External resistance to water vapour transfer of varnishes on wood

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Abstract
This paper reports results of experimental measurements of diffusive water vapour flux through wood specimens coated with varnishes and resins commonly used in the field of restoration. The internal and the external resistance to the transport of water in wood was calculated with a numerical method from sorption tests. The results show that all painting layers reduce the flux. The calculated mass transfer coefficient is an important physical characteristic of the material and it allows improved models for the understanding and prediction of the influence of coatings and painting layers on the hygroscopic and deformative behavior of wooden objects.

1. INTRODUCTION
Wood is an hygroscopic material. Its moisture content (MC) at equilibrium (EMC - Equilibrium Moisture Content) is a function of the relative humidity (RH) and temperature (T) of surrounding air. Whenever the hygro-thermal conditions of the environment change, the wood tends to reach a new EMC, adsorbing or desorbing water. Shrinkage and swelling always accompany the variation of MC and they are probably the main source of problems for the conservation of wooden artefacts because they can cause deformations, internal stresses, cracks of the wooden support and degenerative phenomena of the painted layers such as delamination [1].

During the transient phases of sorption (absorption or desorption) in response to a RH change, the water -in the form of bound water and vapour in the cell cavities- diffuses from the region of high moisture concentration to one of lower moisture concentration. The transport rate of water between wood and surrounding air is controlled by two resistances, namely the external resistance due to the boundary layer at the surface and the internal resistance due to the wood structure. For a porous and hygroscopic media such as wood, the internal molecular flow under the influence of a concentration gradient is represented, according to many authors, by Fick’s law of diffusion which relates the flux ($J$) to the moisture concentration gradient [2]:

$$ J = -D \nabla c $$

where: $D$ = diffusion coefficient $[m^2 \text{ sec}^{-1}]$; $\nabla c$ = concentration gradient, i.e. the difference of concentration $c$ between two points separated by a distance $x$.

The external transport flux of vapour of the exchange surfaces is defined by:

$$ J = S(c_{surf} - c_{ext}) $$

where $c_{surf}$ is the water concentration of the surface at the equilibrium with air, $c_{ext}$ is the water concentration of the surrounding air and $S$ is the surface emission coefficient $[m \text{ sec}^{-1}]$.

In the case of wood, $D$ depends on many variables, some of which have been investigated in the past years, mostly in the field of applied research of industrial wood drying. It is known that $D$ has a positive relationship with $T$ and $MC$, that it is from 2 to 10 times higher in the longitudinal direction than in the transversal direction and that it is 15% to 25% higher in the radial direction of softwood than in the tangential direction [2]. Significant variability can be observed among wood species where $D$ lies in the range $10^{-8}$ to $10^{-11}$ $m^2 \text{ s}^{-1}$ [2, 3].

External resistance depends on the characteristics at the wood-air interface. It is related to air temperature, humidity, speed and the type of flow (turbulent, laminar) as well as with wood surface characteristics such as roughness, MC and density. Widely variable values of $S$ are found in the literature. This is due to the large number of methods used to measure and calculate $S$ and to the great number of variables influencing the results. Sorption tests in a thin lamella at several temperatures give values in the range of $1-5 \times 10^{-7}$ $m \text{ s}^{-1}$ [4]. Other methods lead to values in the range of $5-20 \times 10^{-6}$ $m \text{ s}^{-1}$ [5].
The presence of paint layers on the surface of a wooden object can increase the resistance at the boundary, influencing the rate of vapour transfer between air and the object, with different consequences on conservation. Paint layers can form a helpful vapour barrier which reduces the influences of environmental climatic variations, above all high frequency fluctuations such as the daily RH variations that affect the superficial zones of the wood. On the other hand, asymmetrical mass transfer in panel paintings due to the different permeability of painted and rear sides can produce cupping deformations in the panel for short periods during transient variations, after a RH change. This phenomenon is well known in the field of restoration and many publications describe practices for the insulation of the rear side of panel paintings using different materials and techniques in the attempt to reduce the effect of asymmetric transfer [6]. However, in this case, good results can be attained only if the permeability properties of the barrier materials are known.

The work described in this paper is in the framework of a larger project aiming to characterise the permeability properties of different families of materials, used in the past for panel paintings and nowadays in the field of restoration. The first results of the permeability of different combinations of painting layers replicated according to techniques and materials used in the period from the the late Middle Ages to the Renaissance are going to be published soon in [7]. In this paper, with the same methods, the results of the tests on nine types of varnishes and resins commonly used in the field of the restoration for the consolidation and protection of painting layers and wood of the support are reported and compared with the permeability of painting layers.

The database developed in the project aims to be a tool providing information to the restorers and conservators in the choice and use of the materials and substances. Moreover it aims to improve the efficiency of numerical models for the understanding and prediction of the influence of coatings and painting layers on the hygroscopic and deformative behaviour of wooden objects subjected to changes in environmental climatic conditions.

2. MEASUREMENT OF DIFFUSION COEFFICIENT

Cup test (steady-state method) and sorption test (unsteady-state method) are the main experimental methods for the measurement of the mass transfer coefficient. Both methods consist in measuring the diffusive flux produced by vapour concentration difference passing through a known exchange surface in the time interval [3]. In theory the two methods should give the same results; this is quite true at lower moisture content but at higher moisture content the cup method $D$-value tends to be about double that the unsteady-state one, because of stress relaxation phenomena involved in the latter case [8, 9]. An experimental comparison between the two methods, performed at the beginning of this work, confirmed the discrepancy between the two methods. Furthermore, in the case of sorption modelling, we are mostly interested in the unsteady-state diffusion coefficient values. and so, for all these reasons, sorption test was preferred.

In the sorption method, the weight change of hygroscopic specimens due to a step change in the external RH is measured from the beginning until the end of the test, when the wood reaches a state of equilibrium (constant weight). The specimens are placed in a climatic chamber and first equilibrated to a given constant climatic condition. When they are equilibrated, the RH in the cell is changed to a new set value. The mass variation of specimens due to sorption of the wood is measured periodically until the specimens reach the new EMC. The gradient (and consequently the flux) is maximum at the beginning and then it decreases, varying during time ($t$) and space ($x$), through the thickness of the specimen. This is an unsteady-state condition described by the Fick’s second law. The result of a sorption measurement is a sorption curve, the plot of the weight change versus time.

Sorption tests can be performed at any $T$ and RH values and in both directions (absorption or desorption). The results have different values and different meaning according to the dependency of $D$ from $T$ and local MC of wood and also according to the hygroscopic hysteresis of wood, a phenomenon responsible for the variation of EMC when reached from adsorption or desorption. The quality of the data from a sorption test mainly depends on the performance of the climatic chamber. It must ensure very stable climatic conditions over time and uniformity throughout the volume of the chamber. The RH change must be very fast and without any significant variation of $T$. For this purpose a special dew-point climatic chamber was designed and built [10]. The volume of the chamber is small ($0.15 \text{ m}^3$) suitable for small specimens. The analytical balance is in the interior of the
chamber, protected against vibrations and air fluxes. Two holes with rubber baffles permit manipulation of the samples during weighing operations without the need to open the door.

The results of sorption tests with the following parameters are reported: T 25° C constant; RH1 40%; RH2 60% (absorption, EMC from 7.6% to 11.1%); air speed: 0.5 m sec⁻¹; time from RH1 to RH2 less than 1 minute; weighing every ½ hour during the first day, then with decreasing frequency.

3. SAMPLES

Brick shape wooden samples ( 8 x 150 x 100 mm) were cut from a sound radial sawn board (quarter sawn board) of Spruce (average normal density: 410 kg m⁻³). The faces of the specimens were carefully oriented according to the three anatomical directions in the tree: Longitudinal (L), Radial (R), Tangential (T). Radial sawn boards are the most commonly utilized for panel paintings because they are more stable than tangential sawn boards (flat sawn boards). In Italy, the recurrence of Spruce wood (*Picea abies*) in panel painting and altarpieces is common in the Alpine regions and sporadic in the pictorial Italian Schools of central Italy [11]. Spruce wood was selected because it is more studied than other wood species, with well-known and documented physical and mechanical characteristics, and because it is easy to find defect-free (knots, spiral grain, reaction wood etc.) and it has homogeneous characteristics (density, rings pattern etc.).

One face (in the radial plane) of each sample was coated with the testing coating substances. The opposite face and the remaining four edges were sealed with aluminium sheet and silicon adhesive. In this configuration the flux of vapour occurs in the T direction only, through the coated surface.

The surface of wood of the specimens without any preparation were coated with a number of layers (from 1 to 3) of 9 types of varnish or resin (directly on the wood surface). Those substances (listed in table 1) were selected among the different products commonly used in the field of restoration for the consolidation and protection of wood and painting layers. Each coating type was replicated on two series of specimens with different dimensions and coming from different sawn boards. One reference specimen (dummy) for each type was kept uncoated. The combination of nine coating types replicated two times plus nine reference case of uncoated bare wood specimen led to 27 specimens.

Currently tests on the following substances for consolidation are in progress: Gelvatol, Klucel G, Aquazol 200, Aquazol 500, Plexisol P550,Paraloid B-72,Paraloid B-67,Primal AC33, Akeogard AT 35, Akeogard AT 40, Plextol B500. Results for those tests will be published in the next CESMAR 7 which will be held in Padova (Italy) next October.

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Table 2 – Name and composition of varnishes and resin used for the series of specimen with varnish only.

4. CALCULATION

During a diffusion experiment the global mass change of the wooden object is measured and this allows the calculation of the apparent diffusion coefficient \( D^* \) which includes both \( S \) and \( D \), i.e. the external and the internal resistances.

\[
D = D^* \quad \text{only if the external resistance is zero (high value of } S) \]

Such an occurrence means that the surface of wood is at an instantaneous equilibrium with the external air conditions.

Different methods can be used to calculate \( D^* \) from a sorption test. The classical way is to calculate \( D^* \) from the slope of the normalized sorption curve (i.e. the fractional weight change \( E \) versus the square root of time) according to eq. 4 representing an analytical solution of Fick’s second law:
where $E$ is the normalized weight change $= \Delta M_t/\Delta m_e$ and $\Delta M_t$ and $\Delta m_e$ are the weight changes at time $t$ and at final equilibrium respectively, and $x$ is the thickness of the sample [12]. The slope $\frac{dE}{dt}$ is usually calculated in the part of the curve from 0 to $E=0.5$ corresponding to the half sorption time ($t_{0.5}$).

In thin samples, in correct experimental conditions, a surface resistance different from zero generates a sigmoid trend of the initial part of the normalized sorption curve [13]. It allows to separate $D$ and $S$ from $D^*$. In this work a numerical model based on the finite element method (FEM) was used for determining the mass transfer coefficients $S$ and $D$ from the shape of the curve. The model was developed on a commercial FEM software package (COMSOL Multiphysics®) with a module for transient analysis of the mass balance governed by diffusion. A 1-D geometry is sufficient to represent the unidirectional flux of the experimental conditions. The problem was hence simplified with a line with length $L = x$ where $x$ is the thickness of the specimen. The line corresponds to the sub-domain where the internal transfer, controlled by $D$, acts. The two ends of the line correspond to the surfaces where the boundary conditions act. According to equation 2, the surface emission coefficient $S$, controls the boundary conditions in terms of the rate of change in the zero thickness layer at the surface. A condition of insulation ($S = 0$) was imposed on one end corresponding to the sealed face of the specimen. The coating of the other end was considered just a surface with a zero thickness influencing the value of $S$.

In order to avoid confusion in the text $S$ refers to the surface emission coefficient of uncoated wood and $P$ to the permeability coefficient of coatings on the wood’s surface. It should be pointed out that in this condition, the thickness of the coating can influence the $P$ value. Further details on the model can be found in [7,10]. The coefficients were determined by inverse method, consisting of finding the values of coefficients which produce the best fit between experimental and simulated curves. The $D$ and $S$ coefficients were previously determined from experimental sorption curves of uncoated specimens. In particular $S$ was determined from the shape of the initial part of the sorption curve. $D$ was considered to be constant in the entire range of variation of MC. This assumption is realistic when the variation is small. The model tuned in $D$ is then used with the same procedure for the determination of $P$ from sorption curves of coated samples, by varying $S$ and assuming that $D$ remains constant.

5. RESULTS

The normalized sorption curves for all of the specimens are reported in figure 1 (left). The total sorption time needed to reach the equilibrium was quite variable, being about 40 days for uncoated specimens (D0 0) and over 200 days for some coated specimens Half sorption time ($t_{0.5}$) ranged from about 2 to 23 days. The half sorption time is a measure of the barrier effect of different materials.

![Normalized sorption curves](image1.jpg)

Figure 1 – Right: Normalized sorption curves for all specimens (first period); black lines: reference uncoated specimens; red lines: coated specimens. Left: comparison between experimental data (continuous lines) and simulated curves (dotted lines); [7 Modified].
The \( D \) and \( S \) coefficients, calculated by reverse method from the average sorption curves of bare wood specimens are \( D = 1.5 \times 10^{-10} \text{ m}^2 \text{ sec}^{-1} \) and \( S = 1.1 \times 10^{-7} \text{ m} \text{ sec}^{-1} \). These data agree with the literature \[2, 3\]. The \( P \) coefficient of each combination of layers was then calculated from the corresponding average sorption curves maintaining \( D \) constant. Experimental average curves and simulated curves are shown in figure 1 (right). The correspondence between them is always excellent demonstrating the good adherence of the model to the physical phenomena.

The average \( P \) values are reported in the left histogram of figure 2. Those data can be compared with the right diagram concerning the \( P \) values of different painting layers replicated according to techniques and materials used in the period from late Middle Age to Renaissance, calculated with the same method \[7\].

In both histograms the \( P \) value of The right Y axis of the graph shows the corresponding scale of the relative permeability \( P^* \) defined as \( S/P \), the ratio between uncoated (\( D_0 \)) and coated surface resistance. \( P^* \) may be also be read as a measure of the asymmetry of the mass transfer responsible for transient deformations in panel painting.

The picture provided by the experimental results presented in this paper should be considered as incomplete because no information was collected concerning the influence of factors such as temperature, RH, hysteresis, the thickness of the coating layers and the consequences of ageing on the barrier effect due to long-term mechanical, physical or chemical processes. It is known that chemical processes occurring for decades and centuries in oil paint (polymerisation, hydrolysis, oxidation, soap formation) accompany changes in the mechanical properties with modification of stiffness and brittleness properties \[14\] and modification of the characteristics of the painted surface (e.g.: occurrence of cracks, detaching, craquelure). The effects of such modifications on permeability is unknown and, because of the large number of variables involved, its quantification is a scientific challenge. Some ongoing experimental measurements of mass variation of 16th century panels, painted with oil on one face and exposed to environmental fluctuation in exhibition conditions show a much higher \( P \)-value than expected. Such data (to be published) seems to confirm a strong effect of ageing factors in increasing the permeability of painting layer.

**CONCLUSIONS**

This paper described a method for the characterisation of water vapour permeability of painting layers on wood. The permeability coefficient described and measured in the paper is a fundamental physical property of the material because it affects the hygroscopic and deformative behaviour of wooden objects. This is an important quantity for improving the efficiency of FEM-based application software which, lately, are becoming powerful tools in the field of restoration and conservation. Because of the small number of samples tested, such results do not have a high statistical relevance but they do provide the first look at data never measured before. Further measurements are needed to assess the influence of thickness of coatings, ageing factors and several climatic parameters such as...
temperature. Moreover, the method could be extended to the characterisation of other materials such as consolidating additives and new substances used in restoration practice.

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