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Study of Air-Induced Paper Discolorations by Infrared Spectroscopy, X-ray Fluorescence, and Scanning Electron Microscopy

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Air-induced paper discoloration is described as being different from other discoloration morphologies. It seems to be the result of prolonged exposure to air in a humid and polluted environment without appropriate protecting coverage. In this work, three folios from the same eighteenth century book, presenting three degrees of discoloration and opacity and subjected to different environmental conditions, were examined and compared. Samples were analyzed and compared by three different instrumental techniques, mid-infrared spectroscopy, X-ray fluorescence (XRF), and scanning electron microscopy (SEM). Chemical and physical changes were confirmed from the data collected by these techniques. The absence of the secondary amide band characteristic of proteins in the infrared spectra of the two discolored folios, accompanied by the appearance and increase of white mineral-like deposits visible in the SEM micrographs, support the idea that oxidation reactions occurred and that these two folios were subjected to more severe degradation hazard.

Index Headings: Art conservation; Discoloration; Oxidation; Paper; Fourier transform infrared spectroscopy; FT-IR spectroscopy; X-ray fluorescence; XRF; Scanning electron microscopy; SEM.

INTRODUCTION

A paper presented at the IIC Congress in 2002[1] described the observation of paper artifacts presenting partial or total discoloration sometimes associated with an increase in opacity. In the conservation literature consulted at the time, no mention was made of air exposure provoking discoloration and opacity, although many research papers on the effect of air pollution, and its control and effects on air quality inside museums, have been published previously. More specifically related to the phenomenon of the gain in opacity, Johansson mentions that the presence of NO_2 allows for a greater pick-up rate of SO_2 on the paper and promotes the formation of gypsum.[2] Since then, Letnar and Muck found that paper samples submitted to accelerated aging registered a decrease of brightness and an increase in yellowness as well as an increase in opacity. They attribute this to an altered gelatine sizing.[3]

Porck et al. reported on a study regarding the differences between identical book copies stored in two different libraries, respectively located in a highly polluted urban area and a less polluted area.[4] They concluded that the paper in the more polluted environment registered a larger amount of sulfur and a greater level of acidity; no mention was made of discoloration. In 2002 Havermans and Pork carried out further tests on the same books and concluded that the margins were not only more acidic but also considerably more discolored.[5]

Although ozone had been overlooked in indoor pollution parameters until quite recently because of its high reactivity and low time existence indoors (6 minutes), it has been more recently studied and published in non-conservation literature.[6,7] Synergetic effects produced by different air contaminants have also started to be considered. Weshler investigated ozone concentration levels in indoor and outdoor areas[8] and concluded that the ozone levels tend to be larger in homes with natural ventilation and that the higher the relative humidity, the larger the deposition velocities to different surfaces. The author also states that ozone can synergistically react with nitrogen dioxide and form nitrate radical, which can accumulate indoors in the absence of direct sunlight.[8] The nitrate radical is short-lived and is ultimately converted to nitric acid in typical indoor environments.[8] Dahlin and Grontoft agree with this and state that the reactions involving NO_2 and O_3 increase in the summer in towns with heavy traffic.[9] Ferm et al. speak of new multi-pollutant situations provoked by the decreasing sulfur dioxide levels in most parts of Europe and the increasing automobile traffic causing an increase of nitrogen compounds, ozone, and particulate matter. Although the dominant reaction for the formation of HNO_3 is between NO_2 and OH radicals, HNO_3 can also be formed by a dark reaction involving O_3 and NO_2.[10]

Relating the present findings with the discoloration study presented in 2002,[1] it seems plausible that papers exposed for prolonged periods to polluted and humid air, without glazing protection in a naturally ventilated dark room overlooking a street with dense traffic, should develop a strong oxidizing process.

Parallel to this, reactions responsible for an increase of opacity also take place. As explained by Johanssons[2] SO_2 from the surrounding environment is physically adsorbed on the paper surface and converted into sulfite S(IV). This thermodynamically unstable substance is further oxidized into sulfate S(VI)[2] in the presence of NO_2. The sulfate further reacts with calcium, present in the paper, to form gypsum ($CaSO_4 \cdot 2H_2O$), which then acts as a filler and the paper increases in opacity.

Preliminary studies through visual characterization and simple analytical tests, namely surface pH measurements and colorimetric tests, have already been published.[1] It was found that pH values on air-induced discolored paper areas were only slightly different from the non-discolored areas, presenting pH values of 4.58 and 4.64, respectively. Measurements on the relative lightness and darkness of the papers (L* value) confirmed that the oxidized C folio became considerably darker than the non-oxidized A folio, presenting an L* value of approximately 88 and 62, respectively.

Fɪɢ. 1. Folios A, B, and C under normal light.

In the present study we intend to characterize and detect differences between the discolored and non-discolored paper samples using chemical and physical analytical instruments, namely mid-infrared (MIR) spectroscopy, energy dispersive X-ray fluorescence (XRF), and scanning electron microscopy (SEM). This article presents some of the results collected.

The use of MIR spectroscopy is not new in the conservation field and in the last decades has been extensively described in the specialized literature; Fourier transform infrared (FT-IR) spectroscopy has been employed in the qualitative study of organic materials such as paper.[11–19]

X-ray fluorescence is also a technique widely used to identify and quantify the elements present in historical documents and aged paper samples.[19–24] This is an analytical technique that provides multi-elemental information in a completely nondestructive way, without sampling or other damage to the artwork. Furthermore, technological advances have allowed such a miniaturization that portable spectrometers are available to provide quality measurements on location. This way, documents of important value or in a severe state of degradation can be analyzed without removal from the museum or archive.

Scanning electron microscopy is also a valuable technique that has been used in the qualitative characterization and degradation of paper.[24,25] SEM has been used for morphological characterizations of fibers, identification of filling materials, and for comparison of physical differences on paper artifacts.

MATERIALS AND METHODS

Specimen Description. The paper samples selected for this study are three folios pertaining to an unbound and incomplete glossarium printed in 1766, donated in 1983 by the Portuguese National Library for experimental conservation treatments. The folios, designated as A, B and C, are rag, gelatine sized handmade papers (Fig. 1). Having in mind the printed date period and the observed light extinction in transmitted light, the paper leaf does not seem to have had china clay incorporated into its paper mesh. Collins and Milner state that the use of china clay was first suggested in 1733 but was in general use only in 1780.[25] From 1983 to 1997, the folios were stored in different environments and were not submitted to any type of treatment. Folio A, which exhibits a light tone, was protected by a folder of tracing paper inside a metal archive drawer in the Paper Conservation Department. Folio C, which corresponds to the brown paper, was shown in 1986 during a six-month exhibition, as an example of a document extremely attacked by insects. It was secured with metal pins onto white painted low density fiberboard. No glass was present. It is interesting to note that the exhibition room was located next to a heavy traffic street with no trees and a narrow sidewalk. After the exhibition, folio C remained in the same position, in the same room, in total darkness, for at least another year and remained on the same exhibition board, unprotected from direct contact with air, for another 10 years in a dim corridor of the building. Folio B was exhibited inside a showcase in the same exhibition room

TABLE I. Mean elemental concentration and standard deviation (μg·g^{-1}) obtained in this work for orchard leaves NBS1571 and certified values.

	P	S	Cl	K	Ca	Mn	Fe	Zn	Cu
Present work	2300 ± 400	3000 ± 1000	760 ± 90	16000 ± 2000	18000 ± 3000	80 ± 10	260 ± 60	19 ± 7	8 ± 2
Certified value	2100 ± 100	2300 ± 100	700 ± 10	14700 ± 300	20900 ± 300	91 ± 4	300 ± 20	25 ± 3	12 ± 1

as folio C and followed the same time path except for the last 10 years, when it was returned to its folder in a metal drawer cabinet.

Comparing the three folios by means of optical properties, it is possible to see that folio A after remaining inside a drawer is non-oxidized and retains its original cream color, while folio C, which had been in direct contact with air, in the conditions stated above, not only became very brown but also acquired a gain in opacity. Folio B also seems oxidized although its tone is mildly intense when compared with the tone presented by C.

Experimental Setup. *Mid-Infrared Spectroscopy.* Infrared spectra obtained in the range from 4000 to 650 cm^{-1} were acquired with a Perkin Elmer 1600 FT-IR spectrometer. Paper samples were analyzed in transmission, with accumulations of 64 scans and a resolution of 4.0 cm^{-1}. The data obtained were further analyzed on a separate work station using Omnic 5.2 software.

The samples were previously prepared by mixing 0.5 mg of defibered paper with 50 mg of anhydrous potassium bromide (Merck, spectroscopy grade). The mixture was ground in an agate mortar and transferred to a die and pressed into a pellet 7 mm in diameter using a press of 8–10 tonnes for 5 minutes, in order to obtain transparent disks.

Energy Dispersive X-ray Fluorescence. The equipment used in this study is a portable instrument consisting of an Oxford X-Ray generator (Model XTF 5011) with Mo. The detector used is a Vortex-EX SDD (Si) thermoelectrically cooled with a nominal area of 50 mm^2 and a Be window. The X-ray generator and detector are coupled to a vacuum chamber in 45° geometry. By using a polycapillary lens to collimate the beam, a spot size of 90 μm is obtained. The chamber also possesses a camera, allowing the visualization of the analyzed area and thus the capture of an image.[26]

All spectra were collected using the polycapillary mode in vacuum, operating conditions of 40 kV, 1 mA, and 300 s. The spectral analyses were performed using the WinAXIL (Analysis of X-ray spectra by Iterative Least-squares fitting) software package and the quantification was made using the compare mode, using three Standard Reference materials (Poplar leaves GBW 07604; Bush branches GBW 07603; Tea leaves GBW 07605).

The accuracy of the method was checked by analyzing a fourth Standard Reference Material, orchard leaves NBS1571, and the results are presented in Table I.

Scanning Electron Microscopy. A Jeol JSM-5310LV SEM with a high voltage of 20 kV was used. Square samples of ~1 cm^2 were removed from all the samples on equivalent paper sections where no printing ink was present. After metallization of the paper specimens with a very thin layer of graphite to assure a good conductivity, they were placed inside the sample holder compartment. SEM images were recorded using the secondary electron detector at two different magnifications: 150× and 500×.

RESULTS AND DISCUSSION

Mid-Infrared Spectroscopy. For the spectra obtained in the range of 4000 to 650 cm^{-1}, a special emphasis was given to the analyses of the region below 2000 cm^{-1}, which normally contains the most interesting and valuable information of the material we are studying. The identification was accomplished either by assigning chemical groups to the peaks in the spectra or by comparing each spectrum to those of known compounds and making the identification by the best match.

Infrared spectra are shown in Fig. 2. The spectra of folios A and B present great similarity and their cellulose character is strongly confirmed by the presence of specific bands identified and listed in Table II. Bands located at 898 cm^{-1} and 1060 cm^{-1} are due to vibration of cellulose structure and to C–O–C glycosidic ether group, respectively. In folio A, the presence of gelatine sizing is revealed by the amide I and II bands at 1545 cm^{-1} and 1648 cm^{-1}, respectively.[15] The band at 1648 cm^{-1} seems to be a superimposition of the amide I band and the H–O–H bending mode of hydrogen bonded water in the cellulose. In the folio B spectrum, the band at 1545 cm^{-1} is missing, meaning that the original sizing was subjected to deterioration as there are less peptidic bonds. Here the band at 1639 cm^{-1} must be due to absorbed water.

As for folio C some differences can be pointed out in the region of 1700 cm^{-1} when compared with the other two spectra. Small, sharp bands are observed in this region, leading us to conclude that they are constituents from degradation products such as ketones, aldehydes, and carboxylic acids. The absence of the three characteristic amide bands of proteins in folio C, associated with the loss of the absorption band at 898 cm^{-1} attributed to the cellulose skeletal vibration, reinforces the idea that folio C was subjected to a more severe degradation
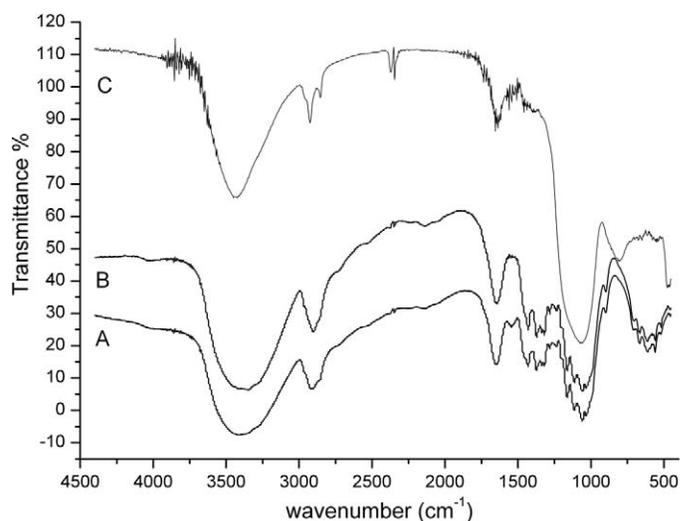
FIG. 2. FT-IR spectra obtained for paper samples of folios (**A**) A, (**B**) B, and (**C**) C.

TABLE II. Peak wavenumber (cm^{-1}) and interpretation for folios A, B, and C.

Wavenumber (cm^{-1})			Assignment	Interpretation
Folio A	Folio B	Folio C		
3406	3345		O–H stretching	Hydroxyl group of cellulose
			N–H stretching	
2902	2902	2927	C–H stretching	Aliphatic hydrocarbons
		2854		
		1777	C=O stretching	Acetones, aldehydes and/or carboxylic acids
		1753		
		1721		
		1709		
1648	1639		C=O stretching	Amide I
			COO$^-$ stretching	Carboxilic groups/ions
			O–H stretching	Water in cellulose
1545			C–N stretching	Amide II
			N–H bending	
1373	1372		CO–H bending	
1318	1318			
1282	1282		–CH$_3$ stretching	
1163	1163		C–OH stretching	
1113	1113		C–O–C symmetric stretching	
1060	1060	1060	C–O–C asymmetric stretching	Cellulose, aliphatic ethers -glucose
898	898		Skeletal vibration	Cellulose
704			CH$_2$ rocking	Cellulose
665	664	669	C–OH bending	Out of plane

hazard. The formation of carbonyl groups points to an oxidation process induced by air pollutants as the main reaction responsible for discoloration, as previously hypothesized.

Furthermore, in the region of 2800–3000 cm^{-1}, attributed to the stretching vibration of CH, CH$_2$ groups, folio C presents two peaks at 2927 cm^{-1} and 2854 cm^{-1}, revealing that this folio contained more methylene groups than the other two folios.

X-ray Fluorescence. The mean elemental concentrations of Al, Si, K, S, Ca, Mn, and Fe for the three folios are presented in Table III. A slight increase of the potassium content was observed for the stained folios (B and C) when compared with folio A, as shown in Fig. 3. This behavior has already been found in studies regarding paper degradation.[21] No other elemental variation was found, namely for Ca, leading us to believe that the formation of gypsum was due to a rearrangement of the elements constituting the paper.

Scanning Electron Microscopy. Scanning electron microscopy results corroborate the conclusions made from the MIR spectra: micrographs show the presence of a cellulosic matrix for all three samples; however, the three samples show

different stages of deterioration. The results of the inner surface of the paper samples, shown in Fig. 4, show that the fibrous structure is still pristine in folio A while in folios B and C the fibrous structure is progressively more flattened. Fibers in folio C are not only more flat but also appear to be considerably more fibrillated and therefore shorter in length. They also have blunter ends.

In the micrograph of folio A short white thin lines are observed within the fiber filaments. This differs from the small, white mineral-like deposits agglomerated on the surface or between the fibers in the other two folios. These same mineral-like deposits are quite numerous on folio C.

The thin lines may be attributed to the presence of calcium carbonate within the fiber structure. Dabrowski et al.[27] spoke of early European handmade papers as having a buffer of calcium carbonate natural filler conveyed by the manufacturing process, which added lime to the beating process.

TABLE III. Mean elemental concentration and standard deviation (µg·g^{-1}) in the three studied folios (A, B and C).

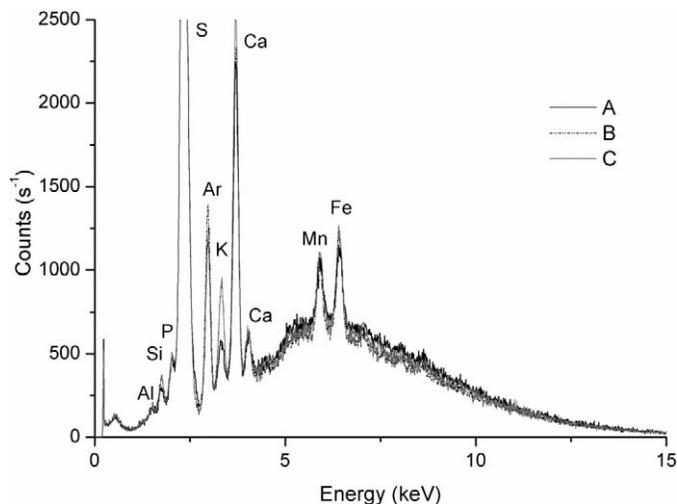|	A	B	C
Element	Mean ± SD	Mean ± SD	Mean ± SD
Al	2480 ± 420	2250 ± 150	2600 ± 100
Si	4500 ± 600	4400 ± 700	5500 ± 500
P	1200 ± 100	1400 ± 100	1300 ± 100
S	3000 ± 100	3000 ± 100	3000 ± 100
K	250 ± 50	400 ± 50	400 ± 80
Ca	1250 ± 250	1100 ± 100	1100 ± 1000
Mn	60 ± 10	50 ± 10	60 ± 10
Fe	70 ± 10	80 ± 10	70 ± 10

FIG. 3. Comparison of the obtained XRF spectra for folios A, B, and C.

Fig. 4. SEM observation on the surface structure of paper folios A, B, and C at 500× magnification.

As for the other two folios, the presence of the small white mineral-like deposits outside the fiber filaments may suggest the presence of fillers. As these forms are only observed in these folios and are absent in folio A, it is plausible to considerer that their formation occurred parallel to or after the air-induced oxidation and that they may be responsible for the increase in opacity.

CONCLUSION

This work is a successful combination of several analytical techniques in the characterization of paper degradation. The results obtained in this study are of importance in preventive conservation and can bring new perspectives to the role of science in artwork conservation.

Chemical and physical changes were confirmed from the data collected using the different analytical methods. The detection of progressively stronger carbonyl bands for folio C, together with the absence of the secondary amide band characteristic of proteins in folios B and C, support the idea that oxidation reactions occurred and that these two folios were subjected to a more severe degradation hazard, not only by presenting a loss of their original gelatine sizing but also by presenting a greater intensity of oxidation.

The appearance and increase of white mineral-like deposits visible in the SEM micrographs of folios B and C seem to confirm the degradation of cellulose structure and the transformation and rearrangement of the original calcium carbonate into gypsum. The thin white straight lines previously visible within the fiber filaments give space to the mineral-like deposits scattered within the fiber structure. The maintenance of the calcium elemental content also supports the rearrangement hypothesis. Gypsum when deposited between the fibers acts as filler and can be responsible for the increase in opacity in folio C. Furthermore, the XRF technique confirmed that no elemental changes occurred in the paper during the discoloration process, except for a slight increase in potassium, confirming that the discoloration progression is not due to metallic ions present in either paper or the environment.

1. F. Figueira, A. M. Fernandes, and A. Ferreira, *in Works of Art on Paper, Books, Documents, and Photographs: Techniques and Conservation*, D. Daniels, A. Donnithorne, and P. Smith, Eds. (IIC, London, 2002), pp. 65–68.
2. A. Johansson, P. Kolseth, and O. Lindqvist, Restaurator **21,** 117 (2000).
3. M. C. Letnar and T. Muck, Restaurator **24,** 240 (2003).
4. H. Porck, W. J. T. Smit, J. Heijst, and I. Leeuwen, in *Paper Preservation Symposium* (Tappi Press, 1988), 74–80.
5. J. Havermans and H. Porck, *La Conservation à l'Ère du Numérique* (ARSAG, Paris, 2002), pp. 173–179.
6. G. Thomson, *The Museum Environment* (Butterworth-Heinemann, Oxford, 1986), 2nd ed.,p. 146.
7. M. Cernic Letnar and V. Kropar Vancina, Restaurator **23,** 118 (2002).
8. C. Weschler, Indoor Air **10,** 269 (2000).
9. E. Dahlin, T. Grontoft, S. Rentmeister, C. Calnan, J. Czop, K. Hallett, D. Howell, C. Pitzen, and A. S. Larsen, The 14th Triennial Meeting, ICOM-CC (James and James, London, 2005), pp. 617–624.
10. M. Ferm, F. De Santis, and C. Varotsos, Atmos. Environ. **39,** 6664 (2005).
11. J. L. Pedersol and F. J. Ligterink, Restaurator **22,** 133 (2001).
12. G. Bitossi, R. Giorgi, M. Mauro, B. Salvadori, and L. Dei, Appl. Spectrosc. Rev. **40,** 187 (2005).
13. L. M. Proniewicz, C. Paluszkiewicz, A. W. Birczyńska, H. Majcherczyk, A. Baránski, and A. Konieczna, J. Mol. Struct. **596,** 163 (2001).
14. K. Castro, S. Pessanha, N. Proietti, E. Princi, D. Capitani, M. L. Carvalho, and J. M. Madariaga, Anal. Bioanal. Chem. **391,** 433 (2008).
15. P. Garside and P. Wyeth, Stud. Conserv. **48,** 269 (2003).
16. M. Baker, D. Reyden, and N. Ravenel, Book Paper Group Annu. **8,** 177 (1989).
17. N. V. Ivanova, E. V. Korolik, R. G. Zhbankov, and N. I. Insarova, J. Appl. Spectrosc. **38,** 937 (1983).
18. R. J. Koestler, N. Indictor, and B. Fiske, Restaurator **13,** 58 (1992).
19. M. Bicchieri, S. Rinconi, F. P. Romano, L. Pappalardo, M. Corsi, G. Cristoforetti, S. Legnaiolo, V. Palleschi, A. Salvetti, and E. Tognoni, Spectrochim. Acta, Part B **57,** 1235 (2002).
20. M. Manso, M. Costa, and M. L. Carvalho, Nucl. Instrum. Meth. A **580,** 732 (2007).
21. M. Manso, S. Pessanha, and M. L. Carvalho, Spectrochim. Acta, Part B **61,** 922 (2006).
22. J. L. Ferrero, C. Roldan, D. Juanes, J. Carballo, J. Pereira, M. Ardid, J. L. Lluch, and R. Vives, Nucl. Instrum. Meth. Phys. Res. B **213,** 729 (2004).
23. K. Castro, N. Proietti, E. Princi, S. Pessanha, M. L. Carvalho, S. Vicini, D. Capitani, and J. M. Madariaga, Anal. Chim. Acta **623,** 187 (2008).
24. E. Princi, S. Vicini, E. Marsano, and V. Trefiletti, Thermochim. Acta **468,** 27 (2008).
25. T. Collings and D. Milner, Paper Conservator, **14,** 58 (1990).
26. M. Manso, S. Pessanha, F. Figueira, S. Valadas, A. Guilherme, M. Afonso, A. C. Rocha, M. J. Oliveira, I. Ribeiro, and M. L. Carvalho, Anal. Bioanal. Chem. **395,** 2029 (2009).
27. J. Dabrowski and J. Simmons, Fibres Textiles Eastern Eur. **11,** 8 (2003).