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An initial investigation into the cleaning of new and naturally aged cotton textiles using laser radiation

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Abstract – A series of tests has been conducted to evaluate the potential for using a Q-switched Nd:YAG laser (wavelengths 1 064, 532 and 266 nm) to clean both new and naturally aged cotton textiles. Tests have been carried out on i) plain weave and velvet cotton and ii) new and naturally aged cotton samples to investigate the possible roles of weave structure and ageing in the cleaning process. Cleaning trials have been carried out on artificially soiled new cotton and compared with results obtained using traditional cleaning techniques: wet cleaning and organic solvent cleaning. Cleaned surfaces were examined using optical and scanning electron microscopy. © 2000 Éditions scientifiques et médicales Elsevier SAS

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1. Introduction

The past 10 years have seen a significant increase in the use of laser cleaning in conservation [1]. Since the pioneering work of John Asmus and colleagues in the 1970s [2] laser technology has developed rapidly so that laser cleaning has become a practical and reliable technique offering the conservator a high level of precision and control. The majority of cleaning work carried out using lasers has focused on the cleaning of sculpture [3, 4]. To date, organic artefacts have received much less attention with the small amount of research that has been carried out concentrating on cleaning paper and parchment: lasers have been used successfully to remove microfungi from paper [5] and dirt from antique parchment [6]. In textile conservation initial research has been carried out on silk and wool [7]. Laser radiation at 1 064 nm has been used to remove dust and pencil marks from silk damask and silk velvet, while dust, fungus and starch paste have been removed from woollen fabrics using laser radiation at 532 nm. Examination of cleaned surfaces by electron microscopy did not detect any fibre damage provided cleaning was carried out at the optimum level of fluence.

The aim of this initial research was to evaluate the potential of the Nd:YAG laser as a textile conservation cleaning method. This focused on investigating whether soiling could be removed from white cotton without causing fibre damage and analysing any chemical or physical changes which may take place at the surface of a textile as a direct result of irradiation. Damage thresholds of new and naturally aged, white, plain weave (bleached) and velvet (unbleached) cotton have been established at infrared (1 064 nm), green (532 nm) and ultraviolet (266 nm) wavelengths. The effectiveness of laser cleaning has been tested using artificially soiled cotton test fabrics and evaluated by comparison with three traditional textile conservation cleaning methods. All tests were carried out using a Lynton Lasers

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Table I. Specifications of the Q-switched Nd:YAG laser used in the tests.

Pulse duration	Pulse energy	Repetition rate
5–10 ns	≤450 mJ @ 1 064 nm ≤230 mJ @ 532 nm ≤50 mJ @ 266 nm	≤10 Hz

Paragon Q-switched Nd:YAG laser with second and fourth harmonic generation (*table I*). The multimode beam was delivered by articulated arm at 1 064 and 532 nm. At 266 nm delivery was direct from the fourth harmonic assembly so there was no means of beam manipulation, i.e. to clean an area of the sample surface involved moving the sample.

2. Damage threshold measurements

2.1. Effect of weave structure

The susceptibility of cotton to damage resulting from direct exposure to the laser beam was investigated by first establishing damage thresholds for clean new cotton at 1 064, 532 and 266 nm. Both plain weave and velvet samples were tested to determine whether weave structure plays an important role in the process. Samples were scoured before testing to remove impurities. Each sample was exposed to 100 pulses at a repetition rate of 2.5 Hz. The number of pulses received by the surface was therefore in excess of the number to which it would be exposed during cleaning. Damage was defined as fibre damage or disruption visible at $\times 40$ magnification or discoloration. Fluence was calculated by dividing pulse energy by spot size (estimated from photosensitive paper) and is therefore an average value.

The results (*table II*) indicate that clean, new, plain weave cotton can be safely exposed to 1 064 nm laser radiation below approximately 2.5 J/cm^2 and to 532 nm radiation below approximately 4.3 J/cm^2. Exposure of the clean surface to 266 nm radiation resulted in damage at a fluence level approximately one order of magnitude lower. Discoloration (yellowing) of the surface was observed at 266 nm only. The low damage threshold at 266 nm may be due in part to strong absorption at this wavelength by bonds within the polymer chains [8].

Similar damage threshold values were recorded for plain weave and velvet fabrics at each wavelength. This suggests that weave structure does not play an important role in determining whether irradiation will result in damage. It is likely that fibre type is more important. *Figure 1b*, *c* shows surfaces exposed to 100 pulses at fluence levels in excess of the damage thresholds. Fibre damage is evident at each wavelength, although the nature of the damage appears very different at 266 nm than at 532 and 1 064 nm. At 1 064 and 532 nm the structure of the textile has been disturbed and cotton fibres damaged. The rapid heating caused by absorption of energy in the laser beam has led to breaking of some of the fibres which are left standing out of the plane of the surface. At 266 nm there is increased removal of material (a hole was left in the centre of the irradiated region) and the cotton fibres appear to have been 'sliced' rather than 'torn'. This is most likely a direct consequence of the increased photon energy at 266 nm, which is 4.8 eV, twice that at 532 nm and four times that at 1 064 nm. This is sufficiently energetic to break C–C, C–O and C–H bonds. This leads to damage via photchemical rather than photothermal processes [9], i.e. direct chemical bond-breaking without heating.

Table II. Damage thresholds for clean new cotton.

Wavelength (nm)	Weave structure	Mean damage threshold (J/cm^2, $\pm$ 25 %)	
		Damage/disruption	Discoloration
1 064	plain weave	2.5–3.0	–
	velvet	2.5–3.0	–
532	plain weave	4.3–4.9	–
	velvet	4.9	0.3
266	plain weave	0.2	0.1
	velvet	0.3	<0.2

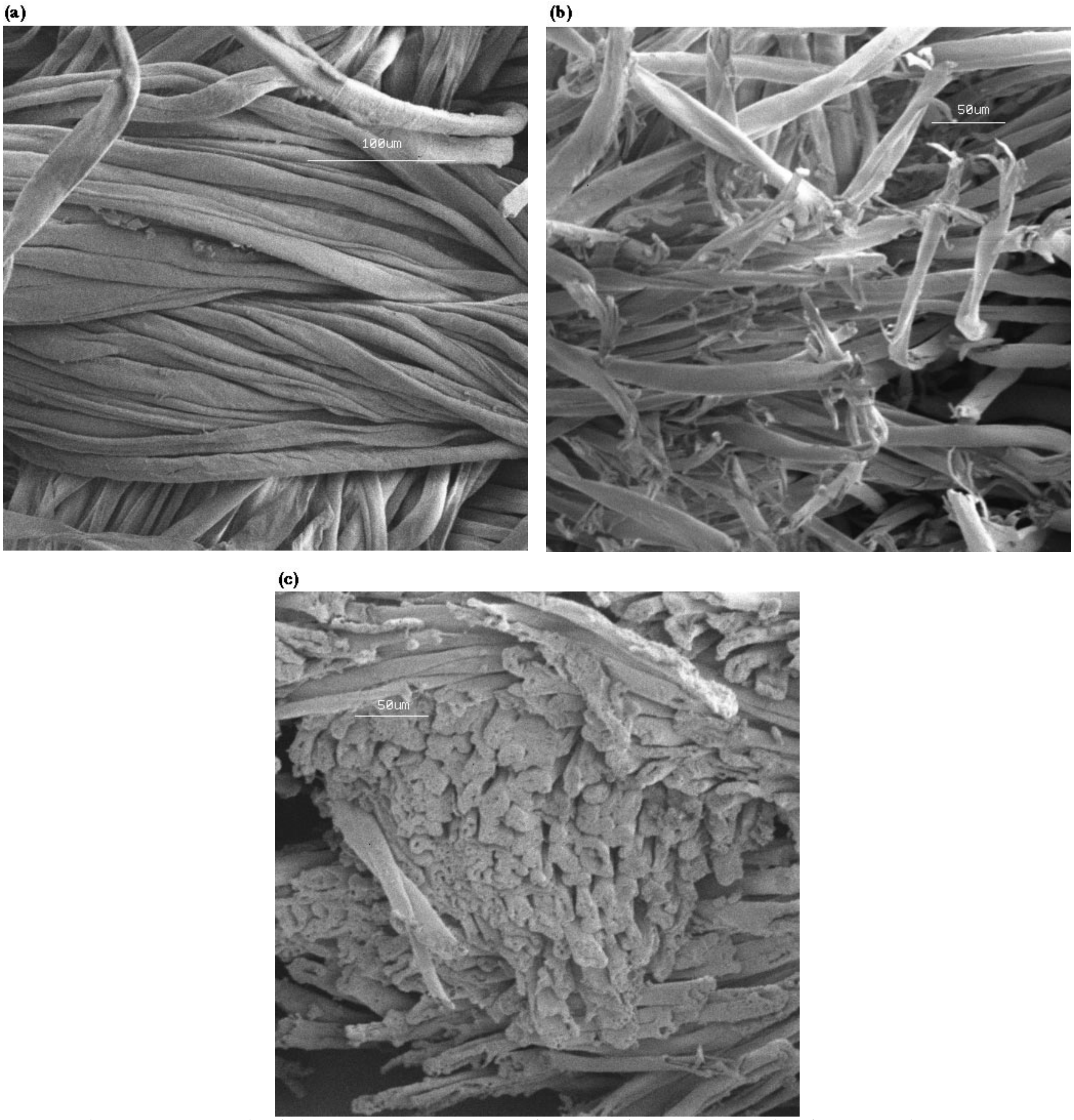


Figure 1. Electron micrograph of clean new white cotton surface: a) before irradiation; b) after 100 pulses, 1 064 nm, 3.7 J/cm^2 (the fibres have been damaged); c) after 100 pulses at 266 nm, 0.5 J/cm^2 (the damaged fibres are on the edge of a hole which has been created through the textile).

2.2. Effect of age

The effect of textile age on damage threshold has been investigated. Three naturally aged, clean, plain weave cotton textiles (of different ages, exact age unknown) were tested. In most cases the effect of irradiation at a particular fluence level varied from sample to sample for each wavelength (*table III*), suggesting that the damage threshold of a cotton textile is dependent on age. Also, overall the damage

Table III. Summary of effects of 532 nm laser radiation on clean naturally aged, plain weave cotton samples.

	Fluence (J/cm^2, ± 25 %)	Fibre damage visible at $\times$ 40 magnification
Cotton 1	3.5	small amount of surface disruption, some fibres tangled together
	3.9	small amount of fibre damage, mainly defibrillation visible in centre of irradiated region
Cotton 2	3.5	none
	3.9	none
Cotton 3	3.5	fibre damage extensive; surface appears abraded, fibres split and frayed; damaged fibres white and opaque
	3.9	fibre damage extensive; surface appears abraded, fibres split and frayed; damaged fibres white and opaque

threshold of aged samples was found to be lower than the damage threshold of a new sample at each of the wavelengths tested, i.e. the susceptibility of cotton to laser-induced damage appears to increase with age.

3. Test cleaning

Cleaning tests were carried out on artificially soiled, new plain weave cotton (*figure 2*) to establish whether effective cleaning was possible at fluence levels below the damage thresholds established at 1 064, 532 and 266 nm (*figure 3*). A standard commercially prepared artificially soiled (carbon and olive oil) cotton test fabric was used.

Examination (at $\times$ 40 magnification) of the artificially soiled cotton after treatment revealed that effective (complete soil removal) and uniform cleaning could be achieved using 1 J/cm^2 at 1 064 nm and 1.1 J/cm^2 at 532 nm (*figure 4*) without causing damage to the underlying fibres. A small amount of soil was still present after cleaning using 0.1 J/cm^2 at 266 nm. No fibre damage or disruption to the textile structure was observed at any of the wavelengths tested (*figure 5a*, *b*). One drawback of the use of artificially soiled test fabrics was the strong discoloration observed at 1 064 nm, and slight discoloration at 532 nm. This is either the result of i) singeing of the surface caused by heating of the fibres through thermal conduction from the heated soil particles or ii) a residue of the soiling layer, possibly the oil component discoloured through heating. Earlier work has shown that it is not due to direct exposure of the cleaned fibres to the laser beam. Although carbon frequently forms a large percentage of soiling found on textiles, the distribution of the test fabric soil is not representative of how soiling often occurs on historic textiles. In

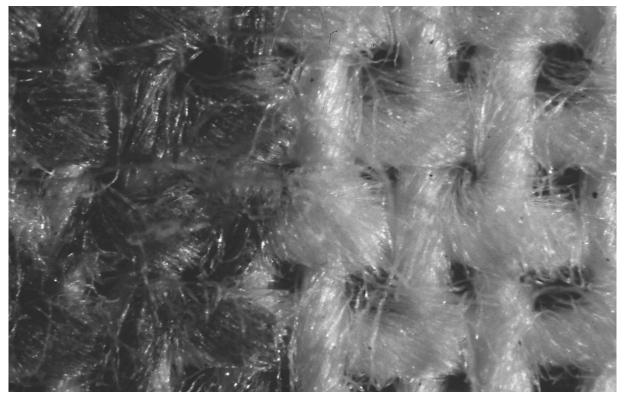


Figure 2. Area of new cotton textile (approximately 4.5 mm $\times$ 4 mm). Left side: artificially soiled; right side: clean.

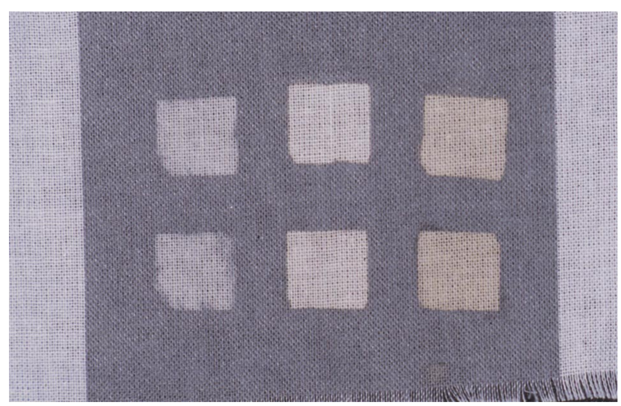


Figure 3. Laser test cleans on artificially soiled new cotton. The test areas are approximately 1.5 cm $\times$ 1.5 cm. Upper row (left to right): 1) 266 nm, 0.15 J/cm^2; 2) 532 nm, 3.2 J/cm^2; 3) 1 064 nm, 2.7 J/cm^2. Lower row (left to right): 1) 266 nm, 0.1 J/cm^2; 2) 532 nm, 1.1 J/cm^2; 3) 1 064 nm, 1.0 J/cm^2.

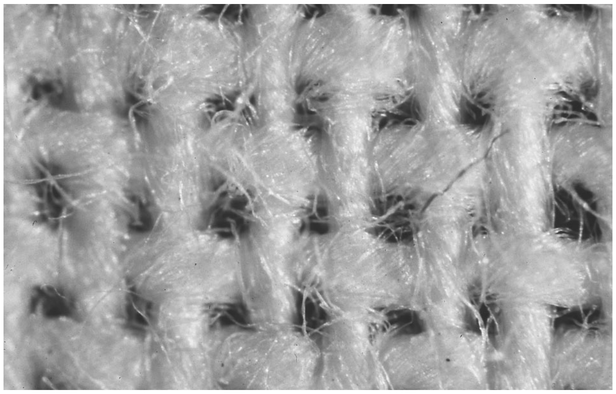


Figure 4. Area of artificially soiled cotton cleaned by 532 nm laser radiation at a fluence of 1.1 J/cm^2. There are no signs of damage (similarly at 1 064 nm, 1 J/cm^2 and 266 nm, 0.1 J/cm^2).

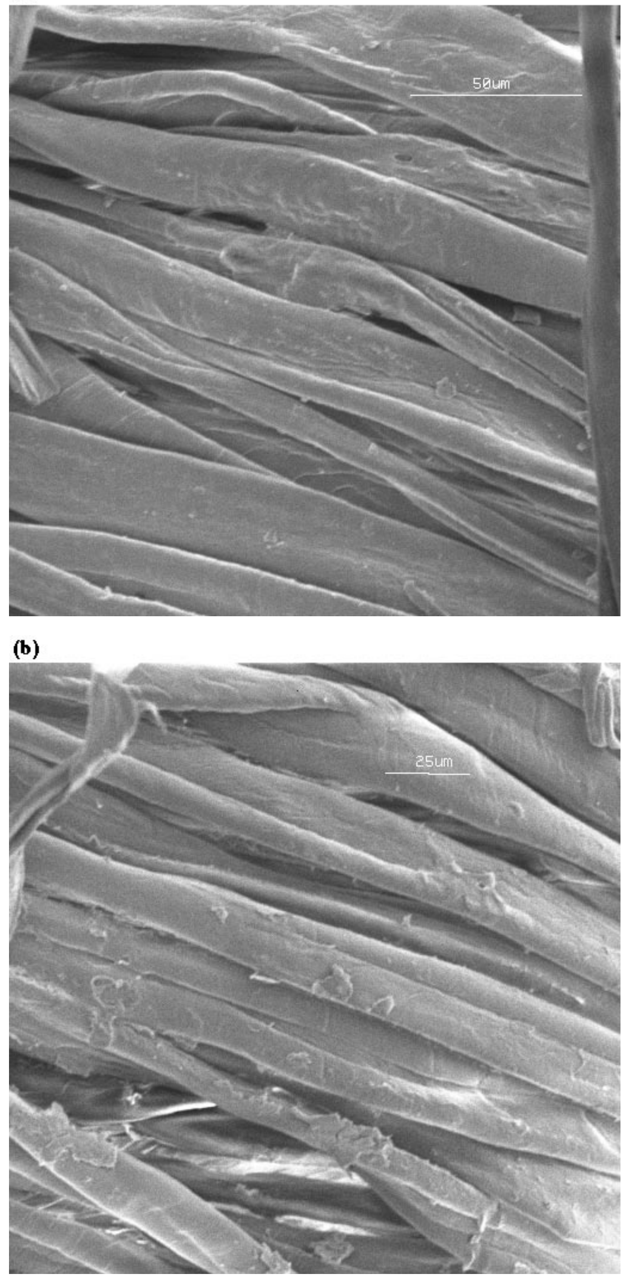
reality soiling is unlikely to be as uniform, and any discoloration (should it occur at all) will probably be much less severe than the levels observed during these tests. The possibility of discoloration does, however, serve to highlight the necessity of testing before treatment. No discoloration was observed at 266 nm owing to the photochemical nature of the process, as discussed in section 2.1 [9].

4. Comparative cleaning tests

The effectiveness of laser cleaning compared to three traditional textile conservation cleaning methods: wet cleaning (the solution used consisted of a non-ionic detergent (Synperonic N), an anionic detergent (Arkopon T) and an anti-redeposition agent in softened water) and organic solvent cleaning using industrial methylated spirits (IMS) and white spirit, has been established (*table IV*). The wet and solvent cleaning methods involved soaking the sample in a bath of cold solution for 30 min, gently sponging the soiled side for 15 min, rinsing and allowing the sample to dry naturally. Cleaning was carried out over larger areas (125 mm × 90 mm) of the same artificially soiled cotton fabric used in the laser cleaning tests.

Laser cleaning (at each wavelength) was much more effective in removing soiling. Wet cleaning and organic solvent cleaning methods were unable to produce a noticeable change in the appearance of the soiled surface. The results obtained at 532 nm were especially promising since soil removal was achieved without any visible fibre disruption or

(a)



(b)

Figure 5. Electron micrograph of new white cotton surface (area 175 μm × 175 μm): a) clean surface (not irradiated); b) artificially soiled surface cleaned by 532 nm laser radiation, 1.1 J/cm^2 (no signs of damage). Similar results were obtained at 1 064 nm, 1 J/cm^2 and 266 nm, 0.1 J/cm^2.

Table IV. Summary of laser cleaning, wet cleaning and organic solvent cleaning results.

Technique	Effectiveness of clean	Colour change in test area	Surface disruption, fibre damage at ×40
Wet clean	ineffective: little soiling removed	negligible	none visible
Organic solvent clean (IMS)	ineffective: little soiling removed	negligible	none visible
Organic solvent clean (white spirit)	ineffective: little soiling removed	negligible	none visible
1 064 nm, 1 J·cm^{-2}	effective: no soil visible	dark grey to yellowish-brown	none visible
532 nm, 1.1 J·cm^{-2}	effective: no soil visible	dark grey to off-white	none visible
266 nm, 0.15 J·cm^{-2}	fairly effective: small amount of soil visible	dark grey to greyish-white	small amount of fibre damage visible in isolated areas

damage and with only very slight discoloration of the textile surface. Cleaning at 2.5 Hz took approximately 45 min, which compares favourably with traditional techniques. At 1 064 nm cleaning was equally as effective but discoloration was stronger. At 266 nm cleaning was slightly less effective and slight fibre damage was visible in a few small localised areas, although there appeared to be no discoloration of the cotton surface.

5. Conclusion

On the basis of these experimental findings laser cleaning has definite potential as a method of cleaning both new and naturally aged cotton textiles. Provided laser parameters, such as wavelength and fluence, are carefully chosen artificial soiling can be removed from white plain weave cotton without fibre disruption or damage, in a way which is not possible using wet cleaning and solvent cleaning methods. At 532 nm, discoloration of the cleaned cotton surface is only slight. The work has shown laser cleaning to be an extremely selective method of cleaning under the right conditions. It is a very precise and localised method well-suited to extremely fragile surfaces. However, further research and testing on genuine articles is necessary before a firm mandate recommending its use can be made. Further work is needed to investigate the cause of the discoloration at 1 064 and 532 nm and whether it can be removed using a combination of gentle traditional methods. It is important to stress that no fibre damage or disruption has been seen to accompany the slight discoloration. This work has been carried out on white cotton and further work is needed to investigate the importance of textile colour in the laser cleaning process.

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