THE INTRODUCTION OF LASERS AS A TOOL IN REMOVING CONTAMINANTS FROM PAINTED SURFACES

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Abstract: *We have demonstrated the safe removal of contaminants from painted surfaces using a pulsed Er: YAG laser at 2.94 µm, avoiding solvent saturation of the paint film. A hollow waveguide coupled to the laser allows fine control of moderate-energy pulse delivery to the targeted surface. Spectroscopic analysis of the ablated material indicates that no pigment is removed in the cleaning process.*

Résumé: *Nous avons démontré avec succès une méthode sans risque pour retirer les contaminants des surfaces peintes en utilisant un laser Er: YAG à 2,94 µm, qui épargne le film de peinture de toute saturation en dissolvants. Un guide d'ondes creux couplé avec le laser permet de contrôler minutieusement l'envoi, sur la surface ciblée, de pulsations à énergie modérée. Une analyse spectroscopique du matériel ôté indique qu'aucun pigment n'est supprimé lors de l'opération.*

Introduction

Ever since Stolow, Feller and Jones [1] first defined the chemical and physical processes which endanger oil paint films when natural resin and synthetic varnishes are removed by aromatic solvents, conservators have been aware of the problems surrounding the cleaning of paint surfaces. All varnish layers discolor and yellow over time, obscuring the color surface. This problem is compounded when the original color surface has been overpainted or covered with media which dry to form films of long-chain hydrocarbons (25 units or more), or when soot, dust, or wax are embedded in the paint matrix of a surface that has never been varnished.

As de Cruz first wrote in 1979 [2], when power, exposure time, pulse width, repetition rate and wavelength have been properly selected for specific paint surface encrustations, lasers can safely remove varnish and overpaint without endangering the oil paint film. Theoretically, the ability of a laser to remove inorganic and organic substances at a wavelength of 2.94 µm has been known for fifteen years [3], while the ArF-Excimer laser's ability to remove organic contaminants at 193 nm was demonstrated by Adele de Cruz and Stephen Trokel in experiments performed in April, 1995.

Because the laser beam is almost monochromatic, it is possible to excite specific molecular entities in a mixture while leaving others unaffected. Objections to the use of lasers have been centered around the cumulative thermal effects of the pulse on the organic paint film. This objection is valid when purely heating effects are used to remove contaminant layers. We demonstrate the success of safe laser removal of contaminants from paint films with the proper wavelength [4], and describe the interactions of photons with the contaminants in the ablation process.

From the various problems encountered in the use of lasers in art conservation to date, it is clear that the proper choice of lasing parameters is crucial in determining the ultimate utility of the laser as a conservation tool. For example, the tests with the Excimer ArF_2 ultraviolet laser at 193 nm showed that it removes hydrocarbons in shallow layers extremely well, allowing the operator to exert fine control over ablation depths. However, its use in conservation presents three major difficulties: 1) the 193 nm photons are ineffective if inorganic salts are present in the contaminant; 2) there is no reliable delivery system currently available that is compatible with the conservator's needs; and 3) the high energy of UV photons has the potential for introducing a photochemical reaction in the paint surface once the contaminant layer has been penetrated.

In the infrared, the CO_2 laser at a wavelength of 10.6 µm removes organic substances effectively by burning them away; unfortunately, the areas adjoining the targeted region are potentially damaged by the heat carried to them through thermal diffusion. The Nd: YAG laser wavelength of 1.06 µm has a strong affinity to calcium sulfate deposits, which are inorganic. Since the degradation of marble and stone is primarily an inorganic process, the Nd: YAG has been shown to be quite useful in the cleaning of sculptures. However, its high power and deep penetration make it unsuitable for the more delicate requirements of painting surfaces, where the cleaning process is generally targeted towards organic substances such as varnish and soot.

Experiments and results

We therefore sought a wavelength which provided greater promise in the safe removal of hydrocarbons from the surfaces of art works. Our work was done with a pulsed Er: YAG laser [5], which emits radiation at 2.94 µm in the mid-infrared. This choice of wavelength has long been theoretically motivated because of several characteristics which make it an ideal candidate for the cleaning of delicate painted surfaces.

1) 2.94 µm corresponds to a strong absorption peak in the infrared spectra of OH- or NH-containing organic molecules. The energy of photons at this wavelength excites bond vibrational stretching modes. 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 [3]. 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.

2) The selectivity of laser absorption due to the strong absorption peak makes the use of 2.94 µm radiation effective even at relatively low pulse energies, generally between 5 and 20 mJ/pulse. For a spot size of 1 mm diameter, this corresponds to an irradiance of approximately 2.5-10 kW/cm^2.

3) The energy per photon of the Er: YAG radiation is not high enough 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 3 µm wavelength have an energy of only 0.4 eV. Furthermore, the irradiance of the laser is too small to allow for multi-photon effects, which might provide the necessary dissociation energy.

4) The process as used (with adjustable moderate pulse energies at a 10 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 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 [3], and 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. The underlying non-absorbent film does not undergo significant heating because the photon energy does not penetrate past the ejectum layer.

5) The highly reliable and safe Er: YAG laser is commercially available. For relatively low-energy pulses, good delivery systems (hollow glass waveguide, articulated arm) have been developed and provide essential control of laser action on the surface to be cleaned.

The characteristics of 2.94 µm radiation described above are especially important for the safe cleaning of sensitive paint surfaces. For the small pulse energies employed, the selectivity of the absorption protects the paint while targeting the contaminants to be removed. The ablation process is confined to very thin surface layers, so that in cases of multiple varnish films, for example, layers can be removed one at a time with good control.

The advantage of this technique over the sole use of solvents is clear, especially where the nature of the contaminant requires substantial solvent strength and cleaning endangers the substrate through saturation, swelling and leaching. A 14th-century-style Italian Madonna we have treated with the Er: YAG, for example, has multiple layers of natural resin varnish on extremely delicate films of egg tempera and gold on gesso ground. The solvent strength required to remove the varnish traditionally causes penetration into the gesso and subsequent weakening and abrasion of the paint and gold layers. At modest pulse energies the laser does not affect the paint or the gold (metals in general reflect almost 100 % of infrared radiation), but cleanly removes the varnish with very light pretreatments of isopropyl alcohol (see Figs. 1-3).

Because of space constraints, we give a detailed report of the cleaning results from only one representative work here. Our example is a 1859 French painting entitled the « Turkish Noble (Bashi Bazouk) », dated and signed by Bargue. The piece measures 11.5 x 16.5 cm and is oil and bitumen on academy board (Fig. 4, before cleaning).

The painting was covered with a natural resin varnish to which oil and bitumen had been added. Bitumen was also present in the oil colors. As the gases escaped from the oil-rich color surface during the drying process, the varnish layer contracted, turning amber and opaque. The resulting alligator-skin-textured surface of the varnish layer obscured the paint and especially the signature, of which only the number "59" was faintly visible. Various solvents in which the varnish was partially soluble were tested, but were found to soften and abrade the paint on penetration. We therefore proceeded to laser-clean the painting.

Figure 1: 14th-century-style Italian Madonna by an anonymous artist. The right half of the painting has been laser cleaned. On the left the brownish resin covering the paint surface can be seen.

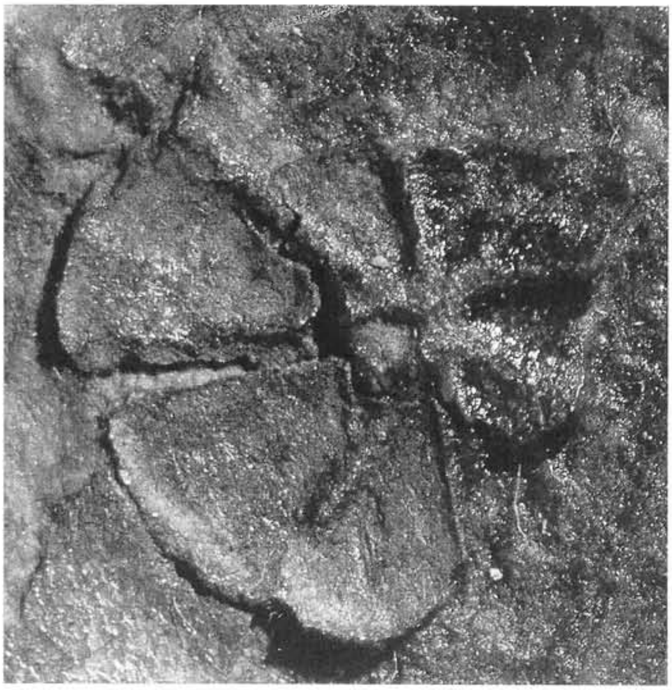

Figure 2: Detail of gold-covered punch work on the halo of the Madonna, before cleaning.

Figure 3: Same detail after laser cleaning. The delicate gold leaf is undamaged by the laser.

The surface of the varnish was lightly moistened with ethanol and then exposed to laser pulses of about 9 mJ energy (corresponding to an irradiance of about 4.6 kW/cm^2) at the rate of ca. 700 pulses/cm^2. Some of the varnish volatilized and was deposited on the glass coverslip used to protect the hollow fiber [5]; the remainder of the varnish residue was safely removed from the surface with an alcohol-moistened swab. After various tests we found that the introduction of the ethanol before lasing was unnecessary, as the pulse energy was effectively absorbed by the untreated contaminant. Fig. 5 shows the cleaned painting. Figs. 6 and 7 illustrate the results of cleaning for a detail of the foot. The uneven varnish surface before cleaning is clearly visible in Fig. 6. The texture of the paint is preserved after lasing, with no visible damage to individual brush strokes. Figure 8 shows part of the painter's signature before and after laser treatment. A spectro-

Figure 4: The « Turkish Noble » (Bargue, 1859), before cleaning. The varnish has partially obscured the color surface and has a rough, alligator-skin texture.

Figure 5: The « Turkish Noble » after laser treatment.

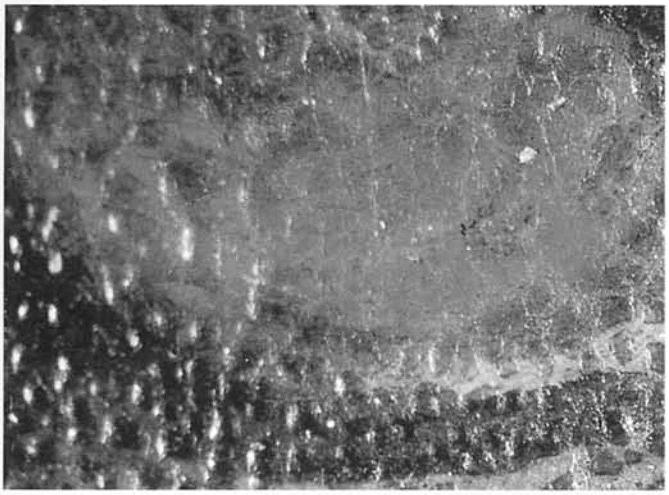

Figure 6: Detail of the slipper in the « Turkish Noble », before cleaning. Again, the uneven varnish texture is clearly visible.

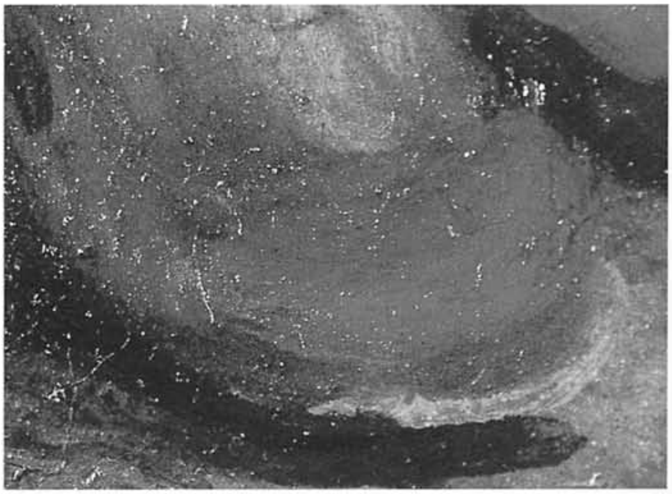

Figure 7: Detail of the slipper after laser cleaning. The varnish has been removed; the delicate red pigment is undamaged.

Figure 8: Part of the painter's signature before and after laser treatment.

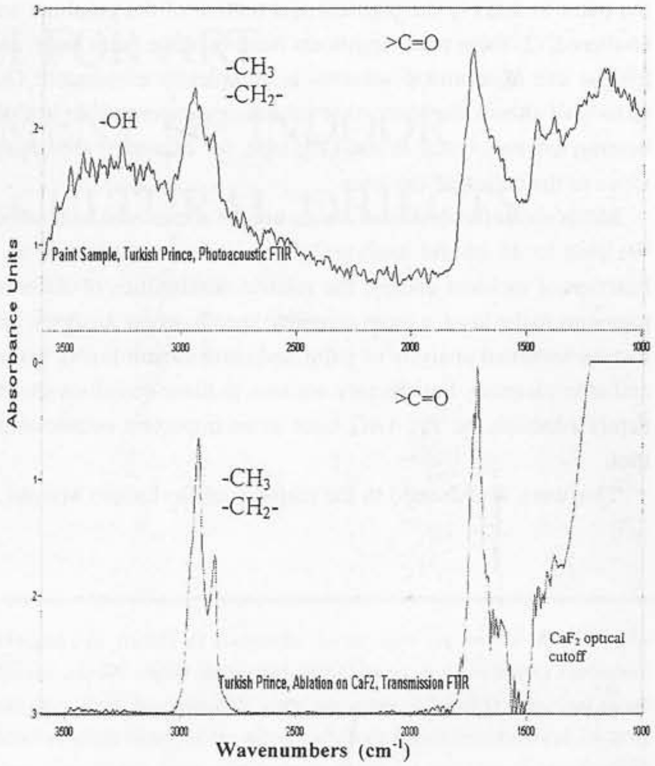

Figure 9: Photoacoustic spectrum of uncleaned paint sample (top) and phototransmission spectrum of ablated contaminant (bottom) from the « Turkish Noble ». The mid-IR bands in the excised paint sample correspond to functional groups (-CH_2-, -CH_3, -COOH) found commonly in soot, tars, and varnishes. The spectrum of the laser-ablated material contains these same organic moieties corresponding to surface treatments and contaminants with an apparent loss in hydroxy content. Analysis of the aliphatic region in the ablated material spectrum indicates a hydrocarbon chain length of about 20 carbon units. *(Courtesy of G.D. Smith, E.B. Phifer, and R.A. Palmer, Dept. of Chemistry, Duke University.)*

scopic examination (see below) of the ablated debris collected on the coverslip indicates that no pigment is removed in the laser cleaning process.

The temperature rise due to cleaning with the Er: YAG is principally limited to the affected contaminant volume and reaches its vaporization maximum of over 100 °C for a few milliseconds at most [6]. 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 lining processes often involve heating of the paint layer to much higher temperatures for much longer time periods.

The ejection of contaminants from the surface onto small microscope cover slips provides ideal samples for examination using transmission spectroscopy. For comparison, small uncleaned pigment samples taken from the paintings were tested with photoacoustic spectroscopy. Both spectroscopic methods yield equivalent infrared transmission spectra [7]. In comparing the spectra we find that, while the pigment samples reveal complicated structure over the whole spectral range, the ejected contaminant has two isolated peaks corresponding to organic moieties consistent with surface treatments, with no indication of the complex structure seen in the pigments (see Fig. 9). We conclude that no pigment is removed in the ablation process. As an additional check, much of the cleaning is done under a stereoscopic microscope, with which any change in surface texture is carefully monitored. We see no effect of the laser on fine brushwork or other small surface details.

Conclusion

In conclusion, the work we have done thus far in Er: YAG laser cleaning of painted surfaces indicates that our method is safe for the paint in that (1) the pigment and texture of the paint are left unaltered, (2) there is no significant heating of the paint layer, and (3) the use of aromatic solvents is completely eliminated. Our tests have shown, however, that substances impermeable to OH-bearing solvents (such as masking tape, for example) are impervious to the action of the laser.

Much about the details of the technique remains to be studied. We plan to do careful analyses of the surface temperature as a function of incident energy, the relative sensitivities of different pigments to the laser, a more complete spectroscopic analysis, and a cross-sectional analysis of paint and contaminant layers before and after cleaning. Satisfactory answers to these questions should firmly establish the Er: YAG laser as an important conservation tool.

This work is dedicated to the memory of Dr. Lazaro Mandel.

Acknowledgements

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Notes and bibliography

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[3] Wolbarsht, Myron L. «Laser Surgery: CO_2 or HF» IEEE Journal of Quantum Electronics, **QE-20** (1984), pp 1427-1432.

[4] The laser-cleaning technique described here is the subject of a patent pending: U.S and International Patent Serial No. 09/151, p. 161

[5] Model «Conservator 2940», Schwartz Electro-Optics, Orlando, FL, coupled into a hollow glass wareguide made by J.A. Harrington, Rutgers University, Piscataway, NJ.

[6] The Er: YAG emits pulses of approximately 250 µs duration (depending on pulse energy), each consisting of a train of about ten 1-2 µs micro-pulses.

[7] To verify this, photoacoustic as well as transmission spectra were obtained for some of the slides containing contaminant, and were found to be identical