

Analytical Study of the Chemical and Physical Changes Induced by KrF Laser Cleaning of Tempera Paints

Marta Castillejo,* Margarita Martín, Mohamed Oujja, Diego Silva, and Ricardo Torres

Instituto de Química Física Rocasolano, CSIC, Serrano 119, 28006 Madrid, Spain

Alexandra Manousaki and Vassilis Zafiropulos

Foundation for Research and Technology-Hellas, Institute of Electronic Structure and Laser, P.O. Box 1527, 71110 Heraklion, Crete, Greece

Oscar F. van den Brink† and Ron M. A. Heeren

FOM-Institute for Atomic and Molecular Physics (AMOLF), Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

Rianne Teule

Art Innovation b.v., Westermaatsweg 11, 7556 BW Hengelo, The Netherlands

Alberto Silva and Helena Gouveia

Instituto de Soldadura e Qualidade, Taguspark, Oeiras 2780, Portugal

The cleaning of paintings using UV lasers is a growing field of interest in the practice of conservation. In this work, we have studied the chemical and physical changes induced by KrF excimer laser at 248 nm of tempera paint dosimeter systems. The changes have been evaluated by using a range of analytical techniques. These include profilometry; colorimetry; optical and vibrational spectroscopies, such as laser-induced fluorescence (LIF), laser-induced breakdown spectroscopy (LIBS), Fourier transform Raman (FTR), and infrared (FT-IR); and analytical mass spectrometric techniques, such as direct-temperature-resolved mass spectrometry (DTMS) and matrix-assisted laser desorption and ionization mass spectrometry (MALDI-MS). Integration of the results obtained by these techniques allowed the investigation of the nature and degree of change of the irradiated paint systems. Direct laser irradiation induces various degrees of discoloration that depend strongly on the nature of the pigment. This effect takes place mainly on the surface layer of the sample. Degradation of the binding medium occurs in the presence of inorganic pigments, and in some cases, evidence of alterations in the molecular composition of the pigment has been obtained. Varnished systems do not display this discoloration when a thin protective layer is left on the paint. A laser cleaning strategy for varnished paintings should be based on the partial removal of the varnish, leaving a residual layer that shields the underlying pigments from direct laser exposure.

Laser techniques are being widely used in conservation as advanced tools for cleaning artwork surfaces, for analysis of cultural heritage artifacts and materials, and to study the processes of aging and the effects of the environment on artworks.¹ Laser cleaning is a well-accepted restoration method for the removal of black crusts or other unwanted layers from sculptures made of stone and marble or architectural surfaces.² In the case of painting conservation, active research on the use of lasers has resulted in the discovery that UV excimer lasers can efficiently remove oxidized varnish layers and over-paintings with minimal light penetration and thermal effects to the underlying paint layers.^{3–5} Noncontact etching of the unwanted superficial layers can be performed with in-depth resolution as high as 0.1 μm /pulse and lateral resolution of the order of 50 μm , allowing accurate control of the amount of removed material. UV laser cleaning can be a safe and efficient method when applied together with an on-line diagnostic tool, such as laser-induced breakdown spectroscopy (LIBS),^{5,6} which can also serve as an independent in situ analytical technique.⁷

- (1) Fotakis, C.; Anglos, D.; Balas, C.; Georgiou, S.; Vainos, N. A.; Zergioti, I.; Zafiropulos, V. *Laser Technology in Art Conservation*. In *OSA TOPS on Lasers and Optics for Manufacturing*; Tam, A. C., Ed.; Optical Society of America: 1997; Vol. 9, pp 99–104.
- (2) *Lasers in the Conservation of Painted Artworks in Laser in Conservation: an Introduction*; Cooper, M., Ed.; Butterworth Heineman: Oxford, 1998.
- (3) Georgiu, S.; Zafiropulos, V.; Anglos, D.; Balas, C.; Tornari, V.; Fotakis, C. *Appl. Surf. Sci.* **1998**, 127–129, 738–745.
- (4) Zafiropulos, V.; Galyfianali, A.; Boyatzis, S.; Fostiridou, A.; Ioakimoglou, E. In *Optics and Lasers in Biomedicine and Culture*; von Bally, G., Ed.; Series of the International Society on Optics within Life Sciences; Springer-Verlag: Berlin, 2000; pp 115–122.
- (5) Zafiropulos, V. *Laser Ablation in cleaning of Artworks*. In *Laser Cleaning*; Luk'yanchuk, B., Ed.; World Scientific: Singapore, 2002, in press.
- (6) Klein, S.; Stratoudaki, T.; Zafiropulos, V.; Hildenhagen, J.; Dickmann, K.; Lehmkuhl, T. *Appl. Phys. A* **1999**, 69, 441–444.

* Corresponding author. E-mail: marta.castillejo@iqfr.csic.es.

† Present address: Akzo Nobel—Chemicals Research Arnhem, P.O. Box 9300, 6800 SB Arnhem, The Netherlands.

The high sensitivity to light of the components of pictorial artworks, including pigments and binders, requires a careful study to characterize and quantify the effects of the transmitted UV radiation reaching the paint layers. Previous works^{8–12} have used various techniques to investigate the damaging effects on pigments in powder form or in mixtures with different binding media caused by exposure to laser light of different wavelengths. To validate the cleaning of paintings with UV laser radiation, fundamental research on the interaction of a laser with a painting is imperative for the acceptance of the technique in the restoration community. Knowledge about the immediate and long-term effects of laser radiation on the organic constituents of artists' materials is essential in the evaluation of the cleaning method. However, because of the complexity of the subject, a systematic study is necessary for deriving safe conclusions.

Work done within the framework of a cooperative research project "Advanced Workstation for Controlled Laser Cleaning of Artworks" funded by the European Union^{13,14} has allowed conservators, researchers and engineers to collaborate in a multidisciplinary research effort. The aim was to investigate the viability of the UV excimer laser (KrF, 248 nm) as an additional tool in the practice of painting conservation, to define the boundary conditions in which laser cleaning can be safely applied, to evaluate long-term effects, and to validate the LIBS technique for on-line control of the cleaning procedure. In this paper, we present the results of a systematic analytical study of the effects of laser cleaning performed on a well-defined set of samples through the characterization of the changes induced by laser irradiation in their chemical and physical properties.

A systematic study was carried out on egg-tempera paint-based dosimeters prepared by following a well-defined procedure. These types of model systems were chosen because their aging mechanisms have been previously studied¹⁵ and because it is possible to age them with artificial light in a short period of time. The tempera paints included paints that were pigmented with traditional inorganic pigments, such as lead white and sienna, and organic pigments, such as alizarin. Two types of egg tempera systems were made in order to address different issues of laser cleaning. One-layer samples of unvarnished tempera paint served to determine the nature and extent of physical and chemical changes induced by laser irradiation on paint materials. These samples allowed investigation of the effects of direct laser irradiation and defined the worst case scenario of laser cleaning,

that is, when no protective varnish or over-paint layer has been left and the laser hits the paint surface directly. In a previous paper¹⁶ we gave a preliminary account of the corresponding results. Two-layer samples, constituted by a tempera paint layer covered with a layer of varnish, served to define the laser conditions for efficient laser removal of the varnish layer. These systems were also used to determine the effect of the UV laser light transmitted through the external varnish layer. Laser irradiation of samples was compared with conventional UV lamp irradiation. To study and compare long-term effects, the samples were artificially aged after UV lamp and laser treatment.

A broad range of physical and chemical properties of the prepared samples were measured to study the effects of the treatments applied to them. Profilometry determined morphological changes on the paint surface. Colorimetry was used to measure the discoloration of the paints. Chemical changes in the pigments and also in the binding medium were investigated by optical and vibrational spectroscopic techniques, including laser-induced fluorescence (LIF), laser-induced breakdown spectroscopy (LIBS), Fourier transform Raman (FTR), and infrared (FT-IR). Analytical mass spectrometric techniques, such as direct-temperature-resolved mass spectrometry (DTMS) and matrix-assisted laser desorption and ionization MS (MALDI-MS), allowed the detailed determination of the nature of the chemical changes in the binding medium of the paints. The particular properties of the samples required the development of new MALDI-MS methodologies, as will be shown below.

SAMPLE DESCRIPTION AND LASER AND UV TREATMENT

Sample Preparation. Results obtained on two types of test systems will be described here: (a) systems with a single layer of tempera paint and (b) systems with a layer of tempera paint covered with a layer of shellac varnish. One-layer samples were prepared by adding a selection of pigments to an egg-based binding medium and applying a layer of the mixture on a Melinex support or on a synthetic primed panel. Details on the preparation procedure of the Melinex samples have been given elsewhere,^{15,17,18} and a short description is presented as a guide for the reader. The pigmented tempera paint, consisting of a mixture of egg, mastic, and pigment was deposited on a sheet of Melinex using a Byk Gardner (Geretsried, Germany) film applicator at 200 μm wet layer thickness. For the preparation of the samples on panel, the pigment was mixed with egg yolk using a spatula and a glass plate. Paint layers of around 100 μm thickness were applied on the primed panels by using a stopping-knife, which was fortified with a horizontal brace to prevent it from bending.

The pigments were selected to provide a representative series used in traditional painting practice with various chemical characteristics. Inorganic pigments containing a variety of metal ions included azurite (basic copper carbonate, $2\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$), lead white (basic lead carbonate, $2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$), lead chromate, (PbCrO_4), Naples yellow (lead antimoniate, $\text{Pb}_2\text{Sb}_2\text{O}_7$), cinnabar

- (7) Anglos, D. *Appl. Spectrosc.* **2001**, *55*, 186A–205A.
- (8) Athanassiou, A.; Hill, A. E.; Fourrier, T.; Burgio, L.; Clark, R. J. H. *J. Cult. Herit.* **2000**, *1*, S209–S213.
- (9) Zafiropulos, V.; Stratoudaki, T.; Manousaki, A.; Melesanaki, K.; Orial, G. *Surf. Eng.* **2001**, *17*, 249–253.
- (10) Sansonetti, A.; Realini, M. *J. Cult. Herit.* **2000**, *1*, S189–S198.
- (11) Pouli, P.; Emmony, D. C.; Madden, C. E.; Sutherland, I. *Appl. Surf. Sci.* **2001**, *173*, 252–261.
- (12) Zafiropulos, V.; Balas, C.; Manousaki, A.; Maraki, G.; Marvelaki-Kalaitzaki, P.; Melesanaki, K.; Pouli, P.; Stratoudaki, T.; Klein, S.; Hildenhagen, J.; Dickmann, K.; Luk'yanchuk, B. S.; Mujat, C.; Dogariu, A. *J. Cult. Herit.* **2002**, in press.
- (13) Scholten, J. H.; Teule, J. M.; Zafiropulos, V.; Heeren, R. M. A. *J. Cult. Herit.* **2000**, *1*, S215–S220.
- (14) Teule, R.; Scholten, J. H.; Van den Brink, O. F.; Heeren, R. M. A.; Hesterman, R.; Ullenius, U.; Larsson, I.; Zafiropulos, V.; Castillejo, M.; Martin, M.; Guerra-Librero, F.; Silva, A.; Gouveia, H.; Albuquerque, M. B. *J. Cult. Herit.* **2002**, in press.
- (15) Van den Brink, O. F.; Eijkel, G. B.; Boon, J. J. *Thermochim. Acta* **2000**, *365*, 1–23.

- (16) Castillejo, M.; Martin, M.; Oujja, M.; Santamaría, J.; Silva, D.; Torres, R.; Manousaki, A.; Zafiropulos, V.; Van den Brink, O. F.; Heeren, R. M. A.; Teule, R.; Silva, A. *J. Cult. Herit.* **2002**, in press.
- (17) Van den Brink, O. F.; Boon, J. J.; O'Connor, P. B.; Duursma, M. C.; Heeren, R. M. A. *J. Mass Spectrom.* **2001**, *36*, 479–492.
- (18) Van den Brink, O. F. Ph.D. Thesis, University of Amsterdam, 2001.

(mercuric sulfide, HgS), zinc white (zinc oxide, ZnO), sienna (a mixture of α -goethite, FeOOH and α -haematite, Fe₂O₃), and smalt (glass sintered with cobalt oxide). Paint systems containing organic pigments prone to photodegradation and oxidative changes included curcumin (1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5,-dione, C₂₁H₂₀O₆), alizarin (1,2-dihydroxyanthraquinone, C₁₄H₈O₄), and indigo (C₁₆H₁₀N₂O₂). To investigate the modifications of the binding medium upon laser exposure, samples of the unpigmented paint were used as reference.

The samples on Melinex were cured for a period of 3 weeks and then light-aged for 4 weeks to mimic real aged paints. The periods of curing and light aging were shortened to 14 and 2 days, respectively, in the case of the pigmented paints on panel. Light aging was performed in the MolArt light aging facility at The Limburg Conservation Institute (SRAL Maastricht, The Netherlands) by using 12 Philips TLD-36W/96 fluorescent daylight tubes providing an intensity of 9200 lux. Perspex (PMMA) filters were used to absorb the already low intensities of UV radiation produced by the fluorescent lamps. During aging, the temperature and relative humidity were kept constant at values of 22 °C and 40–44%, respectively.

The varnished test systems were prepared by applying shellac varnish in multiple layers over the tempera paints on panel using a wide paintbrush to obtain an estimated varnish layer thickness of 20 μ m. The varnish was prepared by dissolving shellac resin (from Istituto Centrale del Restauro, Roma, Italy) in ethanol (96%). Because shellac is known to dry very fast, no artificial light aging was needed in these samples.

Laser Treatment. The unvarnished and varnished test systems were treated with a KrF excimer laser producing pulses of ~ 25 ns at 248 nm. The test systems were irradiated by scanning the laser beam over the sample surface. The irradiation parameters, fluence, number of pulses per step and repetition rate, were chosen on the basis of ablation rate measurements and transmission studies (see below). In some cases, LIBS control was used to determine the end of the cleaning action.

The laser beam had a rectangular cross-section with a Gaussian intensity profile in the direction of the smaller dimension and a top hat intensity profile in the longer perpendicular direction. The beam was directed to the surface of the sample by the use of mirrors and was focused onto it by a cylindrical planoconvex quartz lens ($f = 300$ mm). The position of the lens with respect to the sample surface determined the width of the focused beam, and hence, the energy fluence in J cm⁻² on the sample surface. The pulse energy was measured by a joulemeter (Molelectron J4-09), and the spot area, by imaging the focused beam on an unplasticized PVC sheet, reflecting the size of the trace of the laser beam on a varnished surface. To achieve a homogeneously treated surface area, the laser had to be scanned over the sample. It was found that the right overlap during scanning was critical in the smaller dimension of the beam cross section (Gaussian profile), and the optimum overlap was 80% in this direction. For the longer perpendicular dimension, an overlap of 15–20% was found to be adequate.

The unvarnished systems were treated with laser light as to define three data points in each paint system. The first data point is the control nonirradiated sample. Two cases of laser treatment of the surface define two more data points: namely, the worst

case scenario in which the paint layer is severely ablated by the laser, unvarnished laser ablated area; and a milder irradiation not leading to ablation, unvarnished laser irradiated area. The unvarnished ablated data point is obtained by strong laser irradiation above the ablation threshold of the paint surface, at a fluence of ~ 0.4 J cm⁻² close to the optimal fluence for the removal of most aged varnishes.^{3–5} The number of pulses was determined on the basis of the ablation rate of the paint system (see Ablation Rate Studies). These conditions were chosen to typically remove 20% of the paint layer thickness. In the case of the temperas that contained lead salts, the layer removed was thinner than for the other paint systems. The irradiation conditions used to create the unvarnished laser ablated data point on the panel samples are given in Table 1, together with the total UV laser radiation received by the paint surface. Finally, the unvarnished laser irradiated data point was created by delivering 2 pulses/step at a lower fluence of 0.11 J cm⁻², which is below the ablation threshold for all paint systems treated. These irradiation conditions correspond to the practice of laser cleaning in which the varnish layer is barely removed, leaving the underlying paint exposed to low levels of laser radiation. Laser-ablated and -irradiated areas of the unvarnished test samples on Melinex were created at correspondingly similar laser fluences.

Four data points were created from the varnished systems. The first one corresponds to the control nonirradiated data point. A second point was created by removing the varnish layer according to conventional cleaning methods using chemical solvents. The third type of system resulted from best practice laser cleaning, in which part of the varnish was removed using the optimal fluence for varnish removal, leaving a thin layer of varnish. The remaining varnish layer absorbs the residual UV light and acts as a protection for the underlying paint system. The fourth series of varnished systems were treated with elevated laser fluence employing LIBS control to determine the exact number of pulses to reach the paint substrate. This was the worst case scenario in the removal of aged varnish using laser. On the test systems, it was more difficult to determine suitable control parameters than in the laser removal of naturally aged varnish. For the latter, the ablation is usually stopped when the intensity ratio of the CO and the C₂ bands in the LIBS spectrum reaches a predefined value that indicates that the very top layers of oxidized varnish have been removed.^{2,5} Table 1 gives a detailed account of the irradiation conditions of the laser treated varnished samples and the total amount of UV radiation received by the sample. The LIBS criteria used for the process control were chosen on the basis of a range of tests. Starting with relatively low laser fluences (~ 0.45 J cm⁻²), the varnish layer was completely removed from the sample on one position, while continuously recording LIBS spectra (on-line) from the sample surface. If no sufficient LIBS signal was observed, the fluence was raised to 0.6 J cm⁻². The spectra showed mainly a broad signal with no distinct features, characteristic of the case of nonpolymerized varnish. Therefore, the criterion defined in the control software generally included an increase in intensity of a characteristic peak of the underlying pigments. The background signal close to the specific peak was subtracted in the criterion to account for fluctuations in the signal intensity. Small areas were cleaned, varying the signal-to-background ratio in the criterion. The final criterion used for

Table 1. Laser Treatment of Tempera Systems

system	laser ablation of unvarnished systems				best practice laser treatment of varnished systems				laser treatment at elevated fluence of varnished systems					
	ablation threshold J cm ⁻²	mean ablation rate μm/pulse	fluence J cm ⁻²	pulses per step	total radiation on the paint surface J cm ⁻²	fluence J cm ⁻²	pulses per step	total dose accepted by the varnish J cm ⁻²	abladed depth μm	fluence J cm ⁻²	pulses per step	total dose accepted by the varnish J cm ⁻²	abladed depth μm	LIBS criterion peak [nm] ^c
alizarin	0.11–0.24	0.15 ^a	0.41	50	102.5	0.40	2	4	4.1	0.6	3–4	10.5	11.4	([344] – bkg)/(shbkg[435.8] – bkg) < 0.65
cinnabar	0.20	0.11 ^a	0.35	50	87.5	0.40	2	4	4.1	0.46	6	13.8	14.4	(egg[336] – bkg)/(shbkg[435.8] – bkg) < 1.3
unpigmented	0.17	0.68 ^b	0.40	50	100	0.40	2	4	4.1	0.47	4	9.4	10	(Pb[405.8] – Pb _{bkg} [416])/Pb _{bkg} [416] < 0.04
Naples yellow	0.11–0.24	0.017 ^a	0.35	190	332.5	0.32	3	4.8	4.8	0.47	4	4.7	5	(Pb[405.8] – Pb _{bkg} [395])/Pb _{bkg} [395] < 0.03
lead white	0.11–0.24	0.14 ^a	0.39	50	97.5	0.40	2	4	4.1	0.47	2	12.9	13.7	Fe[383.1] – Fe _{bkg} [394.7]/Fe _{bkg} [394.7] < 0.75
sienna	0.27	0.03 ^b	0.35	50	87.5	0.40	2	4	4.1	0.47	5–6	15	16.3	(Co[344] – bkg)/(shbkg[435.8] – bkg) < 0.6
smalt	0.35	0.23 ^b	0.45	50	112.5	0.32	3	4.8	4.8	0.6	5	16.1	16.8	(CN[387.5] – bkg)/(shbkg[435.8] – bkg) < 5
zinc white	0.34	0.13 ^b	0.11	2	1.1	0.40	2	4	4.1	0.46	7	16.1	16.8	(CN[387.5] – bkg)/(shbkg[435.8] – bkg) < 5
shellac	0.21	0.41 ^b												

^a Measured at 0.24 J cm⁻². ^b Measured at 0.4 J cm⁻². ^c The characteristic atomic line or molecular band chosen to apply the LIBS criterion (see text) is expressed by the symbol of the atomic element for the molecular formula and the corresponding wavelength in nm; bkg and shbkg stand for background and broad band signal of shellac, respectively.

^a Measured at 0.24 J cm⁻². ^b Measured at 0.4 J cm⁻². ^c The characteristic atomic line or molecular band chosen to apply the LIBS criterion (see text) is expressed by the symbol of the atomic element or the molecular formula and the corresponding wavelength in nm; bkg and shbkg stand for background and broad band signal of shellac, respectively.

the treatment of the varnished samples at elevated laser fluence was chosen by examining the different test areas. The criteria eventually used on the varnished test systems are listed in Table 1.

UV Irradiation. To identify and calibrate the processes that occur as a result of UV exposure, the unvarnished samples were artificially aged by UV light emitted by a conventional lamp under controlled environmental conditions. The aging cabinet consisted of a climate chamber at constant temperature (22 °C) and relative humidity (55%) that contained eight 15 W UV-C lamps (Philips) that emitted at 254 nm, a wavelength close to that of the laser used for cleaning. Four data points were created by irradiating during periods of 4, 24, 96.5, and 240 h. These irradiation times delivered UV radiation doses of 12.7, 76.0, 306.0, and 761.0 J cm⁻² respectively, estimated on the specification of the effective intensity of the lamps (200–240 $\mu\text{W cm}^{-2}$ at a distance of 20–30 cm).

After laser and UV lamp irradiation and subsequent analysis, the samples on panel were again artificially light aged (with visible light) for a period of 4 weeks in order to assess the long-term effects of the treatments.

EXPERIMENTAL METHODOLOGY

Ablation Rate Studies. To be able to define the data points described in the preceding section, a full laser ablation study was required that included the determination of the ablation rate at a range of laser fluences. The ablation threshold was determined from the obtained ablation rate curve. For measuring ablation rates of the unvarnished tempera paints and of the shellac varnish (applied on a quartz plate), craters were created by delivering a number of laser pulses on the surface of the sample. The depth of the craters was measured by stylus profilometry. The mean ablation rate at a given fluence was obtained by dividing the total resulting depth volume by the spot size and by the number of pulses. The measured ablation thresholds and typical ablation rates at a representative laser fluence for the samples on panel are presented in Table 1. It should be noted that the threshold fluence for removal of shellac varnish, 0.21 J cm⁻², is below the corresponding value for the removal of most of the inorganic paint systems of this study.

Analytical Techniques to Study the Effects of Laser Cleaning. The morphological changes induced by laser irradiation of the surface of the samples were assessed by profilometry using a Mahr Perthner perthometer. The roughness of the surface was evaluated through measurements of R_a , the arithmetic mean deviation of the roughness profile and R_{max} , the maximum roughness depth.

A Minolta CM 408 spectrophotometer was used to record the reflectance spectrum of the paint samples and characterize their chromatic properties. Three spectra were averaged to obtain one data point. Changes in the reflectance spectra were expressed in colorimetric values using the CIELAB procedure. Color shifts are expressed in three variables, namely, ΔL (+ = lighter, – = darker), Δa (+ = shift to red; – = greener), Δb (+ = yellow; – = bluer). The magnitude of the color change is given by $\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$.

Four other spectroscopic techniques, LIF, LIBS, FTR and FT-IR, were employed to characterize the changes induced in the pigment and binding medium as a result of the treatments. These techniques provide information on the molecular structure of the

paint components and allow the identification of pigments in paintings.^{7,20–25} LIF measurements were carried out with the unfocused output of a KrF laser (248 nm), illuminating the sample at an incidence angle of 45° and at a typical laser fluence of 1.25 mJ cm⁻². The induced fluorescence was collected at right angles with respect to the laser beam and imaged onto the entrance slit of a monochromator coupled to a photomultiplier. The spectra were obtained by scanning the grating of the monochromator and averaging at each position over typically five laser shots.

In addition to its use as tool for on-line control of the cleaning procedure, LIBS was used in the research as an analytical technique. In LIBS measurements, the output of the KrF laser was focused on the surface of the samples by a quartz lens to reach the high-energy fluence needed for the formation of a plasma plume (0.5–1 J cm⁻²). The light emitted from energetically excited atoms and molecular fragments in the plasma plume was collected at right angles to the laser beam and analyzed with a spectrograph coupled to a CCD/ICCD detector or an optical multichannel analyzer. The spectra were recorded in the 200–600-nm wavelength range. They were captured choosing the most suitable time delay (100–500 ns after the laser pulse impinged on the surface) and window of observation (200–1000 ns). For some measurements, the total time-integrated signal was collected.

FTR spectra were recorded with an RFS 100/S–G Bruker spectrometer. The excitation source consisted of a Nd:YAG laser emitting at 1064 nm. Low laser power outputs, in the range of 10–20 mW, were used. Only ~1/3 of this power illuminated the sample surface, preventing damage or laser-induced degradation of the samples during measurements. The light scattered from a surface of ~0.01 cm² was collected in backscattering (or 180°) geometry. Each data point was the result of the accumulation of 200 scans. The wavenumber resolution was 8 cm⁻¹. FT-IR spectra were recorded with a Bruker IFS 66 FT-IR spectrometer equipped with a DTGS detector and taken in the reflection mode at 45° using a variable angle reflectance accessory, Specac SC 19650. Areas of ~0.5 × 0.5 cm² were sampled. The reflectance spectra were collected between 4000 and 400 cm⁻¹ as the sum of 512 or 1024 scans at a resolution of 8 cm⁻¹ and were transformed to absorbance units by using the Kramers–Kronig algorithm. Each spectrum was normalized to the absorbance intensity measured at 4000 cm⁻¹.

Mass spectrometric techniques that allowed the investigation of the effects of laser irradiation on the chemical composition of the tempera test systems include direct temperature-resolved mass spectrometry (DTMS)¹⁵ and matrix-assisted laser desorption/ionization MS (MALDI-MS).¹⁷

DTMS is a bulk analysis technique that is able to determine qualitative and quantitative changes on the molecular level. The technique allows the analysis of particulate material on an analytical probe. A detailed description of the technique is given

in ref 19. Applied to the analysis of egg tempera paints, DTMS focuses on the chemical changes in the lipidic part of the binding medium and allows the identification of processes such as oxidation and hydrolysis of triglycerides. Using the multivariate technique of discriminant analysis (DA),¹⁵ the degree of change in the complex mass spectra can be expressed as the score on a set of discriminant functions. Details on the combined use of DTMS and discriminant analysis have been given elsewhere,^{15,17,18} and only a short description will be given here. For the samples of this study, the extraction of the material of the exposed samples by scraping off the Melinex or panel support was found to greatly enhance the efficacy of the determination of the degree of chemical change in the lipidic part of the systems. To prepare a sample for DTMS analysis, ~1 mg of material was scraped off its support and extracted twice with 400 µL of dichloromethane/ethanol (7:3, v/v). A drop (~1 µL) of the combined extracts was applied on the filament of the DTMS probe. After evaporation of the solvent, the probe was inserted into the ion source of a JEOL SX 102A mass spectrometer and heated from ambient temperature to 800 °C in 2 min by ramping the current through the filament. Desorbed and pyrolyzed material was ionized by 16 eV electron impact ionization. Spectra were acquired using a 1-s cycle time. Discriminant analysis of the mass spectrometric data was performed using the ChemomeTricks toolbox, developed at the FOM Institute, which runs under Matlab.

As observed by optical microscopy (see below) the majority of the changes that result from laser irradiation or ablation of the samples occur directly on the top layer (of typical depth 1–2 µm) of the surface of the samples. Therefore, a methodology was developed to investigate the oxidative changes in the lipid compounds present on the surface of the samples. This new methodology builds on the knowledge obtained by using MALDI Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) on similar egg tempera paint systems.¹⁷ In the present study, two MALDI-TOFMS methods (on a Bruker BiFlex instrument) were employed to investigate the oxidative changes on the surface of the UV-treated paint systems. Both methods use dihydroxybenzoic acid as a matrix and 4 pulses of 337-nm UV light from a nitrogen laser to produce analyte ions. In the first method, small samples (9 mm²) were excised from the paint system, mounted on a probe, and sprayed with a wetting agent and a matrix solution. Although the spectra of samples prepared according to this method showed peaks from (oxidized) phospholipids and triglycerides, the signal intensity was spot-dependent. Moreover, the sample preparation was very time-consuming. Therefore, a second method was developed that uses a small piece of a (cellulose) thin-layer chromatography (TLC) plate as surface for MALDI. The TLC miniplate is wetted with cyclohexane and shortly brought in contact with the paint surface. It is subsequently mounted on a modified probe of the MALDI-TOF instrument and sprayed with a 0.5 M solution of 2,5-dihydroxybenzoic acid (DHB) in ethanol. This method was found to be more selective than the direct method and resulted in peaks from pseudomolecular ions of phospholipids (protonated, M + H⁺, and sodiated, M + Na⁺, molecular ions), avoiding fragmentation by loss of trimethylamine from the pseudomolecular ions, which was observed when using the MALDI–FTMS method.¹⁷ The samples investigated were found to contain natural phosphatidylcholines and their (single)

- (19) Boon, J. J. *Int. J. Mass Spectrosc. Ion Proc.* **1992**, 118/119, 755–787.
- (20) Anglos, D.; Solomidou, M.; Zergioti, I.; Zafiropoulos, V.; Papazoglou, T. G.; Fotakis, C. *Appl. Spectrosc.* **1996**, 50, 1331–1334.
- (21) Anglos, D.; Couris, S.; Fotakis, C. *Appl. Spectrosc.* **1997**, 51, 1125–1129.
- (22) Burgio, L.; Clark, R. J. H. *Spectrochim. Acta A* **2001**, 57, 1491–1521.
- (23) Vandenabeele, P.; Moens, L.; Edwards, H.; De Reu, M.; Van Hooydonk, G. *Anal. Chim. Acta* **2000**, 407, 261–274.
- (24) Bruni, S.; Cariati, F.; Casadio, F.; Toniolo, L. *Spectrochim. Acta A* **1999**, 55, 1371–1377.
- (25) Shearer, J. C.; Peters, D. C.; Hoepfner, G.; Newton, T. *Anal. Chem.* **1983**, 55, 875A–880A.

Table 2. Magnitude of Color Changes and Color Shift of Unvarnished Systems on Melinex

	unvarnished laser-ablated		unvarnished laser-irradiated		UV-exposed for 240 h	
	ΔE	shift	ΔE	shift	ΔE	shift
alizarin	2.7	dark	1.2	dark	0.7	<i>a</i>
cinnabar	18.5	green	13.5	green	1.5	green
unpigmented	8.7	yellow	2.4	yellow	10.0	blue
Naples yellow	57.3	blue	1.8	<i>a</i>	3.1	blue
lead white	54.0	dark	28.5	dark	4.9	blue
sienna	37.8	dark	6.8	blue	0.4	<i>a</i>
Ssmalt	6.9	dark	0.9	<i>a</i>	4.3	blue
zinc white	36.8	dark	0.7	<i>a</i>	2.1	<i>a</i>
curcumin	0.9	<i>a</i>	4.7	blue	3.0	blue
indigo	4.5	dark	2.9	dark	0.2	<i>a</i>
azurite	32.8	yellow	7.3	yellow	2.6	blue

^a More than one important shift.

oxygenation products. Doubly oxygenated phospholipids were observed at low intensity and in extreme cases of deterioration only. Using the MALDI-TOFMS results, the degree of oxygenation of the surface of paint samples could be determined as the summed relative intensity of the oxygenated phospholipids.

RESULTS AND DISCUSSION

Profilometry. Detailed measurements of the roughness of the surface of the tempera samples were performed before and after cleaning (conventional and laser), after UV treatment, and after varnishing. The initial roughness R_a of the paint systems was between 5 and 10 μm for all systems, except the unpigmented and lead white systems that yielded very low values, around 1–2 μm . After cleaning (solvent or laser) the roughness increased ~ 20 –50% in all test systems. Varnishing with shellac generally reduced the surface roughness to a greater extent than other varnishes such as ketone or dammar. This is due to the faster drying of shellac varnish compared to other varnishes, as mentioned previously.

Colorimetry. Colorimetric measurements performed on the samples on panel yielded results similar to those on samples with a Melinex support. The colorimetric results obtained on the laser-treated unvarnished systems on Melinex are summarized in Table 2. The results obtained on the samples illuminated with a UV lamp during the longest irradiation period of 240 h are given for comparison. The Table indicates the values of ΔE and which color shift (red-green; yellow-blue; light-dark) contributes most to this magnitude.

As seen in Table 2, the chromatic properties of the unpigmented (binding medium) and organic paint systems remain practically unaltered under low fluence laser irradiation; they discolor only slightly when the surface of the sample is ablated at high fluence. The unpigmented (binding medium) laser-ablated sample shows a somewhat higher discoloration of $\Delta E = 8.7$. In contrast to this behavior, direct interaction of the laser radiation with the inorganic pigmented paint systems at high fluence (unvarnished laser-ablated samples) results in strong discoloration with lead chromate, Naples yellow and lead white suffered the highest effect, ΔE of 74.8, 57.3, and 54.0, respectively. Microscopic and UV fluorescence cross-sectional analysis of the laser treated samples, as exemplified for Naples yellow tempera in Figure 1e,

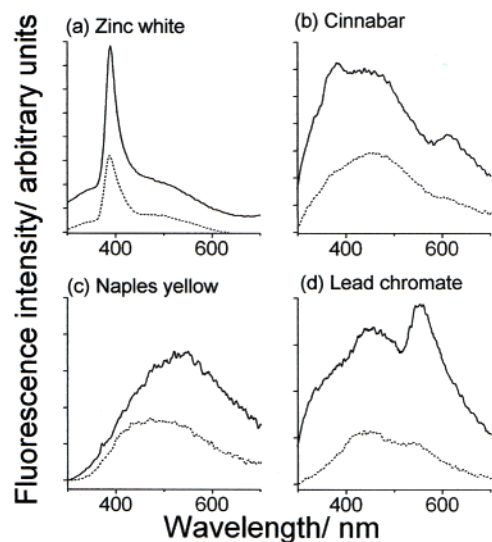


Figure 1. LIF spectra of unvarnished tempera systems taken at a resolution of 1 nm with a laser fluence of 1.2 mJ cm^{-2} : (a) zinc white, (b) cinnabar, (c) Naples yellow, and (d) lead chromate. The exciting laser wavelength is 248 nm. A cutoff filter at 298 nm was used in front of the monochromator to reject scattering light from the laser. The spectra have not been corrected for the spectral response of the detection system. The continuous and dotted lines correspond to the control samples and 20% ablated by laser respectively (see text). (e) UV fluorescence image of a cross section of an unvarnished laser-ablated region of a Naples yellow tempera sample. Magnification is $500\times$. The layer thickness is 20 μm ; the size of the charring particles, $<1 \mu\text{m}$; and the charring layer thickness, $\sim 2 \mu\text{m}$. The underlying paint appears unaltered.

revealed that discoloration takes place on the uppermost layer (of about 1–2 μm) of the sample, as was initially observed for cinnabar and lead white.^{9,12}

The UV aging series showed a trend in discoloration for each of the tempera systems. The colorimetry data indicate that UV aging has a distinctively different effect on the color appearance of the samples, as compared with the laser-cleaned samples. The sienna samples, for example, exhibit no discoloration after 4-day UV exposure ($\Delta E = 0.4$), whereas laser ablation resulted in severe darkening, constituting a high ΔE value of 37.8. These results indicate that effects induced by UV lamp irradiation are of a nature that is different from those induced by a UV laser.

Colorimetric measurements also indicated that varnish application causes a small spectral shift toward the paint's complementary color, resulting in better color saturation. Laser cleaning of the varnished samples, both in the conditions of best practice and at elevated fluence, has no significant effect on the color of the samples, indicating that the varnish protects the paint against discoloration by impeding direct interaction with the laser beam.

In specific cases, as for cinnabar and lead white systems, post aging of the test systems reversed the discoloring effects of laser irradiation and ablation. Upon post aging, the color of the nonvarnished laser-ablated cinnabar and lead white systems shifted back to red ($\Delta a = +1.5$) and to white ($\Delta L = +14.5$), respectively. None of the paint systems showed an enhancement of the laser-induced discoloration upon post aging.

Laser-Induced Fluorescence and LIBS. The LIF spectra of the unpigmented nonvarnished system consist of a broad feature around 450 nm. Extra bands related to the pigments appear in the spectra of the pigmented paints. Curcumin and zinc white contribute with an intense band at 560 and 385 nm respectively that can be readily assigned to the pigment emission.^{26,27} The LIF spectra of azurite, lead white, and lead chromate display features at 380, 490, and 560 nm, respectively, which are tentatively assigned to the specific pigment. Selected LIF spectra of unvarnished systems on panel are shown in Figure 1. Similar results were obtained for the samples on Melinex. Laser treatment, either ablation or irradiation, does not modify substantially the intensity of the fluorescence bands of the systems based on the organic pigments. However, contrary to what is observed in organic systems, laser ablation of inorganic pigment sample areas results in a significant reduction of the LIF emission intensity (cf. Figure 1). In all cases, the LIF spectra of laser irradiated areas are less affected or, as for lead chromate, show negligible intensity modifications.

Irradiation with 254-nm UV light does not alter the fluorescence spectra of the unvarnished samples, although an increase in the total fluorescence signal intensity proportional to the exposure time is observed in all systems. This is possibly related to the formation of oxygenated material upon UV irradiation.

Application of the varnish layer does not substantially modify the spectral shape of the fluorescence of the tempera systems; i.e., spectra taken at the nontreated sampled areas are similar to the ones measured at the corresponding unvarnished areas, although the intensity is much lower. The fluorescence produced by the varnished samples is due to the transmitted laser light that reaches the underlying pigment layer. The total fluorescence intensity is observed to increase upon cleaning, either conventional, or laser. In the case of zinc white, the intensity of the pigment band is much higher after conventional cleaning, indicating that this procedure has removed more varnish than laser cleaning.

The effect of conventional and laser cleaning of varnished samples is reflected in the changes observed in the LIBS spectra taken at elevated fluence in order to ensure a bright ablation plume. As an example, we show in Figure 2 the results obtained for the varnished zinc white samples. Unlike the LIBS spectra at lower fluence for on-line control of the laser treatment of the samples, the LIBS spectra of the reference sample showed the molecular CN and C₂ Swan bands centered at 386 and 478 nm, respectively, that originate from the varnish. Atomic Ca emissions at 393.36 and 396.84 nm were also visible. Removal of the varnish by conventional methods resulted in a disappearance of the organic CN and C₂ bands and the emergence of prominent atomic Zn bands at 468.01, 472.21, and 481.05 nm, indicating that this

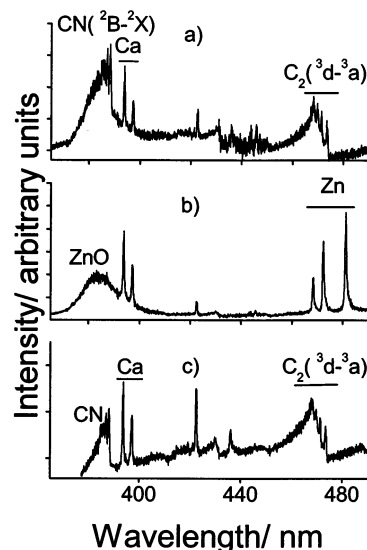


Figure 2. LIBS spectra of varnished zinc white tempera samples: (a) untreated sample, (b) cleaned with solvent, and (c) best-practice laser-cleaned.

cleaning procedure has exposed the pigment layer surface. The spectrum of the sample cleaned at low laser fluences is similar to the spectrum of untreated varnished sample. This is consistent with the fact that a layer of varnish has been left to protect the paint and demonstrates that laser cleaning can be used for the controlled removal of part of the varnish layer. This is not possible using conventional methods.

The above example and previous results on unvarnished lead chromate samples¹² indicate that LIBS, in addition to its use as on-line monitoring technique, also serves as analytical tool for the evaluation of changes on the surface of laser-treated paints immediately after treatment.

FTR and FT-IR. The FTR spectra of the pigmented tempera systems display the characteristic bands of the corresponding pigment.²² The egg binding medium contributes to the spectra with bands of aliphatic compounds in the 2000–3000 cm⁻¹ region, (assigned to the $\nu(\text{C-H})$ mode) and organic bands near 2100 cm⁻¹. Figure 3 shows FTR spectra of the unvarnished cinnabar, Naples yellow, lead chromate, azurite, and alizarin tempera, where the pigment bands have been readily assigned. Strong laser irradiation leading to ablation induces noticeable modifications in the Raman spectra of the inorganic pigment samples and leaves unaffected the spectra of the organic ones. This is exemplified in Figure 3 for alizarin. Laser irradiation at lower fluence does not modify the spectra of either inorganic or organic systems significantly (data not shown). The modifications induced by laser ablation on inorganic systems include a decrease in intensity of the pigment bands, an increase in some cases of the blackbody emission at high wavenumbers (e.g., for lead chromate, azurite, zinc white, and lead white tempera), and the appearance of extra features in the spectra. We have observed the build-up of extra bands characteristic of amorphous carbon at 1325 and 1580 cm⁻¹²² upon laser ablation of the azurite, sienna, and zinc white paint systems. In the case of azurite, new bands indicating a change in the chemical composition of the pigment appear around 143 and 640 cm⁻¹ as a result of laser exposure.¹⁶ These have been assigned to the reddish semiconductor compound cuprite Cu₂O.²⁸ In fact,

(26) Chignell, C. F.; Bilski, P.; Reszka, K. J.; Motten, A. G.; Sik, R. H.; Dahl, T. A. *Photochem. Photobiol.* **1994**, *59*, 295–302.

(27) Srikant, V.; Clarke, D. R. *J. Appl. Phys.* **1998**, *83*, 5447–5451.

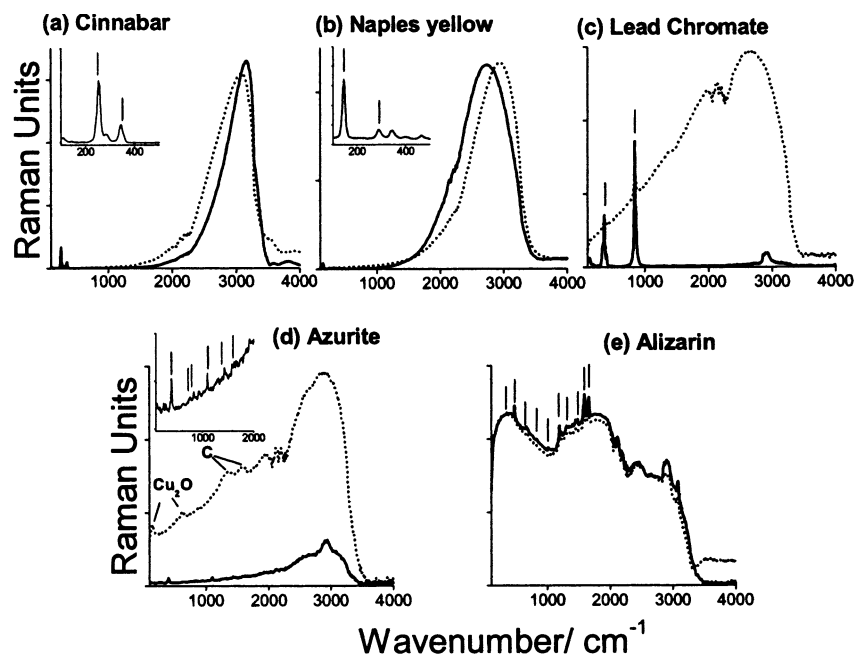


Figure 3. Fourier Transform Raman spectra of unvarnished tempera systems: (a) cinnabar, (b) Naples yellow, (c) lead chromate, (d) azurite, and (e) alizarin. Continuous lines represent untreated samples, and dotted lines, laser-ablated samples. Assigned pigment lines are indicated by vertical bars. The insets show in detail the characteristic pigment bands.

a shift to red is observed by colorimetry measurements on this paint sample.

The spectral modifications can be correlated with changes in the chemical physical properties of the sample surface. The increase in the continuous signal (blackbody emission) in the Raman spectra of the laser-treated inorganic pigmented samples correlates well with the increase in roughness, as measured by profilometry, which has revealed a higher surface roughness after laser treatment that certainly modifies the scattering properties of the surface. The observed continuum indicates an additional contribution of blackbody emission that is likely to be due to a more efficient absorption of the exciting laser light at 1064 nm, causing an increase in temperature of the laser-treated surface. These observations are in agreement with colorimetric results. The decrease in intensity of the inorganic pigment bands and the appearance of new bands in the FTR spectra point toward alterations in the molecular composition of the sample surface. In the case of azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), a possible reduction of the copper compound to yield cuprite (Cu_2O) could be taking place under strong laser irradiation. On the other hand, XPS measurements performed in lead chromate samples showed that laser ablation induces a noticeable decrease in the $\text{CrO}_4^{2-}/\text{Cr}^{3+}$ ratio.¹⁶ This is an indication of the formation of the chromium (III) oxide (Cr_2O_3). Oxide formation by reduction of the original salt could explain the color shift to green, as observed by colorimetry, and is also correlated with the relative intensity changes of the Pb and Cr lines in the LIBS spectra of this paint system.¹⁶

UV aging at 254 nm does not induce a significant alteration of the Raman spectra of the unvarnished samples, not even for the longest exposure periods. Only lead white samples are affected by an increase in the continuous blackbody emission proportional to the exposure time. This correlates with the shift to blue

observed in the UV-exposed yellowish lead white systems, as shown in Table 2. These results indicate that laser-induced changes on the pigmented tempera samples are of a different nature from those induced by prolonged UV lamp irradiation. Varnishing the samples does not modify their Raman spectra as a result of the transparency of the varnish to the exciting 1064 nm laser. Laser cleaning of the varnished samples does not result in significant spectral changes, either. Post-ageing does not lead to qualitative changes in the FTR and LIF spectra of any of the paints.

Some examples of the FT-IR spectra of the nonvarnished tempera samples are shown in Figure 4. The spectra of the unpigmented samples show the amide II and I bands at 1539 and 1666 cm^{-1} , respectively, attributed to the proteins of the binding medium^{23,29,30} and the ester carbonyl band at 1740 cm^{-1} assigned to the lipid component of the egg.³⁰ The spectra of the pigmented systems include the above features and the characteristic pigment bands. The intensity ratio of the carbonyl and amide I bands at 1740 and 1666 cm^{-1} , respectively, increases upon laser ablation. For inorganic systems, the spectra of laser-exposed samples show a considerable decrease in the relative intensity of the pigment bands, as shown in Figure 4 for the lead white, lead chromate, and azurite tempera paints. In the case of the organic systems, the relative intensity of all spectral bands does not change to a great extent (see Figure 4 for the example of alizarin tempera).

The absence of changes in the color and spectroscopic properties of the unvarnished samples based on organic pigments under low fluence laser irradiation, and the low extent of the modifications observed under strong laser irradiation give a firm indication of the stability of the binding medium itself and in

(28) Ivanda, M.; Waasmaier, D.; Endriss, E.; Ihringer, J.; Kirfel, A.; Kiefer, W. *J. Raman Spectrosc.* **1997**, *28*, 478–493.

(29) Castillejo, M.; Martin, M.; Oujja, M.; Silva, D.; Torres, R.; Domingo, C.; García-Ramos, J. V.; Sánchez-Cortés, S. *Appl. Spectrosc.* **2001**, *55*, 992–998.

(30) Cohen N. S.; Odlyha, M.; Campan, R.; Foster, G. M. *Thermochim. Acta* **2000**, *365*, 45–52.

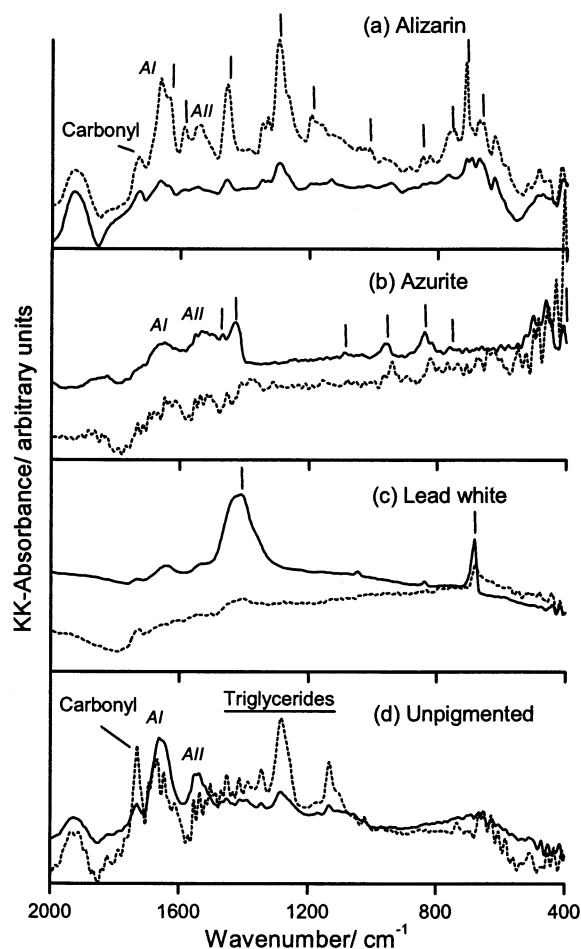


Figure 4. FT-IR spectra of (a) alizarin, (b) azurite, (c) lead white, and (d) unpigmented tempera samples. Continuous lines represent untreated samples, and dotted lines, laser-ablated samples. Assigned pigment lines are indicated by vertical bars and amide bands of the egg albumen at 1539 and 1666 cm^{-1} by AII and AI, respectively.

combination with organic pigments. These results suggest that the laser ablation mechanism is mainly photochemical by nature and that contributions of further thermal effects on the surface of the samples play a minor role. However, the drastic color changes, the quenching of the fluorescence emissions, and the modifications of LIBS, FTR, and FT-IR spectra indicate that alterations of the pigment and degradation and charring of the binding medium (as shown in Figure 1e) take place in the presence of the inorganic pigments.

Mass Spectrometry. Mass spectrometric analysis further supports the above observations. The DTMS/DA results on the unvarnished laser-ablated and irradiated samples of the unpigmented egg tempera showed a low degree of chemical change in the bulk material. This provides additional proof of the dominance of a photochemical ablation mechanism induced in the egg-binding medium by the KrF laser. DTMS/DA results showed a correlation between the exposure under UV lamps and the degree of chemical change, which is constituted by oxidation and cross-linking. This indicates that the laser treatment initially induces little change in the bulk of the unpigmented paint sample, as compared to prolonged UV exposure. On the other hand, DTMS/DA measurements confirmed the occurrence of important modifications in the inorganic paint systems. Chemical changes were observed in the laser-treated inorganic systems.¹⁶

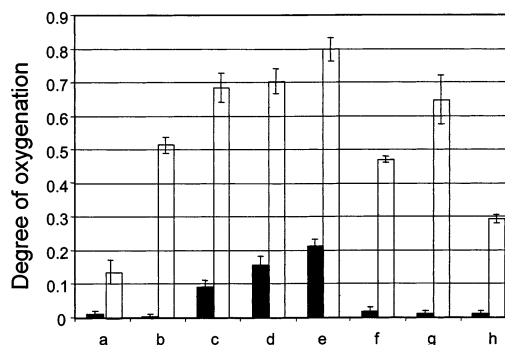


Figure 5. Degree of oxygenation of phosphatidylcholines, as defined in the text, measured on the surface of egg tempera paint systems: (a) unvarnished nontreated; (b–e) UV-exposed for 4, 24, 96.5, and 240 h, respectively; (f) unvarnished laser-ablated; (g) unvarnished laser-irradiated, (h) varnished, laser-treated at elevated fluence. Full and empty bars are for the unaged and post-aged samples, respectively.

MALDI-MS measurements of prints on the surface of the treated paint systems on TLC plates were performed in order to focus more on the changes on the surface of the paint samples. The degree of oxygenation of phosphatidylcholines (PCs) was determined. It is defined as the product of the intensity of the peaks attributed to oxygenated PCs as a fraction of the total PC signal and the number of oxygen atoms introduced into the PCs. The calculation of the degree of oxygenation from MALDI-FTMS results obtained on oxidized egg tempera samples is described elsewhere.¹⁷ The results, presented in Figure 5, indicate that the surface of the unvarnished nontreated control sample shows a low degree of oxygenation, ~ 0.01 . Laser treatment does not lead to a significant increase in the degree of oxygenation after exposure. The degree of oxygenation of the varnished sample laser-cleaned at elevated fluence is negligible, too. On the contrary, the samples exposed to UV light (at 254 nm) for different periods of time¹⁴ showed significant degrees of oxygenation of phospholipids on the surface that increase with the exposure time. Thus, these results indicate once again that aging with a UV lamp yields different photochemical effects, as compared to the irradiation with the KrF cleaning laser. Hence, a modeling study of the effects of laser cleaning can be validated only on actual laser-treated samples.

The effect of post-ageing on the degree of oxygenation of the phospholipids on the surface of the paint systems is also shown in Figure 5. After post-ageing, the degree of oxygenation of all the samples increased. The lowest value was observed for the untreated sample; all other samples showed a higher value. This is attributed to UV-induced formation of relatively stable radicals or small quantities of labile material (peroxides), which serve as an initiator or catalyst of oxidative processes that take place during visible light exposure. After post-ageing the paint sample irradiated at low fluence showed a higher degree of oxygenation than the ablated paint sample. This is tentatively explained as follows: During laser irradiation, all the energy of the laser beam is absorbed by the surface of the paint layer. However, during laser ablation, the plasma plume formed by the ablated material shields the underlying sample material from laser light, so that fewer photons are absorbed. In a similar way, the lower degree of oxygenation (after post-ageing) observed for the varnished sample

cleaned with laser at elevated fluence suggests that the varnish absorbs most of the photon energy during laser cleaning.

CONCLUSIONS

The combined use of several analytical techniques is necessary to characterize and quantify the chemical and physical effects induced by KrF excimer laser cleaning of tempera paint systems. The understanding of the effects of the UV laser radiation reaching the paint layers is very much required in order to define the consequences that could result from the total removal of a protective varnish or over-paint layer in a worst case scenario of laser cleaning. The direct interaction with the laser at high fluence can result in irreversible unwanted changes, although these effects are constrained to the surface of the sample and are strongly dependent on the nature and chemical characteristics of the paint. Organic tempera paint systems feature a high degree of stability under intense laser treatment. In contrast, strong direct laser irradiation of the inorganic paint systems induces various types and degrees of alterations in the properties of both the pigment and the binding medium, which are not a mere addition of effects on individual components in the mixture. The observed discoloration could be due to a modification of the pigment chemical composition through a change in its state of oxidation or due to a change in the pigment crystalline phase.⁹ Evidence of such phenomena is given in this and previous work¹⁶ for the cases of azurite, lead chromate, and Naples yellow tempera. The ablation of organic material leads to the formation of a thin layer of char that covers the original paint surface. This layer is not produced in the absence of the inorganic pigment in the paint, indicating that pigment particles mediate the char formation through an energy-transfer mechanism. Clearly, the actual paint/pigment composition will determine which of the two effects, change of

pigment chemical composition or charring of the outermost paint layer, is dominant. In all cases, it has been shown that modifications induced by laser irradiation at a fluence below the ablation threshold in both organic and inorganic paint systems were found consistently less severe or undetectable. On the other hand, the results shown in this work suggest an adequate strategy for laser cleaning consisting of a controlled partial removal of the outermost varnish layer, leaving a protective coating that prevents discoloration or other chemically harmful effects.

ACKNOWLEDGMENT

Funding by the European Commission (Project ENV4-CT98-0787) is gratefully acknowledged. The samples were prepared by CORESAL (Madrid, Spain), Bonsoficios (Lisbon, Portugal) and R. Hesterman (Muiden, The Netherlands). Thanks is given to the Limburg Conservation Institute (SRAL, Maastricht, NL), in particular to R. Hoppenbrouwers, for help with the aging of systems and the use of the colorimeter. Prof. Dr J. J. Boon, Ir J. van der Weerd, Drs. M. Geldof, A. E. Kerkhoff, J. van der Horst, M. C. Duursma, and G. B. Eijkel are kindly acknowledged for fruitful discussions and assistance. Thanks is also given to Drs. C. Domingo and J. V. García-Ramos for performing FTR and FT-IR measurements and for useful discussions. This work has benefited from the support of the Ultraviolet Laser Facility operating at Fo.R.T.H. under the Large Installations Plan of the European Union.

Received for review May 17, 2002. Accepted June 25, 2002.

AC025778C