On the Use of OCT to Examine the Varnish Layer of Paintings Cleaned with an Er:YAG Laser

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Abstract: Optical Coherence Tomography (OCT) was used to visualize and quantify the varnish layer of paintings. And to verify the success of efforts by conservators to remove the varnish using laser ablation. An Er:YAG laser (λ = 2.94µm) with a repetition rate of 15Hz and an optical power of 1mW was used to remove the varnish. A spectral domain OCT system with a Michelson topology was constructed using a broadband super-luminescent diode (λ = 840±25nm). The OCT system provided an 8µm resolution, and a field of view of 5x5mm. Samples, including pigment, varnish and substrate, approximately 1mm^2 in size, were removed from the oil painting, San Giorgio Maggiore by Martin Rico (1833-1908). Varnish thickness obtained from OCT was validated by similar measurements obtained from SEM analysis. Other paintings, including a late 18th century landscape, signed Thomas Gainsborough, were imaged with OCT to compare neighboring regions before and after laser treatment and to examine the layering of the artist's signature in an effort to determine its authenticity. In conclusion, the non-invasive OCT technique is an efficient tool for measurement of varnish layer thickness, for imaging over-paint under varnish layers, and for assessing the effectiveness of laser assisted varnish removal.

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1 PURPOSE

The purpose of this study is to demonstrate that Optical Coherence Tomography (OCT) can be used to:

1) Measure the varnish layer thickness of paintings, and
2) Verify that the varnish layer has been removed after laser ablation-based conservation without causing changes to the paint layers.

2 INTRODUCTION

To restore the original intent of the artist, art conservation is moving towards an increased use of laser ablation to remove varnish layers, which have become encrusted with contaminants or have been otherwise altered over the years (Asmus, 1986); Maravelaki et al., 1997); Georgious et al., 1998); Kalaitzaki et al., 1999); Scholten et al., 2000); (Klein et al., 2000); (De Cruz et al., 2000); (Branco et al., 2003); (Pouli et al., 2008). It should be possible to guide the restoration process with imaging modalities that provide information about the varnish layer. In paintings where the encrustation has rendered the varnish completely opaque, OCT has the potential to provide details about the structure and thickness of the varnish layer in a non-invasive manner (liang et al., 2005); (Gora et al., 2006).

3 BACKGROUND

Optical coherence tomography enables fast, noninvasive, high resolution, three-dimensional imaging of the internal microstructure of weakly scattering objects. Conventional OCT systems are coherence-gated interferometers wherein the optical measurement technique known as low coherence interferometry is used to measure the magnitude and echo time delay of backscattered light. In its simplest manifestation, time-domain OCT (TDOCT), the illumination is split and sent to both a

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reference arm and to the sample. Light returning from the sample interferes with light returning from the reference arm, and interference fringes are observed provided that the reference and sample path lengths are matched to within the coherence length of the source. Scanning the reference path length results in a series of interference fringes that correspond to different depths in the sample. The photo-detector signal is demodulated to reconstruct each A-scan (Figure 1).

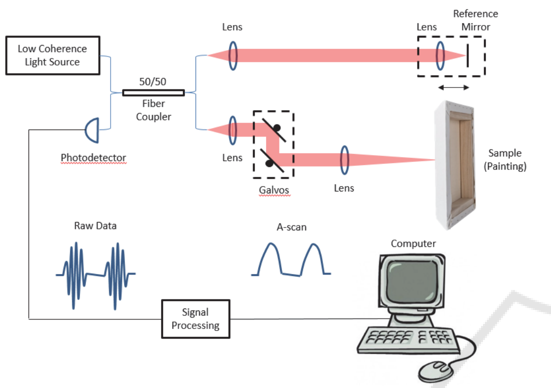

Figure 1: Schematic of a fiber optic TDOCT system. Light blue lines represent fiber optic paths, red lines represent free space optical paths, and thin black lines represent electronic signal paths.

Further, prior work (Figure 2) has shown that using lasers for art conservation offer advantages over conventional methods with solvents and scalpels (Asmus, 1986); Maravelaki et al., 1997); Georgious et al., 1998); Kalaitzaki et al., 1999); Scholten et al., 2000); (Klein et al., 2000); (De Cruz et al., 2000); (Branco et al., 2003); (Pouli et al., 2008). Some contaminants and encrustations require very strong solvents or cannot be removed with a solvent without removing some of the paint itself. Moreover, solvent may saturate the substrate, causing it to swell, materials (from the substrate) may leach into the solvent, and the conservator may be exposed to toxic fumes from the solvent. A brief explanation of the laser cleaning mechanism follows.

The Er:YAG laser, with a wavelength of 2.94 μm, coincides with a strong absorption peak in the infrared spectra of OH- or NH-containing organic molecules. The energy of photons at this wavelength excites a bond vibrational stretching mode. Any substance containing a high concentration of OH bonds at its surface has a strong affinity for photons at 2.94 μm, and confines the absorption of these photons to a surface depth of no more than a few microns. A painting 's organic contaminant, which either contains the OH bonds or has been treated with a thin liquid film (water, alcohol, NH_4^+, OH^-) immediately before lasing, acts as a stain of relatively high concentration and very high absorption, providing a natural barrier to energy penetration into underlying layers.

The energy per photon of the Er:YAG radiation is not sufficient to break bonds. The energy required for OH bond dissociation in most organic molecules ranges from 3.4 to 4.5 eV/molecule, while photons of 2.94 μm wavelength have an energy of only 0.4 eV. Furthermore, the irradiance of the laser is below the level required to generate multi-photon effects, which might provide the necessary dissociation energy. The temperature rise due to cleaning with the Er:YAG is principally limited to the affected contaminant volume and reaches its vaporization maximum of under a 100 °C for a few milliseconds at most. The bulk of the laser energy goes into the ejection of the heated contaminant from the paint surface. The temperature rise in the underlying paint layer is therefore small, and not sufficient to cause thermal decomposition of most materials. As a comparison, surface consolidation or the lining processes often involve heating of the paint layer too much higher temperatures for much longer time periods.

The process as used (with adjustable moderate pulse energies at a 15 Hz repetition rate) volatilizes greases with high vapor pressure and can thus be pictured as a type of steam distillation. Because of the strong absorption, the photon energy is deposited in a layer that is only a couple of microns thick on the targeted surface. This energy goes into near-instantaneous heating of the absorbing contaminant through the vaporization of water or grease. The rapid attendant rise in local pressure causes the affected volume to be ejected forcefully from the surface, taking much of the heat with it. As a result, the underlying non-absorbent film does not undergo significant heating, as estimated in a previous paper (De Cruz et al., 2000); (DeCruz et al., 2014).

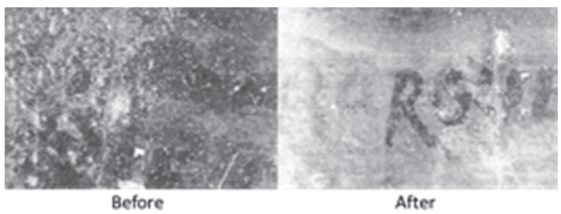

Figure 2: Micro-photo of the signature from an oil painting, The Turkish Noble, by Charles Bargue (1825-1883), date: 1859, showing part of the painter's signature before and after laser treatment.

4 METHODS

In this study, OCT was used to visualize and quantify the varnish layer of paintings. And to verify the success of efforts by conservators to remove the varnish layer using laser ablation. A free-running Er:YAG (MonaLaser, Orlando, Florida) laser with a central wavelength of 2.94 µm, a repetition rate of 15 kHz and an optical power of 1 mW was used to remove the varnish. The IR light couples directly into a 1-mm bore hollow glass fiber about 1-m long. The other end of the fiber can be manipulated like a pen.

A spectral domain OCT (SDOCT) system with a Michelson topology was constructed using a broadband super-luminescent diode (SLD-371, Superlum, Carrigtwohill, Ireland) with a central wavelength of 840 nm and a 50 nm bandwidth and a line scan CMOS sensor (AViiVA, e2v Inc., Milpitas CA) with a 20 kHz line rate. The sample arm design utilized a 4f relay between the first and second galvanometer (scanner) and a telecentric beam delivery system to minimize optical distortions. The OCT system provided an 8.5 µm axial and 7.5 µm lateral resolution, a sensitivity of 105 dB, an imaging range of 0.8 mm (6dB fall off) and a field of view of 5 x 5 mm (Figure 3).

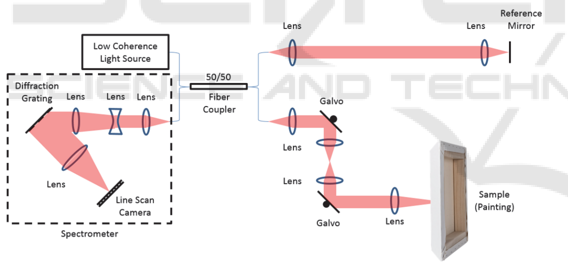

Figure 3: SDOCT system with Michelson topology. SDOCT permits faster image acquisition and higher signal-to-noise ratio than the predecessor TDOCT technology. Through the use of spectral interferometry, depth information is collected without movement of the reference mirror. Backscattered light from the sample and reference interfere, and the broadband interference pattern is measured with the inverse Fourier transform of the broadband interferogram. Thus, measurements of the power spectral density of the interferogram as a function of wavelength are obtained. Since the temporal coherence function (also called the autocorrelation function) and the power spectral density form a Fourier transform pair (Wiener-Khinchin theorem), the A-scan can be reconstructed by merely taking the inverse Fourier transform of the broadband interferogram.

Samples, including pigment, varnish and substrate, approximately 1 mm^2 in size, were removed from an oil painting on panel (San Giorgio Maggiore) by Martin Rico (1833-1908) and imaged using Environmental Scanning Electron Microscopy (ESEM). Varnish thickness obtained from OCT was validated by similar measurements obtained from ESEM.

In addition, other paintings, including a late 18th century landscape, signed Thomas Gainsborough, were imaged with OCT to compare neighboring regions before and after laser treatment and to examine the layering of the artist's signature in an effort to determine its authenticity.

Two Bioptigen Envisu SDOIS (Spectral Domain Ophthalmic Imaging System) systems were also used: 1) R3500 2) R2300. The two systems utilize different sources and spectrometer designs, but both permitted visualization of varnish and paint, at different depths. The 2300 has a lower imaging depth but higher axial resolution, whereas the 3500 can image deeper with a slightly lower resolution. In addition, the 2300 system has an 840 nm SLED, whereas the 3500 has a 1064 nm SLED.

5 RESULTS

The painting San Giorgio Maggiore, Venice, by Martin Rico (1833- 1908) with the signature, Rico in the painting's lower left corner is covered by discolored varnish (Figure 4). In the lighter areas, the discolored yellow-orange varnish has been removed with laser ablation.

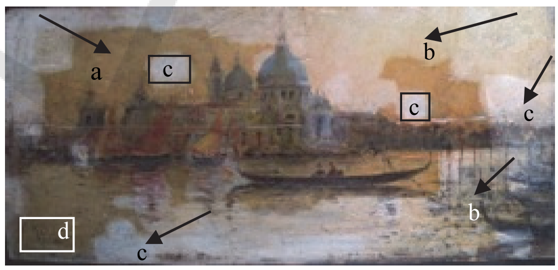

Figure 4: San Giorgio Maggiore, Venice. Martin Rico (1833-1908), oil on panel, 6x12" circa 1890; a) varnished surface before cleaning; b) partially removed varnish; c) surface with varnish completely removed; d) the signature Rico covered by varnish.

The shallow penetration of the laser pulse enables the conservator to remove varnish layers gradually and this difference of thickness is illustrated in area b in Figure 4: the varnish layer, microns thin, can be imaged and measured by OCT (Figure 6).

In figure 5, the OCT scan of the painting layers with near-infrared light creates a cross-sectional view as well as an *en face* projection of the surface. The structure of the paint surface and the varnish layer are clearly visible with the Envisu SDOIS R3500. The first bright layer is the varnish-air interface. The second bright layer is the varnish-pigment interface. The black space in between is the varnish itself, measured in one location using on screen calipers as 65µm. The regions of differing varnish thickness correspond to the variable texture of the paint. Basically, in areas where the texture of the paint made a void or valley, more varnish is present (i.e. the varnish layer is thicker) and vice versa in regions where the texture of the paint made a mound or hill (Figure 7).

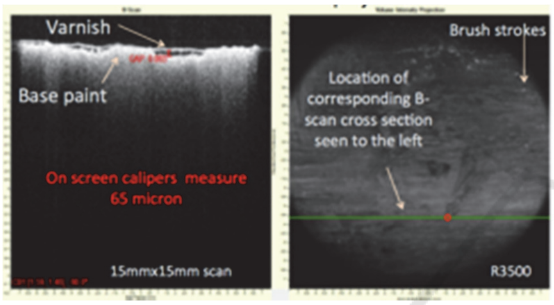

Figure 5: OCT B-scan (left) and volume intensity projection (VIP) of San Giorgio Maggiore acquired with the 3 µm axial resolution SDOIS R3500.

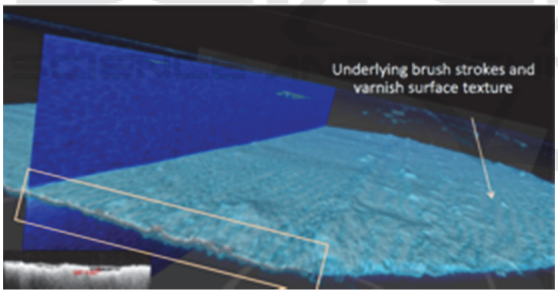

Figure 6: 3D rendering of the San Giorgio Maggiore illustrating the underlying brush strokes and varnish surface texture.

The 3D view (Figure 6), corresponding to the images shown in Figure 5, confirms distinct differences between varnish and paint layers.

The thinning of the varnish layer is confirmed in Figure 7. The thickest layer of varnish is 64.3 µm. In the thinnest regions, the varnish is only 9.6 µm thick.

Interesting results were obtained of the signature Rico in Figure 8 located in the painting's lower left corner, which is covered with a thick layer of discolored varnish.

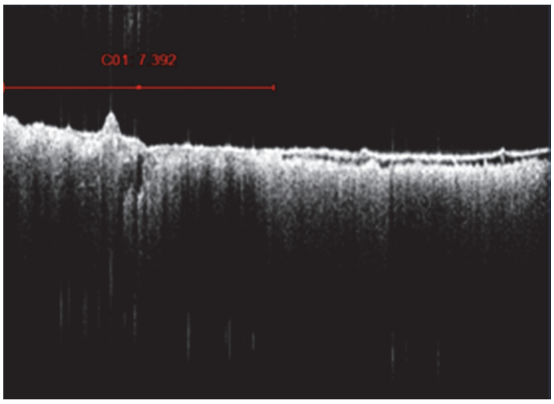

Figure 7: Detail, Rico painting, area b of Figure 4. Left is the thinned partially removed varnish layer (after laser cleaning) and right is the varnish surface before laser ablation.

The shallow depth of penetration of the Er:YAG laser pulse at 2.94µm is demonstrated in figure 9 The texture of the paint is preserved after lasing, with no visible damage to individual brush strokes. To the left in figure 9 is the varnish layer over the paint. The right is the painting surface with the varnish removed by laser ablation.

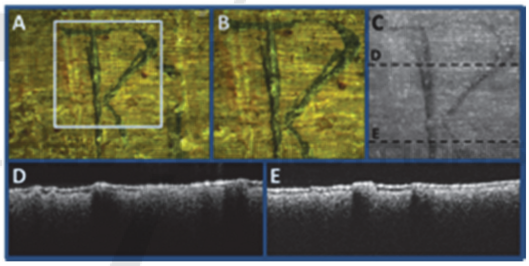

Figure 8: Images of the signature on an oil painting on wood 19th century Venetian landscape panting by Rico. Microscope images of the R in the signature acquired at 4x magnification (A), close-up of R indicated by the light blue box (B), OCT SVP of the same region shown in B (C), OCT cross-sectional images show the layer of paint under the varnish layer and over the painting's surface (D & E) acquired along the dotted lines shown in C.

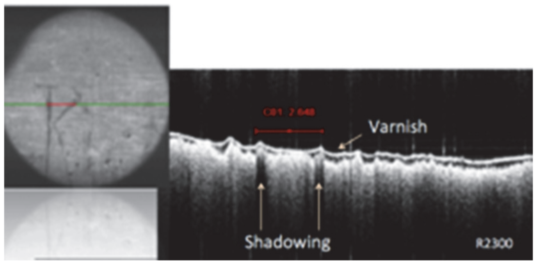

Figure 9: Layers of darker pigmented paint can be distinguished from subsurface paint layers (different optical scattering and absorption properties), as well as the presence of a distinct varnish layer. SDCIS R2300.

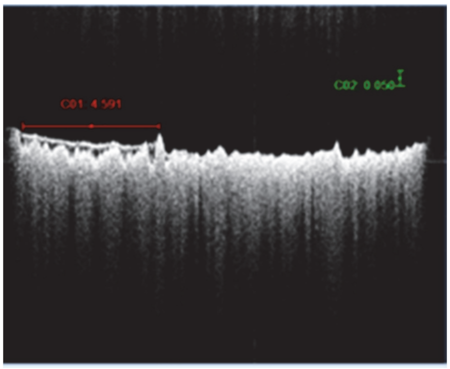

Figure 10: Detail of the varnish and paint surface of Rico painting. Image taken with Bioptigen Envisu SDCIS R2300.

SEM images before and after laser ablation are reported in Figure 11. They were taken to verify the accuracy of the OCT measurements as well as the ablation efficiency.

The varnish layer thickness, on the left of Figure 11, was measured in three locations with the following results: 13.09 µm, 11.87 µm and 13.24 µm. In the image acquired after Er:YAG laser varnish removal, on the right of Figure 11, the surface of the paint appears devoid of varnish, and the texture of the surface of the painting appears fluid-like with pockets of smoothed areas

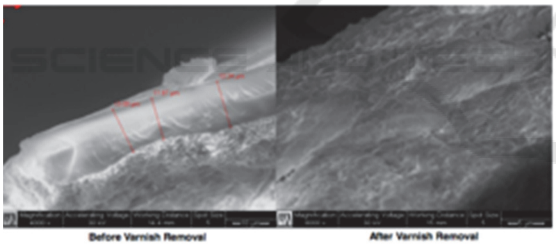

Figure 11: ESEM images before (left) and after (right) varnish removal. Note, ESEM imaging required removal of a small (approximately 1 mm^2) portion of the painting. Visible under the varnish layer before varnish removal is the paint layer.

Varnish layer thickness was 10.8 ± 3.8µm and 12.7 ± 0.7µm measured by OCT and ESEM respectively. Complete varnish layer removal was observed in several regions of the paintings after laser treatment with occasional residual varnish in regions of significant surface topological variation. Additionally, the presence of over-paint and differences in penetration depth were observed in the OCT cross-sections (Figure 7).

In Figure 12, the summed voxel projection (SVP) (top) shows ablation craters in the varnish layer on the left. In addition, the corresponding OCT cross-sections taken at locations 1-3 (bottom) are shown. Notice that there is less varnish with each retreating edge of the varnish layer (from 1 to 3), which has been removed with the Er:YAG laser in each cross-section.

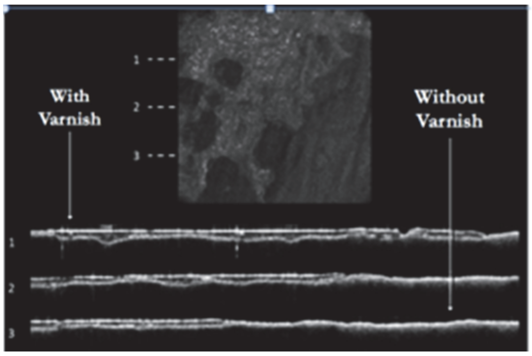

Figure 12: A late 18th century landscape, signed Thomas Gainsborough, imaged in a region with and without varnish.

6 CONCLUSIONS

We believe that this is the first demonstration of the application of OCT to show that the varnish is removed by Er:YAG laser treatment. Given the apparently preserved texture of the underlying pigment after laser treatment, these results suggest that the laser radiation does not penetrate significantly into the paint layer.

In conclusion, we demonstrated that OCT may provide a non-invasive technique that offers measures of the varnish layer thickness and verification of its removal after laser ablation-based conservation efforts.

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