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Colorimetric study of the post-processing effect due to pulsed laser cleaning of paper

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The effect of pulsed laser radiation applied for surface cleaning of historical paper samples from the 17th c. and also samples of newly made paper was investigated by means of measurement of the colorimetric parameters: lightness L^*, chromaticity C^* and yellowness G. For production of the new paper samples the same method and material (linters cellulose) as used in the past were adopted. An artificial sample contamination was simulated by a mixture of charcoal powder with dust. Surface cleaning was performed by means of a Nd:YAG laser (6 ns pulsewidth) at wavelengths from UV, visible, and near IR ranges (355, 532, and 1064 nm). The laser fluence was selected from the range between the ablation and damage thresholds (0.3–0.9 J/cm^2) of the substrate materials. The absolute differences ΔL^*, ΔC^* and ΔG indicate that the smallest changes of the original color parameters and the most effective surface cleaning occurred at 532 nm. Artificial aging equivalent to periods of 25 and 50 years resulted in negligible changes of the L^* and G values of laser cleaned, laboratory soiled samples, while for non-soiled samples a marked enhancement of the surface darkening with time was observed. Changes in L^*, C^*, and G after the laser treatment at 355 nm and 1064 nm are ascribed to the photochemical damage of the cellulose fibers and to enhanced absorption of the laser radiation by soil particles.

Keywords: laser cleaning of paper, colorimetry.

1. Introduction

Cleaning and conservation of historical documents on paper represent a difficult task for restorers because of the delicate substrate material. Mechanical cleaning methods and tools such as erasers or scalpels, and also chemical ones based on use of water and other solvents are traditional and well established. However, these procedures often lead to irreversible changes of the substrate structure and chemical composition, as well as surface damage, which has been a subject of extensive discussions [1], [2].

Recently, use of laser radiation for cleaning and restoration of historical documents was proposed. This technique allows us to avoid the effects encountered when using the traditional, mechanical and chemical procedures of removal of surface impurities. Moreover, the laser assures a non-contact and solvent-free, well localized action, and also allows a computer control of the process. Its progress can be observed by surface analysis methods and also *in-situ* by means of spectroscopic diagnostic techniques such as laser induced plasma spectroscopy (LIPS) and laser induced fluorescence (LIF) [3]–[6].

It is known that even if physical changes to the structure of the cellulose fibers are not observed immediately after the paper restoration, they can appear due to aging. This effect develops over a long time scale and is difficult to notice with the naked eye. However, it can be effectively investigated by using a standard, artificial aging procedure and measuring the absolute color changes. This was confirmed by several spectrocolorimetric studies and allowed better understanding of the chemical and structural processes involved [7]–[9].

The basic compound of paper is cellulose. It is a polysaccharide of linear polymeric structure consisting of D-glucopyranose units joined into chains by β-glycoside bonds between the I and IV carbon atom. The aging process and degradation of cellulose have various effects on the cellulose fibers. Most commonly, there is a drop in the level of polymerization, demonstrated in changes of the amount of glycosidic residue, reticulation, or creation of ether bonds between the glucopyranosal rings [10].

The laser radiation used for ablative cleaning of the paper surface may have various effects on the structure of the cellulose fibers, depending on the laser interaction parameters such as the wavelength, fluence, pulse length and the total energy deposited. There are two groups of interaction effects, depending on the wavelength and the paper substrate: photochemical reactions caused by UV radiation, which lead to photooxidation, and thermochemical ones due to IR radiation, which are responsible for heating and thermal decomposition of the cellulose. In both cases the destruction of the cellulose bonds occurs [11], [12].

In the course of photodegradation process free radicals and chemically active particles are created and initiate reactions in the area of the cellulose chain. If in addition to cellulose also pigments (*e.g.*, titanium white, zinc white), or glues, such as alunite-resin glue, are present in the substrate, further elements come into play and extend the range of absorption of the paper in the ultraviolet region [13]. It was found that pure cellulose absorbs moderately below 340 nm, whereas the addition of photosensitizers widens the absorption band to the range of 355–400 nm [14].

In the case of thermochemical reaction a destruction of the pyrolytic cellulose and also reaction of the II stage hydroxyl groups with atomic oxygen, with simultaneous opening of the glicosidic rings, occur. Both the photooxidation and the thermochemical reactions lead to similar processes that accompany natural aging. The oxidation and photooxidation reactions produce bonds of the cellulose pigment and cellulose chromophores, which are responsible for the paper yellowing, being a clear sign of aging. Cellulose chromophores develop from hydroxyl, aldehyde and ketone groups.

During natural aging appearance of the aldehyde groups around 2-3 atoms of the carbon hydroxyl groups represents the main reason for the changes in color [15].

The above mentioned processes can result due to laser radiation and depend on the interaction parameters. It can be expected in that case that both photochemical as well as thermochemical processes will occur, and damage to the cellulose fibers is possible, too. In order to investigate these effects it is necessary to select carefully the type and structure of the paper as well as the characteristic of the layers, and also to choose the laser interaction parameters accordingly.

In this work, colorimetric measurements were made to estimate the effect of laser cleaning of the paper surface. The surface cleaning was performed by means of laser ablation on a new, hand-made cellulose paper, produced of pulp with and without additional gelatin glue, and also on paper samples from a 17th century document, which was naturally soiled on the surface and brown-yellowish colored. In the experiment, sample irradiation at three laser wavelengths of 1064 nm, 532 nm, and 355 nm was used. For the reference samples (non-irradiated), and for the irradiated ones the artificial aging was applied. Measurements of colorimetric parameters such as yellowing, absolute changes of color and lightness were performed. The results of measurements are compared and discussed.

2. Experiment

The artificial and original paper samples were selected in order to collect a set of substrate materials representative of historical documents as well as for applications in restoration and conservation works. The following samples were investigated in the experiment:

– sample A: purified cotton cellulose,
– samle B: as sample A, gelatin-sized,
– sample C: as sample B, laboratory soiled,
– sample D: gelatin-sized rag paper, originally soiled, from 1650.

Samples A, B, and C were prepared and supplied by the Pulp and Paper Research Institute, Łódź, Poland. For artificial soiling under laboratory conditions an aqueous suspension of charcoal powder and dust was filtered through pulp sheets.

For the ablative laser cleaning a pulsed Nd:YAG laser (Quantel) characterized by a pulse duration of 6 ns (FWHM), pulse repetition of 20 Hz and a nearly Gaussian intensity distribution was adopted at the laboratory of Institute of Fluid-Flow Machinery, Polish Academy of Sciences (PAN). The laser was operated at wavelengths of 1064 nm, and alternatively also at 532 nm and 355 nm with SHG and THG modules, respectively. The spot diameter in the laser interaction region varied with the wavelength from 1.7 mm to 4.5 mm. The fluences were selected and controlled by means of a beam expander together with a focusing lens (f = 200 mm) and a joulemeter (Gentec). Values of fluence were varied between 0.3 and 0.9 J/cm^2 in order to operate in the range between the ablation and damage thresholds for a given material. In this way the occurrence of the minimal cleaning effect as well as prevention of the substrate

damage were assured. The respective threshold values were obtained prior to the sample cleaning experiments.

The accelerated aging was applied to the laser-processed and also non-processed (reference) samples in a closed climatic chamber at a temperature of 353 K and at a relative humidity (RH) of 65% for a period of 5 or 10 days, which was equivalent to aging of the paper under natural conditions for 25 or 50 years, respectively. The aging procedure was in conformance with the ISO 5630-3:1996 standard [16].

In order to analyze the absolute colour changes due to laser processing a spectrophotometer (L&W Elrepho) operating with illuminant CIE *C* and the CIE standard colorimetric observer 2° in conformance with the CIE $L^*a^*b^*$ Color System was used. The entrance port diameter of the integrating sphere was equal to 8 mm, and the measurements were made at a temperature of 297 K and RH of 50%. The data representative of a given surface area were obtained as averages of a series of individual measurements made at various spot locations without overlapping. For data conversion into the $L^*a^*b^*$ colour space a standard numerical code was used, with $L^* = 116[Y/Y_n]^{1/3} - 16$ for lightness, the value of $\pm\Delta a^*$ for red or green color changes ($a^* = 500\{[X/X_n]^{1/3} - [Y/Y_n]^{1/3}\}$), and $\pm\Delta b^*$ for yellow or blue changes ($b^* = 200\{[Y/Y_n]^{1/3} - [Z/Z_n]^{1/3}\}$), respectively. X_n, Y_n and Z_n are trichromatic components of a perfect diffuser. Besides, two descriptive parameters were calculated: the chromatic enhancement $C^* = [(a^*)^2 + (b^*)^2]^{1/2}$, and the yellowing (ger.: Gelbwert) according to DIN 6167, $G = [(a \cdot X - b \cdot Z)/Y] \cdot 100\%$, with $a = 0.78$ and $b = 0.197$ [17], [18].

An additional inspection of the sample surfaces under investigation was carried out by means of the SEM microscope (Phillips XL 30) operating with an acceleration voltage of 15 kV and typical magnification of 50–57. Prior to scanning the samples were placed in a steam environment at a pressure of 20 Pa in order to achieve measurable values of the electron load current in the range of tens of μA. The use of SEM was preferred due to higher contrast and sharpness depth compared to optical microscopy.

3. Results and discussion

Data obtained from the colorimetric measurements were compared for the three samples A, B, C, and for the historical paper (sample D). Samples A, B, C of the pure, contemporary cotton cellulose were hand-made using traditional methods. For reference one of the currently produced samples (A) was made without the usual addition of gelatin glue, and another one (C) was artificially soiled. The substrate of the hand-made, originally soiled sample D from the 17th c. contained the gelatin glue typically used in the past for production of paper.

3.1. Sample A

The sample response to laser irradiation at wavelengths of 1064, 532 and 355 nm, and to aging can be observed via changes of the absolute values of parameters L^*, C^*

and *G*, and also compared with respective values measured for the reference sample (see Fig. 1).

The laser irradiation did not cause a noticeable change of the parameter L^* compared to the value measured for the untreated sample (see Fig. 1**a**). After the 5-days' aging the lightness of the laser treated samples decreased by about $\Delta L^* = 1.6$. The effect seemed to stabilize due to prolonged aging up to 10 days. The total decrease

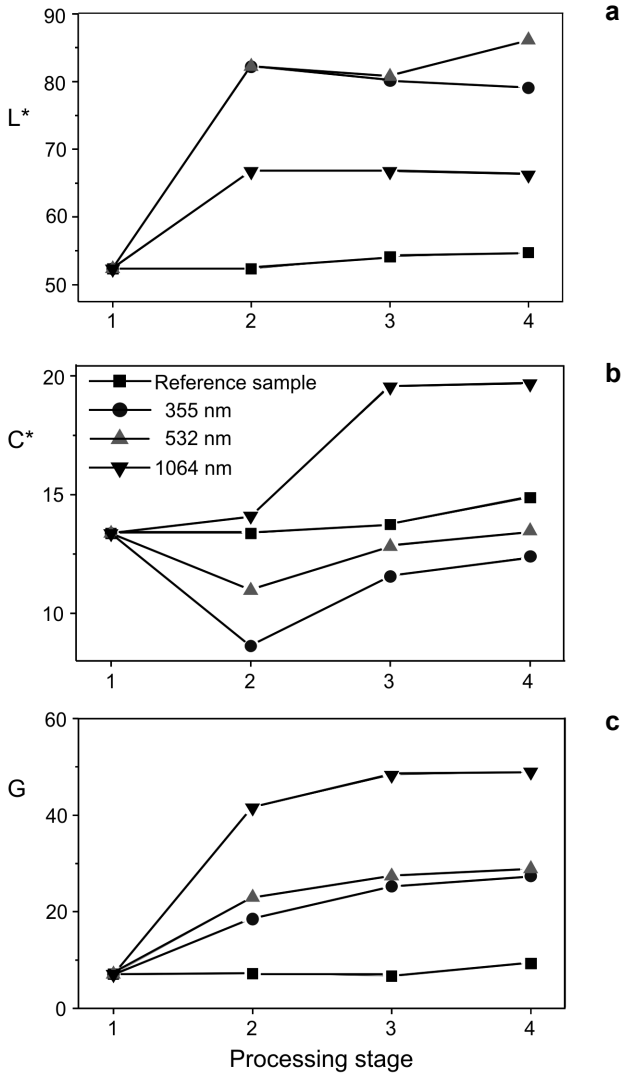

Fig. 1. Sample of a modern cotton cellulose paper; dependence of the colorimetric parameters: lightness L^* (**a**), chromaticity C^* (**b**), and yellowness G (**c**) on the processing stages: 1 – fresh sample; 2 – after pulsed laser irradiation at 355, 532 or 1064 nm (Nd: YAG laser, pulsewidth 6 ns); 3 – after artificial aging during 5 days (equivalent of 25 years under natural conditions); 4 – after prolonged aging of 10 days (50 years).

of $\Delta L^* = 2.3$ was comparable with that observed for the reference sample and lied within the experimental error.

On the contrary, noticeable changes in chromaticity and yellowness were observed. For all irradiation wavelengths an increase in C^* by more than 35% was accompanied by a similar change in yellowness G, compared to the reference sample, Fig. 1**b**, **c**. Aging enhanced both effects. The observations allow us to conclude that the total color change corresponds mostly to yellowing. The strongest dependence corresponding to changes of $\Delta C^* = 2.7$ and $\Delta G = 5.0$ was measured for samples irradiated in the UV at 355 nm and a little bit lower values were obtained for the 532 nm irradiation, whereas the reference sample showed the lowest increase of both values after prolonged aging, *e.g.*, $\Delta C^* = 1.4$ and $\Delta G = 3.1$. It can also be concluded that for samples irradiated at wavelengths shorter than 1064 nm aging was faster than for the reference sample.

3.2. Sample B

For paper samples B prepared from the same cellulose substrate, but sized on the surface with gelatin glue laser treatment at 355 nm and 532 nm resulted in a larger decrease of lightness ΔL^* (Fig. 2). The change in color ΔC^* was greater than that of sample A. Also the level of yellowing of the samples treated previously at those wavelengths grew markedly from 7.2 to 15.9, and from 7.2 to 15.1 after aging. The value of ΔG was higher than that measured for samples not treated by laser prior to aging (growth of G from 7.2 to 9.4), as well as ΔG for samples irradiated at the longest wavelength applied, *i.e.*, 1064 nm.

Again, similarly to the previous case, the above indicates that for the samples processed by the ultraviolet and visible laser radiation at 355 nm and 532 nm, respectively, the accelerated processes of cellulose aging occurred as a result of photooxidation reactions which led to formation of pigmented cellulose chromophores. Undoubtedly, the effect observed was additionally influenced by the presence of gelatin glue, which widens the absorption range of the paper substrate, since pure cellulose is a very poor absorber of radiation longer than 340 nm.

3.3. Sample C

For sample C made of the same kind of material as sample B, *i.e.*, gelatin-sized cotton linters cellulose, and laboratory soiled with a layer of charcoal powder dust, the significant changes were recorded after laser irradiation. Results of measurements of the parameters L^*, C^* and G are shown in Fig. 3. The initial value of surface lightness was lower by about 40% than that of the non-contaminated sample. Again, the most impressive effect appeared due to laser cleaning at 355 nm and 532 nm. This was demonstrated by a drastic increase of the surface lightness after irradiation – the value of ΔL^* grew by nearly 60%. The effect observed for the laser cleaning at 1064 nm was weaker. These results confirm the removal of surface contaminants and show that the most efficient cleaning occurs at shorter wavelengths. In both cases the first aging cycle as well as the prolonged one affected the measured values only slightly.

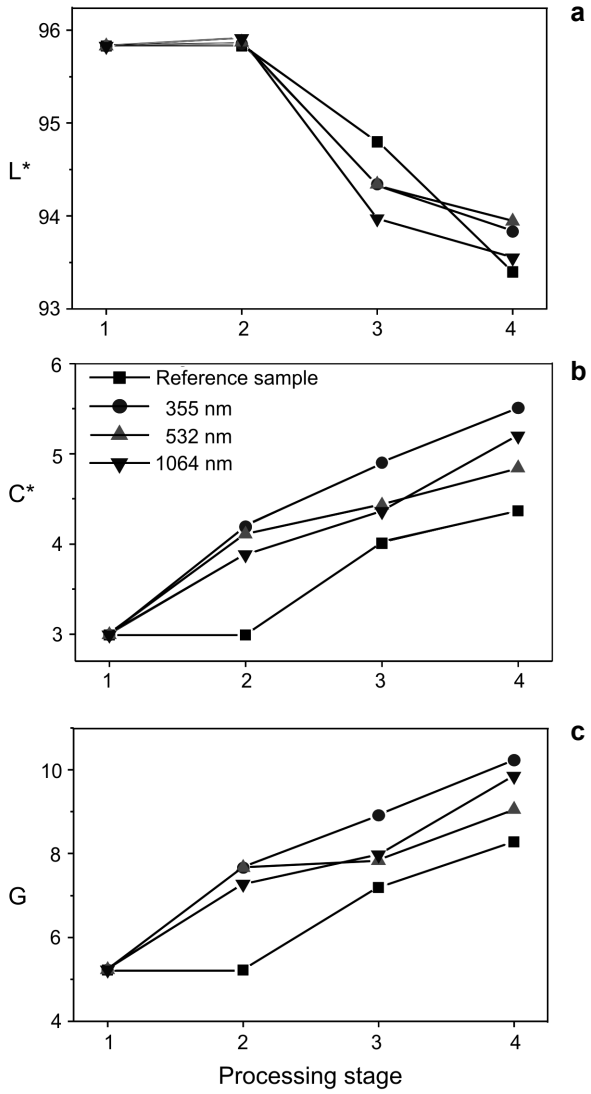

Fig. 2. Same as Fig. 1, but for the modern, gelatine-sized cotton cellulose sample paper.

For type C samples irradiated at both 355 nm and 532 nm the changes in chromaticity were opposite to those for the previously discussed samples A and B. As chromaticity depends on the coordinates a^* and b^*, the observed negative sign corresponds most probably to bleaching of the surface during removal of the contamination. Interestingly, these ΔC^* values were almost completely recovered after prolonged aging and reached values close to those measured for the non-processed sample, see Fig. 3**b**.

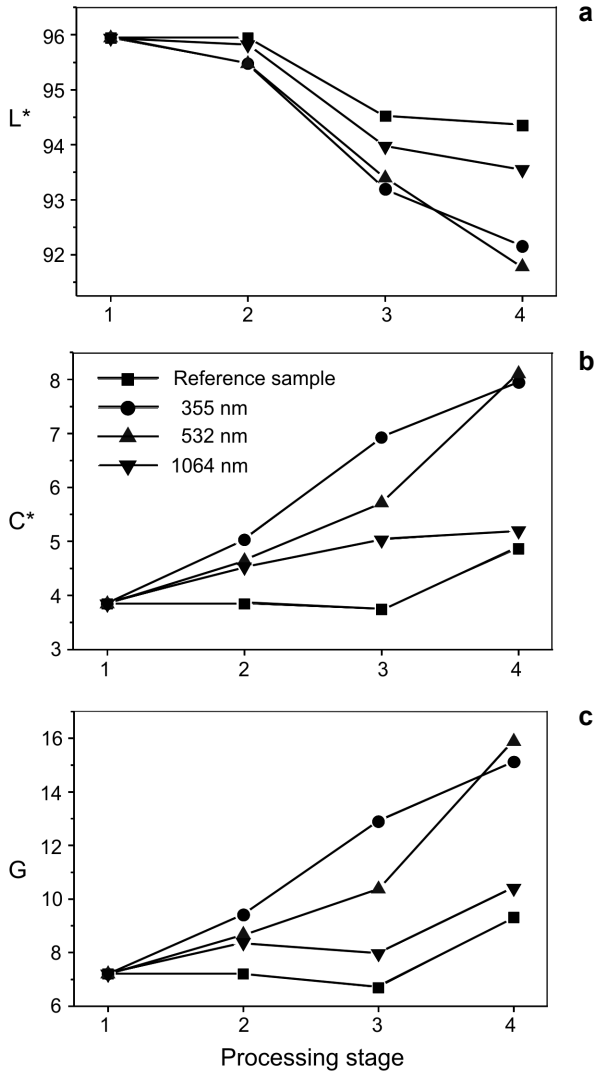

Fig. 3. Same as Fig. 2, but for the laboratory soiled surface of the gelatine-sized cotton cellulose sample.

The cleaning effect of the 1064 nm laser irradiation, as observed through the change of the chromatic coordinate C^*, was relatively small ($\Delta C^* = 0.8$). This value increased to $\Delta C^* = 6.3$ after the first aging cycle and remained almost unchanged after prolonged aging. The positive sign accords with the growth of the yellowing parameter G which can be observed in Fig. 3**c**. It is worth mentioning that the contaminated sample *C* revealed a large, wavelength dependent increase of yellowing, and the largest ΔG value of 34.5 was measured after laser cleaning at 1064 nm. The irradiation at 355 nm and 532 nm resulted in changes of ΔG equal to 11.5 and 15.9, respectively.

The yellowing effect became slightly enhanced after the first aging period, while prolonged aging practically did not influence the measured values.

The results shown in Fig. 3 allow one to conclude on the influence of the artificial surface contamination. The charcoal powder and dust are materials that absorb a great part of the laser radiation energy [8]. During the ablation process the removal of molecules from the substrate surface occurs and the ablated dust contributes to the gas ionization and ignition of the plasma over the surface. This plasma emits radiation in a wide range from far UV into IR. This enhances the energy coupling between the laser beam and the irradiated substrate and in this way contributes to photochemical reactions, which in turn lead to the observed yellowing.

Further, it should be taken into account that there is a transfer of energy from the plasma to the substrate interior, resulting mainly in convection and electronic conduction of heat. This energy transfer occurs during laser interaction with the sample and leads to the yellowing of the sample surface. Thermally stimulated processes lead to production of pigmented chromophores of the cellulose. In this case, the observed result of the degradation process is due to thermochemical processes. These are effectively initiated by the 1064 nm laser irradiation and this result is in agreement with earlier experiments [9].

3.4. Sample D

As an example of a historical, hand-made paper of rags sized with gelatin glue and covered with natural dirt some fragments originating from a 17th c. book were investigated. The paper surface was originally strongly yellowed due to the gelatin and flour glue stains. Also numerous traces of microbiological attack, resulting in light purple spots, were present at numerous locations. The entire surface was covered with a delicate layer of pressed dust penetrating partially the substrate.

The historical paper samples were laser-cleaned using similar procedure as applied for the model samples. Three wavelengths of laser radiation: 1064, 532 and 355 nm were used in the experiment. Results of measurements are shown in Fig. 4.

The greatest change of L^* was recorded for the surface cleaned with the 532 nm laser, and the lightness increased by 11 units relative to the measurement made prior to cleaning (see Fig. 4**a**). A similar increase by approximately 9 units relative to the pre-cleaning state was due to 1064 nm, and the lowest one corresponded to the use of 355 nm laser. In the last case the artificial aging resulted in surface darkening, *i.e.*, the L^* value close to that measured prior to cleaning was recorded again. On the contrary, for the untreated sample a total increase of L^* by 10.2 units after prolonged aging was observed.

An evident change of coordinate C^* was observed under the influence of the 1064 nm radiation, especially after 10 days of aging process, Fig. 4**b**. A similar effect of laser cleaning was observed for irradiation at 532 nm. However, in that case the value of C^* almost recovered to the reference one after 10 days of aging.

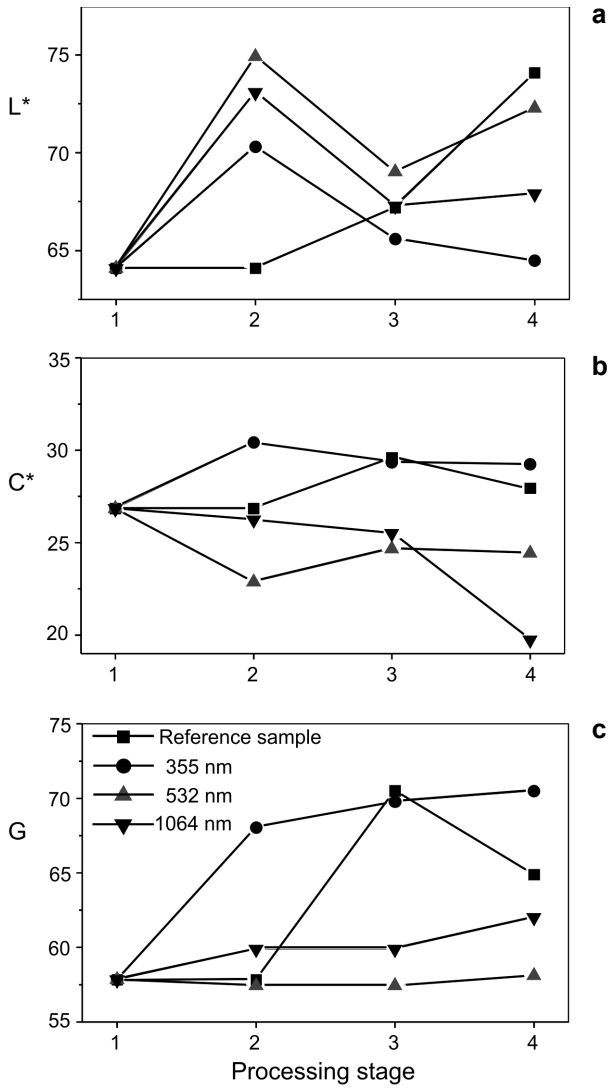

Fig. 4. Same as Fig. 1, but for the historical (17th c.), gelatine-sized rag paper with a surface naturally yellowed, covered by a layer of dust, and also partially contaminated by stains of an organic glue.

The influence of irradiation at 355 nm led to the largest yellowing of $\Delta G = 13$ units, while for the other processing wavelengths the parameter G increased only moderately (1064 nm) to a level comparable with that of the untreated sample, or even negligibly (532 nm). After prolonged aging a slight increase of G by about 1.7 units was observed for samples cleaned at 355 nm and 1064 nm (see Fig. 4**c**). Results reported here agree with data obtained for the paper samples laser-processed under similar conditions and reported by other authors [15].

It is worth mentioning that the yellowing effect due to laser radiation has been discussed extensively in the recent literature. The experimental results published indicate that irreversible changes of the paper chemical composition, which result from the exposure of the surface to the laser radiation, are the most probable reason of yellowing. In particular, the UV photons of energy of 3.5 eV, corresponding to the 355 nm laser wavelength initiate photooxidation of the cellulose. Other organic compounds and particles present in the surface layer can act as photosensitizers, thus enhancing this process [19].

The additionally performed SEM inspection of the sample surface layers revealed no damage to the cellulose fibers for all samples under investigation. However, for sample B (cellulose paper sized with gelatin glue) a partial removal of the gelatin from the surface of the fibers present in the most external substrate layer exposed to the laser beam. In the case of soiled samples C the irregular, structural networking together with empty intersections typically observed for non-contaminated, cellulose-based substrates was partially recovered by the laser treatment. The remaining dirt particles were only observed at greater depths from the substrate surface. A similar effect with no damage to the napped surface of the fibres was observed for the naturally soiled, historical paper samples. Results of the surface analysis will be discussed in detail in a forthcoming paper.

4. Conclusions

For the hand-made, historical and also modern paper samples cleaned by means of the pulsed laser ablation at wavelengths of 355, 532 and 1064 nm and exposed to the artificial aging the colorimetric studies of the post-processing effect, and also SEM surface inspection were performed. Changes due to processing were dependent on the laser wavelength applied, duration of aging, presence of an additive (gelatin glue), and also chemical composition of the surface contamination.

Damage to the substrate structure and cellulose fibers was not observed. This was assured by the choice of laser fluence values from the range of 0.3–0.9 J/cm^2, corresponding to the ablation and damage thresholds, respectively, for the paper substrates under investigation.

For samples produced contemporarily with the gelatine glue additive the increased yellowing of the paper surface after laser cleaning (by 34.5 units compared to the reference value) was revealed, since this additive increased the range of absorption of the paper and the effect was observed for irradiation at 1064 nm. A similar effect was observed for historical samples with remains of organic glue. They demonstrated the strongest yellowing of the surface when exposed to UV radiation at 355 nm.

The pure cellulose paper sample yellowed, however, under the influence of 355 nm radiation, which was not reported in the literature yet. The probable reason for this effect may originate in the paper production method, where water is used for the

molding process. In particular, the elements contained in the water, *e.g.*, the residual content of iron remains in the paper, oxidize with time and contribute to the yellowing.

Samples of paper artificially soiled with the charcoal powder dust were effectively cleaned at all laser wavelengths applied. The strongest surface yellowing was measured for 1064 nm radiation. This was ascribed to the thermally stimulated processes, which lead to the cellulose decomposition due to material ablation induced at the longest wavelength applied.

To sum up, it was found that both the UV radiation at 355 nm and the near IR at 1064 nm had the least beneficial effect on the paper. This is due to the photochemical damage of the cellulose fibers in the first and the enhanced absorption of the laser radiation by the soil particles in the second case, respectively. It can be concluded, in agreement with the literature, that the laser cleaning of hand-made paper by means of pulsed laser radiation at 532 nm represents the preferred solution [5], [9], [20].

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