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FULL PAPER

THE USE OF LASERS FOR THE REMOVAL OF SHELLAC FROM WOOD

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The removal of shellac is a common but challenging task in the conservation of wooden artifacts. In this work, experiments were performed to assess the suitability of lasers for cleaning non aged shellac from pine and oak mock–ups. Optimal laser parameters were determined for preserving the integrity of the original wooden substrate during the cleaning process. In particular, the ablation thresholds for shellac and wood were comparatively examined using excimer (248 nm) and Nd:YAG (1064 nm) lasers, emitting pulses of nanosecond (ns) or picosecond (ps) duration. The induced etching and other morphological alterations to the wood surface were assessed. The results obtained provided strong evidence for the existence of a window of optimal laser parameters for the safe and efficient removal of shellac from wood, in a "self-limiting" process.

1 Introduction

This study focused on investigating the use of lasers for the removal of shellac, a typical coating used on historical wooden artifacts.[1-4] In Greece, shellac is the most commonly used coating since the Byzantine period. Shellac is a natural organic resin, excreted by the insect *Laccifer lacca*, indigenous to India.[5] Even though the chemical composition of shellac is complex, the material is commonly referred to as the polyesters formed by the self-esterification of a mixture of hydroxy acids.[1] Shellac contains 70-80% resin, 6-7% wax and 4-8% coloured matter and moisture. It is insoluble in water but soluble in ethanol and acetone.

Shellac coatings often lose their elasticity and mechanical strength when exposed to environmental parameters such as UV light, temperature and RH. Moreover, they lose their glossiness and transparency and become hard and insoluble.[1,5,6]

The common cleaning procedure for shellac in conservation involves the use of laborious mechanical methods or the use of potentially hazardous solvents. As lasers are now routinely employed for the

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removal of organic coatings from various substrates of cultural heritage objects[7-11], this study aimed to identify whether lasers could be applied in the removal of shellac. Two Nd: YAG (1064 nm) and two excimer (248 nm) laser systems, emitting pulses of nanosecond (ns) and picosecond (ps) duration at each wavelength, were used to determine the optimal laser parameters.

2 Experimental

Hardwood (oak-*Quercus robur* L.) and softwood (pine-*Pinus sylvestris* L.) boards were used to prepare three flat mock-ups (13 × 6 × 1 cm) for each species. Two of them were coated by brush (two layers of shellac - 50% w/v in ethanol) on the tangential surface. Coating thickness was up to 35 µm on the softwood sample and up to 25 µm on the hardwood. The third wooden mock-up was left uncoated and was used as a reference for comparative reasons. Prior to laser ablation studies, mock-ups were left to dry for 2 months, in a controlled environment (25 °C, 45% RH).

Mock-ups were irradiated in order to determine the relationships between the ablation rates of materials used, and laser wavelength, fluence and pulse duration. Four types of laser systems were employed (Table 1).

Laser	Wavelength (nm)	Pulse duration	Repetition Rate (Hz)
Nd:YAG	1064	10 ns	10
Nd:YAG	1064	150 ps	2
Excimer KrF	248	30 ns	20
Excimer Dye	248	0.5 ps	1

Table 1: Laser systems employed in this study.

Following a standard set up procedure, the laser beam was passed through a fused silica glass cell. This cell reflected 10% of the beam onto a joule meter, which monitored the energy of each laser pulse, whilst the remaining 90% of the beam was focused by a cylindrical lens onto the mock-up surfaces.

At all wavelengths and pulse durations, various conditions of energy per pulse were received (±2–3%). In order to calculate the various fluence values, the spot size was measured on blank photo paper. It ranged from 0.2 - 0.3 mm^2 for Nd:YAG lasers and 0.1 - 0.2 mm^2 for excimer lasers and its shape was found to be circular. Thus, the fluence range for the infrared laser systems was from 0.2 to 2 J/cm^2 for a 10 ns pulse duration and between 0.2 to 3.5 J/cm^2 for 150 ps. For the ultraviolet laser systems, a higher fluence range was required than that of the Nd:YAG laser, in order to induce any noticeable results on the photo paper. In particular, for the KrF laser, emitting pulses of 30 ns, a fluence range from 0.2 to 5.7 J/cm^2 was employed, while for pulses of 0.5 ps the corresponding range was from 0.2 to 0.8 J/cm^2.

Finally, for all fluences applied on mock-ups, measurements were taken for both 1 and 5 laser pulses (three to four sets for each spot). However, only results obtained by using 1 laser pulse are presented, as 5 pulses produced analogous results with approximately five times the intensity (crater depth and discoloration) and did not affect the ablation threshold of shellac or wood in all tests carried out.

To asses the suitability of laser cleaning on wooden substrates, it is essential to determine the damage threshold for uncoated wooden surfaces (references). In this work, the damage of wood or varnish was considered as any physical change (discoloration, structural modifications etc) observed by scanning electron microscopy (SEM), stereomicroscopy and using a profilometer. By using SEM in particular, it was possible to document the ablation threshold of wood and shellac by physically illustrating the starting point of the interaction between lasers and these materials. The minimum laser fluence for the removal of shellac and for the damage of uncoated wood was determined in order to asses the so called "self limiting effect".[8]

The ablation curves were formed by plotting the crater depth versus the different fluences applied. Crater profiles and depth, on coated mock-ups and references, were measured with a mechanical stylus profilometer (Parthen Mahr – Profilometer S5P) with a 200 µm resolution. This depth was measured in order to examine the quantity and quality of the varnish removal and assess the etching rate in relation to the laser parameters applied.

3 Results and discussion

Results obtained on the ablation rate of shellac irradiated using the four types of laser systems, are presented in figures 1-4.

The results of laser etching depth measurements, as a function of laser fluence (Figure 1-4), showed noticeable differences in the ablation thresholds for shellac and wood. In all cases, shellac was ablated at lower fluences than wood, creating an optimum (self limit) window of fluence energies that could be applied without altering the wooden surface.

In particular, for coated mock-ups, shellac etching occurred at 0.2 J/cm^2 (the lowest fluence applied), for both wavelengths and pulse durations (Figure 5, 6).

Thereby, based on the ablation threshold of wood (Table 2), at 248 nm and ns pulses, a safe limit window of 1.6 J/cm^2 and 0.8 J/cm^2 was set for oak and pine respectively; while for ps pulses the safe limit window was 0.4 J/cm^2 and 0.3 J/cm^2 respectively for oak and pine.

For laser irradiation at 1064 nm (for both ns and ps pulse durations), the ablation threshold of wood started at higher fluences (Table 2).

Thereby, for ns pulses, a safe limit of 1.8 and 1.7 J/cm^2 was set respectively for oak and pine during the laser cleaning operation. In this case, shellac can be gradually removed up to the point where a thin layer of coating remains.

Using the same wavelength (1064 nm) but ps pulses, a narrower window of 1.1 J/cm^2 and 1 J/cm^2 was obtained respectively for oak and pine for the safe removal of shellac, while avoiding surface morphological alterations on wood.

At 1064 nm, pulse duration, played an important role in the etching depth developed (Figures 1 and 2). In particular, it was noticed that for the removal of shellac, and especially for fluences > 1.5 J/cm^2, the shorter the pulse duration (ps) the smaller the crater depth (etching).

The removal of shellac using excimer lasers was slow compared to Nd:YAG and visible only at high fluences. Shellac strongly absorbs the UV light, resulting in a low etching depth and consequently, in a gradual, but slow removal at 248 nm. In contrast, when Nd:YAG laser was applied, a high etching depth was observed which, along with the wide self limit window, allowed fast and controlled removal of resin.

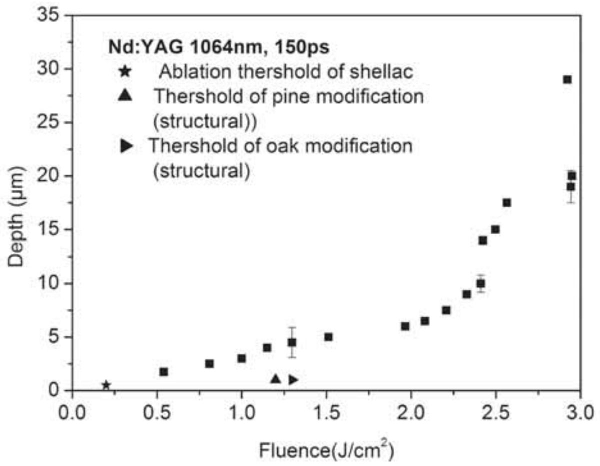

Figure 1: Ablation rate of shellac when irradiated with Nd: YAG 1064 nm, (pulse duration 10 ns). Every datum point is an average of at least 3 to 4 different measurements. The error bars are indicative.

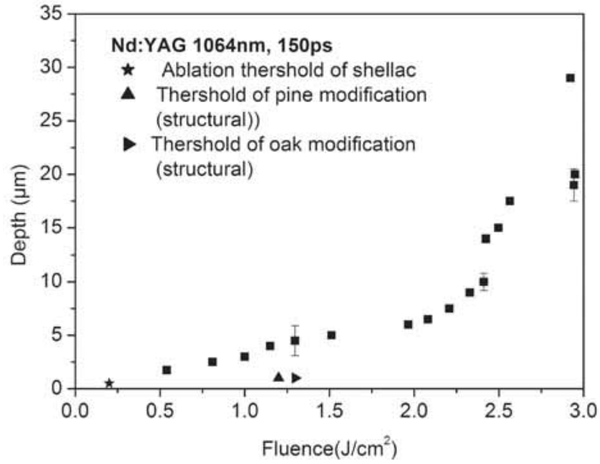

Figure 2: Ablation rate of shellac when irradiated with Nd: YAG 1064 nm, (pulse duration 150 ps). Every datum point is an average of at least 3 to 4 different measurements. The error bars are indicative.

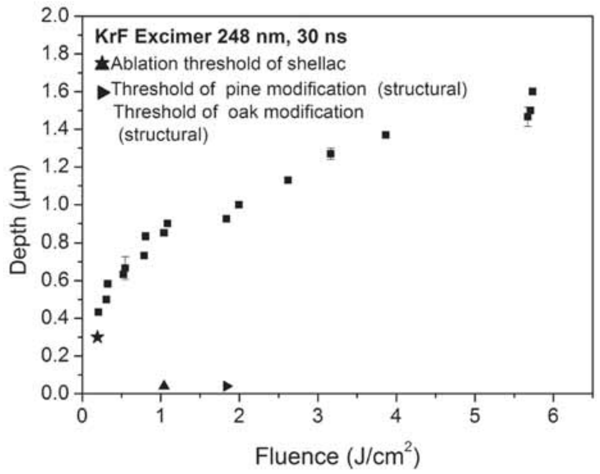

Figure 3: Ablation rate of shellac when irradiated with KrF Excimer 248 nm, (pulse duration 30 ns). Every datum point is an average of at least 3 to 4 different measurements. The error bars are indicative.

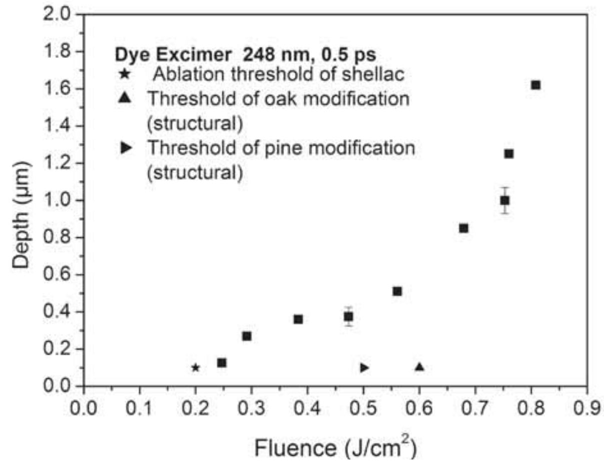

Figure 4: Ablation rate of shellac when irradiated with Dye Excimer 248 nm, (pulse duration 0.5 ps). Every datum point is an average of at least 3 to 4 different measurements. The error bars are indicative.

Above the wood threshold, a noticeable change in the wood morphology was observed, when different wavelengths were used.

Stereoscopic examination of uncoated mock-ups, irradiated at 248 nm, for both ns and ps pulses, showed photochemical alterations to the wooden surface, in the form of yellowing at all fluences applied; while wood etching became visible only at high fluences.

In contrast, at 1064 nm for both ns and ps pulses, no discoloration effects were present; while wood etching became visible at low fluences for ps pulses and at high fluences for ns pulses.

	Ablation threshold of oak	Ablation threshold of pine	Repetition Rate
Laser	(in J/cm2)	(in J/cm2)	(Hz)
Nd:YAG, 1064 nm,10 ns	2	1.9	10
Nd:YAG, 1064 nm,150 ps	1.3	1.2	2
Excimer KrF, 248 nm, 30 ns	1.8	1	20
Excimer Dye, 248 nm, 0.5 ps	0.6	0.5	1

Table 2: The ablation threshold of oak and pine, based on craters depth, for all wavelengths and pulses applied.

However, examination of the same mock-ups by SEM, showed that irradiation with 248 nm caused structural modifications in addition to the photochemical changes (yellowing) observed stereoscopically, for both ns and ps pulse durations, even at very low fluencies (1 J/cm^2 and 0.5 J/cm^2 respectively) (Figure 7, 8).

In summary, it was revealed that at 1064 nm, the self limited window was wider than that observed at 248 nm for both pulse durations. Furthermore, with ps pulse durations a narrower self limited window was obtained than with ns pulses at both wavelengths applied.

Finally, for all wavelengths and pulses applied, the ablation threshold of oak always occurred at higher fluence than pine (Table 2). The higher density of oak ($r_0 \approx 0.62$ g/cm^3)[12] compared to pine ($r_0 \approx 0.46$ g/cm^3)[12], could be an explanation for this difference in fluence required to ablate the two wood species.

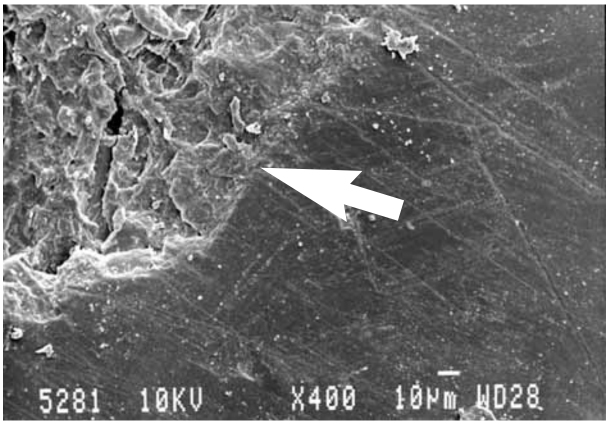

Figure 5: SEM micrograph of spot created (arrowed) on oak coated with shellac with 1 pulse. Fluence: 0.2 J/cm^2. Laser: Nd:YAG 1064 nm, 1 ns. Bar = 10 µm.

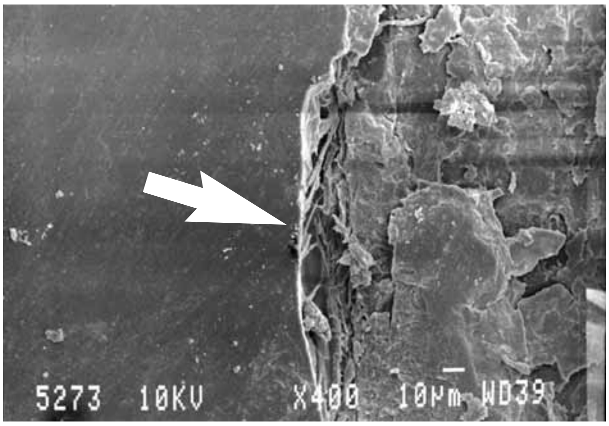

Figure 6: SEM micrograph of spot created (arrowed) on oak coated with shellac with 1 pulse. Fluence: 0.2 J/cm^2. Laser: Nd:YAG 1064 nm, 150 ps. Bar = 10 µm.

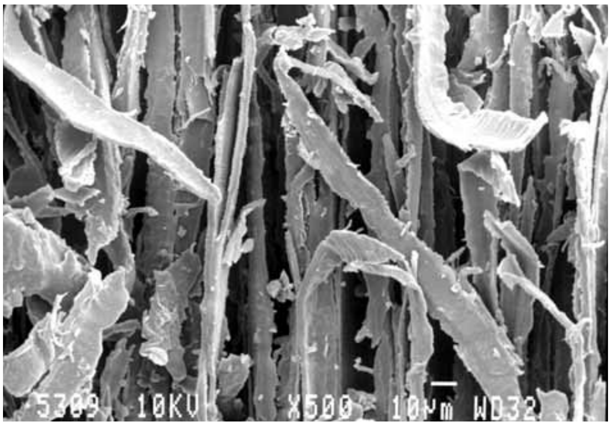

Figure 7: SEM micrograph of spot created on uncoated pine mock-up with 1 pulse. Fluence: 1 J/cm^2. Laser: Excimer 248 nm, 30 ns. Bar = 10 µm.

Figure 8: SEM micrograph of spot created on uncoated oak mock-up with 1 pulse. Fluence: 0.5 J/cm^2. Laser: Excimer 248 nm. 0.5 ps. Bar = 10 µm.

4 Conclusions

The results obtained provide strong evidence for the existence of a window of optimal laser parameters for the safe and effective removal of shellac from wood. This indicates that laser cleaning could be a suitable technique for the removal of shellac varnish.

Stereoscopy and SEM observations revealed that the Excimer KrF lasers used in this work can cause photochemical changes (yellowing) and structural modifications above the wood threshold. In contrast, with Nd:YAG lasers, only structural modifications were observed.

Profilometer results, measuring the laser etching depth, showed that Nd: YAG lasers can ablate shellac faster than excimer. Furthermore, the self limit window with Nd:YAG lasers is wider than that of excimer lasers.

Best cleaning results were achieved using the Nd:YAG laser at 1064 nm and a pulse duration of 10 ns, where shellac could be ablated independently of the wooden substrate. By working with different fluences, a gradual and controlled cleaning of shellac can be achieved, giving conservators the choice of leaving a thin layer of varnish when required.

However, it is important that irradiated mock-ups are subjected to accelerated ageing in further studies. This could provide valuable information on the long term effects of laser cleaning, such as the possible interactions between the shellac and wood during irradiation, which at present, may not be observable using microscopy.

Furthermore, it appears that the fluence required for wood ablation is related to the density of wood species. This physical property depends upon many factors such as the micro-structure of wood (intercellular voids, intercellular canals, size of cells, thickness of cell walls), the width of the annual rings, the percentage of latewood to earlywood, the chemical composition etc. Thus, further work is required in order to better understand how density affects the wood damage threshold. However, knowledge of the wood species used in an artefact may play an important role in designing a laser cleaning method. Additional studies using different wood species are required to confirm this.

Among other factors which may affect the laser cleaning, are possible interactions between the shellac and wood during irradiation, which also require further investigation. Further laser cleaning studies are also in progress to investigate the removal of aged shellac.

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6 References

1. S. Rivers and N. Umney, *Conservation of Furniture*, Butterworth Heinemann, Oxford, 2003.

2. H. Hodges, *Artifacts, An Introduction to Early Materials and Technology*, Duckworth, Great Britain, 1995.

3. F.R. McGiffin, *Furniture care and conservation*, Nashville, American association of state and local history, USA, 1983.

4. G. Richter, *The Furniture of the Greeks, Etruscans and Romans*, Phaidon, London, 1966.

5. W. Xia, L. Jian-Zhang, F. Yong-Ming and J. Xiao-Juan, *Present research on the composition and application of lac,* 2006, 1, 65-69.

6. B.B. Schaeffer, H. Weinberger, and W.M. Howlett Gardner, *Nature and Constitution of Shellac*, Ind. Eng. Chem., 1938, 4, 451 – 454.

7. M.I. Cooper, *Laser Cleaning in Conservation: An Introduction,* Butterworth-Heinemann, Oxford, 1998.

8. C. Fotakis, D. Anglos, V. Zafiropulos, S. Georgiou, V. Tornari, *Lasers in the preservation of cultural heritage,* Principles and applications, Taylor and Francis, 2006.

9. G. Wiedemann, M. Schulz, J. Hauptmann, H. G. Kusch, S. Muller, M. Panzner, H. Wust, *Laser cleaning applied in the restoration of a medieval wooden panel chamber at Pirna*, J. Cult. Her. 2000, 1, 247–258.

10. G. Bounos, A. Nevin, S. Georgiou, C. Fotakis *Laser restoration of painted artworks: Fundamentals, Modeling and Advances*, in: C. Phipps, Ed., *Laser Ablation and its Applications*, Springer Verlag, Berlin Heidelberg, 2007, 549-577.

11. S. Georgiou, V. Zafiropulos, D. Anglos, C. Balas, V. Tornari and C. Fotakis, *Excimer laser restoration of painted artworks: Procedures, Mechanisms and Effects,* Appl. Surf. Sci., 1998, 127-129, 738-745.

12. R. B. Hoadley, *Identifying Wood: Accurate Results with Simple Tools*, The Tauton press, Newtown, USA, 1990.