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# A study of laser cleaning of paper with fat-containing contaminations

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**Abstract.** This paper is devoted to investigation of laser cleaning of paper with fat-containing contaminations. In recent years, laser technologies have been widely used in the preservation of Cultural Heritage (CH). One of the main fields of laser application in this area is the cleaning of CH objects from natural and anthropogenic contaminations. It is known that there exist two main approaches to the laser cleaning, e.g. dry cleaning and wet cleaning. We will present experimental results of wet laser cleaning with the Ytterbium fibre laser (wavelength of 1064 nm) of fat-containing contaminations from model samples and fragments of a real historical artefact such as XIXth century book.

Keywords: heritage science, laser application, laser cleaning

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# Исследование лазерной очистки бумаги от жиросодержащих загрязнений

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Аннотация. Данная работа посвящена исследованию лазерной очистки бумаги от жиросодержащих загрязнений. В последнее время лазерные технологии находят все более широкое применение в сохранении культурно-исторического наследия. Одним из главных направлений применения является лазерная очистка объектов культурно-исторического наследия от природных и антропогенных загрязнений. Известны два подхода к лазерной очистке: сухая очистка и влажная. В данной работе редставлены результаты использования технологии влажной лазерной очистки иттербиевым волоконным импульсным лазером с длиной волны 1064 нм модельных образцов и исторического артефакта такого, как книга XIX века.

Ключевые слова: культурно-исторические наследие, лазерная очистка, применение лазеров

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#### Introduction

Laser technologies have recently begun to be widely embedded not only in industrial and scientific applications but also in the field of restoration and conservation of Cultural Heritage. Laser restoration of stone and metal monuments is the most well developed, while laser cleaning of CH objects made out of organic materials is still at the stage of experimental studies.

Studies conducted in the last decade have brought significant evidence that laser cleaning has a real potential for application in conservation of paper [1–3]. Laser irradiation could be used for treating various deteriorations such as dust, soot, fungi, foxings, etc.

Paper contaminations with fat-containing substances are highly widespread in conservation practice of books and documents on paper base. There could be found vegetable fat or animal fat, or a combination of both. For example, one of the most common contaminations of books and documents is "finger grip", a trace of human skin oils. The removal of such contaminations by traditional conservation methods which imply using organic solvents that could be dangerous for the conservators is a laborious process. Moreover, such solvents could be damaging for the paper as well, which is unacceptable for rare CH objects on paper base. Thus, developing a novel approach to the described problem is an actual scientific task.

The authors of this work have already reported about laser cleaning of different kinds of paper using pulsed Ytterbium fibre laser with the wavelength of 1064 nm [3–5]. Earlier authors presumed that laser cleaning is suitable only for surface paper contaminations. However, it could be different in case of laser cleaning with the use of auxiliary liquid (for example distilled water), so called wet cleaning. The technology of wet laser cleaning is well-known in the field of cleaning stone and metal [6]. Wet laser cleaning is reported to serve not only for removing surface contaminations but also to clean contaminations that are in some depth of the material. Given technology also could be more delicate for the treated material.

The purpose of this work is to investigate the technology of wet laser cleaning of paper from fat-containing contaminations at 1064 nm with pulsed Ytterbium fibre laser performed on paper samples and real historical artefacts.

### **Experiment**

During the experiment model paper samples as well as fragments of a real historical artefact were cleaned with laser irradiation and later studied. Model paper samples were purposefully prepared beforehand. To imitate fat contamination copy paper samples were soaked in olive and castor oils and then put into thermal cabinet with the temperature of  $102-104\,^{\circ}\mathrm{C}$  for 12 days. The latter was performed to simulate the process of paper ageing. Fragments of a real artefact, a book of religious content published in the XIXth century, were laser treated as well. Given fragments were contaminated with lamp oil, wax and traces of soot. In the process of wet laser cleaning 5% aqueous solution of sodium hydrogen carbonate (NaHCO<sub>3</sub>) served as an auxiliary liquid, which is widely used in conservation practice for removing fat contaminations from paper. It is known that sodium hydrogen carbonate decomposes under the temperature higher than 60 °C into sodium carbonate, water and carbon dioxide. By using thermal processes that occur during laser ablation we can achieve such chemical reaction to "whip out" fat molecules from paper fibres.

In the work a laser system with the Ytterbium fiber laser source (1064 nm) was used. The "MiniMarker" laser apparatus is commercially available marking laser system produced by "Laser Center", Ltd., Saint Petersburg.

To evaluate the results of wet laser cleaning of paper optical microscopy as well as scanning electron microscopy were used.

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## **Results and Discussion**

Preliminary study of reflectance of model paper samples contaminated with oils gave us information that dry laser cleaning could not give positive results due to the fact that on the working wavelength of laser (1064 nm) paper samples reflect nearly 90% of the irradiation. Reflection spectra of an artefact paper showed the same results. The fact was proved empirically on paper samples.

Since the dry laser cleaning was proved not to be an option the authors decided to consider the technology of wet laser cleaning. In case of wet laser cleaning, it was shown that use of laser irradiation with following parameters: wavelength of 1064 nm, pulse duration of 100 ns, peak power density from  $1.4 \cdot 10^5$  W/cm² to  $2.0 \cdot 10^5$  W/cm², the pulse repetition frequency of 20 kHz makes possible an effective removal of fat-containing contaminants. The laser system is equipped with the preinstalled scanning system. Scanning parameters for laser cleaning are as follows: beam scanning speed of 800 mm/s with the filling of 40 lines per millimetre. Wet laser cleaning performed on the model paper samples was a success, thus, it became possible to clean an artefact as well. Laser cleaning of fragments of the historical book showed positive results. As it could be seen in Fig. 1, b treated areas were considerably lightened in colour, which imply that the lamp oil was successfully removed. Moreover, it was noticed that wax contamination was removed as well (Fig. 1, c). There are no noticeable damages on the images by optical microscope.

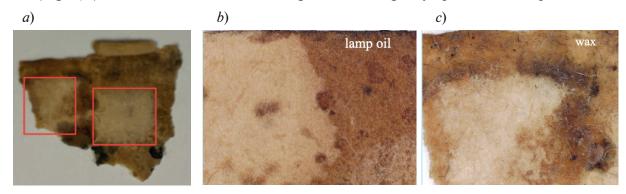


Fig.1. Fragment of artefact book after laser cleaning (a). Cleaned areas are marked in red. Images by optical microscope of laser treated areas with lamp oil (b) and wax (c)

Images obtained by the means of scanning electron microscopy (SEM) proved that the laser cleaning of model samples from oils was efficient (Fig. 2). It could be noted that there are no damages to the paper structure of paper samples (Fig. 2, b).

On the left side of the SEM-image it could be noted that paper fibres are coated with contaminations whereas on the left deteriorated layer is removed. In addition, it could be noted that laser irradiation caused no damage to the paper fibres.

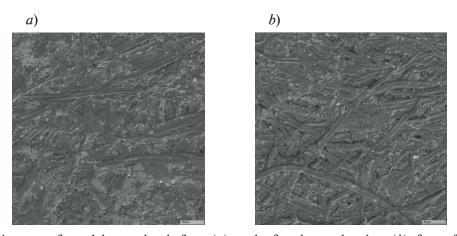


Fig.2. SEM-images of model samples before (a) and after laser cleaning (b) from fat-containing contaminations

SEM-images of laser treated fragment of the artefact proved that the laser cleaning was efficient (Fig. 3, a). On the left side of the SEM-image (Fig. 3, a, b) it could be noted that paper fibres are coated with contaminations consisted of oil and wax with traces of soot whereas on the left the deteriorated layer is removed. In addition, it could be noted in Fig. 3, c that laser irradiation caused no damage to the paper fibres and paper structure as a whole.

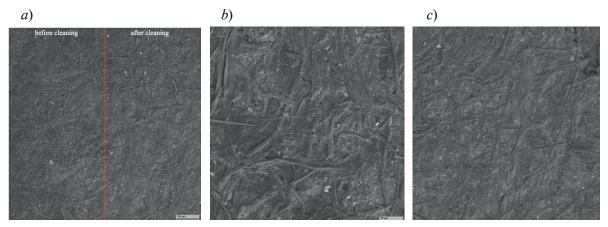


Fig.3. SEM-image of a fragment of the artefact book with the areas before (left) and after (right) laser cleaning (a) from fat-containing contaminations. It could be noted that fibres are coated with contaminated layer (a and b). Fragment of the book after laser treatment (c)

During the experiment FTIR spectroscopy was performed for the fragments of the artefact. By comparing spectra of laser treated fragments and non-treated it could be concluded that contaminated layer was removed successfully since there are no peaks that characterise the substances of contamination layer.

#### **Conclusion**

Removing fat-containing contaminations from paper showed the advantage of wet laser cleaning of paper in relation to the given task. Paper samples as well as fragments of an artefact were successfully cleaned from lamp oil and wax during the experiment with the use of 5% aqueous solution of sodium hydrogen carbonate as an auxiliary liquid. Investigation of laser treatment results by means of optical microscopy and scanning electron microscopy showed no damage to the paper structure and fibres after laser treatment. FTIR spectroscopy proved the efficacy of laser treatment.

To conclude, wet laser cleaning of paper from fat-containing contaminations is proven to be a novel and efficient solution to the very apparent problem in conservation practice. It showed that laser cleaning could be applied not only for surface contaminations but also to the ones that go deep into material such as fat-containing contaminations.

Nevertheless, further investigations of the application of wet laser cleaning for restoration and conservation of Cultural Heritage objects consisted of organic materials are needed as well as studies of the laser irradiation influence on such materials, their chemical and mechanical and other properties.

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