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PAPER

UV laser removal of varnish on tempera paints with nanosecond and femtosecond pulses

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Two laser cleaning approaches based on ablation by ultraviolet laser pulses of femtosecond (fs) and nanosecond (ns) durations for the removal of shellac varnish from egg-yolk based tempera paints are investigated. Laser irradiation effects, induced on the varnish layer and on the underlying temperas by multiple pulses in the fs domain at 398 and 265 nm and single pulses in the ns domain at 213 nm, were examined following a spectroanalytical approach. By using optical microscopy, colorimetry and laser induced fluorescence it was found that irradiation of the varnished temperas with fs pulses changes the texture of the varnish surface and results in degradation of the underlying coloured paint. In contrast, operating with pulses of 15 ns at the highly absorbed wavelength of 213 nm, controlled micrometric layer removal of the varnish is possible without noticeable modification of the coloured temperas. These results widen the choice of laser conditions for painting restoration.

Introduction

Painting conservation relying on laser ablation has been the subject of recent studies to discuss the current possibilities and limitations of the technique.[1–14] Ongoing research is devoted to the use of various types of laser systems operating in different spectral regions and pulse durations, including UV excimers, Nd:YAG and Er:YAG lasers. One of the key parameters to ensure a safe laser cleaning strategy relies on the efficient coupling of laser energy to the unwanted layer, a condition that can be fulfilled when the laser wavelengths fall within the high absorbance spectral region of the material to be removed. Removal of polymerized outer varnish layers and over-paintings with minimal light penetration and thermal effects to the underlying paint has been demonstrated based on the use of a KrF excimer laser operating at 248 nm with a nanosecond (ns) pulse duration.[1,2] With such a system, non-contact etching of the unwanted superficial layers can be performed with in-depth micrometre resolution, allowing accurate control of the amount of removed material.

Paint materials, including pigments, binders and varnishes, are sensitive to light and therefore are prone to physical and chemical modifications during laser irradiation. Detailed studies have been undertaken to investigate these effects[2,7,9–13] in order to offer a safe procedure that can improve and complement traditional painting conservation and restoration practices.

More recently, the use of shorter laser pulses in the picosecond (ps) and femtosecond (fs) domains has been introduced in the field, and investigation of the advantages offered with respect to ns pulses is underway.[1,6,7,9] The prospect of ultrashort pulses for laser removal of unwanted superficial layers and overpaints relies on the minimisation of photo-thermal, photo-mechanical and photo-chemical phenomena, on the possibility of processing even nominally transparent substrates and optimizing morphological aspects to avoid melting, bubbling, crack formation, *etc.* Careful selection of the irradiation conditions of wavelength, fluence and number of pulses widens the scope of application of ultrashort pulses for painting conservation. For example, processing by Ti:Sapphire irradiation (795 nm) with pulses of ∼100 fs has turned out to be ineffective for varnish removal (dammar and mastic); however, irradiation with 248 nm, ∼500 fs laser pulses results in an improved etched morphology as compared with results achieved with ns pulses of the same wavelength.[6]

Aiming at the examination of alternative laser cleaning strategies for paintings, this work focuses on the UV laser removal of varnish applied on tempera paints, investigating two laser processing approaches based on the use of fs and ns pulses. To this end, shellac varnished, egg yolk based model temperas were irradiated in a multipulse approach with pulses in the fs regime at 398 and 265 nm and in a single pulse approach in the ns regime at 213 nm. A spectroanalytical methodology, capable of assessing the physical and chemical

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modifications induced by laser irradiation,[2,4,7,9,14] was adopted based on the use of optical microscopy, colorimetry and laser induced fluorescence (LIF). The obtained results are discussed in the framework of previous studies on laser cleaning of paintings and polychromes using ns KrF excimer and Q-switched Nd:YAG lasers and a fs Ti:Sapphire laser at 795 nm.[2,7,15,16]

Experimental

Samples

The varnish and paints analyzed in this work were specifically selected to reproduce common materials used in artistic paintings. Shellac is a natural organic resin excreted by the insect *Laccifer lacca*. The chemical composition of this varnish is complex with typically 70–80% resin, 6–7% wax and 4–8% coloured matter and moisture, the material being commonly referred to as the polyesters formed by self-esterification of a mixture of hydroxyl acids.[17,18] The paints consisted of egg yolk based temperas coloured with various inorganic pigments of different chemical characteristics. These are vermillion (mercuric sulfide, HgS), lead chromate ($PbCrO_4$), lead white (basic lead carbonate, $2PbCO_3Pb(OH)_2$) and azurite (basic copper carbonate, $Cu_3(CO_3)_2(OH)_2$). While vermillion, lead white and azurite are red, white and blue traditional pigments, respectively, lead chromate is a yellow modern pigment.

The present study is based on model systems of unvarnished and varnished temperas consisting of a single layer of paint and a layer of paint covered with a layer of shellac varnish. The samples were prepared according to a procedure described elsewhere.[2] Pigments in powder were mixed with egg yolk, using a spatula and a glass plate, and applied on primed panels resulting in layers of ~100 μm thickness. Samples of unpigmented tempera were also prepared to allow the comparison with results obtained from the uncoloured binder. For the varnished systems, purified (platina) shellac varnish, prepared by dissolving purified shellac resin in ethanol (1 : 2, w/w), was applied over the tempera layer using a wide paintbrush, resulting in a varnish layer of ~10 μm thickness. Before the present study the samples were subjected to natural ageing for a period of more than eight years by keeping them in the dark at a constant temperature and relative humidity of 22 °C and 40–44% respectively.

Laser irradiation

The unvarnished and varnished systems were treated in air by using two types of laser systems delivering pulses in the fs and ns domains. Irradiation tests were performed for both laser conditions on a single-spot basis for various fluence values, in order to determine ablation thresholds, as well as on a scanning basis in order to achieve a homogeneously irradiated area on the varnished systems in which further analysis could be performed. Once the ablation thresholds (F_{th}) were determined for each system, three different irradiated zones were prepared with fluence values of 0.75, 1.0 and 1.5 times the threshold for varnish removal.

The fs system consists of a commercial Ti:Sapphire oscillator (Tsunami, Spectra Physics) and a regenerative amplifier system (Spitfire, Spectra Physics) based on the chirped pulse amplification technique. The system produces linearly polarized 120 fs pulses at 795 nm with a repetition rate of 1 kHz. The pulse energy can reach a maximum of 1 mJ and it is finely controlled by a half-wave plate and a linear polarizer. Neutral density filters were used when further energy reduction was required. The average power of the beam is measured with a thermopile detector (407A, Spectra Physics). The transversal mode is nearly a Gaussian TEM00 with a 10 mm beam diameter (at $1/e^2$).

The second harmonic of the fundamental laser output (398 nm central wavelength) was generated in a 1 mm thick BBO crystal (type-I, $\theta = 29°$) with a maximum energy per pulse of 0.33 mJ. The pulse duration (measured by cross-correlation with the fundamental pulses) was 150 fs. The third harmonic (265 nm central wavelength) was obtained in a second BBO crystal (1 mm thick, type-I, $\theta = 44°$) by sum-frequency mixing of the fundamental (795 nm) with the second harmonic (398 nm) beams. An estimation of the temporal duration of these pulses is 260 fs (taking into account the group-velocity mismatch of the interacting pulses in the crystal), and the maximum available pulse energy is 40 μJ.

For irradiation of samples, the fs laser beam impinged perpendicularly onto the target surface which was placed on a motorized *XYZ* translation stage where the *Z* axis is perpendicular to the sample surface. The pulses were focused on the surface by a plano-convex cylindrical lens (fused silica, uncoated) with a focal length $f = 75$ mm providing a spot size of 6 × 9000 μm^2 ($1/e^2$ criterion). Motion in the *Z*-axis helped to accurately focus the laser beam on the surface. Homogeneous irradiation within a 10 × 10 mm^2 area[7,9] was achieved by using a squared mask placed on the surface of the sample and by scanning it along the direction of the smallest spot dimension. The scanning speed, and consequently the spatial overlap of successive pulses, was chosen to ensure the delivery of approximately 100 pulses on each point of the sample. After processing the whole square length, the sample was moved in the transverse direction by steps of 1500 μm, resulting in an overlap of 95% with regard to the maximum pulse intensity.

For the irradiation with the 265 nm fs pulses, a tighter focusing was needed because of the smaller energy per pulse available. In order to reach and surpass the ablation thresholds for all the samples, a combination of two cylindrical lenses with their astigmatic axes crossed was arranged. A lens of $f = 20$ mm was used to focus the beam onto the sample in one axis. A second lens with $f = 75$ mm, placed 30 mm in front of the $f = 20$ mm lens, served to reduce the beam size by a factor of three along the opposite axis. Under these conditions, the spot size at the sample was 1 × 2000 μm^2.

The ns system consisted of a Q-switched Nd:YAG laser (Lotis II, LS-2147) operating at the 5th harmonic of the fundamental radiation (213 nm) with pulses of 15 ns at a repetition rate of 1 Hz. Again in this case, surface sample areas of 10 × 10 mm^2 were homogeneously irradiated by scanning of the beam (focused by a cylindrical planoconvex quartz lens with $f = 150$ mm providing a spot size of 1 × 10 mm^2). The chosen scanning speed ensured irradiation with one pulse on each point of the sample surface. The laser fluence was modified in this case by using a high energy variable dielectric attenuator (LaserOptik).

Analytical techniques

To assess the physicochemical changes induced by laser irradiation on the paint systems, a combination of spectroanalytical techniques was used. Optical microscopy and colorimetry served to measure the morphological and colour changes, respectively, while LIF provided information on possible chemical modifications induced on the irradiated surfaces.

Optical microscopy images were taken with an optical microscope (Zeiss Axio Imager Z1m) equipped with a CCD camera. A Minolta CM 700d spectrocolorimeter served to measure the chromatic properties of the samples and specifically the changes induced by laser irradiation. The observation area was circular, of 5 mm diameter, and five spectra were acquired in each zone and averaged to obtain one data point. The CIE-Lab colour space was used to measure colour shifts expressed in three variables, namely, ΔL^* (lightness), Δa^* (red to green), Δb^* (yellow to blue). The magnitude of the overall colour change is given by $\Delta E^* = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$.

LIF measurements were carried out using laser excitation at 266 nm (4th harmonic of a Q-switched Nd:YAG laser, ~6 ns pulses) and a 0.30 m spectrograph with a 300 lines mm^{-1} grating (TMc300 Bentham) coupled to an intensified charged coupled detector (2151 Andor Technologies). The temporal gate was operated at zero time delay with respect to the arrival of the pulse to the surface of the sample and with a width of 3 μs. The sample was illuminated at an incidence angle of 45° with pulses of around 0.1 mJ. For the results presented here, a 420 nm cutoff filter was set in front of the spectrograph to avoid the second order emissions of lower wavelengths. Each spectrum resulted from the average of 20 measurements in five different points of each sample zone.

The UV-Vis absorption spectrum of shellac, shown in Fig. 1, was measured on a film of the varnish deposited by casting on a quartz slide using a SHIMADZU UV-3600 Spectrophotometer. The spectrum of shellac is similar to those of other varnishes commonly used in paintings, such as those based on dammar and mastic resins, featuring an intense absorption band at wavelengths below 250 nm.[6] The measured absorption coefficients of shellac at 213 and 265 nm are 8600 and 500 cm^{-1} respectively. At 398 nm the absorption coefficient is negligible with an estimated value of around 120 cm^{-1}.

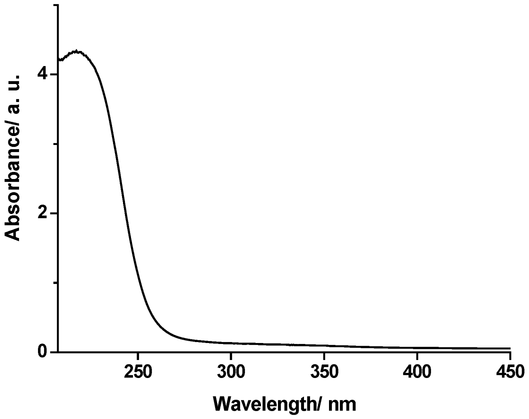

Fig. 1 UV-Vis absorption spectrum taken with a resolution of 2 nm of a 5 μm thick shellac varnish film on a quartz plate.

Results and discussion

Ablation thresholds

Ablation threshold fluences F_{th} for irradiation with fs pulses at 398 and 265 nm were measured as reported previously[7] using the method of Dumitru *et al.*[19] These were determined for $N = 1$, 5, 20 and 100 pulses. The incubation factors ξ were obtained by fitting the results to the expression $F_{\text{th}}(N) = F_{\text{th}}(1) \times N^{(\xi-1)}$.

On the other hand, the fluence thresholds for ablation at 213 nm with one pulse of 15 ns were determined by applying the spot regression method.[20] Assuming pulses with a Gaussian spatial beam profile, the maximum laser fluence on the sample surface and the diameter D of the ablated area are related by $D^2 = 2\omega_0 \ln(F/F_{\text{th}})$, where ω_0 is the $1/e^2$ radius of the Gaussian beam distribution. The fluence at the target surface is calculated by $F = E/\pi\omega_0^2$, where E is the pulse energy. The diameter of the ablated area was determined as observed by optical microscopy. The plot of D^2 *versus* $\ln E$ yields the value of F_{th} in this case.

The values of ablation thresholds and incubation factors obtained for fs multishot irradiation and of ablation thresholds for one pulse ns irradiation are reported in Table 1. Although the linear absorption coefficient of the varnish at 398 and 265 nm is much lower than the value at 213 nm (Fig. 1), multiphoton absorption processes play a relevant role under fs irradiation, thus ensuring good coupling and therefore efficient ablation of the varnish under the present fs irradiation conditions. Inspection of the table reveals that upon irradiation with fs pulses of 398 nm, the threshold of shellac is only lower than the threshold of the temperas in the case of azurite. For the rest of the systems this threshold is higher, or at least comparable. The use of this wavelength of the fs system is therefore not recommended for removal of varnish applied on those pigmented layers, as it may result in the partial ablation or discoloration of the paint. In fact, discoloration of the paint layer was observed upon irradiation because the poorly absorbed laser light at 398 nm is not shielded by the varnish layer. The same conclusion can be extended to the fundamental emission of the Ti:Sapphire laser at 795 nm where the damage induced on the pigmented layer could be even more significant.[6,7]

As also shown in Table 1, by operating at 265 nm the varnish ablation threshold is lower than those of all coloured temperas only when operating with a high number of fs pulses ($N \geq 100$). This is related to the incubation effect that causes the reduction of threshold as the number of applied pulses increases.[7] The incubation effect is high in vermillion ($\xi = 0.35$) and less important, with values in the range from 0.64 to 0.95, for the rest of studied systems.

For irradiation at 213 nm with 15 ns pulses the threshold of shellac is also lower than those of the unpigmented and pigmented temperas. Hence the present measurement of ablation thresholds indicates that varnish removal under multiple pulse ($N \geq 100$) irradiation at 265 nm (260 fs) and single pulse irradiation at 213 nm (15 ns) allows the selection of a fluence range in which partial elimination of the varnish layer would in principle safeguard the underlying paint based

Table 1 Ablation thresholds in J cm^{-2} and incubation factors (ξ) of naturally aged shellac and unvarnished tempera paints irradiated at the indicated laser conditions. Estimated errors are 10%

	Wavelength, pulse duration	$F(100)$	$F(20)$	$F(5)$	$F(1)$	ξ
Shellac	398 nm, 150 fs	0.13	0.26	0.53	0.96	0.57
	265 nm, 260 fs	0.10	0.23	0.52	0.85	0.69
	213 nm, 15 ns				0.14	
Unpigmented tempera	398 nm, 150 fs	0.23	0.22	0.26	0.40	0.85
	265 nm, 260 fs	0.23	0.24	0.34	0.54	0.81
	213 nm, 15 ns				0.45[a]	
Vermillion	398 nm, 150 fs	0.13	0.18	0.28	0.44	0.73
	265 nm, 260 fs	0.17	0.20	0.50	1.41	0.35
	213 nm, 15 ns				0.26[a]	
Lead chromate	398 nm, 150 fs	0.12	0.13	0.14	0.15	0.95
	265 nm, 260 fs	0.20	0.20	0.36	0.51	0.80
	213 nm, 15 ns				0.25[a]	
Lead white	398 nm, 150 fs	0.14	0.20	0.27	0.40	0.77
	265 nm, 260 fs	0.16	0.23	0.37	0.46	0.77
	213 nm, 15 ns				0.30	
Azurite	398 nm, 150 fs	0.21	0.38	0.63	1.13	0.64
	265 nm, 260 fs	0.13	0.17	0.25	0.36	0.78
	213 nm, 15 ns				0.35	

[a] Ref. 9.

on the pigment effects considered here. In fact, measurements of removed layer thickness yield values of about 5 and 2 μm (out of a total 10 μm thickness) under the indicated fs (265 nm) and ns (213 nm) irradiation conditions, thus confirming that sufficiently thick varnish coating protects the light sensitive tempera paints from the effects of direct laser irradiation. Further investigations on the effects induced on the paints by optical microscopy and LIF help to discuss the suitability of the two laser irradiation methods for varnish removal.

Laser induced modifications

Optical microscopy served to determine the fingerprint of UV laser irradiation in the fs and ns domains. Fig. 2 shows images of the samples in the region limiting the irradiated and non-irradiated areas of the varnished samples. As observed, irradiation at 265 nm with 260 fs pulses induces a loss of transparency of the remaining varnish layer which acquires a whitish appearance. Closer inspection of the irradiated region of the samples indicates the formation of micrometric sized bubbles. Formation of a foamy layer upon fs laser irradiation has been observed in polymeric materials of similar composition.[21] However, this detrimental effect is absent when the samples are irradiated at 213 nm with a pulse of 15 ns. In this case, with a fluence of 1.5 F_{th} (F_{th} being the threshold for varnish removal with one pulse at this wavelength), the varnish layer thickness decreases, as mentioned above, by about 2 μm while at the same time it maintains its transparent appearance without any evident morphological change. This result exemplifies the degree of control that can be exerted on the layer-by-layer removal of the varnish under ns 213 nm irradiation and can be compared with the larger thickness removed by a KrF excimer laser (4 μm at 2 F_{th}).[2]

To quantify the colour changes on the irradiated varnish paints, colorimetric measurements were performed on the non-irradiated and irradiated varnished areas. The values of ΔE^* as a function of the irradiation fluence are listed in Table 2.

The fs irradiation at 265 nm (260 fs) leads to noticeable discoloration effects for vermillion, lead chromate and azurite paints, while unpigmented and lead white temperas are less affected. Although the loss of transparency on the outer varnish coating should contribute to the measured value of ΔE^*, discoloration is particularly severe for vermillion, where irradiation at fluences even below the threshold for varnish removal leads to pigment darkening ($\Delta E^* = 5.5$ at 0.75 F_{th}). The mechanisms for laser discoloration of vermillion based tempera have been abundantly discussed in the literature with reference to a change of the crystal system and/or chemical reduction.[2,9–12] On the other hand, the measured low ΔE^* values obtained after fs, 265 nm laser irradiation of the unpigmented and lead white varnished samples are in correspondence with the limited colour changes observed even at the highest fluences of 1.5 F_{th}, as observed in the optical microscopy images of Fig. 2.

In clear contrast with the induced modifications of colour resulting from irradiation of the varnished systems with UV fs pulses, ns irradiation at 213 nm preserves the colour of the tempera paints under the ablated varnish layer. In fact, as reported in Table 2, the overall colour change is limited to values of $\Delta E^* \leq 1.2$. This is in agreement with the optical microscopy observations, and demonstrates that efficient and confined layer-by-layer varnish removal can be carried out by operating with these laser parameters without causing discoloration of the underlying paints. Thus, controlled laser varnish removal is possible at 213 nm with pulses of 15 ns as the remaining varnish layer, highly absorbing the laser radiation at this wavelength ($\alpha = 8600$ cm^{-1}), protects the paint against direct exposure to the laser beam avoiding discoloration of the sensitive pigmented layer.[2]

Further investigation of the modifications induced on the varnished tempera paints by laser irradiation was carried out by measuring the LIF spectra. These are displayed in Fig. 3. The spectrum of shellac (Fig. 3a) consists of a broad feature centred at 450 nm with the addition of peaks at 355 nm, 375 nm,

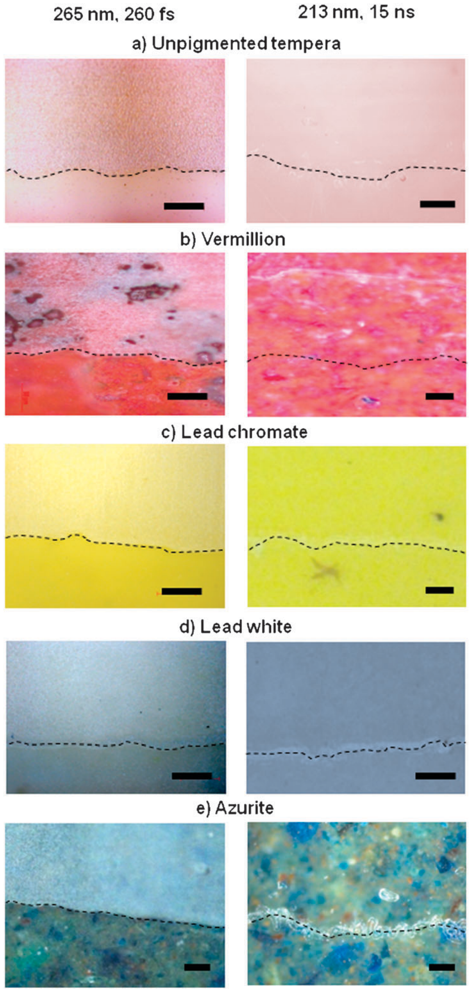

Fig. 2 Optical microscope photographs taken under dark field illumination of irradiated areas of shellac varnished temperas at 1.5 times the fluence threshold for varnish removal. The boundary between the irradiated (upper) and non-irradiated (lower) areas is marked by a discontinuous line. The bar length is 50 μm in all images. Left and right columns correspond to irradiation with 100 pulses at 265 nm with 260 fs and with one pulse at 213 nm with 15 ns respectively.

Table 2 Magnitude of colour changes of varnished tempera paints irradiated at the indicated laser conditions (F_{th} stands for varnish threshold). Errors in ΔE^* are around 10%

	Wavelength, duration and number of pulses	F/F_{th}	ΔE^*
Unpigmented tempera	265 nm, 260 fs	0.75	0.3
	100 pulses	1.0	1.5
		1.5	3.0
	213 nm, 15 ns	0.75	0.1
	1 pulse	1.0	1.0
		1.5	1.2
Vermillion	265 nm, 260 fs	0.75	5.5
	100 pulses	1.0	11.0
		1.5	21.0
	213 nm, 15 ns	0.75	0.1
	1 pulse	1.0	0.3
		1.5	0.5
Lead chromate	265 nm, 260 fs	0.75	2.3
	100 pulses	1.0	24.0
		1.5	29.0
	213 nm, 15 ns	0.75	0.1
	1 pulse	1.0	0.5
		1.5	0.7
Lead white	265 nm, 260 fs	0.75	0.2
	100 pulses	1.0	1.1
		1.5	4.0
	213 nm, 15 ns	0.75	0.1
	1 pulse	1.0	0.5
		1.5	0.6
Azurite	265 nm, 260 fs	0.75	0.4
	100 pulses	1.0	6.0
		1.5	12.0
	213 nm, 15 ns	0.75	0.1
	1 pulse	1.0	1.0
		1.5	1.0

495 nm (assigned to hydroxy acids), and at 630 nm attributed to the fluorescent residual laccaic acids.[18,22]

Fig. 3b–f show the LIF spectra of the unvarnished and varnished temperas (as black dotted and thin lines respectively) and the effects of UV laser irradiation with fs and ns pulses. The fluorescence spectrum of the unvarnished binder (Fig. 3b) consists of a broad band in the 300 to 750 nm with a maximum around 480 nm which results from the contribution of different fluorophores that participate in the composition of egg yolk.[2,7,9] For the unvarnished vermillion and lead chromate, the extra bands observed at 607 nm and 557 nm, respectively, are assigned to the corresponding pigment chromophores, the semiconductor HgS and the chromate ion chromophore (CrO_4^{2-}).[2,9] For lead white and azurite no distinctive pigment bands are observed and the fluorescence spectra of those unvarnished systems resemble that of the binder. The spectra of the varnished systems show both the pigment and varnish features.

Fluorescence spectra of the varnished paint recorded on areas irradiated at 265 nm with pulses of 260 fs, shown in Fig. 3b–f as gray lines, reveal the changes induced. Together with a significant overall reduction of the fluorescence signal and a minor widening of the spectral shape, varnish bands in the short wavelength region below 400 nm and at 630 nm disappear. The change of rugosity on the varnish surface induced by laser irradiation, as evident in the optical microscopy images (Fig. 2), together with photochemical modifications induced on the polymeric material[23,24] are the main factors for the altered spectral shape. Under these laser conditions, a relative noticeable reduction of the band at 607 nm ascribed to vermillion is also evident (Fig. 3c, thick black line). This is in correspondence with the discoloration of this paint reported above. In fact, as mentioned, the shellac layer is partially transparent to the 265 nm laser light, allowing the illumination of the underlying paint which induces degradation of the pigment.[2,7,9]

Irradiation with a 213 nm, 15 ns pulse, black thick lines in Fig. 3b–f, does not alter the fluorescence spectra of the varnished samples, and an increase of the total fluorescence signal intensity is observed in all systems. This is related to the reduction of the thickness of the varnish material. As indicated before, at a fluence of 1.5 F_{th} the thickness decreases by about

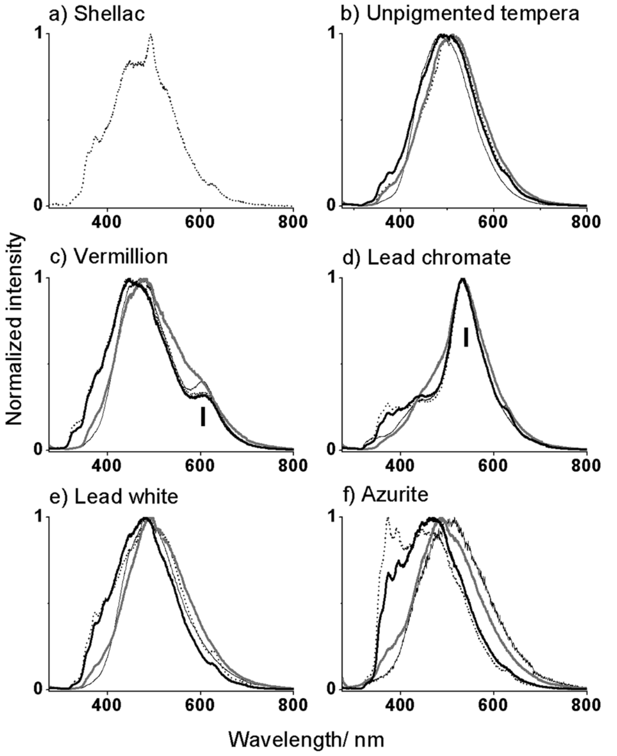

Fig. 3 Normalized LIF spectra (resolution 2.5 nm) on tempera paint samples: (a) shellac, (b) to (f) unpigmented tempera, vermillion, lead chromate, lead white and azurite respectively. Thin black lines are for unvarnished tempera, dotted for varnished tempera, gray for varnished tempera irradiated with 100 pulses at 265 nm (260 fs) and thick black for varnished tempera irradiated with one pulse at 213 nm (15 ns). In both cases the applied fluence was 1.5 times the threshold for varnish removal. The vertical bars in (c) and (d) mark the pigment bands.

2 µm, leaving exposed a less polymerized varnish surface which yields a more intense LIF signal.

Conclusions

Investigations have been carried out on two UV laser irradiation approaches in the fs and ns domains for the removal of shellac varnish on egg yolk based temperas. In a multipulse approach with pulses of fs duration at 398 and 265 nm it was found that the varnish layer either ablates at fluences that exceed the damage threshold of the underlying paint (at 398 nm) or experiences irreversible modifications of the initially smooth superficial texture in the form of a laser generated foam that reduces its transparency (at 265 nm). Together with this unacceptable varnish degradation, the underlying paint layers undergo colour changes, in various extents depending on the nature of the pigment, that are interpreted as due to chemical degradation caused by exposure to the transmitted laser light. In contrast, irradiation with pulses of 15 ns at the highly absorbed wavelength of 213 nm allows the controlled pulse by pulse micrometric layer removal of the varnish and preserves the colorimetric and spectral properties of the underlying paints. Similar results are foreseen for painting varnishes based on dammar and mastic resins, due to the similarity of their absorption spectra to that of shellac. This, together with the increasing availability and compactness of Q-switched Nd:YAG laser systems providing frequency multiplied output, envisages good prospects for this laser cleaning approach in the field of painting conservation. Further investigations on the use of shorter wavelength irradiation at 213 nm, using ps pulses, and 199 nm (4th harmonic of the Ti:Sapphire system), with pulses of fs duration, are in progress. It is foreseen that investigation of the effects under these conditions of irradiation will cast light on the different mechanisms involved in the various temporal regimes and provide new tools for advanced laser cleaning of light sensitive substrates.

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