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Recent Studies of Laser Science in Paintings Conservation and Research

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CONSPECTUS

The removal of aged and deteriorated molecular overlayers from the surface of paintings is a delicate and critical intervention in Cultural Heritage (CH) conservation. This irreversible action gets particularly complicated given the multitude of materials that may be present within a painted work of art (often in ultrathin layers or traces), as well as the exceptional sensitivity of the original surfaces to environmental conditions such as heat, light, and so on. Lasers hold an important role among the available cleaning methodologies, as they enable high control and accuracy, material selectivity, and immediate feedback. Still, prior to their implementation, it is imperative to optimize the cleaning parameters, so to ensure that any potential implications to the remaining materials are minimal and well understood.

Toward this aim, research at IESL-FORTH is focused on both refining and continuously updating the laser-cleaning protocols (by introducing novel laser technologies into the field, i.e., ultrashort laser pulses), as well as on investigating and studying the nature and extent of laser-induced physicochemical alterations to the involved materials. In this Account, extended work for the understanding of ultraviolet (UV) laser ablation of polymers is presented. Emphasis is placed on the use of model systems (polymers doped with chromophores of known photochemistry) to examine the in-depth laser-induced modifications at the processed surfaces and thus to illustrate the dependence of their nature and extent on laser parameters and material properties.

Furthermore, studies for the potential use of femtosecond UV pulses to overcome certain limitations involved with the nanosecond ablation of molecular overlayers from CH surfaces are highlighted. In particular, it is demonstrated that in the femtosecond regime any chemical modifications are, qualitatively and quantitatively, highly defined, limited and nearly independent of the material properties, such as the absorptivity and the degree of polymerization/molecular weight. Thus, they can be highly potent in the treatment of molecular substrates, enabling new material processing schemes that have not been possible with nanosecond laser technology, as for example, processing of ultrathin varnish layers.

Finally, a sensitive indicator is introduced to elucidate the extent of any photochemical or structural modification induced at the substrate on the process of the laser-assisted removal of overpaints. A realistic scenario of an overlayered modern painting is simulated by a sensitive polymer film covered with acrylic paint. The indicator is doped with photosensitizers of known photochemistry and strong fluorescence emission, which allow the employment of laser induced fluorescence (LIF) for the detection of any chemical modifications generated into the substrate during laser cleaning. In addition, nonlinear microscopy techniques are successfully employed to examine the extent of these modifications. The suggested methodology is proven to reliably and accurately detect potential changes, and thus, it can serve as a monitoring tool to fine-tune the cleaning protocol and safeguard the original painting.

Introduction

Cleaning of unwanted surface layers is one of the most critical interventions in Cultural Heritage (CH) conservation. Aiming to enhance the aesthetics and appearance of the artwork, to reveal hidden details or information, and eventually to prolong its life, the conservator interacts directly and irreversibly with the cultural material and thus exceptional control and selectivity are required. Among the cleaning methodologies, lasers hold an impor-

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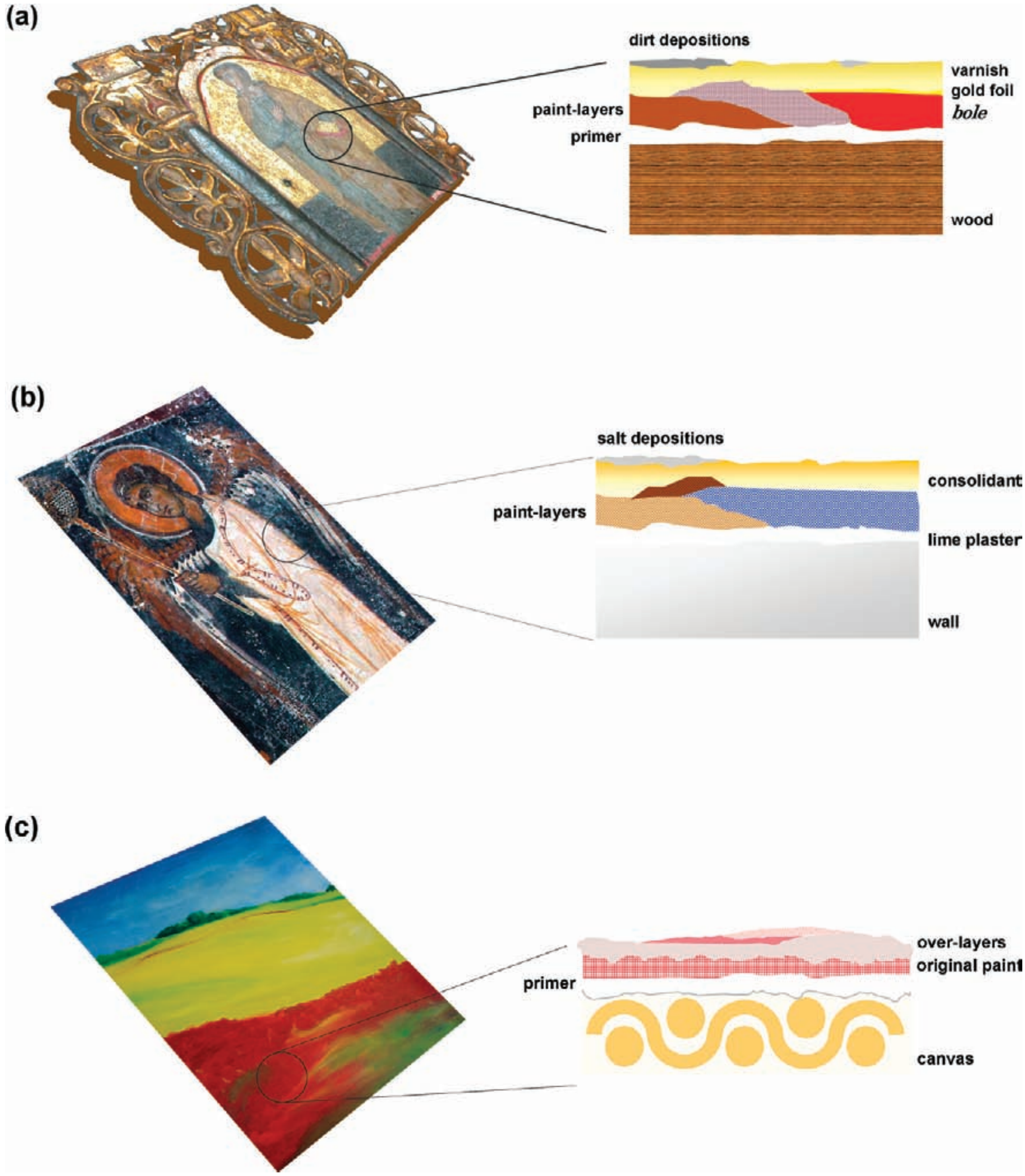

FIGURE 1. Cross-sectional representations of cleaning issues in paintings: (a) cleaning of superficial pollutants and degraded layers on wood-panel icon with gilded decorations; (b) removal of consolidation coatings and salt deposits on fresco wall painting; (c) contemporary painting with several retouching layers which cover the original surface.

tant role, as they enable high control and accuracy, material selectivity, and immediate feedback. Their wide implementation was initially held back due to skepticism originating from the complexity of the involved photosensitive materials, the irreversibility of the intervention, and restrictions in testing on authentic surfaces. Nevertheless, previous knowledge from similar simpler systems, extensive studies on model samples, and technological breakthroughs addressed successfully these challenges, inspired new approaches, and established lasers as highly effective and versatile tools in everyday conservation practice.[1−6]

In the context of paintings restoration, which is the subject of this Account, removal of aged varnish layers, past consolidation treatments, and overpaints are commonly encountered conservation issues. These cases, given the sensitivity of the substrate and the requirements for controlled and selective material removal, call for particular attention.

A typical painting (Figure 1) consists of a number of paint layers having a thickness in the order of tens of micrometers. These can be made of inorganic pigments dispersed in organic media (oil, egg-tempera, etc.) or organic dyes and are usually found on a rather thick primer or ground layer that has been applied to a support (canvas, wood-panel, wall, parchment, etc.). Metal foils (i.e., gold) may also be adhered to the painted surface as decoration.

In their majority, paintings are covered with natural or synthetic varnishes mainly for protective reasons, as well as to enhance colors and to improve their appearance[7,8] (Figure 1a). Their thickness ranges from 10−50 μm, while cases of ultrathin layers (<10 μm) have also been encountered. Natural varnishes derive from tree resins (mastic, copal, and later dammar), contrary to the synthetic ones which are manufactured by processing of organic compounds to obtain enhanced properties. Moreover, synthetic polymer-based coatings have been used extensively as consolidants for protecting fragile, deteriorated, and/or damaged painted surfaces[9] (Figure 1b). It is noted however that these consolidants are practically irreversible treatments and therefore their removal upon aging is particularly demanding.

Under exposure to light and environmental conditions, polymerization processes occur (i.e., cross-linking[7−10]), which alter significantly the appearance and properties of the varnish layers. Hardening and discoloration are the most obvious results. Furthermore, in the case of proprietary synthetic coatings, additional degradation processes may lead to other undesirable surface effects such as loss of transparency, blooming, microcracking, and so on. Thus, the legibility and aesthetic appearance of the coated/protected paintings are seriously affected. Additionally, dirt, pollutants, and various external depositions (i.e., salts) may also be found on paintings, urging their cleaning.

Another important requirement in paintings conservation is the removal of overlayers (Figure 1c), which are usually applied to retouch stains and repair damaged areas. Their removal is particularly delicate, especially in contemporary art, in which retouching materials of synthetic composition are used. These have a very short lifetime and over the years change differently with respect to the original paints. Given the sensitivity of modern painting materials to most organic solvents, the conservator usually avoids their removal and instead applies a new overpaint. Excessive retouchments may jeopardize the value of the original painting and must therefore be removed.[11]

In all these interventions, the restoration aims to remove the altered material, including any superficial pollutants, to the most possible extent, minimizing any interference with the underlying paint surface. In favorable applications of partly degraded varnish (Figure 1a), selective removal of the outermost surface may be adequate, followed by application of a new varnish coating. On the other hand, in cases of degraded polymeric coatings applied on damaged and weathered artworks, which in their original phase were not varnished, that is, wall paintings, cleaning refers to the whole altered film (without necessarily extracting the material penetrated into the substrate) (Figure 1b). Finally, in the case of modern paintings (Figure 1c), the retouching layers and the original surface show very similar optical properties and hence the cleaning limits may not be easily discernible.

These are particularly delicate interventions, in which aggressive chemical methodologies are often avoided, as they have high potential to alter the underlying surface (given that the material to be removed exhibits similar physicochemical properties to the substrate, and consequently uncontrolled solvent penetration into the bulk may occur). Furthermore, issues related to removal of residual conservation materials, health risk, and feasibility (in the case of extended surfaces) may cause additional problems. In such cases, mechanical means are employed, which on the other hand may be highly inefficient on seriously hardened and/or ultrathin coating layers.

Laser-assisted material removal is an effective cleaning alternative offering exceptional control and selectivity. Based on mature technology developed for specific material processing applications, that is, in micromachining and medicine, lasers were successfully introduced in CH conservation. Due to their monochromaticity, focusibility, and short pulse duration, they enable material processing with accuracy (in the range of micrometers), high selectivity, and immediate feedback, and thus, they are effectively used in several examples of demanding CH restoration problems.

This work focuses on the challenges associated with laser conservation of paintings concerning the removal of aged varnishes, altered consolidants, and overpaintings. Practical issues are presented with emphasis on the research carried out on model systems, aiming to elucidate the associated mechanisms and thus refine the cleaning protocols.

Cleaning by Laser Ablation

Laser cleaning relies on the *ablation* effect, as a result of intense and short pulse irradiation at wavelengths that are strongly absorbed by the substrates. This is a quite complex process, closely dependent on material properties and laser parameters, which upon optimization results in layer-by-layer material removal with minimal thermal load or damage to the substrate. Many studies have heretofore been performed concerning UV laser ablation of polymers,[12,13] constituting an essential guide for understanding the fundamental photophysics of laser ablation and the optimization of the cleaning meth-

FIGURE 2. Laser-cleaning tests on oil painting (courtesy of Dr. M. Doulgeridis). Series of preliminary etching-rate studies (left) resulted in the selective removal of 20 μm of varnish layer (0.9 J/cm^2, 12 pulses/spot).

odologies (given that polymers can be considered as an adequate simulation of polymerized varnishes). In the following, a brief description of the parameters affecting the ablation process will be presented with emphasis on the removal of nearly homogeneous organic polymer films (aged varnishes and deteriorated consolidants) and heterogeneous composite material layers (overpaintings).

The minimization of the removed material thickness per pulse, usually referred as *etching depth* (δ), is a crucial parameter for laser cleaning. This, for nanosecond (ns) pulses, depends on the applied laser fluence (F, laser pulse energy per unit irradiated area) as follows: $\delta = (1/\alpha)\ln(F/F_{\mathrm{thr}})$, based on the heuristic "blow-off" or "layer-by-layer" model introduced to describe ablation effected by intense laser pulses. This model assumes that the absorption processes follow Beer's law and that all material absorbing energy within a depth is effectively removed. Therefore, for incident fluences higher than the ablation threshold ($F \geq F_{\mathrm{thr}}$), etching depth depends on the effective absorption coefficient (α) of the material and on laser fluence, and so in-depth control may be achieved using highly absorbed laser radiation. Natural resins (which are triterpenoid compounds, with their basic molecular unit being a tetracyclic or pentacyclic organic ring with carbonyl or hydroxyl groups[7,8]) and their degradation products absorb strongly in UV ($\alpha_{\mathrm{varnish}} \approx 10^5$ cm^{-1} at 248 nm). As a consequence, KrF excimer laser ablation ($\lambda = 248$ nm) may result in resolutions in the range of 0.1−1 μm per pulse,[3] enabling a highly selective and controlled removal of the deteriorated layer. In Figure 2, a successful example of laser-cleaning of aged dammar is shown, proving the effectiveness and the exceptional control that may be obtained in this regime.

ArF excimer lasers have also been considered for optimizing the cleaning methodology. Most of the polymers absorb stronger at 193 nm than at 248 nm, and thus, a much better surface morphology of the treated areas may be achieved. Indeed, the etching depth at 193 nm is significantly low, ensuring a highly confined material removal (potentially applicable to ultrathin applications). Still, the relatively low output power of the ArF laser results in a much longer and inefficient cleaning procedure, and therefore, it is not favored.

Another fundamental parameter which considerably influences laser ablation of aged polymers is their degree of polymerization (DP), which refers to the number of monomer units in an average polymer chain and is a measure of molecular weight (MW). To initiate material ejection from a high MW polymer, more intense conditions must be attained to cause chain decomposition into clusters, which are eventually ejected. As a result, higher fluences are necessary for material removal. This is particularly pronounced upon irradiation at weakly absorbed wavelengths[14] (Figure 3). In practice, upon UV cleaning of paintings, varnishes of the same composition but different aging (DP/MW) will necessitate further adjustments to the operative fluences to achieve efficient material removal. Similarly, fluence adjustements are also necessary in cases of thicker varnishes, in which the polymerization degree gradually decreases from the surface to the bulk of the film (due to differential exposure to weathering conditions). How-

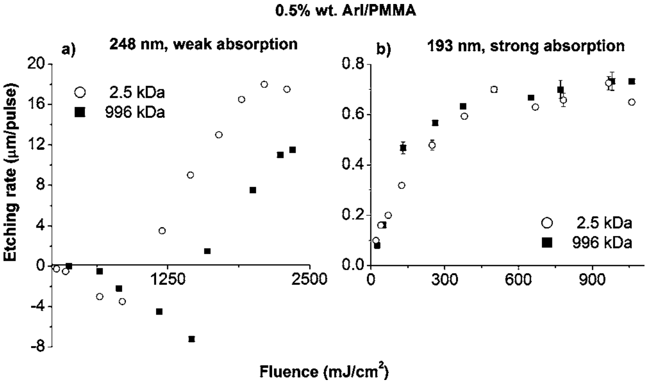

FIGURE 3. Single-pulse etching-rate measurements of ArI/PMMA systems of various MWs upon ns irradiation at (a) 248 nm and (b) 193 nm. Negative etching-rate values in (a) indicate polymer swelling.

ever, at stronger absorption conditions (193 nm), these differences are less pronounced.

Optimization of Laser-Cleaning

For establishing the most appropriate laser parameters for an efficient cleaning process, another highly important issue is the investigation of potential implications to the underlying surfaces. Polychromies and other materials sensitive to laser radiation (i.e., gilding) upon incorrect interventions may suffer from direct and detrimental physicochemical alterations (discoloration, melting, etc.), thus demanding particular attention. Furthermore, molecular substrates, which generally include a wide variety of chromophores, upon UV excitation, may dissociate[13] into highly reactive fragments, while thermal or stress effects may break weak bonds resulting in the formation of additional species. These side products (which may not be easily and immediately distinguished) will probably, in the short or long term, threaten the integrity of the substrate. Consequently, minimization of any thermal, photomechanical, and photochemical effects in the substrate is crucial for the optimization of laser applications.

A major concern in the laser-cleaning of paintings is the thermally induced side effects. As most of the CH materials tend to be thermally sensitive, they may due to heat conduction suffer considerably with detrimental consequences to their appearance and integrity. Although the temperatures attained following laser irradiation at 248 nm may be high in the region to be ablated, these are confined only to the areas in which radiation is absorbed, resulting in minimization[6,13] of the heat flow and thermal load in the neighboring region. In fact, under optimized conditions (ns irradiation at wavelengths strongly absorbed by the irradiated material), the thermal diffusion length (z_{thermal}) is estimated to be significantly smaller or at most comparable to the typical optical penetration depth of most varnishes in the UV (1−10 μm). Indeed, given that $z_{\mathrm{thermal}}(t) \sim (Dt)^{1/2}$, in which t is the time of energy removal (~1−10 μs) and the thermal diffusivity (D) for polymers and amorphous organic materials is[13] in the range of 10^{-3}−10^{-4} cm^2/s, then z_{thermal} is estimated to be 100−500 nm. The extent of heat "damage" upon ns irradiation is closely related to the substrate absorptivity at the irradiation wavelength, which for typical varnishes increases much for shorter wavelengths, and so "clean" etching of aged varnishes with minimal thermal disruption into the bulk is possible for ablation at $\lambda \leq 248$ nm.

It must be also highlighted here the high sensitivity of the majority of pigments in laser radiation, with discoloration being the immediate result.[15,16] Studies on pigment powder have shown that discoloration is independent of the laser wavelength, but still a strong connection was recently found between the wavelength and the paint binding media.[17] Specifically, it was shown that the color and chemistry of egg-tempera cinnabar (HgS) upon 213 nm irradiation (Nd:YAG fifth harmonic) are not affected, although HgS is an extremely sensitive pigment well-known to undergo intense discoloration upon exposure to both environmental conditions (due to transformation[18] from red hexagonal cinnabar, a-HgS, to black cubic meta-cinnabar, a′-HgS) and laser irradiation (due to reduction mechanisms as confirmed by XPS analysis,[15,16] intense thermal conduction phenomena,[15] etc.). The authors[17] attribute this behavior to the strong absorptivity of the egg medium at 213 nm.

Another important issue in the laser processing of molecular substrates is the generation of structural modifications induced by high-amplitude stress waves produced upon irradiation. Their sources may be the back-momentum exerted by the ejected material, the pressure rise caused by the rapid thermal expansion, and/or the expansion of gases formed within the substrate upon material decomposition. Still, what is important is that they are not restricted within the ablation spot (in contrast to the photochemical effects) but they may be expanded at delocalized areas. The propagation of delaminations and cracks at various distances from the irradiation area was found to be closely dependent on the number of applied pulses, the laser fluences, and the relaxation time and thus must be carefully monitored. To this end, double-exposure holographic interferometry[19] is a unique and versatile tool for evaluating and observing these mechanical effects.

Laser-induced chemical modifications in polymers have been systematically investigated in studies based on various model systems.[12,13] On the same basis, to assess the nature and extent of laser-induced photochemical modifications upon

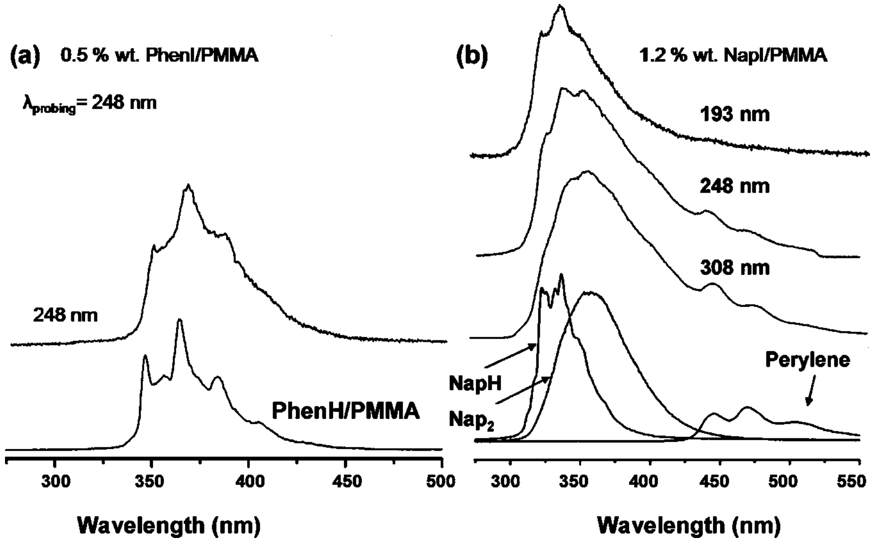

FIGURE 4. Probe product LIF spectra following single pulse irradiation of (a) PhenI/PMMA and (b) NapI/PMMA at the indicated wavelengths close to the F_{thr} (LIF spectra recorded from PMMA doped with the indicated compounds are also presented).

removal of molecular overlayers from CH surfaces, a series of studies on model samples based on doped polymeric systems were undertaken. The idea was motivated from the nature of the paint layers (chromophores dispersed within an organic medium), and, even if idealized, they represent well the painted surfaces. The study over realistic or original samples is advantageous, as it allows systematic investigation of the responsible mechanisms without tedious and impractical analysis of the numerous parameters that a case-by-case study of real situations may entail. Furthermore, detailed knowledge of the dopant photoproducts enables the systematic characterization of the induced modifications as a function of laser parameters (wavelength, fluence, number of pulses) and materials properties (MW, absorptivity).

Model systems of polymers (PMMA, poly(methyl methacrylate) and PS, polystyrene) doped with photolabile haloaromatic compounds (NapI, iodonaphthalene and PhenI, iodophenanthrene)[3,6,20] were employed. The aryl chromophores, ArI (Ar = Nap, Phen), upon UV irradiation, undergo a homolytic dissociation to aryl radicals, which may abstract a hydrogen atom from the polymer to form ArH (NapH, naphthalene and PhenH, phenanthrene)[21] via a thermally activated process:

$$\mathrm{ArI} + h\nu \rightarrow \mathrm{Ar} + \mathrm{I}$$

$$\mathrm{Ar} + \text{polymer} \rightarrow \text{ArH-like}$$

$$\mathrm{Ar} + \mathrm{Ar} \rightarrow \mathrm{Ar_2}$$

In contrast to their photoproducts, the dispersed chromophores and the host polymers do not fluoresce, and as a result the laser-induced products, ArH-like, can be detected and monitored efficiently via laser-induced fluorescence (LIF) in a "pump-probe" scheme, constituting a highly sensitive "indicator" of the in-depth polymer modification upon laser irradiation.

Indeed, upon irradiation of NapI or PhenI (<1 wt %) doped PMMA and PS films, the aromatic $^1B_{3u} \rightarrow {}^1A_{1\,g}$ emission (at ~330 nm for NapH and ~375 nm for PhenH), which dominates the fluorescence spectra, is recorded and monitored (Figure 4). Their presence denotes photochemical activity in the irradiated system, while their yield reflects the temperature evolution in the substrate following irradiation. Furthermore, under certain conditions (high fluence, dopant concentrations > 1% wt, and low polymer absorptivity), biaryl species are also detected upon irradiation of NapI/PMMA. These species (a broad band around 360 nm ascribed to 1,1-binaphthalene (Nap_2) and a double peak structure at 430 and 450 nm attributed to perylene[21]) are formed via diffusion-limited reactions, and they may be considered as experimental probes for evaluating the degree and the extent of substrate structure disruption (melting) and polymer viscosity changes upon irradiation. On this basis, the most important conclusions derived from these studies are highlighted in the following.

Selecting a laser wavelength which is strongly absorbed is critical for high etching efficiency, good surface morphology, and minimal thermal load to the irradiated material. This fact was further supported in studies on the chromophore/polymer model systems. Indeed, upon UV (193, 248, and 308 nm) irradiation of ArI/PMMA and ArI/PS systems, laser-induced photoproducts are detected which, in all wavelengths, are qualitatively the same. Still, the extent of the induced photochemical modifications was found to be well reduced for highly absorbing systems (193 nm, ArI/PMMA). Furthermore,

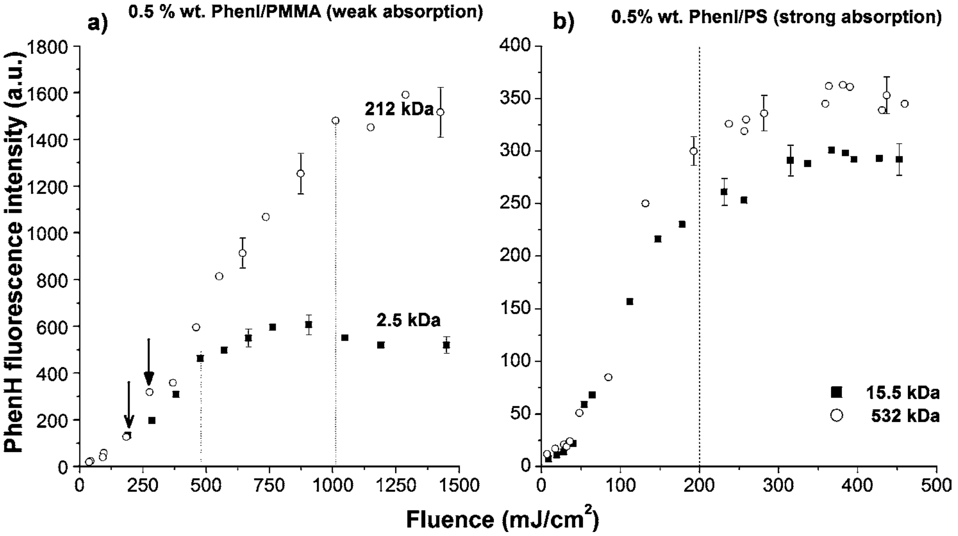

FIGURE 5. Fluence evolution of PhenH photoproduct emission upon a single 248 nm laser pulse of doped (a) PMMA and (b) PS films with various MWs. Arrows indicate the swelling onset values for each system, while lines designate the F_{thr}.

it was also shown that, for a given fluence, biaryl species formation is much reduced with increasing substrate absorptivity and consequently side product formation is restrained. This dependence is explained as the relative ratio of etching depth versus optical penetration depth is much reduced with increasing substrate absorptivity and thus the depth over which products remain in the substrate becomes limited. Correspondingly, for highly absorbing systems, F_{thr} decreases also and similarly the photon flux affecting the substrate decreases.

The dependence of the photoproduct emission intensity on the applied laser fluences has also been examined. Figure 5 shows the fluence evolution of the ArH photoproduct emission intensity following irradiation by a single pump-pulse on the doped polymer for (a) weakly and (b) strongly absorbed wavelengths and for different polymer MWs. A linear increase of the photoproduct yield at low *F*, a subsequent abrupt rise for the range of *F* responsible for surface "swelling",[12] and finally a further, although slower, increase above the F_{thr} was recorded for the weakly absorbing systems (Figure 5a). It is evident that, above the swelling threshold, photodegradation of the haloaromatic dopants per unit volume is enhanced. This enhancement is particularly intense for polymers with higher MW, indicating that higher temperatures are attained at those systems. Conversely, a quite different behavior is observed for strongly absorbing systems (Figure 5b) in which the F_{thr} denotes stabilization of the photoproduct yield to a limiting value (obviously due to material removal). It must be also noted that in this regime PhenH production appears to be less influenced by the MW.

Another crucial parameter which may affect photoproduct accumulation in the substrate is the number of the applied laser pulses. This particularly concerns thicker overlayers which require multipulse irradiation protocols. As shown by experimental results, product formation in the substrate is closely related to the number of pulses and the applied fluence. For irradiation above F_{thr}, material removal balances side product formation and consequently photoproduct accumulation in the substrate is much reduced (as it is practically limited to a smaller depth). On the contrary, at fluences close and below F_{thr}, due to thermal desorption mechanisms, the removal of the "heavy" (strongly bound to the matrix) fragments is inefficient and successive laser pulses favor the accumulation of ill-defined side products in the material. This effect is particularly pronounced for irradiation at weakly absorbed wavelengths.[20]

In all, to avoid accumulation of side products that may be detrimental for the chemical integrity of the substrate, a balance must be established between the chosen wavelength (which must be highly absorbed by the polymer), the applied laser fluence (able to effectively remove the overlayer), the number of pulses (sufficiently low to restrict photochemical effects), and, last but not least, the aging condition and the particular requirements of the object.

The above studies refer mainly to the investigation of laser-induced effects in the processed polymeric coatings upon layer-by-layer removal of their outermost degraded layers. Another critical issue in laser cleaning of paintings refers to the extent of the laser-induced side effects on the original surface upon removal of overpaintings (Figure 1c). This is particularly important and common for contemporary art interventions, in which the aim is to remove aged retouching overlayers (mostly of acrylic composition) and reveal safely the

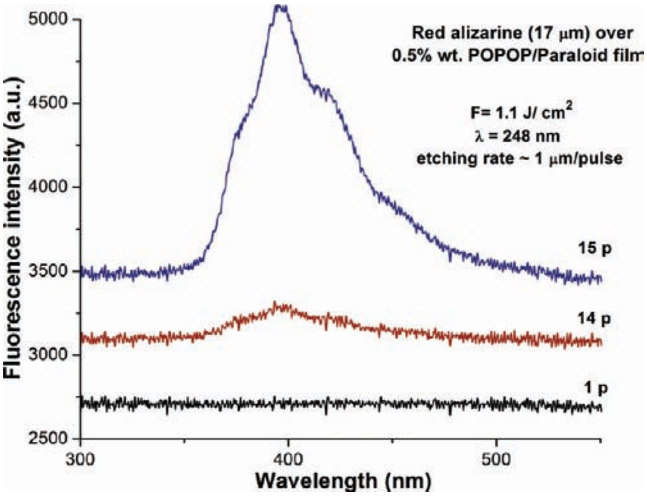

FIGURE 6. Probe product LIF spectra recorded following UV irradiation of doped Paraloid-B72 film overpainted with alizarine.

original painting. In this case, one of the most demanding cleaning problems refers to the removal of overlayers of the same composition to the underlying layer. A method for the in-depth assessment of such modifications induced during laser cleaning of modern paintings has been proposed.[22]

To simulate the case of an overlayered modern acrylic painting, a sensitive polymer indicator covered with acrylic paint was examined. The overpainting, a 20−120 μm layer of red acrylic paint (Rowney 513, 1:2 dihydroxyanthraquivone), was casted over the doped polymer film. The polymer indicator substrate (10−20 μm) (simulating the original acrylic surface) consists of Paraloid-B72 doped with 0.5% wt of a known photochemistry photosensitizer. POPOP (1,4-di[2-(5-phenyloxazolyl)]benzene), a common laser dye, was used, as it fluoresces strongly and consequently the detection of its LIF spectra following irradiation of the acrylic paint denotes the removal of the overlayer and the exposure of the underlying polymer. From this critical point and on, photochemical changes to the substrate may potentially be induced. Thus, laser removal of the acrylic overpaint may be qualitatively monitored by means of a "pump-probe" fluorescence scheme at 248 nm.

The fluorescence spectra collected from the irradiated surface of an overpainted POPOP/Paraloid-B72 film upon KrF irradiation is shown in Figure 6. No fluorescence is collected upon the first pulses (the acrylic paint does not fluoresce when excited at 248 nm), whereas the fluorescence emission from the POPOP appears to be distinguishable at the 14th pulse, indicating partial removal of the overpaint. The clear and characteristic POPOP fluorescence peak recorded at the 15th pulse denotes efficient paint removal and, potentially, initiation of laser-induced effects to the substrate.

Furthermore, for the in-depth assessment of modifications potentially induced at the underlying polymer substrate during the laser removal process, the technique of nonlinear microscopy was applied. The unique advantage of multiphoton excitation fluorescence (MPEF)[23] over conventional confocal fluorescence microscopy relies on its intrinsic three-dimensionality, which allows one to section deep (due to the use of 1028 nm light as the excitation source) within the samples. MPEF spot measurements on the model samples (following total removal of the overpaint) indicated photochemical modifications to the underlying substrate, as the fluorescence properties of the exposed surface were altered in comparison to the reference measurements (recorded as a 5 μm reduction in the FWHM of the MPEF spectra).[22]

The potential of using the suggested photosensitive indicator to monitor the presence and extent of photochemical modifications at the underlying surfaces upon laser removal of overlayers is of great importance. LIF and nonlinear microscopy may reliably and accurately detect potential changes and serve as monitoring tools to safeguard the original painting.[22] Of course, optimization of the parameters and development of an appropriate laser-cleaning methodology are imperative and under study.

Ablation by Ultrashort Laser Pulses

From the above, it is evident that UV ablation of aged polymer layers using short laser pulses may be an efficient and highly selective tool in CH conservation. There are, however, several exceptionally demanding cases in which the use of ns lasers is of limited scope. These include paintings with very thin varnish layers (<10 μm) or painted surfaces in which, due to unsuccessful past conservation treatments, the whole overlayer film must be removed. In such cases, there is a risk for direct exposure of the laser-sensitive original surfaces to irradiation. To overcome these limitations, ultrashort laser pulses have been considered, as they have been shown to offer exceptional capabilities for material processing.[12,13,24]

A major advantage in using ultrashort lasers is that heat diffusion effects are minimized[13] and consequently the thermal load to the substrate is negligible. Furthermore, in the absence of plasma shielding, the laser energy is efficiently coupled into the substrate,[24] enabling processing at much lower fluences. Finally, due to the efficient energy absorbance and the enhanced possibility of multiphoton processes, the effective optical penetration depth is much reduced and side effects on the substrate are unlikely. In fact, the F_{thr} is much reduced and processing of even nominally transparent or weakly absorbing substrates can be effected.

These advantageous features of ultrafast irradiation were further illustrated in a series of comparative studies on both neat and ArI-doped model polymeric films. Their aim was to critically assess a number of issues which are vital for the laser cleaning of CH surfaces and, given that several aspects of the interaction of femtosecond (fs) laser pulses with materials differ even qualitatively from that of ns laser interaction, they must be carefully examined prior to their implementation. These include the etching resolution, the morphology of the etched areas, and the affected depth.

It was indeed demonstrated that 500 fs laser pulses at 248 nm offer higher etching resolution and cleaning control over the ns ones,[25] as F_{thr} and etching rates are much reduced. Furthermore, the sharply defined craters with clear edges confirmed the improved "quality" of processing. Moreover, it was shown that varnishes with different linear absorption coefficients at 248 nm show similar etching rates in the ultrashort cleaning regime,[25] and thus, materials with unknown absorption properties (i.e., commercial varnishes of unidentified exact composition) or multilayered coatings of variable absorptivities may be uniformly treated with UV fs irradiation.

On the basis of assessing the extent of laser-induced photochemical alterations to the irradiated surfaces, comparative LIF analysis on NapI–PMMA and PhenI–varnish systems demonstrated the superiority of fs laser ablation. Specifically, it was shown that:

(a) Photochemistry is well-defined. Indeed, the spectra recorded upon fs KrF pulses (above F_{thr}) on NapI–PMMA are indicative of NapH-like products, and no additional peaks (i.e., Nap_2) were recorded even for high dopant concentrations.[20] In contrast, at low fluences, a number of byproducts are observed upon successive laser pulses; evidently, the accumulating radicals react with each other to produce ill-defined products. Most interestingly, ill-defined species are not observed above F_{thr} even after extensive irradiation.

(b) The affected depth is highly restricted, as indicated by the much lower ArH yield recorded and consequently the reduced depth over which ArI photolyzes. This can be explained on the basis of multiphoton processes much reducing the "effective" optical penetration depth. In the case of mastic, this difference is estimated to be nearly an order of magnitude (Figure 7).

(c) Heat diffusion is limited, and product formation is instead determined by multiphoton processes. This is supported from the supralinear increment of ArH formation with "pump" laser fluences and the plateau reached above F_{thr} in contrast to the ns irradiation.

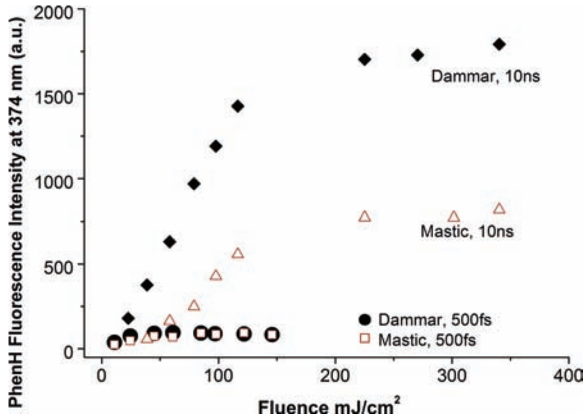

FIGURE 7. PhenH product fluorescence intensity versus fluence following irradiation with a single 248 nm "pump-pulse" of PhenI-doped varnishes with fs and ns laser pulses.

(d) Laser-induced changes in the substrate are largely independent of the (small signal) absorption of the irradiated varnish. Indeed (Figure 7), the PhenH yields of the different varnishes in the fs irradiation are nearly independent of their absorptivity at the applied wavelength. This fact (also confirmed by the similar dependences upon etching-rate studies) enables processing independently of the optical properties of the unwanted layers.

(e) Upon successive laser pulses, the accumulated PhenH product amount in the remaining varnish (Figure 8) decreases sharply for increasing fluences above F_{thr}. Although in the subablative range the two irradiation regimes show similar behavior (PhenH accumulates in the remaining varnish, nearly exponentially, until reaching a plateau), this advantageous behavior of the fs pulses above F_{thr} indicates that the ratio of the optically affected depth in the remaining substrate versus etched/removed thickness decreases.

Therefore, it can be tentatively said that UV fs ablation of varnishes may be dominated by avalanche ionization, in which multiphoton processes result in few quasi-free electrons. These are subsequently accelerated to high energies, and (upon collision with the atoms) they are ionized to generate further "free" electrons. When a sufficiently high density of such electrons[13] is reached ($\sim 10^{21}$ cm^{-3}), optical breakdown and material ejection will occur. Avalanche ionization is expected to be largely independent of the optical characteristics of the substrate, and thus, it can account for the weak dependence of the etching rates and PhenH yield on varnish absorptivity. In consequence, the effective optical penetration depth is limited to the submicrometer scale. It is expected that, with increasing F, instead of increasing the affected depth, higher energy is deposited in this depth, improving the etching versus affected depth. Such an optimization cannot be generally achieved in the ns regime.

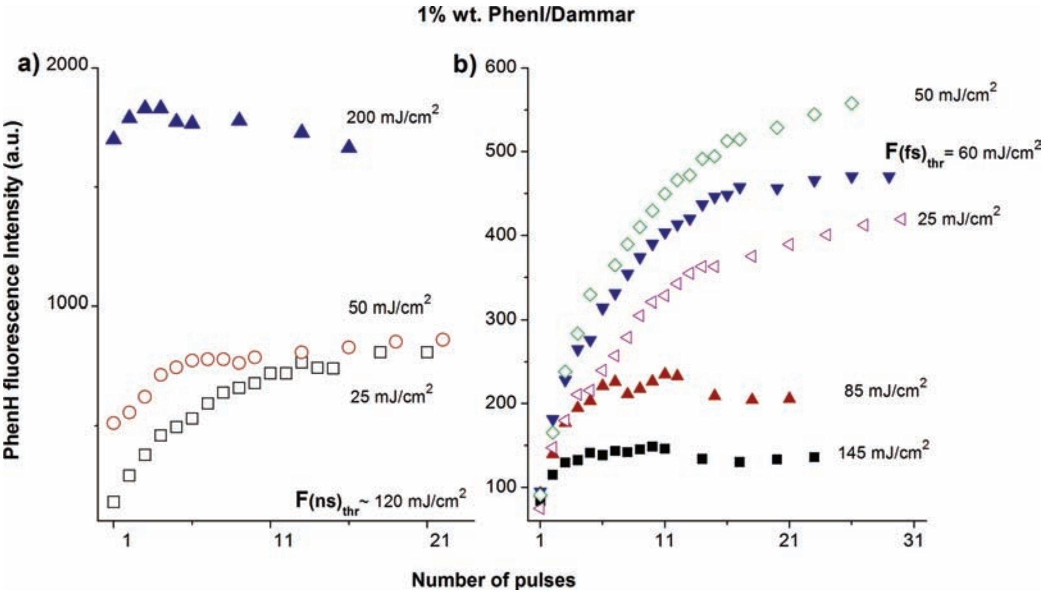

FIGURE 8. Pulse evolution of the intensity of the PhenH product formed upon irradiation of PhenI/dammar with (a) ns and (b) fs laser pulses at the indicated fluences.

In conclusion, it is evident that ultrashort pulses are superior to the ns ones regarding the etching resolution, the affected depth, and the extent of the observed physicochemical alterations in the remaining and/or underlying material. Furthermore, the potential to process polymeric materials independently of their optical properties and their improved surface quality opens new perspectives in CH cleaning interventions.

Conclusions

In this work, current possibilities and limitations in the use of lasers in paintings conservation are discussed. The review focuses on issues associated with UV laser processing of unwanted polymeric overlayers on paintings, aiming for their removal. Toward the optimization of irradiation parameters, studies on model doped polymer samples have shown that, upon irradiation in the ns regime, the physicochemical properties of the material (absorption, degree of polymerization/MW) as well as the applied laser fluences and number of pulses are crucial parameters for the minimization of potential photochemical alterations and should be carefully assessed.

Also, photochemical effects in UV ablation with fs laser pulses are reduced, highly defined, and nearly independent of the material properties. Hence, they may open new avenues for the treatment of molecular substrates, enabling novel material processing schemes that have not been possible with ns laser technology.

Finally, aiming to assess the in-depth laser induced modifications at the original painting upon laser cleaning, a sensitive polymer sensor was introduced. This, together with analytical methodologies based on LIF and nonlinear microscopy, may reliably and accurately detect potential changes and serve as a monitoring tool to fine-tune the cleaning protocol and to safeguard the original painting.

BIOGRAPHICAL INFORMATION

Paraskevi Pouli holds a degree in Physics from Aristotle University of Thessaloniki, Greece and a Ph.D. in Physics from Loughborough University, U.K. She joined IESL-FORTH on 2000. Her research interests include the investigation of laser-ablation mechanisms with emphasis on CH applications and the development of laser-cleaning methodologies on a variety of real cases. She is also responsible for the laser-cleaning projects on the Athens Parthenon sculptures.

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Savas Georgiou received his B.Sc. in chemistry and mathematics from Knox College, Illinois, and his Ph.D. in physical chemistry from the University of Utah. He subsequently performed postdoctoral work at Princeton University. In 1993, he joined IESL-FORTH as Research Director. He has also held position as a Visiting Assistant Professor of Chemistry (University of Crete) and as an Assistant Professor of Physics (University of Ioannina, Greece). He has received various awards and has participated in several European Union research projects. He has coauthored more than 80 articles in international scientific journals on photophysics/chemistry and particularly on laser-materials interactions. He was guest editor for the special issue of *Chemical Reviews* on "Laser Ablation of Molecular Substrates" (2003).

Costas Fotakis is Director of IESL-FORTH and Professor of Physics at the University of Crete. He is also Director of the European Ultraviolet Laser Facility operating at FORTH ("LASERLAB-Europe" project). His research interests include laser physics and related applications. He has been chair of several international conferences on these topics. He has over 230 publications and belongs to the editorial boards of several scientific journals. He is a life member and Fellow of the Optical Society of America from which he received the "Leadership Award/New-Focus Prize" in 2004.

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