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Laser-induced alteration of contaminated papers

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ABSTRACT Cleaning of paper objects represents one of the most complex cases of laser ablation, since low volumes of dispersed material phases are evaporated while a sensitive and fragile fibrous organic matrix has to be preserved. Conventional chemical and mechanical cleaning methods suffer from the common phenomenon that the foreign matter is diluted into the substrate rather than removed. The application of a laser beam allows highly localized and optically specific interaction. However, the occurrence of extreme temperatures and light intensities may cause irreversible alteration of the paper matrix. Further, incomplete removal and/or chemical conversion of contaminations may result in insufficient cleaning or affect the ageing behaviour. Laser treatments were performed by Q-switched Nd : YAG lasers at three wavelengths (355 nm, 532 nm, and 1064 nm). Papers contaminated with inks and adhesive-tape remnants served as model samples. Multispectral imaging and colorimetric results served to quantify and systematize the results.

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1 Introduction

Laser cleaning of paper has attracted much interest in respect of the conservation of cultural and historic objects [1–6]. Recently, optical and chemical laser-induced alterations of various uncontaminated, pre-aged, and post-aged paper types have been characterized by spectral reflectance colorimetry, size-exclusion chromatography (SEC), and photon counting, in order to measure colour changes, the weight-average molecular mass (M_w) of cellulose, and chemiluminescence (CL), respectively [7]. Thus, the weight-average molecular mass or, interconvertibly, the average degree of polymerization (DP) and chemiluminescence allowed quantitative monitoring of the degradation of paper. Colour changes after laser irradiation were more pronounced for pre-aged samples than for fresh ones. The laser treatment with second-harmonic green light at 532 nm below the ablation threshold fluence gave the most promising results on pure papers, with no discoloration and no other visible alteration, nor detectable chemical changes as a further proof of earlier findings [4, 5]. On the other hand, chemical alterations of the pure paper samples occurred as a result of UV laser treatment: the cellulose was depolymerized and luminescent species were formed due to photosensitized radical degradation reactions. These initial degradation products turned into coloured products, yielding significant discoloration after artificial post-ageing.

In this study, papers contaminated with ink and glue were laser treated at $\lambda = 355$ nm, 532 nm, and 1064 nm and diagnosed with colorimetry and multispectral imaging in respect of the complex interrelationship of incongruent material ablation and preservation of paper-fibre matrices.

2 Experimental

Three paper types were used in this study: bleached sulphite softwood cellulose paper with no fillers and no sizing (P1), additive-free cotton linters cellulose paper with no fillers and no sizing (P2), and acid mechanical pulp paper, alum-rosin sized and kaolin coated (P3). In certain instances, pre-ageing was performed by exposure to air at 90 °C and 50% relative humidity, in the dark, for 12 days.

Laser treatments were undertaken by three different laser wavelengths (355 nm, 532 nm, and 1064 nm) at the Federal Institute for Materials Research and Testing, Berlin. The wavelength $\lambda = 355$ nm was generated as the third harmonic of a Nd : YAG laser system (Spectron Laser Systems, SL 852) yielding a maximum energy of 16 mJ with a pulse duration of 13 ns and a repetition rate of 1.25 Hz. The beam was focused by a quartz cylinder lens (310-mm focal length) to a spot dimension of $200 \times 2000\,\mu m^2$ (area 0.04 cm^2). Samples were mounted and scanned on a controlled x–y–z stage. The wavelengths of $\lambda = 1064$ nm and 532 nm were delivered by a com-

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puterized prototype laser cleaning system, based on a high pulse energy diode pumped Q-switched Nd : YAG laser operating with a pulse duration of approximately 10 ns and a maximum energy of 5 mJ (1064 nm) and of 2.5 mJ (532 nm), respectively. The set-up consisted of a scanning optical system (254-mm focal length) which delivered a spot size of approximately 100 μm and energy densities (fluences) in the range of up to $F_{max}(1064) = 21\ \mathrm{J\,cm^{-2}}$ and $F_{max}(532) = 10\ \mathrm{J\,cm^{-2}}$. The repetition rate could be chosen up to 1 kHz.

Colour measurements on laser-treated areas and untreated background were carried out using a spectrophotometer (Minolta CM-2002) equipped with a 5-mm-aperture sample holder (CM-A49). The spectrophotometer was connected to an integrating sphere, illuminated with a UV-filtered pulsed xenon arc lamp. CIE-$L^*a^*b^*$ colour coordinates were calculated for the 10 standard observer and illuminant D65. The vector between both points is the colour difference between two colours ΔE^*:

$$\Delta E^* = \sqrt{L^{*2} + a^{*2} + b^{*2}}. \qquad (1)$$

Humans can detect $\Delta E^* > 1$.

The multispectral imaging system (MuSIS 2007, Art Innovation, Hengelo, The Netherlands) operated in a spectral range from 320 nm to 1550 nm [6]. Several imaging modes were employed: visible reflection, infrared reflection, visible fluorescence, and ultraviolet reflection.

3 Results and discussion

The removal of contaminating ink script and stamps, or ink 'bleeding' areas is an often-encountered complicated task in paper conservation. Several ink–paper models have been treated.

Ballpoint ink is a very common contaminant on paper. An image of a pre-aged acid mechanical pulp paper (P3) laser treated at $\lambda = 532$ nm at various fluences is depicted in Fig. 1. The judgment of the cleaning effect by the naked eye can be quantified by the colorimetric evaluation (Table 1). The colour difference ΔE^* in dependence on the applied laser fluence F is depicted in Fig. 2. The pre-aged pure pulp paper shows a slight ΔE^* change to approximately 2.5 upon illumination above $F = 0.5\ \mathrm{J\,cm^{-2}}$. The CIE-$L^*a^*b^*$ colour-coordinate change indicates less saturation of a yellowish appearance, i.e. a kind of bleaching occurred (Table 1). The laser removal of the ink is not complete in the F range of $F < 0.5\ \mathrm{J\,cm^{-2}}$, where the original paper colour is not changed. However, the original blue saturation with $b^* = -9$ has already turned into $b^* = +14$, not far from the original paper value of $b^* \sim +17$. Only in the region $F > 1\ \mathrm{J\,cm^{-2}}$ is the ink practically removed; however, the paper attains the same colour change observed without ink in the same fluence regime.

Red felt-tip pen ink has been applied as a model system to bleached sulphite softwood cellulose paper (P1, Fig. 3) and to acid mechanical pulp paper (P3, Fig. 4). A matrix of 6×5 or 5×4 squares (approx. $8 \times 8\ \mathrm{mm^2}$) for each wavelength/substrate combination was laser treated with increasing fluences (F, top down) and pulse numbers ($N = 1, 2, 3, 5$, and 9, from left to right). The ultraviolet laser (355 nm) was varied from $F = 0.25$ to $1.9\ \mathrm{J\,cm^{-2}}$, the green laser (532 nm) from $F = 0.1$ to $2.5\ \mathrm{J\,cm^{-2}}$ (shown in Figs. 3 and 4), and the infrared laser (1064 nm) from $F = 1.2$ to $6.7\ \mathrm{J\,cm^{-2}}$.

	$F/\mathrm{J\,cm^{-2}}$	L^*	a^*	b^*	ΔE^*
No ink	0	81.53	2.00	17.17	0
	0.1	81.67	1.82	16.95	0.31
	0.2	81.70	1.79	17.04	0.29
	0.4	81.82	1.66	17.02	0.47
	0.8	82.45	1.25	16.01	1.66
	1.5	83.06	0.98	15.60	2.41
	2.5	82.97	0.75	15.37	2.62
With ink	0	58.11	−0.23	−9.00	35.18
	0.1	67.75	−4.32	0.87	22.26
	0.2	73.77	−3.44	8.57	12.80
	0.4	78.24	−1.23	13.91	5.64
	0.8	80.94	−0.03	14.73	3.23
	1.5	81.83	0.35	14.89	2.83
	2.5	82.45	0.53	15.32	2.54

TABLE 1 Laser cleaning ($\lambda = 532$ nm) of ballpoint ink on pre-aged acid mechanical pulp paper (P3); pre-ageing at 90 °C, 50% relative humidity, in the dark, 12 days; colorimetric data ΔE^* vs. laser fluence F: CIE-$L^*a^*b^*$ colour coordinates, colour difference ΔE^*, L^*, a^*, blue saturation b^*

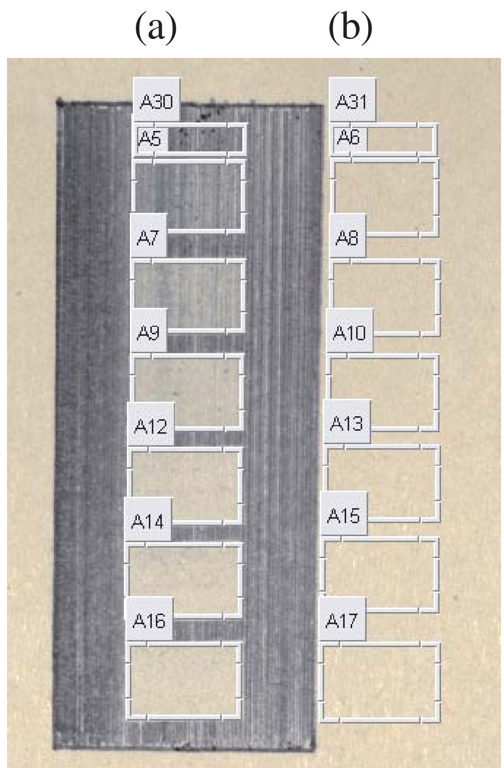


FIGURE 1 Laser treatment of pre-aged acid mechanical pulp paper (P3). $\lambda = 532$ nm; pre-ageing at 90 °C, 50% relative humidity, in the dark, 12 days; (a) bulb paper with ballpoint ink, (b) pure bulb paper

Multispectral imaging is an advantageous diagnostic tool on contaminated surfaces, where colorimetry is less meaningful in contrast to pure substrates. It allowed a fast and semi-quantitative strategy to not only document colour changes (see above) but also diagnose invisible absorption changes in the UV and IR due to irreversible chemical degradations.

The unsized softwood cellulose paper (P1) showed a cleaning effect up to $F = 1\ \mathrm{J\,cm^{-2}}$. The UV, VIS, and IR reflectivity increased with F. Degradation was observed above approxi-

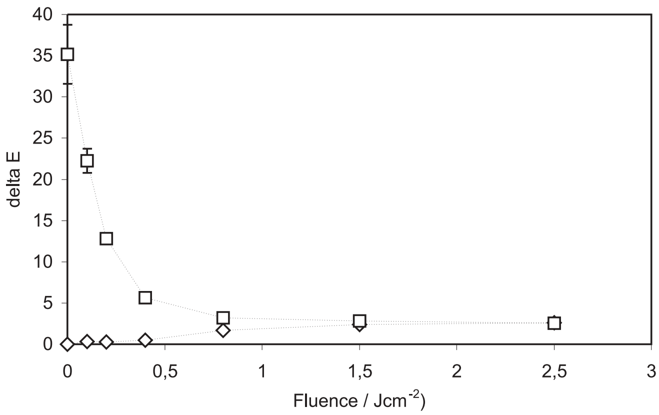


FIGURE 2 Colorimetric data of laser treatment with $\lambda = 532$ nm on ball-point ink and pure bulb paper (P3). Colour difference ΔE^* vs. fluence F; ◇ without ink, □ with ink

mately $F = 1\,\mathrm{J\,cm^{-2}}$, according to an increase of UV absorption indicated by a decrease of UV reflectance (Fig. 3c). Charring occurred above $F = 2\,\mathrm{J\,cm^{-2}}$, as can be seen in the visible, the IR (Fig. 3b), and the UV reflectance images. The optimum cleaning result (circles) can be discriminated both by the naked eye (Fig. 3a) and by the invisible information from IR (Fig. 3b) and UV (Fig. 3c) at $F = 0.8\,\mathrm{J\,cm^{-2}}$ and a number of pulses $N = 9$.

Ink removal from alum-rosin sized and kaolin-coated acid mechanical pulp paper (P3) was more difficult because this paper type is much more sensitive to chemical changes and charring. Even though the cleaning status was not yet optimum at $F = 0.4\,\mathrm{J\,cm^{-2}}$ (Fig. 4a), higher fluences were prohibitive because the IR (Fig. 4b) and the UV reflectance images (Fig. 4c) indicated irreversible chemical changes even for the lowest number of pulses $N = 1$. This is due to the complex fibre composition of the pulp paper type, whereas the inorganic additives are not expected to react at these fluences.

An example of oil-based postage-stamp ink was located exclusively on the surface of the paper. Laser radiation of $\lambda = 532$ nm could remove the aged cross-linked ink, whereas the UV wavelength achieved only partial removal paralleled by yellowing (not shown here). A treatment with $\lambda = 1064$ nm led to brown deposits on the recto side and print removal on the verso side due to radiation penetration throughout the entire paper.

Tests with a red felt-tip pen writing on modern alkaline office paper, which has been deliberately caused to 'bleed' by adding a small volume of acetone, also showed the contrasting effects of the laser wavelengths. $\lambda = 532$ nm yielded sufficient cleaning of the bled area, whereas $\lambda = 1064$-nm irradiation even caused deep disruption of the paper bulk (not shown here). An experiment with a KrF-excimer laser radiating at $\lambda = 248$ nm caused the paper to discolour and reduced the fluorescence of the optical whitener present in the paper.

Remnants of adhesive tapes are often a complex problem for paper conservation. Laser treatment with $\lambda = 532$ nm again yielded satisfactory cleaning results with a superficial deposit of rubber-based adhesive (Fig. 5a). However, deep or strong superficial discoloration was caused by laser radiation of $\lambda = 1064$ nm and 248 nm, respectively. The same held for the removal of a superficial layer of a mixed starch- and protein-based adhesive partially covering a printed text on a rag paper (Fig. 5b). The laser beam had to be scanned around the upper-right letter 'u' in order to avoid its ablation.

4 Conclusions

Cleaning of paper objects represents one of the most complex cases of laser ablation, since low volumes of

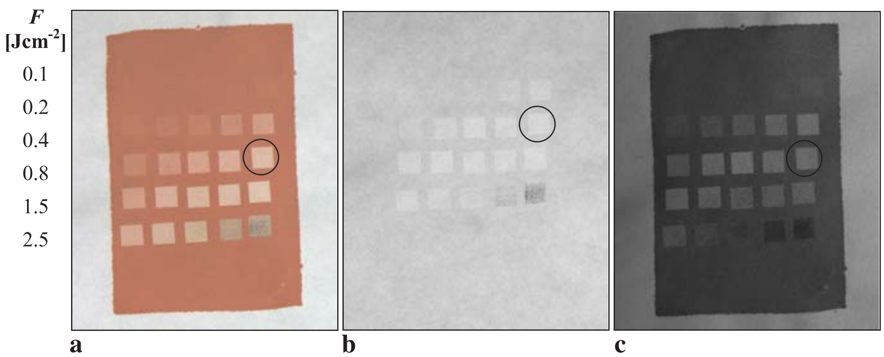


FIGURE 3 Laser cleaning of felt-tip pen ink on bleached sulphite softwood cellulose paper with no fillers and no sizing (P1). $\lambda = 532$ nm, repetition rate $\nu = 500$ Hz, fluences $F = 0.1$ to $2.5\,\mathrm{J\,cm^{-2}}$, *top down*, pulse numbers $N = 1, 2, 3, 5$, and 9, from *left* to *right*. **a** Video image, **b** IR reflectance image, **c** UV reflectance image

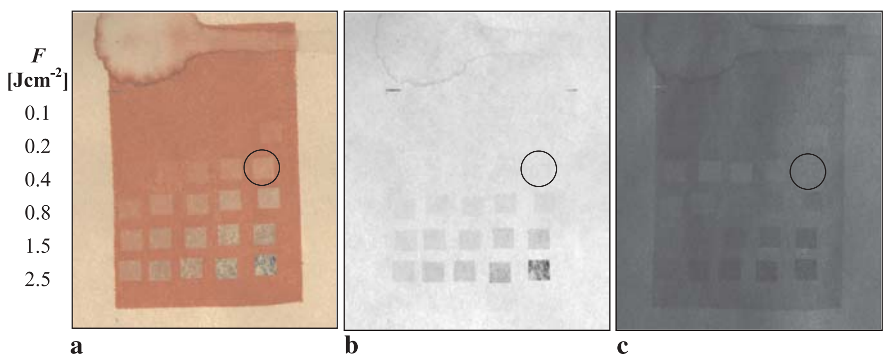
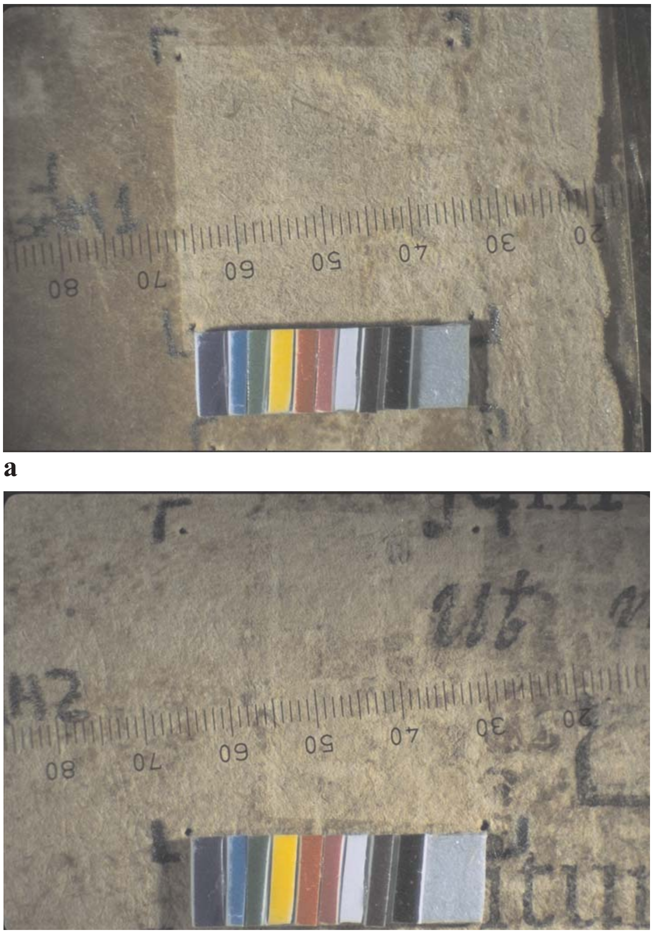


FIGURE 4 Laser cleaning of felt-tip pen ink on acid mechanical pulp paper, alum-rosin sized and kaolin coated (P3). $\lambda = 532$ nm, repetition rate $\nu = 500$ Hz, fluences $F = 0.1$ to $2.5\,\mathrm{J\,cm^{-2}}$, *top down*, pulse numbers $N = 1, 2, 3, 5$, and 9, from *left* to *right*. **a** Video image, **b** IR reflectance image, **c** UV reflectance image



a

b

FIGURE 5 Laser cleaning with $\lambda = 532$ nm of superficial deposits of adhesive glues. **a** Rubber-based adhesive, $F = 0.8\,\mathrm{J\,cm^{-2}}$, $N = 2$; **b** mixed starch- and protein-based adhesive, $F = 0.4\,\mathrm{J\,cm^{-2}}$, $N = 2$

dispersed material phases are evaporated while a sensitive and fragile fibrous organic matrix has to be preserved.

Laser treatments performed by Q-switched Nd : YAG lasers at three wavelengths (355 nm, 532 nm, and 1064 nm) on several paper models contaminated with inks and adhesive-tape remnants were diagnosed by multispectral imaging and colorimetry. Multispectral imaging is an advantageous diagnostic tool on contaminated surfaces, where colorimetry is less meaningful in contrast to pure substrates. It allowed a fast and semiquantitative strategy to not only document colour changes but also diagnose invisible absorption changes in the UV and IR due to irreversible chemical degradations.

Cleaning results with $\lambda = 532$-nm laser wavelength are clearly superior to $\lambda = 248$ nm, 355 nm, and 1064 nm, where respectively photochemical etching and deep disruption of the fibrous paper matrix occur.

Visible laser treatment (532 nm) of pre-aged bulb paper showed a slight colour change with less saturation of a yellowish appearance, i.e. a kind of bleaching. This status is also attained when ballpoint ink is removed completely. Deeply penetrating inks, such as felt-tip pen ink, on bleached sulphite softwood cellulose paper and acid mechanical pulp paper could be removed without damage at $F = 0.8\,\mathrm{J\,cm^{-2}}$ and at $F = 0.4\,\mathrm{J\,cm^{-2}}$, respectively. A higher overlap of laser pulses on the same spot was always superior to faster beam scans. The removal of superficial oil-based postage-stamp ink was successful with laser radiation at $\lambda = 532$ nm.

Remnants of adhesive tapes, both rubber-based and mixed starch- and protein-based, could be successfully removed with $\lambda = 532$-nm laser light. Deep and strong superficial discoloration was caused by laser treatment with $\lambda = 1064$ nm and 248 nm, respectively.

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