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STUDY OF THE EFFECT OF LASER CLEANING ON COLLAGENOUS STRUCTURES

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ABSTRACT

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. This paper contains researches about the effect that the laser restoration procedures (laser cleaning, mainly) induce on organic substrates such as leather and parchment. Laser cleaning of leather & parchment is a novel technique that has the potential to provide contactless, chemical-free cleaning of historically important documents, overall providing a high accuracy successful cleaning. However, the effect of laser cleaning on the collagenous structure of parchment is still poorly understood, as is the effect of the wavelength or the energy density (fluence level). This study comprises aspects of the ageing of the materials and also specific issues concerning conservation of their photomechanical properties, correlating information obtained using specific scientific methods of analysis such as colorimetry, optical microscopy, shrinkage temperature of the organic fibers and NIR Spectroscopy. Surface monitoring based on chromatic modulation has been carried out for the laser cleaning of different types of leather and parchment samples, working with the spectral signature of reflected light from the surface. Results show that the spectral parameters derived from the chromatic detection provide not only clear indication of the surface cleanliness and the substrate damage but also useful chromatic information on the surface. The outcome of these experiments consists in an on-line control of laser induced material removal from artworks under restoration, phenomena encountered in photo-induced ablation.

INTRODUCTION

A primarily objective of this study has been the assessment of the prospects opened by the adaptation of the laser technology in art conservation. Traditional methods of conservation rely on mechanical or chemical techniques. Because these processes are difficult to control, extensive expertise is necessary in order to achieve an optimal result. Furthermore, optical techniques can be applied on-line to evaluate the cleaning process and carefully monitor its progress safeguarding against any damage.

Traditional chemical and mechanical cleaning procedures using chemical solvents and scalpels respectively, may result to a sample’s deterioration and besides it is difficult to discriminate between the surface’s and the substrate’s ablation. Conventional cleaning methods applied on parchment, using alcohol and water may lead to the hydrolysis of collagen fibers, change of molecular structure of proteins and finally to gelatinization. On the other hand, laser cleaning is a non-destructive, non-contact and selective method to be applied on organic materials, namely on parchment. Its efficiency depends on the object’s optical parameters as well as on the laser parameters. However, organic materials are the most sensitive objects on which laser cleaning may be applied, as they are prone to discoloration and degradation induced by photo thermal reactions, which may take place.

CONTEXT

Parchment is commonly manufactured from the dermis layer of animal skin after strong alkaline removal of the epidermis and the subcutaneous tissue layers. It mainly consists of collagen fibers. The molecular subunits of collagen fibers are polypeptide chains with various amino acid side chains Rx: (-NH-CHRx-CO-)n.[1]

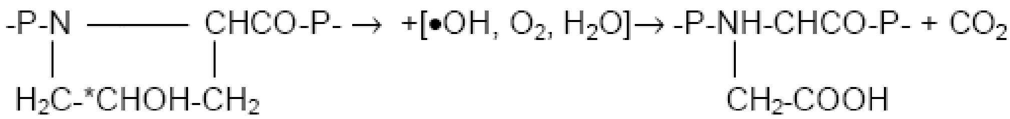
Collagen is composed of three similar strands of a protein containing in greatest amount glycine, alanine, proline, and hydroxyproline. The spatial configurations of repeated triple amino acid sequences involving glycine, alanine, and hydroxyproline or proline are responsible for the helical conformation between the strands. Water molecules are intimately connected with the hydrogen bonding holding the triple helix together [2].

Laser cleaning [3] is a relatively new technique that acquired the attention of many restorers from modern research centers for conservation and restoration, as an outcome of the many advantages envisaged by this non-conventional technique.

Up to now, a small amount of research related to laser cleaning of the collagenous substrates has been made, comparative to the studies and investigations made on inorganic materials (stone, metal). Encouraged by the publications in the international literature [4] we followed with preliminary studies [5,6] in order to see what are the effects that the laser radiation may induce on collagenous structure before starting work on historical parchments.

We must take into consideration the fact that UV radiation (accumulated during its life time) plays an important role in chemical degradation of parchment due to the Oxidative breakdown processes of parchment base on heat and light. Parchment starts degrading at tripeptides in clusters of charged amino acids following the pattern: (1) loss of mainly the basic amino acids Lysine, Arginine, Hydroxylysine, and the amino acids Proline and Hydroxyproline, (2) gain of acidic amino acids, (3) formation of small amounts of breakdown products. Acidic breakdown causes hydrolysis of the peptide bonds in the peptide chains, and amino end groups are generated. So, using the IR wavelength of the laser assured a safer surrounding.

Besides, autoxidation of parchment occurs in the presence of light. Initially, hydroxyl radicals could be generated by the laser irradiation. These may attack carbon atoms in peptide side chains (indicated with an asterix) as shown in an example of Hydroxyproline (most common



in collagen).
where a P means peptide chain rest, and also lysine

$$R\text{-}C^{*}H_2\text{-}NH_2 \rightarrow +[\bullet OH] \rightarrow R\text{-}CHO + NH_3 \rightarrow +[O_2, H_2O] \rightarrow R\text{-}COOH$$

with R the rest of the Lysine side chain, $-(CH2)_3-$, including the peptide main chain. Polar groups, particularly carboxylic acid functions are formed.

Parchment affected by photochemical reactions (photochemical degradation), breaks down and gelatinizes. This seriously damages the cohesion of the fibers and the parchment becomes brittle, fragile and liable to split. Besides, the hard gelatinized mass prevents the fibers in the parchment from moving freely.

EXPERIMENTAL DATA

This studies' purpose was to establish the fluence thresholds adequate to an efficient removal of the dirt layers. In this manner several parchment samples (with different animal provenience) were artificially soiled with natural charcoal in order to simulate impurities over time. The laser used in the experiments was a YAG:Nd Q-Switched that works at fundamental wavelength (1064 nm) as well as at its three harmonics: 532, 355 and 266 nm. This is part of an ample study of the effects of laser radiation on collagenous substrates; the samples were carefully diagnose before and after cleaning using chemical and physical methods such as FT-IR, NIR, UV-VIS Spectrometry, colorimetry, microscopy and *Micro Hot Table*.

Goat Parchment

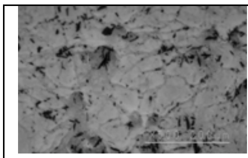
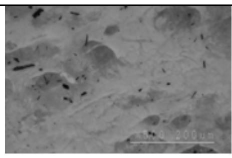
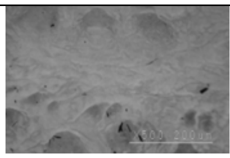
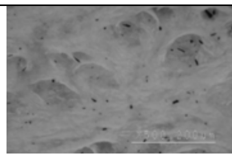
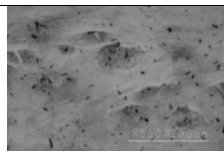
				
dirty	1064 nm – 0.7 J/cm^2	1064 nm – 0.6 J/cm^2	1064 nm – 0.5 J/cm^2	532 nm – 0.5 J/cm^2

Figure 1: Microscopy investigations at 200 X magnification of the goat parchment sample

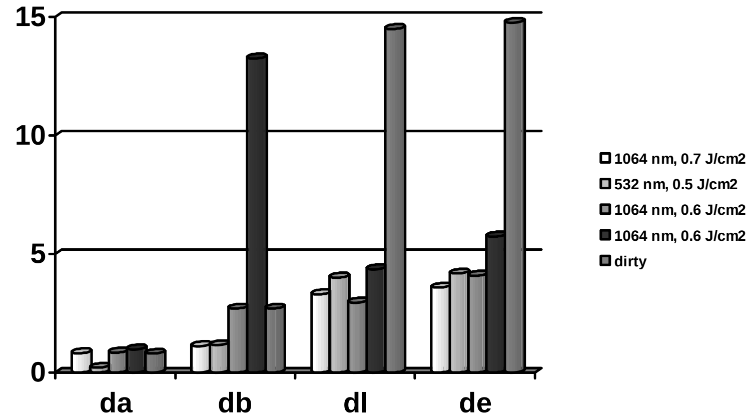


Chart 1: Colorimetry parameters fluctuations for the goat parchment sample

Lamb Parchment

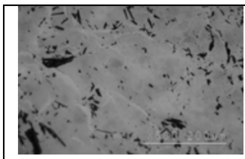
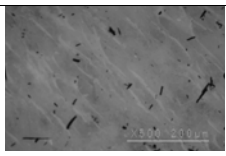
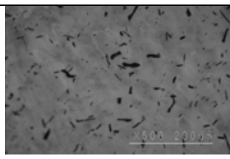
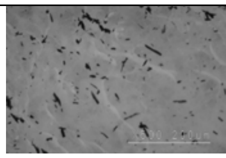
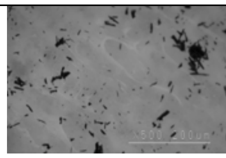
				
dirty	1064 nm – 0.7 J/cm^2	1064 nm – 0.6 J/cm^2	1064 nm – 0.5 J/cm^2	532 nm – 0.5 J/cm^2

Figure 2: Microscopy investigations at 200 X magnification of the lamb parchment sample

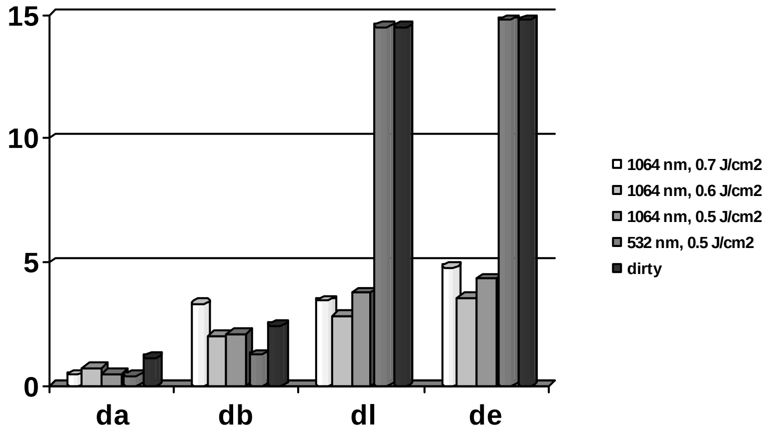


Chart 2: Colorimetry parameters fluctuations for the lamb parchment sample

Young Goat Parchment

dirty	1064 nm – 0.7 J/cm^2	1064 nm – 0.6 J/cm^2	1064 nm – 0.5 J/cm^2	532 nm – 0.5 J/cm^2

Figure 3: Microscopy investigations at 200 X magnification of the young goat parchment sample

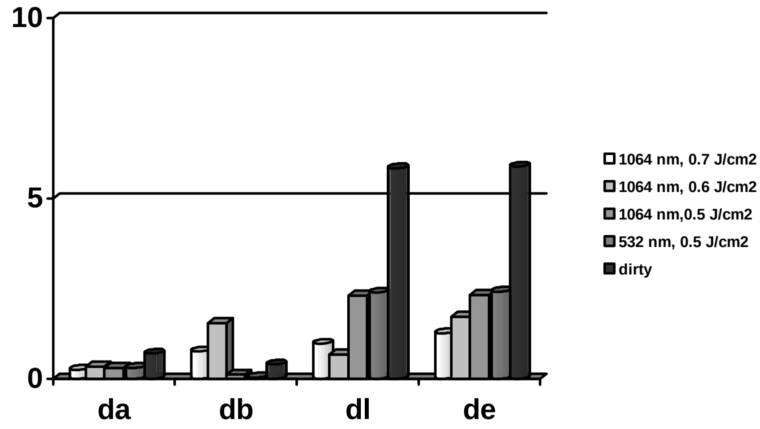


Chart 3: Colorimetry parameters fluctuations for the young goat parchment sample

CONCLUSIONS

The experiments presented in this paper are part of a complex study concerning the consequences that laser cleaning process may induce on the collagenous substrates, such as leather and parchment. The main concern was if laser induces ageing or not. The results were more than satisfactory and concluded that the laser cleaning (applied in correct working regime) induces no harm (*no ageing*) to the collagenous substrates. The most efficient results were obtained using the 1064 nm wavelength at a fluence interval starting from 0.5 mJ/cm^2 to 0.7 J/cm^2.

ENDNOTES

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Back to Top