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Laser cleaning of organic pigments on paper

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Abstract. This paper is devoted to the investigation of laser cleaning of organic pigments on paper. 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 various contaminations of natural or anthropogenic origin. Experimental results of laser cleaning with the Ytterbium pulsed fibre laser (1064 nm wavelength) of model samples of modern organic pigments on paper as well as Raman spectroscopy analysis of the obtained results are presented.

Keywords: cultural heritage, laser cleaning, pigments, contaminations, fibre laser

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Лазерная очистка органических пигментов на бумаге

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Аннотация. Статья посвящена исследованию лазерной очистки органических пигментов на бумаге. В последнее время лазерные технологии все чаще распространяются в сфере сохранение культурно-исторического наследия. Одним из основных направлений применения лазерных технологий в реставрации является очистка объектов культурно- исторического наследия от различных загрязнений естественного и антропогенного происхождений. В данной работе представлены экспериментальные результаты лазерной очистки модельных образцов современных органических пигментов на бумаге при помощи иттербиевого импульсного лазера на длине волны 1064 нм, а также анализ полученных результатов методом спектроскопии комбинационного рассеяния.

Ключевые слова: культурно-историческое наследие, лазерная очистка, загрязнения, пигменты, волоконный лазер

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Introduction

Recent studies have shown that laser cleaning is a safe and efficient instrument for restoration of cultural heritage (CH) objects [1–2]. Laser cleaning of artefacts made out of inorganic materials such as stone and metal is well developed, whereas cleaning CH objects based on organic ones is still in the process of experimental studies. Organic materials in cultural heritage include paper, leather, parchment, textiles and also organic paints and colourants.

Based on scientific literature on the topic and authors' experience laser could be applied for removing various deteriorations such as dust, soot, fungi, foxings, oil and wax from the surface of the paper without causing it any damage [3–5]. CH artefacts on paper base such as books, documents, manuscripts and painting are complex objects and include not only paper but ink, pencil, paint, colourant, etc.

In the given research we will consider laser treatment of organic pigments on paper. Organic pigments for paints and colourants production were used since the dawn of time. A lot of historical paints and colourants are known to be of organic origin, for example, plant derivative ones, such as indigo or madder. These pigments could be found in paintings, books, documents, historical textiles, taxidermy objects, etc. Nowadays organic pigments are even more widely spread in the manufacturing of paints and colourants, apart from their predecessors modern pigments are nearly all synthesised. Therefore, using organic synthetic pigments is a well established practice by contemporary artists. Thus, investigating novel restoration and conservation technics for the future CH objects is an actual scientific task.

Experiment

The authors of this work have already reported about laser cleaning of CH objects on paper base using Ytterbium fibre laser with the wavelength of 1064 nm [3–5]. Given wavelength was chosen based on the reflectance of the paper. Preliminary to the experiment on leaser cleaning reflectance spectra of pigments on paper samples were obtained as well. Reflectance spectra show that up from 800 to 1100 nm about 80–90 % of laser irradiation is reflected from the paint surface (Fig. 1). Therefore, it was proven that laser with the wavelength of 1064 nm is suitable for carrying out the given task.

Investigated pigments are modern organic synthetic pigments most widely used in paint production. These pigments are pigment blue 15 (PB15), pigment green 7 (PG7), pigment violet 19 (PV19), pigment violet 23 (PV23) and pigment yellow 3 (PY3). Pigments were present in different paints such as watercolour, gouache and acrylic. The selection of listed pigments was based on the fact that they make an average palette of a contemporary artist.

Samples were prepared by applying paint on the surface of the paper. To imitate contamination graphite dust was used. During the experiment samples were cleaned from the contamination by laser and then studied by optical microscopy and Raman spectroscopy.

Laser cleaning from contaminations was achieved by laser irradiation with following parameters: wavelength of 1064 nm, pulse duration of 100 ns, pulse repetition frequency of 20 kHz, peak power density about $3{\cdot}10^5$ W/cm^2, beam scanning speed of 800 mm/s. Cleaned area was 10 by 10 mm.

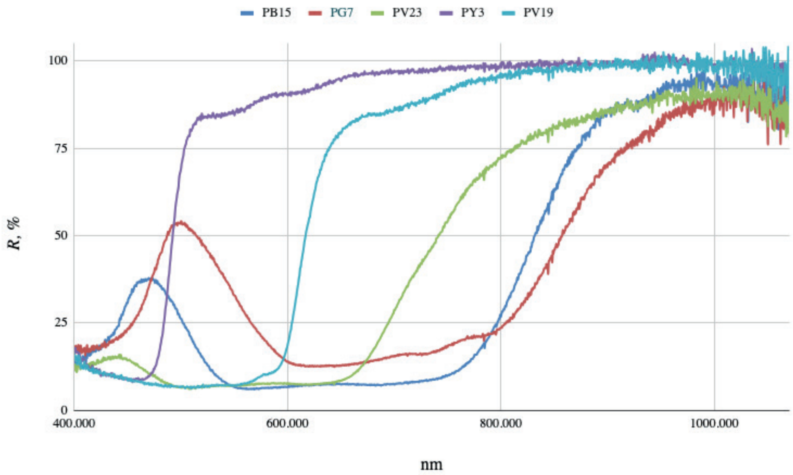

Fig.1. Reflectance spectra of pigments on paper

Results and Discussion

Samples of pigments on paper were successfully cleaned by laser irradiation from contamination without any visual damage. The results of laser cleaning are shown in Fig. 2. Images obtained by the means of optical microscope additionally proved that the laser irradiation caused no damage to the paint layer or any colour degradation in it.

Raman spectroscopy was performed to detect any changes in the chemical composition of pigments caused by laser irradiation and to control the efficacy of laser cleaning. Raman microscope by SOL Instruments (Belarus) was utilised during the experiment with the solid laser irradiation source with the wavelength of 785 nm. Spectra were registered with the diffraction grating of 600 lines per mm, measurement range ran from 100 to 1800 cm^{-1}, integration time for a spectrum was set at 20 seconds. Spectral resolution of a microscope 0.07 nm. Spectra were obtained in two points of a sample: in the untreated area and in the area undergone laser cleaning. In Fig. 2 untreated area labeled by number (1) and cleaned area is within the white square.

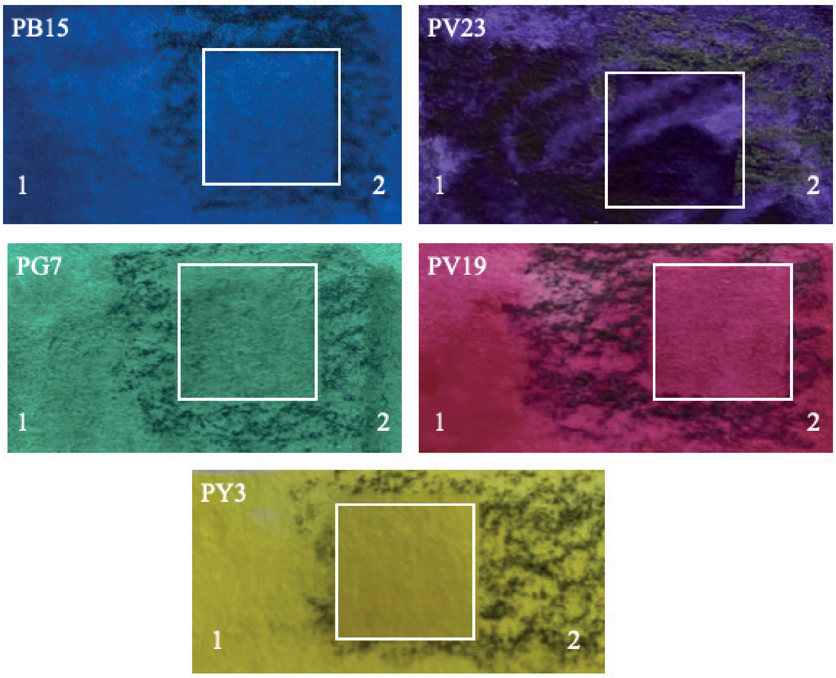

Fig.2. Images of samples after laser cleaning. Cleaned areas are marked with white (10×10 mm). Untreated area of a sample is marked (1) and contaminated area (2)

Summary results of laser cleaning and Raman analysis are presented in Table. It can be seen that cleaning results and spectra analysis correlate. There are no visible changes in the treated areas and there are no changes in a pigment spectrum.

Table

Summary table of laser cleaning results and Raman spectroscopy analysis

Pigment	Class of the chemical substance of a pigment	Laser cleaning result	Raman spectroscopy result	
			Raman wavenumbers (cm^{-1}) before cleaning	Raman wavenumbers (cm^{-1}) after cleaning
PY 3	Azomethine	No damages	Intense peaks at 1619, 1500, 1390, 1338, 1314, 1141; medium peaks at 1678, 1250 and 1198; weak peaks at 1572, 1449, 1282, 1040, 960, 826, 748, 650, 622, 410, 393, 201, 181, 133, 108	Intense peaks at 1618, 1498, 1390, 1341, 1314, 1141; medium peaks at 1685, 1250 and 1198; weak peaks at 1575, 1446, 1295, 1039, 990, 960, 824, 748, 650, 621, 411, 393, 201, 185, 135 and 103
PV 19	Quinacridone	No damages	Intense peaks at 1612 and 1366; medium peaks at 1552, 1519, 1491, 1289, 1250, 1169, 1247, 731; weak peaks at 1433, 1390, 1336, 1117, 1017, 968, 804, 610, 575, 522, 502, 425, 333, 260, 210	Intense peaks at 1613 and 1366; medium peaks at 1553, 1517, 1491, 1287, 1249, 1169, 733; weak peaks at 1428, 1391, 1334, 1121, 1014, 966, 804, 611, 577, 522, 501, 426, 331, 261, 210
PV 23	Dioxazine	No damages	Intense peaks at 1435, 1396, 1349, 1209; medium peaks at 1595, 1260, 1168; weak peaks at 1655, 1533, 1113, 999, 925, 674, 622, 592, 528, 485, 418, 315	Intense peaks at 1435, 1393, 1349, 1209; medium peaks at 1595, 1260, 1168; weak peaks at 1655, 1533, 1113, 999, 925, 674, 622, 592, 528, 485, 418, 315
PB 15	Phthalocyanine	No damages	Intense peaks at 1525, 1338, 746; medium peaks at 1452, 1144, 678; weak peaks at 1637-1578, 1214, 1190, 1010, 953, 879-820, 775, 596, 485, 256, 171	Intense peaks at 1525, 1338, 746; medium peaks at 1452, 1144, 678; weak peaks at 1633-1576, 1216, 1199, 1111, 953, 879-820, 777, 596, 481, 255, 171
PG 7	Phthalocyanine	No damages	Intense peak at 1538, peaks of medium intensity at 1335, 1280, 1206, 772, 741, 685, weak peaks are at 1384, 1077 and 980	Intense peak at 1538, peaks of medium intensity at 1335, 1280, 1206, 772, 741, 685, weak peaks are at 1384, 1077 and 980

Obtained Raman spectra of samples are shown in Fig. 3. The difference in intensity of the spectra before and after cleaning is likely to be due to the unequal distribution of the pigment layer on paper since there is no evidence of any damage done to it during laser treatment.

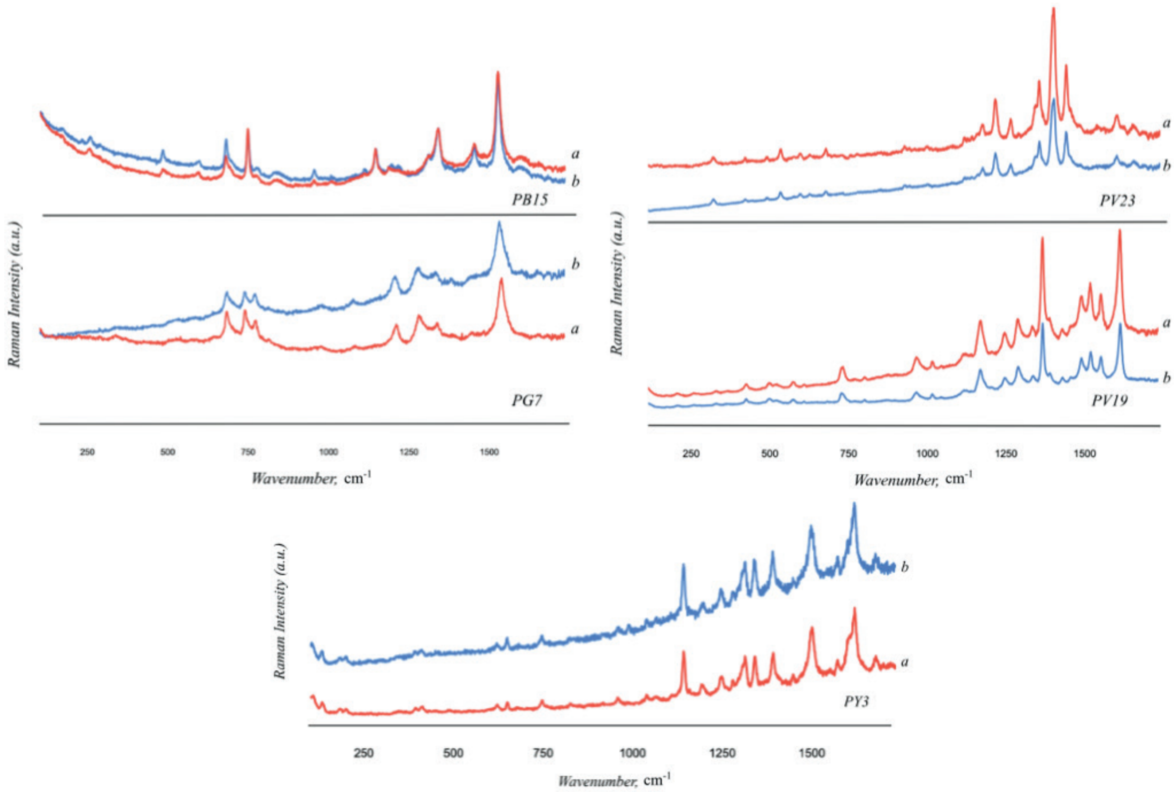

Fig.3. Raman spectra of pigment samples in the untreated area (*a*) and in the laser cleaned area (*b*)

It can be seen that for all of the samples Raman spectra in the untreated area and in the cleaned area do not differ. Main peaks are listed in Table, it can be noted that there is an insignificant shift in the wavenumbers of the corresponding peaks of a sample. Nevertheless, it can be concluded that laser irradiation impact does not lead to any dangerous changes in the pigment layer after removing contaminations.

Conclusion

Samples of organic pigments on paper were successfully cleaned from contaminations by the laser irradiation with the wavelength of 1.06 μm. Investigation of laser treatment results by means of optical microscopy showed no damage to the pigment layer after laser cleaning. A study of the issue using the method of Raman spectroscopy further proved that laser cleaning does not cause damage to the pigment layer as well as chemical transformation in it.

To conclude, it could be presumed that laser cleaning can be safely applied to the restoration of cultural heritage objects containing organic synthetic pigments of paper, such as paintings, book miniatures, documents, etc. Nevertheless, authors will proceed with further investigation on the matter.

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