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# AN EXPERIMENTAL METHOD TO EVALUATE THE CONTRIBUTION OF WOOD SUBSTRATE AND COATING FILM TO THE LIGHT INDUCED COLOUR CHANGES OF WOOD SURFACES

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**Abstract:** The paper presents an original laboratory method developed to determine and compare the light-induced colour changes of uncoated and coated wood surfaces, while also allowing the highlighting and evaluation of the individual contributions of the substrate and coating film to the global effect. Two types of wood test samples: V1 (uncoated) and V2 (coated) and coating films on 1mm thick clear glass slides were employed. The behaviour of the wood substrate under the coating film was simulated on uncoated substrate covered with a coated glass slide. European maple (Acer pseudoplatanus L.) and two types of transparent water-based varnishes with 2k formulations were used. The samples were exposed for up to 72 hours to artificial UV-VIS light in accelerated tests simulating natural light passing through window glass. Colour changes were measured in the CIELab system, as well as the chemical changes of the wood substrate and the coating films by FTIR analysis. Exposure of uncoated maple wood resulted in a total colour difference ( $\Delta E$ ) of 10.83 units and this was only slightly reduced by coating (9.29-9.81 units). Exposure through the glass slide reduced the colour changes of the uncoated and coated wood surfaces by 37-43%. Colour changes of 5.79-6.85 units were measured on the wood substrate exposed under coated glass slides, whilst the colour changes of the coating films on glass slides were only 0.64-1.0 units, which indicates a maximum contribution of the wood substrate to the light-induced colour changes of the coated surfaces. FTIR investigation confirmed this finding.

*Key words:* wood, coatings, colour, CIELab, UV-VIS light exposure, colour changes, experimental method.

#### 1. Introduction

Both uncoated and coated wood surfaces change colour in time, even in

indoor conditions, due to the action of natural and artificial light [9, 34], which is a phenomenon that might have disturbing consequences for the consumers.

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Research has proven that the most aggressive causing factor is the UV radiation (UVA-UVB) of natural light [36] which can partially penetrate through the window glass [2, 11] or might be contained in the emission spectra of various artificial sources. Moreover, part of the visible light (in the violet and blue wavelengths domain) may also contribute to the colour changes of wood surfaces [20, 30, 41].

Both the wood substrate and the finishing film contribute to the light behaviour of transparently finished wood surfaces. Depending on their composition, the finishing films could have a protective effect by partially blocking or reflecting incident light radiation, especially the UV component, or on the contrary, they could contribute to the overall colour change by modifying their own colour [30].

Accordingly, various research approaches have been considered for stabilising the natural colour of wood surfaces. These included pre-treatments/ modification of the wood substrate to increase colour stability [6, 13, 21, 27, 35, 39], modification of the coating materials with different types of UV absorbers, radical scavengers [3-5] or both [33].

Colour measurements in the CIELab system have usually been employed for monitoring colour changes of wood surfaces [7, 10, 22, 25, 29, 31], while FTIR investigation was often the method chosen to analyse the chemical changes brought about by light exposure [24, 34, 36]. However, in most cases these investigations were carried out either on uncoated or coated wood samples, prior and after light exposure, so that the individual contributions of the substrate and of the coating film in the global colour change of the finished wood surfaces could not be determined [1, 28, 29]. At the same time, the FTIR investigation of the coated samples could reveal only the chemical changes of the coating film, but not the chemical changes of the wooden substrate under the transparent film [23, 25]. This was considered a limitation in understanding the occurring phenomena.

There are only a few experimental studies applying methods developed to assess individually the contributions of the wooden substrate and of the coating film to the colour changes of coated wood surfaces. For instance, Capobianco et al. [7] conducted a study on poplar wood exposed to artificial photodegradation, analysing colour and surface chemistry changes for the wood surfaces and the protective coatings. The experimental method used revealed that the coating materials employed (shellac, beeswax, Linfoil) demonstrated a very low protective effect on photodegradation over long periods of exposure. Chou et al. [8], used a light reflection model to evaluate separately the colour changes due to the clear coating film and the underlying wood [8].

In this context, an experimental method adequate for analysing the wood substrate, the coating films, and the finished surfaces from the point of view of colour and surface chemistry changes following light exposure would be important in order to highlight their individual contributions and to better understand the phenomena involved in the resulting global colour change, with a view to identifying and testing novel solutions for improving the light fastness of wood coated surfaces with natural aspect.

Development and testing of such a laboratory experimental method was in

fact the goal of the research presented in this paper. The proposed method should serve the following research objectives: (i) accelerated testing of light induced colour changes of wood surfaces in indoor conditions by exposure to UV-VIS radiation simulating natural light passing through the window glass; (ii) comparative evaluation of the light-induced colour changes for uncoated and coated wood surfaces; (iii) highlighting and evaluation of the individual contributions of the wood substrate and coating film to the global colour changes of finished wood surfaces; and (iv) investigation of the associated surface chemistry changes by FTIR.

# 2. Materials and Methods 2.1. Principle of the Method

From the envisaged objectives, the main challenge was to find a possibility to highlight and evaluate separately the contributions of the wood substrate and of the coating film to the global colour changes of the coated surfaces. For this purpose, it would have been necessary to detach the coating film from the substrate after light exposure for colour measurements and FTIR investigation and reapply it onto the substrate for further exposure. As this was not possible, the solution of a "detachable" coating film was solved by applying the coatings onto thin (1 mm thick) clear glass lamellae (microscope slides) which were then tightly fixed on the uncoated wood substrate. The influence of the clear glass support on the results was considered and evaluated for interpretation of results.

In order to address all the research objectives, two types of test samples, coded V1 (uncoated wood support –

Figure 1a) and V2 (coated wood support – Figure 1b), were designed and employed in this research. Both types of test samples contain more areas differentiated by their actual light exposure situation, including also a colour control area (V1/Z4, V2/Z2) tightly covered with black cardboard and aluminium foil to prevent penetration and the effect of light. Accordingly, it was possible to highlight and measure the light induced colour changes for the uncoated (V1/Z3) and coated wood surfaces (V2/Z1) directly exposed to light, as well as the colour changes when exposure to light was done under a clear glass lamella (areas V1/Z2, respectively V2/Z3), the colour changes of the wood substrate under the coating film (simulation V1/Z1, under coated glass lamella), and the coating films (applied on clear glass lamellae).

# 2.2. Wood Material and Coatings

European maple (*Acer pseudoplatanus* L.) wood was employed to verify the proposed method. It was selected considering its wide use for furniture, panelling, flooring, and other indoor applications, alongside its pale homogeneous natural colour, which was shown as highly sensitive to UV-VIS light [25, 37].

Two types of clear waterborne lacquers produced by Renner – Italy [17] were employed. These were an acrylicpolyurethane lacquer (YO-20-M702 laboratory code FB1) and a polyurethane lacquer (YO-20M838 – laboratory code FB3), prepared as two-component (2K) coatings with the addition of an isocyanate hardener (YCM 403) (Table 1)Error! Reference source not found..



Fig. 1. Test samples: a. V1- Uncoated wood support, coating on glass lamella: dimensions and various specific zones/light exposure situations (Z1-Z4); b. V2 - Coated wood support: dimensions and various specific zones/light exposure situations (Z1-Z3)

Water borne coating materials (2K) [14]

Lab.	Code	Film forming resin	Csu	Density	Isocyanate hardener
code	product	Thin torning resin	[%]	[g/cm³]	YCM 403 [%]
FB1	YO 20-M702	Acryl-polyurethane (non-yellowing)	25±1	1.02	5
FB3	YO 20-M838	Polyurethane	30±1	1.03	10

# 2.3. Preparation of Test Samples V1 (Uncoated Wood)

Glass microscope slides with dimensions of 76 x 26 x 1 (mm x mm x mm) from Distrimed LAB - Bucharest [14] were employed as support for the coating films. A special device and guiding support were employed to apply the clear coating as uniform 100  $\mu$ m thick liquid films onto the glass slides (Figure 2). The coating films were allowed to cure at room temperature for 4 h and then a second layer of 100 µm was applied. After a period of 24 h, the slides were carefully cleaned of any accidental spill and the

thickness of the dry coating film was measured employing HMB dial indicator with 3 decimals accuracy from Select Auto [15].

Table 1

The wood substrate was prepared as pieces of  $120 \times 80 \times 8$  (mm x mm x mm) on the L, Ra, Tg directions, respectively. The surfaces were planned and then manually sanded with grit sizes 100 and 120, prior to marking the limits of the areas Z1-Z4 on the edges with a pencil. The test samples V1, prepared for light exposure, resulted by assembling the corresponding uncoated wood pieces with coated and uncoated glass slides employing tight plastic rods (Figure 3).



Fig. 2. Application of the coating films of 100  $\mu$ m thickness onto clear glass slides: a. coating film application device; b. sketch 2d dimensions; c. introduction of liquid coating; d. application on the glass slide by moving from left to right



Fig. 3. Test sample V1 (uncoated wood) mounted for UV\_VIS exposure: Z1- area covered with coated glass lamella, Z2-area covered with clear glass lamella, Z3-uncovered area (directly exposed), Z4-area covered with black cardboard and aluminium foil

## 2.4. Preparation of Test Samples V2 (Coated Wood)

Clear glass slides and coated wood test pieces were employed for preparing the V2 test samples. Coating of the wood substrate was carried out by manual brushing. A constant amount of 1 ml liquid coating material was used for each sample, achieving an application rate of about 106-110 g/m<sup>2</sup>, respectively a liquid coating film of about 100  $\mu$ m, similarly to the glass slides prepared for the test pieces V1. After 4 h drying at room temperature and sanding with 240 grit size, a second coat of 106-110  $g/m^2$  was applied.

Four replicates were prepared for each coating material: three were assembled as V2 test pieces and exposed to light and one remained as a reference and was not exposed (Figure 4).



Fig. 4. Test sample V2 (Coated wood) mounted for UV\_VIS exposure: Z1- uncovered area (directly exposed), Z2- area covered with cardboard and aluminium, Z3-area covered with glass lamella

#### 2.5. Light exposure

A Feutron FKS 400 environmental climatic chamber, equipped with an ultraviolet radiation source UV-A Spot 400A, covered with an H2 glass filter to cut off UV radiation below 295 nm, was employed to simulate the natural light passing through the window glass. Accordingly, exposure was done to artificial light containing UV-B, UV-A, and VIS radiations with wavelengths between 295-600 nm, as detailed in a previous publication [38]. However, it is important to acknowledge that UV radiation is the main factor causing colour and surface chemistry changes of wood and coatings [12, 28, 36], while visible light in the violet and blue range of wavelengths (up to 496 nm) may contribute to the colour changes

of wood substrate [20], especially for naturally coloured species with a high content of extractives [6, 32, 33, 40]. Accordingly, it seems appropriate to use the term exposure to light/UV radiation within this paper for the experimental situations in the presented research.

The test samples were placed on a rack which was introduced in the climatic chamber (Figure 5). Exposure to light was achieved in cycles of 24 h with several steps, described in Table 2. Cycles of 24 h UV exposure are in accordance with ISO 16474-3 [18] exposure method B: daylight behind window glass. This stepwise cycle was repeated three times to ensure exposure to light for 24, 48, and 72 h, coded 24\_UV, 48\_UV, and 72\_UV.

Steps	Temperature [°C]	RH [%]	UV radiaton	Holding time [h]
1	20	55	OFF	0.5
2	40	-	ON	6
3	20	55	OFF	0.5
4	40	-	ON	6
5	20	55	OFF	0.5
6	40	-	ON	6
7	20	55	OFF	0.5
8	40	-	ON	6
9	20	55	OFF	12

Stages of UV exposure program for one exposure cycle of 24 h Table 2

Total duration of UV exposure at 40°C: 24h; Final conditioning 12h; Total duration of 1 cycle: 38h.



Fig. 5. Experimental test samples on the exposure: a. rack, and b. method of exposure-2D sketch with climate chamber dimensions - made in AutoCAD 2023

Considering the possible differences in the actual exposure of the samples depending on the distance from the lamp source, three zones of exposure were defined and the samples were moved after each exposure cycle of 24 h, so that each of them passed through all three exposure zones to finally reach a similar total light irradiation dose.

#### 2.6. Colour Measurements

Colour measurements in the CIELab reference system were made with an AVA Spec USB 2 spectrometer by Avantes [16]. The equipment was equipped with an integration AvaSphere with a diameter of 80 mm and a circular measurement aperture of 8 mm in diameter. The measurements were made according to ISO 4582 [19], with a standard D65

illuminant and measurement angle set to 10 degrees.

AvaSoft 7.0 colour measurement was software employed for data collection. The measured colour parameters were: lightness value  $(L^*)$ varying from 0 for black to 100 for white, degree of red (redness) on the green-red chromatic axis ( $-a^*$ ,  $+a^*$ ), and degree of yellow (yellowness) on the blue-yellow colour axis (-b\*, +b\*). Colour measurements were done on 12 fixed points (actually circular areas of 8 mm in diameter) on each wood sample (uncoated or coated) and on three fixed points for the coated glass lamellae, prior to assembling the wood specimens with the glass lamellae. After each period of light exposure, the samples were disassembled and colour measurements repeated in the same areas on the wood substrate and the coated lamellae. Measurements were made on three fixed points on each exposure zone (Z1-Z4/V1 and Z2-Z3/V2) of the test samples, which were in triplicates, resulting minimum nine measurements to be averaged for each zone/exposure situation. One exception was the zone Z1/V2 with six measuring points and a total of 18 measurements included in the average.

All colour data were collected and further processed in Excel to calculate the light induced variation of the colour parameters ( $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$ ) and the total (global) colour difference ( $\Delta E$ ) according to Equations (1)-(4):

$$\Delta L^* = Le^* - Li^*$$
 (1)

$$\Delta a^* = a e^* - a i^* \qquad (2)$$

$$\Delta b^* = b_e^* - b_i^* \tag{3}$$

$$\Delta E^{*} = \sqrt{[(\Delta L^{*})^{2} + (\Delta a^{*})^{2} + (\Delta b^{*})^{2}]} \quad (4)$$

where:

- L\* is the lightness;
- a\* the degree of red/green on a scale
  with positive values for red and
  negative values for green;
- b\* the degree of yellow/blue on a scalewith positive values for yellow andnegative values for blue;
- "e" and "i" as indexes indicate the values for the light exposed samples and the initial values before light exposure, respectively.

Reproducible measurements in the same areas were considered essential due to the high colour variability of most wood surfaces, depending on the wood species and reflecting characteristic structural features, such as latewood, earlywood, sapwood-heartwood, by case.

Accordingly, an adjustable device (Figure 6a) was designed and used to perform measurements in fixed areas according to the corresponding templates for wood substrates (Figure 6b) and glass lamellae (Figure 6c), before and after each cycle of 24 h light exposure (24, 48, 72 h).



Fig. 6. Adjustable device for repetitive colour measurements (a.); measuring points for wood substrate (b.); measuring points for coated glass slide (c.)

#### 2.7. FT-IR Investigation

FTIR spectra in the range 4000-400 cm<sup>-1</sup> at a resolution of 4 cm <sup>-1</sup> and 24 scans per spectrum were registered with a FTIR spectrometer ALPHA BRUKER, equipped with an ATR (attenuated total reflection) module.

FTIR spectra were recorded for uncoated and coated maple samples in the different zones before (Figure 7a) and after each cycle of 24 h light/UV exposure. The spectra were recorded directly on the surface of the coated wood samples (V2), while thin chips were extracted with a sharp blade from the surface of the uncoated wood samples covered with coated glass slides (Figure 7b) with three types of lacquers: acrylic-polyurethane (area Z1-FB1), acrylic (area Z2-FB2), polyurethane (area Z3-FB3) and uncoated glass (area Z4-S) for FTIR analysis (Figure 7c). The spectra of the coating films applied on the glass slides were also recorded before and after each cycle of 24 h UV exposure. Minimum three spectra were recorded for each situation and average spectra were then computed employing the OPUS 7.2 software. The normalised (min-max normalisation) average spectra registered before and after light/UV exposure were compared in order to highlight the associated chemical.



Fig. 7. Extraction of thin chips from the uncoated wood sample (V1) Z1-Z4 for FTIR investigation: a. test sample mounted before UV exposure; b. test sample disassembled after UV exposure (Z1-SFB1-area covered with acrylic-polyurethane coated glass slide; Z2-SFB2-area covered with acrylic coated glass slide; Z3-SFB3-area covered with polyurethane coated glass slide); c. FTIR investigation of the thin chips to reveal surface chemistry changes

# 3. Results and Discussion 3.1. Colour Changes

The artificial accelerated testing by exposure to UV-VIS radiation simulating natural light passing through window glass resulted in visible colour changes for both the uncoated (V1) and coated (V2) maple wood samples, with differentiations of the zones (Z1-Z4; Z1-Z3) depending on their specific exposure situation. These colour changes were visible starting from the first cycle of 24 h exposure and evolved in time (Figure 11).

The pictures and the data in Tables 3 and 4 refer to the aspect and colour changes after 72 h light exposure. Each table contains comparative images and data for the uncoated (V1) and coated samples, alongside (V2) test the corresponding coating material, namely the waterborne acrylic-polyurethane lacquer coded FB1 (Table 3) and the waterborne polyurethane lacquer coded

FB3 (Table 4). At first sight, it can be observed that the method succeeded in serving the first two objectives: effects of light exposure in various areas are visible (to human perception and by colour difference data) and a comparison of the light induced colour changes for the uncoated and coated surfaces is clearly revealed by the colour data. A total colour change  $\Delta E$  of 10.83 units was measured for uncoated maple wood after 72 h direct light exposure (V1/Z3), while for the coated samples (V2/Z1) the corresponding values were slightly lower: 9.29 (FB1) and 9.81 (FB3). Exposure under the 1mm thick clear glass lamella reduced the total colour change of uncoated maple by 36.8% to 6.83 units, very likely due to a reduced transmittance of UV light (by 40% according to [11]). Similarly, the total colour changes of the coated wood surfaces under the clear glass (V2/Z3) were reduced by around 40-43% to 5.63 (FB1), respectively 5.55 (FB2), which might indicate some protection of the coating film against the light induced colour changes of the finished surfaces. At the same time the colour of the coating films FB1 and FB3 exposed directly to UV radiation remained nearly unchanged after 72 h light exposure, as resulted from the calculated  $\Delta E$  values of 0.64 and 1.00, respectively, which means a reduced contribution, from 6.9% up to 10.2%, to the overall colour changes of the coated surfaces ( $\Delta E$  9.28; 9.81).

The "protective" effect of the clear glass lamella, by blocking part of the UV radiation, represents a limitation of the method, as all the colour and surface chemistry changes measured in such conditions will be significantly lower than those occurring and measured in real conditions (without а glass slide). Therefore, comparisons within this method should be made for similar exposure situations.

In this context, a closer look and comparative analysis of data in Tables 3 and 4, for the areas V2/Z1 (simulation of wood substrate colour changes under the coating) and V2/Z3 (colour changes of the coated surface exposed covered with a glass slide) show how the method served the third objective, namely the contribution of the wood substrate could be highlighted and evaluated.

According to the data in Table 3, after 72 h light/UV exposure, the colour changes of the wood substrate under the simulated detachable coating (V1/Z1) were close to those measured for the coated surfaces exposed under a similar clear glass slide (V2/Z3): variation of lightness -4.16/-4.53 (91.8%); variation of redness 1.77/1.94 (91.2%); variation of yellowness: 3.61/2.73 (132.2%), resulting in total colour changes of 5.79 units for the maple substrate under the simulated detachable coating compared to 5.63 units for the maple coated with lacquer FB1. All data highlight the major contribution of the substrate under the coating film to the colour changes of the finished surfaces. The higher increase of yellowness for wood under the simulated detachable coating might be associated with lignin photodegradation for the maple wood substrate [26]. In this context, it is also important to note that yellowing of the wood substrate was significantly reduced in the areas covered with clear glass slide (V1/Z2:  $\Delta b^*=4.50$ ), compared to the direct exposed areas (V1/Z3:  $\Delta b^*=8.67$ ), due to the partial blocking of UV radiation by the glass slide, whilst the applied coating brought only a very slight supplementary contribution (V1/Z1:  $\Delta b^*$ =3.61).

In the case of lacquer FB3 (Table 4), the comparative colour for the areas V1/Z1 (substrate under the coated glass slide) and V2/Z3 (coated substrate under clear glass slide) were as follows: variation of lightness -5.02/-4.66 (107.7%); variation of redness 2.10/2.16 (97.2%); variation of yellowness: 4.16/2.11 (197.1%), resulting in total colour changes of 6.85 units for the maple substrate under the simulated coating film, compared to 5.55 units for the maple coated with lacquer FB3, which might indicate a better protective effect of the coating FB3 compared to FB1. In both cases, the major contribution of the substrate under the coating film to the global colour changes of the finished surfaces was evident. This aspect should be considered with priority in future approaches of stabilising the natural colour of wood surfaces.

## Table 1

# Results of colour changes for: A. Test samples V1 Uncoated maple - effect under clear and FB1 coated glass slide compared to direct exposure; B. Test samples V2) Coated maple – coating FB1 (acryl-polyurethane 2K); C. Coating film FB1 (acryl-polyurethane 2K)

ΔL*	∆a*	∆b*	ΔE	A.(V1) Uncoated maple - effect under coated glass lamella FB1		
-4.16	1.77	3.61	5.79	Z1		
-4.77	1.94	4.50	6.84	Z2		
-6.04	2.53	8.67	10.83	Z3		
0.44	-0.26	-1.48	1.57	Z4	lcm	
ΔL*	∆a*	∆b*	ΔE	<b>B.</b> (V2) Coated maple -coating FB1 (acryl-polyurethane 2k)		
-5.97	2.31	6.73	9.29	Z1		
-0.04	-0.20	-0.03	0.21	Z2		
-4.53	1.94	2.73	5.63	Z3		
ΔL*	∆a*	∆b*	ΔE	<b>C.</b> Coating film FB1 (acryl-polyurethane 2k)		
0.45	-0.25	-0.38	0.64			

## Table 4

# Results of colour changes for: A. Test samples V1 Uncoated maple - effect under clear and FB3 coated glass slide compared to direct exposure; B. Test samples V2- Coated maple – coating FB3 (polyurethane 2K); C. Coating film FB3 (polyurethane 2K)

ΔL*	∆a*	∆b*	ΔE	A.(V1) Uncoated maple - effect under coated glass lamella FB3		
-5.02	2.10	4.16	6.85	Z1		
-4.77	1.94	4.50	6.84	Z2		
-6.04	2.53	8.67	10.83	Z3		
0.19	-0.27	-1.94	1.97	Z4	icm	
ΔL*	∆a*	∆b*	ΔE	<b>B.</b> (V2) Coated maple-coating FB3 (polyurethane 2K)		
-6.18	2.53	7.19	9.81	Z1		
-0.15	-0.27	-0.26	0.40	Z2		
-4.66	2.16	2.11	5.55	Z3	1cm	
ΔL*	∆a*	∆b*	ΔE	<b>C.</b> Coating film FB3		
0.33	0.02	-0.95	1.00	(polyurethane 2K)		

#### **3.2. FTIR Investigations**

# **3.2.1.** Chemical Changes of the Maple Wood Substrate

The FTIR spectra, in the range 2,000-600 cm<sup>-1</sup>, for uncoated maple wood samples registered prior (control) and after 72 h UV exposure in different exposure conditions are comparatively presented in Figure 8. Light exposure resulted in degradation of lignin, observed as decrease of absorption at 1,504 cm<sup>-1</sup>

(aromatic skeletal vibration of lignin), occurring in parallel with oxidation processes leading to the formation of unconjugated carbonyl groups (1,730 cm<sup>-1</sup>), these changes being more evident for the directly exposed areas (V1/Z3) than those exposed covered by clear glass slide (V1/Z2) or coated glass slide (V1/Z1). The specific absorption peaks of cellulose (900 cm<sup>-1</sup>) and hollocellulose (1,370 cm<sup>-1</sup>) were unaffected or minimally affected.



Fig. 8. Comparative FTIR spectra in the range 2,000-600 cm<sup>-1</sup> for uncoated maple wood before (P-Control-OUV) and after 72 h UV exposure in different conditions: direct exposure (P-72UV) area V1/Z3, exposure under clear glass slide (P\_S\_72UV) area-V1/Z2, and exposure under coated glass slide (P\_S\_FB1/P\_S\_FB3) areas V1/Z1 for two coatings FB1, FB3

In order to better highlight and compare these light induced chemical changes in direct relation to the exposure situation, integration of selected absorption bands was performed with the OPUS software, and the ratios of the areas of relevant absorption bands were calculated [38]. The chemical changes occurring as a result of light exposure are clearly emphasised by the calculated FTIR ratios (absolute and relative) presented in Table 5, as a decrease of the ratio A1504/A1370 and an increse of ratios A1730/A1370 and A1730/A1504, similarly to previously reported research [1, 26, 38].

The ratios highlight maximum photodegradation of the wood substrate in the case of direct exposure, the "protective" effect of the glass slide and a contribution of the coating materials in reducing lignin degradation of the wood substrate under the coating, though the oxidative phenomena leading to unconjugated carbonyl groups seem to be accentuated under the coated glass. Again, the UV blocking effect of the 1mm thick glass was a limitation of the method, but the chemical changes of the substrate under the coating were demonstrated.

Table 2

Ratios of relevant absorption bands in the FTIR spectra for uncoated maple wood	1
samples (V1) before (control_0UV) and after 72 h UV exposure under different	
conditions, corresponding to the areas V1/Z1, V1/Z2, V1/Z3	

	P_Control _0UV	P_72UV (V1/Z3)	P_S_72UV (V1/Z2)	P_S_FB1_72 UV (V1/Z1)	P_S_FB3_72U V (V1/Z1)		
FTIR Ratio (absolute value)							
A1730/A1370	5,31	6,20	5,37	5,76	5,66		
A 1504/A1370	1,55	0,45	0,88	1,02	1,10		
A1730/A1504	3,43	13,64	6,09	5,67	5,16		
Relative FTIR Ratio (compared to the control)							
A1730/A1370	1,00	1,17	1,01	1,08	1,07		
A 1504/A1370	1,00	0,29	0,57	0,66	0,71		
A1730/A1504	1,00	3,98	1,78	1,65	1,50		

# **3.2.2.** Chemical Changes of the Coated Wood Surfaces

Exposing the coated wood surfaces to UV radiation for 72 hours did not result in any directly visible or significant changes in the FTIR spectra of the coating films presented in Figure 9 for FB1 (acrylic-polyurethane) and Figure 10 for FB3 (polyurethane). This observation seems true regardless of the exposure situation, whether direct exposure (V2/Z1) or under a 1 mm thick clear glass lamella (V2/Z3). This aligns with the minimal colour changes ( $\Delta E$  up to a maximum of 1 unit) determined for the films applied on glass slides and after direct exposure to UV

radiation for 72 h. A more in-depth analysis of the spectra (integration) and longer exposure times might uncover minor chemical changes associated with aging phenomena. This aspect will be explored in future research.

# **3.3.** Evolution in Time of Colour Changes of the Uncoated and Coated Maple Wood Support

Besides the aspects already presented, the proposed method can be employed to study the evolution in time of the light induced colour changes for the uncoated (samples V1) and coated wood surfaces (samples V2), as depicted by the plots in Figures 11a and 11b, respectively. The plots also compare colour changes as a function of the exposure situations characteristic to the different zones of the

two types of test samples employed in the original method developed in this research.



Fig. 9. Comparative FTIR spectra in the range 2,000-600 cm<sup>-1</sup> for coated maple wood before (P-Control-FB1\_0UV) and after 72 h UV exposure in different conditions: direct exposure (P\_FB1\_72UV) area V2/Z1, exposure under clear glass slide (P\_FB1\_S\_72UV) area-V2/Z3 for FB1 (acrylic-polyurethane) coated samples



Fig. 10. Comparative FTIR spectra in the range 2,000-600 cm<sup>-1</sup> for coated maple wood before (P-Control-FB3\_0UV) and after 72 h UV exposure in different conditions: direct exposure (P\_FB3\_72UV) area V2/Z1, exposure under clear glass slide (P\_FB3\_S\_72UV) area V2/Z3 for FB3 (polyurethane) coated samples



Fig. 11. Colour differences ( $\Delta E$ ,  $\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$ ) of uncoated and coated maple wood samples according to exposure time and exposure situation: A: (V1) uncoated wood support: Z3-P (direct exposure), Z2 (exposure under glass slide), Z1 (exposure under coated glass FB1/FB3); B: (V2) coated wood support: Z1FB1/Z1FB3 (direct exposure), Z3FB1/Z3FB3 (exposure under glass slide)

Light exposure of coated wood surfaces (Figure 11a ) resulted generally in lower total colour changes ( $\Delta E$ ) compared to exposure of uncoated surfaces (Figure 11b). In the case of the uncoated samples, the highest colour changes occurred in the first 24 hours of UV exposure (10.43 units), while for the coated samples FB1/FB3, the colour changes were highest after 72 hours of exposure (9.29/9.81 units).

Changes in lightness ( $\Delta L^*$ ) were observed by negative values in both uncoated/coated samples, which means that they darkened as the exposure time increased. In the case of the uncoated substrate, the maximum colour changes of the directly exposed substrate occurred after 24 h of exposure (-9.58 units), while in the case of the FB1/FB3 coated substrate, maximum darkening was registered at the longest exposure time of 72 h (-5.97/units). Longer exposure times are necessary for a better evaluation of the occurring phenomena. For both uncoated and coated samples, exposure behind a 1 mm thick glass slide reduced the lightness changes by approximately (1-2 units).

The evolution of redness changes was not very different for the coated and the uncoated maple samples, the changes reaching values up to about (2.5 units).

A continuous increase of yellowness was registered for both the uncoated and coated maple wood samples, with a trend of relative stabilisation after 72 h. The highest value (8.67 units) was registered for uncoated maple directly exposed to UV radiation, while the corresponding values for the FB1/FB3 coated samples were reduced by 17-23% (6.73/7.19 units). The "protective" effect of glass was observed for both coated and uncoated wood substrate in a reduction of yellowness changes by about 4-5 units. Only minimal differences were observed between changes of wood under coated glass compared to clear glass. Yellowness changes of wood substrate correlate well with FTIR data on lignin degradation (see relative ratios A1504/A1370 in Table 5).

#### 4. Conclusions

Stabilising the natural colour of wood species exposed to light under indoor conditions by coating is a challenge that could be more efficiently addressed based on a better understanding of the occurring phenomena, influencing factors and their specific contributions to the overall colour changes.

An original experimental method was developed and tested in this research. This allowed: testing of light induced colour changes in indoor conditions by an accelerated test under artificial UV-VIS radiation simulating natural light passing through the window glass; comparative evaluation of the light-induced colour changes of the uncoated and coated wood surfaces; highlighting and evaluation of the individual contributions of the substrate and coating film to the global colour changes of finished wood surfaces and investigation of the associated surface chemistry changes by FTIR.

The method, which proposes two types of wood test samples and simulation of a detachable coating film by a coated 1 mm thick clear glass slide, was verified employing European maple as wood substrate and two types of waterborne clear lacquers. Three cycles of 24 h light/UV exposure were run. Exposure of uncoated wood resulted in a total colour difference ( $\Delta E$ ) of 10.83 units, which was only slightly reduced by coating (9.29-9.81 units). Exposure through the glass slide reduced colour changes of uncoated and coated wood surfaces by 37-43% (up to 6.84 units for uncoated wood and 5.6 units for the coated samples), due to a partial blocking of UV light by the 1mm thick glass.

Color changes of (5.79-6.85 units) were measured on the wood substrate exposed through the coated glass slides, while the color changes of the coating films on the glass slides only (0.64-1.0 units), indicated a maximum contribution of the wood substrate to the light-induced colour changes of the coated surfaces.

The FTIR investigation highlighted photo-degradation of the wood substrate under the simulated detachable coating film in good accordance with the colour changes.

The UV blocking effect of the glass slides is the main limitation of the method proposed which will be addressed in future research by replacement with quartz glass slides.

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# References

- Agresti, G., Bonifazi, G., Calienno, L. et al., 2013. Surface investigation of photo-degraded wood by colour monitoring, infrared spectroscopy, and hyperspectral imaging. In: Journal of Spectroscopy, vol. 4, ID article 380536. DOI: <u>10.1155/2013/380536</u>.
- Almutawa, F., Vandal, R., Wang, S.Q. et al., 2013. Current status of photoprotection by window glass, automobile glass, window films, and sunglasses. In: Photodermatology, Photoimmunology an Photomedicine, vol. 29(2), pp. 65-72. DOI: <u>10.1111/phpp.12022</u>.
- Aloui, F., Ahajji, A., Irmouli, Y. et al., 2007. Inorganic UV absorbers for the photostabilisation of woodclearcoating systems: Comparison with organic UV absorbers. In: Applied Surface Science, vol. 253(8), pp. 3737-3745. DOI: <u>10.1016/j.apsusc.2006.08.029</u>.
- Auclair, N., Riedl, B., Blanchard, V. et al., 2011. Improvement of photoprotection of wood coatings by using inorganic nanoparticles as ultraviolet absorbers. In: Forest Products Journal, vol. 61(1), pp. 20-27. DOI: <u>10.13073/0015-7473-</u> 61.1.20.
- Bielerman, J., 1998. Lackadditive, WILEY-VCH, ed., Weinheim; New York; Chichester; Brisbane; Singapore; Toronto, 395 p. DOI:<u>10.1002/9783527624768</u>.

- Blanchet, P., Pepin, S., 2021. Trends in chemical wood surface improvements and modifications: a review of the last five years. In: Coatings, vol. 11(12), ID article 1514. DOI: 10.3390/coatings11121514.
- 7. Capobianco, G., Calienno, L., Pelosi, C. et al., 2017. Protective behaviour monitoring on wood photodegradation by spectroscopic techniques coupled with chemometrics. In: Spectrochim Acta A: Molecular and Biomolecular Spectroscopy, vol. 172, pp. 34-42. DOI: 10.1016/j.saa.2016.05.050.
- Chou, P.L., Chang, H.T., Yeh, T.F. et al., 2008. Characterizing the conservation effect of clear coatings on photodegradation of wood. In: Bioresource Technology, vol. 99(5), pp. 1073-1079. DOI: <u>10.1016/j.biortech.2007.02.027</u>.
- Cirule, D., Kuka, E., Andersone, I. et al., 2022. Wood discoloration patterns depending on the light source. In: Heritage Science, vol. 10(1), ID article 158. DOI: <u>10.1186/s40494-022-00795-2</u>.
- Dong, Y., Yan, Y., Ma, H. et al., 2017. In-situ chemosynthesis of ZnO nanoparticles to endow wood with antibacterial and UV-resistance properties. In: Journal of Materials Science and Technology, vol. 33(3), pp. 266-270. DOI: <u>10.1016/j.jmst.2016.03.018</u>.
- Duarte, I., Rotter, A., Malvestiti, A. et al., 2009. The role of glass as a barrier against the transmission of ultraviolet radiation: an experimental study. In: Photodermatology, Photoimmunology and

Photomedicine, vol. 25(4), pp. 181-184. DOI: <u>10.1111/j.1600-</u> 0781.2009.00434.x.

Müller, 12. Forsthuber, Β., U., Teischinger, Α. et al., 2013. Chemical and mechanical changes during photooxidation of an acrylic clear wood coat and its prevention using UV absorber and micronized TiO<sub>2</sub>. In: Polymer Degradation and Stability, vol. 98(7), pp. 1329-1338. DOI: 10.1016/j.polymdegradstab.2013.0

3.029. 13. Hill, C., 2006. Wood Modification

- Hill, C., 2006. Wood Modification Chemical, Thermal and Other Processes. Wiley Press, 239 p. Available at: <u>https://onlinelibrary.wiley.com/doi/ book/10.1002/0470021748</u>. Accessed on: November 8, 2023.
- 14. <u>https://distrimed.ro/</u>. Accessed on: November 8, 2023.
- 15. <u>https://selectauto.ro/</u>. Accessed on: November 5, 2023.
- 16. <u>https://www.avantes.com/</u>. Accessed on: October 27, 2023.
- 17. <u>https://www.renneritalia.com/en/</u>. Accessed on: October 13, 2023.
- ISO 16474-3, 2021. Paints and varnishes-Methods of exposure to laboratory light sources—Part 3:Fluorescent UV lamps— Requirements. Geneva, Switzerland.
- 19. ISO-4582, 2017. Plastics Determination of changes in colour and variations in properties after exposure to glass-filtered solar radiation, natural weathering or laboratory radiation sources-Requirements. Geneva, Switzerland.
- 20. Kataoka, Y., Kiguchi, M., Williams, R.S. et al., 2007. Violet light causes photodegradation of wood beyond

the zone affected by ultraviolet radiation. In: Holzforschung, vol. 61(1), pp. 23-27. DOI: 10.1515/HF.2007.005.

- Kropat, M., Hubbe, M.A., Laleicke, F., 2020. Natural, accelerated, and simulated weathering of wodd: a review. In: BioResources, vol. 15(4), pp. 9998-10062. DOI: <u>10.15376/biores.15.4.Kropat</u>.
- Kržišnik, D., Lesar, B., Thaler, N. et al., 2018. Influence of natural and artificial weathering on the colour change of different wood and wood-based materials. In: Forests, vol. 9(8), ID article 488. DOI: <u>10.3390/f9080488</u>.
- 23. Liu, X.Y., 2017. Contributions to the study of ageing phenomena of wooden substrate and traditional materials for transparent finishes – a comparative approach for Europe and China with applicability in furniture conservation / restoration. PhD Thesis. Transilvania University, Brasov, Romania.
- 24. Liu, X.Y., Timar, M.C., Varodi, A.M. et al., 2016. An investigation of accelerated temperature-induced ageing of four wood species: colour and FTIR. In: Wood Science and Technology, vol. 51(2), pp. 357-378. DOI: <u>10.1007/s00226-016-0867-4</u>.
- Liu, X.Y., Timar, M.C., Varodi, A.M. et al., 2022. Colour and surface chemistry changes of wood surfaces coated with two types of waxes after seven years exposure to natural light in indoor conditions. In: Coatings, vol. 12(11), ID article 1689. DOI: 10.3390/coatings12111689.
- 26. Müller, U., Rätzsch, M., Schwanninger, M. et al., 2003.

Yellowing and IR-changes of spruce wood as result of UV-irradiation. In: Journal of Photochemistry and Photobiology B: Biology, vol. 69(2), pp. 97-105. DOI: <u>10.1016/S1011-1344(02)00412-8</u>.

- Nair, S., Nagarajappa, G.B., Pandey, K.K., 2018. UV stabilization of wood by nano metal oxides dispersed in propylene glycol. In: Journal of Photochemistry and Photobiology B: Biology, vol. 183, pp. 1-10. DOI: 10.1016/j.jphotobiol.2018.04.007.
- Ncube, E., Meincken, M., 2010. Surface characteristics of coated soft- and hardwoods due to UV-B ageing. In: Applied Surface Science, vol. 256(24), pp. 7504-7509. DOI: <u>10.1016/j.apsusc.2010.05.097</u>.
- 29. Oltean, L., Hansmann, C., Németh, R. et al., 2010. Wood surface discolouration of three hungarian hardwood species due to simulated indoor sunlight exposure. In: Wood Research, vol. 55(1), pp. 49-58.
- Panek, M., Oberhofnerova, E., Hysek, S. et al., 2018. Colour stabilization of oak, spruce, larch and douglas fir heartwood treated with mixtures of nanoparticle dispersions and UV-stabilizers after exposure to UV and VIS-radiation. In: Materials, vol. 11(9), ID article 1653. DOI: <u>10.3390/ma11091653</u>.
- Papp, E.A., Csiha, C., Valent, J., 2012. Colour change of some wood species during artificial xenon radiation. In: Óbuda University e-Bulletin, vol. 3(1), pp. 89-97.
- 32. Passauer, L., Prieto, J., Müller, M. et al., 2015. Novel color stabilization concepts for decorative surfaces of native dark wood and thermally modified timber. In: Progress in

Organic Coatings, vol. 89, pp. 314-322. DOI:

10.1016/j.porgcoat.2015.06.017.

- Rajkovic, J.V., Miklecic, J., 2021. Enhancing weathering resistance of wood - a review. In: Polymers, vol. 13(12), ID article 1980. DOI: <u>10.3390/polym13121980</u>.
- Rosu, D., Teaca, C.A., Bodirlau, R. et al., 2010. FTIR and color change of the modified wood as a result of artificial light irradiation. In: Journal of Photochemistry and Photobiology B: Biology, vol. 99(3), pp. 144-149. DOI: 10.1016/j.jphotobiol.2010.03.010.
- Spear, M.J., Curling, S.F., Dimitriou, A. et al., 2021. Review of functional treatments for modified wood. In: Coatings, vol. 11(3), ID article 327. DOI: <u>10.3390/coatings11030327</u>.
- 36. Teacă, C.A., Roşu, D., Bodîrlău, R. et al., 2013. Structural changes in wood under artificial UV light irradiation determined by FTIR spectroscopy and color measurements – a brief review. In: BioResources, vol. 8(1), pp. 1478-1507. DOI: 10.15376/biores.8.1.1478-1507.
- Timar, M.C., Beldean, E.C., 2022. Modification of shellac with clove (*Eugenia caryophyllata*) and thyme (*Satureja hortensis*) essential oils: compatibility issues and effect on the UV light resistance of wood coated surfaces. In: Coatings, vol. 12(10), ID article 1591. DOI: <u>10.3390/coatings12101591</u>.
- Timar, M.C., Varodi, A.M., Gurau, L., 2016. Comparative study of photodegradation of six wood species after short-time UV exposure. In: Wood Science and

Technology, vol. 50, pp. 135-163. DOI: <u>10.1007/s00226-015-0771-3</u>.

- 39. Yi, T., Morrell, J.J., 2023. Role of  $\alpha/\gamma$ Fe<sub>2</sub>O<sub>3</sub> and ZnO nano-particles in reducing photodegradation of wood components. In: Wood Science and Technology, vol. 57, pp. 427-446. DOI: <u>10.1007/s00226-023-01456-8</u>.
- Zahri, S., Belloncle, C., Charrier, F. et al., 2007. UV light impact on ellagitannins and wood surface colour of European oak (*Quercus petraea* and *Quercus robur*). In: Applied Surface Science, vol. 253(11), pp. 4985-4989. DOI: <u>10.1016/j.apsusc.2006.11.005</u>.
- 41. Živković, V., Arnold, M., Radmanović, K. et al., 2013. Spectral sensitivity in the photodegradation of fir wood (*Abies alba* Mill.) surfaces: colour changes in natural weathering. In: Wood Science and Technology, vol. 48(2), pp. 239-252. DOI: <u>10.1007/s00226-013-0601-4</u>.