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A study of chemical and mechanical properties of paper under its laser cleaning

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Abstract. This paper is devoted to investigation of chemical and mechanical paper properties after laser cleaning. 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 surfaces of CH objects from natural and anthropogenic contaminations. However, cleaning of books and documents on paper basis requires intensive experimental studies. Comparison of paper properties before and after laser cleaning may prove the safety of laser cleaning. One of the most important parameters that characterize paper strength and durability are hydrogen ion concentration (pH) and absorptivity. We will present experimental results on pH value measurements of paper as well as results on paper absorptivity performed on model samples and real historical artefacts such as books and fragments of newspapers. The results of studies indicate on the neutralising effect of laser irradiation which can be used for the conservation of books and documents on paper base.

Keywords: heritage science, laser application, laser cleaning

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Исследование химических и механических свойств бумаги после лазерной очистки

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Аннотация. Данная работа посвящена исследованию химических и механических свойств бумаги после лазерной очистки. В последнее время лазерные технологии стали все шире применятся для сохранения культурно-исторического наследия. В реставрации используют технологию лазерной очистки, которая позволяет решать

задачи по удалению природных наслоений и антропогенных загрязнений с поверхности памятников. На сегодняшний день наиболее отработанной является очистка объектов из камня и металла, лазерная очистка органических материалов, например, бумаги находится в стадии проведения поисковых научно-исследовательских работ. Сравнение химических и механических свойств бумаги до и после воздействия лазера может доказать безопасность лазерной очистки. Наиболее важными параметрами, характеризующим сохранность бумаги являются концентрация ионов водорода (pH) и впитываемость бумаги. В данной работе будут приведены результаты измерения кислотности и впитываемости бумаги после лазерной очистки иттербиевым волоконным импульсным лазером с длиной волны 1064 нм модельных образцов и исторических артефактов. Результаты проведенных исследований указывают на нейтрализующий эффект лазерного излучения, что потенциально может быть использовано для реставрации книг и документов на бумажной основе.

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 paper objects is still at the stage of experimental studies.

For the last decade many research groups have presented the possibility of using laser irradiation to remove paper deteriorations such as dust, soot, fungi, foxings, etc. [1–5]. These studies have shown that laser cleaning has a significant potential for removal of surface contaminations. However, currently there are still debates between professional restorers regarding the safety of laser cleaning for preservation of books and documents, especially in the long term. That is why proving the inalterability of chemical and mechanical properties of paper before and after laser cleaning might be considered as confirmation of its safety.

Most significant parameters of paper in conservation practice are hydrogen ion concentration and absorptivity. The hydrogen ion concentration or pH value of paper characterizes strength and durability of paper. Oxidation processes in paper have a negative effect on its properties, increasing the acidity. Increased acidity is one of the main factors that causes accelerated ageing [6]. Usually paper that is long in storage becomes acidic: pH 3.0–5.0. If the pH is less than 5.5 paper is neutralized. The ability of paper to absorb moisture from the air is determined by its absorptivity [7]. When being stored under conditions with a certain humidity level between the air and the paper there is established a balance. When the balance is disturbed robustness of paper is compromised. In conservation, absorptivity is very important. For example, it influences the possibility to absorb adhesives substances therefore the possibility of conservation itself. If the absorptivity decreases after laser cleaning it raises a question about capability of subsequent conservations of paper documents. Not to say that excessive dryness leads to fragility of paper and its early destruction for dry paper loses its mechanical durability.

Experiment

Earlier the authors of this work reported about laser cleaning of different kinds of paper using Ytterbium fiber laser [8–9]. It was shown that use of laser with following parameters: wavelength of 1064 nm, pulse duration of 100 ns, peak power density varies from $1.6 \cdot 10^5$ W/cm^2 to $3.2 \cdot 10^5$ W/cm^2, the pulse repetition frequency of 20 kHz makes possible effective removal of

contaminants. The purpose of this work is to investigate chemical and mechanical properties of paper after laser cleaning at 1064 nm with Ytterbium fiber laser performed on paper samples and real historical artefacts.

Three types of old paper samples from the Soviet era were cleaned during the experiments and further their chemical and mechanical properties were studied. These samples are: sample 1, thin paper of a light brown shade, sample 2, thicker paper similar in shade to sample 1, sample 3, thin nearly white paper. Soviet paper samples are presented in Fig. 1.

To simulate surface contamination of paper graphite or charcoal dust were rubbed onto the surface of samples.

The other artefacts are the books from the late third of the 18th century to the beginning of the 20th century. Such a choice of books was made to cover a large period of time and to have different kinds of book paper. On top of that, investigated books are relevant to conservation science, especially 19th century books since they were mass produced from raw materials of lesser quality, therefore they are more fragile and unstable towards ageing. In the selection there are books printed in European countries and in the Russian Empire. Contaminations that occur in studied artefacts are typical in conservation, they are worn-in dust, traces of grease and of unknown origin. A list of artefacts is presented in Table 1.

The pH value measurement was carried out by portable pH metres manufactured by Hanna Instruments and Ohaus with plane electrodes and temperature sensitive elements. For the paper absorptivity measurement, analytical balance was utilized.

Table 1

List of historical artefacts

#	Title	Year of printing	Place of printing
1	Sonnets by Petrarca	1778	London, England
2	The Dramatick Writings of Will. Shakspere, Volume the Thirteenth	1788	London, England
3	Application de l'Analyse à la géométrie by M. Monge	1809	Paris, France
4	Collected volume of works by F.M. Dostoyevsky	1866	St. Petersburg, Russia
5	The Complete Works of M.E. Saltykov-Shchedrin, Volume One	1905	St. Petersburg, Russia
6	What are we living for? by L. Tolstoy	1906	Moscow, Russia
7	History of Greece in the classical period. 9th–4th century BC by R. Vipper	1913	St. Petersburg, Russia
8	History of Western Europe, Contemporary Times by N. Kareev	1916	Moscow, Russia
9	Newspaper dated June, 1943	1943	USSR

Results and Discussion

The pH test was performed by the method of aqueous extract in concordance with *Direction of pH value measuring using the contact method* by Mamaeva and Velikova [6] with electronic pH-meter. The measurement was performed in two points on the page of a given sample or artefact: one in the area (Fig. 1) that was treated by the laser and another in the untreated area. Results of pH value measuring are shown in Table 2.

As seen in Table 2, alkalic modern copy paper became more neutral after laser cleaning, pH value decreased. For the samples 1 and 2, pH value increased whereas for the sample 3, it stayed nearly the same.

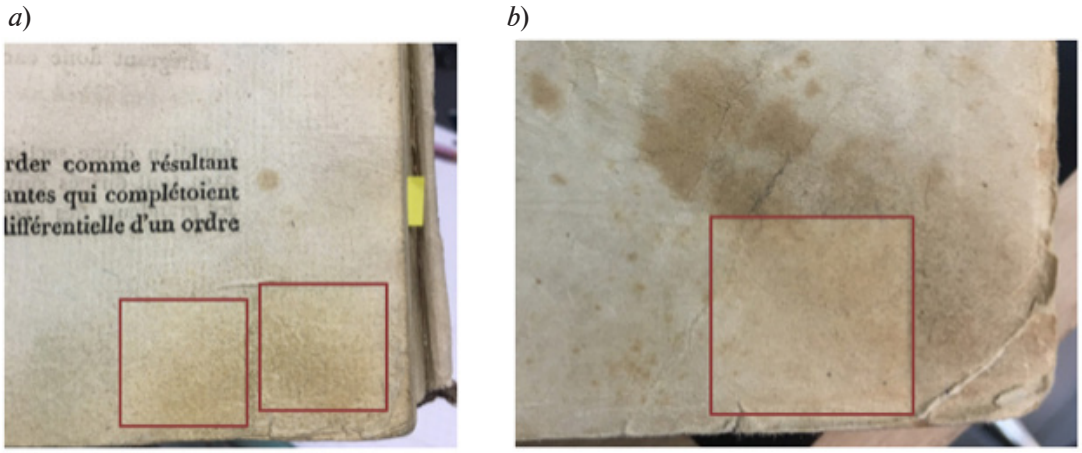

Fig. 1. Books after laser cleaning. Fragment of book *Application de l'Analyse a la géométrie* (*a*). Fragment of *The Complete Works of M.E. Saltykov-Shchedrin, Volume One* (*b*). Laser-treated areas are marked in red

Consider further pH value measurement of historical artefacts. Sample numbers match document titles presented in Table 1. As seen in the table, all of the artefacts excluding 2 became more neutral, their pH values increased after laser treatment. As for artefact 3 its initial pH value is quite neutral and it becomes slightly more acidic. Probably further investigation is needed. Overall pH value tending to neutrality is a positive fact. In general, initially acidic paper became less acidic after laser treatment or did not change its pH value, alkali paper became more neutral. There is no change in pH value for the newspaper after laser cleaning.

To conclude, pH measurement showed overall the tendency for neutralizing of paper after laser irradiation, initially acidic paper became less acidic, alkalic one became less alkalic, although paper samples that had neutral pH-value became more acidic. To ensure general rule it is suggested that another experiment taking place with a sample collection method of pH value measuring. Given results could raise a question about the possibility of neutralizing paper by laser which is an actual conservation task.

While performing pH value measuring it was noted that laser treated areas absorb water differently than non-treated areas (Fig. 2). It was suggested that the absorptivity of paper declines due to processes that happen under laser irradiation. This phenomenon will be considered in the following part.

As it was noted in the previous part that paper presumably loses its ability to absorb moisture, it was decided to perform an experiment to evaluate the absorptivity of paper.

Table 2

Summary table of measured pH values of paper samples

Sample	Without cleaning	After cleaning	Sample	Without cleaning	After cleaning
Model samples			2	4.29	4.55
Copy paper	9.15	8.89	3	6.56	6.23
#	Soviet paper samples		4	5.57	5.66
1	4.75	5.32	5	5.83	6.05
2	4.75	5.32	6	4.20	4.40
3	4.91	4.90	7	4.40	4.60
Artefacts			8	4.00	4.40
1	5.55	5.88	9	5.55	5.55

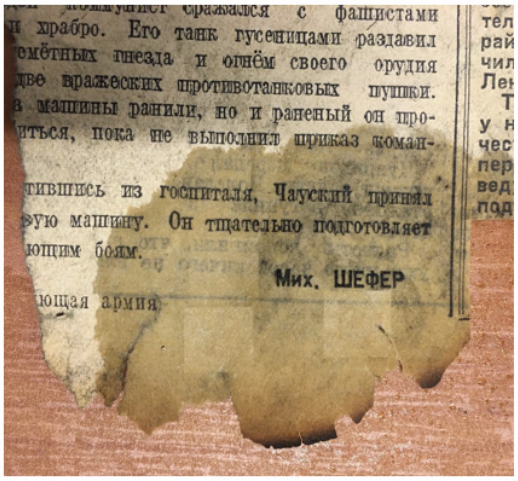

Fig. 2. Fragment of the newspaper wetted with distilled water for pH value estimation. Less absorbent areas are noticeably lighter, they were treated with laser irradiation

The experiment was carried out in accordance with the Soviet Union State Standard 12605-97 *Paper and board. Method for determination of surface water absorptiveness at one-sided wetting (Cobb method)*. Three samples 10 by 10 cm in size of old soviet paper (paper that goes by sample 1 in previous parts) were cleaned from charcoal dust, they were weighed on an analytical balance in dry and wet states and compared with three samples of the same paper which did not undergo the laser treatment. Laser treated samples were wetted from the cleaned side.

The surface water absorptivity of paper with one-sided wetting for each sample is calculated by the following formula

$$Cobb_x = 100(m_2 - m_1), \tag{1}$$

where m_1 is the mass of the sample before the experiment; m_2 is the mass of the sample after the experiment.

There is no difference in values, thus it could not be unambiguously said that paper loses its absorptivity after laser cleaning. Nevertheless, the result observed in Fig. 2 with the piece of a newspaper is significant enough to proceed the investigation of a given question for paper differ drastically in properties depending on many factors. In conclusion, further investigation is needed.

Conclusion

pH measurement of paper samples and artefacts showed overall the tendency for neutralizing of paper after laser irradiation, initially acidic paper became less acidic, alkalic one became less alkalic, although paper samples that had neutral pH-value became more acidic. Considering that generally paper that has been in storage for a long time is acidic and has pH of 3.0–5.0 the tendency of neutralizing paper after laser irradiation is a positive fact. It could raise a question about the possibility of neutralizing paper by laser which is a topical conservation task.

The investigation of the absorptivity of paper gave no unequivocal result, it could be speculated that some paper really loses its absorptivity after laser impact as it was suggested happened with the newspaper fragment, which is a negative fact for it leads to fragility of paper, though some paper does not lose it.

To conclude, laser cleaning of paper has its own benefits, it is a very precise and fast conservation method, though it has a narrow applicability, it could be used in specific conservation tasks and only for surface contaminations. Nevertheless, further investigations of the laser irradiation influence on paper and its chemical and mechanical as well as other properties are needed.

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