JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 8, August 2008, p. 2168 - 2173

Influence of laser restoration method on the collagen based artifacts

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This paper is part of an ample study of the effect that the laser cleaning procedures has on collagenous composites, such as *leather* and parchment. Cleaning procedures applied on organic substrates of artifacts can be challenging due to their high sensitivity to all exterior factors, their fragile nature demanding a high precision and accurate monitoring of the cleaning process. Although the laser cleaning applications on organic materials - leather in particular, are quite avoided, from the reported results [1,2] it proves to be an innovative technique that has the potential to provide contactless, chemical-free cleaning of historically important documents, overall providing a high accuracy cleaning The laser effect on this type of organic materials is still poorly understood The study avers the ageing of the materials and specific issues concerning conservation of their photomechanical properties, by correlating various informations obtained with specific methods of analysis such as optical microscopy, shrinkage temperature of the organic fibers and molecular spectroscopy (FT-IR and UV-VIS-NIR domains).

(Received May 19, 2008; accepted after revision June 30, 2008)

Keywords: Laser cleaning, collagen, FT-IR medium and NIR, UV-VIS spectroscopy, optical microscopy, shrinkage temperature

1. Introduction

In the context of monitoring the preservation state of artworks we come across the necessity of cleaning, which is done with chemical products that may affect the molecular structure of the collagen. That is why we developed the study on the effect of laser cleaning procedures on the molecular structure of collagen; laser cleaning was applied on a series of leather samples with vegetal and mixed (vegetal + chrome salts) tanning.

Collagen is the main composite of skin, conjunctive tissues and bones. From the structural point of view, collagen is a protein made of amino-acids associated by peptide links. The main amino-acids isolated from animal collagen are glycine, proline and hydroxyl-proline. Their structure consists in a three chains spiral that contains the amino-acids, twisted to the left, the glycine taking every third position on the length of the chain; the spiral is stabilized by chemical links between the chains (hydrogen links). These hydrogen links are formed between NH and C=O groups situated in adjacent reactive chains. They have a great importance for the stability of collagen during technological process of skin, as for the destructive conditions that may affect the product during the utilization and long time storage, as in the case of cultural heritage objects.

2. Experimental

The leather samples investigated have different provenance and tanning history (crafted using old traditional methods), as follows:

a. Sample 1, cattle – combined tanning: 15% Mimosa (vegetable condensed tanning) + 4% Chromitan (mineral tanning) [1% Cr_2O_3]

b. Sample 2, cattle - combined tanning: 4% Chromitan (mineral tanning) [1% Cr_2O_3]+15% Mimosa (vegetable condensed tanning)

c. Sample 3, calf – vegetal tanning (20% Mimosa- vegetable condensed tanning)

d. Sample 4, calf - calf, type M –QbC2 - calf, type Q - vegetal tanning (20% Quebracho- vegetable condensed tanning)

e. Sample 5, cattle – vegetal combined tanning (10% Quebracho + 10% Mimosa, vegetables condensed tanning)

The leather samples were artificially soiled with candle smoke in order to simulate the impurities that can be accumulated on historical and religious documents kept in various cult locations.

The chemical characteristics of the leather samples are presented in the following table:

Table 1. Chemical characteristics of the leather samples.

Analysis	Samples				
	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**
Humidity %	15.63	12.61	14.07	11.86	13.10
Extractable matter %	5.72-6.77*	9.82-11.23*	8.41-9.79*	13.90-15.77*	4.41-5.07*
Total ash %	1.60-2.03*	2.54-3.27*	0.77-0.99*	0.65-0.88*	1.22-1.48*
Cr_2O_3 %	0.90-1.14*	1.30-1.68*	0.35-0.45*	-	-
Hide substance %	52.10-66.24*	48.06-63.22*	51.98-67.05*	45.75-61.62*	50.36-61.05*
Total soluble %	2.01-2.56*	2.45-3.15*	3.77-4.86*	2.71-3.65*	2.8.-3.43*
Inorganic solubles %	0.80-1.02*	0.37-0.48*	0.68-0.88*	0.22-0.30*	0.36-0.44*
Organic solubles %	1.21-1.54*	2.08-2.67*	3.09-3.98*	2.49-3.35*	2.47-2.99*
Combined tannin %	23.74	23.90	21.68	25.35	28.44
Tanning factor %	45.57	48.72	41.71	55.41	56.47
pH	5.00	5.15	5.91	4.4	4.6

*) The values are calculated without considering the humidity.

The study was developed on two directions of investigation of the laser cleaning effects:

1. From the visual assessment and aesthetical point of view:

- *Colorimetry* – determination of the color parameters CIELab and color spectra - surface monitoring based on chromatic modulation has been carried out for the laser cleaning of different types of leather (calf and cattle), working with the spectral signature of reflected light from the surface. We used a portable colorimeter.
- *Microscopy* investigations – in order to monitor characteristics of the samples' relief - before and after laser cleaning, revealing any deteriorations on the surface morphology that may be induced by the laser radiation

2. Probability of causing induced ageing:

- *Shrinkage temperature* – present practice utilizes the measurement of hydrothermal shrinkage observed when a sample is subjected to a controlled temperature dynamics. When collagen leather fibres are heated in water they deform over a distinct temperature interval. The deformation is seen as shrinkage on fibres, which is dependent on the strength or the quality of the leather material and on the degree of its deterioration. Thus, it can serve as a measure of the combined chemical and physical stability of the material. The micro hot table method (MHT) for measuring the shrinkage activity of micro samples of collagen fibrous materials has been used in the study of historic vegetable tanned leathers [3,4,5,6].
- *NIR* – Near-infrared spectroscopy is based on molecular overtone and combination vibrations. Such transitions are forbidden by the selection rules of quantum mechanics. As a result, the molar absorptivity in the near IR region is typically quite small. The molecular overtone and combination bands seen in the near-IR are typically very broad, leading to complex spectra. NIR spectroscopy consists in the measurement of the wavelength and intensity of the absorption of near-infrared light by a sample

3. Results and discussion

All the leather samples were artificially soiled in the same manner, using candle smoke, in order to simulate the soil/dirt that can be accumulated by historical documents kept in churches and other cult locations. The cleaning was done with a Q-switched YAG:Nd laser using its fundamental wavelength – 1064 nm and its third harmonics: 532 nm, 355 nm and 266 nm, at different fluencies – according to the cleaning thresholds previously established.

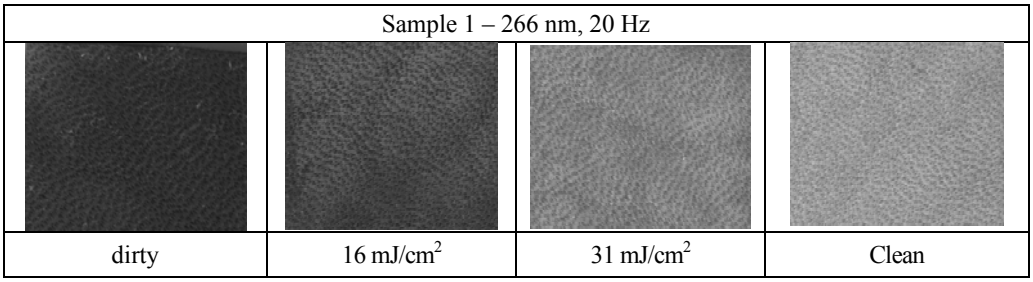


Fig. 1. Extract from visual investigation data base of Sample 1.

3.1. Colorimetry

The chromatic characteristics determined and analyzed were lightness (L*), and the color coordinates a* and b* using a portable colorimeter [7].

Table 2. The chromatic characteristics of Sample 1.

Sample 1	**L***	**a***	**B***	**Efficiency %**
clean area	37.59	11.34	18.54	100
1064 nm - 350 mJ/cm^2	34.64	10.91	16.35	92.15
532 nm - 185 mJ/cm^2	33.12	10.32	15.64	88.11
355 nm - 94 mJ/cm^2	31.52	9.66	16.02	83.85
266 nm - 31 mJ/cm^2	28.26	9.19	15.83	75.00
dirty area	19.69	1.72	3.11	

The efficiency was calculated considering the lightness data and it is with the wavelength and the intensity of the laser beam. From the colorimetric point of view the most efficient results (good cleaning, irrelevant color modifications in comparison with the original area) were obtained using the 1064 nm wavelength at fluencies from 500 mJ/cm^2 to 300 mJ/cm^2, as well as at 532 nm at fluencies around 180 mJ/cm^2.

3.2. Microscopy investigations

Optical microscopy investigations were made using a portable digital microscope with magnifications from 20x to 1000x, in order to monitor the laser cleaning process, the efficiency of laser cleaning and also to notice any morphological changes that may occur.

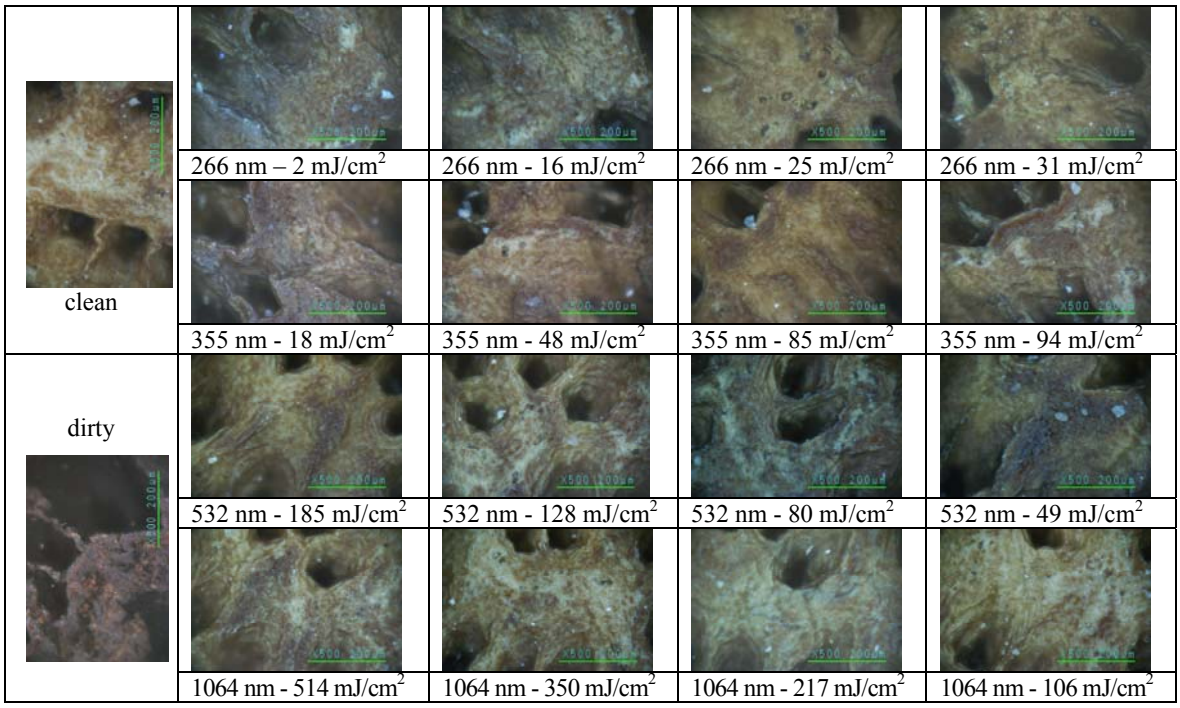


Fig. 2. Optical microscopy images for Sample 1.

From the optical microscopy point of view the laser cleaning didn't induce any morphology changes on the irradiated material, it followed closely the surface relief. The best removal of the impurities was obtained using the 1064 wavelength at 514 mJ/cm^2. In the table below we present the microscopy results for Sample 1.

3.2.1 Shrinkage temperature

This investigation is based on Micro Hot Table (MHT) method with CALORIS equipment (Stereomicroscop Wild Heergbrugg/ Hot Table Caloris/ webcam/ computer) and F.L.T.K. 1.1.X Software for reaching the temperature in the imagine place.

Experimental procedure:

A sample of around 0.1 mg fiber from the corium part (flesh side) of the leather is wetted with demineralized water from 10 to 20 minutes on a microscope slide with a concavity. The measurements are performed on only a few fibers.

The slide is placed on the hot table (Caloris) and heated at a rate of 2ºC/min.

The highest controlled level of temperature used is 100 degree for leathers and the magnification used was around x40.

The shrinkage of the leather fibers can be described in three temperature intervals with the following characteristics:

- Interval A1/A2: Distinct shrinkage activity is observed on individual fibers.
- Interval B1/B2: Shrinkage activity on one fiber (occasionally more) is immediately followed by shrinkage activity on another fiber.
- Interval C: At least two fibers show shrinkage activity simultaneously and continuously. The start temperature of this main interval of shrinkage is the shrinkage temperature, T_S.

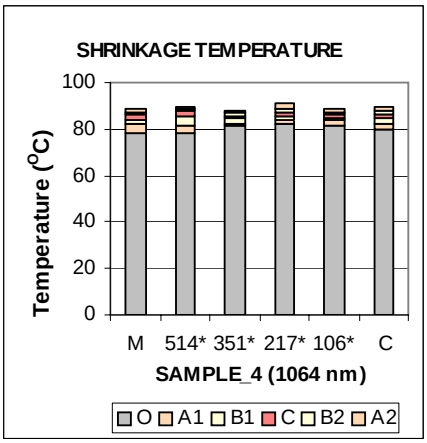
The shrinkage activity can be observed as a function of temperature for the fiber sample undergoes the following changes:

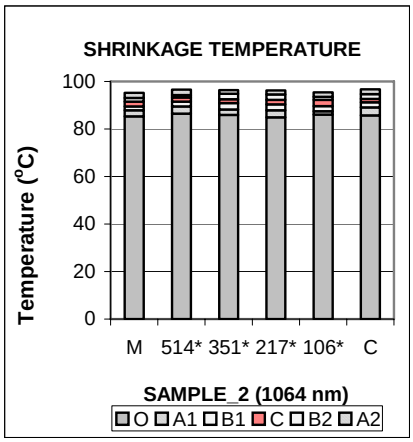
no activity ► A1 ► B1 ► C ► B2 ► A2 ► complete shrinkage

A typical shrinkage activity example is shown in *Fig. 3* for 6MaC3 leather sample, irradiated with the 1064 nm wavelength at a fluence of 514 mJ/cm^2.

$T_{initial}$	A_1	B_1	C	B_2	A_2	T_{final}
						
23.6	78.4	82.0	**84.0**	86.3	87.3	89.1

Fig. 3. Shrinkage activity images for Sample 1, cleaned with 1064 nm, 514 mJ/cm^2





Graph 1. Shrinkage activity images for Sample 4 (left) and Sample 2 (right) cleaned with 1064 nm.

The contraction intervals are illustrated in the following graphs.

The data obtained using this method are presented in the following table.

From the shrinkage temperature point of view the laser cleaning technique can be applied safely on leather, because the fibril structure is not affected. Laser cleaning process didn't induce any significant modifications in the shrinkage temperature of the leather fibers, fact that proves the geometry of the catena was not affected.

3.3 Wear infrared spectra

- Structural characteristics are deduced from IR spectra. In the medium – IR domain the characteristic bands for amidic structure of the collagen are as follows:

- 3425 – 3450 cm^{-1} – CH and OH, valence vibrations
- 1650 – 1655 cm $^{-1}$ – C=O amide I, valence vibrations
- 1550 – 1530 cm^{-1} – NH amide II, deformation vibrations
- 1240 – 1235 cm^{-1} – valence vibrations of C-N structure, amide III [8]

These bands are usedto identify of the damage processes (hydrolysis or denature) that may affect the collagen catena. Following these steps the proportions A_I/A_{II} and A_{OH}/A_I give us information about the hydrolysis degree, and $\Delta\nu$ (ν_I/ν_{II}) about the denaturation degree. [9]

Table 3. Shrinkage temperature values using MHT method.

Wavelength	**Shrinkage temperature**					
266 nm	*Clean*	*31 mJ/cm²*	*25 mJ/cm²*	*16 mJ/cm²*	*2 mJ/cm²*	*Dirty*
Sample 1	99.0	99.2	99.1	98.9	98.7	99.3
Sample 2	92.6	92.1	93.0	92.6	93.0	92.9
Sample 3	79.4	79.3	78.5	78.9	79.2	79.0
Sample 4	84.5	85.4	84.9	84.6	85.2	85.0
Sample 5	76.1	75.8	76.4	76.2	75.9	76.2
355 nm	*Clean*	*94 mJ/cm²*	*85 mJ/cm²*	*48 mJ/cm²*	*18 mJ/cm²*	*Dirty*
Sample 1	98.8	99.1	99.2	99.6	99.0	99.3
Sample 2	92.1	92.5	92.3	91.8	92.3	92.5
Sample 3	79.0	78.7	79.5	79.6	79.5	79.3
Sample 4	84.1	84.6	85.2	85.0	84.9	84.9
Sample 5	75.6	76.2	76.3	76.8	76.4	
532 nm	*Clean*	*185 mJ/cm²*	*128 mJ/cm²*	*80 mJ/cm²*	*49 mJ/cm²*	*Dirty*
Sample 1	98.6	98.9	99.1	99.3	99.0	99.1
Sample 2	91.9	92.3	92.3	93.0	92.8	92.9
Sample 3	79.2	78.9	79.1	79.6	79.5	79.0
Sample 4	84.7	84.5	85.1	84.9	84.5	85.0
1064 nm	*Clean*	*514 mJ/cm²*	*351 mJ/cm²*	*217 mJ/cm²*	*106 mJ/cm²*	*Dirty*
Sample 1	99.6	99.3	98.4	98.6	99.3	99.2
Sample 2	92.3	91.9	92.6	93.0	92.6	93.3
Sample 3	79.5	79.0	78.9	79.3	78.8	79.4
Sample 4	84.0	85.3	84.5	85.8	84.5	84.3

Any movement of the 1240 cm^{-1} band indicates the elongation/contraction of the fibril on the C-N link. *Table 4* presents the data obtained for the leather sample 6MaC3.

Table 4. Structural characteristics from medium - IR domain.

Sample area	A_I/A_{II}	$\Delta\nu$	A_{OH}/A_I
clean	1.00	96	1.10
1064 nm - 350 mJ/cm^2	1.05	98	1.13
532 nm - 185 mJ/cm^2	1.03	97	1.12
355 nm - 94 mJ/cm^2	1.02	97	1.12
266 nm - 31 mJ/cm^2	1.00	96	1.11

From the analysis of the acquired data we can say that the laser cleaning process has not induced any significant changes of the hydrolysis and denaturing degrees. Also, neither movements of the 1240 cm^{-1} band, nor the occurence of the oxygenate groups specific to a destructive process of the peptide catena at 1720 cm^{-1} were found.

In the NIR domain we attribute the 1450 – 1520 cm^{-1} band to the free and associated hydrogen links [10,11] (see Table 5).

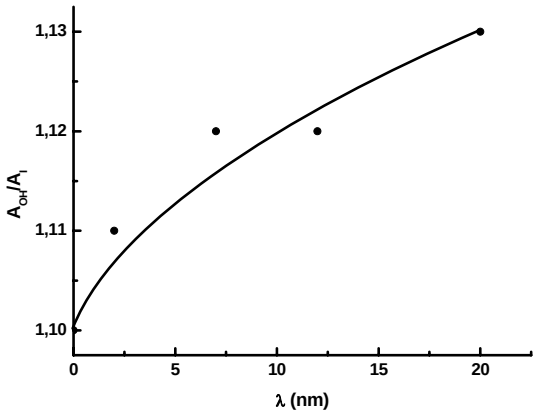
Table 5. NIR characteristics of Sample 1.

Sample 1	λ (nm)	Δλ (nm)
clean	1484	-
1064 nm - 350 mJ/cm^2	1504	+20
532 nm - 185 mJ/cm^2	1496	+12
355 nm - 94 mJ/cm^2	1491	+7
266 nm - 31 mJ/cm^2	1486	+2

In the clean area of Sample 1, the band is placed at 1484 nm, which points out the existence of some partially free hydrogen links. The movement of the band (Δλ) as an effect of the laser irradiation produces a monotonous increase of the association process.

The results obtained for all the samples are quite similar, but we noticed that the sample 4, tanned with Quebracho, is most sensitive one, and the one tanned with Mimosa – sample 3 - the most proof resistant one.

These data correlated with the medium – IR information help us determine the hydrolysis degree (A_{OH}/A_I), as you can see in *Graph 2*.



Graph 2. Movement of υ_{OH} due to the hydrolysis degree given by A_{OH}/A_I.

The movement of the υ_{OH} band that occurs after the laser cleaning process indicates an increase of the association in the peptide catena, due to a light diminution of the OH groups. From the spectral data point of view we conclude that laser cleaning does not affect the structural characteristics of the collagen fibers.

4. Conclusions

The paper reports a synthesis of a large study regarding the behavior of the leather samples after laser cleaning protocol of restoration-conservation. Several cases have been validated based on morphological evaluation of old leather, mainly from libraries or book – restoration workshops.

For the first time an advanced study is done on a large series of fresh samples crafted following traditional recipes; modifications of leather samples' properties were controlled for dirty and cleaned by laser cases.

After macroscopic control and aesthetical evaluation that shown an efficient cleaning (with over 75% efficiency) they have been tested for control of induced ageing effects.

Proper selection of the laser regime proved conservation of the fibril structure - testify by shrinkage temperature activity monitoring of all samples.

Positive results were obtained by NIR that - in specific bands – shows no modification of collagen catena.

References

[1] R. Salimbeni, V. Zafiropulos, R. Radvan, V. Verges-Belmin, W. Kautek, A. Andreoni, G. Sliwinski, M. Castillejo, S. R. Ahmad, Coalition – CSIC Thematic Network on Cultural Heritage, Newsletter no.9, pp. 2- 8, 2005.

[2] M. Simileanu, R. Rădvan, J. Striber, W. Mărăcineanu, C. Deciu, N. Herăscu, Tehnici fotonice de restaurare şi conservare a operelor de artă ce au în componenţă materiale organice, Proc. Simpozionul "Patrimoniu cultural din piele şi pergament – abordări abordări moderne pentru caracterizare, conservare şi/sau restaurare", Bucureşti, 2006, p. 45, ISBN: 973-87211-9-9

[3] R. Larsen, M. Vest, K. Nielsen, Journal of Society of Leather Technologist and Chemist **77**, 151 (1933).

[4] R. Larsen, M. Vest, K. Nielsen, In STEP Leather Project. European Commission DG XII, Research Report No.1, The Royal Danish Academy of Fine Arts, School Of Conservation, Denmark, 1994, p.151-164.

[5] R. Larsen, M. Vest, D. V. Poulsen, U. B. Kejser, in Environment Leather Project. European Commission DG XII, Research Report No.6, The Royal Danish Academy of Fine Arts, School Of Conservation, Copenhagen, 1996, p.145-165.

[6] R. Larsen, Thermochimica Acta **365**, 85 (2000).

[7] DIN 174-1976, CIE-Lab Germania

[8] M. Avram, C. D. Mateescu, Spectroscopia in IR. Aplicatii in chimia organica, Ed. Tehnica, Bucuresti 1966.

[9] M. Derrick, Evaluation of state of degradation of dead sea scroll samples using FT-IR spectroscopy, Annual of the Book and Paper Group, American Institit for Conservation, 10, 1991.

[10] M. Egawa, T. Furukara, M. Takahaski, Y. Ozaki, Applied Spectroscopy **57**(4), 473 (2003).

[11] S. Sasic, V. H. Segtman, Y. Ozaki, J. Phys. Chem. **A106**, 760 (2002).

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