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OVERVIEW ON LASER CLEANING OF LEATHER OBJECTS

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In această lucrare sunt investigate pragurile de fluenţă aferente curăţării laser a obiectelor din piele. Restaurarea obiectelor de arta organice poate fi problematică fiind necesar să luăm în considerare fragilitatea materialelor, structura tridimesională a acestora, să ne ferim de apariţia unor schimbări dimensionale etc. în condiţiile în care petele şi depunerile aderente trebuie îndepărtate pentru a diminua degradarea artefactelor.

This paper presents investigation of the laser cleaning fluence thresholds of leather patrimony objects. Cleaning of organic materials can be problematic for a variety of reasons: fragility of the materials, unwanted dimensional changes, three-dimensional structure, etc. yet stains and dirt will promote its degradation.

Keywords: laser cleaning threshold, paper, leather, parchment

1. Introduction

Laser cleaning is a relatively new application that is based on laser – surface interaction, selective due to its unique properties, firstly its monocromaticity. This method allows us to avoid mechanical disruptions and keeps aside the disadvantages of fluid means traditional cleaning – chemical or just water- that may produce long term degradations of the material's substrate. More than that, laser cleaning may accelerate the conservation work, offering a higher cleaning quality, a high level of control and precision.

Elaboration of expertise procedures, material studies and technical structure of the artefacts based exclusively on physical and chemical methods, upgrading them to the latest technological innovations, can only be benefit to restoration and conservation, bringing a high level of quality, no secondary effects [1]. International studies and researches aim at setting up these non-conventional methods of restoration and conservation of the artworks that will submit to the fields' requirements: rapid technique, high accuracy, well determined depth and surface action, no induced chromatic modifications, no chemical residuu.

Paper, parchment or leather are mostly affected by dust, pollutants from the surrounding environment, and corroborate different laser conservation and

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restoration regimes [2]. The photonic technologies and laser equipments are going through a period of investigation and enlargement of the application spectra in the field of restoration/conservation of cultural heritage artworks. Besides the laser cleaning techniques, the non-destructive laser methods of analysis and diagnosis come next, giving a lot of information about the chemical and physical structure of the studied artworks. The modern European conservation normative that allow us a permanent monitoring of the cleaning process will become mandatory in the near future (Fotakis 1995, Fotakis 1997, Maravelaki 1997, Gobernado-Mitre 1997, [3]). The field literature classifies and explains several distinct mechanisms on which laser cleaning may be based on. In this context, laser cleaning is a generically given name that in order to be defined must imply the entire object (substrate) - deposition (pollutant layer) information. In all the mentioned cases all the risks that may be inflicted on the substrate were removed. Lack of danger, lack of any deterioration to the substrate implies a subtle cognisance of the phenomena that may occur to the surface of the cleaned object and sometimes brings into discussion subjective arguments or one dependent on the restorer's experience and working principles.

2. Experimental procedure and results

Leather and parchment are substrates of the object included in our cultural heritage. Parchment is made from most animal skins and consists in a collagen fibres network. Its type and age influence its opacity, colour and texture. Interfibre cohesion is much smaller in these cases due to the large spaces between fibres' that allow hygroscopic liquids absorption. Their organic nature, as well as their microclimate influence development of bio-deteriogens factors.

Based on study previously published on the effect that the laser cleaning procedures has on collagenous composites such as leather and parchment [4], the purpose of these investigation was to establish the fluence thresholds that allows us to have an efficient cleaning without affecting the surface of the artwork. Corresponding tests are addressed to different types of animal leather (cattle, goat, sheep) [5], that are often used in the context of the organic artworks.

The leather samples comprised in this study have different provenience and tanning history, as follows:

a. 6MaC3 - cattle, type 6M – combined tanning: Mimosa +Chromium
b. 6Mbi - cattle, type 6M - combined tanning: Mimosa + Chromium
c. MbC2 - calf, type M – vegetal tanning (Mimosa)
d. QbC2 - calf, type Q - vegetal tanning (Quebracho)
e. TC2 - cattle, type T – vegetal tanning (Quebracho + Mimosa)

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.

In these experiments we used a pulsed YAG :Nd laser [6]. In q-switched regime for intensities ~ 107 – 1010 W/cm2, the assumed mechanism of cleaning is the spallation [7]. The temperature of the evaporated material reaches ~104-105 K, becomes partially ionized, and absorbs a lot of laser radiation. Thus, evaporation on material's surface is stopped, being « shadowed » by the plasma, and the radiation doesn't reach the substrate's surface. The plasma gets warmer and warmer until the pressure reaches very high values (~1-100 Kbar), resulting in a shock wave. This shock wave produces a microscopically compression on the surface of the material. After the laser pulse has ended, the plasma is expanding to the surface of the material, and the surface of the material – in the relaxing process - expulses a layer out of it. Although in the substrate the temperatures aren't so high, the rapidity of the process implies some deterioration risks. Substrate melting is in all cases undesirable since morphological change in the substrate will be implied in this situation.

The leather samples were subjected to precise colorimetry investigations before and after laser cleaning was applied in order to evaluate the laser cleaning by matter of alteration of colour. The Colour System exploited was CIE L*a*b* [8] - a uniform device independent colour space in which colours are located within a three-dimensional rectangular coordinate system.

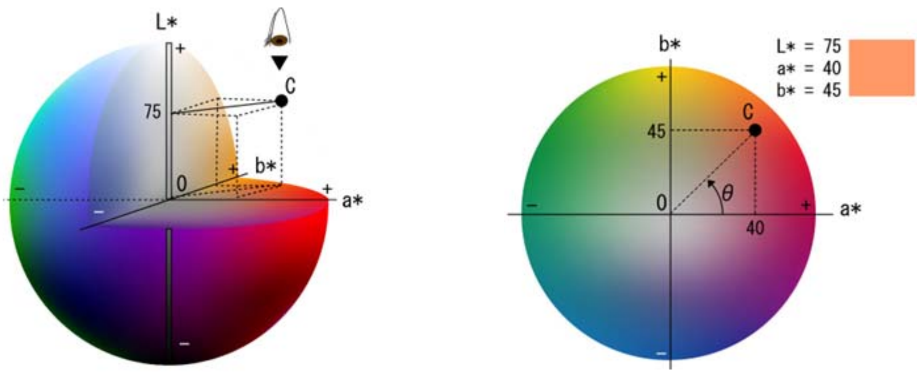


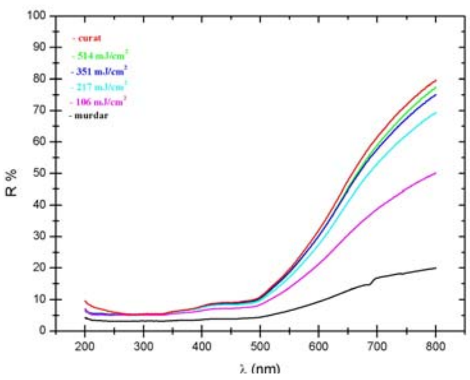
Fig. 2.1. L*a*b* Color System representation of color point **C**

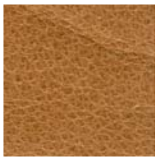
The three dimensions are L* luminosity (between 0 and 100); a* red – green axis (with values between -60 and 60); b* yellow – blue axis (with values between -60 and 60) of the samples in "Uniform Color Space" defined by CIE. In general, the following variables are used: E* = [(L*)2 + (a*)2 + (b*)2]1/2 and ΔE* = [(ΔL*)2 + (Δa*)2 + (Δb*)2]1/2; where E* is a color index and ΔE* is a color difference index..

The laser cleaning was accompanied and monitored using optical microscopy, in order to make sure and prove that the surface original relief is completely preserved.

For all the five leather samples the results proven to be similar, so we present in the investigation charts below the extent for one of them, submersed to all four laser cleaning regimes used. Results show that the spectral parameters derived from the chromatic detection correlated with the optical microscopy information provide us clear indication of the surface cleanliness and the substrate safeguarding.

Sample QbC2: calf leather, vegetal tanning (Quebracho) – laser regime: λ = 1064 nm, ν = 20 Hz



		
dirty	106 mJ/cm^2	217 mJ/cm^2
		
sample	514 mJ/cm^2	351 mJ/cm^2

Colorimetry investigations: L*a*b* Color System, Data pitch: 5(nm)

sample	**106 mJ/cm^2**	**217 mJ/cm^2**	**351 mJ/cm^2**	**514 mJ/cm^2**	**dirty**
L* = 54.75	L* = 46.43	L* = 51.46	L* = 53.56	L* = 53.44	L* = 32.20
a* = 17.66	a* = 13.68	a* = 16.61	a* = 16.95	a* = 17.49	a* = 8.62
b* = 31.11	b* = 23.63	b* = 28.26	b* = 29.91	b* = 30.38	b* = 14.89
	dL* = -8.32	dL* = -3.30	dL* = -1.19	dL* = -1.31	dL* = -22.56
	da* = -3.99	da* = -1.05	da* = -0.72	da* = -0.17	da* = -9.04
	db* = -7.48	db* = -2.85	db* = -1.20	db* = -0.73	db* = -16.23
	dE*ab = 11.88	dE*ab = 4.48	dE*ab = 1.84	dE*ab = 1.51	dE*ab = 29.22

Optical Microscopy Investigations – 200X

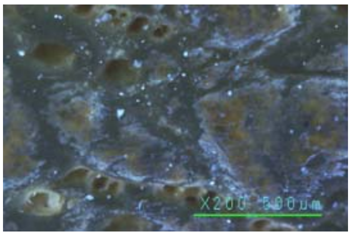
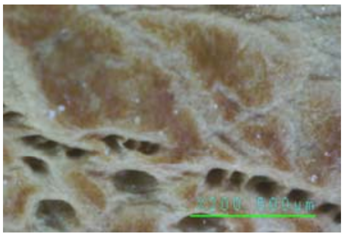
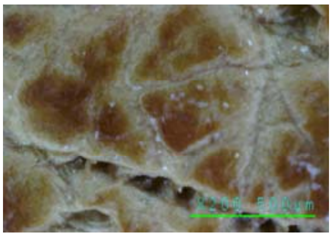
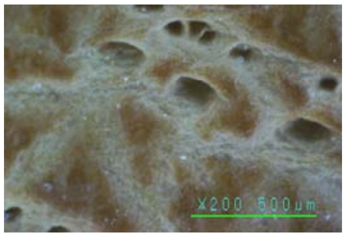
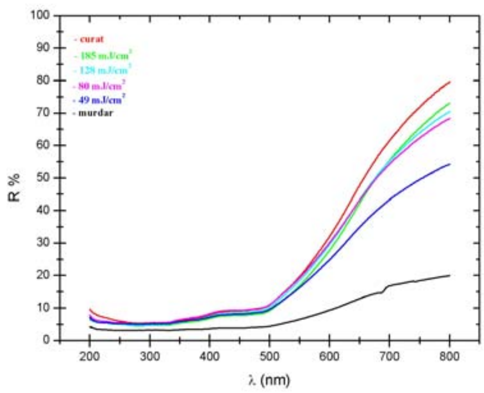
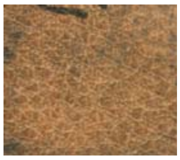
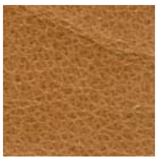
 dirty	 1064 nm - 514 mJ/cm^2	 1064 nm - 350 mJ/cm^2
 sample	 1064 nm - 106 mJ/cm^2	 1064 nm - 217 mJ/cm^2

Table 2.1: Investigation chart corresponding to laser cleaning of QbC2 leather sample at 1064 nm

Calf leather, vegetal tanning (Quebracho) – laser regime: λ = 532 nm, ν = 20 Hz

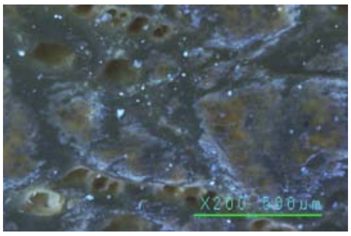


 dirty	 49 mJ/cm^2	 80 mJ/cm^2
 sample	 185 mJ/cm^2	 128 mJ/cm^2

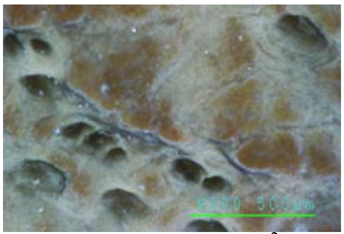
Colorimetry investigations: L*a*b* Color System, Data pitch: 5(nm)

sample	**49 mJ/cm^2**	**80 mJ/cm^2**	**128 mJ/cm^2**	**185 mJ/cm^2**	**dirty**
L* = 54.75	L* = 49.77	L* = 53.77	L* = 53.03	L* = 51.35	L* = 32.20
a* = 17.66	a* = 13.72	a* = 15.70	a* = 16.56	a* = 17.56	a* = 8.62
b* = 31.11	b* = 25.96	b* = 28.74	b* = 29.95	b* = 30.19	b* = 14.89
	dL* = -4.98	dL* = -0.98	dL* = -1.72	dL* = -3.41	dL* = -22.56
	da* = -3.94	da* = -1.97	da* = -1.10	da* = -0.10	da* = -9.04
	db* = -5.15	db* = -2.37	db* = -1.16	db* = -0.92	db* = -16.23
	dE*ab = 8.18	dE*ab = 3.23	dE*ab = 2.35	dE*ab = 3.53	dE*ab = 29.22

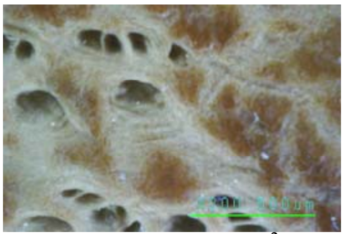
Optical Microscopy Investigations – 200X



dirty



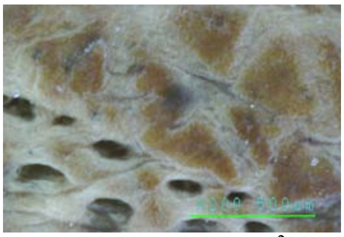
532 nm - 49 mJ/cm^2



532 nm - 80 mJ/cm^2

sample

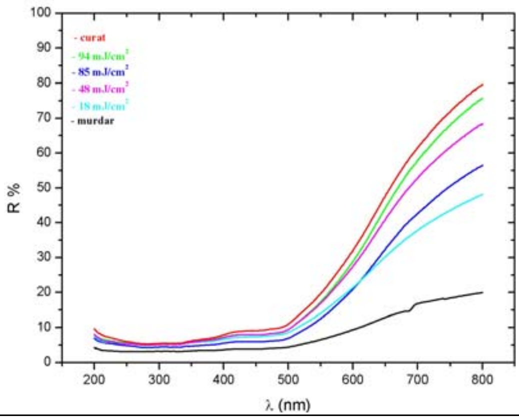
532 nm - 185 mJ/cm^2



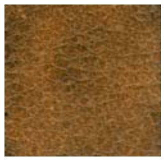
532 nm - 128 mJ/cm^2

Table 2.2 Investigation chart corresponding to laser cleaning of QbC2 leather sample at 532 nm

Calf leather, vegetal tanning (Quebracho) – laser regime: λ = 355 nm, ν = 20 Hz

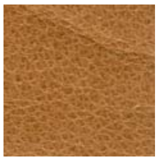


dirty



18 mJ/cm^2

48 mJ/cm^2



sample

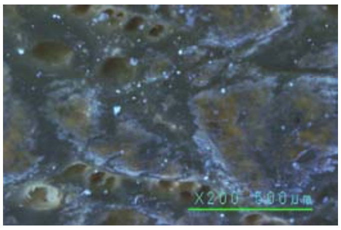
94 mJ/cm^2

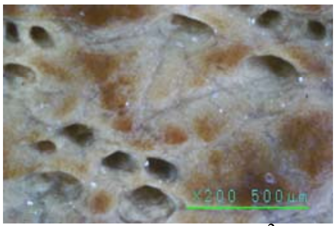
85 mJ/cm^2

Colorimetry investigations: L*a*b* Color System, Data pitch: 5(nm)

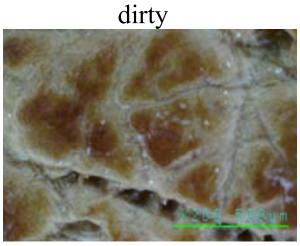
dirty	**18 mJ/cm²**	**48 mJ/cm²**	**85 mJ/cm²**	**94 mJ/cm²**	**sample**
L* = 32.20	L* = 46.69	L* = 51.26	L* = 45.22	L* = 52.10	L* = 54.75
a* = 8.62	a* = 13.16	a* = 16.83	a* = 16.69	a* = 18.25	a* = 17.66
b* = 14.89	b* = 23.60	b* = 29.10	b* = 26.76	b* = 30.57	b* = 31.11
dL* = -22.56	dL* = -8.06	dL* = -3.49	dL* = -9.54	dL* = -2.66	
da* = -9.04	da* = -4.50	da* = -0.83	da* = -0.97	da* = 0.58	
db* = -16.23	db* = -7.51	db* = -2.01	db* = -4.35	db* = -0.54	
dE*ab = 29.22	dE*ab = 11.90	dE*ab = 4.11	dE*ab = 10.53	dE*ab = 2.78	

Optical Microscopy Investigations – 200X


dirty


355 nm - 18 mJ/cm^2


355 nm - 48 mJ/cm^2


sample


355 nm - 94 mJ/cm^2

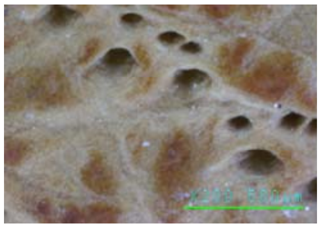
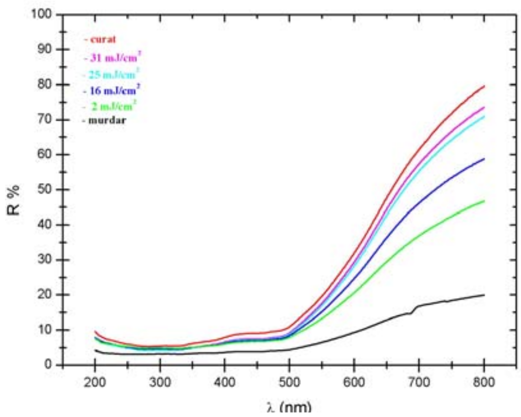
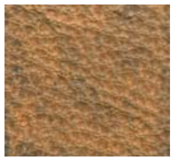

355 nm - 85 mJ/cm^2

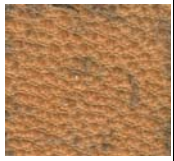
Table 2.3 Investigation chart corresponding to laser cleaning of QbC2 leather sample at 355 nm

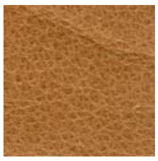
Calf leather, vegetal tanning (Quebracho) – laser regime: λ = 266 nm, ν = 20 Hz




dirty


2 mJ/cm^2


16 mJ/cm^2


sample

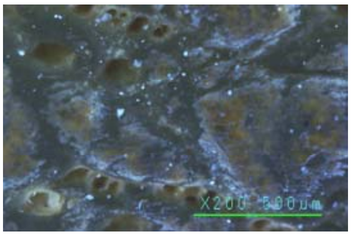

31 mJ/cm^2


25 mJ/cm^2

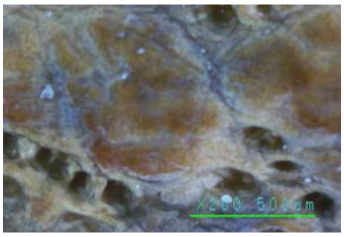
Colorimetry investigations: L*a*b* Color System, Data pitch: 5(nm)

dirty	**2 mJ/cm^2**	**16 mJ/cm^2**	**25 mJ/cm^2**	**31 mJ/cm^2**	**sample**
L* = 32.20	L* = 45.72	L* = 48.91	L* = 51.54	L* = 52.43	L* = 54.75
a* = 8.62	a* = 13.57	a* = 15.88	a* = 17.86	a* = 18.02	a* = 17.66
b* = 14.89	b* = 24.41	b* = 28.68	b* = 32.16	b* = 32.66	b* = 31.11
dL* = -22.56	dL* = -9.04	dL* = -5.84	dL* = -3.21	dL* = -2.33	
da* = -9.04	da* = -4.09	da* = -1.79	da* = 0.20	da* = 0.35	
db* = -16.23	db* = -6.70	db* = -2.43	db* = 1.05	db* = 1.55	
dE*ab = 29.22	dE*ab = 11.97	dE*ab = 6.57	dE*ab = 3.38	dE*ab = 2.82	

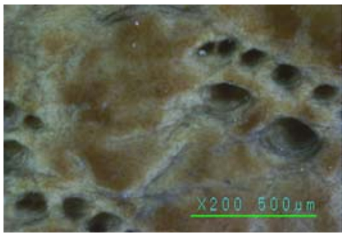
Optical Microscopy Investigations – 200X



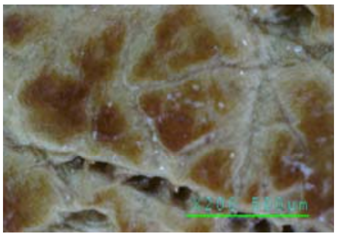
dirty



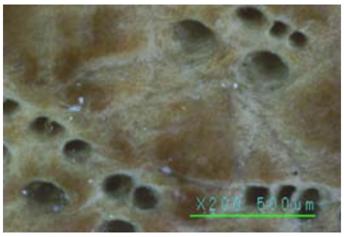
266 nm – 2 mJ/cm^2



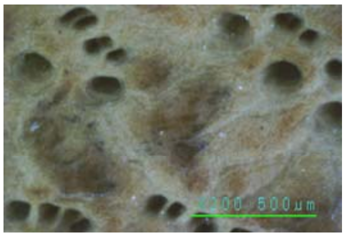
266 nm - 16 mJ/cm^2



sample



266 nm - 31 mJ/cm^2



266 nm - 25 mJ/cm^2

Table 2.4 Investigation chart corresponding to laser cleaning of QbC2 leather sample at 266 nm

4. Conclusions

The laser cleaning working regime that uses the 1064 nm wavelength has proven to be the optimal one due to the fact that its color index value is the closest to the original (color index difference between the section cleaned at a fluence of 514 mJ/cm^2 and the sample one: dE*ab = 1.51). As you can conclude from the investigation charts presented above, where the green-red colour axe (a*) is concerned the colour fluctuation are small (under 0.5 %), the closest value to the initial one being the same one mentioned above. Considering the blue-yellow axe (b*), we see a slight yellowing, not noticeable with open eye. The leather's structure wasn't affected, the relief of the surface was preserved, and the colour differences were very small, not noticeable by open eye analysis. The 532 nm wavelength offered us good results also, but there were cases where slight yellowing appeared; 355 and 266 nm were not satisfactory.

The outcome of these experiments, combined with the one made on parchment samples will develop an on-line control of laser induced material removal from artworks under restoration, phenomena encountered in photo-induced ablation.

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