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Some Methods for the Degradation-Fragility Degree Determination and for the Consolidation of Treatments with Paraloid B72 of Wood Panels from Icon-Type Heritage Objects

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Abstract: The main objective of this paper is to develop methods for assessing the deterioration of wooden panels of iconic heritage objects and the effectiveness of consolidation treatments, methods that are easy to apply to the field of wood restoration. During the research, four evaluation methods were identified, respectively: the density method, the excessive porosity method, the Brinell hardness method, and the Mark hardness method. Each method was exemplified on five wooden panels (icons), and when needed, degraded specimens were used and/or treated with Paraloid B72. One of the main conclusions of the research is that, although all methods are minimally invasive and do not require cutting of these heritage objects, the applicability of each is done depending on the type of degradation, often requiring a combined analysis between two or several methods. Additionally, the classification of the cultural good in one of the five degrees of embrittlement-degradation help to design a technological flow regarding the treatments of consolidation/restoration of the heritage object.

Keywords: fragility degree; restoration; icon; heritage objects; consolidation; wood; degradation evaluation

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1. Introduction

Heritage objects are valuable objects for a certain community or a certain geographical space, from the cultural, artistic, historical, faith, etc., points of view. The concept of heritage is constantly evolving through its traditional, chronological, and geographical character. In parallel with this aspect, the selection criteria of a heritage object have been extended [1] adding to the historical and artistic value, other values such as the cultural one, the national identity one, and the memory interaction one. The new heritage concept was structured on two levels: material and immaterial heritage, respectively, tangible and intangible.

The degradation and fragility of wood from heritage objects are determined by the fact that wood is a biological material conducting the development of wood-decaying insects and fungi, these being the main factors of its degradation and fragility [2]. Damage can sometimes be so severe, especially for small heritage objects (icons) [3,4] that it jeopardizes their continued existence. Figure 1 shows the three important stages of a heritage object, namely the initial stage as a new object, the intermediate degradation stage (with several stages), and the final stage when the degradation is so strong that the object can no longer be restored.

Wood degradation depends on its structure, especially its density but also the content of secondary chemicals [4]. For example, dense wood of 1260 kg/m^3 such as *Guaiacum officinale* [5] is more difficult to be attacked by fungi and insects, and wood containing a considerable percentage of tannins or resins is also less susceptible to insect–fungus attack. Several types of wood degradation are known [4], the most important of which are: cracking, deformations, insect holes, galleries, mold, rot, etc. (Figures 2 and 3).

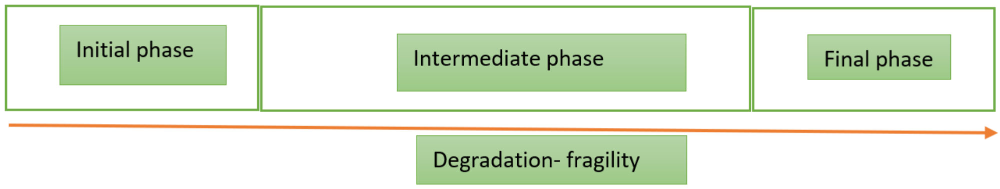


Figure 1. The stages of wood degradation-fragility from heritage objects.

(**a**) (**b**) (**c**)

Figure 2. Degradation of wood support: mold (**a**) and rot (**b**,**c**).

(**a**) (**b**) (**c**)

Figure 3. Wood degradation: (**a**) *Coniophora puteana*, (**b**) *Serpula lacrymans* and (**c**) *Anobidae* insects.

The main wood-decaying fungi that attack wood from heritage objects are *Coniophora puteana* (wet rot) and *Serpula lacrymans* (dry rot); they cannot grow at negative temperatures, but always at a wood moisture content of optimal 22–25%. The mycelium and hyphae of these wood-eating fungi can penetrate the masonry to reach the wood [4].

Macchioni et al. [6] highlighted the need to revise international standards for the evaluation of wooden structures from heritage objects. Macchioni et al. [7] studied the state of conservation of wood from artifacts. The research was subject to the guiding principles of the standard UNI 11161: 05 [8] on species determination, anatomical recognition of wood structure, mechanical properties, identification of biological attack, and assessment of the damage caused by fungi and insects. Fassina [9] described the legal regulation on specific European standardization work in the field of cultural heritage conservation as essential for a common, unified approach to the conservation and restoration of cultural heritage. Wood damage is a natural process that depends on a number of factors, be they biotic or abiotic. The temperature considered optimal for the installation and development of xylophagous insects has values between 18–25 °C and the relative humidity of 55–95% [10], both values are slightly variable for the different types of xylophagous insects that are frequently found in heritage assets with wooden support (*Anobium punctatum*, *Lyctus linearis*, *Xestobium rufovillosum*, etc.). The optimum moisture content of wood for insect development is 26–32%, and when it falls below 17%, insects can reduce their activity [11]. The larvae, in a life cycle of 1–2 years, produce galleries with diameters between 1.5 and 4 mm, decaying the wood along the fibers, the exit galleries become sinuous and with diameters of 0.5–2.2 mm.

Sakuno and Schniewind [12] showed the importance of the quality of the reinforcement materials used during the restoration, using old Douglas wood (*Pseutdosuga menziesii*). Three types of synthetic polymers were used in the experiments, namely Acrylic B72, Butylul B98 polyvinyl butyral, and Ayat polyvinyl acetate in 15% solution, each of the three with two types of solvents. For experimental research, old wood was taken in the form of poles, extracted from an old construction, where they stayed 70 years underground.

Cataldi et al. [13] investigated the use of other thermoplastic composites made of microcrystalline cellulose powder or even bamboo paper [14] in various percentages (up to 30%, mass basis) as a consolidator and Paraloid B72 as a matrix, in order to grow mechanical properties of the composite. During the experiment, microcrystalline cellulose powder (Sigma-Aldrich) with a specific gravity of 1.56 g/cm^3 was used as the reinforcing filler. Resin Paraloid B72 procured by Rohm and Haas (Germany) with a specific gravity of 1.15 g/cm^3 was also used as the polymer matrix. The works elaborated by Cataldi et al. [15–17], made an analysis of the use of microcrystalline cellulose as a filler-consolidator in composite materials that will be used to strengthen the wooden support of heritage objects. For the experimental analysis, two types of historical wood from the 18th century were used, walnut (*Juglans regia*) and white fir (*Abies alba*), which showed deep degradations. This old wood was reinforced with a composite material made from the commercial polymer Paraloid B72 which is often used to strengthen the wood, in combination with two different amounts of 5 and 30% (weight basis) microcrystalline cellulose. As a comparison, the same tests were performed on clean and fresh wood specimens from the same species. The presence of this filler in the composite has increased its resistance to static or impact tests. Mańkowski et al. [18] only used Paraloid B72 on old linden wood (*Tilia cordata*). The paper looked at the retention of the consolidating Paraloid B72 solution in butyl acetate. During the first cycle of impregnation, the retention of Paraloid B72 was double that of the second cycle of impregnation.

Charola et al. [19] state that the applied treatment will not protect the wood from further deterioration, but will slow down the deterioration process and give the heritage object a longer lifespan so that in the future a new treatment can be applied if it is necessary. Timar et al. [20] addressed the issue of consolidant retention, its depth of penetration, and uniform distribution on the surface and inside the wood. The reinforcing products were Paraloid B72, beeswax, and two other types of paraffin. The consolidant retention was low by 2–4% in the case of Paraloid B72 (dilute solutions 50–100 g/L), but much higher in wax and paraffin-based products, by 20–26%.

Deng et al. [21] proved how much electron tomography means in the analysis of the degree of degradation and fragility of heritage objects, by analyzing the missing areas, sometimes even on a sub-microscopic scale. The paper uses electron tomography and develops an algorithm to identify and reconstruct the missing areas and information in 3D space. Schniewind and Eastman [22] used the scanning method Scan Electron Microscopy (SEM) to observe the percentage of wood cells filling with the reinforcing material. Three different consolidants were used (Butvar B98, Acryloid B72, and Butvar B90) and applied on damaged wood by vacuum impregnation. The Douglas pillars from a 70-year-old house, the part buried in the ground, on the shore of a lake, with obvious bacteriological degradation, were used as wood specimens. It has been shown that the number of consolidants decreases from the surface to the core of the specimen. Pavlidis et al. [23] showed the importance of 3D digitization scanning of the heritage object. The study identified three main factors influencing 3D digitization: the complexity of shape and size, the level of detail, and the diversity of materials used. Rivers and Umney [24] analyze in their book the history of furniture restoration, as well as the classical and modern materials and techniques used in this case. Siau et al. [25] made a foray into the phenomena and processes that occur in wood and especially those related to moisture content transfer.

The most common treatment used to harden wood is acrylic polymers (often Paraloid B-72). The choice of solvent, its toxicity, explosiveness, and flammability must also be taken into account [18]. For example, the highest degree of wood saturation was obtained using Paraloid dissolved in methanol; however, due to the strong swelling caused by methanol, it could not be applied in conservation practice. High saturation causes a low penetration of the solvent into the depth of the wood [18]. In their research, they determined polymer content in damaged wood samples impregnated with Paraloid solution 20% B-72 in toluene and found that there is polymer at a depth greater than 7 mm in about 10% of wood vessels. A better supersaturation was obtained by dissolving the Paraloid in acetone [18], except that acetone produces dimensional instability of the wood, and its use in restoration should be judiciously observed. One of the main advantages of B-72 as a consolidator is that it is stronger and harder than others, without being extremely brittle. This consolidator is more flexible than many of the other typically used consolidators and tolerates more stress on jointing. Along with Paraloid B72, another synthetic product used to strengthen the wood support is polyethylene glycol. However, the disadvantages of reduced penetration in the cell membrane for concentrations higher than 10%, lack of antibacterial properties, increased acidity of the treated product, and reduced depth of penetration into the wood must be overcome [22].

The degree of impregnation will depend on the consolidating material, the solvent used, the concentration and the viscosity of the solution, the permeability of the wood to be consolidated, the technique used (brushing, injection, immersion, vacuum impregnation, etc.), and other treatment parameters such as duration and temperature [20]. Higher concentration solutions store more resin and will therefore give more strength. Another material used in restoration is Regalrez 1126—a saturated cyclic hydrocarbon similar to wax and paraffin. It was found that a concomitant mixture of the two substances (Paraloid B72 dissolved in toluene and ethyl acetate and Regalrez 1126) could cause precipitation, resulting in a suspension that would make the injection difficult, which could have a negative effect on the expected effect. Paduretu and Ghiorghita [3] stated that a restored object must remain original, without noticing the interventions that were operated on it. That is why the materials used for restoration must be compatible with the old wood from the heritage object. Walsh-Korbs and Avérous [26] argued that the reduction in density can also be explained as a decrease in the structural components of wood. Bucsa and Bucsa [4] showed that a humid space and a reduced air circulation are the main factors for the development of the attack of fungi and/or xylophagous, independent or combined. This attack causes rot or larval galleries, and these lead to chromatic changes or loss of mechanical strength of the wood. Other authors have analyzed the restoration process [27–29], others have noticed that the visual inspection of the surface is not enough [30], that a chemical cleaning of the surface is needed [31–33], a preliminary diagnosis is needed [34], even 3D digitization [35], the use of Paraloid B72 [36,37], or the use of new wood of the same species for comparison [38]. It has also been proposed to use heat-treated wood as an artificial degradation process [39,40] and to use modern FT-IR and X-ray tomography methods [41,42].

Many researchers in the field of wood restoration and conservation addressed in detail the analysis of the factors and mechanisms that produce the degradation, fragility, and even partial destruction of wood in heritage objects. They identify the problem and improve it, but do not establish a scale of these degradations, an index, or a percentage of the degradation. Following the critical analysis of the literature, three main objectives of the paper were identified. The first objective is to find some practical methods for assessing the degradation of the wooden support of the heritage object at the entrance to the restoration laboratory. The second objective is to evaluate the effectiveness of the wood reinforcement treatment, by the same methods specific to the first objective. The third objective is to develop a ranking of the level of wood degradation, simultaneously with the measures to consolidate the wood support for each level.

2. Materials and Methods

The experimental studies were carried out in the research and restoration laboratory ("Restaurare Ionescu", Sibiu, Romania), and the analyzed icons were 150–350 years old. Four new methods for wood degradation degrees have been developed:

- Determining the comparative density of healthy wood and degraded wood;
- Determination of excessive wood porosity caused by insect holes and galleries;
- Determination of Brinell hardness and comparison of the values obtained for healthy wood with degraded wood;
- Determination of hardness by means of the wood-pricking device, Mark 10, as a minimally destructive and alternative method.

Xylophagous insects, by the nature of the attack and the attacked wood species, can be classified as xylophagous insects that feed and grow on single wood and xylomycetophagous insects that grow in symbiosis with fungi. For many types of insects, which cause wood degradation, the action develops symbiotically (Figure 4) and is constantly preceded by the development of fungi [4].

(**a**) (**b**) (**c**)

Figure 4. Degradation of the wood support; (**a**) fungal attack (*Serpula lacrymas*); (**b**) symbiotic attack; (**c**) xylophagous attack.

2.1. Determination of the Degree of Fragility by the Method of Comparative Densities

This method is intended to obtain an answer for the differences in mass (density) between the two panels (healthy and degraded), considering that the initial density of the degraded panel is the same as that of new, healthy wood specimens without defects and degradations of the same species. The density method determines the total density difference between the panels at the same percentage of wood moisture (degraded and the new reference). Moisture content measurement was performed with Gann HT65 Humidifier with M20 hammer (GANN Mess. Regeltechnik GmbH, Nürnberg, Germany), measuring range 4–60%, analytical balance, EWJ 600–2M Kern (Merck KGaA, Darmstadt, Germany), with an accuracy of 0.01 g. For this study, 5 icons on linden wood (*Tillia cordata* Mill.) degraded by intense and medium xylophagous attack (visible on the outside) were considered from the laboratory. Because we did not want to intervene in the moisture content of the wood panel, the following density transformation ratio was used at a certain moisture content (under fiber saturation point) to another one (Equation (1)):

$$\rho_{MC2} = \rho_{MC1} \frac{1 + MC_2}{1 + MC_1 + (MC_2 + MC_1) \cdot \rho_{MC1}} \left[\mathrm{kg/m^3}\right] \quad (1)$$

where: ρ_{MC2}—density at moisture content MC_2, in $\mathrm{kg/m^3}$; ρ_{MC1}—density at moisture content MC_1, in $\mathrm{kg/m^3}$; MC_2—Moisture content tip 2, in %; MC_1—Moisture content tip 1, in %.

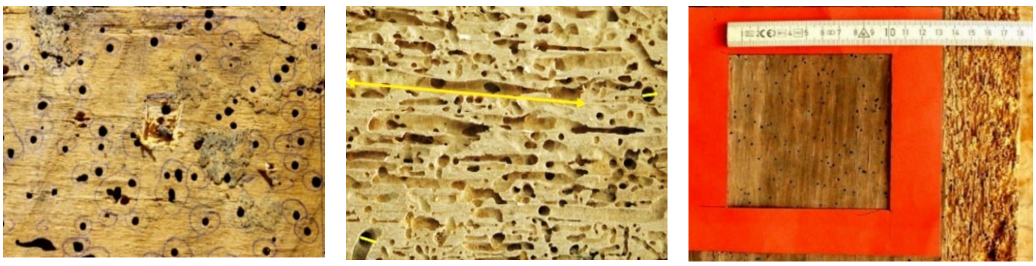
The density of lime wood introduced into heritage objects 200 years ago is not precisely known and depends on the vegetation conditions of the tree and other biotic and abiotic factors. As there are no precise methods for evaluating it, it was considered the equivalence-approximation of density with that of the existing species (lime) to the required moisture content. Beyond these limitations, the assessment is within ±5% of current statistical analyzes. New 50 × 50 mm specimens, made of healthy wood, of the same essence, with the same thickness, conditioned at a moisture content of 6% or 8%, depending on the moisture content of the analyzed icon, were used for the sharing. The density of the degraded panel was determined, as a ratio between the mass and the degraded volume, obtaining the value of 290.69 kg/m^3. For comparison, several rulers of timber of the same species were taken, brimstone linden, brought to the same moisture of 6% by conditioning, from which were cut 6 specimens with dimensions of 20 × 20 × 30 mm, at which the density was determined as the ratio between their mass and volume (EN 323: 1993). The determination of the degree of degradation-fragility by the density method is based on determining the density of the degraded wood support and the density of the original wood support, the non-degraded one, respectively, using the following relationship (Equation (2)):

$$G_{f\rho} = \frac{\rho_i - \rho_d}{\rho_i} \cdot 100\ [\%] \quad (2)$$

where: $G_{f\rho}$—the degree of fragility-degradation by the density method, when the panels have the same moisture, in %; ρ_i—the density of the healthy wood specimen, at the same moisture, expressed in kg/m^3; ρ_d—density of degraded wood specimens, at the same moisture content, expressed in kg/m^3.

2.2. Determination of the Degree of Degradation by the Method of Excessive Porosity Caused by Xylophagous Attack

The excessive porosity of heritage objects is determined by the attack of wood-decaying insects inside the wood, causing holes and larval galleries, especially by the group of insects *Anobiidae*. The holes visible in the wood surface are multiplied inwards compared to the surface holes several times (Figure 5). Initially, an area of the outer surface was colored black and there was a color difference between the areas with holes and those without holes. The two surfaces were determined by color scanning. Then, the outer part was excavated on the same surface, revealing the holes and inner galleries, much more complex than those on the surface. The surface was dyed black, with darker and lighter areas appearing. The area of the two areas was determined by scanning. The ratio between the two surfaces was made, obtaining the coefficient of 3.89 for the 5 different surfaces taken into account. This value was used for all icons.



(**a**) (**b**) (**c**)

Figure 5. Insect holes and galleries: (**a**) at surface; (**b**) at interior; (**c**) comparative.

In the literature, this porosity is expressed as the number of holes per dm^2 [4], with current values of 40–200 holes/dm^2. Taking into account the volume/surface lost through these holes in the volume/surface of the clean wood, it is possible to quantify how much a consolidant solution is needed to restore the mechanical strength and hardness of the restored object. The principle of the method consists in observing a small perimeter, in shape and size, usually a square with a side of 100 mm (Figure 6) in order to analyze it. The flight holes are counted for at least 5 attacked areas. The average number of holes/dm^2 is multiplied by the area in dm^2 of a hole, depending on the average diameter of the holes. Diameters had to be measured at two perpendicular diameters for each hole and the average value was the reference.

Figure 6. Marking and counting of flight holes per dm^2.

The known number of flight holes is determined on this known surface, but also their average diameter is determined. In general, the intensity of the degradation is determined as the ratio between the area of the insect holes and the area taken into account (Equation (3)):

$$G_{fs} = \frac{k \cdot n \cdot \pi \cdot d^2}{4 \cdot A_{fh}} \cdot 100 \ [\%] \quad (3)$$

where: G_{fs}—degree of fragility-surface degradation as intensity of flight holes, in %; k—multiplication coefficient of the core holes, equal with 3.89; n—the number of flight holes on the entire analyzed surface; d—average diameter of flight holes, in mm; A_{fh}—the plane area of the surface that is taken into account, in mm^2.

In the conditions in which the number of holes per dm^2 was previously determined, the relation (4) was transformed into a simpler one, respectively:

$$G_{fs} = \frac{3.89 \cdot n_d \cdot \pi \cdot d^2}{400} \ [\%] \quad (4)$$

where: n_d—number of holes per dm^2.

The procedure was applied to 5 icons in the laboratory, each analyzing 5 distinct areas.

2.3. Determination of the Degree of Fragility by the Brinell Hardness Method

The degradation and fragility of wood are not uniform and can be on the surface, interior, or combined for the entire wooden support of the heritage object. Thus, one method of assessing the degradation of the wood surface is to compare the hardness of the degraded wood with that of the original wood introduced in the heritage object (equivalent to that of the wood species identified in the restored heritage object). If the Brinell hardness (Hardness Brinell) is noted with HB, the degree of degradation-fragility (expressed as a percentage loss of wood hardness) will be determined by the following relation (Equation (5)):

$$G_{fHB} = \frac{HB_i - HB_d}{HB_i} \cdot 100 \ [\%] \quad (5)$$

where: G_{fHB}—degree of fragility by Brinell hardness method, in%; HB_i—initial Brinell hardness, in N/mm^2; HB_d—Brinell hardness of the panel damaged, in N/mm^2.

The purpose of Brinell hardness method is to determine the strength of the wood surface. Brinell hardness can be interpreted as the property of wood to resist the penetration of a 10 mm diameter penetrator (Figure 7), under the action of a constant force. The force tends to change its surface (EN 1534-2003) [43]. As the determination could not be made directly on icon surfaces because of the risk of their destruction, the research was organized in two directions. In the case of the first direction, more than 60 healthy specimens of lime and balsa wood were used, with or without Paraloid B72 consolidator, with a concentration of 10% in ethyl acetate and toluene 1:1, in order to determine the effectiveness of the treatment on new or degraded wood. In the second research direction, 30 pieces of 50 × 50 mm lime specimens with various degradations were used. These specimens were treated or untreated with 10% B72, being taken from old, abandoned panels, recovered, and kept in the laboratory archives. In this way, the degrees of fragility-degradation of the analyzed specimens were determined.

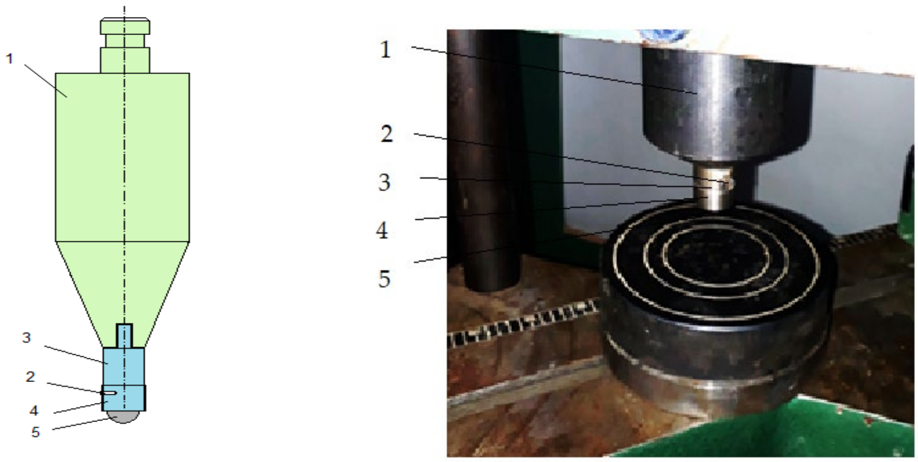


Figure 7. Brinell hardness tester: 1—device body; 2—threaded pin; 3—additional punch; 4—bushing; 5—metal ball.

The Brinell hardness calculation relationship was as follows (Equation (6)):

$$HB = \frac{2 \cdot F}{\pi \cdot D(D - \sqrt{D^2 - d^2})} \left[\frac{N}{mm^2}\right] \quad (6)$$

where: HB—Brinell hardness, in N/mm^2; F—pressure force, 100 N; D—diameter of the tip penetrator Ø10, in mm; d—the diameter of the imprint left on the wood, in mm.

For this research, a special stand with a magnifying glass of 5x magnification was used in the Brinell tests, and a copying indigo sheet was inserted between the penetrator and the test ball to highlight the diameters.

In order to compare, hardness determinations were performed for healthy new wood specimens for which consolidation treatment was applied with Paraloid B72, having a concentration of 10% in ethyl acetate, by immersion for one hour, for lime species and balsa (as a complement-consolidation wood).

The following formula was used to calculate the effectiveness of the hardening reinforcement treatment (Equation (7)):

$$E_{HB} = \frac{HB_{B72} - HB_i}{HB_i} \cdot 100\ [\%] \quad (7)$$

where: E_{HB}—hardness efficiency after consolidation treatment, in %; HB_{B72}—hardness after consolidation with Paraloid B72; HB_i—initial Brinell hardness, before treatment.

2.4. Determination of Mark Hardness as a Minimally Invasive Method

The hardness test, with the Mark 10 dynamometer equipped with a pressing-extraction device (Mark-10 Corporation, Copiague, NY, USA), is based on the penetration into the wood of a thin cylindrical-conical tip with a diameter of 1.34 mm and a length of 6 mm (consisting of a conical area of 2 mm and a cylindrical area of 4 mm), with a pressing force indicated on the digital screen of the dynamometer, expressed in [N]. The principle of operation of the device is based on the stinging of the wood and the determination of the opposite force of the wood when the needle penetrates inside it. The Mark-10 digital camera (type M3-200) measures forces in N, in a range of 0–1000 N. The Mark 10 M3-200 series dynamometer and the S10 fixing-testing stand are manufactured by Mark-10 Corporation. For these tests, the 5 icons used in the first two methods (of excessive density and porosity) were used. A total of 5 areas with different degradations were chosen for each icon. As materials for comparative testing, the same specimens that were previously tested with the Brinell stand were used, and the determination of HM (Hardness Mark) was performed in the vicinity of the Brinell test. The total lateral area of the penetrator tip was calculated as the sum of the lateral areas of the two geometric bodies (cylinder and cone), obtaining the value of the total lateral area of the penetrator of 21.28 mm^2. Based on this area, Mark hardness was determined with the following relationship (Equation (8)):

$$HM = \frac{F}{A_{lt}} = \frac{F}{21.28} \qquad \left[\frac{N}{mm^2}\right] \tag{8}$$

where: HM—Mark hardness, in N/mm^2; F—Force read on dynamometer Mark 10, in N; A_{lt}—the total lateral surface of the tip penetrator; 21.28—lateral contact area between wood and the tip of the penetrator, in mm^2.

The degree of fragility by the Mark hardness method was determined by the following relationship (Equation (9)):

$$G_{fHM} = \frac{HM_i - HM_d}{HM_i} \cdot 100\ [\%] \tag{9}$$

where: G_{fHM}—degree of embrittlement obtained with the Mark hardness method, in %; HM_d—Mark hardness of degraded wood, in N/mm^2; HM_i—initial Mark hardness of new and healthy wood (reference), in N/mm^2.

Since the reporting area is a constant (21.28 mm^2), the embrittlement-degradation formula can be simplified, taking into account only the compression force, respectively (Equation (10)):

$$G_{fFM} = \frac{FM_i - FM_d}{FM_i} \cdot 100\ [\%] \tag{10}$$

where: G_{fFM}—degree of embrittlement obtained with the method of Mark force, in %; FM_d—Mark force of degraded wood, in N; FM_i—Mark force of initial new and healthy wood (reference), in N.

3. Results

3.1. Density Method Results

The degree of fragility by the density method (Gfρ) was determined for five examples of icons in the laboratory. The analyses of the results were performed separately for each icon, according to the European standard EN 17121 [44]. For example, the initial data of the icon were first recorded (example 1), at the entrance to the restoration laboratory, which was the following: mass of the panel degraded before restoration of 791 g and 818 g after the evaluation of the losses from the panel of 3.3%, the external dimensions 280 × 335 × 30 mm (V = 0.002814 m^3), the moisture content of 6% and the wood species linden (*Tilia cordata* Mill.) was obtained [45]. An average density of 509.8 kg/m^3 was obtained (Table 1). Using the formula (Equation (2)), applying the values of a new panel and for the degraded panel to 6% moisture content, total degradation of 42.97% was obtained. This degradation-fragility coefficient contained all wood losses, whether they are due to wood-decaying insects, wood-decaying fungi, fungal attach, or other physical damages.

Table 1. Degree of degradation-fragility obtained by the density method.

Icon	Initial Mass, g	Loss of Wood, %	Reconstituted Mass, g	Panel Dimensions, mm	Icon Density, kg/m^3	New Wood Density, kg/m^3	Loss of Density, %
1	791	3.3	818	280 × 335 × 30	290.69	509.8	42.97
2	1243	2.1	1270	415 × 345 × 28	316.7	509.8	37.87
3	1380	0	1380	415 × 345 × 28	344.3	509.8	32.46
4	9494	1.2	9610	970 × 730 × 34	399.1	514.4	22.41
5	5135	0	5135	780 × 630 × 24	435.4	514.4	15.35

The degree of fragility by the density method (Gfρ) was determined for five examples of icons, and they are recorded in Table 1, where all the values for the presented examples are highlighted.

Further analysis of the values was made and correlated with the visual aspect of the heritage objects, and classification was found from the point of view of the degrees of degradation-fragility in three categories: 15–25%—weak degradations, 25–35% medium degradation, and 35–45% as severe degradation.

3.2. Results of Xylophagous Insect Attack

The results obtained in the case of the attack of xylophagous insects were centralized in Table 2. The analysis was done for the same five icons used in the case of the density method, evaluating their back, without pictorial support. For example, for the number 1 icon, the analyzed surfaces had dimensions of 172 × 100 mm. An average number of 346 insect holes was obtained on the total surface and a specific one of 201 holes/dm^2. The diameter of the flight holes was between 1.4–2.6 mm, with an average value of 2.03 mm. Introducing in relation (5) a degree of fragility-degradation of 25.2% was obtained.

Table 2. Degree of fragility-degradation by the method of excessive porosity given by insect holes.

Icon	Planar Dimensions, mm	Total Number of Holes	Average Diameter, mm	Number of Holes/dm^2	Fragility, %
1	172 × 100	346	2.03	201	25.2
2	80 × 100	122	1.92	152	17.1
3	180 × 150	390	2.11	144	19.5
4	100 × 35	46	1.91	131	14.5
5	170 × 125	252	1.84	118	12.1

Based on the results obtained during the research of the five types of icons, but also on the mathematical modeling of the relation (4), the graph from Figure 8 was obtained. A slight increase in degradation was observed with an increase in the number of holes and an increase in the average diameter of the holes.

In practice, in real situations, these galleries can never be completely emptied of the sawdust inside them, so the degradation is not fully estimated, in fact, there are differences in mass and mechanical strength [4]. This explained the small amount of consolidant used during consolidation research, by about 10% less than the theoretical evaluations of consolidator Paraloid B72.

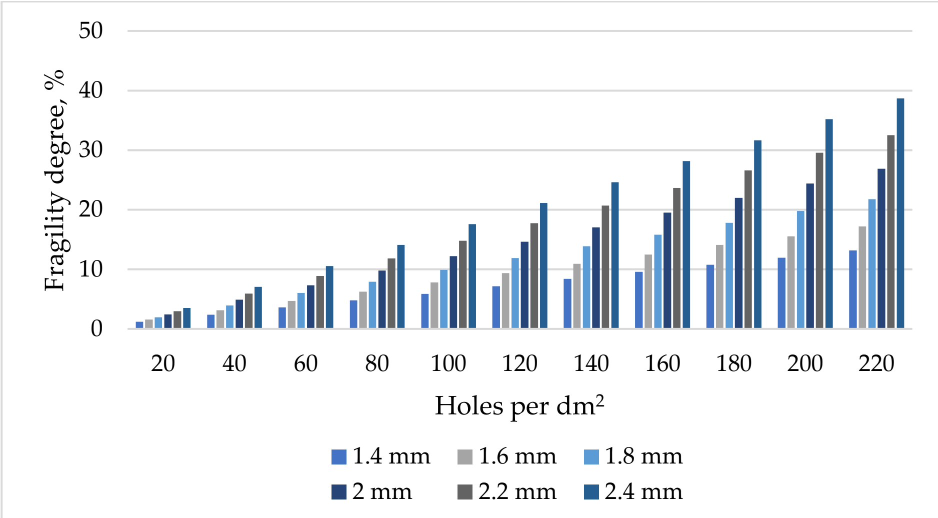


Figure 8. Fragility-degradation degree caused by xylophagous insects.

3.3. Results of Brinell Methods

In the first part of the research, namely that of establishing the effectiveness of the chemical consolidation treatment, the next Brinell hardness values were obtained: 17–22 N/mm^2 (with an average of 20.2 N/mm^2) on tangential surfaces in the case of untreated *Tilia cordata* and of 1.3–2.2 N/mm^2 (with an average of 1.8 N/mm^2) on the same radial-tangential surfaces in the case of *Ochroma pyramidale* (one of the usual species used in restoration works to complete the fragmentary losses, due to its very low density). The faces of the new wood were tangential, the direction of action of the forces being the radial one. The two species used in the research (balsa and lime) are frequently used in restoration. Analyzing the lime and balsa wood specimens, it can be seen that the new wood specimens that were treated with Paraloid B72 (the consolidation retention was about 3%, by dry mass), had an increased efficiency of Brinell hardness by 5.23% for lime and 7.22% for balsa. The growths are modest, which is why the treatment with the consolidant for new wood introduced in the heritage objects is not recommended. In the same way, the hardness of the wood degraded by xylophagous insects was determined, for the two types of specimens, respectively, degraded wood without treatment and with consolidation treatment with Paraloid B72 10%, for *Tillia cordata*. There were obtained the following values:

- 17–24 N/mm^2 (with an average of 21.5 N/mm^2) for new *Tillia cordata* wood;
- 15.1–18.7 N/mm^2 (with an average of 17.2 N/mm^2) for slightly degraded and untreated lime;
- 16.9–19.3 N/mm^2 (with an average of 18.3 N/mm^2) for lime treated with B72 10% in case of light xylophagous degradation;
- 10.8–15.2 N/mm^2 (with an average of 12.9 N/mm^2) for medium and untreated degraded lime;
- 12.5–17.5 N/mm^2 (with an average of 15.9 N/mm^2) for lime treated for an average degradation;
- 4.1–9.2 N/mm^2 (with an average of 6.4 N/mm^2) for strongly degraded and untreated lime;
- 7.7–13.1 N/mm^2 (with an average of 10.2 N/mm^2) for high xylophagous degradation and B72 treatment.

Analyzing the values in Figure 9, it is found that the slightly damaged wood had an improvement-efficiency of the hardness of 6.18% for medium degraded lime, then an increase in hardness by 23.33% for medium degraded lime wood, and in the case of highly degraded wood, the improvement was 60.46%. Even if this value (60.46%) seems very high, in fact, the Brinell hardness value of the very damaged wood increases from 6.40 N/mm^2 to 10.27 N/mm^2, but still does not reach the value of the average wood degraded before the treatment with B72. The Pearson coefficient of determination with values above 0.97 shows that the linear distribution of values best characterizes the modeling of values.

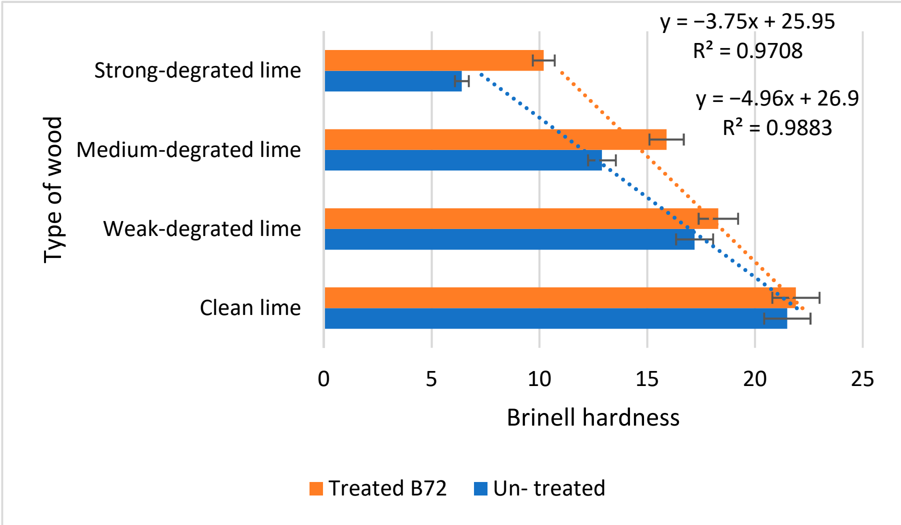


Figure 9. Brinell hardness of new and old degraded lime specimens, treated and untreated B72.

The degree of fragility-degradation in the case of Brinell hardness, determined with Equation (6), for slightly degraded lime wood was 20% for no-treated samples and 14.8% for lime treated with B72. In the case of medium-degraded specimens, the degree of fragility-degradation was 40% when the specimens were not treated and 26% when the specimens had B72 consolidation treatment. In highly degraded specimens, the degree of fragility-degradation was 70.2% when the specimens were not treated and 52.5% when treated with B72. In conclusion, the degradation-fragility values were identified by the Brinell method as 15–25% in case of light degradations, 30–45% in case of medium degradations, and 60–80% in case of strong degradations. Consolidated treatment reduced this degree of fragility by 26% in the case of light degradation, 35% in the case of medium degradations, and 25.2% in the case of strong degradations.

3.4. Mark Hardness Results

The results regarding the degree of fragility-degradation of the wood in the icons in the case of the Mark hardness were extended in two directions, respectively, for the degraded pieces of wood existing in the laboratory (at which the Brinell hardness was determined, for comparison) and for the five icons, which were analyzed in the first two methods. It was determined in both directions, Mark force as well as its corresponding strength, Mark hardness.

For the first part of the results, the obtained values are visible in Figure 10. This figure shows the Mark penetration force for both degraded and ungraded linden, in a probability plot statistical diagram. A degree of fragility-degradation was found, obtained with the relationship (11), of 74.1%, within the area of extended degradations, both the framing of the values between the limits on the graph, as well as two of the statistical parameters of the diagram, respectively, Anderson–Darling and *p*-value show the normality of the values in the 95% confidence interval. If the two values of the standard deviation and the 95% confidence interval are taken into account, the force variation intervals for the degraded lime and freshly clean lime of 153.5–242.7 N and 27.8–74.7 N, respectively, are found by calculation. These intervals are also found on the chart in its central area, for 50% values.

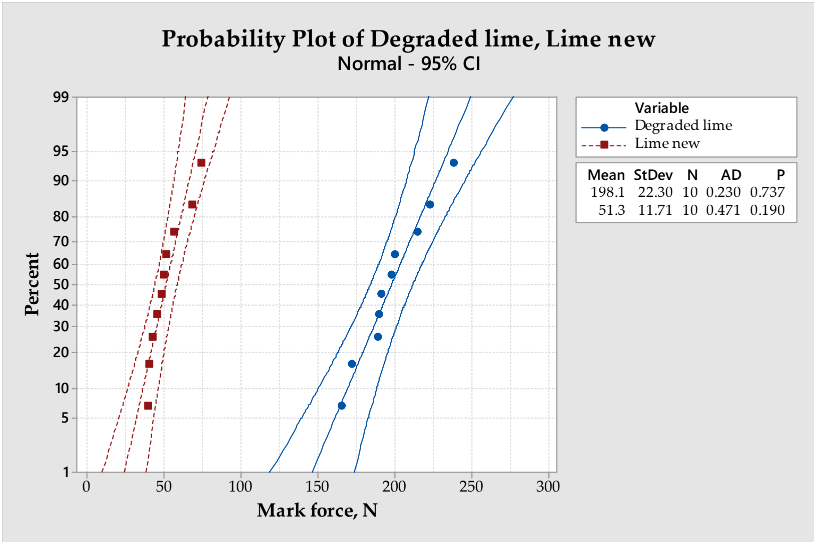


Figure 10. Pressure force obtained with the Mark10 dynamometer.

The results obtained in the second part of the research, respectively, based on the five analyzed icons, are visible in Table 3. In the example for icon 1, an area with medium and extended degradation was chosen on the back of the icons, obtaining a force of 73 N and 21 N, and a Mark hardness of 3.43 N/mm^2 and 0.98 N/mm^2. For comparison, healthy/new lime was used, without defects, on which measurements were made with the Mark 10 dynamometer, obtaining an average force of 205 N, respectively, a Mark hardness of 9.63 N/mm^2. Using the Formulas (10) and (11) a degree of fragility was determined of 64.38% for the area with medium degradation and 89.8% for the area with extended degradation.

Table 3. Degree of fragility with the Mark hardness method.

Icon	1		2		3		4	5	
Xylophagous Evaluation	**Avg. ***	**Ext. ****	**Avg.**	**Ext.**	**Ext.**	**Ext.**	**Ext.**	**Avg.**	**Low**
Force, N	73	21	79	36	36	25	36	84	127
Mark hardness, N/mm^2	3.43	0.98	3.71	1.69	1.69	1.17	1.69	3.94	5.96
Fragility degree, %	64.38	89.8	61.47	82.45	82.45	87.85	82.45	59.08	38.1

* Avg.—Average xylophagous damage; ** Ext.—Extend xylophagous damage; Low—low xylophagous damage.

Figure 11 shows a statistical graph made with the program Minitab 18, respectively, Empirical Cumulative Distribution Function (eCDF), which shows the curves in the form of “S” for clean lime, untreated degraded lime, and degraded lime—treated with B72. It is observed that the curve for degraded and treated lime has a more inclined curve, respectively, a larger variation (3.6–14.4 N/mm^2) than the other two (0.4–6.4 N/mm^2, 15.9–19.5 N/mm^2), this inclination gives the standard deviation of 2.7 N/mm^2, much higher than the other two groups of values of 1.5 N/mm^2 and 0.9 N/mm^2, respectively.

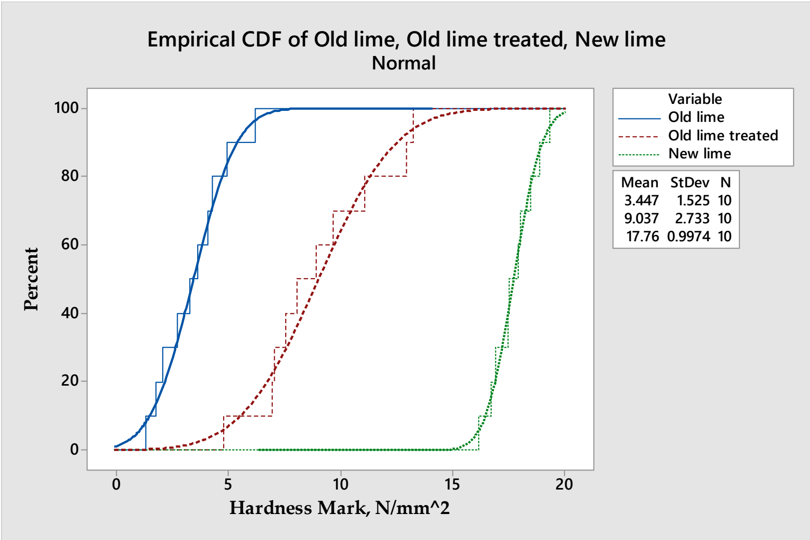


Figure 11. Mark hardness of 3 types of lime wood.

4. Discussion

Discussions about methods. In order to determine the destructive level of the methods that determine the hardness of the wood, the different areas of the imprint left by the penetrator were compared: for example, for the Janka hardness, it is found that the imprint left measures 100 mm^2, maximum 78 mm^2 for Brinell hardness, and at the Mark method the footprint is only 1.41 mm^2. Although all three methods can be considered destructive, it is still found that the footprint left by the penetrator adapted for the Mark dynamometer is very small and compared to Brinell is 98.19% smaller. The footprint of the Mark 10 penetrator is even smaller than that of an insect hole (Figure 12).

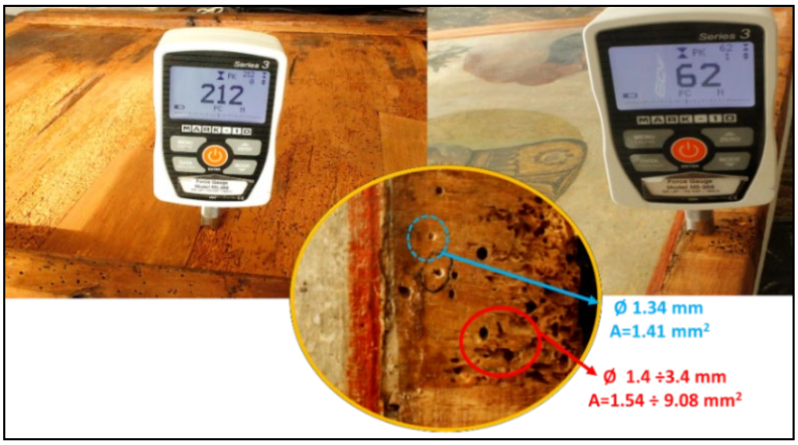


Figure 12. Comparison of the trace of the measuring tip with the flight hole caused by xylophagous insects: Mark 10 tip, Ø 1.34 mm A = 1.41 mm^2, flight hole, Ø 1.4–3.4 mm, A = 1.54–9.08 mm^2.

As Figure 10 shows, in most cases, the wood in the cultural goods is so degraded that, by pressing a force of even 20–80 N, the wood changes its flatness. For a force considered the minimum in the case of the Brinell hardness measurement of 100 N an imprint area eight times larger and a force ten times larger is used, causing deep damage, at least in the same ratio. As some of the recent studies stated [9,26,44] the strength of degraded wood must be evaluated. Even a 3D evaluation [21,23,35] should be performed, and Paraloid B72 is one of the best consolidators that can be used for wood strengthening in the restoration process [18,20] besides natural materials [22].

During the HB hardness determinations, for the degraded wood specimen, the values were measured at 100 N, and at the test of a force of 150 N, the wood split, not in the direction of the pressing force, but the sectioning occurred perpendicular to the direction of the pressing force; the minimal cohesion and strength between the anatomical elements of the wood gave way, producing the splitting of the specimen. If these measurements would take place for a cultural good, it would have resulted in its irreversible destruction [29].

Analyzing the average values between Brinell and Mark hardness, it is found that the ratios between the two methods of measuring hardness are below 1 N/mm^2, resulting in an overall average percentage difference of about ±3.34%. It can be seen that the least destructive method can be used, at least, to determine the hardness directly on the back of heritage assets, which have wooden support, especially when they are in different levels of degradation. Values of 17.2 N/mm^2 and 16.8 N/mm^2 were found in HB and HM for healthy lime, 4.6 and 4.7 N/mm^2 for highly degraded lime, 1.47 and 2.03 N/mm^2 for balsa wood, 9.66 and 10.64 N/mm^2 for old lime with B72 treatment and of 1.79 and 2.5 N/mm^2 for B72 treated balsa wood.

Using the formula for determining the Mark hardness [10,11], a degree of fragility was determined of 89.76% for the strongly degraded area, and 64.29% for the one with medium degradation; on the whole panel, the average degree of fragility was 77.02%, lower than a healthy wooden panel. For such a panel, whose hardness is reduced by 98.47% (on the most affected area, where HM = 1.97 N/mm^2) compared to a similar panel, made of healthy wood, there is the problem of the existence of the heritage object, whose support is extremely damaged. Such a value determines the time and level of the rescue intervention on the heritage object. When the Mark hardness was determined, a very degraded lime had a Mark hardness of 3.08 N/mm^2, compared to the healthy lime which had a Mark hardness of 10.39 N/mm^2, the ratio of these values being found in the case of Brinell hardness. The alternative to the Brinell hardness measurement, performed with the least destructive method MARK 10 starts from the premise that the degradation produced by the penetrator is very small.

Based on the values obtained with the Mark method, the lime degraded panel lost 81.18% of its hardness compared to a healthy panel; after the consolidation treatment, even if it produced an increase of 2.83 times compared to the strongly degraded panel, it can conclude that, in fact, the panel, after the treatment, improves in terms of hardness, only up to 46.59%, in relation with the reference panel.

It has been observed from Figure 13 that the weakening by the method of attack of xylophagous insects depends very much on the number of holes of xylophagous insects expressed per dm^2 [17], which is why the data from previous research have been centralized, obtaining a diagram that expresses the compression force related to flight holes. This diagram also has a linear regression equation, which best models the degradation phenomena, with a very good Pearson coefficient R^2 = 0.989, proving once again the dependence between the number of holes and the Mark hardness.

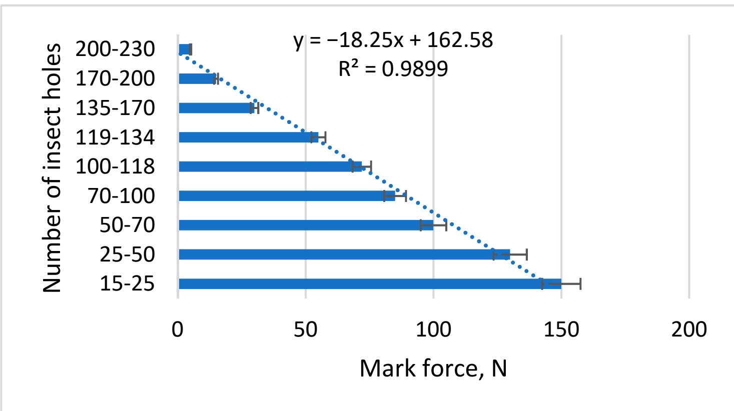


Figure 13. Influence of the number of holes on the Mark force stiffness.

When the intensity of the xylophagous attack exceeds 100 holes/dm^2, the wood becomes fragile [14,16,17] and the hardness is considerably reduced, the pressure of the penetrator falls below the average level, respectively, 70–80 N. As a general conclusion, it can be shown that if the number of holes flight increases, the hardness of Brinell and Mark decreases. Increasing the number of flight holes per dm^2 reduces the penetration resistance of the measuring tip. In this respect, a number of more than 60 flight holes/dm^2 reduces the puncture force to 110 N; at more than 100 holes/dm^2 the force decreases to 40 N, and at more than 220 holes/dm^2 the force is reduced below 10 N, the data refer to new, healthy and/or damaged linden wood.

The efficacy of Paraloid B72 treatment on medium degradation lime was analyzed from the point of view of the Brinell hardness method using ANOVA One-Way (Table 4), using null hypothesis, when all means are equal for a significance level alpha of 0.05. In this case, equal variances were assumed for the analysis. It is observed that the two values F-value and *p*-value correspond to significance assumed level alpha.

Table 4. Analysis of Variance (ANOVA) of Brinell Hardness for untreated and treated B72 medium-degraded lime.

Source	DF	Adj SS	Adj MS	F-Value	*p*-Value
Un-treated	9	0.8760	0.09733	*	*
Error	0	*	*		
Total	9	0.8760			

* These values are below 0.001.

On the same basis, by using the Minitab 18 statistical program, it found the interval plot of treated lime with Paraloid B72, comparative with un-treated lime, with medium degradation (Figure 14). There is a good correlation between the two groups of values when the confidence interval of the values is 95%, which shows once again the normality of the distribution of values.

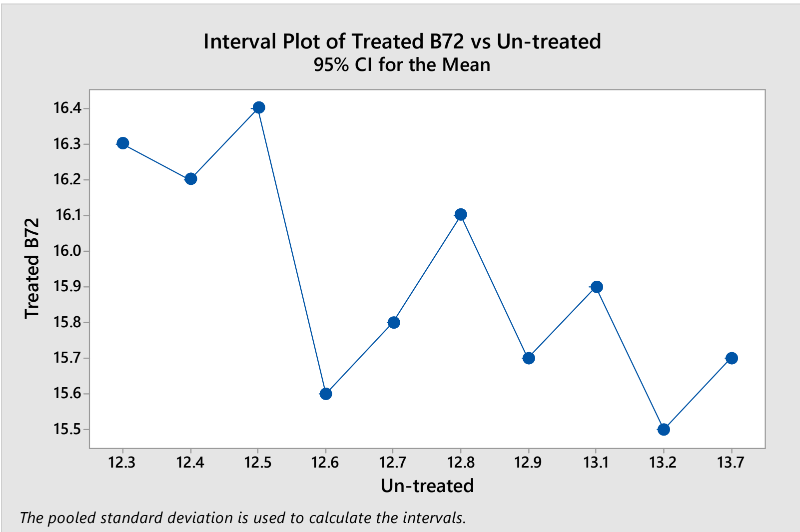


Figure 14. Interval plot of treated B72 vs. untreated medium-degraded lime values of Brinell hardness.

Establishing a hierarchy regarding the degree of degradation. According to the results obtained in this research, a differentiated ranking of the degradation level could be obtained. First of all, a visual instability was observed (visual method) with cracks, fissures, deformations, and gaps in the pictorial layer due to the successive swelling and contraction of the wooden panel in the icon. As other authors have noted before [3,7,30], simple visual inspection is not sufficient, requiring other methods of qualitative and quantitative quantification of degradation [41,42]. In this context, as was observed in the results, three degrees of fragility-degradation were obtained for all four methods. If it adds to these an incipient area in which the icon is not restored yet and a final one in which the heritage object can no longer be used, there were obtained the five levels of degradation-fragility of heritage objects (Table 5).

Table 5. Defining the degree and ranking level of degradation-fragility.

Degree	Level	Method	Fragility-Degradation Values	Icon Status
1.	Good	Density method, % Excessive porosity Number of holes/dm^2 Brinell hardness Hardness Mark	10–15 2–10 20–40 4–35 4–35	Acceptable. It is not being restored
2.	Weak	Density method, % Number of holes/dm^2 Excessive porosity Hardness Mark Brinell hardness	15.1–25 40.1–80 10.1–15 35–50 35.1–50	Worrying. Light restoration activities (surface consolidation treatments are needed)
3.	Average	Density method, % Number of holes/dm^2 Excessive porosity Hardness Mark Brinell hardness	25.1–35 80–160 15.1–20 36–50 50.1–65	Alarming. Medium restoration activities (surface and internal treatments are needed)
4.	Extended	Density method, % Number of holes/dm^2 Excessive porosity Brinell hardness Hardness Mark	35.1–45 160–200 20.1–25 65.1–80 51–60	Critical. Complex restoration activities, including replacement of wooden areas, are needed
5.	Exitus	Visual, all methods	Exceeding previous values	Unrecoverable icon. It is not being restored

A first observation obtained from Table 5 is that the two harnesses Brinell and Mark have very appropriate values for the first levels of degradation and quite appropriate for the following ones. A second observation is that there are different correlations of degradation levels between the four methods. Thus, there is a 5/1/2/2 ratio for the good level, 3/2/7/7 for the week level, 5/3/7/10 for the average level, and 7/4/13/10 for the extended level. These reports may amount to a certain method when there is no material possibility to carry it out effectively.

5. Conclusions

Each of the four simple and easy methods for assessing the degree of fragility-degradation has specific values and is characteristic of a certain type of degradation of the substrate. For example, the method of insect holes is specific to surface degradation, the density method is specific to the total evaluation of the wood support, the Brinell method for surface, and the Mark hardness method is specific to total complex degradation.

All four evaluation methods can be used both for the primary evaluation of the heritage object and also during the investigations and interventions of conservation and restoration of icons with wooden support.

The advantages of using the Mark 10 device are highlighted by the fact that the type of measurement is minimally invasive, and the hole left by the penetrating tip with a diameter of 1.34 mm is almost imperceptible (even smaller than a hole of wood-eating insects). Additionally, the operating time is short (a few seconds), the mobility of the device is higher with small dimensions, the device is portable, and the intervention has low costs.

The methods of assessing the fragility of wood panels are practical and concrete indicators for assessing their degradation and can indicate the nature and volume of consolidation materials that will be used in the time of restoration, but also the restoration techniques that will be put into practice.

In a general conclusion, it can be said that the use of these methods to determine the degree of fragility-degradation may be relevant in assessing the level of degradation or the effectiveness of the wood reinforcement treatment.

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