Izvirni znanstveni članek / Original scientific paper

INFLUENCE OF MICROWAVE HEATING IN WOOD PRESERVATION ON TRADITIONAL SURFACE COATINGS

VPLIV MIKROVALOVNEGA SEGREVANJA PRI ZAŠČITI LESA NA TRADICIONALNE POVRŠINSKE PREMAZE

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ABSTRACT

Microwaves are very effective at wood pest eradication. However, elevated temperatures may pose a risk of damaging surface coatings used on cultural and historical artefacts. Therefore, we monitored changes in patterns of the original paint taken from such objects along with newly prepared coatings. We evaluated visual, mechanical, and chemical modifications of coatings when exposed to microwaves (750W, 2.4GHz), at 60°C or 80°C for 10 min. Whether old or new, only water-based coatings have proven to be resistant to elevated temperatures and no damage was observed at 80°C. Blisters have formed on layers of new oil paints and natural resins due to insufficiently cured film. Temperatures above 80°C may cause melting of coniferous wood resin and thus transport of resin to the surface; on the other hand, temperatures up to 60°C are completely harmless. Mechanical and chemical changes of coatings exposed to microwaves were not observed, but the studies showed that colour and gloss exhibited minor changes.

Key words: objects, wood, wood coatings, wood protection, microwaves, heating

IZVLEČEK

Mikrovalovi so zelo učinkoviti pri zatiranju lesnih škodljivcev. Lahko pa povišane temperature pomenijo tveganje za nastanek poškodb površinskih premazov, uporabljenih na kulturnozgodovinskih predmetih. Zato smo spremembe spremljali na vzorcih originalnih premazov, odvzetih s kulturnozgodovinskih predmetov, ter na novo pripravljenih premazih. Ocenili smo vizualne, mehanske in kemične spremembe premazov, izpostavljenih mikrovalovom (750W, 2,4 GHz) pri 60 °C ali 80 °C za 10 min. Stari premazi in novi, a le tisti na vodni osnovi, so se izkazali odpornejši proti povišanim temperaturam in poškodb pri 80 °C nismo opazili. Poškodbe v obliki mehurjenja so nastajale pri slojih nove oljne barve in naravnih smol, kot posledica premalo utrjenega filma. Temperatura nad 80 °C lahko povzroči taljenje smole v lesu iglavcev in tako prodiranje na površino vzorca pod premaz, medtem ko so temperature do 60 °C povsem neškodljive. Mehanskih in kemičnih sprememb premazov, izpostavljenih mikrovalovom, raziskave niso pokazale, sta pa se minimalno spremenila barva in sijaj.

Ključne besede: kulturnozgodovinski predmeti, les, premazi, zaščita lesa, mikrovalovi, segrevanje

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1 INTRODUCTION

1 UVOD

Useful wooden artefacts of cultural heritage are, due to the characteristics of materials used, extremely sensitive materials, furniture and polychrome wooden plastics in particular. Wood insects and fungi constantly threaten them, which can completely destroy a wooden object in a short time period (Pohleven, 2000). Therefore, in order to eradicate them, different methods are used, including microwave heating. Pest control with microwaves is based on achieving pest's lethal temperature as quickly as possible and without complex interventions. In contrast to classical methods of heating, microwaves heat the volume of the timber from the inside out (Andreuccetti et al., 1995). This method is faster and more efficient for all development stages of the pest (Bini et al., 1997), but some authors do not advise it because of the possibility of damage of surface coatings as well as the possibility of fire due to metal parts inside the objects (Unger et al., 2001). In a previous study, we established the necessary conditions for the destruction of House Longhorn Beetle (*Hylotrupes bajulus*) larvae, which are more resistant to higher temperatures than other types of insects (Becker and Loeb, 1961). The timber's surface had to be heated up from 49°C to 65°C for a time ranging from

10 seconds to 10 minutes, depending on the thickness and the method of irradiation; fungi are on average destroyed at temperatures of about 70°C with a heating time period of 5 to 15 min.

Heat poses a risk to wooden objects and may lead to a reduction of moisture in wood, which causes wood shrinkage. These processes are non-uniform in different directions, because the wood is shrinking particularly in the tangential direction and much less in the longitudinal direction (Gorišek, 2009). Thus, an asymmetric change of the object causes internal tensions which can lead to damage, especially for complex objects consisting of several parts or different materials such as polychrome wooden plastics (Strang, 1995). The shrinkage of wood is then transmitted to surface materials that have different elongation properties. This leads to cracking and peeling of the coating film (Strang, 2001).

The list of materials that are traditionally used for surface treatment of wood is short and includes: natural resins, drying oils, waxes, eggs, glue and natural pigments. All these media are amorphous or semi-amorphous polymers. If they are elastic (oil paints and adhesives) they stretch without damage and better withstand elevated temperatures, just as rigid materials (wood, paper, papyrus) better withstand low temperatures (Michalski, 1991). Beiner and Ogilvie (2005) report that the thermal method of eradicating pests, freezing and warming with regulation of moisture (Thermo Lignum®) do not cause injury or chemical changes in wood polychrome objects, while heating has caused changes in papyrus and leather.

Each individual material constituting the object absorbs heat differently. A dark area heats up to 30% more than bright areas, leading to thermal stress and deformation of thermoplastic dark films which, due to a higher temperature, soften while the light area remains unchanged (Nicolaus, 1999). Resin varnishes and adhesives begin to soften at 60°C (Michalski, 1991). Due to the excessive warming above 75°C, volatile compounds begin to evaporate from the coating, which causes considerable pressure to the softened layer of the coating and results in the formation of heat blisters. Their volume depends on the temperature and duration of the procedure, as well as the type, thickness and age of the surface layer (Nicolaus, 1999). If the temperature exceeds the melting point of a particular material, waxes being the exception, pyrolysis decomposition commences (Wolfmeier, 2003). Binders with high molecular components are split into low molecular components, thereby emitting volatile gases, water, carbon dioxide and products of organic acid decomposition (Nicolaus, 1999). With further heating the situation worsens; the coating loses elasticity and becomes fragile and finally carbonized.

Together with the above described destructive processes, other processes such as oxidation, polymerization and photochemical reactions that cause accelerated aging and yellowing of surface coatings take place (Nicolaus, 1999). Coatings with water-borne binders, (egg and glue) are less responsive than oil paints to the heating up to a temperature of 280 °C. In tempera colours, the colour layer gets brighter (Newman, 1998), while oil paintings darken (Erhardt 1998). Oil paints darken due to degradation of drying oil; at the same time a result of heating is an increase in carbon content. The darkening of the colour is closely linked to the quantity of the binder (Nicolaus, 1999). Irreversible colour changes may occur due to pigments, such as lead-white, yellow ochre, iron oxide yellow and burnt sienna, becoming more reddish to brown (Nicolaus, 1999).

2 MATERIALS AND METHODS

2 MATERIALI IN METODE DELA

2.1 Sample preparation

2.1 Priprava vzorcev

In this study we used samples of eight original coatings from cultural objects, which were removed in the process of conservation and restoration. Coatings were categorized by the art of manufacture and the type of binder. These were: oil, wax, polish, tempera paint, oil paint, oil paint with sandarac lacquer, oil gilding and water gilding. The samples were of different sizes depending on the availability of the material.

We also prepared new samples from spruce (*Picea Abies* (L.) Karst.) and linden (*Tilia platyphillos* Scop.) planks, with dimensions of 300 mm × 100 mm × 20 mm, on which we applied ten different coatings that were, and still are, most often used on objects of cultural heritage. We have prepared the coatings ourselves according to traditional recipes. For each type of coating we prepared three samples. On the linden wood, all of the prepared coatings were applied, while on the spruce only ground, egg tempera, oil paints and oil paints with sandarac lacquer were applied.

2.2 Materials for the surface treatment of wood

2.2 Materiali za površinsko obdelavo lesa

Oiling: linseed oil (Chemcolor Sevnica, d.o.o.) was applied in six thin layers with a cloth. 24 hours elapsed between applications in order for the individual layers to cure.

Waxing: 250 g of beeswax (Samson Kamnik d.o.o.)

was dissolved in 750 ml of turpentine (Chemcolor Sevnica, d.o.o.) and applied with a brush, as thin as possible, in six layers. 24 hours elapsed between applications in order for the individual layers to dry. After drying of the last layer, the surface was wiped with a linen cloth to a matte gloss.

Sandarac varnish: 150 g of sandarac resin in granular form (Samson Kamnik d.o.o.) was dissolved in 850 ml of 96% ethanol (Chemcolor Sevnica, d.o.o.), which was then strained and applied with a brush in three layers. The time elapsed between applying the individual layers was 24 hours.

Polish: 150 g of shellac resin (Samson Kamnik d.o.o.) was dissolved in 850 ml of 96% ethanol (Chemcolor Sevnica, d.o.o.) and then applied to the surface of the wood with a soaked swab made from linseed canvas in 20 layers with time elapsed between the application of individual layers ranging from 10 min to up to 2 days. Towards the end of the treatment process we reduced the percentage of shellac and increased the proportion of the solvent.

Ground: 100 g of rabbit-skin glue (Samson Kamnik d.o.o.) in 1 litre of water was heated in a water bath and dissolved. Samples were then coated with this solution twice. To 1 litre of lukewarm glue solution, 1,200 g of Bologna chalk (Samson Kamnik d.o.o.) was added slowly and stirred. The warm substance was applied with a brush in seven layers with 6 hours of time elapsing between applications.

Egg tempera: 100 g of dry ochre pigment (Samson Kamnik d.o.o.) with added water was, with mortar and pestle, crushed into a paste, then 100 ml of egg yolk (domestic farming) and 50 ml of water was added and mixed together in a beaker. On the ground base we applied three layers with a brush with 12 hours of time elapsing between applications.

Oil paint: to linseed oil (Chemcolor Sevnica, d.o.o.) we added ground pigment of burnt sienna (Samson Kamnik d.o.o.) to make pasty mixture. The mixture was then diluted with pure linseed oil (80 ml / 100 g). The surface of the base was saturated with two layers of a 15 % solution of shellac. The oil paint was applied with a brush to the surface in three layers with 6 days elapsing between applications.

To the other half of the samples with oil paint, we applied sandarac varnish 2 weeks later by brush in two layers.

Oil silvering: on the base we applied dissolved shellac in two layers. When the shellac was dry we applied 12 Hour Oil Mixtion (Lefranc & Bourgeois). 14 hours later, when the surface was just sticky enough, we applied silver stripes (Samson Kamnik d.o.o.) with a goldsmith brush. Excess silver was then removed with a soft brush.

The water silvering in egg technique: on the ground base, first yellow and then red Poliment was applied by brush. The Poliment was prepared from 60 g of bolus (Samson Kamnik d.o.o.) which was dissolved in 50 ml of water and then admixed with 50 ml of egg white (domestic farming); the whole mixture was then strained through a fine sieve. The ready Poliment was then applied on the ground base and tested. The Poliment was wet with 40% alcohol and the silver strip was applied by goldsmith brush. After 7 hours we used a polishing stone to smooth the surface to a shine.

Samples dried for 1 month; oil paint and natural resins took as long as 6 months.

2.3 Exposure of coatings to microwave radiation
2.3 Izpostavitev premazov mikrovalovnemu sevanju

We exposed the samples with the coating systems to microwave radiation for 10 minutes to heat them to two different temperatures: 60°C and 80°C. All the coating systems, apart from silvering, were irradiated in the commercial microwave chamber of a 750 W Whirlpool AT 329 ALU. Glossy and oil silvering was exposed to microwaves by using a microwave device with a horn antenna for targeted irradiance; it had a power output of 800 W and a frequency of 2.45 GHz. In this case, the samples were irradiated from the back side, with the silvering facing downwards due to the fact that the microwaves can't penetrate the layer of silver because they are reflected from it. The temperature was controlled manually by turning on and off the magnetron while we tried to get as close as possible to the desired temperature. These intervals had different times depending on the heating and cooling rate of the sample.

2.4 Determination and monitoring of the temperature
2.4 Določanje in spremljanje temperature

The temperature of coatings was measured, before and after the exposure to microwave radiation, with a Trotec IC 080 LV infrared thermal camera with a resolution of 384 × 288 pixels. The camera used is able to measure temperatures between -20°C and to +600°C with a measurement accuracy of ±2°C and thermal sensitivity of 0.05°C. Since we were using a surface method we only measured the side on which the surface coating was applied; the exception was the silvering where we followed the temperature from the rear side and took reference temperature readings from the front where the silvering was applied. Metal reflects infrared rays (high reflectivity and low emissivity); so in order to have accurate measurements we placed a white sticker with high emissivity on the surface and the surface temperature of the sticker was measured. For the processing of the thermographs, we used the computer program IC IR Report.

2.5 Determination of wood moisture
2.5 Določanje vlažnosti lesa

Samples of spruce and linden wood (300 mm × 100 mm × 20 mm) were weighed before and after exposure to an accuracy of 0.001 g. We then dried them in a laboratory oven for 24 hours at a temperature of (103 ± 2)°C to achieve absolute dryness. The humidity was then calculated using the following equation:

$$u(\%) = \frac{m_z - m_0}{m_0} \times 100\%$$

where the symbol u (%) means the humidity of wood, m_z is the mass of the sample before or after microwave radiation (g) and m_0 is the mass of the absolutely dry wood sample (g). Finally, we calculated the difference in wood moisture before exposure and after it.

For measuring the change of moisture at the surface we used a GANN Hydrometter RTU 600 moisture meter.

2.6 Evaluating the appearance of the samples
2.6 Ocenjevanje videza vzorcev

Before and after the exposure we observed the surface coatings of the samples: blistering in accordance with ISO 4628/2:1982, cracking in accordance with ISO 4628/4:1982, flaking in accordance with ISO 4628/5:1982 and chalking in accordance with SIST EN ISO 4628-6:2002. Changes were observed with the naked eye and by stereo microscope at 10 times magnification.

2.7 Determination of the adhesion of coatings and their resistance to impact
2.7 Določanje oprijemnosti premazov in njihove odpornosti proti udarcu

Adhesion was determined by using a cross-cut test standard SIST EN 927-3:2001 and a modified procedure of the standard SIST EN ISO 2409:1997. We used a special knife with six blades embedded. On each sample, we made an incision of three gratings with a spacing of 2 mm between the blades. Results were calculated by taking an average value of the share of the surface that was discarded after three measurements [with ratings ranking from best (0) to worst (5)].

Surface resistance to impact was measured using a method according to ISO 4211-4:1995. A 500 g weight was dropped from a height of 10 mm and 25 mm. After each executed impact, injuries were closely assessed through a magnifying glass with a 10 times magnification, numerically evaluated and average value established.

Hollows in the wooden substrate caused by insects with varying degrees of damage, inhomogeneities, relief, uneven thickness of the layer, impurities and varying degrees of degradation of the coating systems had an impact on the measurements and the usefulness of certain methods. Therefore, it was necessary in some cases to carry out more measurement repetitions.

2.8 Gloss measurement
2.8 Merjenje sijaja

The samples gloss was measured with an X-Rite AcuGloss TRI Gloss Meter prior and following the exposure according to the standard SIST EN ISO 2813:1999. On each sample, ten measurements were performed at random positions (five from one direction and five from another). Measurements were carried out at a 60° angle in the longitudinal direction of incident light, parallel to the wood fibres and direction of applied coatings. Changes in gloss were calculated from the difference between the average gloss measurements prior to and after the exposure.

2.9 Colour measurement
2.9 Merjenje barve

Prior to and after exposure, the colour of the samples was measured in accordance with ISO/DIS 7724-2:1997. Using a spectrophotometer SP62 manufactured by X-Rite GmbH - Optronik ™, ten measurements were performed on each sample. When measuring the colour of the samples, we used the following parameters: measurement geometry d/8°, 2° standard observer, direct reflected component included (SPIN; Specular-Included), D65 standardized light and CIEL*a*b* system for the numerical evaluation of colour.

We also used the method of scanning samples prior to irradiation and after it, with the optical scanner HP Scanjet G4050, with a resolution of 200 ppi. Measurements of colour in the CIEL*a*b* colour space were measured with the program PHOTO-PAINT 8.

Based on the measurement of colour before and after exposure we calculated, using the CIEL*a*b* system, the colour change of samples by the following equation (ISO/DIS 7724-3:1997)

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

The symbol Δ in the above equation denotes a change (before and after the exposure), *E* is a common colour in the CIELAB system, *L**, *a** and *b** are the values of colour coordinates in the colour space according to the CIELLAB system.

2.10 The surface FT-IR spectroscopic analysis
2.10 FT-IR-spektroskopske analize površin

The FT-IR spectroscopy method was used to determine possible chemical changes in the surface coatings which might occur due to irradiation with microwaves, specifically due to heating. A FT-IR Spectrometer Spectrum One (Perkin-Elmer Instruments) was used for the analysis. From each type of coating, 4 samples were taken by gentle rubbing with a special abrasive product and inserted into the spectrometer. Spectra were recorded using the ATR technique in the range of 4,000 cm^{-1} to 450 cm^{-1} at a spectral resolution of 4 cm^{-1}.

3 RESULTS AND DISCUSSION
3 REZULTATI IN RAZPRAVA

3.1 The influence of microwave irradiation on wood moisture content
3.1 Vpliv obsevanja z mikrovalovi na vlažnost lesa

Maximum damage in thermal treatment arises from the drying, and thus shrinkage, of the wood. Therefore, we have studied the impact of warming on wood moisture of spruce and linden wood samples with approximately 12% initial moisture content (MC). Spruce, on average, lost more moisture than linden wood. When heated to 60°C (10 min), the MC of spruce wood has lowered by 1.9 percentage points on average, and MC of linden wood by 1.3 percentage points, while at 80°C (10 min) the moisture of spruce samples decreased by 2.9 percentage points, and linden by 2.1 percentage points. The surface, however, in contrast to conventional heating, increased in moisture by up to 1.8 percentage points since the microwaves started to heat the interior of the wood firstly, thereby pushing moisture towards the outer surface. This reduced the possibility of cracking of the wood and the coating systems.

3.2 Heating of the coating systems
3.2 Segrevanje premaznih sistemov

Materials which were used as components of the coating systems or cured coatings did not heat up during the microwave radiation. The majority of them do not contain water, which is necessary for the absorption of microwaves, so the surface materials are indirectly heated by timber underneath.

In order to achieve a target temperature of 60°C, the samples were initially exposed to the full power of the microwave for 30 seconds and, to achieve 80°C, for 40 seconds. During the time of 10 minutes all samples had to be constantly heated to 60°C; we irradiated them at intervals altogether for 90 s to 130 s and, for retaining temperature at 80°C, for 130 s to 224 s. Differences between linden and spruce wood were not observed. Samples were heated to the greatest extent in the middle of the surface and less towards the edges (Figure 1). The difference between the maximum and minimum measured temperature was 25°C and more. We did not observe temperature differences between the front and the rear (untreated) sides. Also, we did not note that the dark areas heated up more than the bright ones, as indicated by Nicolaus (1999) with conventional heating. Other research and validations were

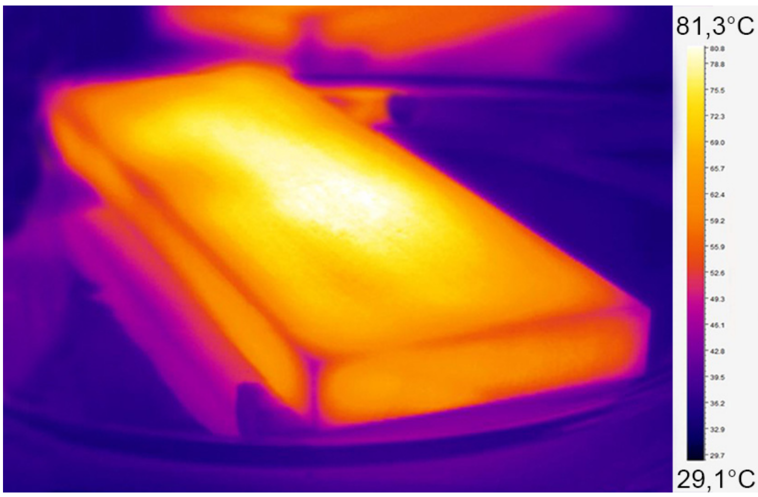

Fig. 1: Heating the surface of the sample with sandarac lacquer

Slika 1: Segrevanje površine vzorca s sandarakovim lakom performed on the parts where the samples were heated the most. The results of the heating of individual samples are summarized in Tables 1 and 2.

3.3 Damage to the coating systems after exposure to microwaves

3.3 Poškodbe na premaznih sistemih po izpostavitvi mikrovalovom

Flaking and chalking of the coatings was not observed in any of the exposures. Blistering on the cultural heritage samples was not observed either (Table 1). Blisters only formed on the newly prepared coatings from the natural shellac resin, sandarac and oil paints, where some very small blisters were formed at 60°C. When exposed to about 80°C, blisters were more frequent (Figure 2) and larger (Table 2). This can be attributed to the process of consolidation of natural resins and oils, due to the volatile substances starting to evaporate more quickly at elevated temperatures, which cause the coating to blister. The curing time of one month was obviously too short, so we carried out a simulation on 6 month old samples. At 60°C, the surface did not change, and at 80°C a few tiny bubbles were formed. By this we can confirm that the blistering appeared mainly due to noncomplete polymerisation of natural oils and resins and not due to the influence of microwave heating, given that blistering did not occur on the old samples cured for more than 100 years. Smaller blisters in spruce wood samples were caused by a leakage of resin to the surface. This phenomenon was observed at temperatures above 82.7°C (Figure 3), although the melting point of the wood resin is between 62 and 65°C (Rivers and Umney, 2003). While we could not detect blistering of the ground on the radial surface of the sample, the blisters were formed in a transverse plane at temperatures higher than 80°C (Figure 3). This is most likely caused by water vapour pressure which in the heating process passes from the

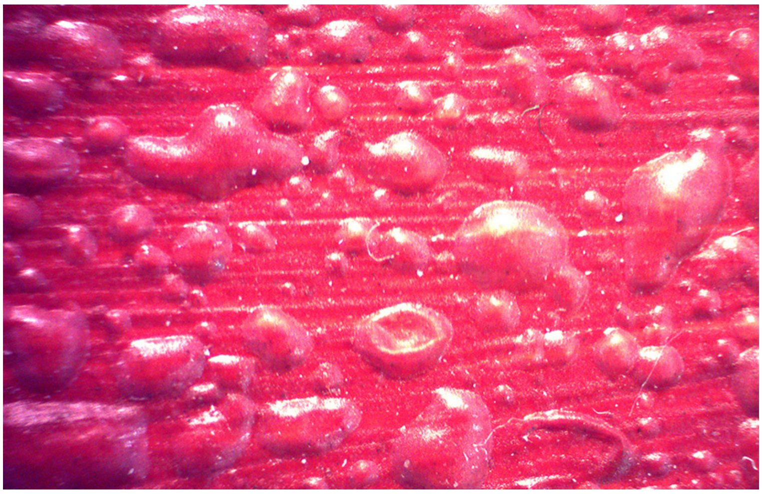

Fig. 2: Blistering of incompletely cured oil paints when exposed to 79.5° C for 10 minutes. 10 times magnification

Slika 2: Zamehurjenje nepopolno utrjene oljne barve pri izpostavitvi 79,5 °C za 10 minut. 10-kratna povečava

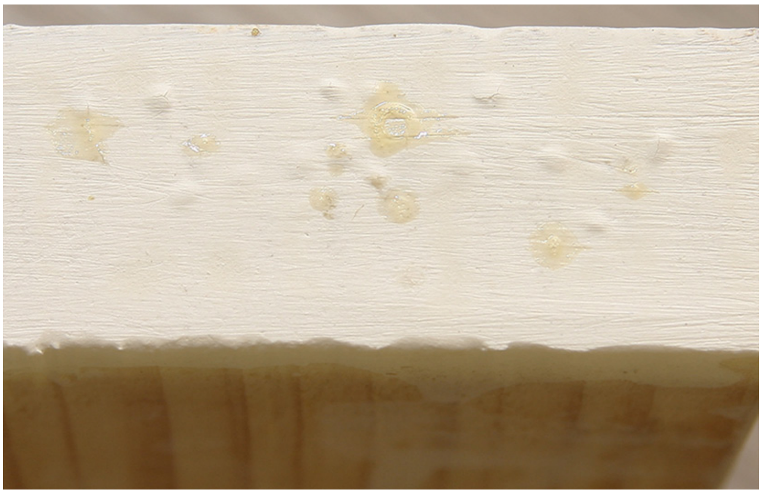

Fig. 3: Blisters formed at a temperature of 82.7 °C on the front side of the sample, and leakage of the resin

Slika 3: Pri temperaturi 82,7 °C nastali mehurji na čelni strani vzorca ter iztekanje smole interior of the wood towards the outer surfaces to interact with the glue, which acts as a binder; glue is sensitive to excessive moisture and elevated heat. The glue softens and blisters form on the coating.

Cracking of the surface coatings is largely dependent on the drying of the wood. Samples exposed to 60°C or 80°C for 10 minutes lost an insufficient amount of water in order to create damage in the form of cracks, which would be noticeable in the majority of old and new coating materials. The existing cracks in the old coatings did not expand (Figure 4), because the moisture that penetrates from the interior of the wood towards the surface prevents cracking of the wood surface and thus the coatings. Only the cross-linked oil paint cracked, due to accelerated hardening at an elevated temperature, while the base remained unchanged. Micro-cracks occurred on water silvering exposed to 80°C. Cracks were observed at 10 times magnification and evaluated with the assessment of 3 (S1) a (medium cracks, visible at 10 times magnification, on surface of coating) (Figure 5; Table 2). The cause for these cracks is most likely, in addition to exposure to high temperature, the silvering technique itself, where the surface is strongly pressed with a polishing stone in order to smoothen silver leaves to a shine; when irradiating samples of old gilding, no newly formed cracks were observed. Due to the resin leakage from the spruce wood when exposed to 80°C, the exposure resulted in cracks of the new sample prepared by ground technique and the old oil marbling sample (Figure 6).

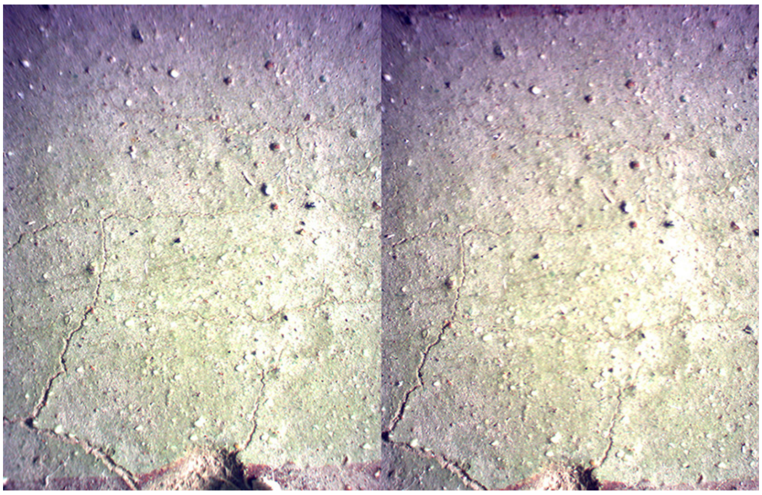

Fig. 4: Comparison of the oil paints with sandarac varnish at 10 times magnification before exposure at 80°C for 10 minutes and after it

Slika 4: Primerjava oljne barve s sandarakovim lakom pri 10-kratni povečavi pred izpostavitvijo 80 °C za 10 minut in po njej

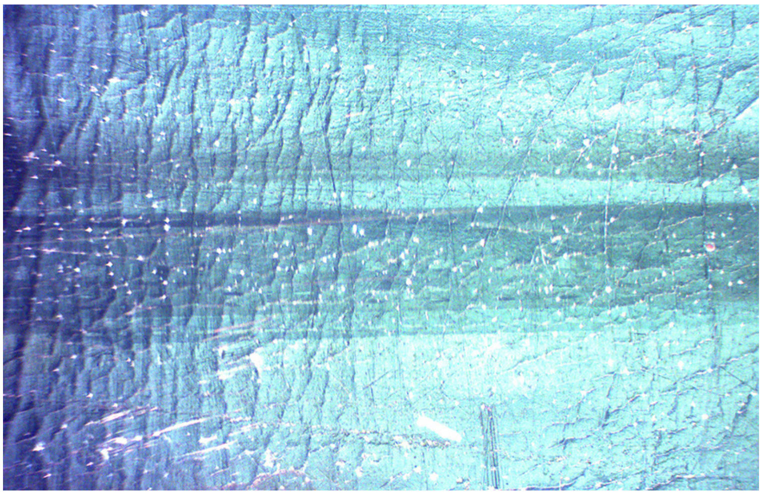

Fig. 5: The resulting cracks on the sample with polished silvering on exposure to 79° C and 10 minutes. 10 times magnification.

Slika 5: Nastale mikrorazpoke na vzorcu s polirano posrebritvijo pri izpostavitvi 79 °C in 10 minut. 10-kratna povečava.

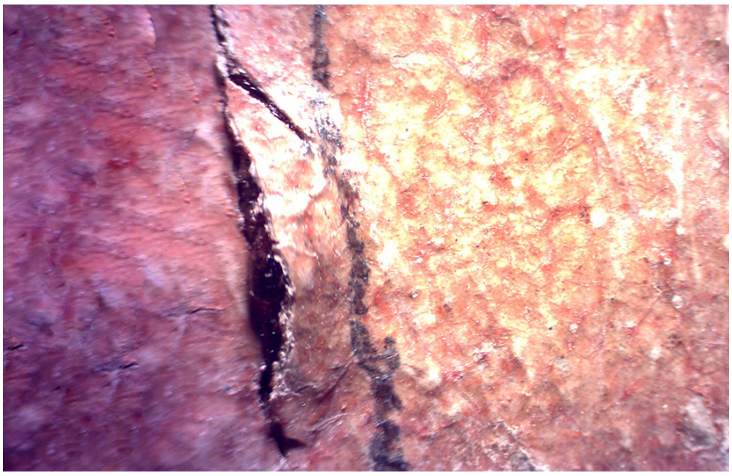

Fig. 6: An oil marbling crack formed due to the melting and penetration of wood resins to the surface at a temperature of 78.5°C. 10 times magnification.

Slika 6: Na oljni marmoraciji je nastala razpoka zaradi taljenja in prodiranja smole na površje pri temperaturi 78,5 °C. 10-kratna povečava.

3.4 The impact of microwave heating on gloss of coating systems

3.4 Vpliv segrevanja z mikrovalovi na sijaj premaznih sistemov

From the gloss measurements before and after the exposure, we have concluded that the change in gloss at temperatures 60°C and 80°C was very small in the case of old coatings (from -2.15 to 0.88; Table 1) and in case of new well cured coatings such as ground, tempera paint and water silvering with changes only to -0.3 units (Table 2). The maximum allowed value for the average change in gloss is up to 5 units for gloss ratings above 25 units, and -2 to +3 units for gloss ratings below 25 units (Kričej and Pavlič, 2007). Greater changes were visual on specimens treated with natural oils and resins in cases where the coating system was not completely cured. Exposure temperature strongly influenced the differences in the values of the gloss; coating films were blistering and cracking more at 80°C. This caused changes in the gloss to an unacceptable -69.37 units. Big differences in the value of gloss happened on beeswax as well. At an elevated temperature of wood the beeswax melted on the surface and penetrated into the wooden substrate. Only a small amount of wax was left on the surface and that greatly reduced the gloss. When exposed to 80°C, the difference in gloss was as high as 40.5 units.

3.5 Changes in the colour of coating systems

3.5 Sprememba barve premaznih sistemov

Exposure to 60°C for 10 min caused minimal changes in colour. Increasing the temperature to 80°C resulted in more pronounced changes. Changes *ΔE* * of old coating systems were slightly lower (0.12 to

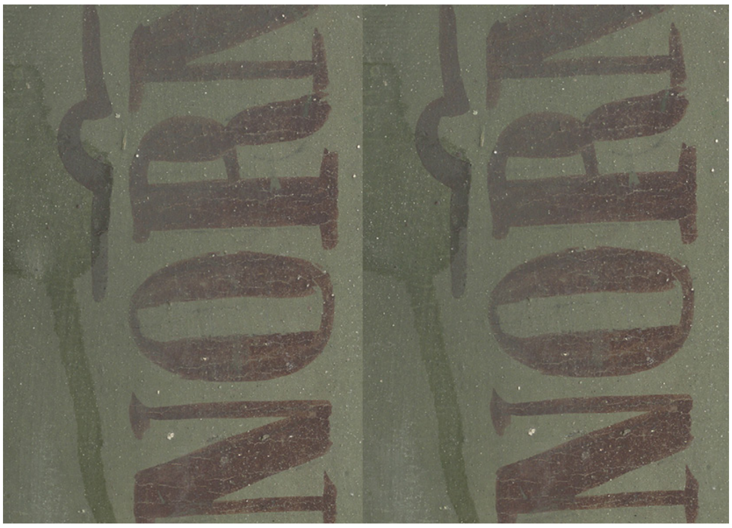

Fig. 7: Maximum measured colour difference (ΔE* = 0.84) in the old sandarac lacquered oil painting before and after the microwave irradiation of 80°C (10 min)

Slika 7: Največja izmerjena barvna razlika (ΔE*= 0,84) pri stari s sandarakom lakirani oljni poslikavi pred in po mikrovalovnem obsevanju 80°C (10 min)

Table 1: Damage and changes in gloss and colour on old coating systems during microwave exposure of about 60°C and 80°C for 10 minutes

Preglednica 1: Nastale poškodbe, spremembe sijaja ter barve na starih vzorcih premaznih sistemov ob mikrovalovni izpostavitvi okrog 60 °C in 80 °C v 10 minutah

Coating *Premaz*	Substrate *Podlaga*	The average temp. / *Povprečna temp.* (°C)	Blistering *Mehurjenje*	Cracking *Pokanje*	Changes in gloss / *Spremembe sijaja*	Changes in colour / *Sprememba barve* (ΔE^*)	
						Spectrophotometer *Spektrofotometer*	Scanner *Optični bralnik*
Linseed oil *Laneno olje*	Walnut *Oreh*	59,51	0	0	-0,21	0,35	0,30
		79,17	0	0	-0,29	0,42	0,45
Beeswax *Čebelji vosek*	Walnut *Oreh*	60,12	0	0	-1.02	0,49	0,35
		78,91	0	0	-2.15	0,64	0,67
Shellac polish *Politura iz šelaka*	Spruce+ veneer *Smreka+ furnirana*	58,92	0	0	-0,73	0,20	0,44
		78,90	0	0	-0,78	0,60	0,81
Tempera *Tempera*	Spruce *Smreka*	58,60	0	0	0,02	0,14	0,06
		79,70	0	0	0,03	0,17	0,09
Oil paint *Oljna barva*	Spruce *Smreka*	59,70	0	0	0,83	0,28	0,33
		78,47	*1(S3)	**2(S1)c	0,88	0,67	0,82
Oil paint + sandarac lacquer *Oljna barva + lak*	Spruce *Smreka*	57,15	0	0	0,07	0,51	0,32
		80,87	0	0	0,35	0,84	0,48
Oil gilding *Mat pozlata*	Linden *Lipa*	61,21	0	0	-0,09	0,21	0,18
		78,92	0	0	-0,13	0,24	0,31
Water gilding *Sijajna pozlata*	Linden *Lipa*	60,51	0	0	-0,03	0,12	0,13
		81,31	0	0	-0,09	0,15	0,19

*Blistering due to leakage of wood resins
**Mehurjenje zaradi iztekanja drevesne smole*

**The crack due to leakage of wood resins
***Razpoka zaradi izteka drevesne smole*

0.84) (Table 1) than the changes in the new (1-month old) coating systems (from 0.23 to 2.52) (Table 2) at the same exposure. Water-borne coatings expressed smaller changes in colour (from 0.23 to 0.65) than natural oil and resin coatings (from 0.56 to 2.52), because they are cured better and do not blister at all. So blistering caused by irradiation can change colour of coating. All coatings darkened with increased temperature, while water-borne coatings (ground and egg tempera) darkened to a lesser extent. At 80°C the least amount of changes occurred in water silvering (ΔE^* = 0.23) and only slightly more in oil silvering (ΔE^* = 0.56). Since the reliability of measurement is influenced by the various texture of coatings, their colour and inhomogeneity, we also used the method of scanning the samples to determine the change in the total surface of the coating; this method expressed lesser changes in the colours (Tables 1 and 2). The samples were also checked with the naked eye, when changes of colour were not detected (Figure 7). The measured values of colour change up to 2.3 after Sandermann and Schlumbom (1962) were undetectable; after Biffle (1985), all the changes up to 1.5 are hardly visually perceptible.

3.6 Adhesion of coatings and their impact resistance

3.6 Oprijemnost premazov in njihova odpornost proti udarcem

The cross-cut method showed no changes in the adhesion of coating systems after 10 minute exposure, regardless of the exposure temperature (60 and 80°C). As expected due to already mentioned curing problems, the only big change occurred on the new samples of oil paints and oil paints with lacquer, where the colour film strongly blistered during exposure to heating. After the initial evaluation of 2 (up to 15% of peeled surface) after exposure to 60°C, adhesion worsened to an average grade of 3.3 (51%) and 3.7 (59%) and at 80°C to 5 (over 65%); at this point the colour film was almost completely separated, while the ground adhered well to the substrate and its adhesion did not deteriorate. Despite the few occurrences of blistering on polish and sandarac lacquer, we could determine no deterioration in adhesion of these two coatings. We concluded that blistering on these samples occurred due to leakage of resin from spruce wood at 82.7°C; in cases without resin leakage the adhesion was good and did not deteriorate with rising temperature.

Changes in impact resistance were not confirmed either. Most coatings received rating 2 (numerous crackles which are maintained the area of deformation) for impact resistance, before and after exposure, except for the oiled and waxed samples where the rating was 4 (there are no cracks in the layer of varnish, on the spot of impact there is just deformation which, however, is visible only in reflection of light). Differences on the imprint into blistered areas and sound areas of natural resins were not observed; with the blistered oil paints varnished with natural resin and not varnished we did not get the right results. It was also

Table 2: Damage and changes in gloss and colour on one-month old coating systems during microwave exposure of about 60°C and 80°C for 10 minutes

Preglednica 2: Nastale poškodbe, spremembe sijaja ter barve na 1 mesec starih premaznih sistemih ob mikrovalovni izpostavitvi okrog 60 °C in 80 °C v 10 minutah

Coating *Premaz*	Substrate *Podlaga*	The average temp. / *Povpreč-na temp.* (°C)	Blistering *Mehurjenje*	Cracking *Pokanje*	Changes in gloss *Spremembe sijaja*	Changes in colour / *Sprememba barve* (ΔE*) Spectrophotometer *Spektrofotometer*	Scanner *Optični bralnik*
Linseed oil *Laneno olje*	Linden	61,65	*0*	0	-0,26	0,61	0,59
	Lipa	80,17	*0*	0	-0,38	0,89	0,75
Beeswax *Čebelji vosek*	Linden	59,23	*0*	0	-39,39	1,28	1,50
	Lipa	79,50	*0*	0	-40,50	1,60	1,68
Sandarac lacquer *Lak iz sandaraka*	Linden	57,05	*1 (S1)*	0	-7,65	0,58	0,45
	Lipa	79,30	*2 (S1)*	0	-14,78	1,59	0,94
Shellac polish / *Politura iz šelaka*	Linden	59,90	*1 (S1)*	0	-13,98	1,40	1,11
	Lipa	78,75	*3 (S1)*	0	-57,16	2,52	1,43
Ground *Klejno-kredna osnova*	Linden *Lipa*	58,05	*0*	0	0,01	0,35	0,29
		78,20	*0*	0	0,06	0,50	0,32
	Spruce *Smreka*	58,80	*0*	0	0,03	0,38	0,29
		78,60	**1 (S2)*	**1 (S2)c	0,08	0,44	0,35
Egg tempera *Jajčna tempera*	Linden *Lipa*	56,55	*0*	0	0,02	0,35	0,36
		77,67	*0*	0	0,14	0,41	0,39
	Spruce *Smreka*	57,24	*0*	0	0,04	0,31	0,36
		80,55	*0*	0	0,08	0,46	0,40
Oil paint *Oljna barva*	Linden *Lipa*	58,96	*1 (S1)*	0	-0,22	0,96	0,85
		78,47	*4 (S4)*	0	-1,87	0,99	0,93
	Spruce *Smreka*	61,35	*1 (S1)*	0	-0,66	1,02	0,90
		79,53	*4 (S4)*	0	-2,64	1,16	1,12
Oil paint + sandarac lacquer *Oljna barva + lak*	Linden *Lipa*	61,20	*2 (S2)*	3 (S3)b	-14,83	0,97	1,08
		78,18	*4 (S3)*	3 (S4)b	-60,16	1,26	1,18
	Spruce *Smreka*	60,17	*2 (S2)*	3 (S3)b	-31,56	1,24	1,13
		79,67	*4 (S5)*	3 (S4)b	-69,37	1,48	1,28
Oil silvering *Mat posrebritev*	Linden	60,11	*0*	0	-0,39	0,53	0,50
	Lipa	80,37	*0*	0	-0,46	0,56	0,54
Water silvering *Sijajna posrebritev*	Linden	59,92	*0*	0	-0,22	0,23	0,17
	Lipa	78,97	*0*	3 (S1)a	-0,29	0,28	0,27

*Blistering due to leakage of wood resins
**Mehurjenje zaradi iztekanja drevesne smole*

**The crack due to leakage of wood resins
***Razpoka zaradi izteka drevesne smole*

difficult to determine the mechanical change on old specimens, while certain standard methods proved unsuitable due to the different condition of the samples.

3.8 FT-IR analysis of the irradiated coated surfaces
3.8 FT-IR analiza obsevanih premazanih površin

FT-IR analysis of the irradiation did not establish any signs of chemical changes in any of the sample materials. Not even in the non-crosslinked oil paint, shellac and sandarac, which were left to cure for only one month and showed the most prominent visual changes. The displayed example of selected spectra in Figure 8 illustrates how FT-IR spectra of the coated surfaces have not changed due to heating with microwaves. It can be concluded that a 10 minute exposure to microwaves does not cause chemical changes of tested wood coatings. This is also the proof that the previously described blistering is not due to chemical changes in the coatings but to the evaporation of moisture from the wood beneath the coating.

3.9 Heating of metal
3.9 Segrevanje kovine

One of the major problems with microwave irradiation, which is noted in the literature by different authors, is the presence of metals in wooden objects that can cause inflammation and damage to the object's surface coatings (Unger et al., 2001). Therefore, we studied the consequences of metal parts presence inside wood. Wood with two nails hammered into the interior of the wood was, from an initial temperature of 24.3°C, exposed to direct current microwave irradiation and heated to an average temperature of 57°C; the nails in the area where they were surrounded by timber warmed up to 33.5 and 38.9°C and in the area where they protruded from the timber to 25.7°C and 27.4°C. This suggests that the metal is indirectly heated by the wood, because the microwaves are reflected from metal. Wood directly surrounding the nails was heated up to about 1°C more than wood, which was further away from the nails (Figure 9). Thus, the microwaves do not cause ignitions, but can affect the ef-

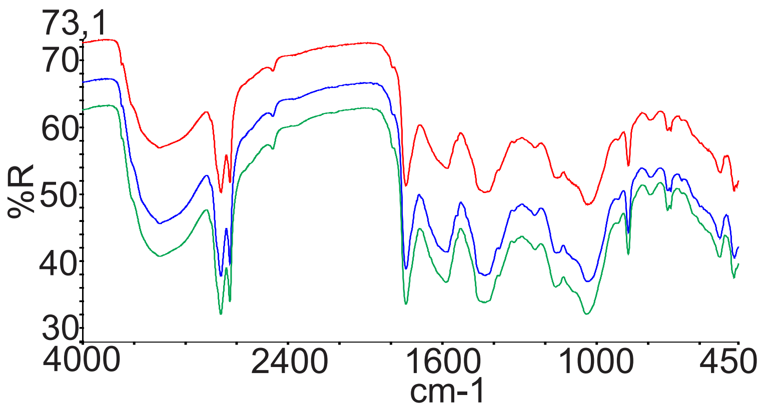

Fig. 8: FT-IR spectra of oil paint that was dried for 6 months (above) and then exposed to 60°C (middle) or 80°C (below)

Slika 8: FT-IR spektri nove oljne barve, ki je bila sušena 6 mesecev (zgoraj) in nato izpostavljena temperaturi 60 °C (na sredini) ali 80 °C (spodaj)

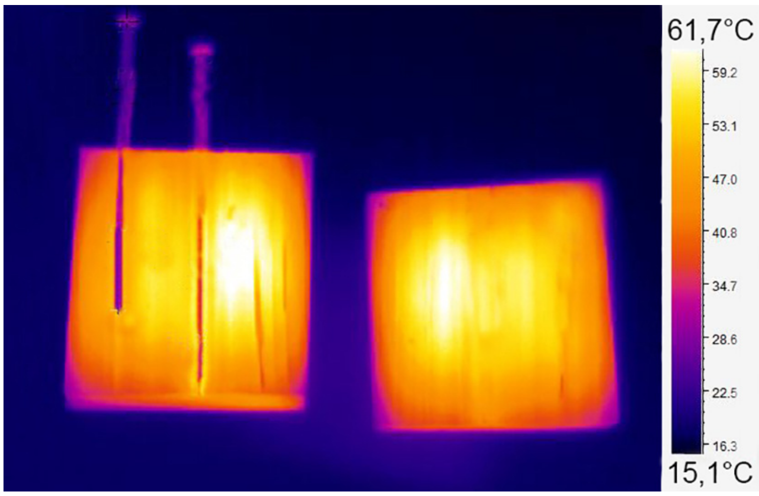

Fig. 9: Heating of metal in the wood

Slika 9: Segrevanje kovine v lesu

fectiveness of the pest eradication in the subject if, for example, the object is mostly covered with metal, as is the case of gilded statues where the microwaves cannot penetrate through the gilt.

4 CONCLUSIONS
4 ZAKLJUČKI

We have verified whether or not the heating of wood with microwaves affects the traditional surface coatings in any way. We have found that heating up to 80°C for 10 min slightly affects colour and shine, but these changes are small enough that they cannot be detected with the naked eye. There was no damage done to the coatings, no change of adhesion, impact resistance or chemical changes (as shown with the FT-IR analysis); some exceptions have appeared due to the heating of wax, which started to melt, and due to transport of melted spruce wood resin to the surface. For wood pest eradication, temperatures from 50°C to 70°C are required; this means that the use of microwaves for pest eradication in the treatment of objects of cultural heritage, including gilded and those that contain metal parts, is safe. So we can conclude on the basis of the test results of the newly prepared surface coatings. Even on new samples no major changes were observed, except for oil paints and varnishes from natural resins where cracking and blistering occurred as a result of subsequent consolidation of previously incompletely cured new surface systems due to exposure to an elevated temperature. These damages were not caused on the real samples of coatings on the ancient cultural objects.

5 POVZETEK

Predmete kulturne dediščine nenehno ogrožajo lesni škodljivci. Za njihovo uničenje je zelo učinkovita in hitra metoda segrevanje z mikrovalovi. Vendar pa povišane temperature pomenijo tveganje za nastanek poškodb ali propadanje predmetov kulturne dediščine, ki vsebujejo veliko različnih materialov. Zato smo preverili, ali segrevanje z mikrovalovi kakorkoli vpliva na tradicionalne površinske premaze.

Preučili smo 7 tradicionalnih premazov, odvzetih s predmetov kulturne dediščine, in deset novo pripravljenih premaznih sistemov, ki se uporabljajo pri pohištvu in umetniških predmetih, kot so: laneno olje, čebelji vosek, sandarak, politura, klejno-kredna osnova, jajčna tempera, oljna barva, lakirana oljna barva ter mat in sijajna posrebritev, ki smo jih nanesli na smrekove (*Picea abies*) in lipove (*Tilia platyphyllos*) vzorce (300 mm × 100 mm × 20 mm) s približno 12 % vlažnostjo lesa. Ocenili smo vizualne, mehanske in kemične spremembe na vzorcih, izpostavljenih v mikrovalovni komori pri moči 750 W in frekvenci 2,4 GHz. Vzorce smo obsevali 10 min pri povprečni temperaturi površine premaza 60 °C ali 80 °C.

Ugotovili smo, da se utrjeni premazni sistemi pri obsevanju z mikrovalovi ne segrevajo neposredno, temveč le posredno zaradi segrevanja lesa. Les se v nasprotju s konvencionalnim segrevanjem s toplim zrakom v notranjosti segreva bolj in s tem sta na površini lesa nižja temperatura in višja vlažnost, kar zmanjšuje tveganje za nastanek razpok lesa in s tem površinskih premazov. Razpok tako pri naši raziskavi nismo zaznali. Segrevanje do 80 °C (/10 min) nekoliko vpliva na spremembo barve (vrednosti ΔE^* od 0,12 do 0,84) in sijaja (od -2,15 od 0,88), vendar so te spremembe tako majhne, da jih s prostim očesom nismo zaznali. Poškodb premazov ter mehanskih in kemičnih sprememb nismo opazili, razen pri segrevanju voska, ki se začne taliti nad 65 °C, in pri premazih, nanesenih na smrekov les, ko smo jih segreli nad 80°C, kjer je ponekod na površino prodrla smola. Za uničenje larv hišnega kozlička (*Hylotrupes bajulus*) je po preliminarnih raziskavah (Klinc, 2016) treba površino lesa segreti od 49 °C do 65 °C in v časovnem razponu od 10 sekund do 10 minut, odvisno od debeline lesa in načina obsevanja, medtem ko glive v povprečju propadejo pri temperaturi okrog 70 °C in času od 5 do 15 min. To pomeni, da je uporaba mikrovalov v večini primerov varna za obsevanje predmetov kulturne dediščine. V ta namen smo testirali novo izvedene premazne sisteme historičnih površinskih obdelav in tudi pri njih ni prišlo do večjih sprememb. Izjemi sta bili oljna barva in oljna barva z lakom iz naravnih smol, kjer prihaja do pokanja in močnega mehurjenja pri en mesec starih vzorcih, medtem ko so se površine, obdelane le z laki iz naravnih smol, samo mehurile, kar je posledica predhodno nepopolno utrjenih premaznih sistemov. Že pri šest mesecev starih in bolj utrjenih premazih so bile namreč opisane spremembe bistveno manjše. Mehurji in razpoke močno vplivajo na oprijem površinske obdelave in odpornost površine proti udarcem ter na sijaj. Prej naštetih poškodb zaradi obsevanja pa ne bi bilo, če bi bili premazi dovolj utrjeni.

Preverili smo tudi vpliv prisotnosti različnih kovin na nastanek poškodb. Mikrovalovi se od kovine odbijajo in kovine neposredno ne segrevajo. Posredno se kovina segreva zaradi segrevanja lesa v neposredni okolici. Tako mikrovalovi ne povzročajo vžigov ali poškodb površinskih premazov zaradi žebljev ali vijakov. Kovine pa lahko vplivajo na učinkovitost zatiranja škodljivcev v predmetu, katerega površino večidel prekriva kovina, ki lahko še povečuje uporabnost obravnavane metode, če predmet obsevamo z nepozlačene/neposrebrene strani. Od pozlate se namreč mikrovalovi odbijajo nazaj v predmet ter ga tako še dodatno hitreje segrejejo.

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