

Original article

Chromatic alterations induced by preservation treatments on paper: The case of Ag-functionalized nanocrystalline cellulose

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ABSTRACT

Artifacts made of paper (books, manuscripts, and other documents) represent a valuable part of cultural heritage. They are particularly fragile compared to other objects due to the multiple physical, chemical, and biological factors able to degrade the paper basic constituents, i.e., cellulose, hemicellulose, and lignin. Moreover, hemicellulose and lignin represent an ideal growth substrate for proliferation of microorganisms and fungi. Regarding this latter aspect, researchers have experimented several methods to prevent and control fungal development on paper documents, but, sometimes, these treatments present themselves collateral effects, being responsible for the variation of paper chromatic appearance. Recently, a suspension made of crystalline nanocellulose with the adding of silver nanoparticles was tested as antifungal method. Actually, the crystalline nanocellulose has been already experimented as starting material for preservation and consolidation treatments on paper, but the adding of silver nanoparticles also provided the suspension with a broad-spectrum antimicrobial action. The aim of the research is to investigate the potential effects of the so-prepared suspension in modifying the optical characteristics of the treated paper. To do that, two different types of paper were analyzed: Whatman and Amalfi. Squared paper samples (3 cm side) were prepared, subjected to artificial ageing, and then inoculated with nanocrystalline cellulose (CNC) and with Ag-functionalized nanocrystalline cellulose (CNC/Ag). Spectral reflectance measurements were performed on the samples, and the CIE L*a*b* chromatic coordinates under D65 were obtained. Comparing the measurements referred to samples treated with CNC and those treated with CNC/Ag, it has been possible to describe the effects due to the presence of silver in the suspension. Obtained results demonstrate that the chromatic variations of the samples treated with CNC/Ag are higher than those referred to the samples treated with CNC. Specifically, the chromatic variations ΔE^*_{D65} range from 0.2 to 10.5 for the Whatman paper and from 0.3 to 5.1 for the Amalfi one. Moreover, it has been shown that the two types of paper react in a different way to the treatments and that the alterations are not homogenous on the entire paper sample, but more evident in the inoculation region in which pinkish spots arise. Finally, it has been proved that the alterations are not stable over time, but, especially for Whatman paper, they become more evident after one month and half from the preparation of the samples.

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Introduction

A great part of the human history is registered in books or other types of documents made of paper-based materials with finite life, that are slowly but irreversibly disappearing [1,2]. Indeed, paper inevitably degrades over time, due to several factors, mainly

humidity, pollution, oxygen or light. Deterioration of paper due to acidity derived from absorption of pollutants that can promote acidic hydrolysis of cellulose fibers is also observed [3]. Protective and non-invasive treatments are required to stop this natural loss [4,5].

The degradation of cellulose, hemicellulose and lignin is due to physical, chemical, and biological factors. Physical and chemical factors include heat, humidity, radiation, acidity derived from absorption of atmospheric pollutants, and oxidation of additives used during the papermaking process, acting as catalysts for cel-

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lulose acidic hydrolysis [3] and leading to the decrease of paper mechanical strength. Moreover, the organic components of paper represent an ideal growth substrate for microorganisms responsible of biological degradation of paper [6]. In general, a bacterial predominance (mainly Gram Positive) has been observed on paper, photographic paper, and glass slides, but fungi can be very harmful as well, being able to thrive also at lower rates of relative humidity [7]. Fungi can also attack other organic materials as parchment, inks, and many types of glues and fillers [8] and produce pigments [9] that, once released in the surrounding environment, contribute to foxing processes [10].

Different treatments regarding the prevention and control of fungal development on paper documents and their recovery have been assessed [11–16]. The most common preventive measures against fungal infestations deal with control of environmental conditions, such as relative humidity and temperature, in storage and display rooms, together with the regular inspection of paper for signs of visible fungal growth. Measuring RH and temperature in archives and libraries can provide a general indication of the risk of microbial biodegradation of paper objects. However, these measurements are usually made in specific areas of the rooms, thus neglecting the conditions of each individual corner of the monitored room. Local microclimates with very high water activity (a_w) can result from inadequate ventilation and irregular surface temperatures in a room with an otherwise low RH [8]. By keeping the a_w value of the paper below 0.60 and the temperature below 20 °C, the development of fungi can be avoided with good air circulation [17]. A common practice to reduce RH and a_w in the paper is to use dehumidifiers. However, paper artifacts are often books with stacked pages and closed by an outer cover or are placed on shelves or stored in sealed frames. Under these conditions, there is a constant but very slow diffusion of moisture from the outside into the paper volume due to a self-buffering effect, so the paper's response to thermo-hygrometric changes is much slower [18]. Moreover, if paper-based materials are already colonized by biofilm, the latter facilitates the survival of fungi even in a low RH and a_w environmental conditions [19]. The only control of indoor environmental conditions is not effective to counteract the development of fungi on paper-based materials. Therefore, it is important to use an integrated approach using both environmental control and cleaning and/or preventive treatments of paper-based materials. Another of the most used practices to stop fungal development is the dry surface cleaning on affected paper objects [20–22]. Numerous chemical treatments have been also attempted; the effectiveness of mitigation methods strongly depends on the fungal strain responsible for the degradation of the paper, its stage of development and whether it is part of a biofilm [23]. Thus, the antifungal or fungistatic chemical compounds applied as restorative methods are chosen on a case-by-case approach, adopting a multidisciplinary research strategy. Enzymatic mixtures based on lipase and proteases gave promising results, but a drawback of this treatment is due to the dark coloration of the enzymatic solution, which is difficult to remove completely, except after numerous aqueous washes, not feasible on paper media. Fumigations of a mixture of methyl bromide and ethanol, or 70% ethanol have been applied on fungal communities growing on paper. The 70% water solution of ethanol is safer and gave promising results against different bacteria and fungi, particularly when the paper was immersed in the ethanol solution. However, this procedure caused dehydration of cellulose, and also a mild treatment based on a 45% ethanol solution induced a decrease of tear resistance of paper and caused significant color alterations [24,25]. Vaporized hydrogen peroxide has also been applied on paper documents, even though it is an oxidizing agent, and its use could lead to the damage of paper [25]. Treatments based on essential oils extracted from higher plants were also proposed to control the

growth of microbial community on paper, by spreading the oils directly where paper staining was visible by naked eye. Also in this case, the dark color of the oil produced an unwanted pigmentation of paper [26]. Thymol fumigation treatments have been tested giving limited antifungal effect and causing paper discoloration [27].

Recently a suspension made of crystalline nanocellulose with the adding of silver nanoparticles has been tested as treatment to control fungal development on paper. Nanocrystalline cellulose (CNC) has been already used as starting material for paper preservation and consolidation due to its excellent properties such as high elastic modulus, optical transparency, low thermal expansion coefficient, biocompatibility, biodegradability, and low toxicity. The adding of silver nanoparticles to the CNC provides the suspension with an antifungal action, since silver has broad-spectrum antimicrobial activity and high toxicity to different type of microorganisms [28–31].

One of the most common drawbacks of the above cited treatments is that they all seem potentially interfere with the optical properties of paper, and usually there is a lack of thorough testing in log-term. In [28] this topic was investigated. The authors prepared suspensions of CNC by sulfuric acid hydrolysis using wastepaper as cellulose source (CNC_{WP}) and of CNC from cotton linter (CNC_{CL}). Then CNCs were mixed with silver nanoparticles (CNC/Ag), the treatments were applied on samples made of Whatman paper and the color difference ΔE^*_{D65} was calculated for 7 regions of the samples before and after the treatments. The authors found that ΔE^* for both CNCs is 0.8 ± 0.1 , whereas the addition of Ag nanoparticles determined higher values ($\Delta E^*=1.8 \pm 0.4$ for CNC_{CL}/Ag and 1.5 ± 0.3 for CNC_{WP}/Ag).

Research aim

The present work was planned to deepen the topic and better evaluate the effects of the CNC/Ag treatment on the paper. Specifically, the novelty consists in:

- Proposing a detailed procedure for testing the chromatic alterations on paper that could be applied also for treatments other than the CNC/Ag: The study analyses the effects determined by the CNC/Ag in terms of variations of spectral reflectance, total reflectance and L*a*b* chromatic coordinates under D65, investigating which color attribute (lightness, hue or chroma) is mainly affected by the treatment and deeply describing the phenomenon.
- Extending the analysis to different types of papers: Whatman and Amalfi papers were used for the experiment, to understand if the effects of the substances are the same on different materials.
- Analyzing the effects of the treatment over time: The chromatic coordinates of the paper samples treated with CNC/Ag were monitored over time to observe if they maintain stable or not.

Materials and methods

The experiment consisted of the three phases.

Preparation of the samples to analyze

Two different types of paper were selected, and their morphological characteristics were determined by using a Leitz Ortholux metallographic microscope, equipped with a ultrapack objective, at a magnification of 6.5×. They are:

- Whatman #1 paper (hereinafter called WP) that is frequently used in paper conservation and biodeterioration research, allowing easy comparisons with results of other studies. It is made of 100% pure cotton linter, characterized by a compact structure and high fibre elongation,

• Amalfi paper (hereinafter called AP) is a well-known kind of fine paper, produced in the homonymous town in Campania region (southern Italy) since the XIII century. The quality watermark made it much more valuable than the other papers and that is why it was commonly used for official documents. Currently, Amalfi paper is made using cellulose and cotton fiber and the paper making process is still the same as in the past. It is used for Vatican City State official documents, for high-end literary publication and for wedding invitations [32].

For each type of paper four different square samples (3 cm side) were cut. One of them was used as reference control, to study papers' basic chromatic characteristics; the other three were subjected to accelerated ageing. Then, two of the artificial aged samples were furtherly treated, the former with CNC, and the latter with CNC/Ag. The CNC and the CNC/Ag were inoculated on the aged samples, since in practical applications they are used to protect aged paper.

From now on, the samples are named by means of a code made of letters. The first group of letters indicates the type of paper (WP or AP) and the second one the considered sample: "Ctrl" is used for the control one, "AA" for the artificial aged one, "CNC" indicates the use of nanocrystalline cellulose and "CNC/Ag" the use of Ag-functionalized nanocrystalline cellulose. For example, the AP_AA_CNC/Ag is the Amalfi paper sample treated with Ag-functionalized nanocrystalline cellulose after artificial ageing process.

In total 8 samples were studied:

- 2 control paper samples (WP_Ctrl and AP_Ctrl),
- 2 artificial aged paper samples (WP_AA and AP_AA),
- 2 artificial aged paper samples, treated with CNC (WP_AA_CNC and AP_AA_CNC),
- 2 artificial aged paper samples, treated with CNC/Ag (WP_AA_CNC/Ag and AP_AA_CNC/Ag).

The selection of the samples was driven by the following reasoning. The final goal of the research is to investigate the chromatic alterations due to the addition of Ag in CNC. However, some alterations could be determined by the ageing process itself or by the CNC. Thus, the comparison between the artificial aged samples and the control ones allowed to quantify the chromatic differences due to the ageing. Then the comparison of the samples treated with CNC and CNC/Ag with the aged ones allowed to quantify the differences due to the inoculation of both suspensions. Finally, the comparison between the samples treated with CNC and those treated with CNC/Ag gave an idea about the effect due to the Ag addition, reaching the final goal.

In more detail, the samples were prepared as it follows. As concerns the accelerated ageing, the samples of WP and AP were put in a temperature and relative humidity chamber (DESPATCH LEA 1–69) at 80 °C and 65% of relative humidity following the ISO 5630–3 1996 standard [33] for 30 days. They were aged in stacked configuration according to Boruvka [34] to reproduce the stacking of pages in books to obtain the greatest amount of ageing in the relatively short time of 30 days, chosen for the experiment.

The treatments based on nanocrystalline cellulose and Ag nanoparticles were synthesized according to Bergamonti et al. (2020) [28]. Cotton linters were hydrolyzed by sulfuric acid (64%) at 60 °C for 40 min. The obtained product (CNC) was repeatedly washed, resuspended by centrifugation and purified in dialysis tube for one week up to neutral pH. 100 ml of suspension of silver nanoparticles (1000 ppm) were obtained by chemical reduction in water of a solution of AgNO₃ with NaBH₄ (Ag/NaBH₄ ratio 5/1) in presence of PVA 1% (ratio Ag/PVA 100/1 v/v) as stabilizing agent. CNC suspension (1% w/v) was mixed with the colloidal suspension of silver NPs (1000 ppm), with volume ratio 9/1 to obtain final suspensions 100 ppm (Ag).

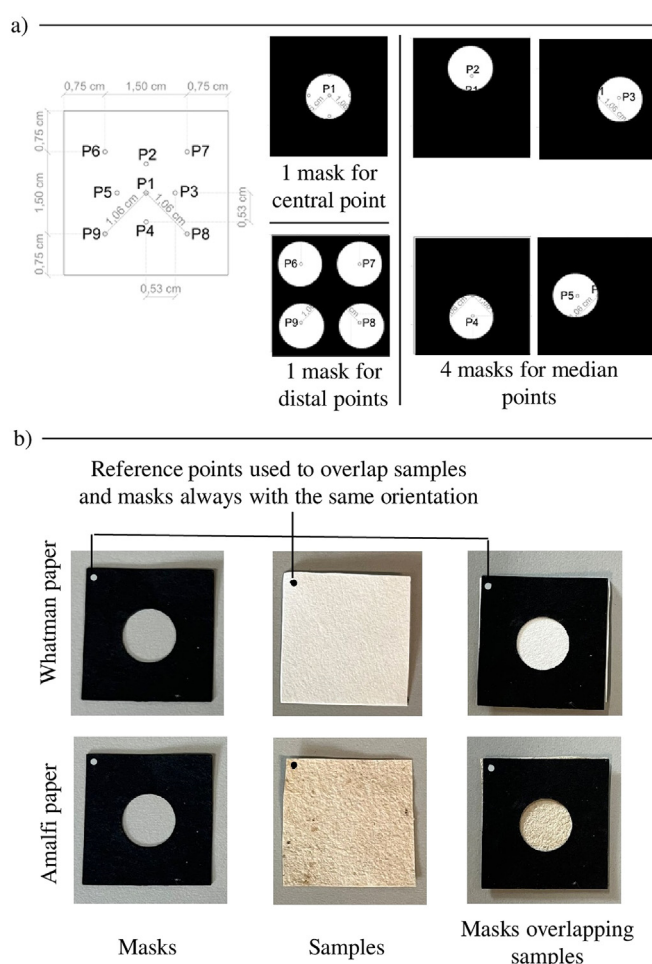


Fig. 1. Scheme of the measurement grid and of the masks (a) and photo of the masks and samples (b).

Once the suspensions were prepared, artificial aged WP and AP samples were sterilized in autoclave at 120 °C for 20 min, dried in an oven to remove the excess of water after the sterilization cycle and displaced in Petri glass dishes. Under laminar flow hood, 1 ml of CNC and CNC/Ag suspensions was inoculated on Whatman and Amalfi paper samples in 3 passes with an interval of 20 min from each other.

Spectral reflectance measurements

Spectral reflectance measurements were performed with a Konica Minolta CM-2600d spectrophotometer.

Preliminary tests showed that, over time, the inoculum of CNC/Ag suspension on aged paper samples, showed chromatic variations that could be perceived by the naked eye. Thus, the measurements of the spectral reflectance were performed twice: immediately after the inoculum of the CNC/Ag suspension on aged WP and aged AP (1st measurement campaign) and 1 month and half later from the inoculum (2nd measurement campaign) on the same aged and treated paper samples. All the other samples were measured only during the 2nd campaign.

Measurements were repeated for 9 different points (see Fig. 1a). The central point coincided with the one in which the suspensions were inoculated. The other eight were considered to verify if the effects of the treatments were homogeneous. Specifically, four points were placed in a median region (0.53 cm from the center),

in shape of a cross, the other four in a distal region (1.06 cm from the center), in shape of a “X”.

To correctly point the instrument towards the points, the following procedure was adopted. 6 patches in black cardboard of the same shape of the samples were prepared. They were punched to obtain circle holes corresponding to the 9 points and with diameter (1 cm) equal to that of the aperture hole of the instrument, producing the masks represented in Fig. 1a. To perform the measurements, each mask was overlapped to the sample (see Fig. 1b) and then the spectrophotometer was located such that its aperture hole coincided with the holes in the masks. It must be noticed that the spectrophotometer measures the reflectance of an area corresponding to its circular aperture hole. Consequently, due to the small dimensions of the samples, part of the measured areas corresponding to each one of the 9 points overlapped. For example, part of the area around P2 coincides with the measurement area around P1, P6 and P7. However, as shown in the results, despite this limit, the used method was effective in highlighting the differences among the 9 areas.

The papers were not completely opaque, but they transmitted part of the incident radiation. So, when performing the measurements, the samples were located on an opaque black almost non-reflective base. In this way it was reduced the risk to measure light reflected by the base on which the paper samples were positioned and transmitted by the paper itself. To guarantee the repeatability of the experiment, the NCS S9000N color target was used as base. Black color was selected for the following reason. The reflected light measured by the instrument, would have been the sum of the light reflected by the paper sample and that reflected by the background and then transmitted by the paper. So, the lower the component reflected by the background, the more precise the measurements. For example, using a white background, it would have been impossible to identify the incidence of the background in affecting measurements. Consequently, an almost completely absorbent background was used.

Post-processing of the measured data

The following data were obtained from the measurements:

- spectral reflectance values in SCI (specular component included) mode,
- corresponding total reflectance under D65 illuminant (ρ_{D65}),
- corresponding CIE L*a*b* chromatic coordinates under D65 illuminant.

Then the following analyses were performed:

1. To describe the differences between WP and AP, WP_Ctrl and AP_Ctrl, were compared one each other.
2. To quantify the variations due to the ageing process, WP_AA and AP_AA were compared with the WP_Ctrl and AP_Ctrl in the following way.

On one hand, as regards the spectral reflectance, for each wavelength λ the average value $\rho_{\lambda,av}$ was calculated as:

$$\rho_{\lambda,av} = \frac{1}{n} \sum_{i=1}^n \rho_{\lambda,i}$$

Where i corresponds to the measurement points and runs from 1 to 9. In this way an average spectrum was obtained. Then, for each point i, the root-mean-square deviation (RMSD_i) was calculated comparing each measured spectrum with the average one, as:

$$RMSD_i = \sqrt{\frac{\sum_{\lambda=1}^m (\rho_{\lambda} - \rho_{\lambda,av})^2}{m}}$$

where ρ_{λ} is the measured spectral reflectance value at each wavelength λ , and λ varies in the range 360 nm to 740 nm with 10 nm step.

The measured spectral reflectance curve for which the RMSDi was minimum was chosen as reference and then all the others were compared with it.

On the other hand, as concerns the differences in the total reflectance ($\Delta\rho_{D65}$) and in the chromatic coordinates (ΔL^*_{D65} , Δh^*_{D65} , ΔC^*_{D65} and ΔE^*_{D65}) the following procedure was used. Considering that, as stated before, the chosen papers were not homogeneous, comparing each point of the aged samples with the corresponding one on the control samples would have given partial information, not representative of the actual differences. For this reason, each point of the aged samples was compared with all the nine points of the Ctrl one obtaining 9 different values of $\Delta\rho_{D65}$, ΔE^*_{D65} , ΔL^*_{D65} , Δh^*_{D65} and ΔC^*_{D65} .

1. To analyze the differences due to the suspensions' addition, the aged and treated samples were compared with the aged ones. The comparison was conducted in the same way described at point 2, but in this case the references for comparisons were not the WP_Ctrl and AP_Ctrl samples, but the aged ones. In this phase, by comparing the results obtained for WP_AA_CNC and AP_AA_CNC, with those obtained for WP_AA_CNC/Ag and AP_AA_CNC/Ag respectively, it was also possible to infer the effects of the Ag addition in the suspension.
2. Finally, to monitor the chromatic variations over time on WP_AA_CNC/Ag and AP_AA_CNC/Ag, the results related to the first campaign were compared with those of the second one. In this case, since the same sample was measured twice, for each point reflectance and chromatic differences were calculated by simply comparing the two measurements obtained in the two different moments.

The analysis method is summarized in Fig. 2.

A specification about the analysis of the obtained results is needed. Given papers' non-homogeneity, it was necessary to understand if the variations obtained as described at point 2 and 3 were due to the applied treatments or to the intrinsic non-homogeneity of the paper. For this purpose, the differences in total reflectance and chromatic coordinates among all the points belonging to each control sample were quantified. These differences, being characteristic of the specific type of paper were named typical and indicated with the “typ” subscript ($\Delta\rho_{typ}$ -typical total reflectance difference-, ΔL^*_{typ} -typical lightness difference-, Δh^*_{typ} -typical hue difference-, ΔC^*_{typ} -typical chroma difference-). Generically indicating each difference as Δx_{typ} , to calculate the corresponding values, each point was compared with the others belonging to the same control sample, building a matrix as it follows.

$$\begin{bmatrix} \Delta x_{typ,1-1} = x_{p1} - x_{p1} & \cdots & \Delta x_{typ,9-1} = x_{p9} - x_{p1} \\ \vdots & \ddots & \vdots \\ \Delta x_{typ,1-9} = x_{p1} - x_{p9} & \cdots & \Delta x_{typ,9-9} = x_{p9} - x_{p9} \end{bmatrix}$$

The matrix is an antisymmetric one, having as minimum $\Delta x_{typ,min}$ and maximum $\Delta x_{typ,max}$ values two opposite numbers. A similar procedure was applied to calculate ΔE_{typ} values. In this case, the obtained matrix was a symmetric one with all positive elements and null diagonal.

For example, for WP it was obtained that $\Delta\rho_{typ,min}$ was -1.0% and the $\Delta\rho_{typ,max}$ was 1.0%. Thus, it can be said that the typical reflectance difference was comprised between -1.0% and 1.0%. The $\Delta E_{typ,max}$ was equal to 0.5 and so it can be said that the typical chromatic differences were at most equal to 0.5.

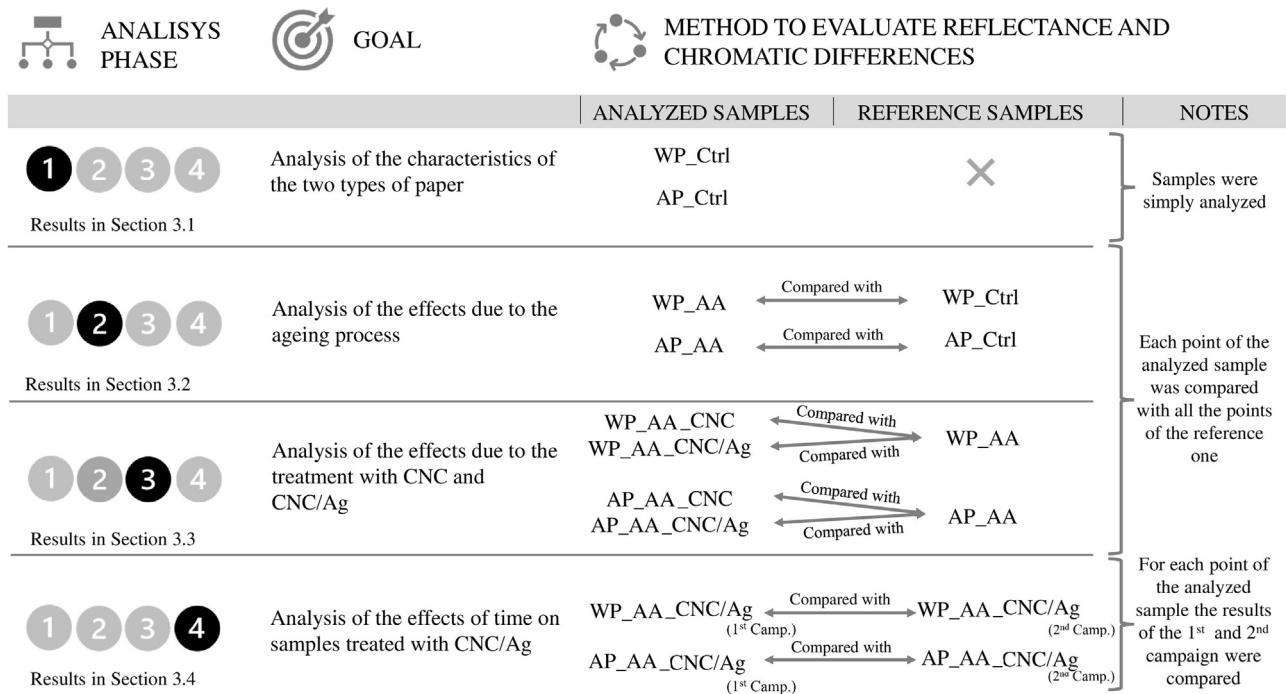


Fig. 2. Scheme of the method used to post-process measured data.

This analysis was conducted also for the aged samples. To distinguish the typical differences of the control and aged samples, they were indicated with the subscript “ctrl” and “aged” respectively. For example $\Delta\rho_{\text{typ,aged}}$, is the typical reflectance difference for the aged samples and $\Delta L^*_{\text{typ,ctrl}}$ is the typical lightness difference for the control samples.

Once obtained the typical variation ranges, the interpretation of the results became easier, since the reflectance and the chromatic differences due to ageing process were considered significant when out of the typical variation ranges of the control samples and those due to the suspensions additions, when out of the typical variation ranges of the aged samples.

Results

Comparison between WP_Ctrl and AP_Ctrl

Fig. 3 describes the two papers. Spectral and total reflectance values for the 9 points are reported in Fig. 3a for WP and in Fig. 3c for AP. The analysed points are represented in the CIE $L^*a^*b^*$ color space in Fig. 3b for WP and in Fig. 3d for AP, where the corresponding L^*_{D65} , h^*_{D65} , and C^*_{D65} values are listed as well. $\Delta E^*_{\text{max,typ,ctrl}}$, $\Delta L^*_{\text{typ,ctrl}}$, $\Delta h^*_{\text{typ,ctrl}}$, and $\Delta C^*_{\text{typ,ctrl}}$ are reported on the graphs. Notice that a^* and b^* axes are not represented in the same scale for readability reasons.

The WP spectral reflectance curves have an almost constant trend from 420 nm on, with values around 78.0%, and lower from 360 nm to 420 nm. The ρ_{D65} values range from 77.3% to 78.3%. As regards the AP, the spectral reflectance values grow with the wavelength and are about 30% corresponding to 360 nm and around 70% from 680 nm on. The corresponding ρ_{D65} values are consequently lower than WP ones, ranging from 58.6% to 61.7%.

As predictable from the reflectance analysis, the L^*_{D65} values are higher for WP (ranging from 90.4 to 90.9) than for the AP (ranging from 81.1 to 82.8). In the case of WP all the measured points are included in the second quarter of the color space (yellow-green quarter) and are very close to the center of the diagram (C^*_{D65} values ranging from 0.1 to 0.2). As concerns AP, the

points are all located in the first quarter of the diagram (red-yellow quarter) and are near to the b^* axis (h^*_{D65} values comprised between 82.8° and 84.8°). They are more saturated and farther from the center of the diagram compared to WP (C^*_{D65} values between 11.0 and 12.3).

Finally, WP is more homogeneous than the AP, being the $\Delta E^*_{\text{max,typ,ctrl}}$ equal to 0.5. On the contrary, for the AP the $\Delta E^*_{\text{max,typ,ctrl}}$ is equal to 2.1.

Effect of the ageing process

Fig. 4 and Table 1 describe the effects of the ageing process for both types of paper. Spectral reflectance curves are represented in Fig. 4a. In the graphs black continuous line represents the reference. $\Delta\rho_{D65}$ and ΔE^*_{D65} values are reported in Figs. 4b and 4c. In the graphs the typical variation ranges for each quantity are indicated with black dashed lines, to make easier to identify significant differences. ΔL^*_{D65} , Δh^*_{D65} and ΔC^*_{D65} are analyzed in Table 1, where for each point the maximum and minimum values and the percentage of significant reductions (S.R.) and significant increments (S.I.) are reported. For example, looking at Table 1 referred to WP, it arises that for P1 the ΔL^*_{D65} values range between -1.2 and -0.8 and that in 100% of the cases the L^*_{D65} reduction is significant, i.e., out of the typical variation range.

The effects of the ageing process on WP and AP are only in part comparable.

As regards WP, the 9 spectral reflectance curves are all under the reference but show a similar shape. This means that the ageing process determined a reduction in the spectral reflectance almost constant for all the wavelengths. Of course, the total reflectance values decreased (see Fig. 4b). The reductions are out of the typical variation range, fluctuating from -3.9% to -1.4% . In the case of AP, the ageing process determines a variation in the shape of the spectral reflectance curves. In the range 360 nm - 560 nm the values are higher than the reference one, whereas from 560 nm on, they are lower. Therefore, the total reflectance values do not vary significantly. Only for points P3, P4, P5, P8 and P9 reductions

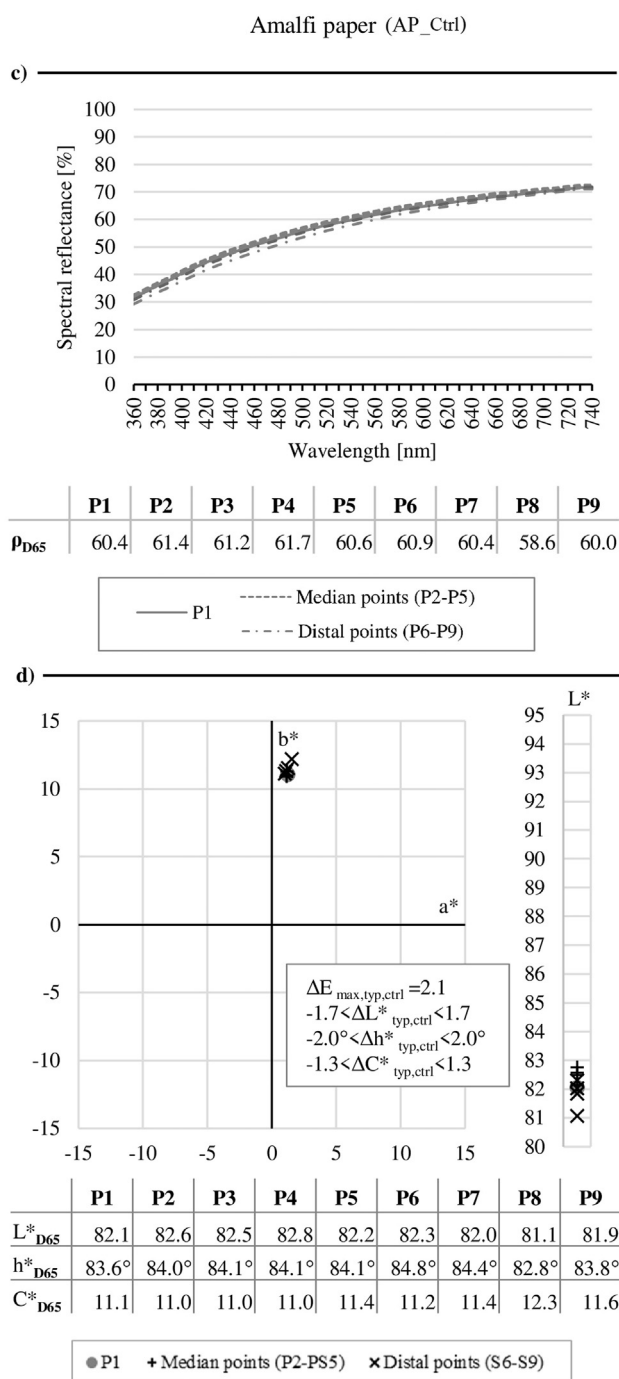
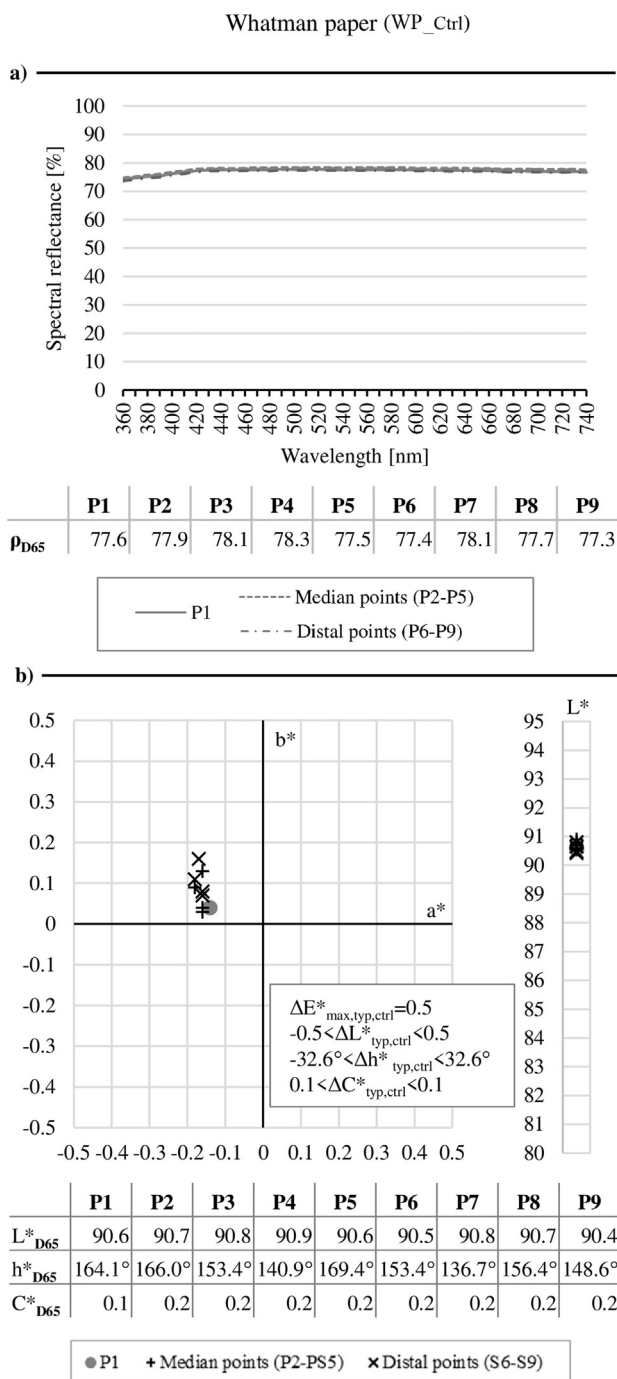


Fig. 3. Measured data referred to control samples (WP_Ctrl and AP_Ctrl): spectral and total reflectance of WP_Ctrl (a) and AP_Ctrl (c), chromatic coordinates of WP_Ctrl (b) and AP_Ctrl (d).

higher than 2.5% are observed and these cases cover only the 29.6% of all the observed ones (see Fig. 4b).

The ageing process determines for WP ΔE^*_{D65} values higher than the typical threshold limit. Moreover, in 84.0% of the cases these differences are higher than 1, so perceptible by the human eye. The maximum observed value is equal to 1.8. As shown in Table 1, these differences are due to a reduction of the L^*_{D65} (significant reductions for all the points), in 44.4% of the cases there are also significant reductions of the hue and in 63.0% of the cases significant reductions of the chroma. For the AP, ΔE^*_{D65} values are out of the typical ranges only in 22.2% of the cases (maximum ob-

served value 2.7), but in this case the main phenomenon is a reduction of the chroma (45.7% of the cases with significant alterations), whereas significant reduction of L^*_{D65} are observed only for 29.6% of the cases and no significant alterations are found for hue values (see Table 1).

Effect of the use of CNC and CNC/Ag

Fig. 5 and Tables 2 and 3 describe the effects of the use of CNC and CNC/Ag on WP and AP with the same approach used in Fig. 4 and Tables 1.

Table 1
Chromatic differences due to the ageing effects on WP and AP (Comparison between WP_AA and WP_Ctrl samples and between AP_AA samples and AP_Ctrl).

		WP				AP			
		Min	Max	S. R.	S. I.	Min	Max	S. R.	S. I.
ΔL^*_{D65}	P1	-1.2	-0.8	100	0	-1.5	0.2	0	0
	P2	-1.6	-1.1	100	0	-1.2	0.5	0	0
	P3	-1.8	-1.3	100	0	-2.5	-0.8	77.8	0
	P4	-1.3	-0.9	100	0	-2.2	-0.5	44.4	0
	P5	-1.1	-0.7	100	0	-2.2	-0.5	44.4	0
	P6	-1.8	-1.3	100	0	-1	0.7	0	0
	P7	-1.8	-1.3	100	0	-1.5	0.2	0	0
	P8	-1.7	-1.3	100	0	-2.3	-0.6	44.4	0
	P9	-1.6	-1.1	100	0	-2.4	-0.7	55.6	0
$\Delta h^*_{D65} [^\circ]$	P1	-32.6	0	0	0	-1.1	0.9	0	0
	P2	-54	-21.4	77.8	0	-0.3	1.7	0	0
	P3	-18.2	14.5	0	0	-1.5	0.5	0	0
	P4	-44.6	-11.9	33.3	0	-1.1	0.9	0	0
	P5	-31	1.6	0	0	-1.8	0.2	0	0
	P6	-55.4	-22.8	77.8	0	-0.2	1.9	0	0
	P7	-60	-27.4	77.8	0	-0.5	1.5	0	0
	P8	-49.2	-16.6	66.7	0	-1.6	0.4	0	0
	P9	-50.3	-17.7	66.7	0	-1.7	0.3	0	0
ΔC^*_{D65}	P1	0	0.1	0	0	-2.4	-1.1	44.4	0
	P2	0.2	0.3	0	100	-2.7	-1.4	100	0
	P3	0	0.1	0	0	-1.9	-0.6	11.1	0
	P4	0	0.1	0	55.6	-2.2	-0.9	44.4	0
	P5	0	0.1	0	11.1	-1.5	-0.3	11.1	0
	P6	0.2	0.2	0	100	-2.6	-1.3	100	0
	P7	0.3	0.4	0	100	-2.6	-1.3	77.8	0
	P8	0.1	0.2	0	100	-1.9	-0.6	11.1	0
	P9	0.2	0.3	0	100	-1.6	-0.3	11.1	0

Table 2
Chromatic differences due to the use of CNC on aged WP and AP (Comparison between WP_AA_CNC and WP_AA samples and between AP_AA_CNC and AP_AA samples).

		WP				AP			
		Min	Max	S. R.	S. I.	Min	Max	S. R.	S. I.
ΔL^*_{D65}	P1	-1	-0.3	33.3	0	-0.1	1.4	0	0
	P2	-1.2	-0.5	55.6	0	-0.2	1.3	0	0
	P3	-0.7	0	11.1	0	-0.1	1.4	0	0
	P4	-0.6	0.1	0	0	0.3	1.8	0	44.4
	P5	-0.9	-0.3	33.3	0	0.1	1.6	0	11.1
	P6	-0.8	-0.1	11.1	0	-0.1	1.4	0	0
	P7	-0.6	0	0	0	-0.1	1.4	0	0
	P8	-0.5	0.2	0	0	-0.2	1.3	0	0
	P9	-0.5	0.2	0	0	-0.6	0.9	0	0
$\Delta h^*_{D65} [^\circ]$	P1	-48.4	-6.6	11.1	0	-0.3	1.4	0	0
	P2	-49.9	-8.1	11.1	0	-0.7	1	0	0
	P3	-45.2	-3.4	11.1	0	-0.3	1.4	0	0
	P4	-36.4	5.4	0	0	-0.1	1.6	0	0
	P5	-47.2	-5.3	11.1	0	-0.5	1.1	0	0
	P6	-48.8	-7	11.1	0	-0.6	1.1	0	0
	P7	-28.2	13.6	0	0	-0.2	1.5	0	0
	P8	-27.5	14.3	0	0	0.7	2.3	0	44.4
	P9	-26.2	15.6	0	0	0.6	2.2	0	44.4
ΔC^*_{D65}	P1	-0.1	0.2	0	0	-2.8	-1.7	100	0
	P2	0	0.3	0	0	-2.3	-1.1	100	0
	P3	-0.2	0.1	0	0	-2.3	-1.2	100	0
	P4	-0.3	0.1	0	0	-2.6	-1.5	100	0
	P5	-0.1	0.2	0	0	-2	-0.8	66.7	0
	P6	-0.1	0.3	0	0	-2	-0.9	66.7	0
	P7	-0.3	0	0	0	-2	-0.8	66.7	0
	P8	-0.4	0	11.1	0	-2.4	-1.3	100	0
	P9	-0.3	0	0	0	-2.4	-1.2	100	0

The use of CNC and CNC/Ag determines different effects and the reaction of the two types of paper to the treatments is diverse.

Specifically, as regards the use of CNC on aged WP the following observations can be stated:

- Spectral reflectance curves are only slightly lower than the reference one and they almost overlap it (see Fig. 5a).

- Consequently, the variations in total reflectance values (see Fig. 5b) are almost always not significant. They are included in the $\Delta\rho_{\text{typ,aged}}$ range, except than sometimes for P1, P2, P5 and P6 (16.0% of the observed cases).
- ΔE^*_{D65} assumes significant values only in 13.6% of the observed cases corresponding to P1, P2, P5 and P6 (see Fig. 5c), but only

Table 3

Chromatic differences due to the use of CNC/Ag on aged WP and AP (Comparison between WP_AA_CNC/Ag and WP_AA samples and between AP_AA_CNC/Ag and AP_AA samples).

		WP				AP			
		Min	Max	S. R.	S. I.	Min	Max	S. R.	S. I.
ΔL^*_{D65}	P1	-8.5	-7.8	100	0	-3.2	-1.7	100	0
	P2	-3.4	-2.8	100	0	-3.4	-1.9	100	0
	P3	-4.7	-4	100	0	-1.9	-0.4	22.2	0
	P4	-3.7	-3	100	0	-4.4	-2.9	100	0
	P5	-2.4	-1.7	100	0	-2.4	-0.9	44.4	0
	P6	-1.5	-0.8	100	0	-0.9	0.6	0	0
	P7	-0.3	0.3	0	0	-0.9	0.6	0	0
	P8	-0.6	0	0	0	-4	-2.5	100	0
	P9	-1	-0.3	33.3	0	-4.4	-2.9	100	0
$\Delta h^*_{D65} [^\circ]$	P1	-107.2	-65.4	100	0	-6.8	-5.1	100	0
	P2	-89.1	-47.3	100	0	-6.3	-4.6	100	0
	P3	-88	-46.2	100	0	-3.8	-2.2	100	0
	P4	-82.8	-41	88.9	0	-7.5	-5.8	100	0
	P5	-85.7	-43.9	100	0	-5.9	-4.3	100	0
	P6	-59.3	-17.5	33.3	0	-1.7	0	11.1	0
	P7	-48.2	-6.4	11.1	0	-1.7	-0.1	11.1	0
	P8	-56.3	-14.5	33.3	0	-5.1	-3.5	100	0
	P9	-53.1	-11.3	11.1	0	-4.7	-3.1	100	0
ΔC^*_{D65}	P1	5.7	6	0	100	0.3	1.4	0	33.3
	P2	1.6	1.9	0	100	0.3	1.4	0	33.3
	P3	3.2	3.5	0	100	-0.5	0.6	0	0
	P4	2.6	2.9	0	100	1	2.2	0	77.8
	P5	1.5	1.9	0	100	0.2	1.3	0	33.3
	P6	0.7	1	0	100	-0.7	0.4	0	0
	P7	0	0.3	0	0	-0.9	0.2	0	0
	P8	0.4	0.7	0	100	1.2	2.3	0	100
	P9	0.3	0.6	0	88.9	1	2.1	0	77.8

for 4.9% of all the cases it is higher than 1 and specifically for P1 and P2. These differences, as shown in Table 2, are due to reductions of L^*_{D65} values and in few cases to reductions of h^*_{D65} , whereas the chroma is not affected by the treatment.

The use of CNC on aged AP has the following consequences:

- It determines a slight increase of the spectral reflectance values (see Fig. 5a). This increase is maximum at 360 nm for all the curves (on the average about 5.0%) and reduces with wavelength increasing. From 620 nm on, the curves almost overlap the reference one.
- The differences in total reflectance values (see Fig. 5b) are always not significant except than in the 7.4% of the cases and specifically for P4 and P5.
- ΔE^*_{D65} is higher than the threshold limit in 58% of the observed cases and the maximum values, equal to 3.0 and 3.1, are obtained for P1 and P4 respectively (see Fig. 5c). As shown in Table 2, the differences are mainly due to the reduction of the chroma, whereas only in some cases the differences in L^*_{D65} and the h^*_{D65} coordinates are significant.

As regards the use of CNC/Ag on aged WP it can be stated that:

- The variations in the spectral reflectance trends are really evident (see Fig. 5d), and differ depending on the observed points, being more relevant for P1. Specifically, the P1 curve presents lower values than the reference one (on the average 20% less) and almost constant till 500 nm; then it starts to increase getting closer to the reference curve from about 640 nm on. For the median points this trend is confirmed, but the curves appear closer to the reference one.
- Therefore, the reductions in total reflectance are noticeable especially for P1 (see Fig. 5e). In this case the average reduction in the ρ_{D65} is 15.9%. P1 is followed by P3, P4, P2, P5 and P6 for which average values of $\Delta\rho_{D65}$ equal to 8.7%, 6.7%, 6.3%, 4.2%, 2.2% are observed respectively. For the other points $\Delta\rho_{D65}$ values are not significant.

- The average ΔE^*_{D65} values are significant for points from P1 to P6, and are equal to 10.2, 3.6, 5.6, 4.4, 2.8 and 1.4 respectively (see Fig. 5f). The differences are due to reductions in L^*_{D65} and h^*_{D65} and increases of C^*_{D65} , as it can be seen in Table 3.

As regards the use of CNC/Ag for aged AP, the following observations arise:

- The treatment determines a general reduction of the spectral reflectance values, and also in this case the differences are lower for longer wavelengths (see Fig. 5d).
- Only P6 and P7 present reductions included in the $\Delta\rho_{typ,aged}$ range, whereas for P1, P2, P3, P4, P5, P8 and P9 the $\Delta\rho_{D65}$ values are on the average -4.1%, -4.6%, -1.9%, -6.3%, -2.7%, -5.5% and -6.2% respectively (see Fig. 5e).
- ΔE^*_{D65} values are out of the typical range for P1, P2, P4, P8 and P9 points, and on the average equal to 2.7, 2.9, 4.2, 3.7 and 4.0 respectively (see Fig. 5f). For these points, the chromatic differences are caused by reductions of L^*_{D65} and h^*_{D65} , whereas the difference of the chroma are less significant, as it is reported in Table 3.

Fig. 6 clarifies the chromatic alterations due to the treatments. It shows that, for both papers the use of CNC/Ag determines more effective variations than CNC. In general, the variations consist in reductions of lightness and hue, and in increases of chroma. So, the papers get darker, more pinkish, and more saturated. The effects are not equal for all the points and manifests themselves with different strength for the two types of papers, being stronger for WP.

Effect of time

Fig. 7 describes the effects of time on WP_AA_CNC/Ag and AP_AA_CNC/Ag. In Fig. 7a the spectral reflectance curves of P1 (considered representative) in 1st and 2nd campaign are reported for both papers. AP remains more stable over time; the curve maintains its trend, slightly shifting downwards. On the contrary,

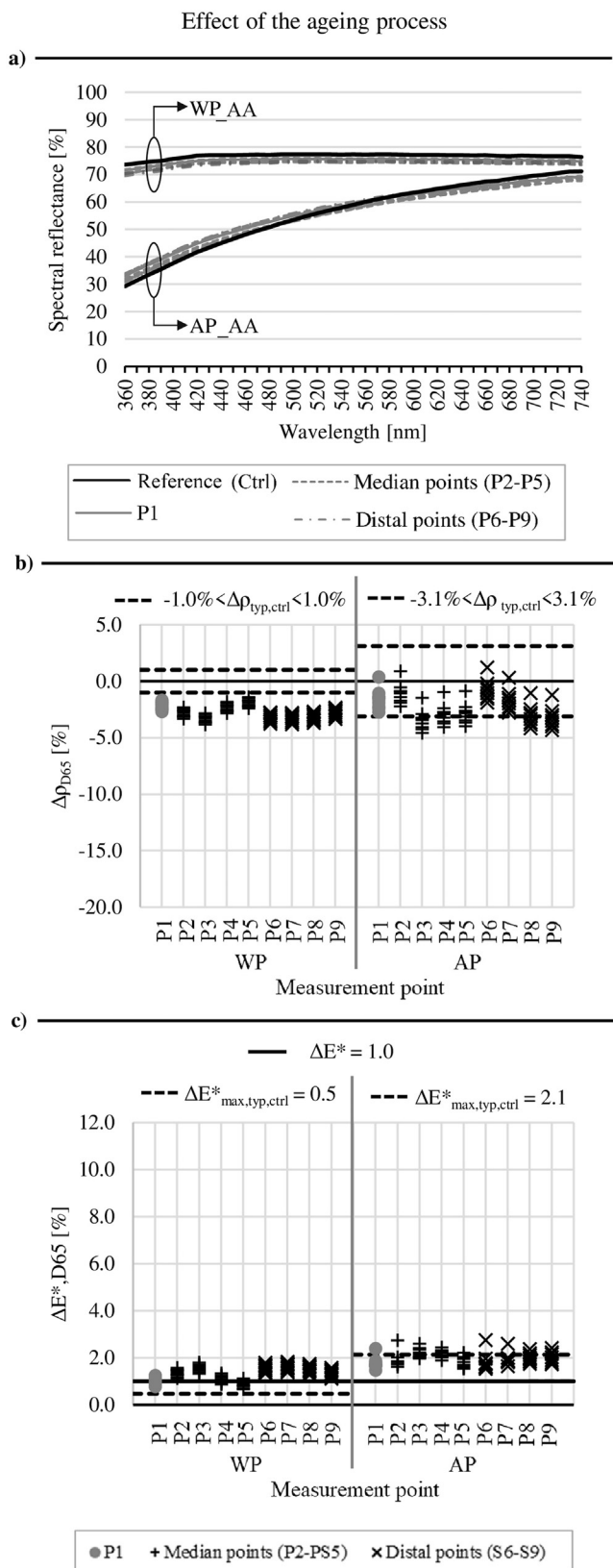


Fig. 4. Effect of the ageing process on WP and AP: spectral reflectance (a), $\Delta\rho_{D65}$ values (b), ΔE^*_{D65} (c). Comparison between WP_AA and WP_Ctrl samples and between AP_AA samples and AP_Ctrl.

WP curve completely changes its shape, assuming the trend described in Section 4.3. Therefore, for WP the reductions in total reflectance are higher ($\Delta\rho^*_{D65} = -6.2$) than the AP ($\Delta\rho^*_{D65} = -1.2$). As regards the chromatic coordinates (see Fig. 7b), for WP the ΔE^*_{D65} equal is 5.5 for P1. As shown by the graph, some of the points (the central and the median ones) are characterized by a reduction of the h^*_{D65} and by an increase of the C^*_{D65} assuming a pinkish appearance and becoming more saturated. On the contrary, the AP stays more stable, and the only relevant differences are those referred to the h^*_{D65} that is slightly reduced.

Discussion and conclusions

From the analysis of the results, it can be concluded that:

- Despite the CNC itself determines significant alterations, the addition of Ag surely makes the effect worse, since the variations observed for WP_AA_CNC and AP_AA_CNC are lower than those observed for WP_AA_CNC/Ag and AP_AA_CNC/Ag. This is in accordance with what reported in [28].
- The use of CNC/Ag determined chromatic variations ranging from 0.2 to 10.5 for WP and from 0.3 to 5.1 for AP. In summary, for both types of paper the variations are due to reductions of L^*_{D65} and h^*_{D65} (the paper gets darker and assumes a pinkish coloration) and increases of C^*_{D65} (the paper gets more saturated). These effects manifest in a different way on the two types of paper. For example, the increase of the chroma is lower for AP.
- The fact that the two types of paper show a different behavior when exposed to the same treatments prompts us to extend the analysis to other kinds of papers in future works.
- The effects of the treatments are not the same for all the points of the measurement grid. For example, for WP the effects due to the addition of CNC/Ag are more evident for central, median point and P6, whereas for AP the points mostly affected are P1, P2, P4, P5, P8 and P9. When the samples were prepared, they seemed completely soaked by the substance that, inoculated at the center, then spread around. The results suggest that the diffusion was not homogeneous and that the coloring agents remained concentrated in the center. Further assays need to be performed to consider other inoculation mode, to try to better diffuse the substances on the paper, avoiding the arise of colored pinkish spots and, hopefully, obtaining a general reduction of the chromatic alterations.
- The variations induced by the CNC/Ag are not stable over time. The AP presents slight differences between the first and the second measurements campaign, but for WP greater variations manifest with time. Further studies are needed to deepen this topic and monitor the possible further changes over longer periods or after further artificial ageing treatments.

An observation must be done. Surely, the presented method could be improved. One of the key issues is the choice to use the black NCS background to perform measurements. When measuring paper capability in reflecting radiation, considering that it is not a completely opaque material, it would be better to refer not to reflectance, but to “reflectivity”. As reported in CIE E-ILV [35], the reflectivity can be defined as the “reflectance of a layer of a material that is of sufficient thickness so that there is no change in reflectance with increase in thickness”. In case of paper, that can be obtained by overlapping a proper amount of paper layers. Of course, each layer should be of the same paper typology of the measured one. However, this method has been considered not appropriate for the specific case. Indeed, as demonstrated in the analysis, papers samples (and especially the Amalfi ones) are not homogeneous and present some spots. It would have been impossible to overlap paper samples characterized by the same spots,

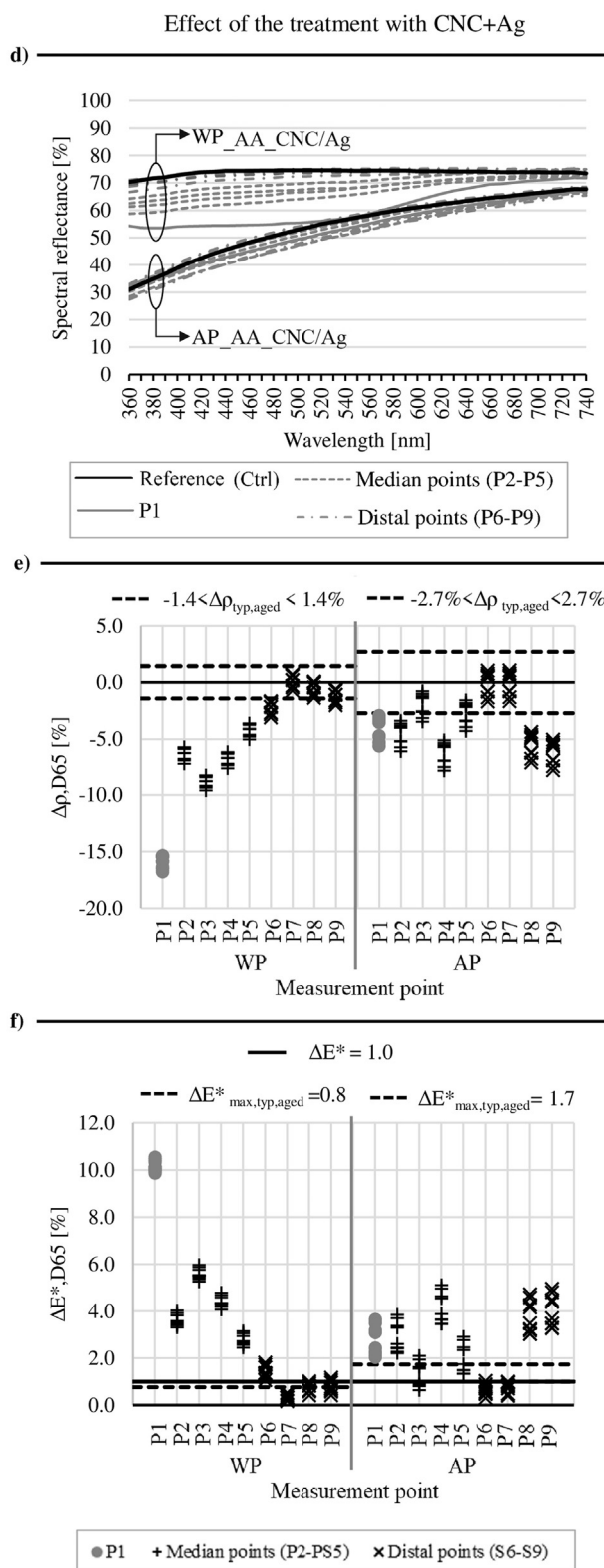
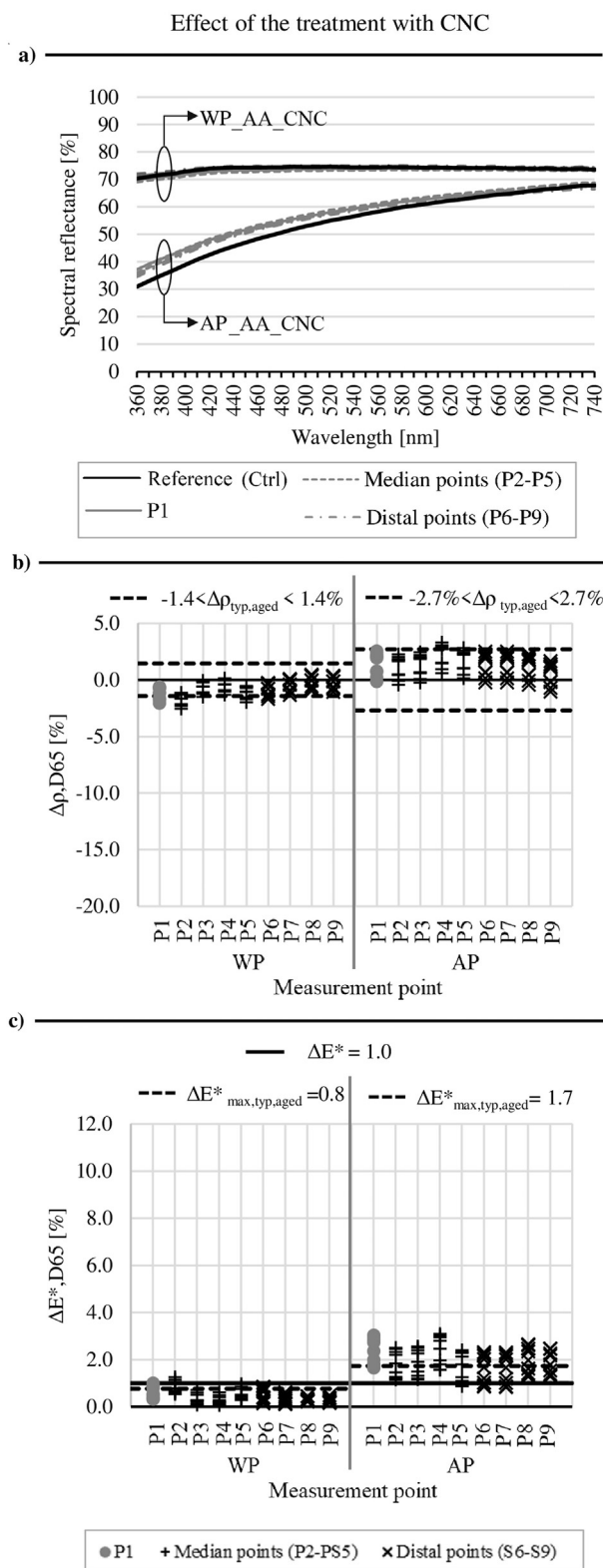


Fig. 5. Effect of the use of CNC and CNC/Ag for WP and AP on spectral reflectance (a and d), $\Delta\rho_{D65}$ values (b and e), and ΔE^*_{D65} values (c and f). Comparison between WP_AA_CNC and WP_AA samples and between AP_AA_CNC and AP_AA samples on the left. Comparison between WP_AA_CNC/Ag and WP_AA samples and between AP_AA_CNC/Ag and AP_AA samples on the right.

Effects of different treatments on chromatic coordinates

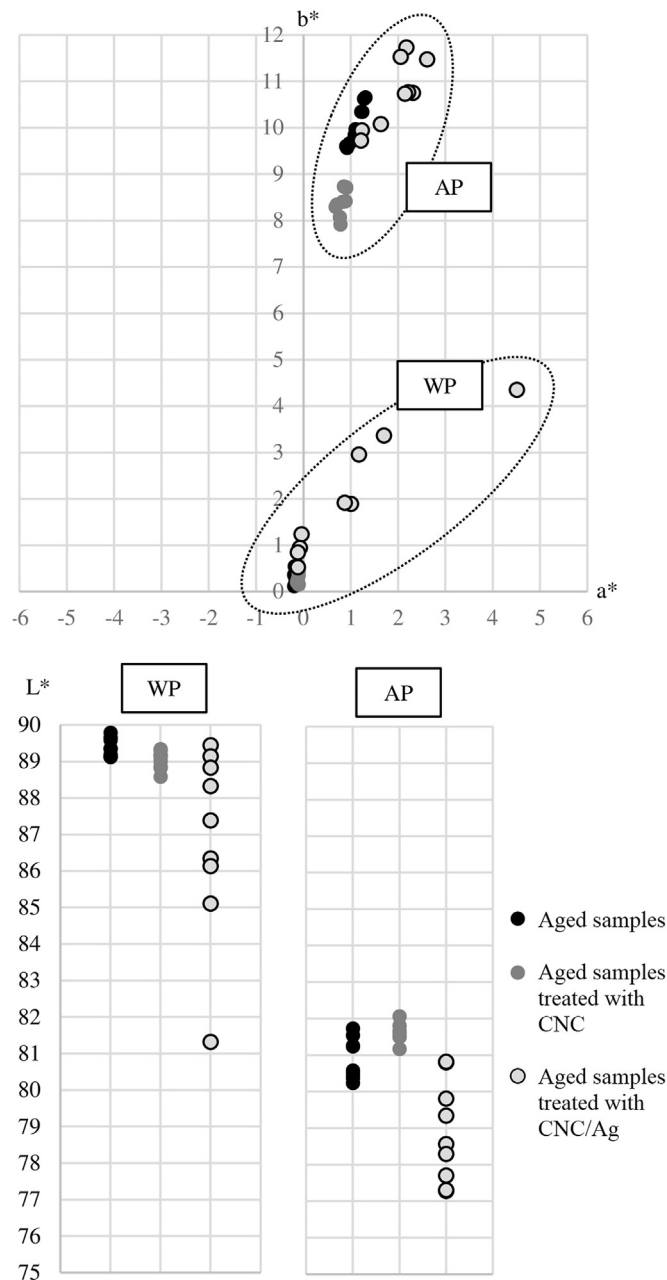


Fig. 6. Overview about the effects of all the treatments on chromatic coordinates for both WP and AP.

so to precisely describe the spots themselves. Moreover, when the treatments were applied, the substances did not spread in homogeneous way. So, again, it would have been impossible to obtain equal samples to overlap and then measure. For this reason, it was considered more appropriate to use as background for measurements a completely homogeneous material, with standardized optical properties and very low spectral reflectance values. This approach determines some limitations in analyzing results. For example, when describing the effects of the treatments, a reduction in reflectance was often noticed. This variation could correspond both to an increase in the absorbance of the material, but also to an increase of the transmittance, meaning that the paper loses its opacity, becoming more transparent, perhaps for alterations in fibers structure. The analysis here conducted allows to explain re-

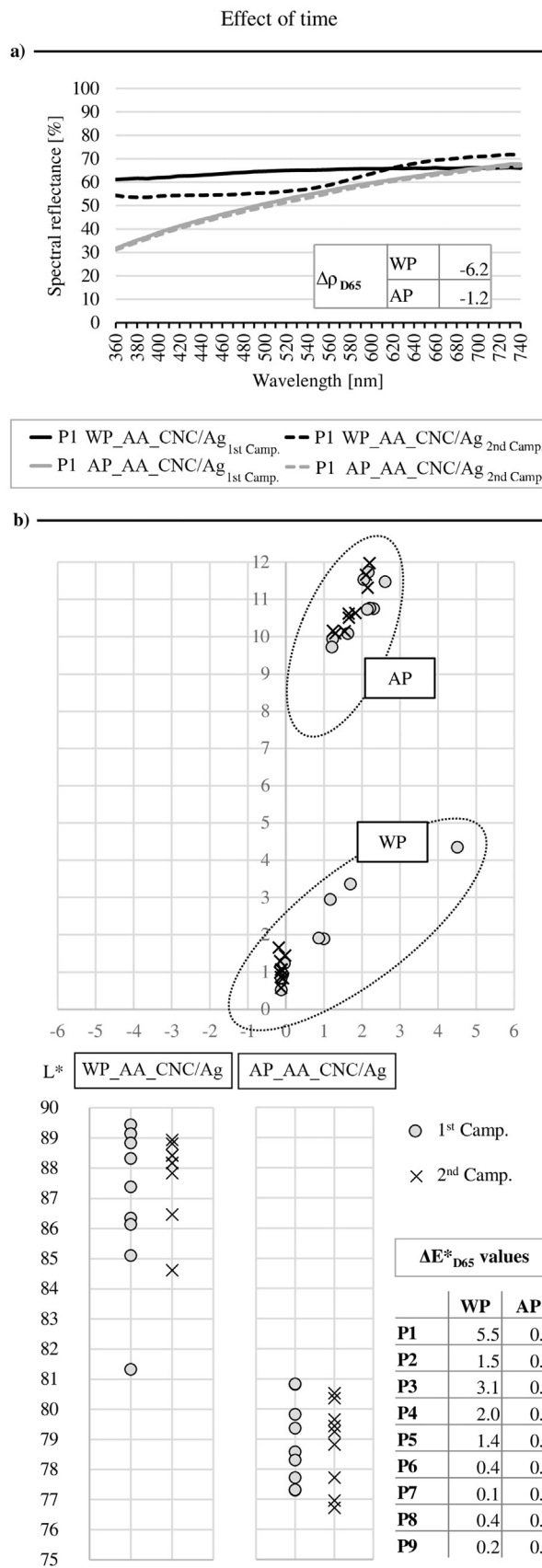


Fig. 7. Effect of time on spectral reflectance for WP_AA_CNC/Ag and AP_AA_CNC/Ag samples (a) and on $L^*a^*b^*$ chromatic coordinates under D65 for the same samples (b).

ductions in reflectance values, but not to understand their causes. Further studies should be conducted to deepen these aspects and provide information also about paper transmittance.

Irrespective of these lacks and of the specific results, the proposed method is general and can be applied to evaluate the alterations of optical properties of paper due to any type of treatment. In any case, it is hoped that the use of this technique will lead to a better understanding of the effects of CNC and CNC/Ag treatments to develop an innovative restorative system of paper artworks that is respectful of their uniqueness.

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