, 55, 56]. For these reasons, the experimental protocol provided that specimens of different species of wood, old or new, be cut in *rectangular* shapes respecting surface displacement in the three sections (T, R and L) cut from homogeneous areas and with the dimension ratio of T:R:L = 4:2:1.

In 2008, a method for the determination of the normal range of variation of moisture content of wood has been developed [51-53]. It has been successfully tested on various species of wood [57-60]. According to the new method, the normal range of variation of the fluid balance (reversible hygroscopic moisture content of the woodwork) is close to a minimum limit (0.5...1.5%, depending on the species, the age of the tree, wood age, state of preservation, etc.). This minimum limit influences wood destructions at a fibre and cellular level. The maximum limit is represented by *the fibre saturation point* (32...36%, depending on the same already mentioned variables). This method has wide applications in archaeometry (to establish the temporal evolution characteristics) and in impact studies of active preservation treatments [16, 18-20, 52, 53].

The purpose of this paper is to study the influence of two organic solvents (alcohol and Red Petroleum) on wooden supports. The organic solvents are mixed with bee propolis, often used by our team in the preservation of wood fibre and cleaning and repair operations [16, 18-20, 57-63]. Propolis has often been used in the synergistic systems along with tannins, both of which are compatible with various types of wood used in the installation of artefacts. The impact of these solvents was evaluated by studying the dynamic physical and structural characteristics of treated samples in relation to untreated samples (considered standard).

The study focused on shrinkage in three sections (longitudinal - L, tangential - T, radial - R). The types of wood studied were linden tree, poplar, fir and oak for four RH values (100, 85, 65 and 25%). There was a gradual value reduction (100% $\rightarrow$ 85%, 85% $\rightarrow$ 65%, 65%$\rightarrow$25% and 25%$\rightarrow$0%). The assessment of treatment impact of organic solutions took into consideration two chemometrical characteristics: *shrinkage discrepancy* (ΔL, ΔR and ΔT) and *the relationship between these discrepancies* (ΔT/ΔL, ΔT/ΔR and ΔR/ΔL). Finally, the studies focused on volume shrinkage, wood porosity and density variation with a summative assessment of gradual decrease in atmospheric humidity. The impact evaluation was conducted using the following chemometric characteristics: ΔV, $\Delta\rho$ and Δp.

Experimental part

The study focused on four wood species. These were most commonly used in Romania in the manufacturing of painting woodwork, namely: lime (*Tilia sp.*), poplar (*Populus L.*), fir (*Abies L.*) and oak (*Quercus petraea L.*). New untreated wood with a stable fluid content was considered as reference. The study focused on new wood treated by submerging it in Red Petroleum from Campeni and 30% alcohol propolis solution dispersed in Red Petroleum. The volume ratio of the two solutions, Red Petroleum: alcoholic propolis solution was 5:1. The samples had *a rectangular shape.* The sample surface were displaced according to the three sections (T, R and L) cut from homogeneous areas and their size being T:R:L=80:40:20 mm or 40:20:10 mm. Before the samples were treated, the content of fluid was stabilised by heating them in the oven at 103±5°C until their mass become constant. A set of three samples, one for each type of wood, was used as a reference set and the other sets containing three samples each were immersed for 60 min in Red Petroleum and alcoholic propolis solution dispersed in Red Petroleum, according to a previous study [16, 18-20, 57-59]. After the samples were wiped with filter paper they were weighed and measured radially, tangentially and longitudinally. The next step was to subject the samples to a hydration process in a climate chamber with a constant temperature of 20°C with a maximum humidity of 100%, until their weight become constant. The new dimensions were measured. The next step was to subject the samples to a gradual process of dehydration in the same climate chamber. They were kept inside the chamber until constant mass was achieved at different levels of humidity (85, 65,

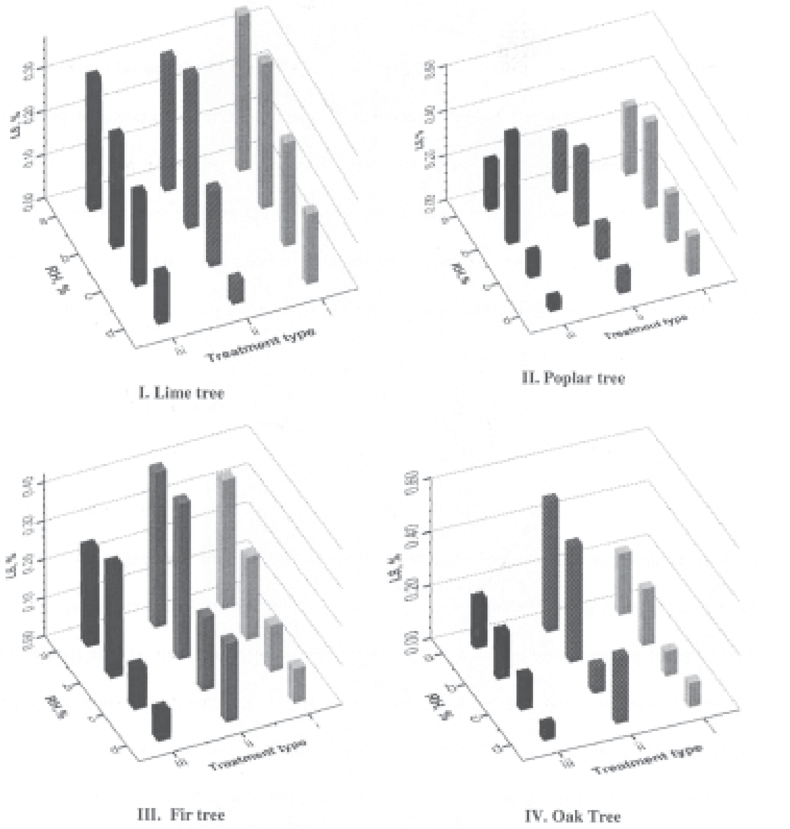

Fig. 1. Variation of longitudinal shrinkage (LS): Type of treatment with the following specifications: a - standard (no treatment); b - treated with Red Petroleum; c - treated with alcoholic solution of propolis dispersed in Red Petroleum; Relative humidity (RH) with the following specifications: a- 100%; b - 85%; c - 65%; d - 25%

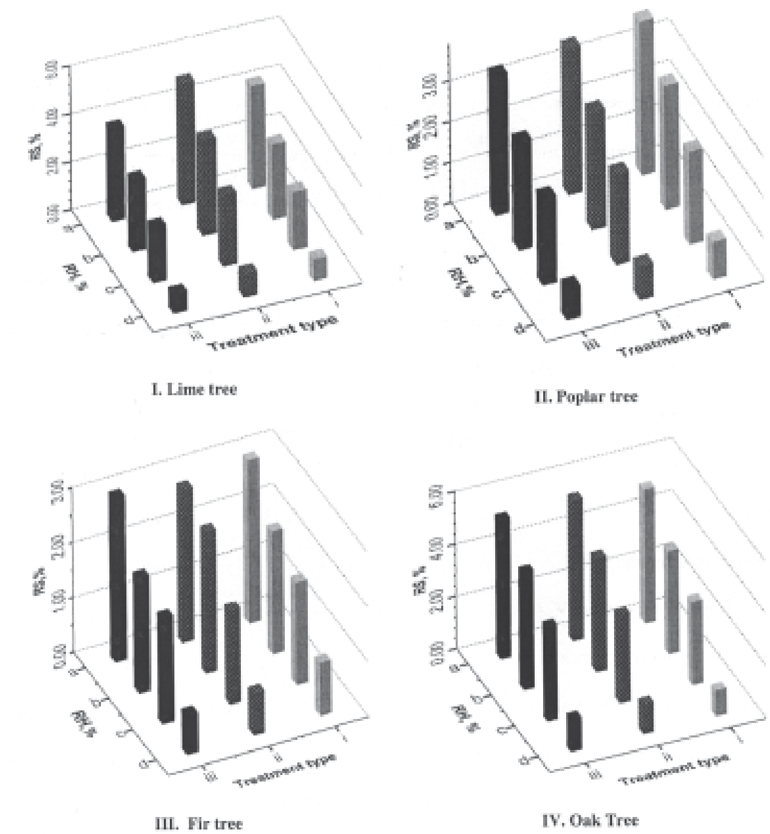

Fig. 2. Variation of radial shrinkage (RS): Type of treatment with the following specifications: a - standard (no treatment); b - treated with Red Petroleum; c - treated with alcoholic solution of propolis dispersed in Red Petroleum; Relative humidity (RH) with the following specifications: a- 100%; b - 85%; c - 65%; d - 25%

25 and 0%). The shrinkage was measured after each step of dehydration. The volume, specific weight and porosity variation were measured based on the dehydration shrinkage of the samples, by gradually transitioning through the four atmospheric humidity levels (100%→ 85%, 85% → 65%, 65% → 25%, 25%→ 0%) Two levels of relative humidity were also considered: “before treatment” and “after treatment” humidity.

Results and discussions

Figures 1, 2 and 3 show the variation of longitudinal, radial and tangential shrinkage of the four species of wood under study. The samples were treated with an alcoholic solution of propolis dispersed in Red Petroleum from Câmpeni, under the influence of environmental moisture, in comparison with the new untreated wood and wood only treated with Red Petroleum.

If we consider the linden wood, the longitudinal shrinkage of the samples treated with Red Petroleum varies

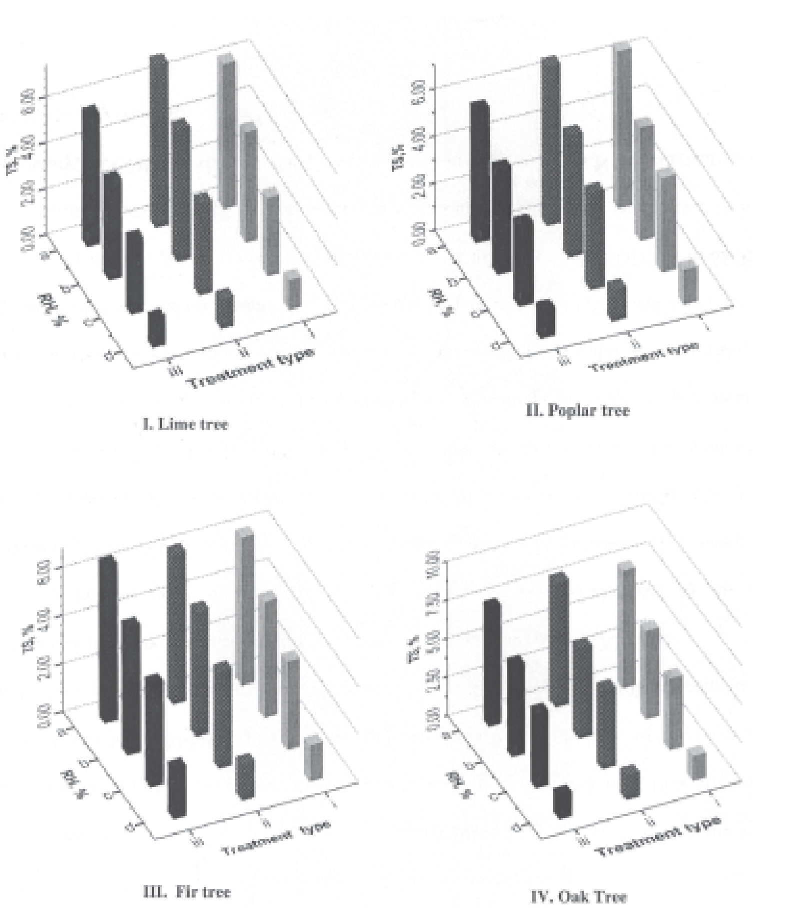

Fig. 3. Variation of tangential shrinkage (TS): Type of treatment with the following specifications: a - standard (no treatment); b - treated with Red Petroleum; c - treated with alcoholic solution of propolis dispersed in Red Petroleum; Relative humidity (RH) with the following specifications: a- 100%; b - 85%; c - 65%; d - 25%

from untreated wood (standard) and samples treated with alcoholic dispersion in Red Petroleum based on propolis. Compared to the control, which shrinks by approx. 0.20%, the samples only treated with Red Petroleum, initially expand after treatment with 0.07% and then shrink with 0.17%, whereas the samples treated with the propolis dispersion initially shrink after treatment with 0.08% and after the atmospheric humidity drops there is a final shrinkage of 0.12%.

The radial shrinkage of samples treated with Red Petroleum is higher and varies differently from untreated wood (standard) and samples treated with alcoholic dispersion of propolis in Red Petroleum. Thus, compared to the control, which shrinks by approx. 0.30%, the samples only treated with Red Petroleum, initially expand after treatment with 0.08% and then shrink with 0.36%, whereas the samples treated with the propolis dispersion initially shrink after treatment with 0.04% and after the atmospheric humidity drops there is a final shrinkage of 0.26%.

The tangential shrinkage is the largest, almost double compared to the longitudinal shrinkage and 1.5 greater than radial shrinkage. In this case, the samples treated with Red Petroleum are different from untreated wood (standard) samples and those treated with alcoholic dispersion of propolis in red petroleum. Thus, compared to the control, which shrinks by approx. 0.48%, the samples only treated with Red Petroleum, initially expand after treatment by 0.07% and then contracted by 0.55%, whereas the samples treated with the propolis dispersion initially shrink after treatment by 0.06% and after the atmospheric humidity drops there is a final shrinkage of 0.42%.

A similar analysis of other species shows that longitudinal variations are totally different and radial and tangential variations are somewhat similar. Worth noting is the fact that compared to lime tree and fir tree, the poplar and oak have small longitudinal shrinkages, whereas the radial and tangential shrinkage variations are similar to lime, poplar and fir and totally different regarding the oak.

The shrinkage difference of the three wood samples depending on each direction varied (when the atmospheric humidity dropped from 100 to 25%) according to this relation: T> R> L (table 1).

Although lime and poplar wood are soft essences in contrast to fir tree and oak, they should react to organic solution treatments in a similar manner. The experimental data in table 1 confirms this.

Shrinkage variation regarding the three directions is very different for the two groups (soft and hard essences). Thus, the most obvious poplar tangential (T) shrinkage differences grow gradually, almost linear according to the relation: i<ii<iii, while the lime tangential (T) shrinkage differences decrease according to the same relation. The fir and oak trees vary according to similar relations, the ii treatment being the one with the highest value (i and iii having extreme smaller values). The fir tree and oak have different variation regularities than the lime tree and poplar.

The poplar and fir tree behave similar radial (R) shrinkage variations in the three cases: (i) - untreated samples

Table 1
SAMPLE SHRINKAGE VARIATION (%) DEPENDING ON DIRECTION (ΔL, ΔR AND ΔT) WHEN ATMOSPHERIC HUMIDITY DECREASED FROM 100% TO 25%

Sample	ΔL (%)			ΔR (%)			ΔT (%)		
	i	ii	iii	i	ii	iii	i	ii	iii
Lime tree	0.20	0.24	0.18	3.20	4.20	3.00	6.00	5.30	4.70
Poplar	0.14	0.18	0.20	3.00	3.00	3.00	4.80	5.20	5.40
Fir	0.27	0.20	0.27	2.00	2.00	2.00	4.60	4.80	4.30
Oak	0.13	0.26	0.10	4.00	4.40	4.40	6.30	6.40	6.20

* There are three cases: i - untreated samples (standard); ii - Red Petroleum treated samples; iii - samples treated with propolis alcoholic solution dispersed in Red Petroleum

Table 2
RATIO VALUES OF SHRINKAGE DIFFERENCES RELATIVE TO THE THREE DIRECTIONS

Wood species	Type of treatment *	Shrinkage difference ratio for the three directions		
		ΔT/ΔL	ΔR/ΔL	ΔT/ΔR
Lime tree	i	28.57	15.24	1.88
	ii	22.08	17.50	1.26
	iii	26.67	16.67	1.60
Poplar tree	i	34.29	21.43	1.60
	ii	28.89	16.67	1.73
	iii	27.00	15.00	1.80
Fir tree	i	17.04	7.41	2.30
	ii	24.00	10.00	2.40
	iii	21.50	10.50	2.05
Oak tree	i	48.46	30.77	1.58
	ii	24.62	16.92	1.45
	iii	62.00	44.00	1.41

* There are three cases: i - untreated samples (standard); ii - Red Petroleum treated samples; iii - samples treated with propolis alcoholic solution dispersed in Red Petroleum

(standard); (ii) - samples treated with Red Petroleum; (iii) - samples treated with propolis alcoholic solution dispersed in Red Petroleum). Compared to the other two essences, the lime tree has a maximum value for (ii), while oak has maximum values for (ii) and (iii).

Longitudinal shrinkage (L) has very small difference values, about 25 ... 30 times smaller than the tangential shrinkage (T), with some exceptions in oak: 10 to 18 times smaller values than radial shrinkage (R). In case of the poplar, these differences in shrinkage increases almost linearly for the three groups, while lime and oak have a maximum value for (ii) while the fir tree has a minimum value.

Oak and fir tree samples, which have higher density, interacted more strongly with the organic solutions used in the experiment, so their dimensional characteristics varied differently and between broader value intervals. The difference between the behaviour of the three samples in relation to the three directions was due to the internal structure and dispersion compatibility of the systems used in the experiment with the volatile components of the four essences.

Table 2 presents a new dimensionless chemometric mode of highlighting treatment impact on differential shrinkage characteristic of each of the three directions, when transitioning from an atmospheric humidity (RH) of 100% to an atmospheric humidity of 25%, using the in-between ratio values. The obtained values confirm specific behaviours that are very different from one essence to another and vary according to the same regularities based on the data of table 1.

In case of the lime tree, ΔT/ΔL and ΔT/ΔR have minimum values for (ii) while ΔR/ΔL has maximum values.

In case of the poplar tree, ΔT/ΔL has gradually declining values and a bit higher than the lime and fir tree, while ΔT/ΔR and ΔR/ΔL are similar, the first ration having an almost linear increase and second an almost linear decrease. Compared to the other samples, the oak tree has higher ΔT/ΔL and ΔR/ΔL values and lower ΔT/ΔR values. In case of treatment (ii) all values are low.

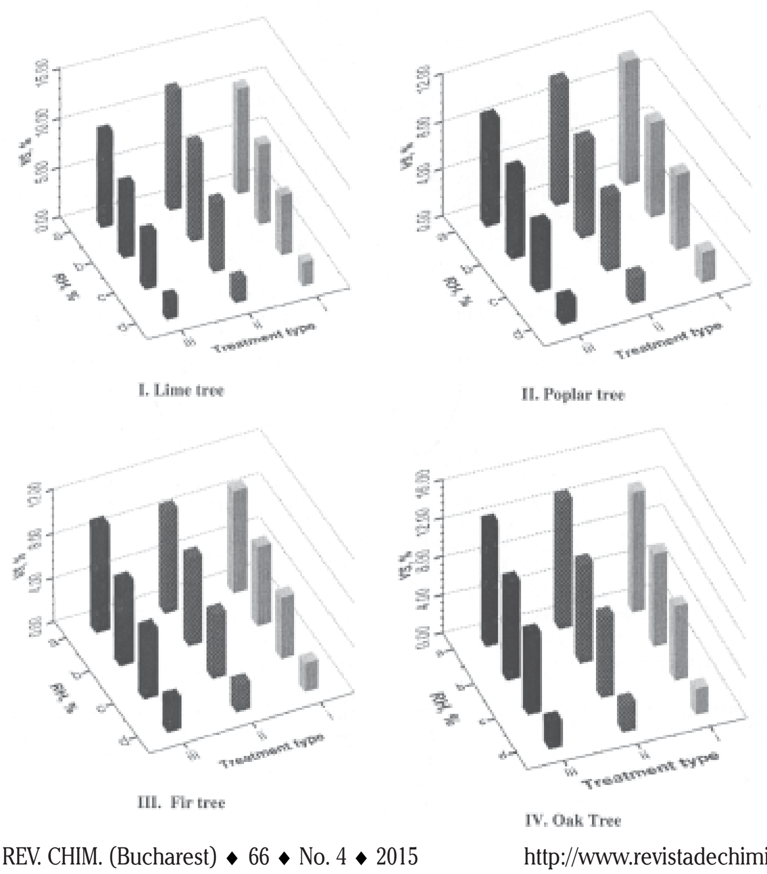

Fig. 4. Volume shrinkage variations (VS): Type of treatment with the following specifications: a - standard (no treatment); b - treated with Red Petroleum; c - treated with alcoholic solution of propolis dispersed in Red Petroleum; Relative humidity (RH) with the following specifications: a- 100%; b - 85%; c - 65%; d - 25%

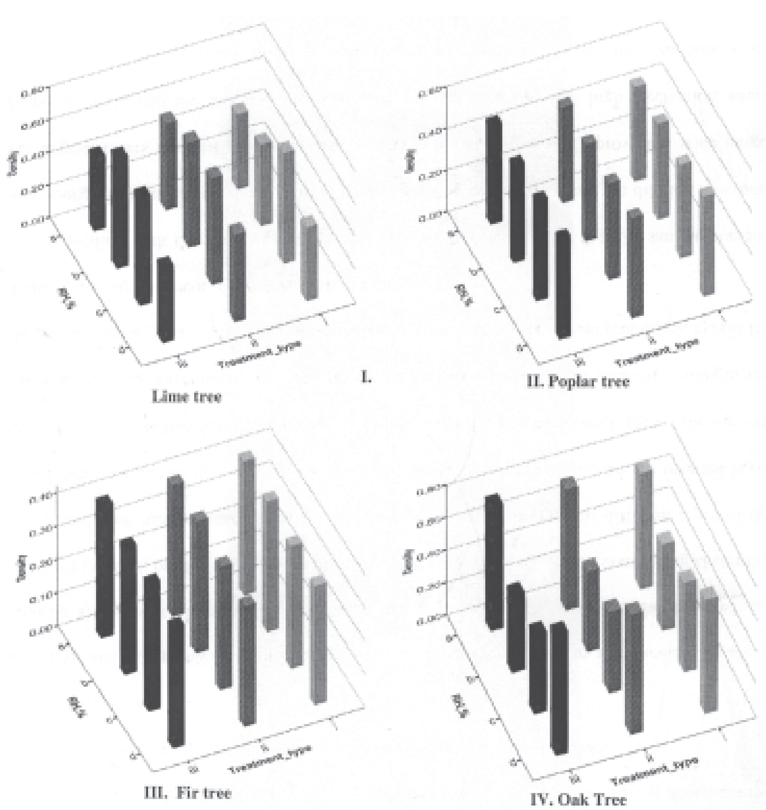

Fig. 5. Specific gravity or density variations (ρ):
Type of treatment with the following specifications: a - standard (no treatment); b - treated with Red Petroleum; c - treated with alcoholic solution of propolis dispersed in Red Petroleum;
Relative humidity (RH) with the following specifications: a- 100%; b - 85%; c - 65%; d - 25%

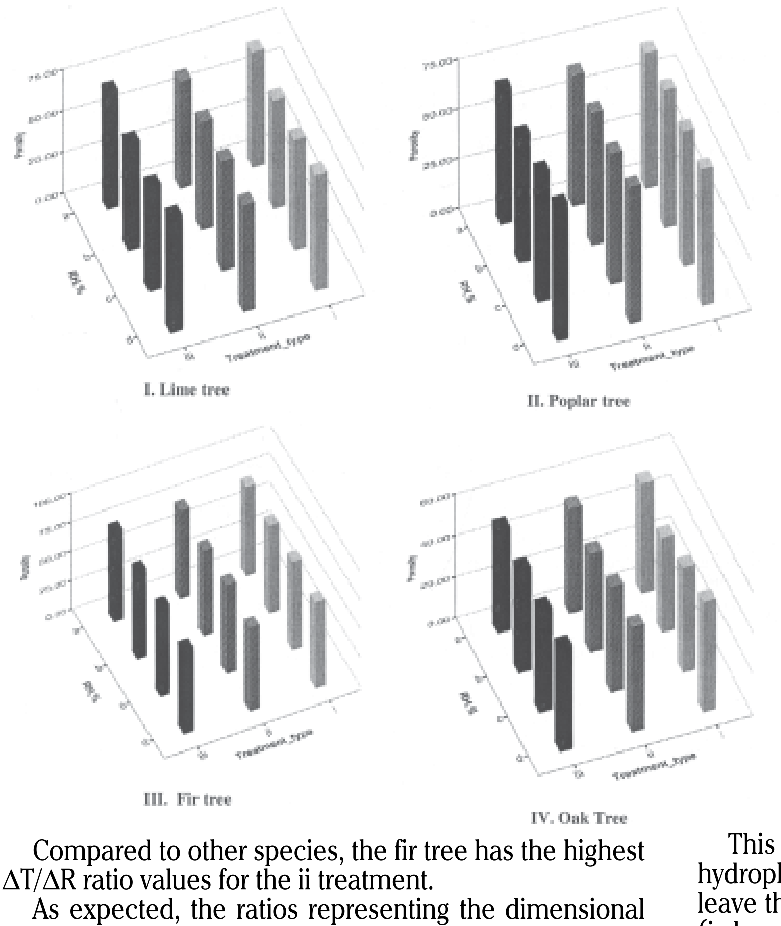

Fig. 6. Porosity variation (p):
Type of treatment with the following specifications: a - standard (no treatment); b - treated with Red Petroleum; c - treated with alcoholic solution of propolis dispersed in Red Petroleum;
Relative humidity (RH) with the following specifications: a- 100%; b - 85%; c - 65%; d - 25%

Compared to other species, the fir tree has the highest $\Delta T/\Delta R$ ratio values for the ii treatment.

As expected, the ratios representing the dimensional shrinkage differences for the three directions varies from one species to another, whereas the penetration and wood retention of organic solutions after the treatment depends on the density and porosity of the wood, the nature of volatile components remaining after fluid stabilization, the state of wood preservation and others. These characteristics induce different speeds of penetration and retention from one species to another.

This explains the fact that after the treatment, most hydrophobic activated components of the Red Petroleum leave the matrix system of wood while propolis and wax (in low concentration) form a thin membrane on the wood cell surface that is permeable for reverse circuit water.

For better measuring of the treatment and RH influence over dimensional shrinkage of the four species samples, volume, density and porosity shrinkage were analysed when passing from air humidity (RH) of 100 to 25%. These features should correlate the regularities of variation for each species.

Species	Type of treatment *	Shrinkage difference (%) for		
		Volume (ΔV)	Density (Δρ)	Porosity (Δp)
Lime tree	i	7.50	0.21	2.64
	ii	9.50	0.14	3.34
	iii	6.50	0.26	2.29
Poplar tree	i	7.10	0.00	1.44
	ii	7.10	0.00	1.44
	iii	7.10	0.00	1.44
Fir tree	i	6.50	0.06	0.50
	ii	6.70	0.03	3.00
	iii	6.80	0.01	5.00
Oak tree	i	9.00	0.03	0.40
	ii	10.20	0.01	1.20
	iii	9.50	0.02	0.80

* There are three cases: i - untreated samples (standard); ii - Red Petroleum treated samples; iii - samples treated with propolis alcoholic solution dispersed in Red Petroleum

Table 3
SHRINKAGE VARIATION DIFFERENCES* FOR VOLUME (ΔV) SHRINKAGE (%), DENSITY (Δρ) AND POROSITY (Ap) FOR THE FOUR SPECIES OF WOOD WHEN ATMOSPHERIC HUMIDITY DECREASED FROM 100% TO 25%

Thus, figures 4, 5 and 6 show the shrinkage variations of volume (V), density (ρ), and porosity (p) for the four wood species under study, after conducting the 30% alcoholic solution of propolis dispersed in Red Petroleum treatment (volumetric ratio of alcohol solution: Red Petroleum = 1:5), under the influence of environmental humidity, as compared to the untreated fresh wood.

Using the same chemometric analysis approach, table 3 presents the data on shrinkage variation differences * (%) for volume (ΔV), density (Δρ) and porosity (Δp) of the four species of wood when the atmospheric humidity decreases from 100 to 25%.

The analysis of these data shows that the poplar tree is virtually unaffected by the two treatments, the lime tree is slightly influenced, while the fir tree and oak tree are the most affected, because the used solutions easily dissolve their organic components (ex. fir tree's resin and terpineol and oak tree's tannins or other glucoses). These components leave the resinous channels and pores of the oak tree, thus changing the specific weight and porosity. This is attributed to the strong penetration of the two solutions. After the dissolution of the organic components present in natural wood, these solutions create a nano-coating on the surface of the anatomical elements. These nano-coatings will confer detectable behaviours only to the wood species containing volatile components that are not compatible with the studied organic solutions. The behaviours can be detected during the interactions of the above mentioned wood species with the hygroscopic moisture in the atmosphere.

Conclusions

Based on studies regarding shrinkage due to the reduction of atmospheric moisture and as a result of treatments involving ethanol-based solutions and Red Petroleum, multiple conclusions may be drawn regarding the four indigenous species of wood (lime tree, poplar tree, fir tree and oak tree).

In case of the lime tree, the samples longitudinally treated with Red Petroleum are different from untreated wood (standard) samples and those treated with propolis alcoholic dispersion in Red Petroleum solution. The *radial shrinkage* is similar. The tangential shrinkage is the largest, almost double compared to the longitudinal shrinkage and 1.5 greater than radial shrinkage.

A similar analysis of other species shows that longitudinal variations are totally different and radial and tangential variations are somewhat similar. Worth noting is the fact that compared to lime tree and fir tree, the poplar and oak have small longitudinal shrinkages, whereas the radial and tangential shrinkage variations are similar to lime, poplar and fir and totally different regarding the oak.

All essences show shrinkage in all three directions (when the atmospheric humidity decreases from 100% to 25%) according to the relation: T>R>L.

The lime tree and poplar tree are considered softwood and react differently than the pine tree and oak tree. Tangential shrinkage differences the biggest, which gradually grow, almost linearly, in case of the poplar tree, according to the relation: i<ii<iii (*i - untreated samples (standard); ii - Red Petroleum treated samples; iii - alcoholic propolis dispersion in Red Petroleum solution*). In case of the lime tree the relation decreases in a similar way. The fir tree and the oak tree shrinkages vary in a similar manner: i<iii<ii.

The poplar and fir tree have similar radial (R) shrinkage variations, the lime tree has a maximum shrinkage in case of treatment (ii) and the oak tree in case of treatments (ii) and (iii).

Longitudinal shrinkage (L) has very small difference values, about 25 ... 30 times smaller than the tangential shrinkage (T), with some exceptions in oak: 10 to 18 times smaller values than radial shrinkage (R). In case of the poplar, these differences in shrinkage increases almost linearly for the three groups, while lime and oak have a maximum value for (ii) while the fir tree has a minimum value.

The difference between the behaviour of the three samples in relation to the three directions was due to the internal structure and dispersion compatibility of the systems used in the experiment with the volatile components of the four essences.

Thus, considering the two analyses groups (longitudinal, radial and transversal shrinkage and volume, density and porosity variation), wood behaviour can be easily evaluated using specific chemometric characteristics such as: variation differences in the three directions (ΔL, ΔR and ΔT), their ratios (ΔT/ΔL, ΔR/ΔL, ΔT/ΔR) and differences in volume, density and porosity variation (ΔV, Δρ, Δp) when transitioning from an atmospheric humidity of 100 to 25%

As expected, the ratios representing the dimensional shrinkage differences for the three directions varies from one species to another, whereas the penetration and wood retention of organic solutions after the treatment depends on the density and porosity of the wood, the nature of volatile components remaining after fluid stabilization, the state of wood preservation and others. These characteristics induce different speeds of penetration and retention from one species to another. This explains the fact that after the treatment, most hydrophobic activated components of the

Red Petroleum leave the matrix system of wood while propolis and wax (in low concentration) form a thin membrane on the wood cell surface that is permeable for reverse circuit water.

For better measuring of the treatment and RH influence over dimensional shrinkage of the four species, volume, density and porosity shrinkage were analysed when passing from air humidity (RH) of 100 to 25%, cumulating the shrinkage related to the tree directions (longitudinal, radial and transversal).

The analysis of these data shows that the poplar tree is virtually unaffected by the two treatments, the lime tree is slightly influenced, while the fir tree and oak tree are the most affected, because the used solutions easily dissolve their organic components (ex. fir tree resin and terpineol and oak tree tannins or other glucoses).These components leave the resinous channels and pores of the oak tree, thus changing the specific weight and porosity. This is attributed to the strong penetration of the two solutions. After the dissolution of the organic components present in natural wood, these solutions create a nano-coating on the surface of the anatomical elements. These nano-coatings will confer detectable behaviours only to the wood species containing volatile components that are not compatible with the studied organic solutions. The behaviours can be detected during the interactions of the above mentioned wood species with the hygroscopic moisture in the atmosphere.

References

1.SANDU, I., SANDU, I.C.A., Chemistry of Conservation and Restoration, Ed. Corson, Iasi, 2002.

2.SANDU, I.C.A., Sandu, I., Luca, C., Modern Aspects of Cultural Heritage Conservation, Vol. II, Ed. Performantica, Iasi, 2005.

3.SANDU, I., Modern Aspects of Cultural Heritage Conservation**,** Vol. V, Ed. Performantica, Iasi, 2007.

4.SANDU, I., Degradation and Deterioration of the Cultural Heritage, Vol. II, "Al.I.Cuza" University Publishing House, Iaşi, 2008.

5.KNUT, N., The Restoration of Paintings, Ed. Konemann, Verlagsgeselshaft GmbH, Erfuhrt, Cologne, 1999.

6.HORIE, C.V., Materials for conservation: Organic consolidators, adhesives and coatings, Ed. Butterworths, London, 1987.

7.MATTEINI, M., MOLES, A., La Chimica nel Restauro. I materiali dell'arte pittorica, Ed. Nardini, Firenze, 1989.

8.STOUT, G., Museum, **8**, No. 5, 1955, p. 139.

9.CASTELLI, C., CIATTI, M., PARRI, M., SANTACESARIA, A., Considerazioni e novita sulla costruzione dei supporti lignei nel quattrocento, OPD Restauro (Rivista delle Opificio delle Pietre Dure e Laboratorio di Restauro di Firenze), **9,** 1997, p. 162.

10.CASTELLI, C., Techniques of Construction of Wood Supports for Panel Painting, Panel Painting: Technique and Conservation of Wood Supports, Edifir, Florence, Italy, 2006, p. 81.

11.BREWER, A., The effects of reinforcements on the preservation of paintings on wood panels: Introduction and results of research on unreinforced panels, Hamilton Kerr Institute Bulletin**,** No 3, (Editor Massing, Ann), University of Cambridge. Hamilton Kerr, Institute, Cambridge, 2000, p. 41.

12.TAUBE, E., Querleisten an Holztafelbildern, Zeitschrift für Kunsttechnologie und Konservierung, **19**, No 2, 2005, p. 231.

13.WADUM, J., Mikroklimavitrinen ohne Feuchtigkeitspuffer, **106**, No. 2, 2000, p. 96.

14.HAYASHI, M., VASILACHE, V., MACCHIONI, N., CAPRETTI, C., SANDU, I., Impact of moisture conditioning on polychrome wood with artificial tempera, in Cultural Heritage Meet Practice (Editors: J. Kolar and M. Strlic), Proceeding of 8th European Conference on Research for Protection, Conservation and Enhancement of Cultural Heritage, Ed. National and University Library, Ljubljana, 2008, p. 94.

15.HAYASHI, M., SANDU, I., CIOCAN, A., VASILACHE, V., SANDU, I.C.A., The impact of some active compounds implied in the preservation, upon physical-structural wood's Characteristics, in 7th International Conference Wood Science and Engineering in the Third Millennium – ICWSE 2009", Transilvania University Press, Braşov, 2009, p. 441.

16.HAYASHI, M., SANDU, I., TIANO, P., MACCHIONI, N., The Effect of Preservative Intervention on the Chemical-Physical and Structural Characteristics of Panel Painting, "Al.I.Cuza" University Publishing House, Iaşi, 2010.

17.HAYASHI, M., MACCHIONI, N., TIANO, P., YOSHIDA, N., SANO, C., SANDU, I., The Effect of Traditional Preservative Interventions for Panel Painting, Hozon Kagaku (Science for Conservation), **49**, 2010, p. 197.

18.SANDU, I., VASILACHE, V., SANDU, I.C.A., HAYASHI, M., Rev. Chim. (Bucharest), **61**, no. 12, 2010, p. 1212.

19.VASILACHE, V., SANDU, I., LUCA, C., SANDU, I.C.A., New in Scientific Conservation of Old Polychrome Wood, Ed. Universitãii Alexandru Ioan Cuza Iasi, 2009.

20.VASILACHE, V., SANDU, I.C.A., CIOCAN, A., SANDU, I., HAYASHI, M., Retention of permethrin-Red Petroleum system during the wood process of preservation, in 7th International Conference Wood Science and Engineering in the Third Millennium – ICWSE 2009, Transilvania University Press, Braşov, 2009, p. 466.

21.HUNTER, A.J., Equilibrium moisture content and the movement of water through wood above fibre saturation, Wood Science and Technology, **29,** 1995, p. 129.

22.SIAU, J.F., Wood—Influence of Moisture on Physical Properties, Virginia Polytechnic Institute and State University, Blacksburg, VA, 1995

23.INAGAKI, T., YONENOBU, H., TSUCHIKAWA S., NIR Spectroscopic Monitoring of Water Adsorption/Desorption Process in Modern and Archaeological Wood, in Conference Proceedings. Wood Science for the Conservation of Cultural Heritage, 5-7 November, Braga 2008. Firenze University Press, 2010, p. 199.

24.KLEIN, P., BRÖKER, F.W., Investigation on Swelling and Shrinkage of Panels with Wooden Supports, ICOM Committee for Conservation 9th Triennial Meeting, Dresden, German Democratic Republic, 26-31 August 1990, Preprints, vol. 1, (Editor: K. Grimstad), 1990, p. 41.

25.GRABNER, M., KOTLINOVA, M., Ageing of Wood – Described by the Analysis of Old Beams, in Conference Proceedings. Wood Science for the Conservation of Cultural Heritage, 5-7 November, Braga 2008. Firenze University Press, 2010, p. 42.

26.KAWAI, S., YOKOYAMA, M., MATSUO, M., SUGIYAMA, J., Research on the Ageing of Wood in RISH, in Conference Proceedings. Wood Science for the Conservation of Cultural Heritage, 5-7 November, Braga, 2008. Firenze University Press, 2010, p. 52.

27.ALTAMURA, M.L., BELLUCCI, R., CASTELLI, C., CIATTI, M., FROSININI, C., NIERI, P., PARRI, M., ROSSI, E., SANTACESARIA, A., La pittura a Pisa nel Duecento: osservazioni sulla tecnica artistica, OPD Restauro **(**Rivista dell'Opificio delle Pietre Dure e Laboratorio di Restauro di Firenze), **17**, 2005, p. 239.

28.BISACCA, G., DE LA FUENTE MARTINEZ, J., The Treatment of Durer's Adam and Eve Panels at the Prado Museum, Facing the Challenges of Panel Painting Conservation: Trends, Treatments, and Training, in The Proceedings of a Symposium at the Getty Centre, 17-18 May 2009. (Editors: Phenix, Alan and Chui, Sue Ann), The Getty Conservation Institute, Los Angeles, California, 2011, p. 10.

29.HOADLEY, R.B., Chemical and Physical Properties of Wood, The structural Conservation of Panel Paintings, in The Proceedings of a Symposium at the J. Paul Getty Museum, 24-28 April 1995. (Editors: Dardes, Kathleen and Rothe, Andrea), The Getty Conservation Institute, Los Angeles, California, 1998, p. 2.

30.MAZZANTI, P., UZIELLI, L., Strength and MOE of Poplar Wood (Populus Alba L) Across the Grain: Experimental Data, in Conference Proceedings. Wood Science for the Conservation of Cultural Heritage, 5-7 November, Braga, 2008, Firenze University Press, 2010, p. 62.

31.RIEF, M., Eingekerbte Hausmarken auf baltischen Wagenschott-Brettern des 14-16, Jahrhunderts, Zeitschrift für Kunsttechnologie und Konservierung, **20**, No. 2, 2006, p. 309.
32.KRETSCHMANN, D.E., Material Mechanical Properties of Wood, in Wood Handbook- Wood as an Engineering Material, Forest Products Laboratory, United States Department of Agriculture Forest Service, Madison, Wisconsin, 2010.
33.DINWOODIE, J.M., Timber Its Nature and Behaviour, E & FN Spon, London, 2000.
34.FUESERS, O., KRIEG, V., KÜHNEN, R., Studie zum hygroskopischen Verhalten von Holz: Dehnungsmessstreifen zur Dokumentation von Materialeigenschaften, Zeitschrift für Kunsttechnologie und Konservierung, **19**, No. 1, 2005, p. 129.
35.RIJSDIJK, J.F., LAMING, P.B., Physical and Related Properties of 145 Timbers, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1994
36.RICHARD, M., Further Studies on the Benefits of Adding Silica Gel to Micro-climate Packages for Panel Paintings, Facing the Challenges of Panel Painting Conservation: Trends, Treatments, and Training, in The Proceedings of a Symposium at the Getty Centre, 17-18 May 2009. (Editors: Phenix, Alan and Chui, Sue Ann). The Getty Conservation Institute, Los Angeles, California, 2011, p. 140.
37.BOUCHAIR, A. VERGNE, A., An application of Tsai criterion as a plastic flow law for timber bolted modelling, Wood Sci. Technol., **30**, No. 1, 1995, p. 3
38.CHEUNG, C.K., SORENSEN, H.C., Effect of axial loads on radial stress in curved beams, Wood Fibre Sci., **15**, No. 3, 1983, p. 263.
39.PELLICANE, P.J., FRANCO, N., Modelling wood pole failure. Part 1: Finite element stress analysis, Wood Sci. Technol., **28**, No. 3, 1994, p. 219.
40.ZALPH, B.L., MCLAIN, T.E., Strength of wood beams with fillet interior notches: A new model, Wood Fiber Sci., **24**, No. 2, 1992, p. 204.
41.ZANDBERG, J.G., SMITH, F.W., Finite element fracture prediction for wood with knots and cross grain, Wood Fiber Sci., **20**, No. 1, 1988, p. 97.
42.ANKERSMIT, B., KRAGT, W., VAN LEEUWEN, I., GOMBAUD, C., The climate in pastel micro-climate cardboard boxes when exposed to fluctuating climates, in Preprints to the ICOM- CC 16th Triennial Conference Lisbon, 19-23 September 2011, 2011.
43.BRATASZ, L., KOZLOWSKI, R., KOZLOWSKA A., Conservation of the Mazarin Chest: Structural Response of Japanese Lacquer to Variations in Relative Humidity, in ICOM Committee for Conservation 15th Triennial Meeting, 22 to 26 September 2008, New Delhi, India, Vol. 2, 2008, p. 1086.
44.MILLER, M.A., Marvelseal Envelopes at the Metropolitan Museum of Art, Facing the Challenges of Panel Painting Conservation: Trends, Treatments, and Training, in The Proceedings of a Symposium at the Getty Centre, 17-18 May 2009 (Editors: Phenix, Alan and Chui, Sue Ann). The Getty Conservation Institute, Los Angeles, California, 2011, p. 207.
45.TOLVAJ, L., MOLNAR, S., Photo degradation and Thermal Degradation of Outdoor Wood, in Conference Proceedings. Wood Science for the Conservation of Cultural Heritage, 5-7 November, Braga, 2008, Firenze University Press, 2010, p. 67.
46.ALLEGRETTI, O., RAFFAELLI, F., Barrier effect to water vapour of early European painting materials on wood panels, Studies in Conservation, **53**, No. 3, 2008, p. 187.
47.DIONISI VICI, P., MAZZANTI P., UZIELLI, L., Mechanical response of wooden boards subjected to humidity step variations: climatic chamber measurements and fitted mathematical models, Journal of Cultural Heritage, **7**, 2006, p. 37.
48.FRAGIACOMO, M., FORTINO, S., TONONI, D., USARDI. I., TORATTI, T., Moisture-Induced Stresses Perpendicular to Grain in Cross-Sections of Timber Members Exposed to Different Climates, Engineering Structures, **33**, 2011, p. 3071.
49.DVINSKIKH, H.S.V., MENDICINO, M., FORTINO, A.L., TORATTI, T., NMR Imaging Study and Multi-Fickian Simulation of Moisture Transfer in Norway Spruce Samples, Engineering Structures, **33,** 2011, p. 3079.
50.SANDU, I., LUPASCU, T., SANDU, I.C.A., LUCA, C., SANDU, I.G., VASILACHE, V., HAYASHI, M., Ecological organic solution for the treatment against insects and fungal attack of the old wood-made artefacts, in Proceedings of the International Conference on Ecological Materials and Technologies ECOMAT 2008, Ed. Printech, Bucureşti, 2008, p.79.
51.SANDU, I., LUPASCU, T., SANDU, I.C.A., LUCA, C., VASILACHE, V., SANDU, I.G., HAYASHI, M., SANDU, A.V., CIOBANU, M., Method for determining the normal range of variation of hydric equilibrium, Patent MD5651G2/15.07, 2008.
52.SANDU, I., VASILACHE, V., SANDU, I.C.A., HAYASHI, M., CIOCAN, A., A new method for determination of the normal range of variation of the hydrous equilibrium for wood, in 7th International Conference Wood Science and Engineering in the Third Millennium – ICWSE 2009", "Transilvania" University Press, Braşov, 2009, p. 471.
53.1.SANDU, I., LUPASCU, T., SANDU, I.C.A., LUCA, C., SANDU, I.G., VASILACHE, V., HAYASHI, M., CIOBANU, M., New method for the evaluation of the characteristics on the old wood used in preservation process and authentication, Proceedings of the 2nd International Conference Advances Materials and Systems – ICAMS, Certex, Bucharest, 2008, p. 490.
54.YOSHIHARA, H., OHSAKI, H., KUBOJIMA, Y., OHTA, M., Applicability of the Iosipescu shear test on the measurement of the shear properties of wood, J. Wood Sci., **45**, 1999, p. 24.
55.UNGER, A., SCHNIEWIND, A.F., UNGER, W., Conservation of Wood Artefacts: A Handbook, Springer, 2001.
56.WALKER, J.C.F., Primary Wood Processing. Principles and Practice, Springer**,** 2006, p. 69.
57.SANDU, I., LUPASCU, T., SANDU, I.C.A., VASILACHE, V., SANDU, I.G., BOTAN, V., SANDU, A.V., CIOCAN, A.C., Process for Insectofungicization and Fireproofing of Age-old Artworks, Patent MD4018(G2)/2010.02.26, 2010.
58.SANDU, I., LUPASCU, T., LUCA, C., SANDU, I.C.A., LUCA, C., VASILACHE, V., HAYASHI, M., VLAD, F.D., SANDU, I.G., Insectofungicidal Composition as an Alcohol Solution and Process for Preparing The Same, PatentRO123353 (B1)/2011-10-28, 2011.
59.SANDU, I.C.A., VASILACHE, V., SANDU, I., VRINCEANU, N., SANDU, I.G., CIOCAN, A.C., SANDU, A.V., Process for actively preserving old water-soaked wood, involves submerging the wood into petroleum-based organic solutions containing specified amounts of tannin and propolis, Patent RO126102-A2/2011-03-30, 2011.
60.SANDU, I., SCUTĂRITA (GHERMAN), L.G., CRISTACHE, M., HAYASHI, M., SANDU, I.C.A., VASILACHE, V., Applications of the normal range of hydric-equilibrium variation in old wood, Proligno, **9**, No. 4, 2013, p. 276
61.PRUTEANU, S., VASILACHE, V., SANDU, I.C.A., BUDU, A.M., SANDU, I., Assessment of Cleaning Effectiveness for New Ecological Systems on Ancient Tempera Icon by Complementary Microscopy Techniques, Microscopy Research and Techniques, **77**, No. 12, 2014, p. 1060.
62.PRUTEANU, S., SANDU, I., TIMAR, M.C., MUNTEANU, M., VASILACHE, V., SANDU, I.C.A., Rev. Chim. (Bucharest), **65,** no. 12, 2014, p. 1467.
63.PRUTEANU, S., SPIRIDON, P., VASILACHE, V., SANDU, I., Ecological cleaning systems for old icons painted in tempera, Chemistry Journal of Moldova, **9**, No. 2, 2014, p. 26.

Manuscript received: 22.12.2014