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The Effect of Preservative Interventions on the Chemical-Physical and Structural Characteristics of Panel Painting

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Abstract

This work studies the impact of two traditional Romanian treatments, Red Petroleum and Propolis, in terms of real efficiency and consequence on the wooden artifacts. The application of these solutions is still a widely adopted and popular technique in preservative conservation but the impact of these solutions is not well known. It is important to know the effect of treatments on chemical-physical and structural characteristics of the artifacts, not only for understanding the influence on present conditions but also for foreseeing the future behavior. These treatments with Romanian traditional products are compared with a commercial antifungal product, Biotin R, which is utilized as reference to control the effectiveness of Red Petroleum and Propolis.

Colour is measured before and after treatments and during the exposure at different RH (100% - 65% 25%) at constant temperature (20 °C). The colour in panel painting has a fundamental importance during the process of conservation and restoration. It is one of the most vital missions to keep original colour as much as possible in conservation and restoration processes. The penetration of solutions (Red Petroleum and Propolis) is fully characterized by FTIR-ATR analysis, providing suitable markers for the identification of the solutions. Treatment by immersion has impact on wood physical parameter while treatment by brushing does not have significant impact.

Red Petroleum and Propolis are not active against mould while Biotin R is very active. Mould attack is mostly concentrated in the painted layer, where the tempera, containing glue and egg, enhance nutrition availability for moulds. Biotin R, even if is not a real insecticide but a fungicide, was the most active product against insect attack of the three products, followed by Red Petroleum, Propolis and untreated reference.

As for colour, varnish does not affect it, while there are some differences after treatments application. Colour did not change so much after the application of Red Petroleum and Biotin R and the colour difference was almost not perceptible. On the contrary, Propolis affected the colour a lot. During the exposure at different RH, the colour changes significantly at 100% RH at equilibrium and this is mainly due to the mould attack.

Red Petroleum penetrates deeply into wood, while Propolis does not penetrate and remains only on the surface. However, Red Petroleum does not interact chemically with wood substance and it is easy volatilized in oven-dry condition. On the contrary Propolis interacts chemically with wood substance and hardly volatilized, even in oven-dry condition and consequently Propolis remains where it penetrated, mostly on the surface.

Treatment by immersion has impact on wood physical parameters while treatment by brushing does not have significant impact. Especially Red Petroleum has an apparent impact on moisture content (MC) due to the penetration of solution, while Propolis does not penetrate so much and remains only on surface therefore Propolis does not have so much impact as Red Petroleum. However, if the weight of the solution penetrated in wood is eliminated, there is not significant difference in MC between treated and untreated samples. Considering physical parameters, dimensional stability is an important parameter. The variation of wood moisture content causes shrinkages/swelling of the wood that polychrome layer can only partially follow. The dimension of wooden supports varied under different moisture conditioning; the painted layer cannot completely follow this deformation, and consequently a degradation and deterioration caused by detachment, occurs. That detachment affects the polychrome stratification of the panel painting and eventually the connections between the different layer compositions of the panel painting.

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CHAPTER 1: INTRODUCTION

1.1 Need and issues for preservative interventions for panel paintings

For this thesis, *preservative intervention* is defined as preventive conservation for wooden support by use of treatment solutions in order to conserve panel paintings in good condition or not to get them in worse condition for panel painting. Physical parameters (density, porosity, shrinkage and moisture content) are indicators for evaluating the effectiveness after treatment, through the comparison with the same parameters measured before the treatments.

Panel paintings are essential components of Cultural Heritage all over the world (Arbizzan 2004). Especially in Romania, icons are one of the most important heritages. Recently their protection and conservation has become more and more important, and scientific analysis can offer the physical, chemical and structural characterization of the material composing panel paintings.

Wooden support is the main material for panel paintings. The most important part is surely a painted layer, but the painted layer cannot exist without a support: the artifact is a unique composed object, made of a wooden support and a composed painted layer, which are inseparable. This material (wood) reacts to the environment, in which it is conserved. It expands and contracts as the temperature increases or decrease respectively. Furthermore, as many hygroscopic materials, it will adsorb water vapor when the relative humidity (RH) increases, which will cause it to expand. On the contrary when the RH decreases, it will release moisture, causing a contraction. Wood is extremely sensitive to RH (more than to temperature), however, not all materials expand and contract at the same rate. Thus, stresses are created at the interfaces between different materials, such as the stratifications present in a panel painting, as they push and pull against each other. Over time, these stresses can cause the deterioration of panel paintings.

Taking into account that, preventive conservation is ideal, it is necessary to improve storage conditions of panel paintings, in order to avoid the necessity of restoration. The condition of storage (factors of environment) consist of all the factors around or surrounding the panel painting. These elements should not be allowed to influence panel paintings in a negative way. In Romania many panel paintings lay in uncontrolled conditions, inside historic buildings (museums, churches, monasteries and storages), where it is very difficult to constantly maintain the climate condition, even if they are equipped with a climate control system. Variations of temperature and RH are principle hazards for preservation of panel paintings. In that case, treatment interventions can be necessary for their longevity and durability.

Investigation of the response of wood to the variations of RH showed that the external zone of wooden supports, at least to the depth of several millimeters, continuously absorbs and releases water vapor, which results in a gradient of moisture content and stress development (Time 2002; Jakiela 2007) The most extensive efforts to determine the response of the wood to fast RH variations have been undertaken so far in the context of conservation science. Dionisi Vici et al. (2006) have reported an extensive research on wooden boards 4 cm thick, simulating the supports of panel paintings, subjected to different RH. Jakiel et al. (2007) have found that the systematic numerical modeling of the moisture changes and resulting stress field has provided insight into the response of wooden cylinder, an important case imitating wooden sculptures. Due to the climatic condition, wooden support is under the hazard of a biological attack, by insects and fungi.

1.2 Scope of thesis

There are numerous preservative solutions to treat panel painting; however, there are few published resources that show the impact of traditional Romanian treatments such as Red Petroleum and Propolis used for the conservation interventions. The advantage of these solutions is considered ecological, lower cost and without health risks (Sandu 2008). The application of these solutions is still a widely adopted and popular technique in preservative conservation but the impact of these solutions, in terms of real efficiency and consequence on the artifacts, is not well known. It is important to know the effect of treatments on chemical-physical and structural characteristics of the artifacts, not only for understanding the influence on present conditions but also for foreseeing the future behavior.

These treatments with Romanian traditional products were compared with a commercial antifungal product, Biotin R and it was utilized as reference control of effectiveness of Red Petroleum and Propolis for mould and insect attack.

Experiments were conducted on wood samples made of fir (*Abies alba* Mill.), poplar (*Populus* sp.), lime (*Tilia* sp.), and oak (*Quercus petraea* Liebl) because they were the most widespread and important species used to manufacture wooden supports of panel paintings. All the samples of each species were obtained from the same plank, in order to be well matched and reduce the problems due to the natural variability of wood.

This thesis will provide conservators, restorers and other preservation professionals with one of the first resources to compare the effectiveness, colour, penetration and physical parameters of the wood treated with Red Petroleum and Propolis.

CHAPTER 2: BACKGROUND

2.1 Panel painting

In this research, icons have been supposed to be a representative of panel painting in Romania. Icons play a leading role in the liturgy and became major cult object in the Orthodox Church. Its intercessory role between heaven and earth and the prayers have been made the icons a necessity for an individual to gain moral strength, salvation of the soul, and spiritual exaltation (Popovska-Korobar 2004). The icons are an integral part of public and private life and one of the most important cultural and religious heritages in Romania. The medium used in most icons is traditionally egg tempera. For this reason, small wood samples with tempera painting have been used in the experiment of this research.

2.1.1 Structure of panel painting

There is stratification in panel painting as following Fig.2.1., mainly support (wood panel), ground layer, paint and varnish layer (Gettens 1966).

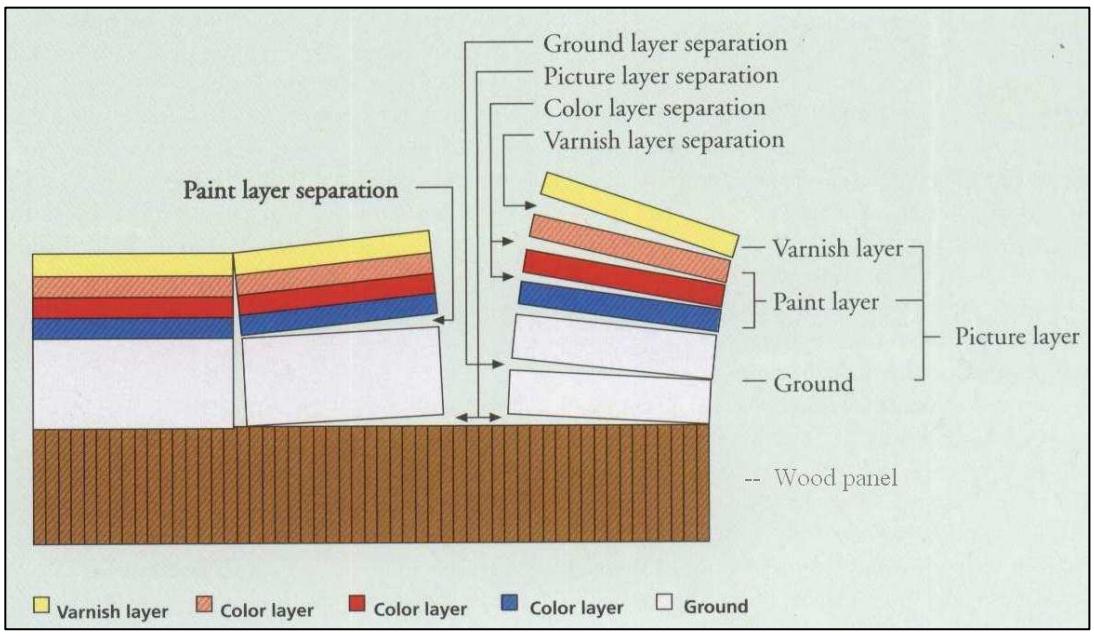


Fig.2.1. Structure of panel painting

Support refers to any material onto which paint is applied. Wood, canvas and paper are common painting support, but the type of supports used for the artwork is very variable. In this research, wood is used as a support of panel painting. Wood has served for centuries as a support for painting, largely because of its strength and availability. The support is without doubt the portion of artwork which has suffered the greatest neglect in contemporary restoration, as this inevitably tends to concentrate on the images (painted layer). However, it is extremely important to control the behavior of wood support in order to conserve panel painting in good condition.

Ground layer is applied on the support to provide a painting surface with the desired colour, texture and porosity and for egg tempera this should be a traditional gesso. This layer is a mixture of some form of whitening (in this research gypsum was used, being the most popular material for icons) rabbit skin glue and water. The support must first be sized with a layer of rabbit skin glue which acts as an isolating coat and helps to bind the gesso to the support.

Paint layer is composed by medium and pigment. Egg tempera is one of the oldest mediums in painting. It consists of dry pigment, water, egg yolk, vinegar and albumen. Medium is the vehicle that binds pigment particles together to make the paint. Egg yolk, vinegar and albumen are the medium for tempera. Pigments are not only used in tempera, but can be used for fresco, encaustic and watercolour paints as well. Painting layer is not only tempera painting but also oil painting, using pigment dispersed in oil. It is not well known how oil painting was first developed, but in Western Europe there are indications of its use from at least the 12^{th} century AD, and it was widely used from the Renaissance time.

Varnish is a final layer applied to a painting after it is finished and completely dry. It is a natural or synthetic resinous coating. Its function is:

- to protect the paint layer from dirt, dust and pollution in the environment

- to modify the optical effects of the paint surface

- to increase colour saturation

- to control the glossiness

It is important to consider that panel painting is composed by these different layers and different materials.

2.1.2 Typology of the conservation state

The resistance of the wooden panels or elements of paintings depends on the environmental agents and on the chemical or biological attack. Also species, age and complexity of the structural and functional elements are fundamental for the preservation of wood's state against the aggressiveness of the environment. In order to increase the resistance to all these agents, the present practice of restoration applies various **treatments** with multiple protection purposes: *anti-insect, anti fungal* (*mould*), *fireproofing* and *waterproofing* treatments, that should not damage the esthetical appearance and that can assure the structural stabilization and the preservation of the chromatic palette and integrity. These treatments have to be applied according to the principles of conservation, considering the age, the structural complexity and cultural value of the object.

The analysis of the conservation state of wooden objects deals with the deterioration and degradation effects of the constitutive elements of panel painting: support, paint layer and varnish layer. (Sandu 1998)

(a) Carbonized and rotted wood (b) Fungal attack (c) Xylophagous insect attack

Fig.2.2. Damages of wooden panel

2.1.3 Typology of degradation and deterioration of panel painting

Degradation changes the chemical nature of a material and it is related to chemical, electrochemical and microbiological and it is related to physical-mechanical and climatic processes.

In Table.2.1., the specific process is given for each type of degradation and deterioration effects, considering the order of their frequency.

Table.2.1. Typology of the defects and deteriorations of ancient panel paintings

(Sandu 1998)

No.	Structural element	Defects	Deteriorations
I. Support			
1.	**Wood**	Knots, rough finishing, surface small cuts and removal of wooden materials etc.	Contractions, erosions, fragility, fessures, holes, galleries and cavities of insects, cracks, looses and displacement of slats, warping, detachments of planks, deposits.
II. Painting layer			
2.	**Grounds (preparation)**	Non-even and inhomogeneous layers, mechanical impurities, loss of binder, adherent deposits etc.	Cracks or craquelures, slitting, loss of cohesion, loss of adhesion from the support, lacunas, alveolar blisters, exfoliations, holes, fragility, erosion.

3.	**Color layer**	Non-even and inhomogeneous layers, mechanical impurities, loss of binder or varnish, adherent deposits etc.	Craquelures, cupping, blind scales, exfoliations, fragility, erosion and abrasions, lacunas, loss of adhesion from the ground, brittleness, blisters.
III. Protective layers			
4.	**Varnishes and lacquers with protection and aesthetical function**	Non-even and inhomogeneous layers, mechanical coarse impurities, looses of materials, ageing micro cracks, loss of adhesion etc.	Cracks, wrinkling, fragility, exfoliations, scales, lacunas, semi-adherent deposits, matting or whitening, blooming, erosion and abrasion, spots, etc.
IV. Other structural elements			
5.	**Frames**	Defects in the reinforcing systems, rough finishing, surface cuts	Detachments, cracks, losses of material, fissures, warping, holes and galleries of insects, biological deposit.
6.	**Ornamental wooden decorations and metallic "rizas" or covers**	Assembling and mounting in a wrong way	Detachments, cracks, losses of material, fissures, warping, holes and galleries of insects, biological deposits, erosion and abrasions, punching etc.
7.	**Stretcher**	Defects in the reinforcing systems, rough finishing, surface cuts and loses of wooden material	Detachments, cracks, losses of material, fissures, warping, holes and galleries of insects, biological deposits
8.	**Angle and metallic elements**	Sharp angles or corners in contact with surface of the structural elements	Detachments, cracks, losses of material, fissures, warping, holes, biological deposits, erosion, abrasion, punching
9.	**Reinforcing systems**	Defects in re-assembling the planks, fissures and detachments of planks, loss of wedges or slats	Detachments, cracks, losses of material, fissures, warping, holes and galleries of insects, biological deposit, displacement or loss of slats
10.	**Handles, rings, nails**	Sharp angles, corners or borders in contact with surface of the structural elements	Detachments, cracks, losses of material, fissures, biological deposits, displacement or loss of metallic elements

2.2 Behavior of wood used for support of panel painting

There are four important wood technological characteristics: Anisotropy, Hygroscopicity, Biological resistance and Variability.

2.2.1 Wood structure

Fig.2.3. shows wood structure in a trunk. Starting from the **central pith**, a fresh layer of wood is formed each year surrounding that of previous year and lying underneath the **bark**. Year by year a fresh **ring** is added to those already formed.

As the process of formation of new rings continues, the inner or older rings cease to constitute part of the living portion of the wood body of the tree, becoming a central column of support, and acting as a storehouse of water.

Surrounding this central **heartwood**, which is sometimes darker in color, is a zone of wood consisting of varying number of year rings, usually lighter in color than the heartwood and is called **sapwood**.

This sapwood is still alive, and takes part in conducting water from the roots to the leaves of the tree. Between the outermost year ring and the bark is a ring of actively growing tissue called the **cambium**.

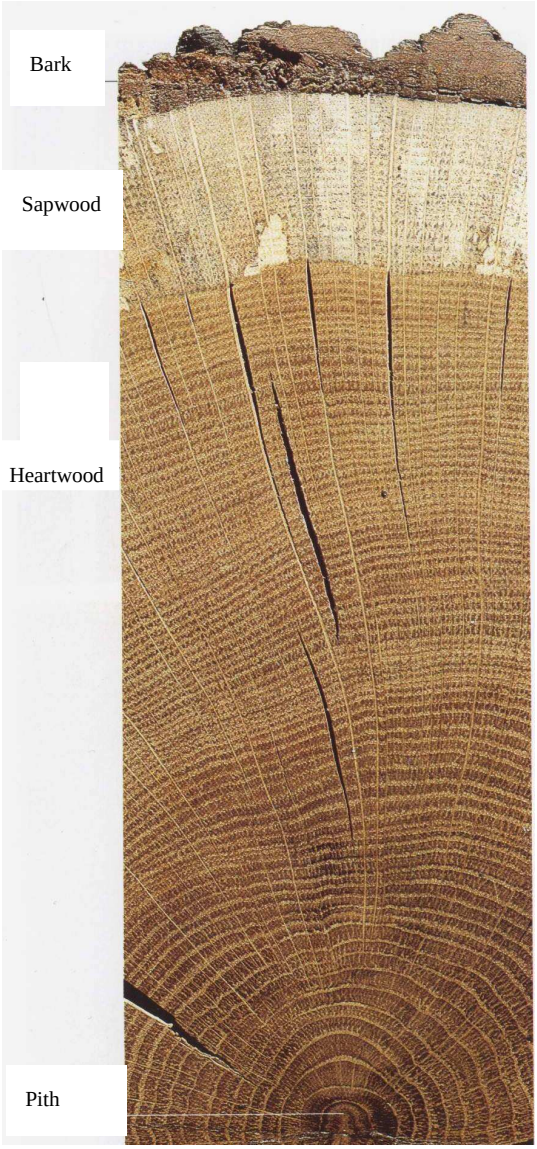
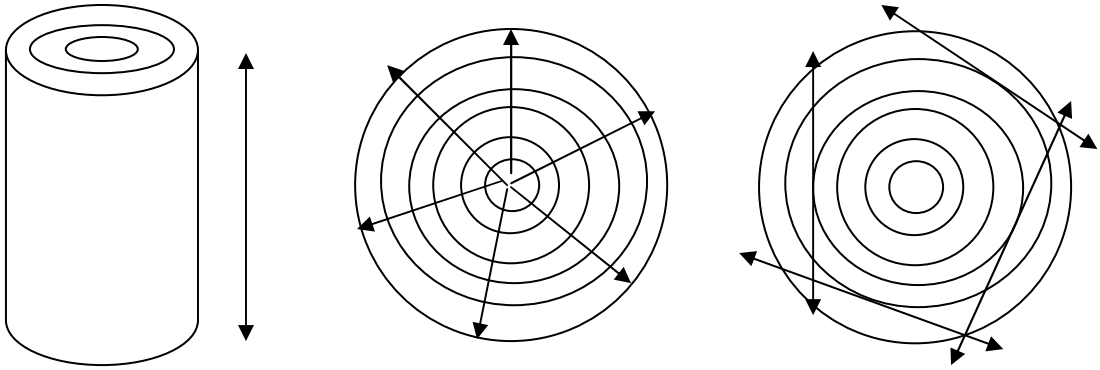


Fig.2.3. Wood structure in trunk (transverse section of an oak) (Nicolaus 1999)

2.2.2 Wood direction and cut

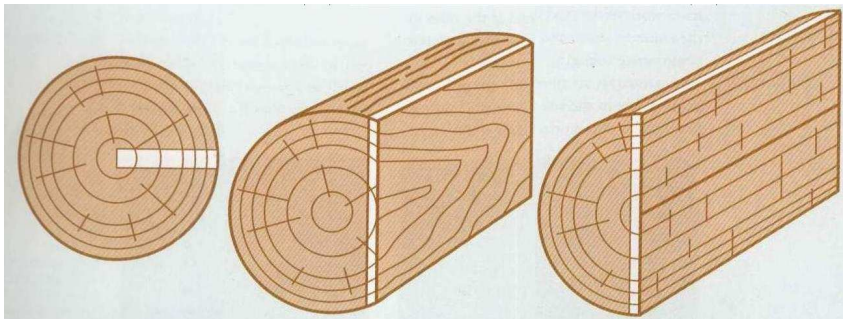
The combination of the axial direction of longitudinal cells and cell arrangement in growth rings gives to wood tissue its **anisotropy**: its properties are significantly different in its three structural directions (Fig.2.4.).



(a) Longitudinal direction (b) Radial direction (c) Tangential direction

Fig.2.4. Three structural directions of wood

Tangential sections and radial sections are used for support of panel painting. Tangential sections are made perpendicular to the rays and tangential to the annual rings and face of log. Radial sections are made along the rays or radius of the log, at right angles to the annual rings (Fig.2.5.).



(Left) Transversal section (Center) Tangential section (Right) Radial section

Fig.2.5. Fundamental anatomical plane (Nicolaus 1999)

It is essential to understand the anisotropic behavior of wood, which manifests itself in many of its properties, in particular shrinking and swelling, mechanical characteristics etc (Uzielli 2006).

2.2.3 Seasoning of wood

Wood used for panel painting has to be seasoned, because natural wood has certain defects, such as the tendency to warp and crack. The wood should be free of resin and gums and grown on poor soil in temperate climates and cut down in winter as the best period. In Italy, the white poplar was largely used for panel paintings, while in Flanders oak tree was mostly used.

In order to understand the seasoning process through which wood devolves, it is necessary to know something of the microscopic structure of the wood. Wood consists of cells, with an external thick wall and an inner hollow space (the lumen), which in the greenwood is more or less full of water. The walls of these cells also consist of material by which water is absorbed and which is able to take in or to give up water according to the amount of humidity in the air.

When the wood is allowed to dry, the lumen's water first disappear and then the cell walls begin to lose water progressively. They never lose the water completely until the wood is heated to a temperature at which begins to decompose. Therefore, the seasoning of the timber is the reduction in the amount of water it contains, to an average, in equilibrium with the storage environment, and as long as this amount is maintained, the wood does not warp or crack. The seasoning in bulk is a slow process and after the wood is cut it requires to be seasoned again. The processes for seasoning make use of natural air storage or hot air and steam.

Pre (or post) treatment before/after real seasoning

Cennino Cennini recommends boiling in water and then drying afresh (Cennini 1954). Sir Arthur Church advises soaking in water at 50 °C degrees and then steaming (Laurie 1967). Kiplik speaks of treating the wood against cracking by boiling it in water for 4 – 8 hours (the soluble components are eliminated from the fibers) followed by steaming at 40 – 50 °C. The Russian iconographers used to treat

the seasoned and dried panels for icons by immersion in water at 50 °C, followed by drying and swabbing with mercury chloride (Nicolaus 1999).

2.2.4 Physical parameter

Moisture Content (MC)

Many of the technological peculiarities which distinguish wood from other materials derive from its particular affinity to water (hygroscopicity). The degree of MC greatly influences almost all the technological characteristics of wood, such as dimensional variations, mechanical strength, elasticity, susceptibility to be decayed by fungal attack, and strongly conditions of the conservation of wood objects (Tsoumis 1991; Uzielli 2006).

The moisture content of wood in living trees, varies from about 30 to 300%. This variation is influenced by different factors, such as tree species, position of wood in the tree, and season of the year.

In softwoods, heartwood has lower moisture content than sapwood. In hardwoods, the differences are not so pronounced, and sometimes the situation may be opposite. Vertical variation of moisture is also more pronounced in softwoods, where an increase was observed from the base to the top of the trees. In hardwoods, the differences are comparatively small, and there is no definite tendency in the vertical direction (Tsoumis 1991).

Moisture held in wood

The basic reason for moisture entering into the mass of wood is the attraction of water molecules by the hydroxyls groups of cellulose, its mainly chemical constituents. There are the following phases of water in the mass of wood (Takahashi 1995):

Bound Water (in cell walls) (moisture content < 30%: Fiber Saturation Point)

- *Monomolecular adsorbed water* (moisture content < 5-6%)

A monomolecular layer of water is formed and held by these hydroxyls with strong hydrogen bonds and Van der Waals force. Formation of this layer results in pushing apart chains of cellulose molecules in the amorphous regions and between the crystallites of the microfibrils, so that wood starts to swell.

- *Polymolecular adsorbed water* (moisture content > 5-6%)

Under the effect of secondary attractive forces, more water molecules enter and form a polymolecular layer. Polymolecular layer of water is held by Van der Waals force one after another.

- *Capillary condensed water* (moisture content < 30%)

Capillary condensed water is the water in cell-wall voids and pit features (pit membrane openings, small pit mouths), which is produced when the relative humidity gets more than around 90%.

The fluctuation of monomolecular adsorbed water and polymolecular adsorbed water affects the physical and mechanical characteristics of the wood. These two kinds of water are held with wood substances directly or indirectly.

The above phases (monomolecular, polymolecular, capillary condensation) are not clearly separated.

Free Water (in cavities) (moisture content > 30%: FSP)

After saturation of the walls, liquid water may also enter cell cavities. Free water is held by capillary attractive force, which is not held with wood substances directly or indirectly. The fluctuation of free water affects the gravity, thermal, and electrical properties of wood.

Hygroscopic equilibrium

Wood exposed to constant conditions of temperature and relative humidity, for a sufficient time, desorbs or absorbs moisture, depending on its original hygrometric condition, and finally retains a certain quantity of moisture. This is called *equilibrium moisture content*. Equilibrium moisture content does not exist in an uncontrolled atmosphere, because both temperature and relative humidity are subject to continuous change. To achieve an equilibrium condition, wood must be placed in a closed container, where temperature and relative humidity can be kept constant.

When relative humidity increases, equilibrium moisture content also increases; however, when temperature increases, equilibrium moisture content is reduced. Differences exist between different species, but they are exhibited mainly at high relative humidity. Low values of equilibrium at high relative humidity may be attributed, as a rule, to a high content of extractives.

Equilibrium moisture content shows differences when wood loses moisture for the first time, or adsorbs moisture after drying, or desorbs moisture, which has been previously adsorbed. Equilibrium is greater in desorption than in adsorption. The phenomenon is called *hysteresis*, and it is a characteristic property of all cellulosic materials. It should be noted that, after the initial desorption of green wood, its hygroscopicity is permanently reduced at high relative humidity (Tsoumis 1991).

It may be concluded that equilibrium moisture content is affected by wood species, especially at high relative humidity, and by hysteresis; however, these effects are small and practically unimportant. Also, equilibrium is independent on the condition of the surface of wood (rough, smooth, **painted,** etc.), air velocity, and growth-ring orientation (transverse, radial, tangential). These factors do not affect the final equilibrium although they do affect the rate of moisture exchange between wood and atmosphere.

Table.2.2. Characteristic wood moisture content values (Nicolaus 1999)

Oven-dried wood	0%
Equilibrium moisture content (EMC) in central-heated rooms	6-8%
EMC in stove heated rooms	8-10%
EMC in normal conditions: (20°C, 65% relative humidity)	12%
EMC of wood stored in open air (air-dried wood, summer approx. 15%, winter approx. 20%)	14-20%
Minimum wood moisture content at which staining and wood-rotting fungi attack	18-20%
EMC at approximately 100% relative humidity (fiber saturation point)	28-32%

Moisture under variable atmospheric conditions

The moisture content of wood does not remain constant; it is subject to change, because the atmospheric conditions of temperature and relative humidity are continuously changing from hour to hour, day to day, month to month, and so on. Aside from temperature and relative humidity, air velocity may exercise a considerable influence, because it affects the rate of moisture evaporation.

The moisture that wood holds at a certain moment depends on species, source (heartwood, sapwood), thickness, surface condition, and direction of moisture movement. These factors affect the rate of moisture movement in the mass of wood. Higher density, greater thickness, and non-hygroscopic cover (ex. paint) have a retarding influence; whereas movement of moisture trough transverse surfaces (parallel to grain) is 10-15 times faster in comparison to movement from radial and tangential surfaces.

Importance of Hygroscopicity

Hygroscopicity is an important property of wood. It affects all other basic wood properties (density, shrinkage, mechanical properties, etc.). Hygroscopicity is a

disadvantage property of the wood as a material, from a dimensional stability point of view. Deep knowledge of the relationship between moisture and the properties and processing is necessary to avoid adverse consequences in practice.

Density

Wood density (or specific gravity) is probably the most extensively studied and widely used indicator of timber quality (Dickson, 1997; Zhang, 1997; Macdonald 2002). Wood is a porous material made of wood substances, water, and air. The air in the cell's lumen is unrelated with the weight but related with the volume. Wood density is a measure of the amount of cell walls material and gives no indication of the anatomy of the cell walls or of its properties (Kollmann 1968; Takahashi 1995).

The density of wood is influenced by moisture, structure, extractives, and chemical composition (Tsoumis 1991). Furthermore, for the same specimen of wood, the density may change over time with variations of the wood's moisture content, and its eventual decay (pyrolysis due to high temperatures, attacks of xylophagous fungi and presence of insect tunnels). As a result, the absolute density of wood may also change because of the eventual presence or leaching of extractives, or because of impregnation with various substances (preservatives, consolidating materials, adhesives, etc.)

Moisture

Hygrometric condition of wood should be stated in each case because adsorption of moisture increases both its weight and volume and desorption has opposite effect. However, there are certain conditions under which wood attains constant weight and volume.

Increasing moisture content increases the density of wood. While the weight of wood increases with increasing moisture content, volume increases at first, but remains constant thereafter irrespective of moisture retained.

Structure

Wood is mostly made of dead cells, which are composed of cell walls and cells cavities. The density of wood varies, depending on the amount of material and voids (lumina) present in a certain volume. Differences in density and porosity (void volume) derive from anatomical differences, such as differences in cell types (tracheids, vessel members, parenchyma cells) and their quantitative distribution, thickness of cell walls, and size of cell cavities (Tsoumis 1991).

Width of growth rings

In softwoods, the statistical correlation between ring width and density is low, but density tends to decrease with increasing ring width. In opposite, in ring-porous hard-woods, density increases, up to a certain level, with increasing ring width, but diffuse-porous hardwoods ring width is not a clear criterion of density.

Proportion of latewood

Latewood is made of cells which have thicker walls and smaller cavities in comparison to earlywood, then normally latewood is denser than earlywood. The relationship is clear in softwoods and rig-porous hardwoods. In diffuse-porous hardwoods, latewood is not clearly discernible. In softwoods, the proportion of latewood (and density) tends to decrease with increasing ring width, but the correlation is statistically low. The relationship is clear in ring-porous hardwoods, where an increase of width is associated with the increase of latewood proportion. In diffuse-porous hardwood, there is no practical way to study the correlation.

Extractives

Extractives are compounds of varying chemical composition (gums, fats, resins, sugars, oil, tannins, alkaloids, etc.) that are not part of the wood substance, but are deposited within cell walls and in cavities; their removal does not affect the cellular structure of wood.

Chemical composition

The chemical components of cell walls differ in density. Therefore, the differences of their presence may contribute to density differences. Cellulose (40-45%) variation is small. However, although the variation of lignin is greater (17-35%) larger differences exist in compression and tension wood.

Swelling/Shrinkage

Wood has many advantages as a constructional and decorative material, but perhaps its drawback is its tendency to swell or shrink when exposed to environment with variable humidity (Laidlaw 1970).

Shrinkage is reduction, and *swelling* is an increase of the dimensions of wood due to changes of its moisture content. Such dimensional changes occur when the moisture of wood fluctuates below the fiber saturation, respective of their magnitude which has no effect on dimensions. Wood is anisotropic with regard to shrinkage and swelling. Specially, the change of dimensions is the least in the longitudinal direction, much greater in the radial direction (averagely ten times than the longitudinal), and still greater in a direction tangential to growth rings (averagely the double than the radial).

Shrinkage and swelling of wood are affected by many factors, such as moisture content, density, anatomical structure, extractives, chemical composition, and mechanical stress.

Moisture

The magnitude of shrinkage and swelling is affected by the amount of moisture, which is lost or gained by wood when its moisture fluctuates between zero to the FSP, and vice versa. The relationship is practically linear and applied to all growth direction (longitudinal, radial, tangential) and therefore to volumetric changes.

It has been observed that the relationship between shrinkage or swelling and moisture change is affected by the size of the specimen used for their measurement. Large specimens do not give consistent results due to lack of uniformity of moisture content distribution.

Density

The magnitude of shrinkage and swelling is higher with higher density. This is due to the larger amount of wood substance (cell walls) in woods of higher density, and to the exterior change of cell dimensions. It has been observed that, when moisture is lost or gained, the size of cell cavities remain practically unchanged.

The coefficient (ratio of tangential and radial shrinkage or swelling) becomes smaller with increasing density (Kollmann 1968). This means that in woods of higher density, the difference between tangential and radial shrinkage or swelling is smaller.

Anatomical structure

The anatomical structure of wood is the basic reason for anisotropic shrinkage and swelling. The difference in different growth directions is attributed mainly to cell wall structure. When moisture is adsorbed, the middle layer of cell wall (S2) tends to swell proportionally to the number of microfibrils, but the other two layers exhibit a restraining effect due to the differing orientation of their microfibrils. The small axial (longitudinal) shrinkage is due to the orientation of microfibrils in the S2 layer, small deviations from parallelism (Fig.2.6.).

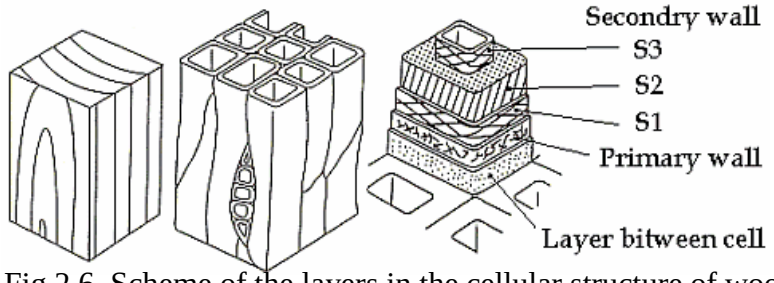


Fig.2.6. Scheme of the layers in the cellular structure of wood

The reasons for the difference between radial and tangential shrinkage and swelling are not well known. Partially, this is attributed to the presence of rays, which

due to their radial orientation, exhibit a restraining influence to the radial shrinkage and swelling. A relationship between shrinkage and the number of rays has been observed, especially in hardwoods. Another factor that is considered to produce a lower radial shrinkage, at least in softwoods, is the deviations of microfibrils caused by the presence of a greater number of pits in the radial walls of axial tracheids. The difference in density between earlywood and latewood is also considered a cause of anisotropy. Latewood shrinks and swells up to 3.5 times due to its high density.

Extractive

A large extractive content contributes to the reduction of shrinkage and swelling. The reduction is proportional to the space occupied by the extractives in the cell walls. Removal of extractives increases shrinkage and swelling (Brown 1952; Tsoumis 1991).

Chemical composition

Lignin exhibits a restraining effect on shrinkage and swelling. Hardwoods shrink more than softwoods at similar wood densities, and this is attributed to lower lignin content of hardwoods. The lignin is an amorphous polymeric material that can be considered as an isotropic material (Davalos-Sotelo 2005). The lignin has stiffness properties dependent on moisture, decreasing as the moisture content increases.

Mechanical stress

Large compression results in a shrinkage greater than normal, when cross section cell dimensions are permanently reduced. Inversely, under the influence of large tension stress, shrinkage becomes smaller than normal (Tsoumi 1991).

2.3 Treatment of wood

The old painted layers were unevenly afflicted by problems of extensive detachment, lifting and flaking, which had increased over time (Payer 1998). The detachment is the most frequent degradation and happens between the ground layer and the wood support. Therefore, the first task for treatment after the degradation is the systematic consolidation of the lifted layers. Various methods and materials have been considered for consolidation: animal glue, wax-resin mixtures, acrylic, polyethylene glycol (PEG), polyvinyl acetate (PVA), methyl methacrylate, allyl alcohol and so on (Payer 1998; Dilek 2000). The most important goal is to find an adhesive that is simple and safe to use. In this research, preservative intervention is considered as treatment. However, in this chapter some important treatment technique, from preservation to conservation, is mentioned.

Surface cleaning

The cleaning of painted surfaces is one of the most critical operations in conservation. Concurrent with the surface consolidation, the surfaces should be cleaned. First, dust and debris were removed with a brush and a vacuum cleaner. Then the water-sensitive and other surfaces should be cleaned respectively. It is an irreversible removal of very thin, non-homogeneous layers, which alter the aesthetics, falsify the image or affect the physical and chemical stability. Traditional cleaning methods were based on mechanical tools, which require great skill and experience and are long-lasting procedures and chemical agents. There are several problems in the operations (Bracco 2003):

- The spatial expansion of solvents is difficult to control;
- The majority of the efficient solvents is toxic;

- Many materials to be removed are sometimes insoluble in any solvent tolerated by the paint surface and make mechanical intervention the only alternative.

Wood consolidation

There are two ways of consolidation: one is preventive consolidation, which is focused in this research, and the other is consolidation for the conservation. The success of the consolidation depends on the impregnation of sufficient monomer into the wood and the degree of polymerization. The most important stage in the consolidation of wood is the selection of a monomer that can protect and consolidate the wood when polymerized within wood. The ideal consolidant action can be obtained if the polymer is fully compatible with the chemical constituents of wood, cellulose, lignin and hemicelluloses (Dilek 2000).

Undesirable changes in panel painting by wood preservatives can be caused by their composition as well as by improper application. Biocide, solvents, binders, pigments and dyes in preservative can all have an affect in the objects (Unger 2001). It is important to do pre-experiment before treatment application in order to observe the compatibility.

Processes and operations for scientific conservation

Main treatment processes and operations for scientific conservation is as following;

- Preventive consolidation of painting layer (facing)
- Controlling fungal and insect attacks (identifying a live attack)
- Disinfection/disinfestation (application of biocides by injection, sealing flight holes, fumigation, inert atmospheres, thermal, X-ray and gamma irradiation)
- Definitive consolidation of painting layer

- Structural consolidation of the panel (straightening and reinforcements, replacing or renewing damaged supports, protective backings, replacing wedges etc.)

- Cleaning of the painting layer and verso of the support

- Puttying or filling of painting layer/lacunas

- Chromatic reintegration

- Varnishing

- Assembling of the picture frames.

Table.2.3. Processes and operations for scientific conservation (Sandu 1998)

Process and its main effect	**Operant system**	
	Aqueous solution	**Organic solution**
Emollient application	Soaps andsurfactants, tannates, bile	Detersives, tannates, bile
Mordant application	Fluorides, alauns Urea	Urea
Waterproofing	Polymers and water soluble resins	Polymers and organic solvents soluble resins, wax, colophany, paraffin
Fireproofing	Ammonium phosphate, sodium silicate, aluminium and ammonium alauns	Halogenated derivatives, phosphohalogenated derivatives, xiloxanes, silicones
Consolidation	Inorganic fillings based on zinc and phosphorus	Natural and artificial waxes and resins
Rheological improvement of nano-structural protective layers	Tannnets, bile, saponins, camphor	camphor
Re-establishment of hydrous equilibrium after treatments and interventions	Natural and chemically modified resins	Natural and chemically modified resins
Structural reintegration	Natural and synthetic glues and adhesives (pertinacious, glucosidal glues and synthetic: PEG, PVA, acrylics)	Natural adhesives and fillings (stuccoes) or artificial (silicones, polyesters, polyamides etc.)
Chromatic reintegration	Watercolours	Oil or resinous colours

2.4. Durability of wood against fungi and insects

The ability of any wood species to resist degradation is called natural *durability*. For practical purpose sapwood is always considered as having low natural durability, although many species of wood may have little or indistinct sapwood (Eaton and Hale 1993). The heartwood resistance to decay is provided by several compounds, called extractives, produced by the tree during heartwood formation. Usually these compounds confer the heartwood a darker coloration, so that the colour is often taken as an indicator of good natural durability. is Wood is degraded by many organisms, such as fungi, insects and marine organisms. The occurrence of these organisms in different environments and conditions exposes the wood to different decay hazards; consequently, wood should be treated with an appropriate biocide in order to increase the durability against the highest threatening organism acting in a specific situation. Because of little importance of marine borers on degradation for panel painting, only insects and fungi are presented as factors of degradation (Tsoumis 1991).

Fungi

Mould fungi

Moulds are described to an artificial group of fungi called Deuteromycetes or fungi imperfecti, obtain their food from nutrients in the parenchyma cells of the sapwood (Schmidt 2006). Their proliferation in indoor environments is favoured by high substrate moisture, high air humidity, warmth and insufficient ventilation (Viitanen and Ritschoff 1991). Moulds do not cause structural damage to wood but they can affect some technological characteristics, for example the gluing of plywood (Wolf and Liese 1977); moulded wood is also unsuitable for decorative use, e.g. wall paneling, as the colour spots are not mechanically removable. The reproductive units of moulds are called spores, and these can be seen on the surface of materials

colonized by them. These small spores are pigmented and, depending on the mould species, may be black, green, red, yellow or other colours.

Stain fungi

Blue Stain fungi belonging the Ascomycetes and Deuteromycetes groups cause discoloration of sapwood. They usually attack softwoods and seldom hardwoods. Hyphae penetrate into stem via medullary rays, giving the discoloration a radially striped shape. Blue stain of pines is the most common and serious consequence of attack by stain fungi. Blue stain is prone to cause bluish or greyish discoloration of the wood but they do not cause decay. Blue stain has little effect on the strength of the wood, being toughness the property most seriously affected (Schmidt 2006). Stain fungi may cause considerable reduction of the market value of wood, mainly due to discoloration.

Decay fungi

Decay fungi constitute the most important factor that affects the durability of wood. Two main categories of decay fungi are recognized: brown rot and white rot. A third category of decay fungi is called soft rot. Decay fungi consume cell walls by secretion of enzymes, which possess the ability to dissolve many organic substances after their change to forms that may be assimilated. Decay fungi cause sensible changes of structure and chemical composition of wood, until its complete degradation. Brown rot results from the degradation of carbohydrates, cellulose and hemicelluloses by Basidiomycetes. These fungi do not produce lignin-degrading enzymes; the brown colour of rotted wood is due to the lignin left in the cell walls. White rot means the degradation of cellulose, hemicelluloses and lignin usually acted by Basidiomycetes and rarely by Ascomycetes. White-rot fungi attack predominantly hardwoods; they reduce the wood strength properties to a lesser extent than brown-rot

fungi, because at the same mass loss, lesser cellulose is consumed, and it does not come to cracking or cubical rot (Schmidt 2006).

Soft-rot fungi differ from the previous ones by growing mainly inside the woody cell wall, producing typical chain of cavities within the S_2 layer of soft and hardwood in terrestrial and aquatic environment. They belong to the Ascomycetes and Deuteromycets groups. A 5% mass loss caused by soft-rot fungi already causes about 50% decrease of impact bending. Soft rot usually decays wood under extreme ecological conditions, which are unsuitable for Basidiomycetes. Their optimal environments are constantly wet wood.

The resistance of various woods to fungal attack varies, but no wood is immune. Differences are due mainly to variations in content of toxic extractives.

Insects

A number of insects have evolved to attack wood. Insects open bore holes and galleries (tunnels) of varying size, up to 2.5 cm in diameter, and some species change the interior of wood to dust, leaving a thin exterior layer. Generally insects attack sapwood and the resistance of wood species depends on different factors such as insect nutritional requirements, presence of symbiotic organism into the gut or presence of enzymatic activity , different composition of wood, hygrometric condition of wood, age from cutting of wood.

Some insects bear decay fungi into wood. The most serious damage to timber is usually caused by species in the three orders *Coleoptera* (beetles), *Isoptera* (termites) and *Hymeno*ptera (ants and bees) as following.

Coleoptera

These insects are characterized by two hard outer wings, which cover and protect the real wings. In relation to the main occurrence and type of damage, the main Coleoptera families may be listed in the following groups (Bletchly, 1969):

- Furniture beetles: Anobiidae (*Anobium punctatum* De G., *Ptillinus pectinicornis*),

- Powder-post beetles: Lyctidae (*Lyctus brunneus* Steph) and Bostrychidae (*Bostrychus capucinus* L)

- Ambrosia beetle (pinhole borers): Platypodidae, Scolytidae, Lymexylidae

- Longhorn beetles: Cerambicydae (*Hylotrupes bajulus* L., *Trichoferus holosericeus* (Rossi) =.*Hesperophanes cinereus* Villers)

Many species excavate tunnels in wood or under bark.

Isoptera

Isoptera are the termites, which cause severe damage to wood. They are very destructive and particularly dangerous because the damage is not visible externally. Termites live in complicated colonies and not as solitary individuals. A colony is made of a "king," "queen" (laying many thousands of eggs every day and for many years), numerous "workers" (responsible for damage to wood), "soldiers" (engaged in defense of the colony), and a number of immature individuals in various stages of development. There are two main groups in termites: dry-wood termites (*Kalotermes*, *Cryptotermes*, etc), and moist-wood or subterranean termites (*Reticulitermes*, *Coptotermes*, etc).

Hymenoptera

These insects have four (two pair) of membranous wings, of which the back ones are shorter. Hymenoptera includes the ants, bees, wasps and sawflies. Few species of Hymenoptera are harmful, they usually bore into wood for egg-laying (*Urocerus gigas* L.) or to excavate nests (carpenter ants). However, the presence of tunnels and holes into wood represents a commercial depreciation. Wood-boring larvae, in association with fungi, can cause extensive damage to plantation of conifers.

CHAPTER 3:

MATERIALS AND METHODS

3.1 Wood species

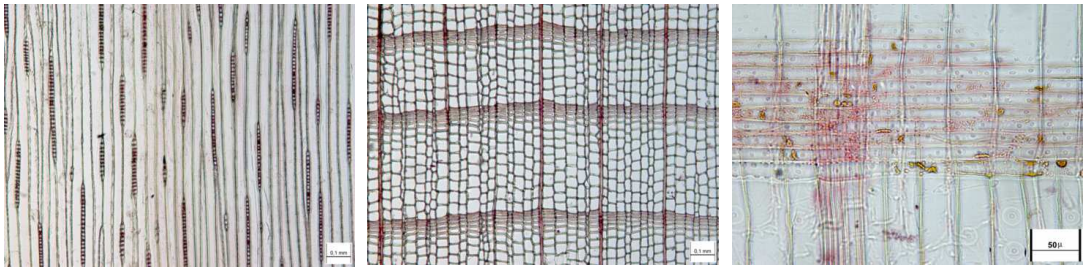
Over centuries, many species of wood have been used as support of panel painting, with each geographic region favoring certain woods for reasons of trend, ease of use, and availability. Today there are thousands of species of wood which have been identified, but only several hundred of these have actually been used in the present or past in each region for the production of timber for working purposes, and not more than a few dozen were regularly used for making support for painting (Uzielli 2006). Painters from northern Germany and Holland preferred oak while those in southern Germany favored such woods as pine, fir, larch, lime and ash. In Italy, poplar and cypress were commonly used (Doerner 1962).

In this research, fir (*Abies alba* Mill.), poplar (*Populus* sp.), lime (*Tilia* sp.) and oak (*Quercus petraea* Liebel) were selected for the experiment. Those wood species are the most widespread species used to manufacture the wooden supports of panel paintings and polychromies for the Cultural Heritage in Romania and Europe generally. Strictly speaking, only fir is really a species; poplar and lime are reported as *Populus* sp. and *Tilia* sp. Because they are two groups of species belonging to the same genus. The species belonging to those groups are distinguishable only on botanical bases different from wood characteristics, which are, indeed, identical from anatomical and technological points of view. The same is for *Quercus* sp.: we utilized a wood declared as *Q. petraea* Liebl.(Sessile oak) but it could also be *Q. robur* L. (English or Pedunculate oak).

Fir (*Abies alba* Mill.)

Abies alba Mill. is softwood and has a density of about 0.44 g/cm³ (RH=12%), widely distributed coniferous in Europe and it is well known as Christmas tree (together with *Picea abies* Karst., Norway spruce). Primary resin canals are absent

(Fig.3.1.). Fir wood is lightweight, light-coloured, finegrained, even-textured and longfibered. It is moderately soft and easily worked, used for general construction, furniture, plywood and pulpwood, and paper manufacture (Rolland 1993). Sapwood and heartwood cannot be distinguished by colour. The leaves are needle-like, flattened, 1.8-3 cm long and 2 mm wide by 0.5 mm thick, glossy dark green above, and with two greenish-white bands of stomata below.



(a)Tangential section (b)Transversal section (c)Radial section

Fig.3.1. Anatomical photos of fir (*Abies alba* Mill.) (Photo from IVALSA)

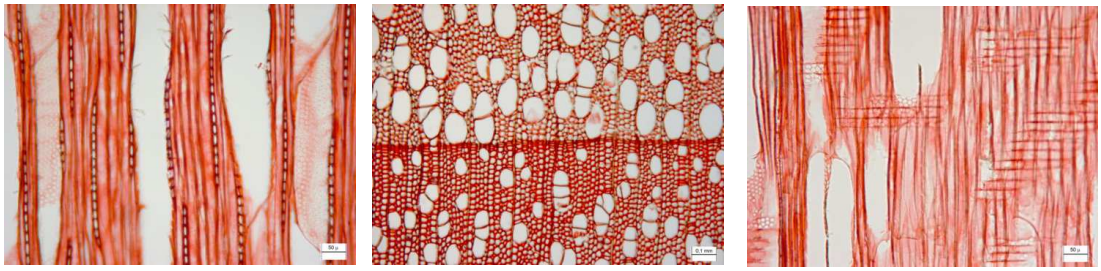
Poplar (*Populus* sp.)

Poplar is diffuse-porous hardwood and has a density of about 0.48 g/cm^3 (RH=12%). It was the most common wood used in Europe for panel paintings; the Mona Lisa and indeed most famous early renaissance Italian paintings are on poplar. The wood is generally white, often with a slightly yellowish cast.

The bark on young trees is different between species, it could be smooth, white to greenish or dark grey, often with conspicuous lenticels. The leaves are spirally arranged, and vary in shape from triangular to circular or (rarely) lobed, and with a long petiole. Leaf size is very variable even on a single tree, typically with small leaves on side shoots, and very large leaves on strong-growing lead shoots. The leaves often turn bright gold to yellow before they fall during autumn.

In wood, on cross sections viewed with a hand lens, the appearance of the pores may suggest a semi-ring-porous arrangement. Tangential section of poplar

shows uniseriate rays with flattened cells (Fig.3.2.(a)). Pores appear numerous, and multiples are common; the rays appear extremely narrow and are barely visible (Fig.3.2.(b)). Radial section of poplar shows the large ray-vessel pits in the marginal rows of procumbent ray cells in contact with a vessel element (Fig.3.2.(c)). (Hoadley 1998)



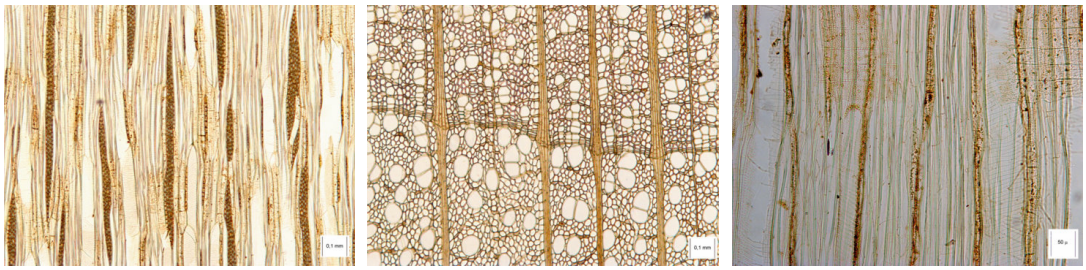
(a)Tangential section (b)Transversal section (c)Radial section

Fig.3.2. Anatomical photos of poplar (*Populus* sp.) (Photo from IVALSA)

Lime (*Tilia* sp.)

Lime is diffuse-porous hardwood and has a density of about 0.65 g/cm³ (RH=12%). It is large deciduous tree, reaching typically 20–40 m tall, with oblique-cordate leaves 6–20 cm across, and is found through the north temperate regions. The sapwood of lime is indistinguishable from the white to pale yellow heartwood, which turns pale brown on exposure. It has a straight grain with a fine, even texture.Lime wood is the tree of legend of the Slavs. In the Slavic Orthodox Christian world, lime was the preferred wood for panel icon painting.

Hand-lens examination of transverse surfaces shows evidence of growth rings by slightly denser latewood fiber mass, the growth-ring boundary often delineated by lighter line of latewood parenchyma (Fig.3.3.(b)). A key feature is the very thick spiral thickenings, which are conspicuous in the vessels. Tangential section shows that the rays are mostly 1-4 seriate, the ray cells appearing flattened or oval rather than rounded (Fig.3.3.(a)). (Hoadly 1998)



(a) Tangential section (b) Transversal section (c) Radial section

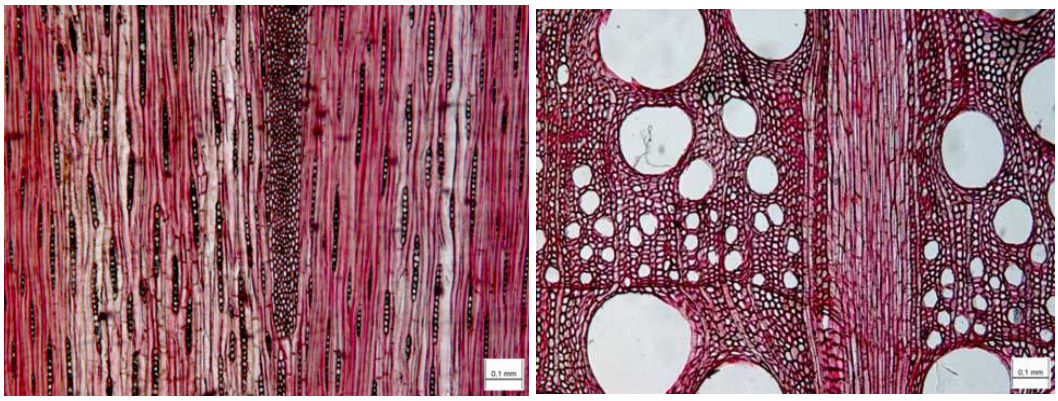
Fig.3.3. Anatomical photos of lime (*Tilia* sp.) (Photo from IVALSA)

Oak (*Quercus petraea* Liebl)

Oak wood is ring-porous hardwood and has a density of about 0.75 g/cm³, great strength and hardness, and is generally resistant to insect and fungal attack because of its high tannin content. It also has very attractive grain markings, particularly when quarter-sawn and is commonly used in furniture, construction, floor, shipbuilding and barrels for wine. It was used nearly exclusively as a painting support from the fifteenth to the seventeenth century in the northern parts of middle Europe (Klein 1998).

Oaks have spirally arranged leaves, with a lobed margin in many species; some have serrated leaves or entire leaves with a smooth margin. The flowers are catkins, produced in spring. The fruit is a nut called acorn, borne in a cup-like structure known as a cupule; each acorn contains one seed (rarely two or three) and takes 6–18 months to mature, depending on species. Left to grow naturally this oak becomes a high domed tree with a closed crown and tall trunk with grey bark.

In the transversal section of oak (Fig.3.4.), the regular occurrence of very large rays is the key feature; they are visible on virtually any surface, forming conspicuous radial lines across transverse surfaces and visible as distinct lines up to around 10 cm long along tangential surfaces (Hoadley 1998).



(a) Tangential section (b) Transversal section

Fig.3.4. Anatomical photos of oak (*Quercus petraea* Liebl) (Photo from IVALSA)

3.2 Treatment solutions

In this research, Red Petroleum and Propolis solutions are used and those solutions are traditionally used in Romania for the preservative intervention on wooden artistic artefacts. The advantage of these solutions is considered ecological, lower cost and without health risk (Sandu, I.C.A. et al. 1995; Sandu, I. et al. 2008). The application of these solutions is still a widely adopted and popular technique in preservative conservation but the impact of these solutions is not well known, in terms of real efficiency and consequence on the artifacts.

Red Petroleum

Red petroleum is a natural product derived by distillation from the old drills from the 1860 year from the village Campeni, Bacau county, belonging to Modarzau-Moinesti scaffold, Romania. This type of petroleum is known even from the XVIth century and has been summary studied after 1880 year by Poni and Mrazec from the Mihaileana University Iasi, Romania and after 1900 by Edeleanu and Filiti (Edeleanu 1900).

Red petroleum has a series of very special characteristics such as: very small density and viscosity, very large inflammability and evaporation rate, very small concentration of solid paraffin (colorless or white), a quite large concentration of aromatic products and exhibits a large capacity to extract the active principles from plants and other natural products via maceration, at room temperature. This type of petrol is of the consistency of kerosene and is phosphorescent green in emission and rubious red to brown in absorption.

Red petroleum is a complex hydrocarbon multi component which contains predominately light gasoline, kerosene, white-spirit, n-heptane…….decane, different aromatic hydrocarbon and a very small concentration (below 5%) of solid paraffin

colorless or white.

This type of petroleum has the following characteristics:

- density: 0.785 (g/cm^3)
- viscosity: 2.8cP
- boiling point: 65-72^oC
- freezing point: -12^oC
- the color: emission: phosphorescent green and absorption: rubious red to brown

The spectrum of Red Petroleum was obtained with FTIR-ATR (Fig.3.5.).

Propolis

Propolis is made up of resinous, rubbery and balsamic substances collected by bees from buds of trees to reinforce honeycombs, entrance walls and cover cracks in the hive. Propolis has been used as traditional medicine for long time and has become the subject of intense pharmacological and chemical studies as antibiotic remedy, applied for treatment of wounds and burns, sore throat, stomach ulcer etc., for recent several decades (Bankova 2005). Propolis is also known as bee glue for gilding in Italian renaissance paintings (Higgitt 2008). Propolis is a chemically complex sticky, dark-coloured resinous hive product containing material collected by bees from buds or other plant exudates, volatile substances and beeswax.

The composition of propolis varies according to the local flora and flowering, climatic conditions, amount of resin on the buds, collecting time and the inclusion of contaminants such as wax, pollen and substances secreted by bees' metabolism (Marletto 1981; Bevilacqua 1997).

In the last decade, the paradigm concerning propolis chemistry radically changed. In the 1960s, propolis was thought to be of very complex, but more or less

constant chemistry, like beeswax or bee venom (Lindenfelse 1967). In the following years, analysis of numerous samples from different geographic regions led to the disclosure that the chemical composition of bee glue is highly variable. Numerous studies, carried out with the combined efforts of phytochemists and pharmacologists, led in recent years to the idea that different propolis samples could be completely different in their chemistry and biological activity. So it is extremely important to analyze the Propolis used in each case.

In this research, Propolis was prepared with ethyl alcoholic solvent at 20%. The FTIR spectra of Propolis, which was used in this research, was obtained (Fig.3.5.). The spectrum has shown that Propolis is a very complex mixture of components, mainly polyphenols including flavonoids, phenolic acids and esters of aromatic alcohols, but also fatty acids, hydrocarbons and terpenes.

Biotin R

Components of this novelty expressed are two molecules, 25% IPBC (3-Iodo-2-propynyl butyl carbamate) and 5% OIT (2-n-octyl-4-isothiazolin-3-one), both with a low solubility in water (156 ppm and 480 ppm respectively). In this research, Biotin R was prepared with Petroleum ether solvent at 1.5%.

IPBC (3-iodo-2-propynyl-butylcarbamate) is a biocide which was originally mainly used for wood preservation, and which is now also used in cosmetics and cutting oils as a fungicide (Rossmoore 1995; Bryld 2001). IPBC was proven to be satisfactorily effective against decay fungi in laboratory biological tests.

Advantages: Wide antifungal activity, Low water solubility, Cosmetic approved;

Disadvantages: Discolouration possible, UV instability, Sulphite instability

OIT is produced as a replacement for the environmentally problematic tri-butyl tin oxide in marine antifouling applications. It is utilized for antifungal product

as well (Willingham 1996; Jacobson 2000).

Advantages: Wide anti-fungal activity;

Disadvantages: Sulphite instability, harmful if ingested, toxic if inhaled;

Personal protection: Safety glasses, gloves, adequate ventilation.

Biotin R should be diluted in the greater part of the organic solvents (ex. Acetone, fragrant, White Spirit). In this research, Biotin R was diluted with petroleum ether to be 1.5%.

The FTIR spectrum of Biotin R was obtained (Fig.3.5.), although the components of this slution are well known.

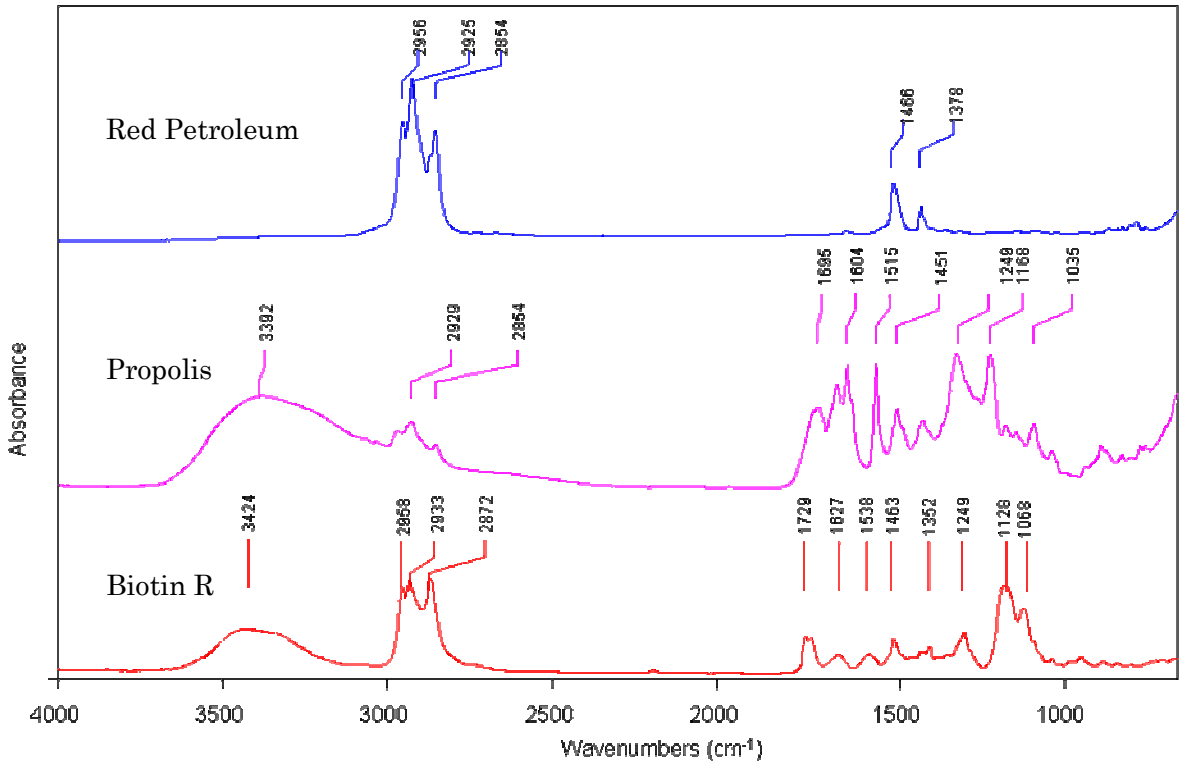


Fig.3.5. FTIR-ATR spectrum of products

3.3 Moisture conditioning

Moisture conditioning approach has been carried out. Fluctuations in ambient relative humidity (RH) produce microbiological (mould) attacks and changes in the materials that make up painted wood objects, resulting in changes in the moisture content in wood and altering their dimensions. Eventually cracks and detachment occur in painting layer. Painted layer can only partially follow. The effect of these processes is due to the fact that the painted layer cannot completely follow the deformation of the wooden support. Eventually it will experience tension leading to irreversible stretching and finally cracking and detachment. The fluctuation of RH and temperature is one of the most vital problems, causing dimensional change.

Many of the technological features, which distinguish wood from other materials, derive from its particular affinity to water. The degree of RH greatly influences almost all other technological properties of wood (dimensional variations, mechanical strength, elasticity, propensity to decay from fungal attack, etc.), and strongly conditions the conservation of wood objects (Uzielli 2006).

In the direction parallel to the grain of a wood substance, applied paint materials are considered to be nearly fully restrained and unaffected because wood's longitudinal dimension remains essentially unchanged by fluctuations in RH. Longitudinal change is almost negligible. However, in the direction across the grain, moisture-related movement of an unrestrained wood substrate may completely override the less responsive painted layers. In this situation, stresses induced in the ground and painted layers due to changes in RH are completely opposite to the stresses parallel to the grain. The anatomical structure of wood is the basic reason for anisotropic shrinkage and swelling. The differential shrinkage and swelling in different growth directions is attributed mainly to cell-wall structure.

The research effort to determine the response of painted wood to RH variation

and to quantify the effects of RH fluctuations on painted wooden object was undertaken first by Mecklenburg, Tumosa and Erhardt (1998). They quantified mechanical properties and dimensional changes of materials constituting painted wooden objects, such as wood itself, glues, gesso, paints, and varnishes. Relating the independent RH responses of each of these materials, the authors could determine the allowable RH fluctuations a particular composite object may ultimately endure without irreversible deformation or damage.

Recently some researches carried out some work in this topic. It was reported that wooden boards, simulating the supports of panel paintings, were subjected to variations of RH (Dionisi Vici et al. 2006). And it was also reported that the allowance thresholds i.e., the amplitude and rate of RH variations that wooden cylindrical objects can safely endure (Kozłowski 2007).

However, nobody has been reported about the combination of treatment and RH. This experiment has been carried out with two scopes. One is for the evaluation of the effectiveness of Romanian traditional preservative treatments (Red Petroleum and Propolis) on wood sample itself and on wood sample with tempera painting, considering chemical-physical and structural characteristics. The other is for the observation between painted layer and wooden support.

For the first scope, the experiment was carried out to evaluate the effectiveness induced by the application of treatment solutions of Red Petroleum, Propolis and Biotin R by immersion and brushing. Biotin R is well known as an effective antifungal product in the market. In this experiment, Biotin R is utilized for comparison to control the efficiency of Red Petroleum and Propolis. The study deals with the assessment of the impact of traditional Romanian treatments, Red Petroleum and Propolis, on wood and the investigations of the possibilities to affect physical characteristics (density, porosity, shrinkage and moisture content (MC)) of wood itself

and panel painting. Regarding the samples with tempera painting, visual assessment (the degree of mould attack), colour measurement were analyzed as well. The penetration of solutions was analyzed with samples without tempera painting with FTIR-ATR.

For the second scope, the interface between painted layer and wood support was observed under different environment causing variations on wood equilibrium moisture contents. The reciprocal behavior of the components of this composite under different environmental conditions was analyzed. A composite made of materials (wood + gypsum and animal glue + tempera) has different physical behavior under varying environmental conditions (Hayashi et al. 2008).

To implement an effective protective strategy for wooden objects, precise cause-effect relationships between the rate of the RH variations and treatments, on the one hand, and the physical-chemical and structural change in the wood, on the other hand, are necessary. A particularly important aim of this experiment was to assess the Romanian traditional treatment effectiveness and to identify the impact of those treatments solutions on wood and on artifacts as a whole.

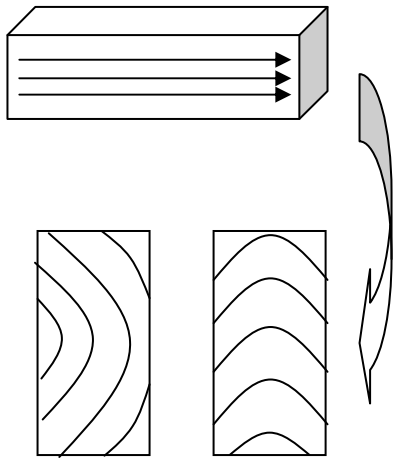
The result of this experiment is useful for the passive preservation strategy for panel painting and polychrome wooden cultural heritage, deciding the solutions of treatment, the environmental condition and the simulation for estimating how the panel paintings will react from one environment to another. The support of panel painting is a good example of work of art particularly vulnerable to RH variations.

3.3.1 Sample without tempera painting

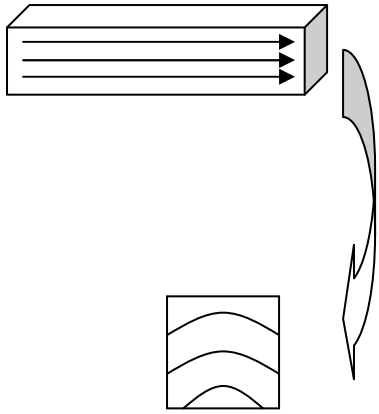
In this experiment, following well oriented samples were prepared for the experiment (Fig.3.6. and Table.3.1.). Treatments solutions were applied by immersion.

- Wood species: Fir (*Abies alba* Mill.);
  Poplar (*Populus* sp.);
  Lime (*Tilia* sp.);
  Oak (*Quercus petraea* L.).
- Dimension: 5x1x1 cm;
  5x2x1 cm.
- Treatments : Red Petroleum;
  Propolis.

- Direction of specimens:



(a) Dimension: 5x2x1 cm



(b) Dimension: 5x1x1 cm

Fig.3.6. Direction and size of sample

- Number of specimens:

Table.3.1. Number of samples without tempera painting

	Red Petroleum	Propolis	References
AI	1	1	2
A2	4	4	6
A3	2	2	5
A4	2	2	5
B1	3	3	4
B2	3	3	6
B3	1	1	4
B4	0	0	0

Preparation and experimental procedure (without tempera)

1. The 4 kinds of species and the 2 kinds of dimension wood bars were prepared (Fig.3.7.(a)) and cut with the machine (Fig.3.7.(b)). every specimen was weighed and the three dimensions (thickness, width, length) measured (Fig.3.7.(c)).



(a) Wood bar (b) Sawing machine (c) Measurement instrument

Fig.3.7 Preparation for the samples without painting

2. All specimens were put in the oven, 103 °C to get oven-dry weight.

3. Specimens were treated by immersion: 20 minutes for 3 times (total 60 minutes) intervalled by 20 minutes on the bench (Fig.3.8.). After treatment, the specimens, once dried, were put in the climatic box at constant temperature (20 °C) but with different RH values (100% → 85% → 65% → 25% → 0% at 103 °C) until equilibrium. At the end the samples were out in oven at 103 °C (RH 0%) until constant weight.

Fig.3.8. Treatment by immersion

4. At each RH, the weight and dimensions were measured and the following parameters were considered.

- MC
- Density
- Shrinkage
- Porosity

5. After the oven dry step the penetration of solutions (Red Petroleum and Propolis) was analyzed with the weight variation and FTIR-ATR.

3.3.2 Sample with tempera painting

In this experiment, there are two kinds of sample with tempera paintings. One was used for the experiment to evaluate effectiveness of Romanian traditional preservative treatments (Red Petroleum and Propolis) **(Sample A)**. The other was for the observation between painted layer and wooden support without treatment **(Sample B)**.

Sample A

The following well oriented samples were prepared for the experiment (Fig.3.9.). Treatments solutions were applied by brushing.

- Wood species: Poplar (*Populus* sp.);
  Lime (*Tilia* sp.);
  Oak (*Quercus petraea* L.).
- Dimension: 5x5x2 cm.
- Treatments : Red Petroleum;
  Propolis;
  Biotin R

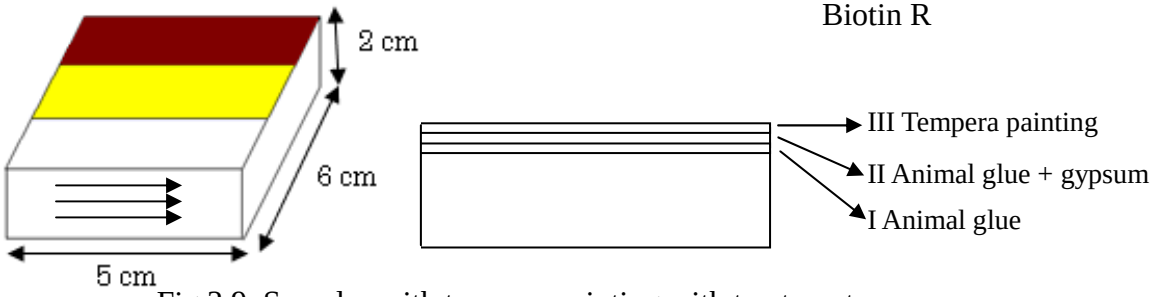


Fig.3.9. Samples with tempera painting with treatments

Sample preparation and experimental procedure (Sample A)

I	Rabbit glue	50 g
	Distilled water	500 ml
II	Rabbit glue	50 g
	Distilled water	650 ml
	Gypsum	988 g

Fig.3.10. Preparation for animal glue

1. Rabbit glue and water were mixed one day in advance. They were heated with bigger bowl with boiling water (bain-marie) and the solution was filtered with a fine cloth (Fig.3.10.). They should not be heated directly. Gypsum was added until saturation little by little. The solution was never mixed until saturation (Fig.3.11.). After saturation, it could be mixed. Before applying I and II on the board, the lateral of sample was taped in order not to spread the glue and gypsum.

Fig.3.11. Preparation of animal glue + gypsum

2. The rabbit glue and the rabbit glue + gypsum were applied. The rabbit glue + gypsum were applied twice (two layers). When the rabbit glue + gypsum were applied on the boards, the boards were beaten in order to let air out from the layer. The boards were dried for one night (Fig.3.12.).

Fig.3.12. Drying boards after applying gypsum

3. After dried, some spots were appeared on the oak boards because of tannin (Fig.3.13.). In case the gypsum is not even, it made smooth with knife. Tapes were removed and the edges were polished with sandpaper. After removing the tapes, the boards were marked, along the length, with creating 3 lines 2 cm width each in order to put tempera painting.

Fig.3.13. Oak after applying gypsum: some spots were appeared for tannin

4. Binder for egg tempera paint was prepared with following components.

- Yolk (the yellow of egg)
- Vinegar
- Albumen (the white of an egg)

Fig.3.14. Preparation for binder

Yolk and albumen are separately well stirred with a mixer (Fig.3.14.). The albumen is stirred to be spongy and leave it for two hours. Then it will separate into liquid and sponge part and is filtered with the fine cloth. Only liquid part (after filtering) is used for tempera painting as binder (Fig.3.14.).

5. Yolk, vinegar, and albumen (Binder) are mixed with the ratio, 2:1:1.

6. Pigment (red, yellow, and white), binder, and water are mixed (Fig.3.15.). The ratio is roughly 1:1:1. But the color for white is 1:0.5:1.

Red : TERRA ROSSA

Yellow : GIALLO OCRA

White : BIANCO TITANIO

Fig.3.15. Mixing tempera painting, red, yellow, and white

7. Tempera was applied on panel three times each color (yellow, red, and white). The order of the color was first yellow, second red, and then white.

8. The boards were cut to 5 cm by sawing machine (5x6x2 cm) and then the samples were polished in order to remove wood hair and gypsum at bottom (Fig.3.16.).

Fig.3.16. Cutting the boards and polishing with sand paper

- The number of samples

Treatment (Red Petroleum, Propolis and Biotin R)	3	54
Varnish (without varnish, with varnish)	2	
Brushing way (bottom, bottom + lateral, all surfaces)	3	
Repetition	3	

54 + 3 (references with varnish) + 3 (references without varnish) = 60

60 + 3 (naked wood) = 63

63 * 3 (species: poplar, lime, and oak) = 189 **Total 189 specimens**

9. Varnish and treatment were applied by brushing. Varnish was applied to the 30 samples per species, total 270 samples and on the painted layer three times by brushing (Fig.3.17.).

Varnish: Vernice per Ritocco (Varnish for retouching)

Fig.3.17. Applying varnish

10. The solutions were applied as preservative treatments were: Red Petroleum, Propolis and Biotin R. Red Petroleum and Propolis were from a region in Romania. Treatments were applied by brush on specimens by three ways i) only bottom (one surface); ii) bottom and lateral (4 surfaces); iii) and all surfaces (6 surfaces). Top and

bottom were treated both lengthwise and widthwise (Fig.3.18.).

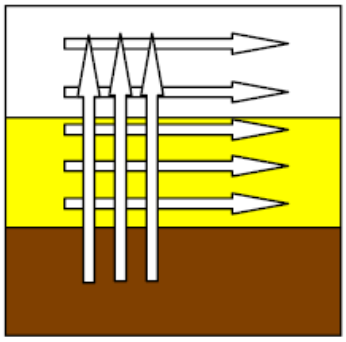


Fig.3.18. Way of brushing for top and bottom

11. Varnish and solutions were applied three times. The quantity of solution penetrated by brushing is less than those applied by immersion for an hour. The difference is as following.

Weight difference (Lime) / cm^2 (Red Petroleum by immersion)

0.040 g

Weight difference (Lime) / cm^2 (Red Petroleum by brushing)

0.011 g

12. After treatment, the specimens were put in the climatic box (100% at 20 °C → 65% at 20 °C → 0% at 103 °C) until equilibrium.

13. At equilibrium at each RH, the weight, dimensions and colour were measured and following parameters were considered.

- Mould attack - Colour - MC
- Density - Shrinkage - Porosity

Sample B

The following samples were prepared (Fig.3.19.). With this experiment, the interface between painted layer and wood support was observed under different environment causing variations on wood equilibrium moisture contents. The direction wood is that poplar and lime samples have sub-tangential rings and fir and oak samples have sub-radial rings (Fig.3.20.).

- Wood species: Fir (*Abies alba* Mill.);
  Poplar (*Populus* sp.);
  Lime (*Tilia* sp.);
  Oak (*Quercus petraea* L.).
- Dimension: 5x5x2 cm.
- Composition of Polychrome layer: Gypsum;
  Animal Glue;
  Pigment (tempera).

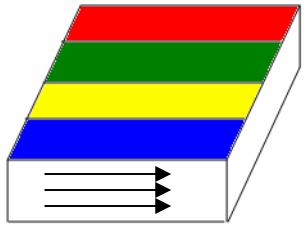


Fig.3.19. Size of sample

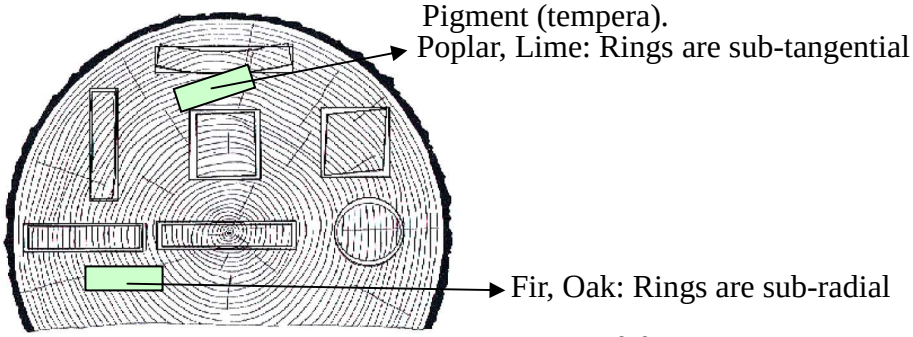


Fig.3.20. Characteristic shrinkage and distortion of flats, squares, and rounds as affected the direction of the annual rings. From US forest Products Laboratory (Kollmann 1968).

Experimental procedure (Sample B)

1. The specimens were put in the climatic box at constant temperature (20 °C) but with different RH values (100% → 85% → 65% → 25% → 0% at 103 °C) until equilibrium.

2. At equilibrium at each RH, the dimensions of sample and the detachment length were measured and the lateral surfaces were scanned to observe the stratification.

3.4 Insect attack test

Insects are the most important and most frequently found living pests attacking wood in panel painting. Wooden support of panel painting is used by insects for food, shelter, and breeding (Unger 2001). Insects can threaten panel painting wherever they are stored, whether in public museum, storage or private home (Florian 1997). Treatments are applied in order to improve the natural durability of support of panel painting. The effective efficiency against insect of Romanian traditional treatments, Red Petroleum and Propolis, is not well known, therefore the aim of this experimental part was to assess the efficacy of these treatments.

The test has been performed in accordance to EN 46-1 (2005) with the aim to assess the preservative action of the wood. This method makes it possible to determine whether recently hatched larvae are capable of boring through the treated surface of susceptible wood species and of surviving in the untreated part of the test specimen. Laboratory tests are commonly used to evaluate the efficacy of wood preservatives (EN 599-1 2006). The performance of wood in service is based on the concept of use classes (EN 335-1 2006) which themselves are based on the biological risk found in different end-use situations. In this research, end-use situations for panel painting is supposed to be interior and covered place, use classes 1 and 2. If the environment situation is a place where the risk of humidity is high, e.g. museum deposit and also some churches, it is necessary to include also class 2. The performance standard for wood preservative products (EN 599-1 2006) requires assessment using test methods which use different organisms dependent on the intended end-use situation. In this whole research the 4 species of wood were used for experiment, 3 species out of 4 were hardwood, which are most widespread and important species used to manufacture the wooden supports of panel paintings and polychrome woods for the Cultural Heritage. The evaluation of efficacy of a wood

preservatives against insects is performed according to EN 46-1 modified for the insect species. The insect utilized for experiment was a south Mediterranean species *Trichoferus holosericeus* (Rossi) that is specialized for hardwood. It was reported that some artifacts had been attacked by this species in an Art and Crafts Museum (Gambetta 1995; Palanti et al. in press).

Wood species

Beech (*Fagus sylvatica* L.), this is the reference hardwood species for European standards because is very susceptible to biological attacks. The sample wood must be exclusively sapwood containing little resin (although beech does not have resin) and having between 2.5 annual rings per 10 mm and 8 annual rings per 10 mm. The sound wood samples were free from visible cracks, stain, insect damage and other defect.

Size and Number of Specimens

The dimensions of each test specimens were 50 x 25 x 15mm (Fig.3.21.). The longitudinal faces were parallel to the direction of grain. The annual ring had a contact angle of (45 ± 15)° to the broad faces. Transversal faces were cut neatly to give sharp edges and a fine-sawn finish to the end-grain surfaces, to give test specimens 50 mm long.

3 specimens for each preservative and 3 untreated control test specimens were prepared. (Red Petroleum: 3, Propolis: 3, Biotin R: 3, Control: 3, Total: 9 specimens)

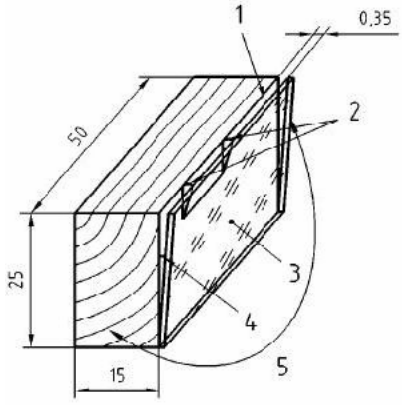


Fig.3.21. Size of specimens for insect attack test (European Standard EN46-1)

Wood preservatives

In this experiment Romanian traditional products (Red Petroleum and Propolis) utilized for wooden cultural heritage and Biotin R (commercial antifungal product used as a reference) were used to assess the efficacy against insect.

Insect species

Trichoferus holosericeus (Rossi) = *Hesperophanes cinereus* Villiers (Linnaeus) (Fig.3.22.).

Fig.3.22. *Trichoferus holosericeus* (Rossi) (Photo from IVALSA)

Sample Preparation Procedure

1. Paraffin wax (Fig.3.23.) was put on transversal section of specimens for sealing the end faces of test specimens to be treated with solutions (Red Petroleum, Propolis and Biotin R). Three coats of the paraffin at about 90 °C were applied so that the first coat adheres closely to the wood and the successive coating bond one to another.

Fig.3.23. Preparation for paraffin wax and put paraffin wax by brushing

2. Specimens except control ones were treated with solutions (Red Petroleum, Propolis and Biotin R) by brushing and mass of absorbed solution per test specimen was determined and reported in Table.3.2. Three specimens with similar retention of applied products were selected for the experiment in each solution.

Table.3.2. Retention of preservative solutions

Specimen	g/m^2
Red Petroleum 1	57,9
Red Petroleum 2	50,6
Red Petroleum 5	51,6
Propolis 1	95,5
Propolis 4	96,2
Propolis 5	96,9
Biotin R 3	67,0
Biotin R 4	64,1
Biotin R 5	63,7

3. Glass plate was put in order to provide a lateral slit on the test specimens for larvae and was fixed with paraffin wax.

4. Recently hatched 10 larvae of *Trichoferus holosericeus* (Rossi) were placed between glass plate and test specimens (Fig.3.24.). Single specimen was put in a Petri dish, one specimen in one Petri dish.

5. All specimens were placed in the testing chamber, ventilated and air conditioned chamber, controlled temperature at (22±2)°C and at a relative humidity (70±5)%.

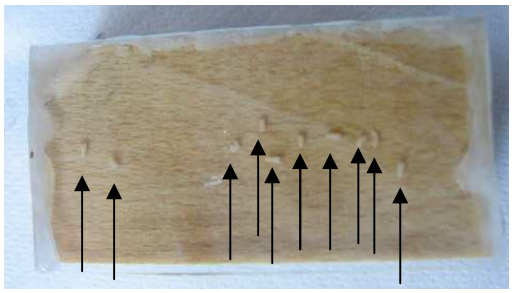


Fig.3.24. Specimen with exposed larvae

Assessment Procedure

After 4 weeks and 12 weeks, all specimens were observed by naked-eye, stereomicroscope and X-ray radiography. In the end specimens were cut up with microtome (Fig.3.25.) in order to count how many larvae were alive in specimen. This microtome is mainly used for slicing animal and plant tissues, being simple to use, easy to operate and highly practical. After specimens were cut up with microtome, slices of specimens were observed with stereomicroscope.

Fig.3.25. Microtome

3.5 Methods and techniques

3.5.1 Physical parameter

Physical parameters of samples such as moisture content (MC), density, porosity, and shrinkages were calculated with the following formula:

$$MC\ (\%) = (W\text{-}W_{od}) / W_{od} \times 100 \quad (3.1)$$

W = the weight of specimen of wood in the conditions of humidity considered ("original" state),

W_{od} = the weight of the same specimen in the oven-dry state;

$$Density\ (\rho) = m / V \quad (3.2)$$

m = mass, V = volume, both at the considered conditions;

$$Shrinkage = (l_1 - l_2) / l_1 \times 100: \quad (3.3)$$

l_1 = the length before shrinking, l_2= the length after shrinking;

$$Porosity\ (Z) = (1 - \rho_0/1530) \times 100(\%) \quad (3.4)$$

ρ_0= oven dry density, $\rho_0 = W_0 / V_0$ (kg/m^3).

The physical parameters of sample without tempera and with tempera (sample A) were considered and compared in order to clarify the impact on wood. Those data were interpreted with statistical software R.

3.5.2 Colorimetry

Colorimetry is non-destructive technique to control pigment colour changes, giving the description and qualification of human colour perception. This includes studies of the colour –matching characteristics of the human visual system, the ability of observers to notice small differences in colour, the phenomenon of adaptation to differently coloured light sources, and studies of human perception of colour in general. Colorimetric evaluation offers the same perception as the human eye, with the benefit of being free from subjective and varying external influences, thus providing objective results. As opposed spectrometry, which can be used to determine, for instance, the decay of a given colour with exposure, colorimetry is used when it is desirable to express changes in terms of appearance (Pinna et al., Eds., 2009).

In the field of art conservation, colorimetry is applied to evaluate the differences between colours of neighbouring areas in artworks before and after conservation, to monitor fading phenomena caused by exposure to specific environmental conditions, and to study colour alteration, for instance resulting from the application or removal of top layer of varnish.

Since the early 1920's, a significant goal of color vision research has been the specification of human color response in a way that can be implemented as electronic color measurement devices-colorimetry. Starting in 1931, much of this work has been done under the auspices of the Commission Internationale de l'Éclairage (CIE), an international clearinghouse for color research at universities and research laboratories. All the CIE and related colorimetric models are based on the trichromatic outputs of the R, G and B cones. This framework allows precise mathematical modeling of color vision using computerized spectrophotometric measurement.

A recent milestone in this effort is the CIE L*a*b* color system (CIELAB for

short), first published in 1976. CIELAB has a long research pedigree, starting from the Munsell color model. In fact, differences in color notation aside, the color spaces defined by CIELAB and Munsell are similar. The CIELAB colour difference between two samples is defined as:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (3.5)$$

where ΔE is the magnitude of the colour difference and ΔL*, Δa* and Δb * are the differences in L*, a* and b*coordinates, respectively, of the two colours.

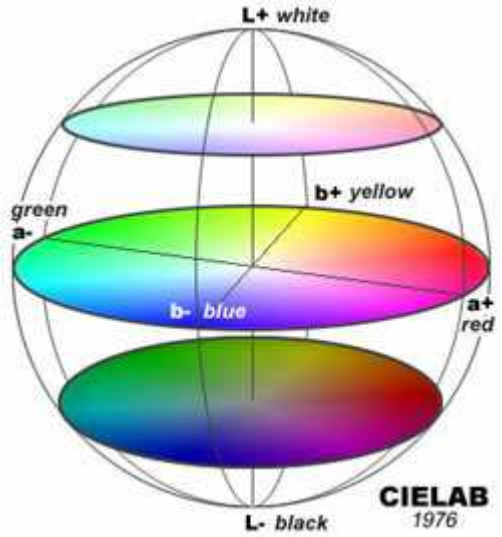


Fig.3.26. CIE L*a*b* 1976 color space appearance (Pinna et al., Eds., 2009)

CIE LAB 1976 made it possible to plot points within a linear structure. It made the shape similar to a sphere (Fig.3.26.) with the lightness axis running through from top to bottom. This enabled mathematical modeling to be used to more easily predict positions of colour within the CIE 1931 Chromatic Diagram. Using the CIE LAB model has some restrictions including that the sphere is effectively sectioned into cubes so there are areas not covered. Extending this into the LCH model (lightness, chroma, hue) helps because the model is cut up so that the curved polar areas fit more precisely.

For the foreseeable future, new standard will be accepted. In the standard, the different calculation is proposed. Because the L*a*b* colour does not have exact equidistance between perceived colours (difference in the saturated colours are more dfficult to perceive), the colour difference formula ΔE_{94} modifies the lightness, chroma and hue (L*C*h*) of L*a*b* colour space by incorporating factors that correct for variation in perceived colour difference magnitude. It is therefore

recommended that the colour differences for each specimens is calculated from the equation $\Delta E^*_{94,}$ between two colours is:

$$\Delta E^*_{94} = \sqrt{\left[\left(\frac{\Delta L^*}{k_L S_L}\right)^2 + \left(\frac{\Delta C^*}{k_C S_C}\right)^2 + \left(\frac{\Delta H^*}{k_H S_H}\right)^2\right]} \quad (3.6)$$

$$C = \sqrt{a^{*2} + b^{*2}}$$

$$\Delta H = \sqrt{(\Delta E^*)^2 - (\Delta L^*)^2 + (\Delta C)^2}$$

$S_L = 1$

$S_C = 1 + 0.045\Delta C^*$

$S_H = 1 + 0.015\Delta C^*$

$k_L = k_C = k_H = 1$ (default)

The parametric factors, k_L, k_C, k_H are correction terms for variation in experimental conditions. Under reference conditions are all set at 1 (CEN/TC 346, 2008). Although this new equation (ΔE^*_{94}) is considered to bring algebra closer to human experience, it is still under the discussion for standard. With this reason, CIE LAB 1976 was used in this research.

Minolta Chroma Meters CR-200 has been used to measure the colour of Sample A. Technical data is as following.

Type: Reflected-light colorimeter;

Receptors: 6 silicon photocells filtered to detect primary stimul stimulus values for red, green, and blue light;

Spectral response: Closely matches CIE Standard Observer curves;

Light source: Pulsed xenon arc lamp;

Illumination/measurement system: Diffuse illumination/0° viewing angle;

Measuring area: Ø8mm.

3.5.3 FTIR-ATR

Infrared spectroscopy allows the chemical characterization of materials, both organic and inorganic. The result of an infrared analysis is a spectrum, where the percentage of transmission/absorbance of the sample is plotted against wavenumbers (cm^{-1}) in which the transmission/absorbance of the analyzed sample occurred (Pinna et al., Eds., 2009). Attenuated total reflectance (ATR) infrared spectroscopy is a measuring technique for superficial analysis of materials.

In this research FTIR-ATR technique has been used to observe the penetration of the treatment solutions with sample without tempera. FTIR-ATR measurements are performed upon contact of the material to be analyzed with a medium of high refractive index (internal reflection element, IRE), the ATR crystal. As infrared radiation impinges on the IRE, it is totally reflected. However, if an IR absorbing medium is placed in contact with the IRE, the evanescent wave becomes attenuated, with specific wavelengths absorbed at each reflection point by the IR absorbing medium. From the attenuated radiation a spectrum is produced which is characteristic of the absorbing material.

The spectra have been recorded with an ALPHA FT-IR spectrophotometer from Bruker Optic, Germany, which is the smallest FTIR spectrometer and an advanced flexible bench-top instrument suitable for routine applications as well as laboratory research (Fig.3.27.). ALPHA is designed for measurements mainly in the mid – infrared region.

Fig.3.27. ALPHA FTIR from Bruker (Image from Bruker)

3.5.4 X-ray Radiography

When in 1895 Wilhelm Röntgen discovered X-rays, this opened up a new way for people to 'look through things' (Röntgen, 1896). Since its invention, the technique has become an invaluable tool for conservators and researchers and has been applied to a great variety of materials (Lang 2005; Berg 2008). X-ray radiography is a very useful technique to investigate the internal structure condition and allows investigating the condition of wood (Pinna et al., Eds., 2009). In this research x-ray radiography technique was used for detecting how many larvae were alive in the specimens. X-ray radiography is an imaging technique applicable for the examination of any art object on a moveable support that allows X-rays, to run through. It is a non-destructive method. The only potential effect to the objects is due to their exposure to the dose of X-rays during the measurement. A limitation of conventional X-ray imaging is that not depth resolved information is obtainable. Therefore to securely interpret the X-ray images, the recorded information has to be evaluated with reference to the visible image and in comparison with other technical images such as IR reflectograms.

In this research X-ray radiography has been carried out to see how many larvae are in specimens. The exposure was obtained by putting the specimens in direct contact with a fine grain radiographic film (Agfa Structurix D7 DW)(Fig.3.28.). The exposure conditions were: voltage 28 kV; anodic current 5 mA; distance X-ray tube–object 700 mm; exposure time 3 min.

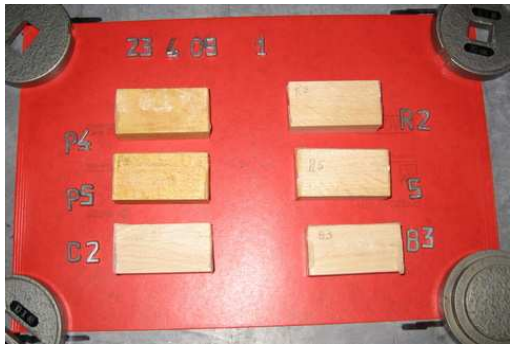


Fig.3.28. Specimens on the film

3.5.5 Naked-Eye Observation

In insect attack test, all specimens were observed with naked-eye without a magnifying lens or a microscope to control how much powdery frass they produced in omaking tunnel galleries in wood samples and how many tunnels larvae made. The first unaided eye observations can give a rough and important information, how active the exposed larvae were. Naked-eye observation is one of the most fundamental ways.

3.5.6 Stereomicroscopy

Micro-structure characterization of specimens has been performed by stereomicroscope (WILD Heerbrugg M420) observations. Stereomicroscope is effective in revealing the details of surface condition and counting exactly how many tunnels larvae made in insect attack test.

Stereomicroscope, also called dissecting microscope, consists in two compound microscopes which focus on the same point from slightly different angles. This allows the specimen to be viewed in three dimensions. As opposed to compound microscopes, the image is upright and laterally correct (not upside down and backwards). Stereomicroscopes are relatively low power compared with compound microscopes, usually below 100x. They can have a single fixed magnification, several discrete magnifications, or a zoom magnification system. (Mabuchi et al., ed., 2003)

3.5.7 Visual assessment

Subjective visual rating of sample is the traditional method for assessing progressive microbial spoilage with samples with tempera painting (sample A) after 100 RH.

Assessment of mould attack has been carried out with simple visual grading criteria (Fig.3.29.). The rating scheme was based on European standard (prEN 927-3 1995).

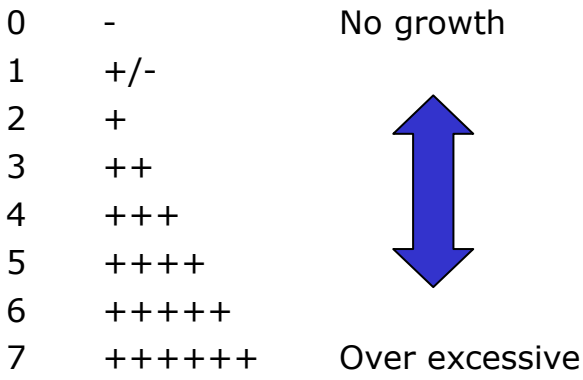


Fig.3.29. Grading of mould attack

Surface discolorations by mould attack degrade the appearance and value of panel painting and are early indicators of susceptibility to general mould attack and environmental condition. The purpose of this assessment is to have a visual idea of the differences between treatments.

3.5.8 Statistical software R

Due to the dispersion of the physical parameters, statistical analysis had been carried out. To do this, the application R (Ihaka and Gentleman, 1996 R Development Core Team, 2008; http://www.r-project.org/) was used. R is a language and environment for statistical computing and graphics. This software is an integrated suite of software facilities for data manipulation, calculation and graphical display. It includes

- an effective data handling and storage facility;
- a suite of operators for calculations on arrays, in particular matrices;
- a large, coherent, integrated collection of intermediate tools for data analysis, graphical facilities for data analysis and display either on-screen or on hardcopy;
- a well-developed, simple and effective programming language which includes conditionals, loops, user-defined recursive functions and input and output facilities.

The interpretation by boxplot with notch was useful to see the result visually (Fig.3.30.). A notch is a V-shaped indentation in the box, centered on the median line. This feature is a quick way to decide if the medians in any two boxes are different from each other at the alpha = 5% significance level. If the notches overlap (looking horizontally across the boxes in the default orientation), they are not different. Separated notches are different.

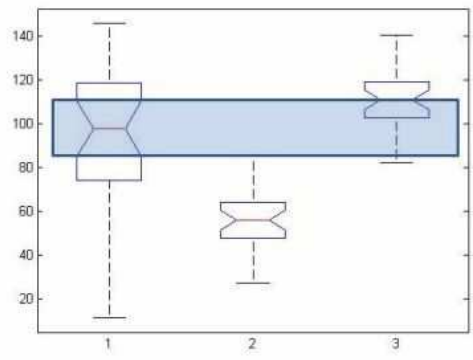


Fig.3.30. Boxplot

The box limits represent the lower quartile Q1 (25th percentile) and upper quartile Q3 (75th percentile), the median is displayed as a line across the box. The median is the position index and the difference between the first and third interquartile IRQ (Q3-Q1) the dispersion index. Whiskers are drawn from the upper quartile to 3/2

IRQ value, and from the lower quartile to the -3/2 IRQ value. Outside and far outside values may be displayed as symbols (Fig. 3.31.) (Santoni 2009a, b).

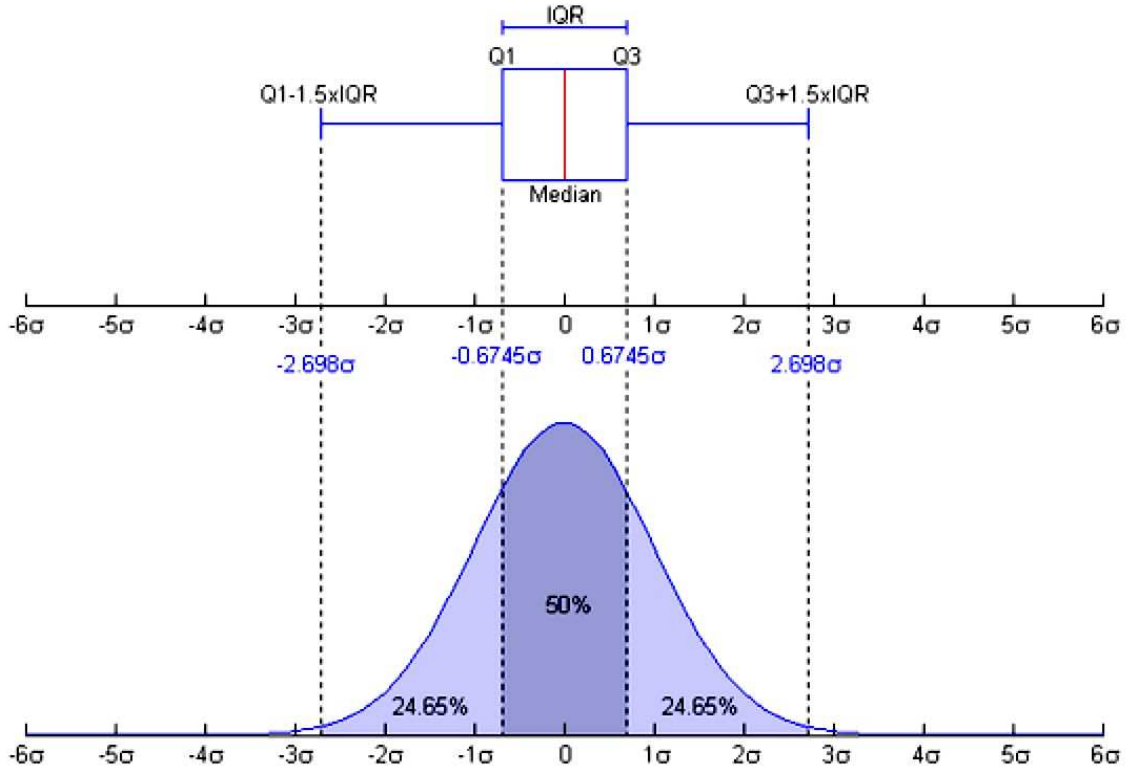


Fig.3.31. Boxplot and a probability density function (pdf) of a Normal $N(0,1\sigma^2)$ Population (http://en.wikipedia.org/wiki/Box_plot)

CHAPTER 4:

RESULTS AND DISCUSSION

4.1 Moisture conditioning

4.1.1 Samples without tempera painting

In this experiment, two sizes of samples (5x2x1, 5x1x1 cm) were used. But as there is not significant difference between sizes, all data have been elaborated together.

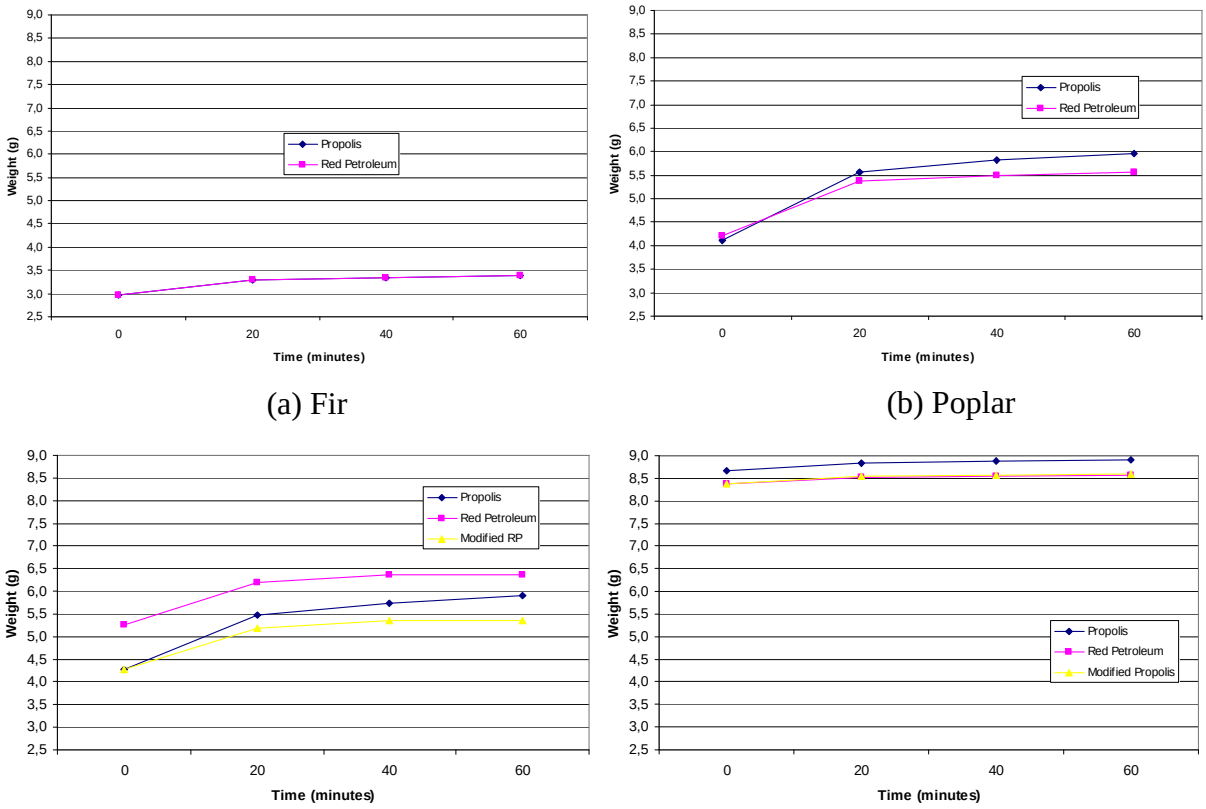
Penetration

The penetration of the solution has been considered by simply weighting the variation of mass during the treatments (Red Petroleum and Propolis) and for each relative humidity (RH) at equilibrium and also using the FTIR-ATR technique.

Weight variation during treatments

The weight of specimens was measured during the treatments and the exposure of each RH at equilibrium. Fig.4.1. shows the weight variation during the treatments. Taking into account the different initial weight of lime and oak, two lines (in Fig.4.1.(c) and (d)), a line treated with Red Petroleum for lime and a line treated with Propolis for oak) were put down parallel in order to have the same initial weight to compare the difference between Red Petroleum and Propolis. Fir and oak samples do not have any difference between the treatment with Red Petroleum and Propolis and the weight increased a little, meaning that the penetration of the products into those woods is very small. On the contrary, poplar and lime have almost the same characteristics as for the specimens treated with Propolis which increases more than for Red Petroleum. The weight of specimens treated with Propolis for poplar increased up to 1.8g for 60 minutes and 1.6g for lime. The weight of specimens treated with Red Petroleum increased 1.3g for poplar and 1.1g for lime respectively. Poplar absorbs products slightly more than lime. From one side it seems that the penetration of Propolis is higher than Red Petroleum, but, considering that the Propolis is diluted into ethyl alcohol, which is very volatile, probably the higher

penetration of substance is for Red Petroleum, which does not have solvent; it is a solution itself.



(a) Fir (b) Poplar

(c) Lime (d) Oak

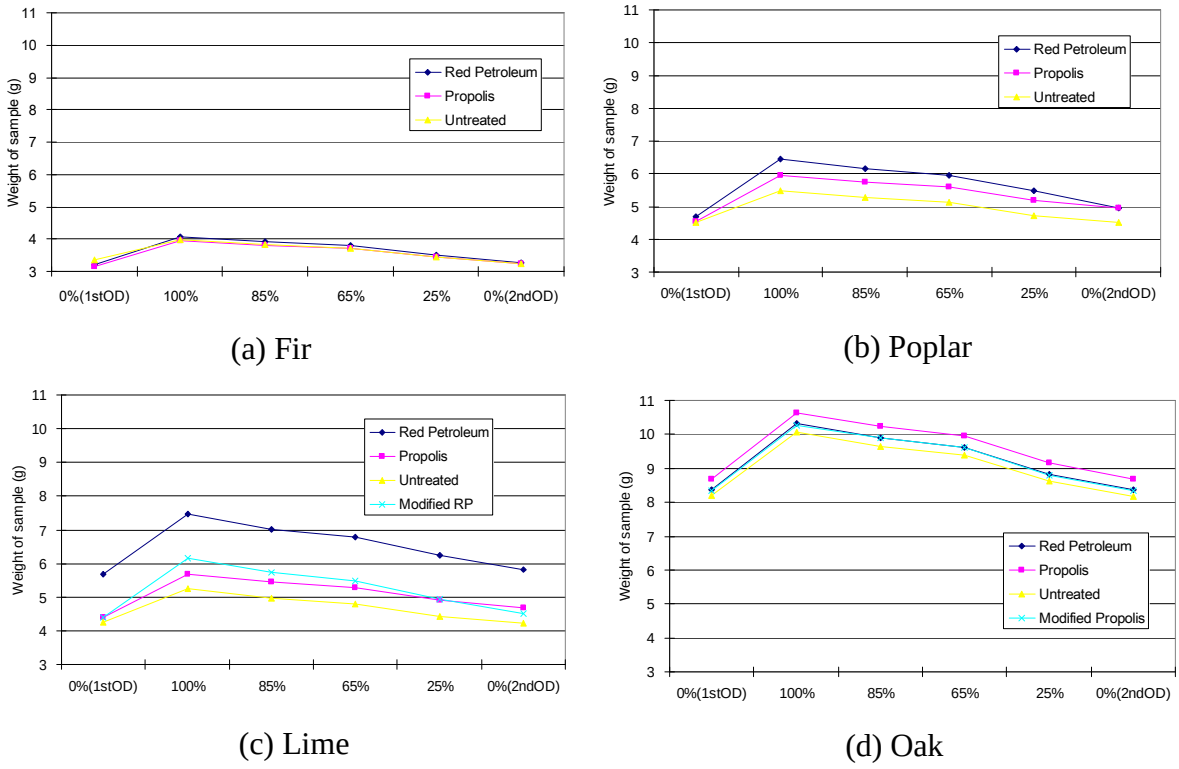
Fig.4.1. Weight variation during treatments

Weight variation for each RH at equilibrium

The weight variation for each RH at equilibrium has been measured (Fig.4.2.). The weight at 0% (1st OD (oven-dry)) is the weight before treatments. Treatment solutions were applied after 1st OD and then specimens were put at each RH until equilibrium. Taking into account the differences of the weight for 1st OD of lime and oak, two lines (in Fig.4.2.(c) and (d)), a line treated with Red Petroleum for lime and a line treated with Propolis for oak) were put down parallel in order to have the same initial weight to compare. Fir and oak samples do not have any difference between Red Petroleum, Propolis and untreated specimens. The weight at each RH at equilibrium is almost the same and the graph lines of fir and oak overlap to each other.

Poplar and lime have almost the same characteristics. Specimens treated with Red Petroleum display a greater weight than Propolis and untreated samples from 100% RH to 25% RH and the weight at 0% (2^{nd} OD) RH is almost the same.

The results of weight variation during treatment (Fig.4.1.) show that fir and oak samples do not absorb any treatment solution but poplar and lime absorb some solutions, more Propolis than Red Petroleum. However, the results of weight variation for each RH at equilibrium (Fig.4.2.) shows that the weight of the specimens treated with Red Petroleum always display greater values than Propolis. As it is discussed in the weight variation during treatments, Propolis is diluted with ethyl alcoholic solvent at 20% and ethyl alcohol is a fast-evaporating solvent (Oh 2003). This evaporated after Propolis treatment. This is the reason why the specimens treated with Propolis have lower weight than Red Petroleum for each RH at equilibrium. These results could explain that penetration of Red Petroleum is higher than Propolis. In addition, it should be underlined that the weight at 2^{nd} OD of specimens treated with Red Petroleum and Propolis is almost same, demonstrating that Red Petroleum is volatile compounds and most of it evaporates at OD state (high temperature). Taking into account these results, Red Petroleum penetrates deeper but it is easy to evaporate and lose the solution from specimens treated with Red Petroleum at high temperature.



(a) Fir (b) Poplar

(c) Lime (d) Oak

Fig.4.2. Weight variation during for each R.H. at equilibrium

FTIR-ATR

FTIR-ATR analysis has been carried out in order to detect the penetration of treatment products (Red Petroleum and Propolis).

- Red Petroleum

In order to detect the penetration of Red Petroleum, three FTIR-ATR spectra (untreated wood, wood treated with Red Petroleum and Red Petroleum solution) have been obtained (Fig.4.3.).

Several points (different depth) were analyzed. However, Red Petroleum has been detected in all points and for this reason only the result in the middle of specimen is included in this thesis.

As for untreated wood, there was a strong broad O–H stretching absorption band around 3425 cm^{-1} and a prominent C–H stretching absorption band around 2931

cm^{-1}. Since these bands have contributions from both carbohydrates and lignin, they have a limited use in analyzing the chemical changes of wood due to treatment (Wang 2008). In the fingerprint region between 800 and 1800 cm^{-1}, there were many well-defined peaks providing abundant information on various functional groups present in wood constituents (Table.4.1.). The stronger absorption at 1735 (3) and 1238 (10) cm^{-1} reflected a higher holocellulose (cellulose and hemicellulose) content present in the hardwood (Wang 2008).

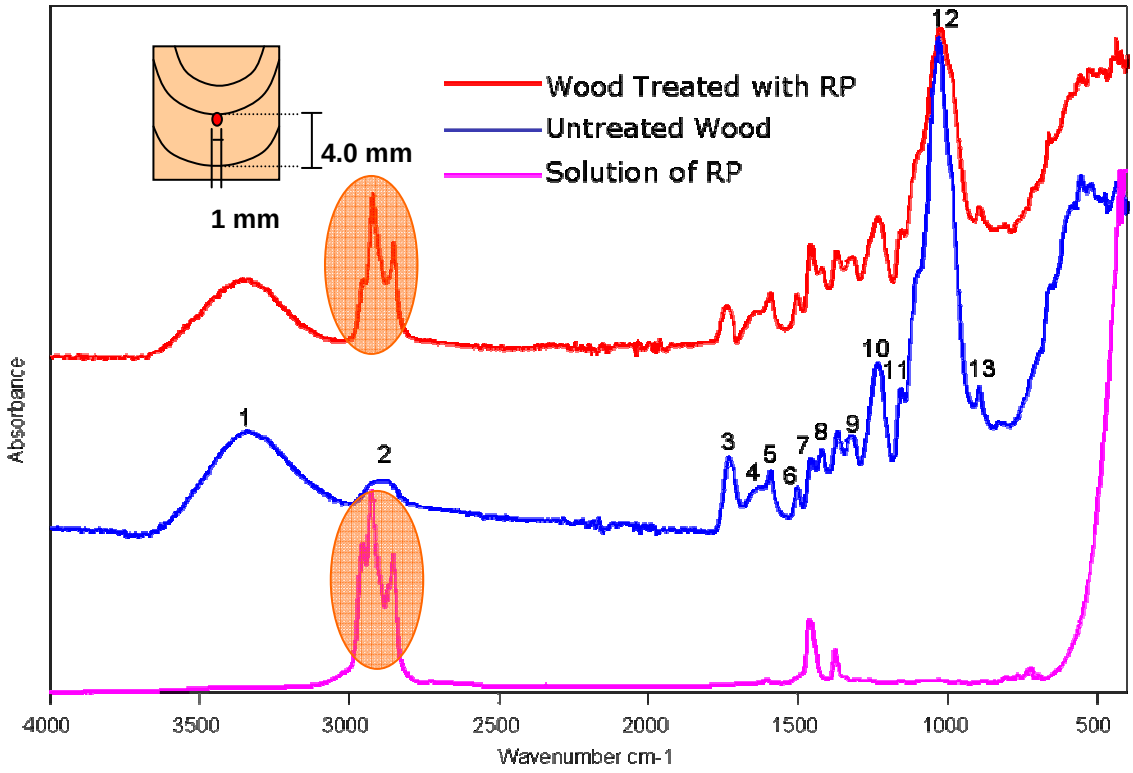


Fig.4.3. FTIR-ATR spectra for specimens treated with Red Petroleum in Lime

Table.4.1. Assignment of absorption IR spectra peaks in wood (Wang 2008)

Wave number (cm^{-1})	Assignments and remarks
3425 (1)	O–H stretching
2931 (2)	C–H stretching
1735 (3)	Non-conjugated C O in hemicellulose (xylans)
1639/1654 (4)	Conjugated C O in lignin
1596/1604 (5)	Aromatic skeletal vibration in lignin
1508/1512 (6)	Aromatic skeletal vibration in lignin
1462 (7)	C–H deformation in lignin and carbohydrates
1377–1423(8)	C–H deformation in lignin and carbohydrates
1330(9)	C–H vibration in cellulose; C–O vibration in syringyl derivatives
1238/1242 (10)	Syringyl ring and C–O stretch in lignin and xylan
1157 (11)	C–O–C vibration in cellulose and hemicellulose
1030–1057 (12)	C–O stretch in cellulose and hemicellulose
898 (13)	C–H deformation in cellulose

Red Petroleum can be easily discriminated in wood. In fact, the three remarkable peaks (2800-3000 cm^{-1}) are good indicators for Red Petroleum, as the wood spectra do not have those peaks in this area (Fig4.3.). However, just to confirm this, the spectra were subtracted in order to detect the solution easier in specimens (Fig.4.4.). This is a good method to detect solutions in wood. The result of manipulation shows that the penetration of Red Petroleum is until the middle of specimen.

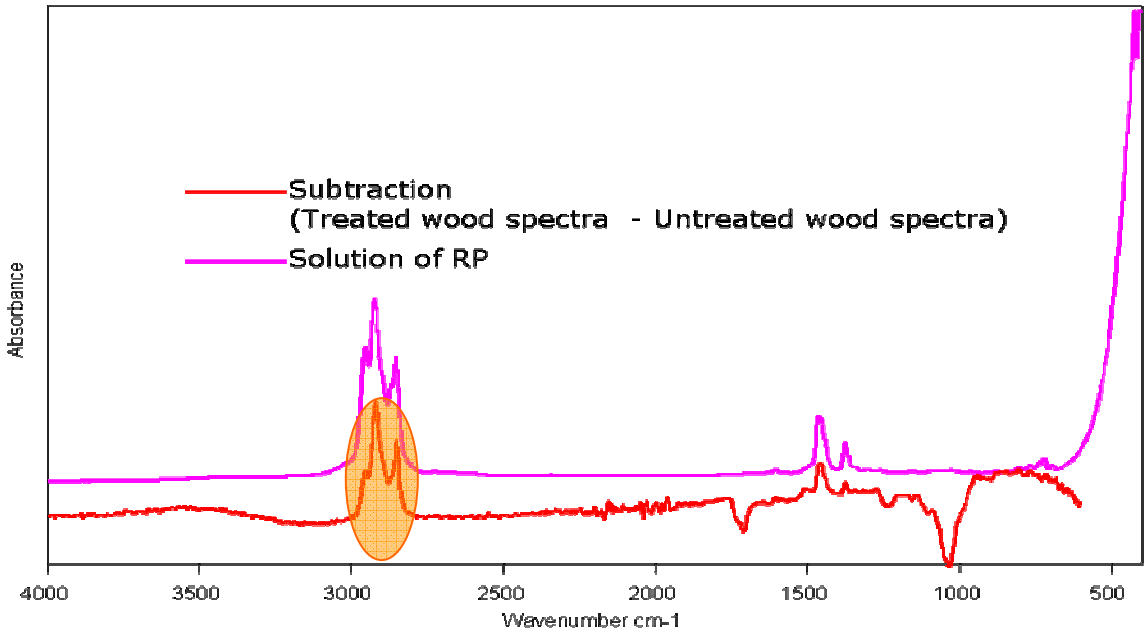


Fig.4.4. Manipulated FTIR-ATR spectra treated with Red Petroleum in Lime

- Propolis

In order to detect the penetration of Propolis, FTIR-ATR spectra of untreated wood, wood treated with Propolis and Propolis solution have been obtained (Fig.4.5.).

Three points (surface, beneath the surface and the middle of specimen) were analyzed in different depth. The spectra of Propolis and wood have similar peaks (Fig.4.5.). Observing the three spectra, it is difficult to detect Propolis in wood. And the same procedure of subtraction was conducted in order to detect Propolis in wood (Fig.4.6.). The spectra after subtraction evidence the presence of Propolis only at the surface, while in the spectra of beneath the surface and in the middle of the sample we can not clearly distinguish any peaks of Propolis. This result shows that Propolis is, most probably, not penetrated inside the wood.

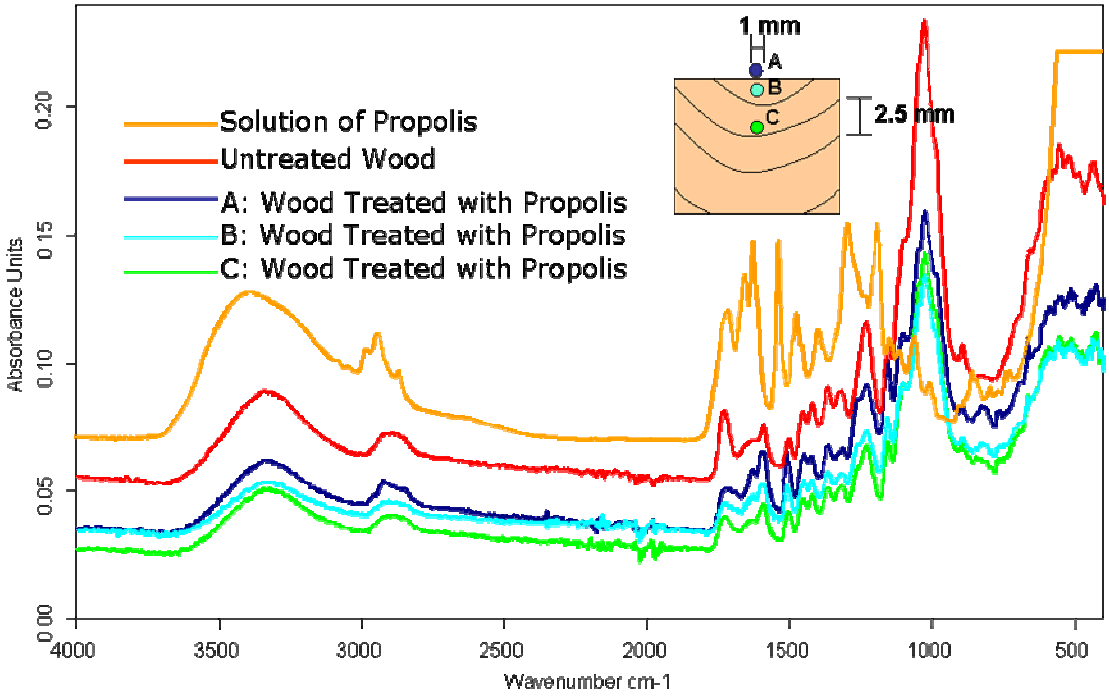


Fig.4.5. FTIR-ATR spectra for specimens treated with Propolis in Lime

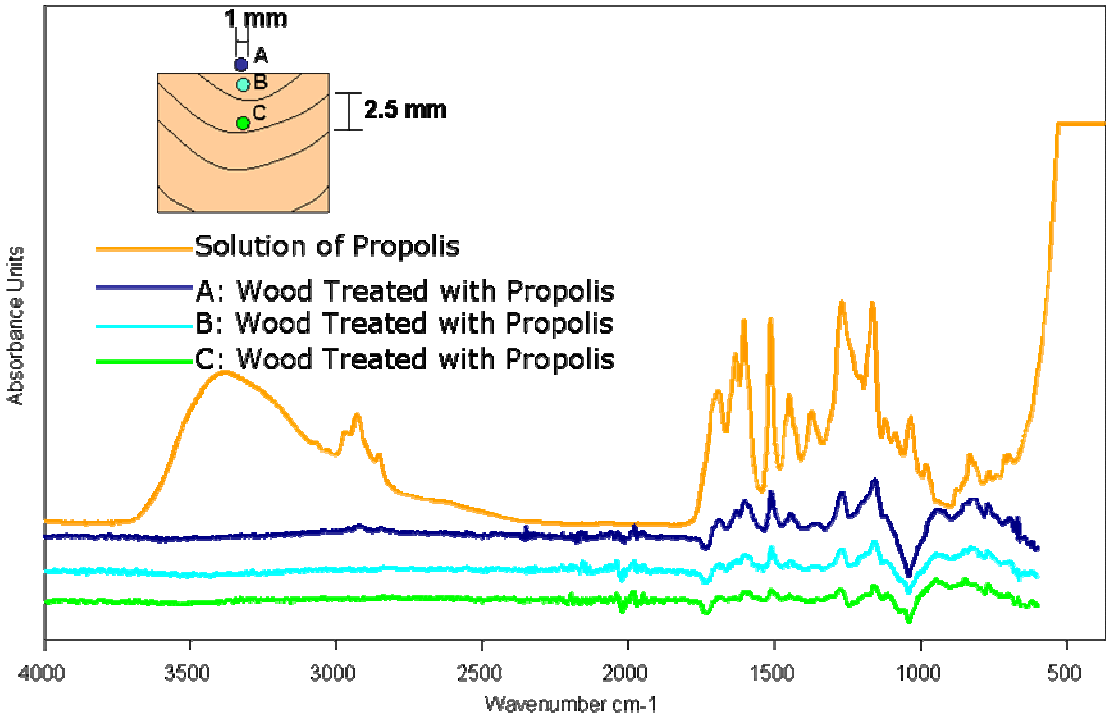


Fig.4.6. Manipulated FTIR-ATR spectra treated with Propolis in Lime

From these FTIR-ATR analysis, it is confirmed that the penetration of Red Petroleum is until the middle of specimens (about 5mm), on the contrary Propolis is only surface.

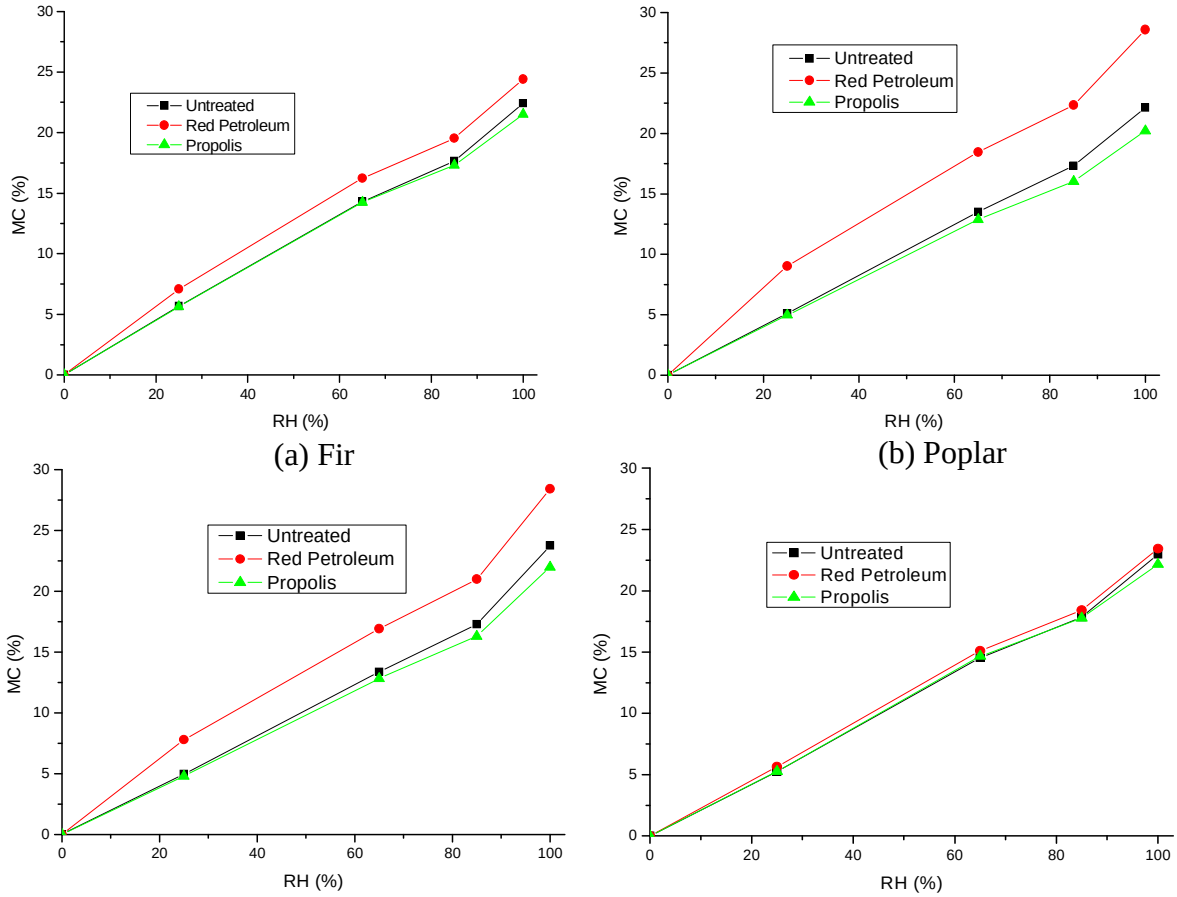
Taking into account the weight variation during treatments and for each RH at equilibrium and FTIR-ATR results, Red Petroleum penetrates a lot, but at low RH condition Red Petroleum evaporates, meaning that the samples treated with Red Petroleum lose the treatment products at low RH condition and mostly at high temperature. On the other hand, higher amount of Propolis solution penetrates more than Red Petroleum during the treatment by immersion, but solvent (ethyl alcohol) evaporates soon and Propolis substance remains only on the surface of samples. Samples treated with Propolis do not lose Propolis substance even in low RH condition or high temperature.

All these results suggest that Red Petroleum does not chemically interact with wood substance so much and it is easier to vaporize at low RH condition or high temperature than Propolis. On the contrary Propolis interacts chemically with wood substance and it is not easy to vaporize even at low RH condition and remains on wood surface.

Physical parameters

Moisture content (MC)

MC for each relative humidity (RH) at equilibrium was calculated with the formula (3.1) (Fig4.7.). In all species of wood, MC of samples treated with Red Petroleum was higher than those treated with Propolis and untreated ones, especially in fir, poplar and lime. Oak (d) sample shows almost no difference between untreated and treated specimens. In fact, the weight of specimens changed very little before and after treatment due to the poor penetration of the treatment solutions.



(a) Fir (b) Poplar

Fig.4.7. MC versus RH of untreated and treated wood

Fig.4.8. shows the sorption hysteresis for the wood samples in climatic cell for 50 weeks, the adsorption process and the desorption process (Ishimaru 2001). Previous hysteresis was traced for not more than several weeks (Stamm 1941; Stamm 1964). There were no significant differences from previous results. In this experiment, the samples were planned to stay in the climatic box until equilibrium but it seems that specimens at 100% RH for 7 weeks were not achieved the equilibrium (Fig4.7.) in all species of wood, while equilibrium moisture content (EMC) at 100 RH at 20 °C is about 30% (Table.4.2.).

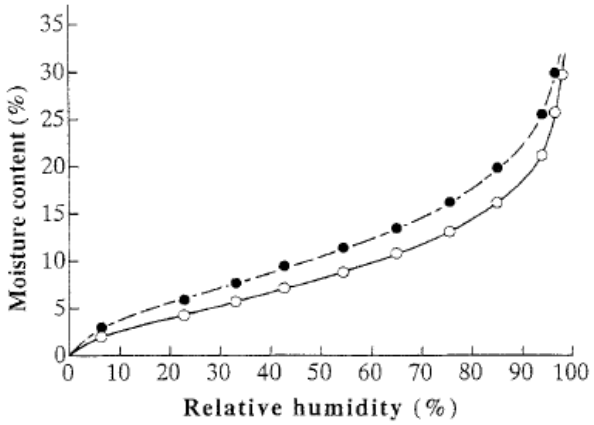


Fig.4.8. Adsorption (*open symbols*) and desorption (*solid symbols*) isotherms of wood moisture-conditioned for a period of 50 weeks (Ishimaru 2001)

MC at 85%, 65% and 25% of specimens can be considered to reach the equilibrium from solid symbols of Fig.4.8. and Table.4.2.

Table.4.2. Typical values of EMC of wood (Uzielli 2006)

RH	Temperature (°C)									
	0	10	20	30	40	50	60	70	80	90
10%	3%	3%	3%	2%	2%	2%	2%	2%	1%	1%
20%	5%	5%	5%	4%	4%	4%	3%	3%	3%	2%
30%	6%	6%	6%	6%	6%	5%	5%	4%	4%	3%
40%	8%	8%	8%	7%	7%	7%	6%	6%	5%	4%
50%	10%	10%	9%	9%	9%	8%	7%	7%	6%	6%
60%	12%	11%	11%	11%	10%	10%	9%	8%	7%	7%
70%	14%	14%	13%	13%	12%	11%	11%	10%	9%	8%
80%	17%	17%	16%	16%	15%	14%	14%	13%	12%	11%
90%	22%	22%	21%	20%	19%	18%	17%	16%	15%	14%
100%	33%	32%	31%	30%	29%	28%	27%	26%	25%	24%

Red Petroleum is hydrophobic solution but MC of samples treated with Red Petroleum is always higer than samples treated with Propolis or untreated samples. MC is calculated with the following formula.

$$MC\ (\%) = (W - W_{od}) / W_{od} \times 100 \qquad (3.1)$$

W should be the weight of sample (the weight of wood substance and the weight of water (moisture) in the wood). But in this experiment W included not only the weight of water but also the weight of treatment products as well. The weight of treatment products has enormous impact on MC due to the penetration of the products, especially in Red Petroleum. Actually MC was not “MC” but “moisture plus treatment product content”. Taking into account that, MC was calculated again with the modification by eliminating the weight of treatment products. As a result MC is

almost the same in different treatmets (Red Petroleum (RP), Propolis (P) and Reference (untreated sample))(Table.4.3.).

Table.4.3. MC before and after modification

(a) Fir								
Before modification					After modification			
	100%RH	85%RH	65%RH	25%RH	100%RH	85%RH	65%RH	25%RH
RP	24,92	19,80	16,49	7,26	23,12	18,37	14,75	5,74
P	21,33	17,24	14,10	5,57	23,74	18,89	15,17	5,90
Reference	22,14	17,61	14,13	5,49	22,14	17,61	14,13	5,49
(b) Poplar								
Before modification					After modification			
	100%RH	85%RH	65%RH	25%RH	100%RH	85%RH	65%RH	25%RH
RP	30,05	24,28	20,34	10,53	20,30	16,42	12,71	4,48
P	19,92	15,96	12,77	4,87	20,96	16,95	13,14	4,64
Reference	21,39	17,35	13,48	4,89	21,39	17,35	13,48	4,89
(c) Lime								
Before modification					After modification			
	100%RH	85%RH	65%RH	25%RH	100%RH	85%RH	65%RH	25%RH
RP	28,68	21,00	16,75	7,50	17,01	12,17	9,13	2,85
P	21,65	16,34	12,79	4,78	22,36	16,09	12,16	4,03
Reference	23,93	17,40	13,31	4,84	23,93	17,40	13,31	4,84
(d) Oak								
Before modification					After modification			
	100%RH	85%RH	65%RH	25%RH	100%RH	85%RH	65%RH	25%RH
RP	23,43	18,41	15,10	5,66	22,52	17,52	14,26	5,15
P	22,17	17,80	14,66	5,26	21,68	16,87	13,74	4,96
Reference	22,96	17,86	14,54	5,25	22,96	17,86	14,54	5,25

According to Table 4.3., the recalculated values for lime are less uniform. Probably the treatment with Red Petroleum removes some terpenic compounds from lime wood. Another physical effect by this removal will be the anomalous shrinkages of Red Petroleum treated lime samples.

The data of MC (original data before modification) were interpreted with statistical software R (Fig.4.9.). The variability of data can be seen visually with boxplot. These boxplots are made with the mixture data of all species of wood at each RH These boxplots show that apparently MC of Red Petroleum displays always higher than Propolis and untreated wood sample due to the penetration of Red Petroleum.

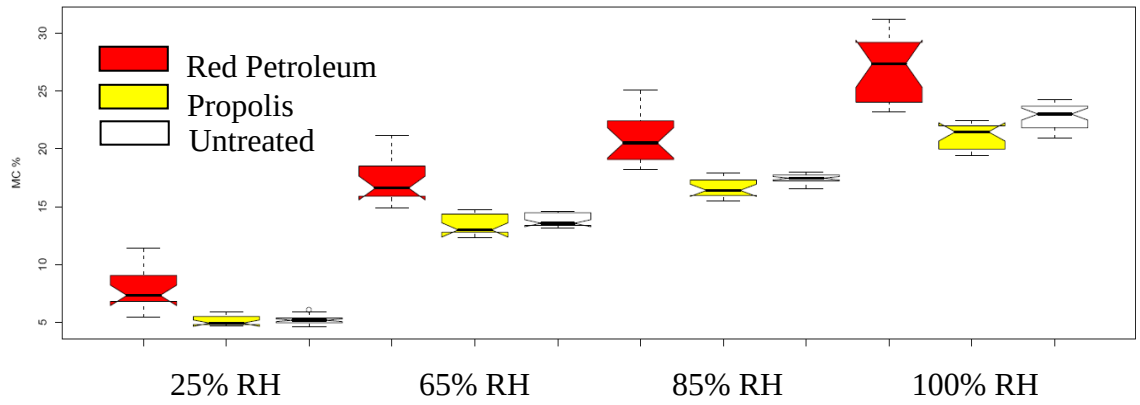


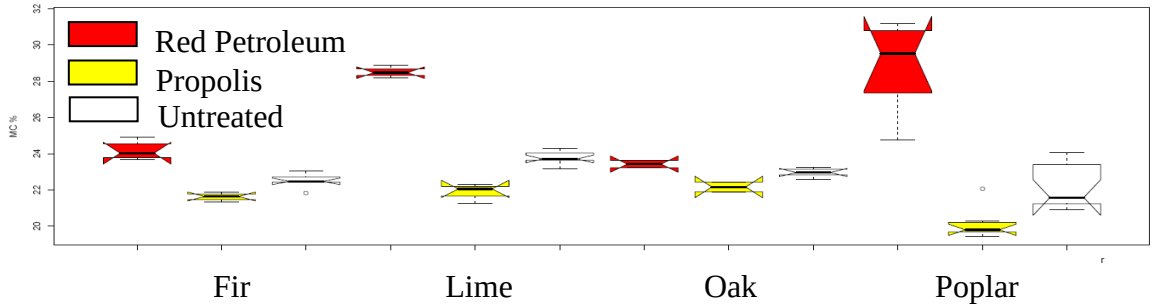
Fig.4.9. Box plots of MC of treatments

Fig.4.10.(a) shows the MC at 100% RH in each species and each treatment. MC of poplar and lime treated with Red Petroleum displayes much higher values than untreated specimens and treated with Propolis. In each species, there is no overlapped area in boxplot, meaning that there is a significant statistic difference between specimens treated with Red Petroleum and untreated and Propolis treated specimens.

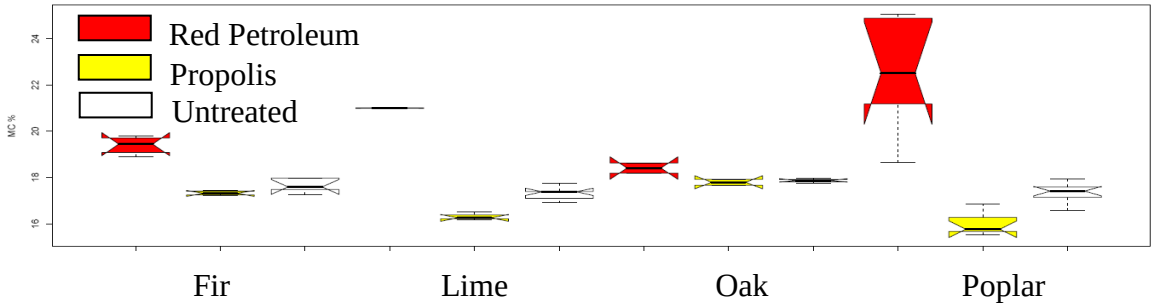
Fig.4.10.(b) shows the MC at 85% RH in each species and each treatments. Distribution is similar as for 100% RH At 85% RH, MC of oak does not have significant difference between treatments, confirming that the amount of treatment penetrated into wood is very small. For fir there is a similar distribution as for oak, although MC treated with Red Petroleum displays still higher values than ohers. Fig.4.10.(c) and (d) show similar distribution as for 85% RH, just the value of MC is shifted at each RH.

For each RH and species, specimens treated with Propolis displayed slightly lower MC than untreated specimens. In poplar, sample treated with Red Petroleum has a large variability than untreated specimens and specimens treated with Propolis. Even the minimun is higher than the maximum value of untreated and Propolis samples.

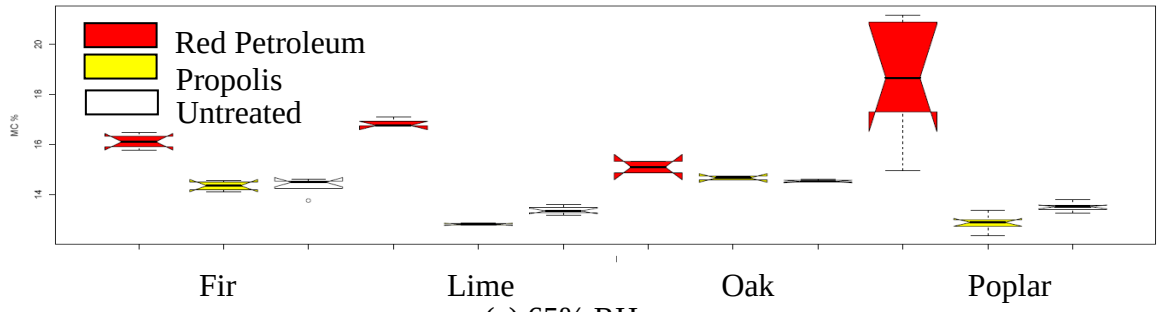
Taking into account all the results of MC, what shoud be underlined is that specimens treated with Red Petroleum always display higher MC, especially in poplar and lime, the difference being remarkable, because in those two species the treatment absorbed by the specimens was higher and it was almost all lost during oven-drying together with water.



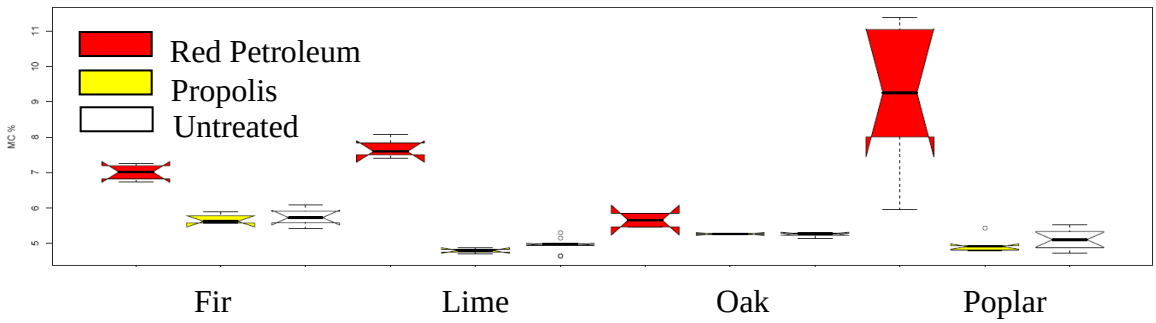
(a) 100% RH



(b) 85% RH



(c) 65% RH



(d) 25% RH

Fig.4.10. Boxplots of MC at each RH

Density

Density at equilibrium at each RH was calculated with the formula (3.2) (Fig.4.11.). From these results there are some differences between species and untreated and treated samples. Fir wood (Fig.4.11.(a)) does not have significant difference between untreated and treated specimens. The graphs of untreated and treated fir overlapped to each other. Poplar samples (Fig.4.11.(b)) have significant difference between untreated and treated samples. From 100% RH to 25% there is a remarkable difference, specimens treated with Red Petroleum displayed the highest density, followed by Propolis and untreated samples. However, when the specimens were put at 0% RH (oven dry), the density at 0% RH has almost the same values in Red Petroleum and Propolis specimens, confirming that the most of the Red Petroleum treatment were lost during the oven drying. As for lime (Fig.4.11.(c)), specimens treated with Red Petroleum always displayed the highest value, followed by Propolis and untreated samples. As for oak (Fig.4.11.(d)), specimens treated with Red Petroleum and Propolis overlapped to each other and untreated samples displayed lower values.

There is a difference between species and treatments but it is extremely important to compare the data with the initial density (before treatment). Initial density is displayed in Table.4.4. Specimens were prepared from the same bars but there is a natural variability in wood (Tsoumis 1991), even if from the same bar. This is one of the most important characteristics of organic materials as wood.

Table.4.4. shows that fir and poplar samples have the same initial density. However, lime and oak samples have a variability (highlighted in yellow). Initial density treated with Red Petroleum was 0.08 g/cm^3 greater in lime and untreated sample was 0.04 g/cm^3 smaller in oak. Taking into account these variability, the whole line of lime sample treated with Red Petroleum and untreated oak sample were

put down parallel in order to have the same initial density with other samples and compare between different treatments of samples (Fig.4.12.).

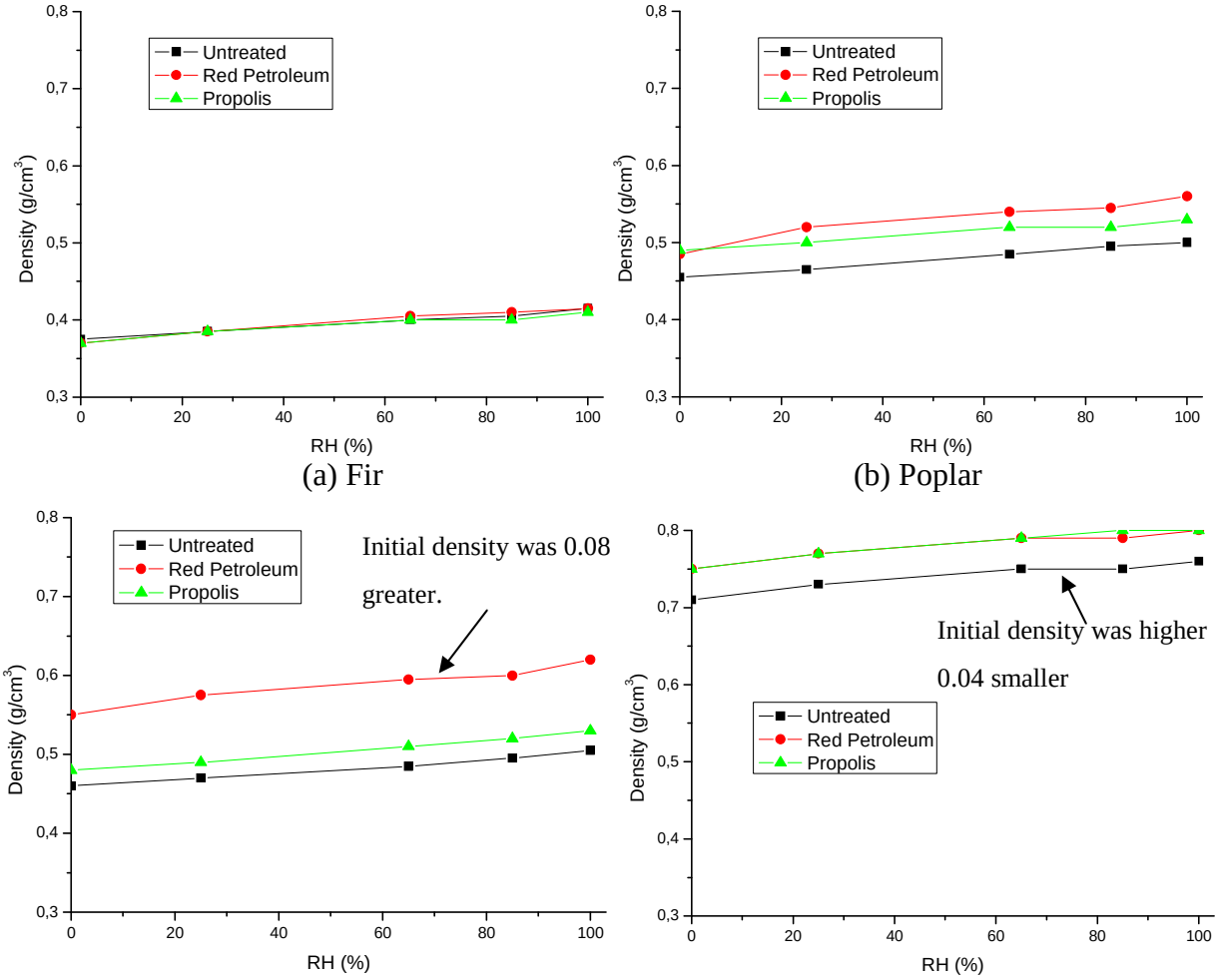
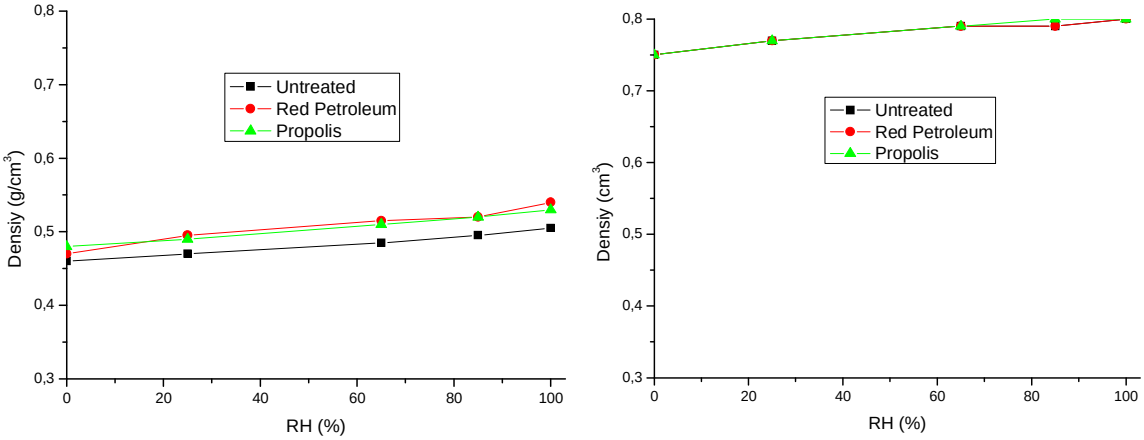


Fig.4.11. Density versus RH of untreated and treated wood

Table.4.4. Initial density (g/cm^3) of specimens

	Fir	Poplar	Lime	Oak
Untreated	0.40	0.48	0.49	0.74
Red Petroleum	0.39	0.49	0.57	0.77
Propolis	0.39	0.49	0.49	0.78

After the correction, the density of untreated lime has smaller density than specimens treated with Red Petroleum and Propolis (Fig.4.12.(a)). The density of oak is almost same in all data (Fig.4.12.(b)) as in the following graphs.



(a) Lime (b)Oak

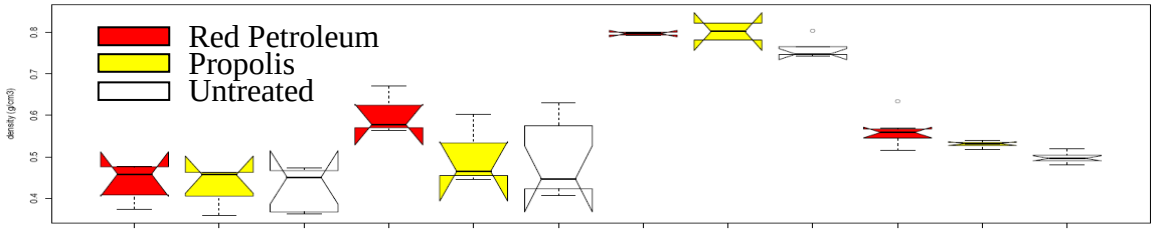
Fig.4.12. Density versus RH after modification

The data of density were interpretedwith statistical software R (Fig4.13.). The variability of data can be seen with boxplots. The samples of lime and poplar treated with Red Petroleum are denser because the amount of product that penetrated into wood is higher. The densities of the oven dry samples demonstrate that most of Red Petroleum treatment evaporates during oven-dry state. As a result the density of sample treated with Red Petroleum and Propolis does not have significant difference, although untreated samples is slightly smaller.

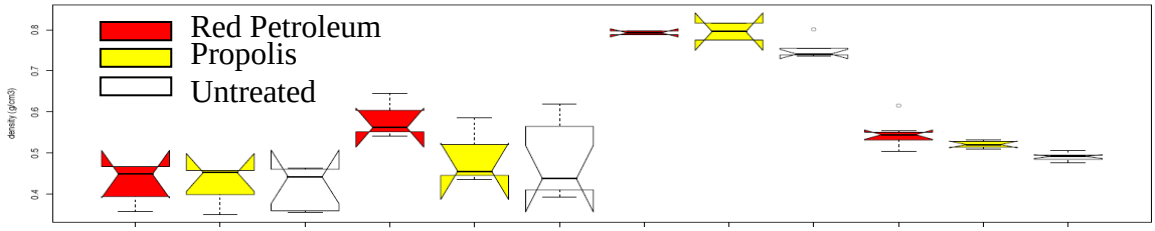
These boxplots were made with original data by statistical software R (Fig.4.13.). Taking into account of initial density, fir, lime and oak samples does not have significant difference between treatments statistically. On the contrary, poplar samples have still significant difference, confirming that there is an impact of Red Petroleum on density, especially at 100% RH and 85% RH.

There is some difference between the result of average (Fig.4.11. and Fig.4.12.) and boxplot with statistical sofware R (Fig.4.13.). With all results of density, it should be mentioned that when data have an extreme outlying number in the group,

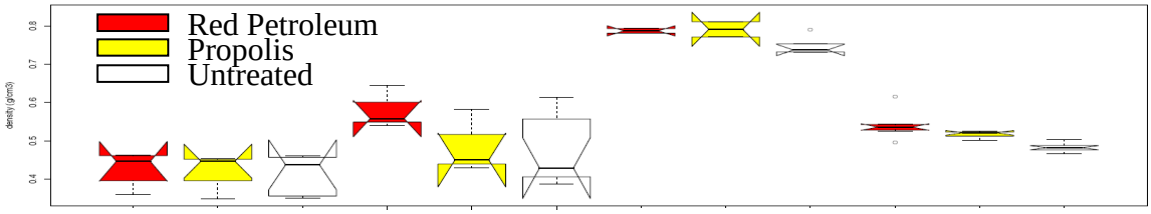
the average can get skewed. With this reason median value is often a better indicator of the middle than the average. Therefore statistical intepretation can be more precise and reliable than average.



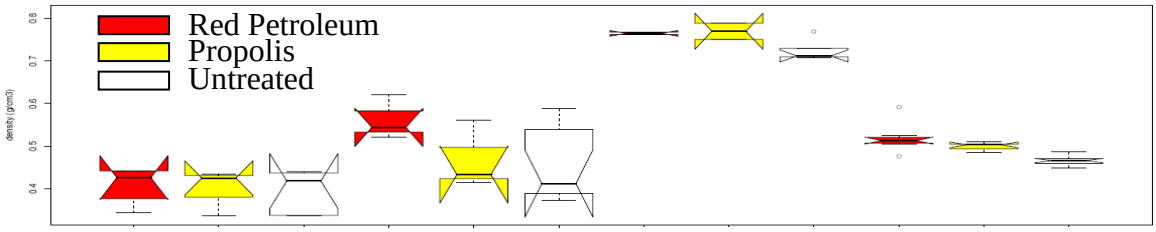
(a) 100% RH



(b) 85% RH



(c) 65% RH



(c) 25% RH

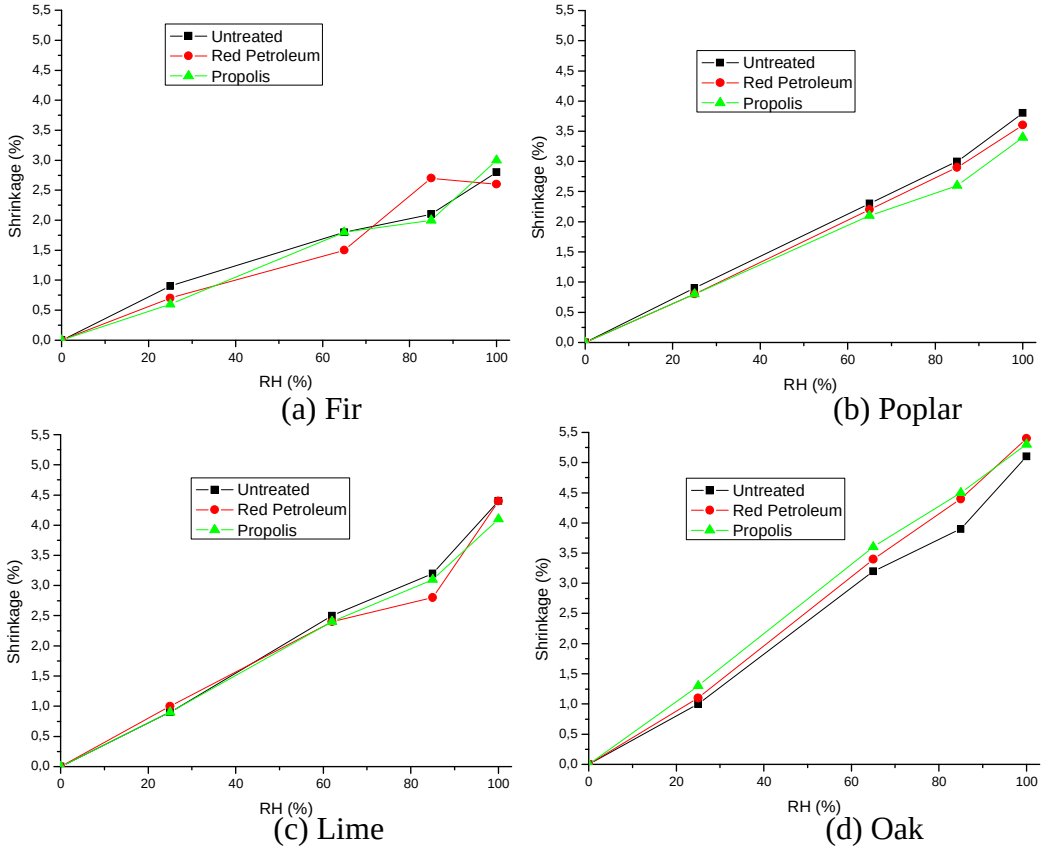
Fig.4.13. Boxplots of density at each RH

Shrinkage

Shrinkage at equilibrium for each RH was calculated with the formula (3.3). Fig.4.14. shows radial shrinkage and Fig.4.15. shows tangential shrinkage for average value.

For radial shrinkage (Fig.4.14.), there is a slight difference between treatments. Fir samples have the lower shrinkage, followed by poplar, lime and oak. The value of shrinkage is higher with higher density (Stamm 1964; Tsoumis 1991). Taking into account the density of specimens: fir (0.40 g/cm^3); poplar (0.48 g/cm^3); lime (0.49 g/cm^3); oak (0.74 g/cm^3), the results of the magnitude of radial shrinkage are exactly in the same order of the density.

For tangential shrinkage (Fig.4.15.), there is also a slight difference between treatments. Fir samples have the lower shrinkage, followed by poplar and lime. They are similar and oak samples have the higher shrinkage. Tangential direction shrinks more than radial one as usual in wood.



(a) Fir (b) Poplar

(c) Lime (d) Oak

Fig.4.14. Radial shrinkage versus RH of wood itself and treated wood

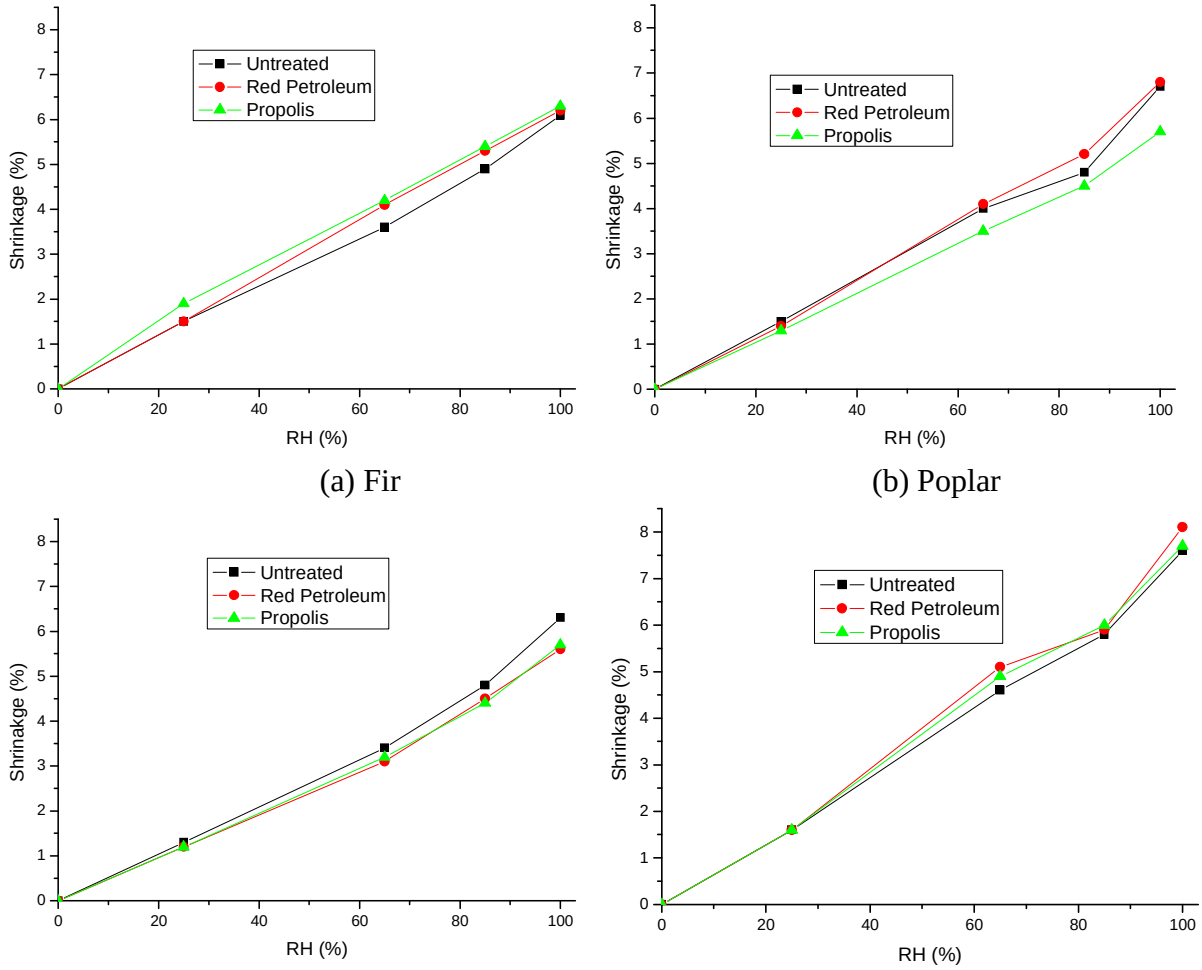
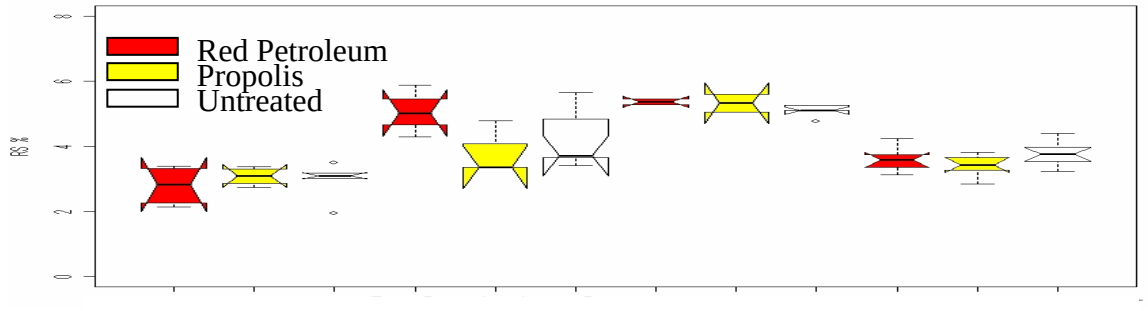


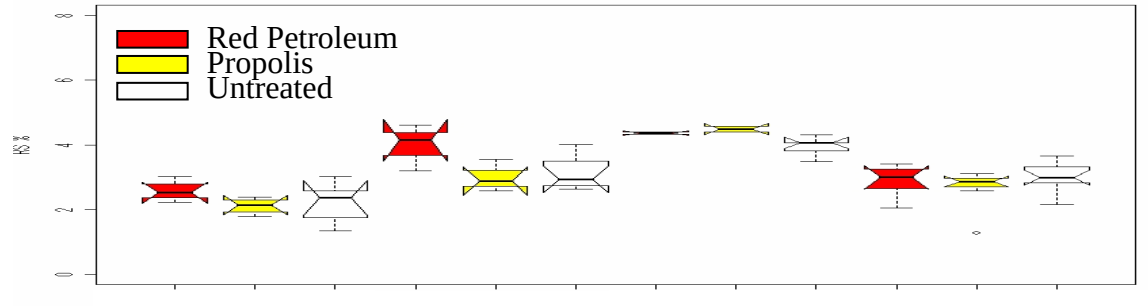
Fig.4.15. Tangential shrinkage versus RH of untreated and treated wood

The data of shrinkage were interpreted with statistical software R with the same considerations made for the density about median and average.

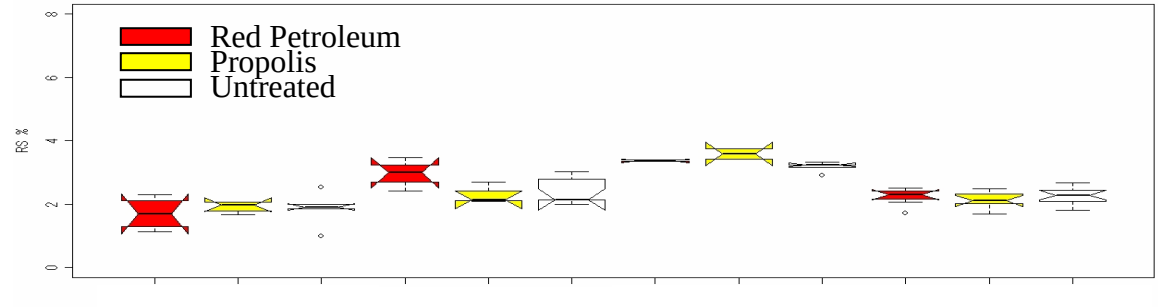
Fig.4.16. shows the boxplots of the radial shrinkage. There is not significant difference between treatments for fir, oak and poplar samples. For lime, the specimens treated with Red Petroleum always display higher shrinkage than untreated ones and Propolis except 25% RH due to the penetration of treatment solution. Tangential shrinkage (Fig.4.17.) displays the same tendency. Probably Red Petroleum act as a solvent of some extractives that interacts with shrinkages, causing a different behaviour of this wood.



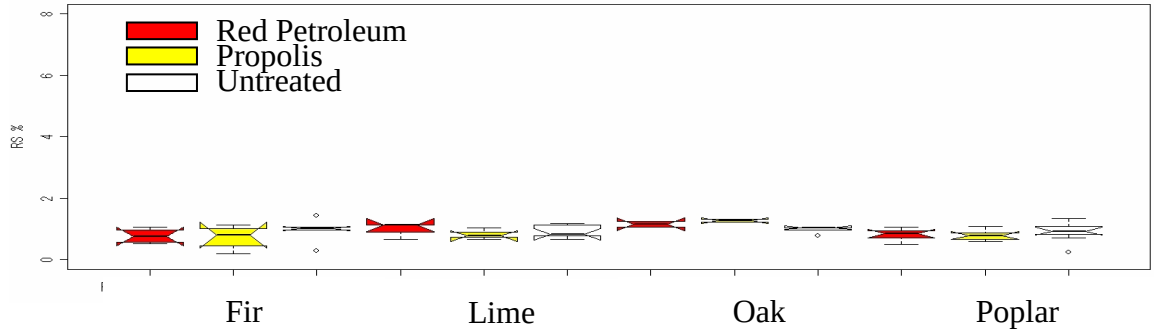
(a) 100% RH



(b) 85% RH

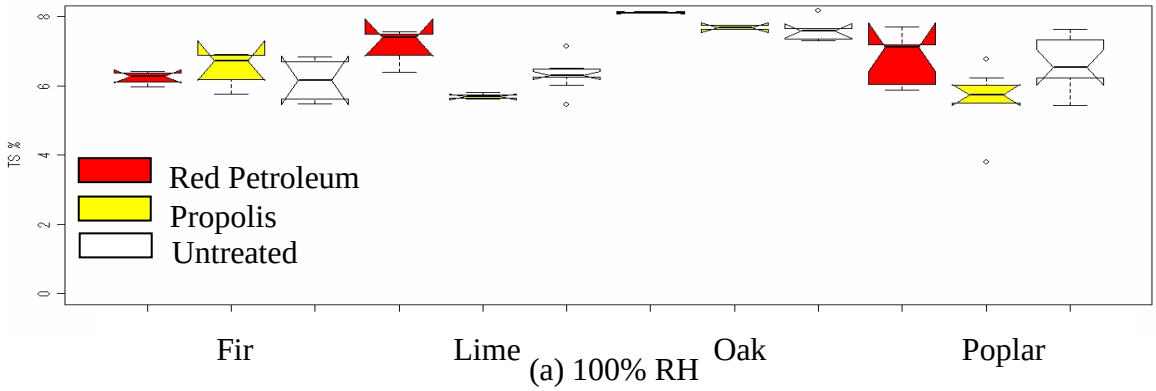


(c) 65% RH

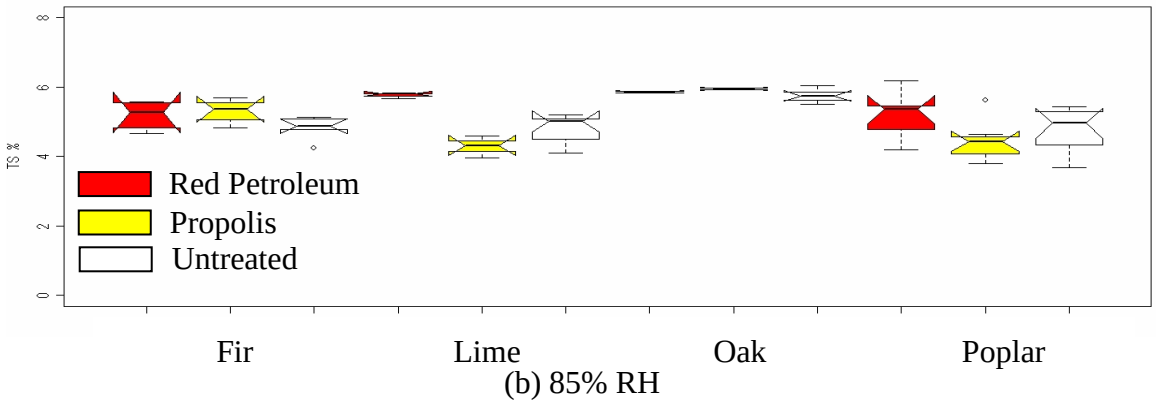


(d) 25% RH

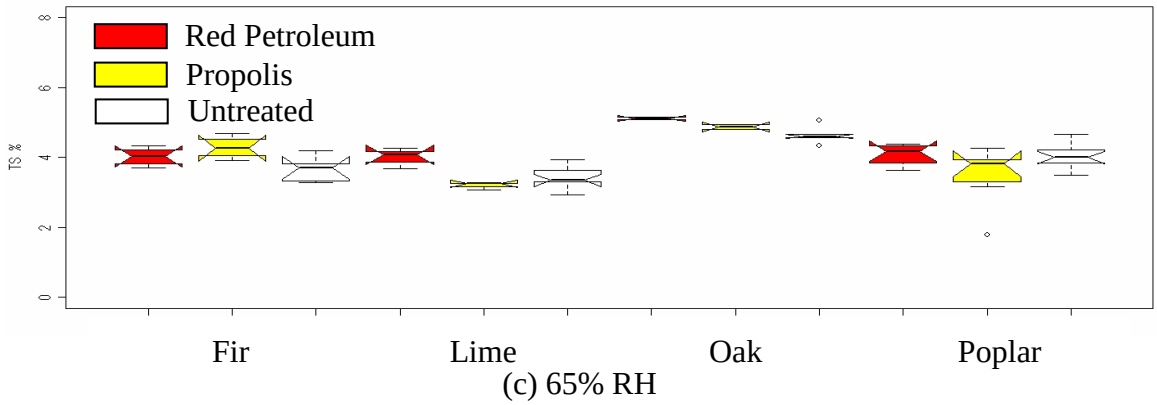
Fig.4.16. Boxplots of radial shrinkage at each RH



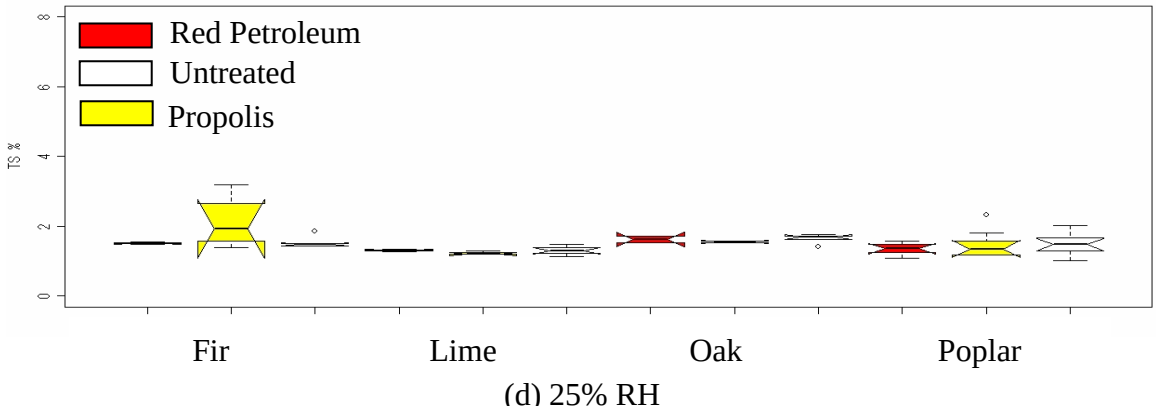
(a) 100% RH



(b) 85% RH



(c) 65% RH



(d) 25% RH

Fig.4.17. Boxplots of tangential shrinkage at each RH

Tangential shrinkage is always higher. Tangential shrinkage varies among species over the range of about 4-12%, with an overall average of about 8%. Average of radial shrinkage values range from about 2% to 8% (Hoadley 1998). In this experiment, there exist small difference from Hoadley's values due to the different conditions (green and 100% RH) and the variability of wood (Table.4.5.). Hoadley's data is from green timber to oven-dry state, this experiment is from 100% RH to oven-dry, and it has been already said that at 100% RH the samples didn't have time to reach the equilibrium moisture content. From green timber the shrinkage should be greater, thus the experimental result can be considered reasonable.

Table.4.5. Values of total shrinkage

(a) Typical value (Hoadley 1998)

	Tangential shrinkage (%)	Radial shrinkage (%)
Fir	7.6	3.8
Poplar	8.5	3.4
Lime	9.5	6.8
Oak	10.2	5.2

(Exposure from green timber to oven-dry state)

(b) Values in this experiment (Untreated)

	Tangential shrinkage (%)	Radial shrinkage (%)
Fir	6.1	2.8
Poplar	6.7	3.8
Lime	6.3	4.4
Oak	7.6	5.1

(Exposure from 100% RH to oven-dry state)

Porosity

Porosity at equilibrium at each RH was calculated with the formula (3.4) (Fig.4.18.). Porosity directly relates density because cell wall specific gravity is constant. Differences in density and porosity derive from anatomical differences, such as differences in cell types (tracheids, vessel member, parenchyma cells) and their quantitative distribution, thickness of cell walls, and size of cell cavities (Boas 1947; Tsoumis 1991). The different anatomical arrangements in the utilized species are clearly visible in the pictures describing the species in the Material and methods chapter.

The results of density and porosity are similar since porosity directly relates with density and it is extremely important to compare porosity and density with their initial values (before treatment). Initial density is displayed in Table.4.6.

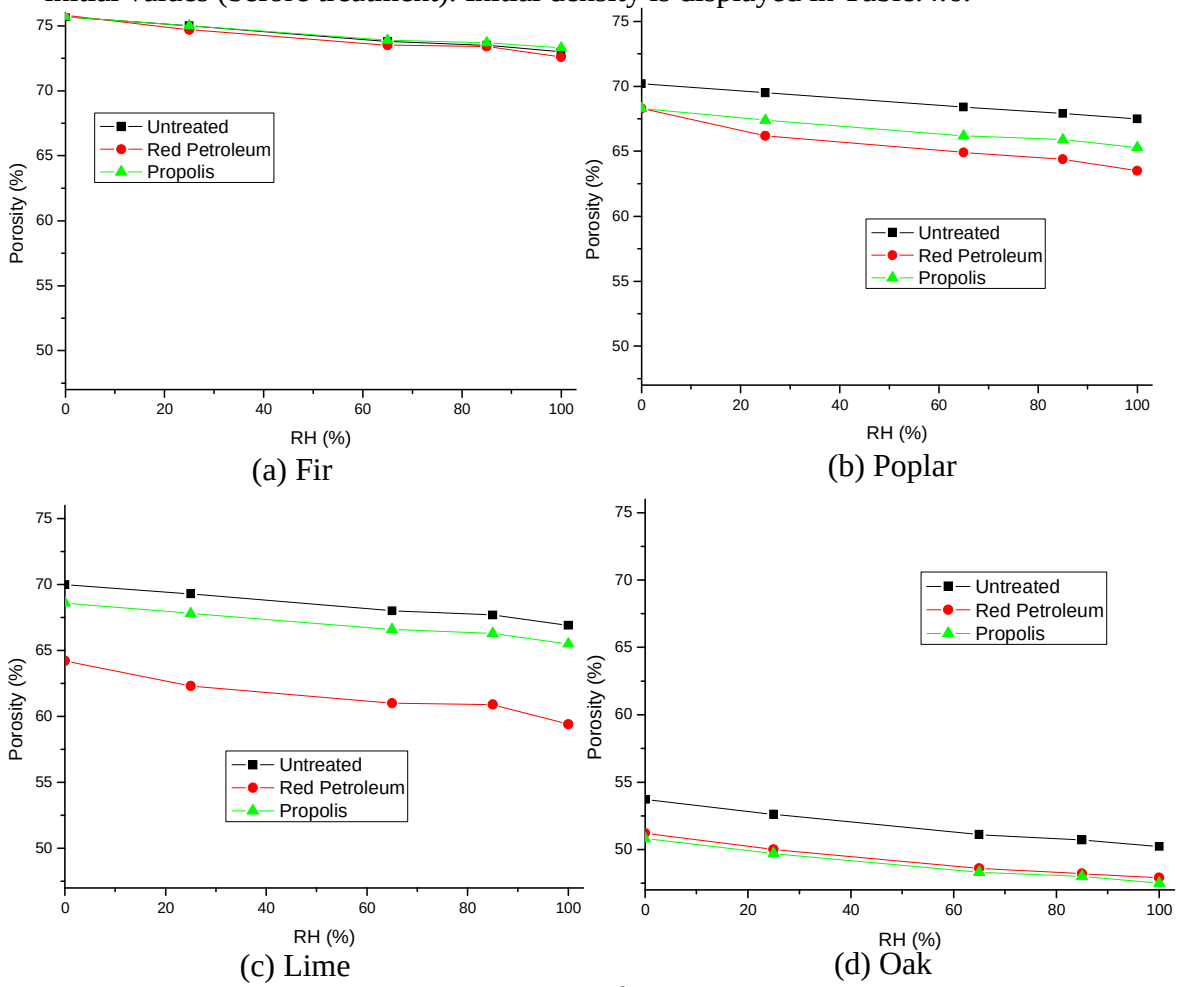
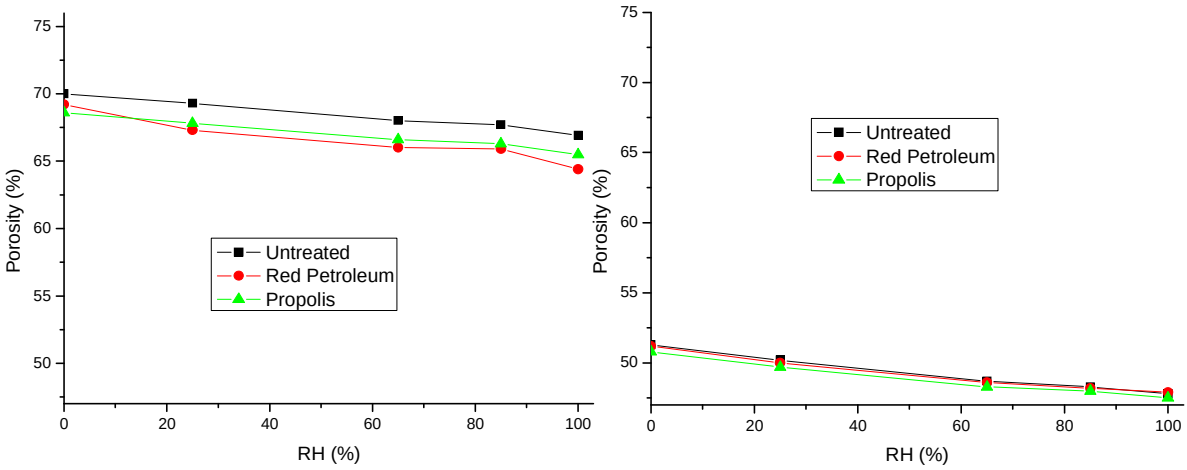


Fig.4.18. Porosity versus RH of untreated and treated wood

Table.4.6. Initial porosity (%) of specimens

	Fir	Poplar	Lime	Oak
Untreated	75.6	70.1	69.4	53.4
Red Petroleum	75.9	69.1	64.4	51.1
Propolis	76.2	69.2	69.3	50.8

Taking into account the initial porosity (Table.4.6.), the porosity data of lime and oak were corrected. Fig.4.19. shows the data after modification. The results of porosity are the same with density. There is not significant difference between density and porosity, deriving these from anatomical difference and the evaluation of the influence of such microscopic characteristics is quite difficult.



(a) Lime (b) Oak

Fig.4.19. Porosity versus RH after modification

4.1.2 Samples with tempera painting

Sample A

Visual assessment

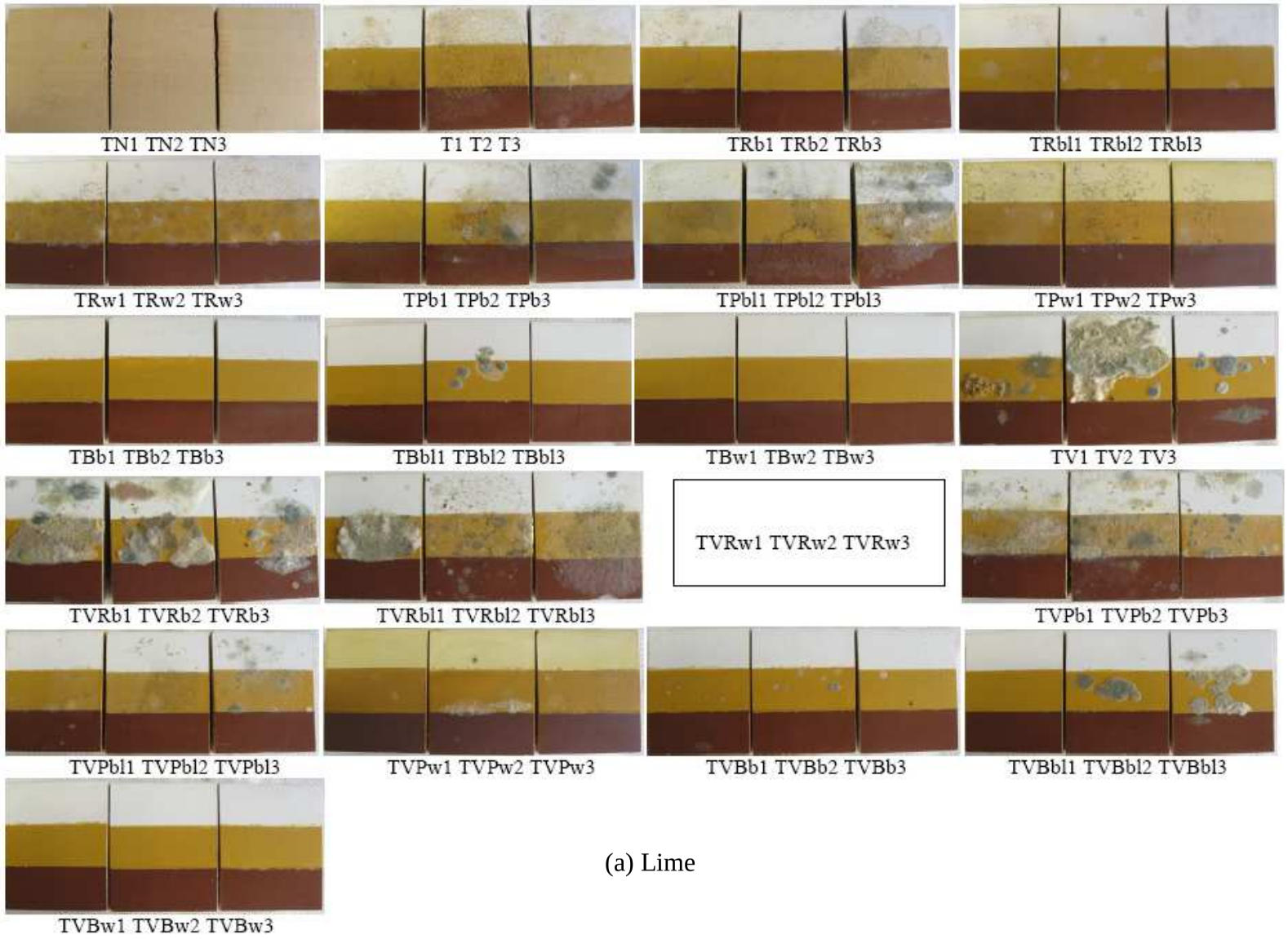
After conditioning at 100 % relative humidity (RH), visual assessment has been carried out for the evaluation of mould attack, ranging from 0 (no growth) to 7 (excessive growth) based on the photographic rating classification in the European standard (EN927-3 1995) for painted layer, lateral and bottom, for 100% RH at equilibrium. Fig.4.20. shows the painted layer of specimens for 100% RH at equilibrium. In these figures, the abbreviations were used for the name of specimens (Table.4.7.). First letter is for species, second for special case (without second letter means only tempera painting), third for treatment solution, fourth letter for brushing way and the last one is numbering. If letters are missing, simply those treatments were not applied on specimens. In these figures, only images of painted layer are shown. The reason is that most important surface of a panel painting is surely the painted layer.

Table.4.7. Abbreviation in Fig.4.20

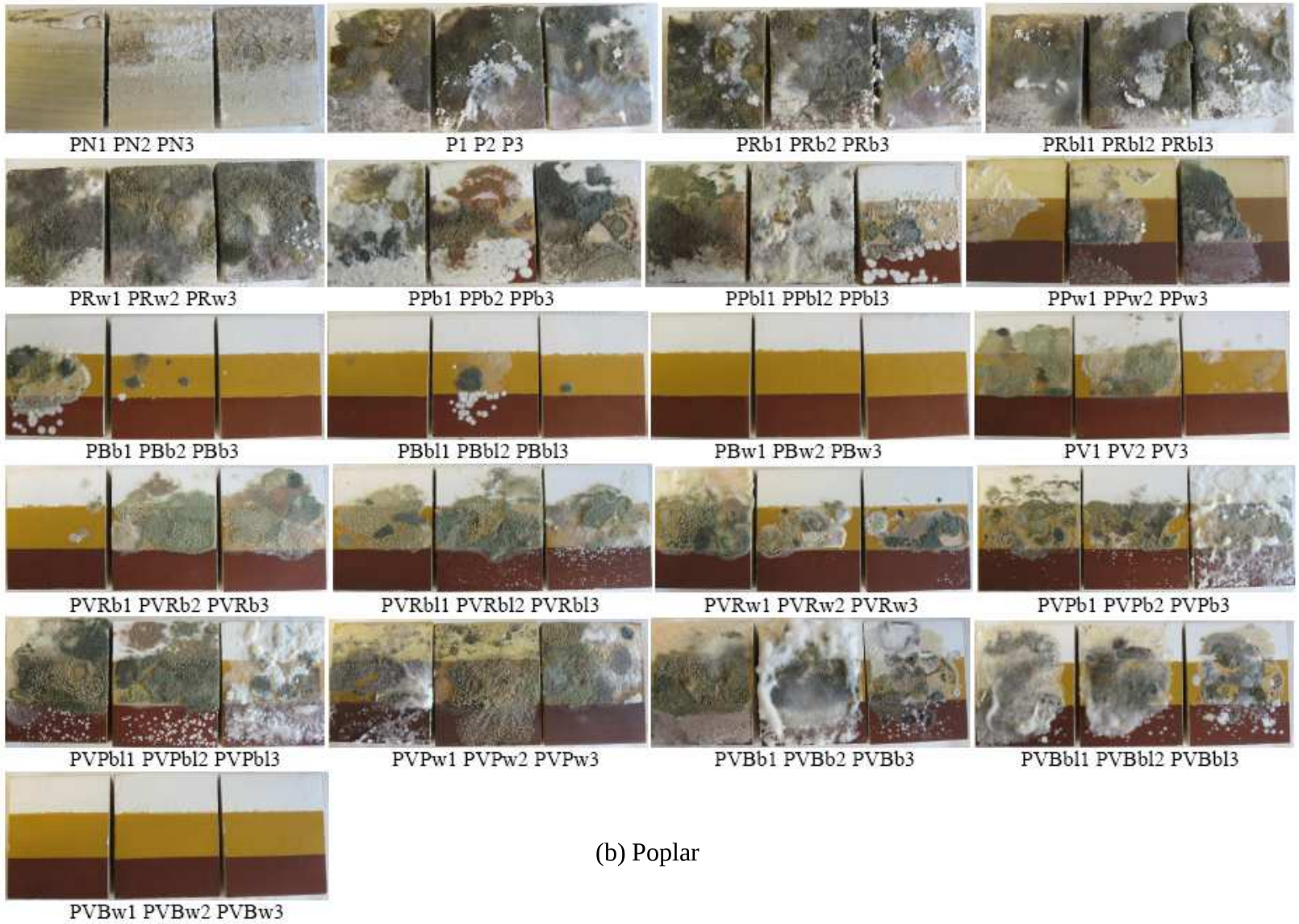
Letter	Meaning	
T	*Tilia* sp. (Lime)	Wood species
P	*Populus* sp. (Poplar)	
Q	*Quercus petraea* Liebl (Oak)	
N	Naked wood (without tempera painting)	Special case
V	With varnish	
R	Red Petroleum	Treatment solutions
P	Propolis	
B	Biotin R	

b	Treatment for only bottom (one surface)	Brushing way
bl	Treatment for bottom and lateral (4 surfaces)	
w	Treatment for whole surface (6 surfaces)	

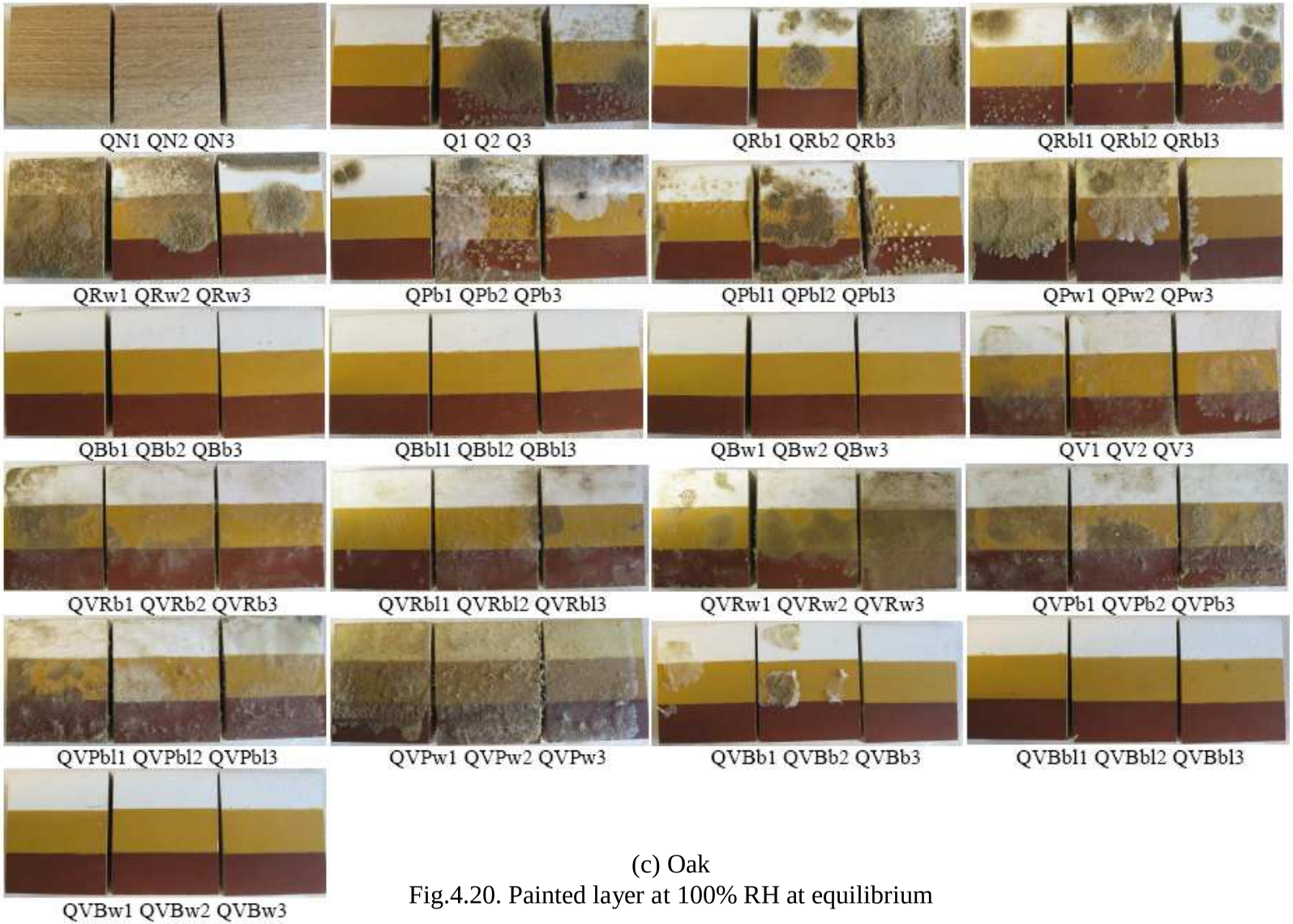
At 100% RH, specimens treated with Red Petroleum and Propolis had mould attack. Biotin R samples were the only samples on which no mould growth was detected. Naked wood performed better with lower degree of mould growth of the tempera specimens in all species of wood.


TN1 TN2 TN3
T1 T2 T3
TRb1 TRb2 TRb3
TRbl1 TRbl2 TRbl3
TRw1 TRw2 TRw3
TPb1 TPb2 TPb3
TPbl1 TPbl2 TPbl3
TPw1 TPw2 TPw3
TBb1 TBb2 TBb3
TBbl1 TBbl2 TBbl3
TBw1 TBw2 TBw3
TV1 TV2 TV3
TVRb1 TVRb2 TVRb3
TVRbl1 TVRbl2 TVRbl3
TVRw1 TVRw2 TVRw3
TVPb1 TVPb2 TVPb3
TVPbl1 TVPbl2 TVPbl3
TVPw1 TVPw2 TVPw3
TVBb1 TVBb2 TVBb3
TVBbl1 TVBbl2 TVBbl3
TVBw1 TVBw2 TVBw3

(a) Lime


PN1 PN2 PN3
P1 P2 P3
PRb1 PRb2 PRb3
PRbl1 PRbl2 PRbl3
PRw1 PRw2 PRw3
PPb1 PPb2 PPb3
PPbl1 PPbl2 PPbl3
PPw1 PPw2 PPw3
PBb1 PBb2 PBb3
PBbl1 PBbl2 PBbl3
PBw1 PBw2 PBw3
PV1 PV2 PV3
PVRb1 PVRb2 PVRb3
PVRbl1 PVRbl2 PVRbl3
PVRw1 PVRw2 PVRw3
PVPb1 PVPb2 PVPb3
PVPbl1 PVPbl2 PVPbl3
PVPw1 PVPw2 PVPw3
PVBb1 PVBb2 PVBb3
PVBbl1 PVBbl2 PVBbl3
PVBw1 PVBw2 PVBw3

(b) Poplar



(c) Oak

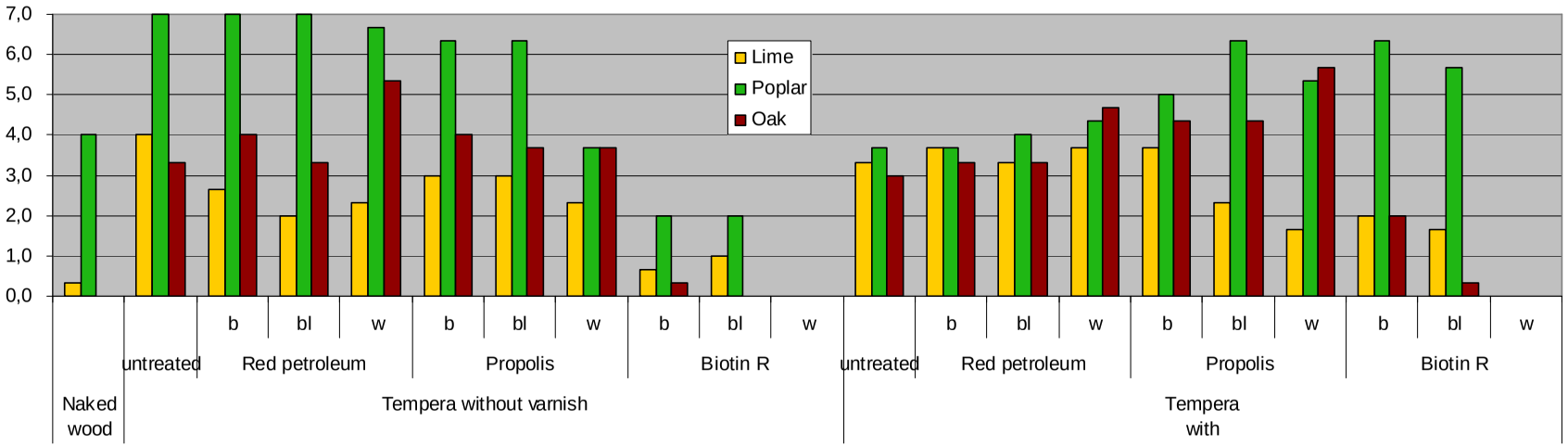
Fig.4.20. Painted layer at 100% RH at equilibrium

Rating for visual assessment of mould attack has been carried out on painted layer, lateral and bottom sides for all specimens (Table.4.7. and Fig.4.20.). Following Table.4.8. and Fig.4.21., some considerations and interpretations have been given with some important criteria.

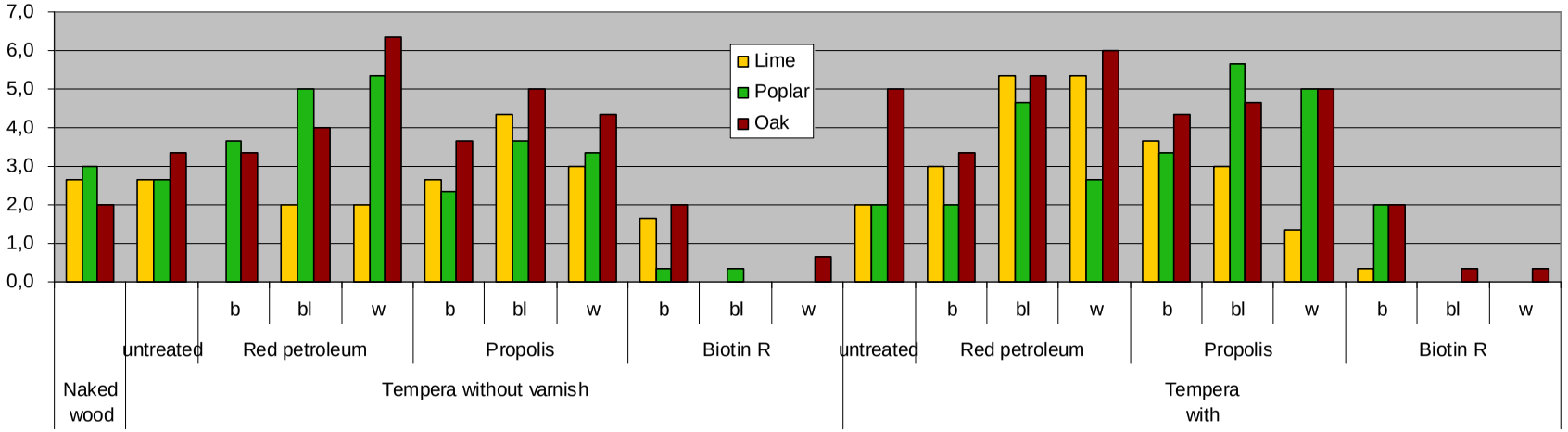
Table.4.8. Visual assessment of specimens

			Lime			Poplar			Oak		
			S	L	B	S	L	B	S	L	B
Naked wood			0.3	2.7	1.0	4.0	3.0	1.7	0.0	2.0	1.0
Tempera without varnish*	untreated		4.0	2.7	1.3	7.0	2.7	0.7	3.3	3.3	1.0
	Red petroleum	b	2.7	0.0	0.0	7.0	3.7	2.0	4.0	3.3	1.7
		bl	2.0	2.0	0.7	7.0	5.0	3.0	3.3	4.0	1.7
		w	2.3	2.0	1.0	6.7	5.3	3.7	5.3	6.3	3.3
	Propolis	b	3.0	2.7	0.3	6.3	2.3	1.3	4.0	3.7	1.0
		bl	3.0	4.3	1.0	6.3	3.7	1.7	3.7	5.0	3.0
		w	2.3	3.0	0.7	3.7	3.3	1.7	3.7	4.3	1.3
	Biotin R	b	0.7	1.7	0.3	2.0	0.3	0.0	0.3	2.0	0.3
		bl	1.0	0.0	0.0	2.0	0.3	0.0	0.0	0.0	0.0
		w	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.7	0.0
Tempera with varnish*	untreated		3.3	2.0	0.3	3.7	2.0	2.3	3.0	5.0	3.0
	Red petroleum	b	3.7	3.0	1.0	3.7	2.0	1.0	3.3	3.3	2.0
		bl	3.3	5.3	1.0	4.0	4.7	2.7	3.3	5.3	2.7
		w	3.7	5.3	0.7	4.3	2.7	1.0	4.7	6.0	3.7
	Propolis	b	3.7	3.7	0.7	5.0	3.3	2.3	4.3	4.3	2.3
		bl	2.3	3.0	0.0	6.3	5.7	2.3	4.3	4.7	3.3
		w	1.7	1.3	0.0	5.3	5.0	3.0	5.7	5.0	2.7
	Biotin R	b	2.0	0.3	0.0	6.3	2.0	0.0	2.0	2.0	0.7
		bl	1.7	0.0	0.0	5.7	0.0	0.0	0.3	0.3	0.0
		w	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.3

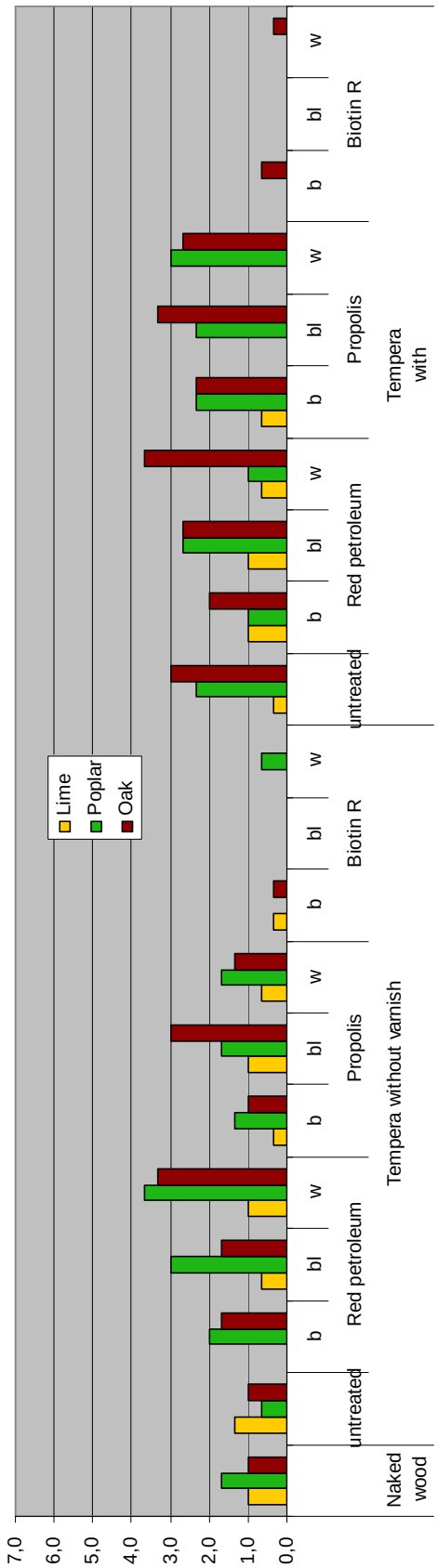
b: bottom (1 surface) **bl**: bottom and lateral (5 surfaces) **w**: whole surfaces (6 surfaces)
S: Surface (painted layer) **L**: Lateral **B**: Bottom
* Varnish was applied only surface before treatment (painted layer)



(a) Painted layer



(b) Lateral



(c) Bottom

Fig.4.21. Visual assessment at 100% RH at equilibrium

Samples with tempera and without tempera

The samples with tempera painting had more mould attack than without (Fig.4.22.). As it is well known, substance that contains organic carbon atoms (organic substance) will provide sufficient nutrients to support mould growth (Moreira 1981). From this experiment the results show that moulds preferred egg tempera containing proteins to simple wood substance containing cellulose; this is not only due to the fact that the feeding compounds of tempera layer are easier to digest, but also to the fact that different species of fungi cause wood decay (the so-called "rot" that degrade cellulose and lignin). Yolk (the yellow of egg), vinegar, albumen (the white of an egg) were used as binders for tempera painting. Additionally it could be possible that some pigments (colors) have also influence on mould growth.

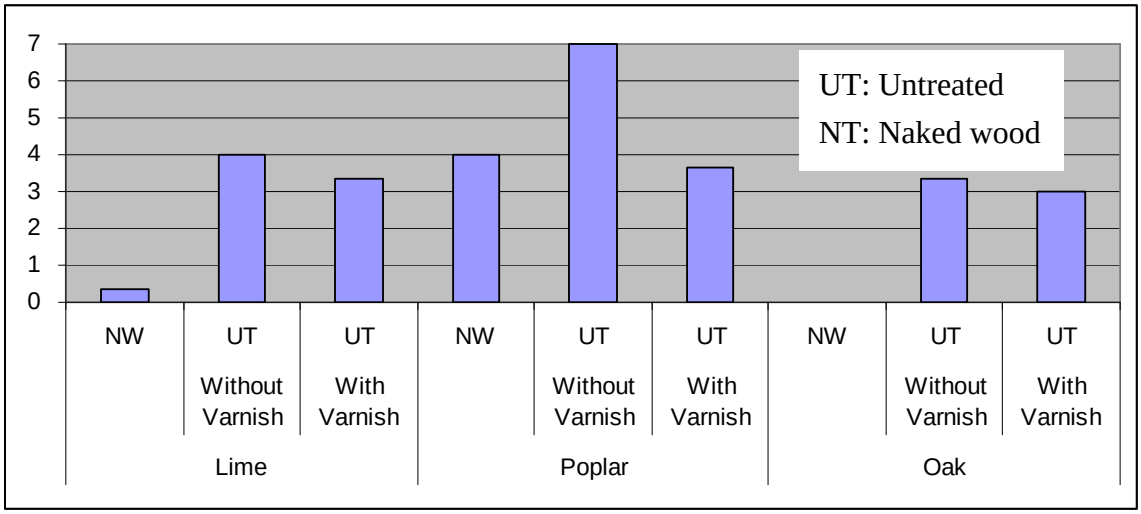


Fig.4.22. Painted layer visual evaluation;

Naked wood, untreated specimens without and with varnish

Wood species

Within the three species of wood, there is a slight difference. Poplar had most mould attack then oak, while lime had the least mould attack (Table.4.9.). Bottom (which is always the non painted face) had the least mould attack than other faces.

Painted layer of poplar has the greatest rating and had the most mould attacks. For lateral side, transversal section was assessed, not longitudinal section, because there was almost no mould attack in longitudinal section. Lime did not have so much variability but oak surface had more variability than others (Fig.4.23.).

Table.4.9.

Visual assessment (including all data)

Lime	1.6
Poplar	2.9
Oak	2.6

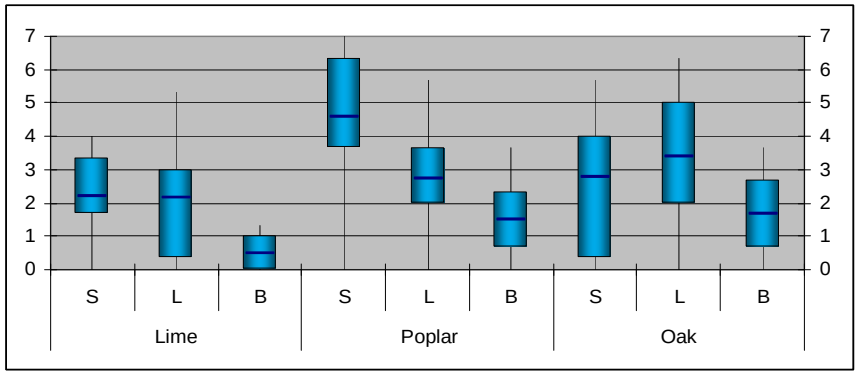


Fig.4.23. Box plot of visual evaluation (including all data)
S: Painted layer L: Lateral B: Bottom

Varnish

It is difficult to assess whether there was a difference in specimens with and without varnish. In lime and oak, specimens with varnish had slightly greater rate than ones without varnish. In poplar specimens with varnish had slightly smaller rate than ones without varnish (Fig.4.24.). Varnish could be a sort of barrier to avoid the penetration of the mould mycelium into the tempera layer, partly justifying the lower presence in the poplar samples, but the results on the two other species seem deny that fact. More probably the barrier effect of this kind of varnish is practically null at 100% RH.

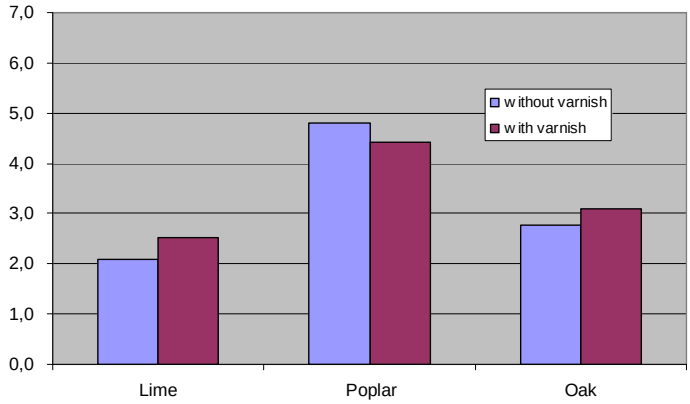


Fig.4.24. Painted layer rate with and without varnish

Treatment solutions

In this experiment, Red Petroleum, Propolis and Biotin R were used as preservative treatment. There is a distinct effect with Biotin R. Biotin R is very effective against mould attack, and it is indeed a well known antifungal product. However, untreated specimens and specimens treated with Red Petroleum and Propolis does not have significant difference for rating (Fig.4.25.). The rating of wood specimens treated with Red Petroleum and Propolis is almost the same for the untreated samples, demonstrating that those products are ineffective against fungal attacks.

Brushing modes

The specimens were treated with three brushing modes, bottom (1 surface), bottom and lateral (5 surfaces) and whole surfaces (6 surfaces). Taking into account the visual evaluation of all surfaces (surface, lateral and bottom), the difference in the brushing mode is not significant (Fig.4.25.). Fig.4.25. shows that, considering only painted layer, Red Petroleum and Propolis do not have any effect on brushing way. However, the effect of Biotin R appears on the surfaces where the solution is applied. There was no mould attack on the painted layer when Biotin R was applied there. Even if Biotin R is applied only at the bottom and lateral, the painted layer has less attack than others.

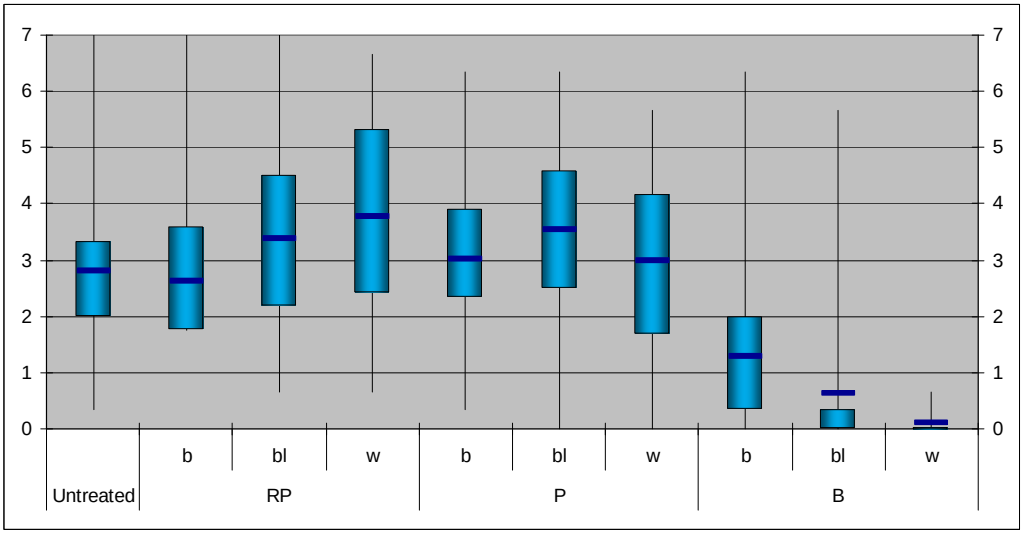


Fig.4.25. Rating by each treatment and each brushing way on painted layer

Colour (pigment)

In general, yellow presents more attack than other colours, followed by white and red. Red has the least attack for three colors. The components of pigments could have influence on mould attack on the painted layer.

White : BIANCO TITANIO

Yellow: GIALLO OCRA

Red : TERRA ROSSA

Fig.4.26. shows the photos of samples with mould attack at 100% RH. The yellow and white part has sufficiently attacked by mould and red part has almost no mould attack. From this result, it is possible to derive a bioinducing effect due to the white and yellow pigment. Fig.4.26.(a) is untreated sample, Fig.4.26.(b) is treated with Red Petroleum and Fig.4.26.(c) is treated with Propolis. All results have a similar tendency.

(a) PV1 PV2 PV3 (b) TVRb1 TVRb2 TVRb3 (c)QPw1 QPw2 QPw3

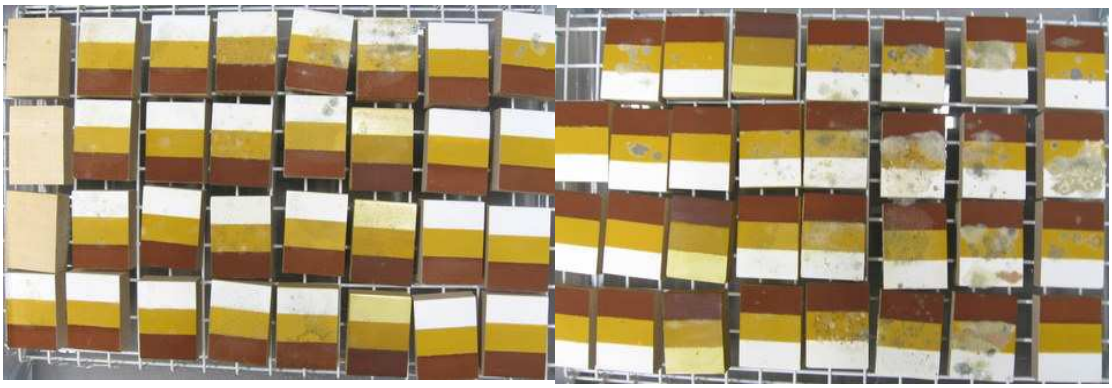
Fig.4.26. Samples with mould attack at 100% RH

All results of visual assessment are in Table.4.8. It is clear that there is a difference between species of wood and treatments. Lime samples have the lowest rate, followed by oak and poplar. Samples treated with Biotin R have the least rate and other samples do not have significant difference in visual assessment.

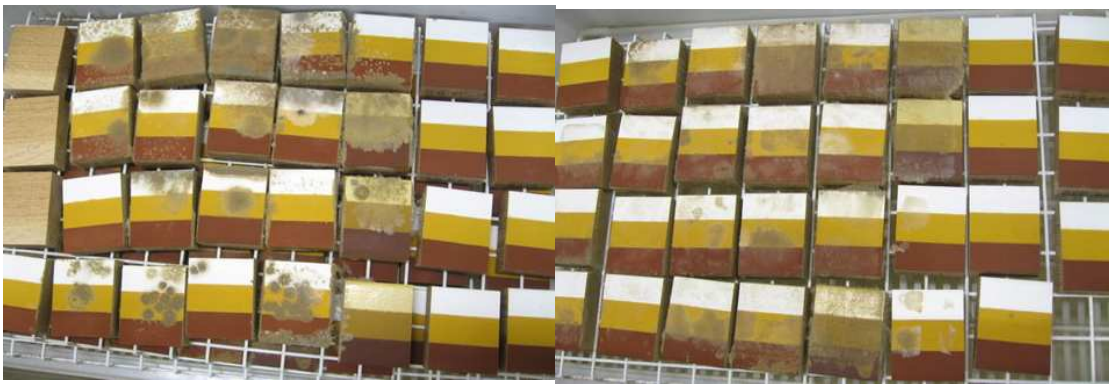
Position in climatic box

The following images are shown the location of all specimens inside the climatic boxes, although this criterion could not be assessed with rating, the position of specimens has little impact on the degree of mould attack. Climatic box was closed therefore if the next specimen was contaminated, it is more probable to have more mould attack (Fig.4.27.). However, in this point, there exists much less influence than treatment coating.

(a) Poplar



(b) Lime



(c) Oak

Fig.4.27. Position in climatic box

Colour measurements

The colours of specimens (painted layer) have been measured with and without varnish, before and after treatments, and at 100% RH and at 65% RH at equilibrium. The CIELAB colour difference has been calculated with the formula (3.5).

Initial colour

There is no difference between species of wood in their initial colour (Table.4.10.). Panel painting has a multilayer above the wood (Fig.4.28.) and the different species do not have any influence on the colour of the painted surface.

Table.4.10. Initial colour

(a) Poplar

	L*	a*	b*
White	95.09	-0.68	3.00
SD	0.21	0.03	0.12
Yellow	63.45	10.30	53.13
SD	1.42	0.52	1.14
Red	37.96	17.90	20.15
SD	0.78	0.22	0.18

(b) Lime

	L*	a*	b*
White	95.04	-0.70	2.91
SD	0.33	0.11	0.14
Yellow	63.54	10.47	53.76
SD	0.66	0.36	0.41
Red	37.61	17.61	19.74
SD	0.37	0.21	0.28

(c) Oak

	L*	a*	b*
White	94.65	-0.76	3.02
SD	0.42	0.13	0.42
Yellow	63.85	10.06	52.89
SD	0.08	0.27	0.49
Red	38.60	17.06	19.09
SD	0.59	0.28	0.25

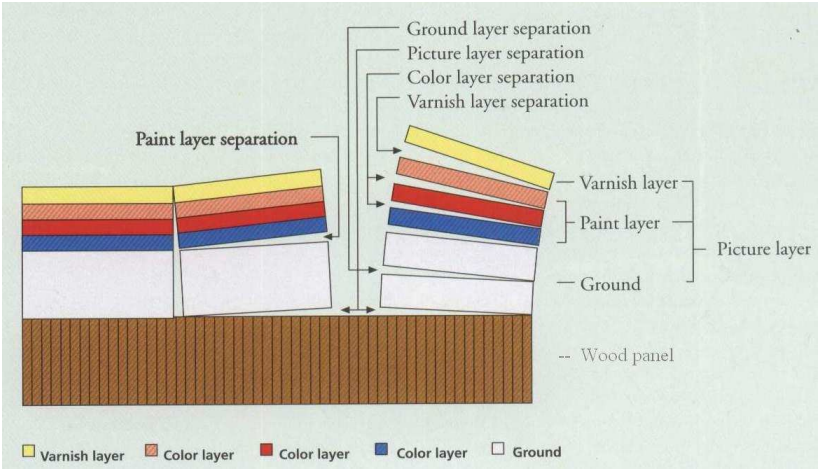


Fig.4.28. Stratification of panel painting

Samples with and without varnish

The varnish did not affect the color so much. The color in L*, a* and b* changed very slightly. L* represents the lightness ranging from 0 (black) to 100 (white), and a* and b* are the chromaticity parameters (+a* for red, -a* for green, +b*

for yellow, and -b* for blue). After applying varnish, white and yellow changed slightly. Red changed a little bit more than other colors. The factor of the overall color change is mainly due to the value of L*, the lightness ranging from 0 (black) to 100 (white). The value of L* decreases slightly for all colors. The overall color change (ΔE*) in red is the largest, followed by yellow and white (Fig.4.29.).

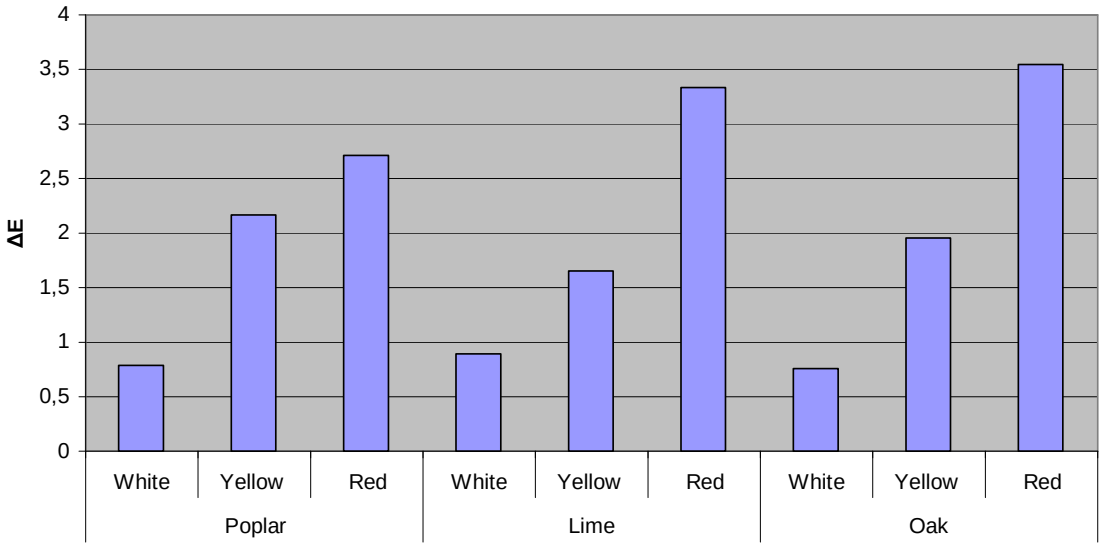


Fig.4.29. Colour difference in varnish

In particular, ΔE is generally used to tell the difference between two colours as indicated by the follow scale (Limbo 2006):

• ΔE < 0.2: not perceptible difference

• 0.2 <ΔE < 0.5: very small difference

• 0.5 <ΔE < 2: small difference

• 2<ΔE < 3: fairly perceptible difference

• 3<ΔE < 6: perceptible difference

• 6<ΔE < 12: strong difference

• ΔE > 12: different colours

Taking account of this scale, the difference for varnish is small difference for white and yellow colours and perceptible for red. In this experiment there is not a

strong difference between the specimens with varnish and without varnish. The data with varnish and without varnish were mixed together in the following results.

Treatment

After treatment, there was no difference between wood species. For this reason we report only the graph of lime as an example (Fig.4.30.). Propolis solution has a great impact on the colour; especially for white colour, with a $\Delta E^* > 12$ (colour changed). Specifically the value of Δb^* changed a lot, which means that the colour becomes yellowish. The change of color in Propolis is outstanding while Red Petroleum is slightly (perceptible difference). In case of Biotin R the overall color change (ΔE^*) is very little (small difference). The differences in Red Petroleum and Biotin R are not so visible with naked eye (Fig.4.31.).

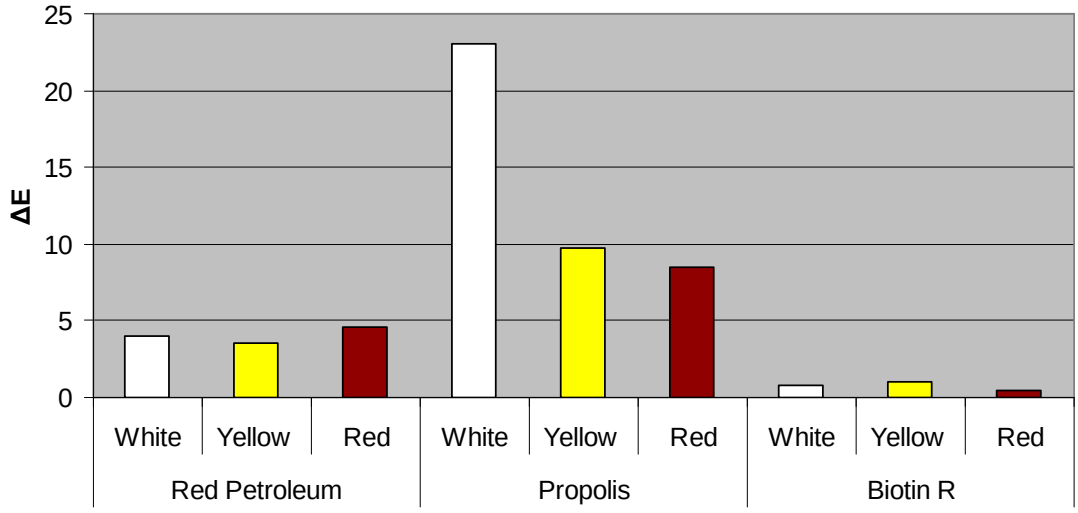
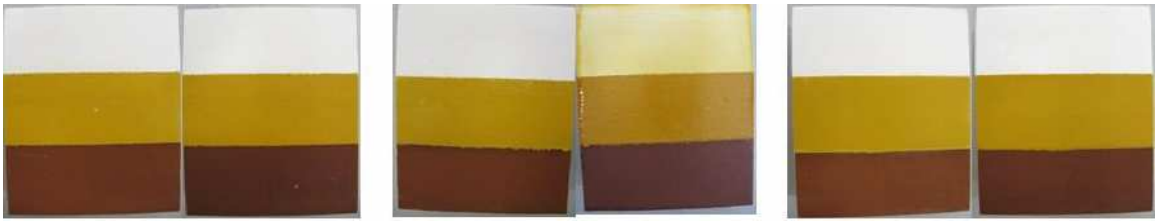


Fig.4.30. Colour difference in treatments (Lime)



(a) Red Petroleum (b) Propolis (c) Biotin R

Fig.4.31. Before (left) and after (right) treatments

100% RH and 65% RH

Colours were affected according to the wood species at 100% RH. Practically mould attack affected the colour and the measured differences are related to the rating of mould attack by visual assessment. Fig.4.32. shows colour difference in treatments at 100% RH. In this case ΔE was calculated as the difference between the colour measurement after treatment and after 100% RH.

The more the mould attack, the more the colour changed. Yellow colour presents most mould attack, followed by white and red colours, as already stated. Even if less attacked, in red colour, mould species have a great impact on colour as in the case of growth of whitish mould on red. However, in case of growth of darkish mould, the red colour changes less than with whitish mould. Whitish mould does not have such a big impact as for white and yellow colour.

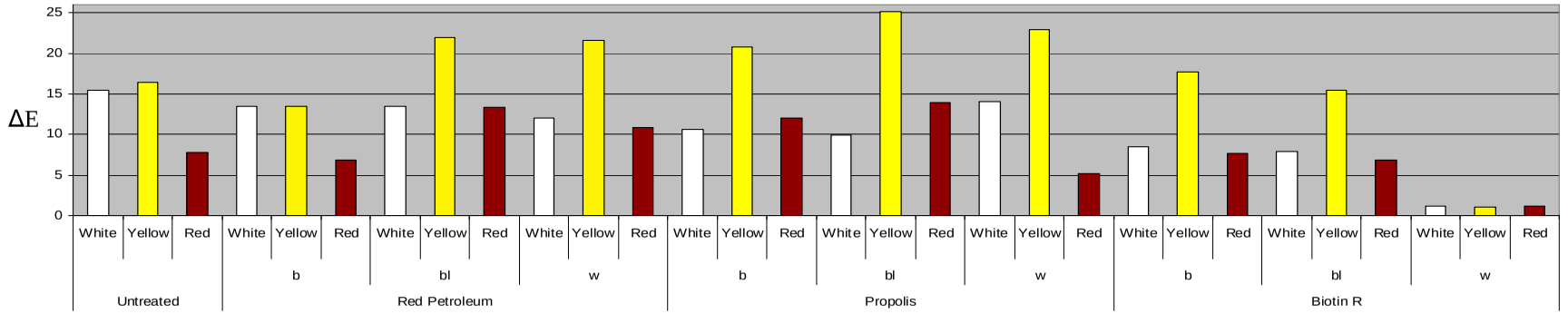
Poplar samples present the most mould attack and the most colour changes, followed by oak and lime. 57% specimens in poplar change to different colour (ΔE>12). Lime samples present the least colour change and actually lime had the least mould attack. For lime, there is no ΔE higher than 12. 13% specimens in oak change to different colour (ΔE>12). Only for poplar samples, partially treated with Biotin R, present mould attack and colour changed. In fact, specimens treated with Biotin R for all surfaces (w) did not have any mould attack for poplar. In the case there is not mould attack, the colour difference can be derived just by time decay. In lime and oak, the specimens treated with Biotin R (only the bottom side (b) and bottom + lateral sides (bl)) have less mould attack and less colour change.

There is not significant difference between Red Petroleum and Propolis, while a little more colour change for Propolis. Propolis itself seems to promote mould attack and consequently the colours changes slightly more, even if it already changed a lot

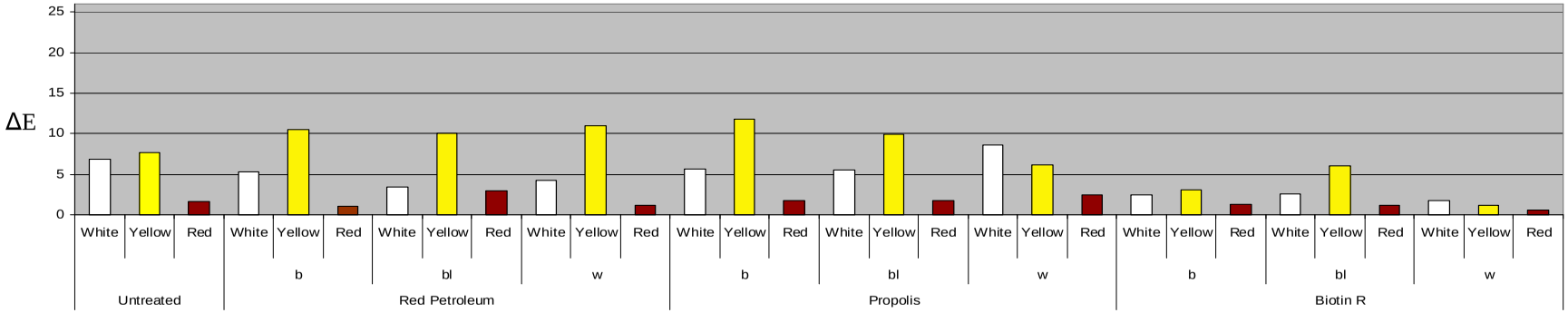
after Propolis brushing. Untreated wood has less colour change than specimens treated with Red Petroleum and Propolis.

Brushing mode does not have significant difference except for Biotin R. Specimens treated with Biotin R on painted layer had no mould attack and their colour changed very little in all species. In lime and oak, specimens treated with Biotin R have almost no mould attack and their colour changes slightly.

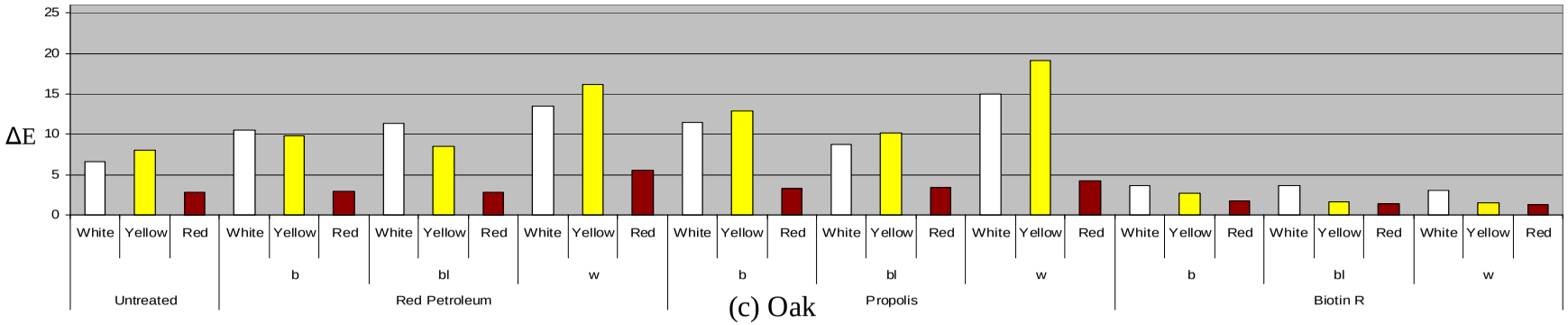
At 65% RH, no mould can grow up. For this reason, there can not be difference in colour of the specimens between 100% RH and 65% RH.



(a) Poplar



(b) Lime

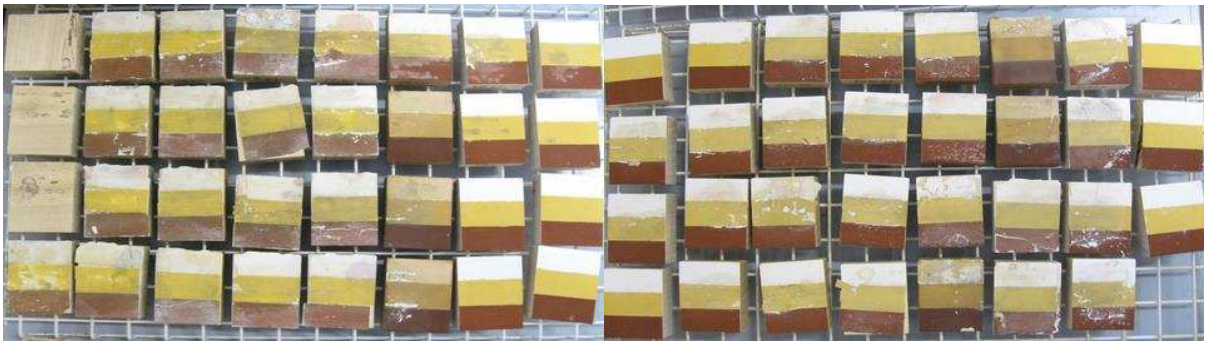


(c) Oak

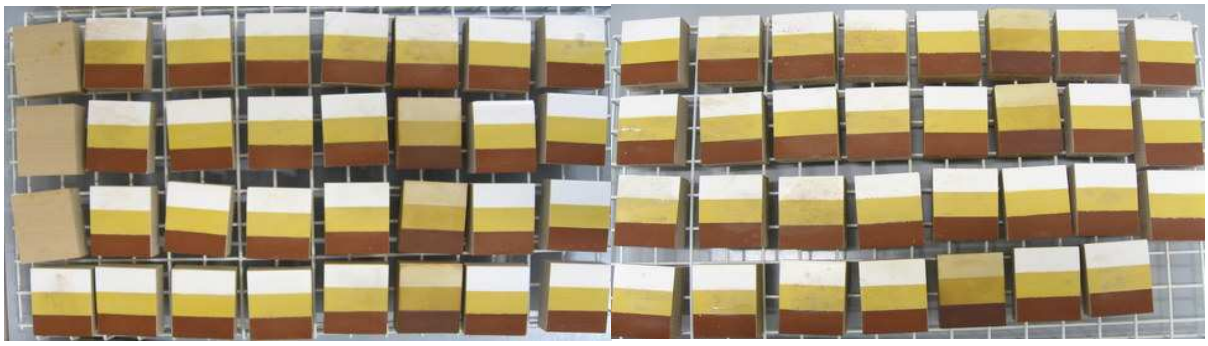
Fig.4.32. Colour difference in treatments at 100% RH

Detachment at oven-dry

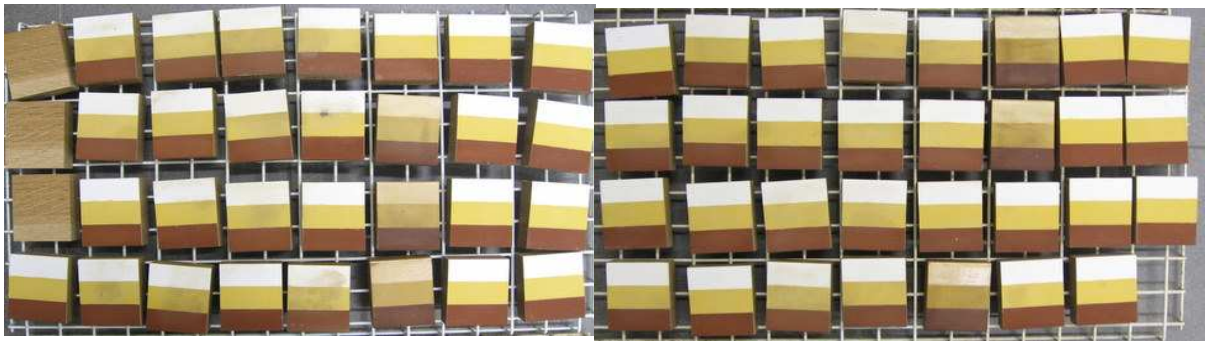
After oven-dry, some detachments of the painted layer occurred in the specimens, which had serious mould attack. Detachment occurred only for poplar, not for lime or oak (Fig.4.33.). For poplar, specimens treated with Biotin R for all surfaces do not have any detachment. This fact proved that mould attack promoted the detachment once the specimens were put in an oven to dry. After oven-dry painted layer broke into pieces and completely detached from wooden support for poplar (Fig.4.34.). Mould hyphae searched for nutrients within the painted layer, producing, in the most active situation, a mycelium felt that dried in oven, causing the apparent detachment.



(a) Poplar



(b) Lime



(c) Oak

Fig.4.33. Specimens after oven-dry

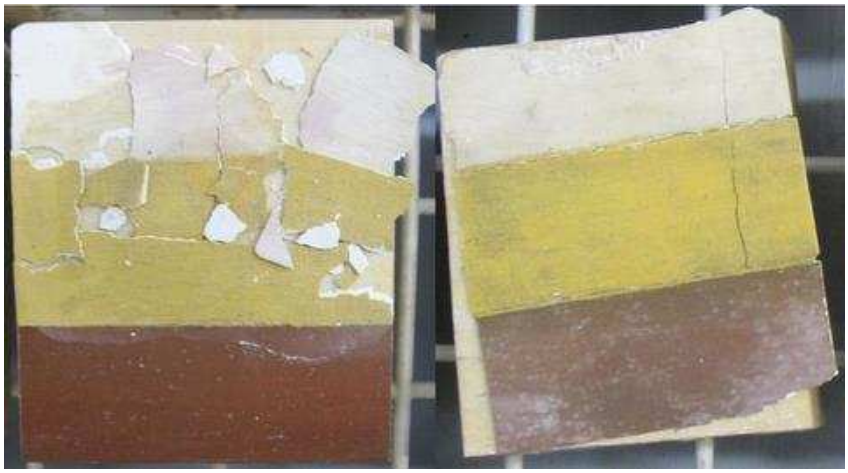


Fig.4.34. Poplar samples after oven-dry

Physical parameter (MC, Density, Shrinkage and Porosity)

In this experiment treatment solutions were applied by brushing and there is not significant difference between treatments (Table.4.11.). The difference is almost the same like variability in wood. When treatment solutions were applied by immersion, there is more variability at 100% RH. However, treatment by brushing does not have such a big difference between treatments.

For example, MC at 100% RH in poplar by immersion has more than 10% difference between the highest and the lowest MC. However MC at 100% RH in poplar by brushing has only 3 % difference. This difference is almost negligible.

In Table.4.11., some abbreviation is used as following.

B Biotin R

R Red Petroleum

P Propolis

U Untreated.

Table.4.11. Physical parameters by brushing

		Naked Wood	Without varnish														With varnish												All Total
			B			B Total	P			P Total	R			R Total	U	Total	B			B Total	P			P Total	R			R Total	U	Total	
			b	bl	w		b	bl	w		b	bl	w				b	bl	w		b	bl	w		b	bl	w				
P	MC before Treatment	11,1	12,8	11,9	11,9	12,2	13,2	12,6	12,8	12,9	12,9	12,3	12,2	12,5	13,1	12,6	13,6	13,1	11,8	12,8	12,5	12,5	12,9	12,6	12,2	11,7	11,5	11,8	11,9	12,4	12,4
	MC at 100% RH	27,4	23,9	24,2	24,2	24,1	25,0	23,9	23,7	24,2	25,6	25,0	24,6	25,1	27,6	24,8	26,6	27,2	28,8	27,5	24,6	25,6	25,7	25,3	23,6	23,7	25,3	24,2	21,5	25,2	25,1
	MC at 65% RH	14,8	15,2	15,0	16,1	15,4	15,6	15,2	15,1	15,3	15,5	15,6	15,6	15,6	15,6	15,4	14,9	14,9	16,2	15,4	15,0	14,9	14,9	14,9	15,1	15,4	15,9	15,4	14,2	15,1	15,3
	Density at 100% RH	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5
	Density at 65% RH	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5
	R shrinkage at 100% RH	3,6	3,3	3,2	3,2	3,2	3,5	3,2	3,2	3,3	3,3	3,3	3,2	3,3	3,6	3,3	3,4	3,3	3,6	3,4	3,4	3,4	3,5	3,4	3,3	3,1	3,4	3,3	3,1	3,4	3,4
	T shrinkage at 100% RH	8,6	7,2	7,7	7,7	7,5	7,3	7,1	7,2	7,2	7,7	7,3	7,3	7,4	8,5	7,5	7,5	8,2	8,6	8,1	7,3	7,7	7,7	7,6	6,8	6,9	7,2	7,0	6,4	7,4	7,5
	R shrinkage at 65% RH	2,4	2,2	2,3	2,2	2,2	2,3	2,1	2,2	2,2	2,2	2,1	2,1	2,1	2,3	2,2	2,2	2,1	2,3	2,2	2,3	2,1	2,3	2,3	2,2	2,1	2,2	2,2	2,1	2,2	2,3
	T shrinkage at 65% RH	4,9	4,8	4,5	4,6	4,6	4,6	4,4	4,4	4,5	4,4	4,7	4,6	4,5	4,9	4,6	4,4	4,4	4,6	4,5	4,5	4,7	4,7	4,6	4,3	4,5	4,4	4,4	4,1	4,4	4,6
Q	MC before Treatment	11,5	15,2	14,8	15,1	15,0	14,4	14,3	15,1	14,6	14,6	14,1	14,4	14,3	15,1	14,7	14,0	13,5	13,8	13,8	14,3	14,4	14,5	14,4	14,2	14,2	14,4	14,3	13,9	14,1	14,3
	MC at 100% RH	23,5	27,3	27,9	26,9	27,4	25,0	25,5	25,6	25,4	24,5	24,7	25,1	24,8	23,9	25,6	24,4	24,8	24,7	24,6	22,6	22,3	24,1	23,0	23,8	24,5	24,9	24,4	22,4	23,9	24,7
	MC at 65% RH	15,8	16,7	16,4	16,3	16,5	16,5	16,5	16,6	16,5	16,4	16,6	16,8	16,6	16,3	16,5	16,4	16,3	16,4	16,4	16,5	16,5	16,5	16,5	16,6	16,8	16,8	16,7	16,3	16,5	16,5
	Density at 100% RH	0,6	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7	0,7
	Density at 65% RH	0,6	0,7	0,6	0,7	0,7	0,6	0,6	0,6	0,6	0,7	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,7	0,6	0,6	0,6	0,7	0,6	0,7	0,6	0,6
	R shrinkage at 100% RH	3,2	2,9	3,2	3,2	3,1	3,0	3,1	3,0	3,0	3,1	2,9	2,9	3,0	3,1	3,0	2,7	2,9	3,1	2,9	2,9	2,7	2,9	2,8	2,9	2,9	2,9	2,9	2,8	2,8	3,0
	T shrinkage at 100% RH	5,7	6,3	7,1	7,1	6,8	6,0	6,5	6,0	6,2	6,1	6,0	5,9	6,0	6,5	6,4	6,0	6,0	6,1	6,0	5,9	5,8	6,3	6,0	5,2	5,6	5,7	5,5	5,1	5,8	6,1
	R shrinkage at 65% RH	2,3	2,1	2,0	2,0	2,1	2,1	2,1	2,0	2,1	1,9	2,1	2,1	2,0	2,1	2,1	1,9	1,9	1,9	1,9	2,1	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,1
	T shrinkage at 65% RH	3,9	3,9	3,9	3,7	3,8	3,7	4,2	3,7	3,9	3,9	4,4	4,4	4,2	4,5	4,1	3,2	3,5	3,5	3,4	3,7	3,7	3,8	3,7	3,8	3,8	3,8	3,7	3,2	3,5	3,8
T	MC before Treatment	10,5	10,7	10,5	10,6	10,6	10,7	10,0	9,9	10,2	10,9	10,2	10,0	10,4	10,9	10,4	10,5	10,2	9,9	10,2	10,7	10,0	9,7	10,1	10,7	10,0	9,8	10,2	10,4	10,2	10,3
	MC at 100% RH	21,6	21,4	22,1	22,1	21,9	18,9	20,6	20,0	19,8	18,8	19,0	19,3	19,0	19,7	20,2	22,2	22,6	23,5	22,8	22,6	21,2	21,5	21,7	23,4	23,8	23,4	23,5	25,1	22,9	21,6
	MC at 65% RH	14,0	14,1	14,0	14,1	14,1	13,0	14,0	14,0	13,7	14,0	14,6	14,7	14,4	14,0	14,1	14,2	14,0	14,0	14,0	14,3	14,0	14,1	14,1	14,4	14,9	14,9	14,7	14,2	14,3	14,2
	Density at 100% RH	0,5	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6
	Density at 65% RH	0,5	0,5	0,6	0,6	0,6	0,5	0,5	0,5	0,5	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,5	0,6	0,6
	R shrinkage at 100% RH	3,9	3,7	4,0	3,8	3,8	3,3	3,7	3,4	3,5	3,4	3,3	3,2	3,3	3,5	3,5	3,9	3,9	4,2	4,0	4,0	3,8	3,9	3,9	4,3	3,1	4,0	3,8	4,4	3,9	3,7
	T shrinkage at 100% RH	6,1	6,4	6,6	6,7	6,6	5,6	6,2	5,9	5,9	5,8	5,4	5,7	5,6	5,8	6,0	6,9	6,6	7,2	6,9	6,9	6,5	6,7	6,7	7,0	6,9	7,1	7,0	7,8	6,9	6,5
	R shrinkage at 65% RH	2,7	2,5	2,4	2,4	2,4	2,4	2,3	2,4	2,4	2,6	2,5	2,6	2,5	2,4	2,4	2,7	2,6	2,6	2,6	2,5	2,5	2,5	2,5	2,5	2,4	2,5	2,5	2,6	2,6	2,5
	T shrinkage at 65% RH	3,9	4,0	3,9	4,2	4,0	3,9	4,2	4,0	4,0	4,2	4,3	4,1	4,2	4,0	4,1	4,2	4,2	4,3	4,2	4,3	4,0	4,1	4,1	4,2	4,1	4,1	4,1	4,5	4,2	4,1
MC before Treatment		11,1	12,9	12,4	12,5	12,6	12,8	12,3	12,6	12,6	12,8	12,2	12,2	12,4	13,0	12,6	12,7	12,3	11,8	12,3	12,5	12,3	12,3	12,4	12,4	12,0	11,9	12,1	12,1	12,2	12,3
MC at 100% RH		24,2	24,2	24,8	24,4	24,5	23,0	23,3	23,1	23,1	23,0	22,9	23,0	23,0	23,7	23,5	24,4	24,9	25,7	25,0	23,3	23,0	23,8	23,3	23,6	24,0	24,6	24,0	23,0	24,0	23,8
MC at 65% RH		14,9	15,3	15,2	15,5	15,3	15,0	15,2	15,2	15,2	15,3	15,6	15,7	15,5	15,3	15,3	15,2	15,1	15,5	15,3	15,3	15,2	15,2	15,2	15,4	15,7	15,9	15,6	14,9	15,3	15,3
Density at 100% RH		0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6
Density at 65% RH		0,5	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6
R shrinkage at 100% RH		3,6	3,3	3,5	3,4	3,4	3,3	3,3	3,2	3,3	3,3	3,2	3,1	3,2	3,4	3,3	3,4	3,4	3,6	3,5	3,4	3,3	3,4	3,4	3,5	3,0	3,4	3,3	3,4	3,4	3,4
T shrinkage at 100% RH		6,8	6,6	7,1	7,2	7,0	6,3	6,6	6,4	6,4	6,5	6,2	6,3	6,3	7,0	6,6	6,8	7,0	7,3	7,0	6,7	6,6	6,9	6,8	6,3	6,5	6,7	6,5	6,4	6,7	6,7
R shrinkage at 65% RH		2,4	2,3	2,2	2,2	2,2	2,3	2,2	2,2	2,2	2,2	2,2	2,3	2,2	2,3	2,2	2,3	2,2	2,3	2,3	2,3	2,2	2,3	2,3	2,2	2,2	2,2	2,2	2,3	2,2	2,3
T shrinkage at 65% RH		4,2	4,2	4,1	4,1	4,2	4,1	4,3	4,0	4,1	4,2	4,4	4,3	4,3	4,4	4,3	3,9	4,0	4,1	4,0	4,2	4,1	4,2	4,2	4,1	4,0	4,0	4,1	3,9	4,0	4,2

4.1.3 Sample with tempera painting

Sample B

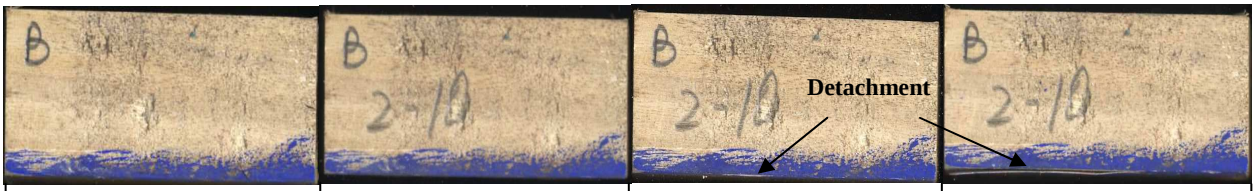
The exposure from high relative humidity to low relative humidity forced wood in loosing water in order to get a moisture content in equilibrium with the environmental relative humidity. Fluctuations in the relative humidity result in changes in the moisture content in wood. These moisture content variations generate the swelling and shrinking of the wood that polychrome layer can only partially follow. The scanned images of each sample help us to see what happened between panel painting support and polychrome layer (Fig.4.35.). It is clearly observed that detachment occurred when the RH was 25% (corresponding to wood equilibrium moisture content between 5 – 6%). The detachment was clearly observed in the following Fig.4.35.

In fir sample (Fig.4.35.(a)) the detachment was 14.80 mm long and the width movement of wood support was 1.50 mm. In poplar sample (Fig.4.35.(b)) the final detachment was 29.12 mm and the width movement of wood support was 2.93 mm. In lime sample (Fig.4.35.(c)) the sub-detachment was observed and the width movement of wood support was 2.81 mm. In oak sample (Fig.4.35.(d)) the detachment was 22.20 mm and the width movement of wood support was 2.39 mm.

The 1% MC difference generates width movement of wood support, fir (sub-radial, 0.08 mm), poplar (sub-tangential, 0.16 mm), lime (sub-tangential, 0.13 mm), oak (sub-radial 0.13 mm).

100%, 24.6%, 52.00mm	85%, 20.0%, 51.70mm	65%, 15.9%, 51.27mm	25%, 11.2%, 50.46mm

(a) Fir



100%, 24.4%, 52.02mm	85%, 19.0%, 51.15mm	65%, 14.9%, 50.53mm	25%, 5.4%, 49.09mm

(b) Poplar

100%, 27.4%, 53.49mm	85%, 19.5%, 52.64mm	65%, 14.5%, 51.87mm	25%, 5.1%, 50.68mm

(c) Lime

100%, 23.6%, 52.69mm	85%, 19.6%, 52.14mm	65%, 16.3%, 51.61mm	25%, 6.0%, 50.30mm

(d) oak

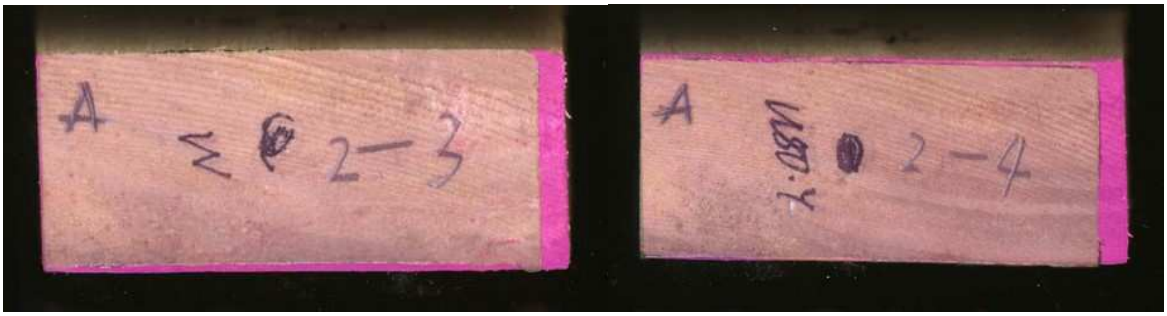
Fig.4.35. Scanned image during exposure of different RH
Values in graph from left to right: RH(%), MC(%), Width of wood support(mm)

It is clear that during exposure from high relative humidity to low relative humidity, dimensional changes occur. Fig.4.36. shows the overlap of two scanning images (normal image: RH 100%, transparent image: 25%). Fig.4.36. allows seeing the dimensional change. Fir and oak shrink a lot in sub-radial direction in width, but mostly in thickness in sub-tangential direction (Fig.4.36.(a), (d)) and on the contrary, poplar and lime shrink in sub-tangential direction in width (Fig.4.36.(b), (c)). Variations of humidity produce dimensional changes and warp and shrinking and swelling of wood. They are strongly influenced by its anisotropy, resulting in changes in form, presence of internal tensions, set warp and cracking. In the case of these samples, thickness and width do not correspond precisely to a wood direction. Radial and tangential directions are mixed on the different faces; this produce distortions

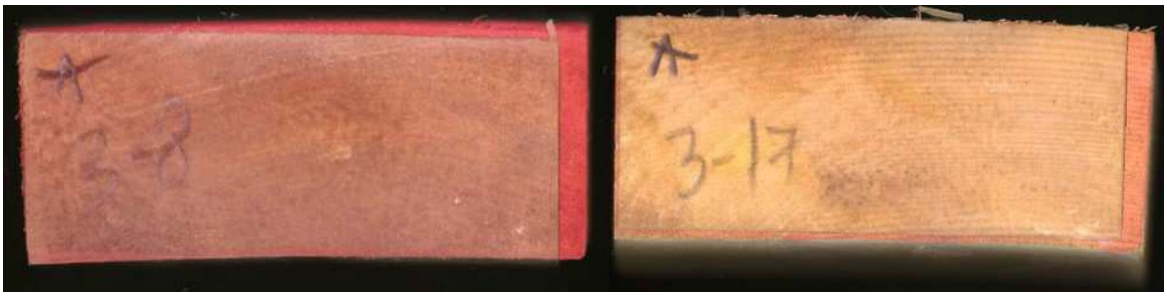
during drying that are clearly visible in the composed pictures, that frequently cause longitudinal surfaces, mostly along width, no more flat (e.g. the 2-8 lime sample in Fig.4.36.(c))

The magnitude of shrinkage is higher with higher density. This is due to the larger amount of wood substance (greater cell wall thickness) with higher density, and to the exterior changes of cell dimensions. It has been observed that, when moisture is lost, the size of the cell cavity remains practically unchanged.

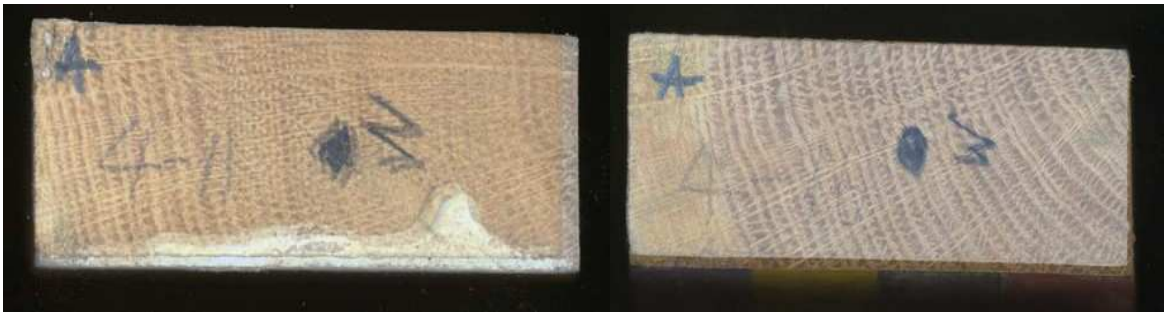
(a) Fir



(b) Poplar



(c) Lime



(d) Oak

Fig.4.36. Overlap image (specimens at 100% RH and 25% RH at equilibrium)

4.2 Insect attack test

4.2.1 Results of insect attack test

The results of the experiments are shown in Table.4.12. The test was considered valid because 70% of larvae exposed to untreated control test specimens survive. It is defined in EN 46-1 (2005).

Table.4.12. Results of insect attack test

Duration of test	Sample number	Retention of preservative g/cm^3	Initial number of larvae	Larvae recovered			Larvae not recovered	Number of tunnells	Larvae recovered with radio-graphy
				dead		live			
				Not having tunnelled	Having tunneled				
Red Petroleum									
15 weeks	R1	57.9	10	9	0	0	1	0	-
	R2	50.6	10	4	2	1	3	4	3
	R5	51.6	10	3	1	3	3	6	0
Propolis									
16 weeks	P1	95.5	10	2	2	5	1	8	4
	P4	96.2	10	3	0	4	3	6	2
	P5	96.9	10	2	3	4	1	7	4
Biotin R									
15 weeks	B3	67.0	10	4	4	0	2	6	3
	B4	64.1	10	9	0	0	1	0	-
	B5	63.7	10	10	0	0	0	0	-
Untreated Controls									
14 weeks	C1	-	10	0	0	8	2	9	8
	C2	-	10	1	0	6	3	9	7
	C3	-	10	0	2	8	0	10	6

Survival, mortality and unrecovered rate (%) after experiment were calculated according to the following equations with the respective numbers in Table.4.12.:

Survival rate (%) =

(the number of live recovered larvae / the initial number of larvae) *100 (%);

(4.1)

Mortality rate (%) =

(the number of dead recovered larvae (the sum of not having tunneled and having tunneled) / the initial number of larvae) *100 (%); (4.2)

Unrecovered rate (%) =

(the number of not recovered larvae / the initial number of larvae) *100 (%).

(4.3)

The average values of survival (4.1), mortality (4.2) and unrecovered (4.3) rate calculated on all treatments are reported in Table.4.13. and, for clarification also in Figure . Significantly there is a difference between preservative treatments in survival rate and mortality rate. But unrecovered rate does not have significant difference; each rate is similar. As reported by other authors (Fox 1975; Kusano et al. 1985), cannibalism is behavioral trait found in wide variety of animals and insects. The reason of unrecovered larvae would be of cannibalism. Or in the end of experiment specimens were cut them up with microtome (Fig.3.25.) and then small tiny larvae could have fallen down.

The survival rate and mortality rate demonstrate that there is a significant difference between treatments. As for survival rate, no live larvae were recovered in specimens treated with Biotin R, it means 0% of survival rate for Biotin R, 13 % for Red Petroleum, 43% for Propolis and 73% for untreated controls. On the contrary 90% of larvae died in the specimens treated with Biotin R, 63% for Red petroleum, 40% for Propolis and 10% for untreated controls.

Table.4.13. Survival, mortality and unrecovered rate of each treatment

	Survival rate	Mortality rate	Unrecovered rate
Red Petroleum	13%	63%	23%
Propolis	43%	40%	17%
Biotin R	0%	90%	10%
Untreated (References)	73%	10%	17%

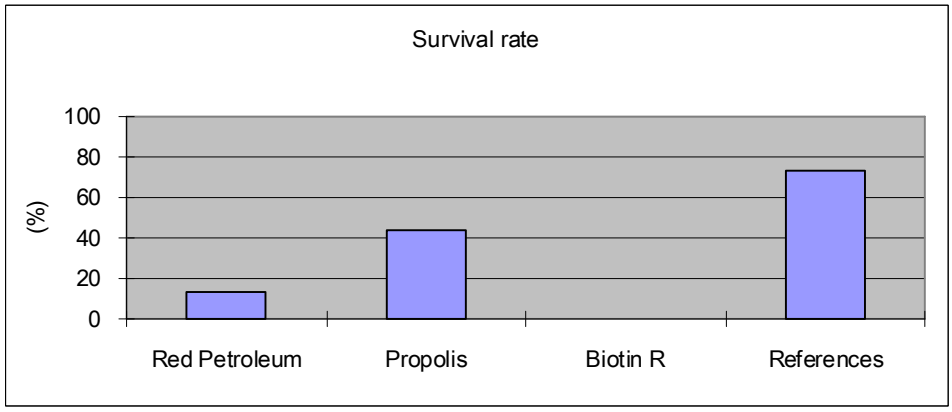
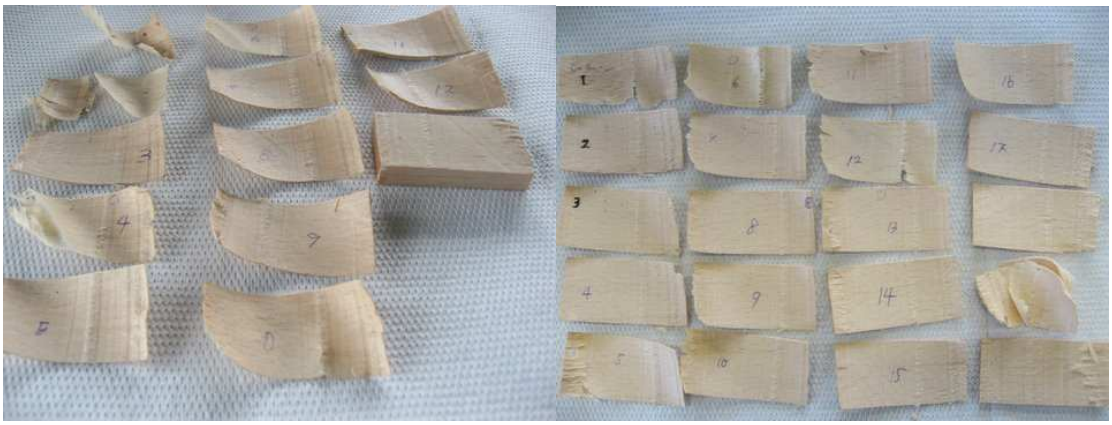


Fig.4.37. Survival rate of each treatment

The number of dead recovered larvae not having tunneled demonstrates how toxic the preservative treatments are. Preservative treatments should have repellent effect. Repellents prevent a pest from reaching a food source or move it away once it is there. (Robinson 2005) 77% of larvae in Biotin R died on the surface of specimens or near the specimens, 53 % for Red Petroleum, 23% for Propolis, 3% for untreated controls. These values were calculates using the following expression, (The number of dead larvae not having tunneled / the initial number of larvae *100). From this number Biotin R has most repellent effect against the larvae, then Red Petroleum, Propolis and untreated controls. On the other hand from the number of tunnels larvae made, the larvae activity can be assessed. (Number of tunnels / the initial number of larvae) This value is maximum 1.0. The larvae activity is 0.2 for Biotin R, 0.3 for Red Petroleum, 0.7 for Propolis, 0.9 for untreated controls.

When specimens were cut them up in the end of experiment, the depth and length of tunnel galleries were deep and long for the specimens treated with Propolis and untreated controls so they were cut them up from the top to the bottom (15 mm long). On the contrary specimens treated with Red Petroleum and Biotin R, tunnel galleries were not as deep and long as the specimens treated with Propolis and untreated controls so they were cut them up until the middle (7-8 mm long).

The value of larvae activity demonstrates not only how many tunnels one larva made but also how active they are and how much they could destroy (make tunnel galleries in specimens) wood specimens. Specimens treated with Propolis and untreated controls were sufficiently infested by larvae and specimens treated with Red Petroleum and Biotin R were not infested as much.



(a) Biotin R (B3) 12 slices and solid (b) Untreated control (C3) 19 slices

Fig.4.38. Thin slices of specimen after cutting

4.2.2 Naked-eye observation

Firstly, after 4 weeks, naked-eye observation was carried out (Fig.4.39.). One specimen in Red Petroleum and two specimens in Biotin R had almost no frass and 9 or 10 dead larvae were recovered on each surface without making tunnels. On the other hand specimens treated with Propolis and untreated control specimens were

observed with a lot of powdery frass. Apparently larvae exposed on the specimens treated with Propolis and untreated references were much more active than ones exposed on specimens treated with Red Petroleum and Biotin R. One mound of frass was almost one tunnel gallery.

The naked eye observation was proved objectively with the value of larvae activity. Preservative treatments were more active, they produce less frass or they cannot pass through the treatment on the surface of wood. It means more frass were detected; the specimens will have more insect attack.

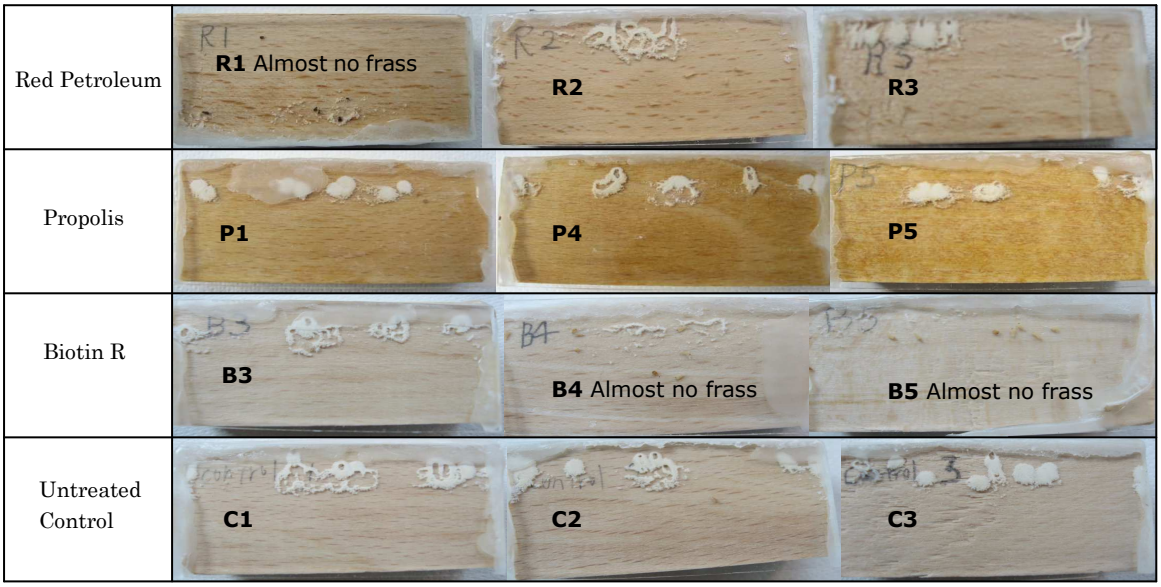


Fig.4.39. Naked-eye observation after 4 weeks before removing covered glass

Secondly, the covered glasses on specimens were removed and powdery frass was cleaned up by brushing in order to count roughly how many holes larvae produced (Fig.4.39.). The specimens (R1, B4 and B5) did not have any holes for tunnel gallery on surface but there was a very little quantity of frass. There were some superficial traces larvae made but they could not make tunnel gallery in wood.

Unaided eye observation was not perfect to count precisely because a small circular entrance hole of tunnel, packed with powdery frass is not so visible and obscure. As a complimentary observation, stereomicroscopy observation was

necessary.

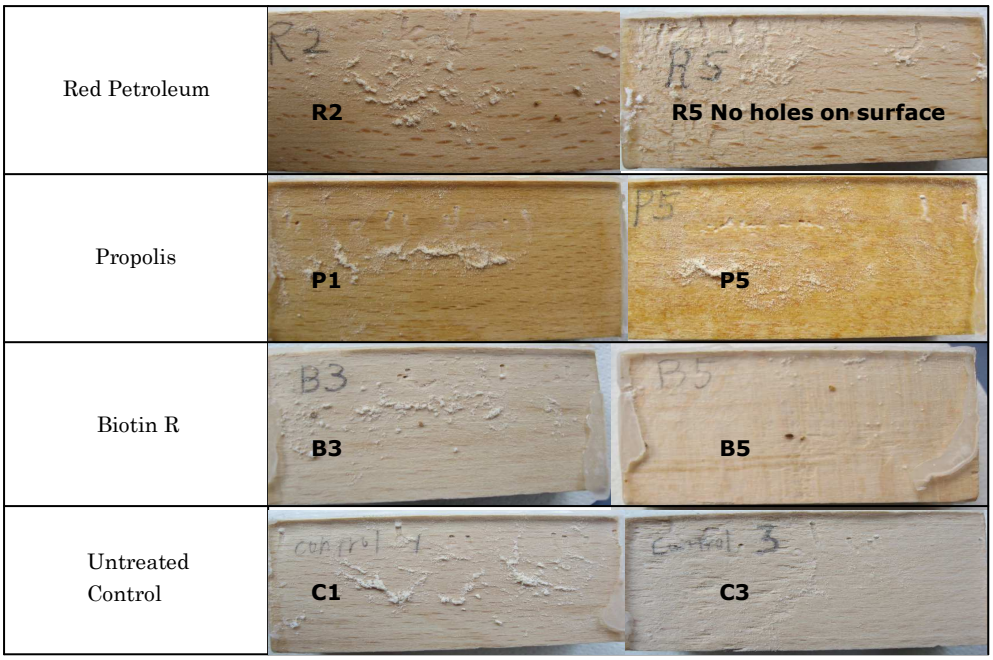


Fig.4.40. Naked-eye observation after 4 weeks after removing covered glass

The surface condition after 12 weeks had no difference after 4 weeks (Fig.4.40.). The reason should be that larvae activity was in the wood specimens to make tunnels after 4 weeks experiment, not superficial.

4.2.3 Stereomicroscopy

After 4 weeks the surface conditions of specimens were observed by stereomicroscope. At the circular gallery the occupied longitudinal tunnel is blocked either by shredded wood or a mixture of shredded wood and frass. Most of the vacated tunnels were blocked by frass (Fig.4.41.(a)). There were some holes without frass after cleaning by brushing (Fig.4.41.(b)). Those holes were possible with no larvae inside. One larva was observed at the entrance of hall by stereomicroscope (Fig.4.41.(c)). Our naked-eye has a limitation to see the detail surface of specimens but by stereomicroscope more detail surface condition could be observed.

(a) Halles filled with frass (b) Hall without frass (c) Larva at the entrance hall

Fig.4.41. Surface conditions after 4 weeks

After 12 weeks specimens were cut up to thin slices with microtome and those thin slices were observed by stereomicroscope. It was difficult to recover live larvae (Fig.4.42.) and dead larvae (Fig.4.43) with unaided eye, particularly dead larvae. Because the body color of dead larvae changed and the body shrunk. The difficulty to recover larvae was that when specimens were cut up to thin layers, it was quite possible to make fall down dead larvae because they shrunk and got dry.

Fig.4.42. Recovered live larva after 12 weeks

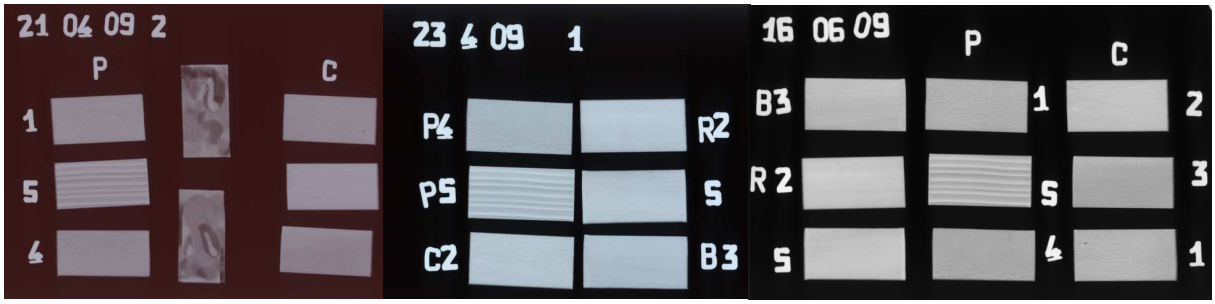
Fig4.43. Recovered dead larvae after 12 weeks

After specimens were cut them up to thin slices, some larvae in tunnel gallery were recovered (Fig.4.44.). It was not easy to recover live larvae due to the similar colour of live larvae and wood substance. When there is a hole packed with frass in tunnel gallery, normally live larvae are the end of the tunnel gallery.

Fig.4.44. Recovered live larvae in tunnel gallery after 12 weeks

4.2.4 X-ray Radiography

After 4 weeks and 12 weeks of experiment, further x-ray radiography analyses were carried out in order to observe how many live larvae were inside the wood specimens (Fig.4.45.). There was some gap between the number of live larvae recovered after cutting them up and the number of larvae recovered by x-ray radiography image. Dark tones identify woodworm tunnels, because that is where the piece of wood worm tunnels, because that is where the piece of wood has been weakened (Pinna et al., Eds., 2009). Light tones identify larvae, because the larvae have rich of quantity of water, and the color becomes lighter than wood substance. After 12 weeks, larvae are still tiny and it is not so visible on the image of radiography but a rough idea can be obtained by x-ray radiography image. When specimens were infested enough, it is easy to see the larvae and damage in wood (Fig.4.45.(a)). X-ray radiography images were observed with magnification in order to check precisely and carefully.



(a) After 4 weeks; Propolis and untreated control specimens, two specimens in the center after 10 months (they were put for comparison)

(b) After 4 weeks; Propolis (P4 and P5), untreated control (C2), Red Petroleum (R2 and R5) and Biotin R (B3)

(c) After 12 weeks; Propolis (P4 and P5), untreated control (C2), Red Petroleum (R2 and R5) and Biotin R (B3)

Fig.4.45. X-ray radiography image after 4 and 12 weeks

CHAPTER 5:

CONCLUSIONS

6.1 Conclusions

In this thesis, Romanian traditional products (Red Petroleum and Propolis) utilized for wood preservation for cultural heritage and Biotin R (commercial antifungal product used as a reference) were analyzed in order to assess the efficacy against mould and insect attack and impact on wood physical parameters. The advantage of these solutions is considered to be ecological, lower cost and without health risk. (Sandu et al. 2008) When the treatment is applied, the first thing to consider is the health hazard for the staff and to ensure that protective measures are used (Florian 1997). From this point of view, Romanian traditional products have some advantages.

Effectiveness against mould and insect attack

Mould attack

Effectiveness for mould attack was studied during the exposure to different relative humidity (RH) at equilibrium. Samples treated with Red Petroleum and Propolis were compared to untreated samples and sample treated with Biotin R. Effectiveness was evaluated with the results of visual assessment for 100% relative humidity at equilibrium as well.

In conclusion, Red Petroleum and Propolis are not active for mould while Biotin R is very active, as it is known for anti-fungal product. Mould attack is mostly concentrated in the painted layer, where the tempera, containing glue and egg, enhance nutrition availability for moulds. Furthermore, materials that are very hygroscopic like wood and materials that have sufficient nutrients are the most susceptible to mould attack (Block 1953) and the type of coating systems had a greater influence on the surface, where the mould grows, than on the wood substrate itself (Ahola et al., 2002). In this research it has been proved that especially the nutrient content of wood surface (tempera painting) intensifies the mould growth and

samples treated with Biotin R (antifungal-product) for the whole surface have no mould attack.

Wood samples without tempera (naked wood) are much more resistant against mould attack than sample with tempera painting. The most resistant species of naked wood is oak, followed by lime and poplar. The most resistant species with tempera painting is lime wood. It is shown that extractives of wood have influence on mould attack. Terpens would have effect on mold attack for lime, and tannin for oak. These minor extractive compounds have antimicrobial activity and could prevent a microbial attack.

The various fungal species generally called “mould fungi” are not able to digest the chemical compounds composing the cell wall (cellulose, hemicellulose and lignin), and in our experiment wood is a support for them. On the contrary, they are able to utilize the substances composing the various layers of what we called the painted layer. Painted layer is more attractive for mould than differences between wood species. It seems that oak and lime wood contain extractives that disturb the presence of mould fungi. On the contrary poplar wood does not disturb the presence of those fungi.

However, the durability of mould attack is dependent on the quality of wood surface. Moreover, the reduction in average moisture content and in the period of time when the wooden artifact is displayed in high RH condition is enough to allow slowing down the rate of mould attack.

The fact that should be underlined is that after oven-drying, the painted layer of the sample which had massive mould attack, broke into pieces or presented serious detachment. It happened only in poplar specimens, which exhibited the most mould attack. Oven-dry state is extreme and it never happens in normal condition but these results show that mould attack has surely an enormous impact on the durability of

painted layer and accelerate the deterioration of panel painting in time, even if structural damage is very small.

Insect attack

Effectiveness for insect attack was studied in accordance to European Standard, EN 46-1 (2005). The efficiency against insect attack of the Romanian traditional treatments (Red Petroleum and Propolis) and Biotin R was assessed.

In conclusion, Bition R, even if is not a real insecticide but a fungicide, is the most active product against insect attack of the three products, followed by Red Petroleum, Propolis and untreated reference. The survival rate of larvae in Biotin R (0%) and Red Petroleum (13%) is smaller than Propolis (43%) and untreated wood control (73%). This result demonstrated that Red Petroleum is slightly active and Propolis is not so active. Objective of an insecticide is primarily a repellent effect against insect inlet so that the fact that some larvae pass the superficial treatment means that the preservative treatment is not active. But it must be emphasized that Red Petroleum and even Propolis had less attack than untreated controls.

Colour measurement

Colorimetry has been used in order to measure the colour before and after varnish and treatment, and during the exposure at different RH at equilibrium.

Varnish does not affect, while there are some differences after treatments application. Colour did not change so much after the application of Red Petroleum and the colour difference was almost not perceptible. On the contrary, Propolis affected a lot the colour. The chromaticity parameters of b* (+b* for yellow and -b* for blue) increased after the treatment of Propolis; the colours become yellowish after the treatment with Propolis on the whole. The difference was obvious, especially for white colour. Light colour is more sensitive than dark one.

During the exposure at different RH, the colour changes significantly at 100% RH at equilibrium and this is mainly due to the mould attack. There are also some other factors as they are mentioned in mould attack part (Chapter 5). The colour difference is dependent on the intensity of mould attack and the colour of mould. Mould attack and the difference of colour are correlated to each other. However, it is not necessarily correlated in case the colour of mould is similar with the colour of the painted layer.

The colour in panel painting has a fundamental importance during the process of conservation and restoration. It is one of the most vital missions to keep original colour as much as possible in conservation and restoration process.

Penetration and chemical interaction between solutions and wood substance

The penetration of solutions (Red Petroleum and Propolis) was fully characterized by FTIR-ATR analysis, providing suitable markers for the identification of the solutions. In particular, FTIR-ATR studies of solutions and treated wood samples proved the penetration of treatment products (Red Petroleum and Propolis) in wood.

In conclusion, Red Petroleum penetrates a lot, while Propolis does not penetrate and remains only on the surface. However, Red Petroleum does not interact chemically with wood substance and it is easy volatilized in oven-dry condition. On the contrary Propolis interacts chemically and strongly with wood substance and hardly volatilized, even in oven-dry condition and consequently Propolis remains where it penetrated, on the surface.

Physical parameter

Treatment by immersion has impact on wood physical parameter while treatment by brushing does not have significant impact. When the treatment is applied by immersion, penetration of solution affects the physical parameters. Especially Red

Petroleum has an apparent impact on moisture content (MC) due to the penetration of solution, while Propolis does not penetrate so much and remains only on surface therefore Propolis does not have so much impact as Red Petroleum. However, if the weight of the solution penetrated in wood is eliminated, there is not significant difference in MC between treated samples and untreated samples.

Considering physical parameter, dimensional stability is an important parameter. The variation of wood moisture content causes shrinkages/swelling of the wood that polychrome layer can only partially follow. The size of wooden support varied under different moisture conditioning; the painted layer cannot completely follow its deformation, and consequently this leads to degradations and deteriorations caused by detachment. That detachment affects the polychrome stratification of the panel painting and eventually the connections between the different layer compositions of the panel painting. In fact, wood is a hygroscopic and anisotropic material while the painted layer is less hygroscopic and isotropic. This wood characteristic produces distortions during drying and promotes detachment of painted layer. Detachment of painted layer is observed not from the edge but from the middle of panel, and the presence of knots (defect) promotes detachment more than normal state wood. A further approach could be the analysis of the behavior of the connections between layers.

6.2 Critical assessment for this research and suggestions for future research

As stated, there are few published resources to refer to the impact of Romanian traditional treatments (Red Petroleum and Propolis) when determining what type of conservative treatment is reasonable for panel painting and a given site's budget and condition. Most of the information regarding to this area is not fully covered in the literature, making this difficult to find all information dedicated for panel painting. While this investigation is an early attempt to determine the impact of treatment, the first recommendation for future research is to continue to study the impact of these traditional treatments and under different environmental conditions. It would be useful to consider new environmental friendly preservative products. This study gives an indication of the impact of treatments, only for some environmental conditions and is not statistically robust enough to determine the whole impact. A study of a greater number of panel paintings would provide a stronger statistical analysis of the impact on panel painting.

Moreover, this study was conducted on small wood samples and, as always, we can not immediately transfer the results obtained on small samples to real case dimensions. Because in real case, there is a larger variability of wood technological characteristics and natural presence of wood defects (grain deflections, knots, localized presence of sapwood, etc.) and presence of insect/fungi attack. Support of panel painting is frequently panels, i.e. it is composed of more than one wooden board. Therefore in real cases, what should be previewed is the presence of connections between single elements and a complex behavior resulting from interactions between single elements. But in order to collect data for eventual future experiments on real painted panels, it was crucial to perform a first set of experiments on small-dimension painted samples as in this research.

The final recommendation for future research is to allow more time to collect data from different conditions. This study was completed over two years and half, yet that was not enough time to do experiments in more different conditions, different species of wood, different pigment and so on. The time necessary for wood until reaching the equilibrium took much longer time than anticipated to obtain data, especially for high relative humidity.

In the end, it is the author's hope that this thesis will lead to more conservators, restorers and other preservation professionals to investigate the treatment for panel paintings, especially those professional in Romania. It should be underlined that this study was conducted, considering wood as a material and support of panel painting. The technological behavior of the support is important to be considered together with the decorated painted layer, they act together to compose the piece of art. This study presents the framework for such kind of investigation, and it is hoped that future researchers will refine and improve it. Doing so will help the preservation community as a whole to find affordable ways to preserve the integrity of panel painting for future generations.

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