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Effects of UV Radiation on Paper: A Chromatic Study

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A study on Whatman#1, bond, rice, kraft, and amate papers in their original condition and exposed to 2.25, 4.5, 6.75, and 9 W of Ultraviolet-C radiation is presented. The techniques used were scanning electron microscopy + energy dispersive X-ray spectrometry (SEM+EDS), differential scanning calorimetry + thermogravimetric analysis (DSC+TGA), Fourier transform infrared spectrometry (FTIR), X-ray diffraction (XRD), Ultraviolet/Visible (UV/Vis) spectrophotometry, pH measurements, and colorimetry. No changes were found in these papers, length and width of fibers, chemical composition, pH, pyrolysis characteristics, or FTIR and XRD patterns after irradiation. Cellulose (all papers), calcite (bond, rice, and kraft), whewellite

(amate), and kaolinite (kraft) were the main components. Non-irradiated bond paper showed a specular effect on the UV spectra, which was progressively reduced by the UV radiation and becoming almost imperceptible at >6 W. Visible spectra of amate paper showed the presence of β carotenoids and chlorophylls, which are degraded by UV radiation. Visible spectra of Kraft paper showed a color reversion at 2.25 W, which progressively diminished as a function of the UV rate energy transfer. UV radiation gradually clarified amate paper. To make a comparison, kraft and amate paper were exposed to gamma radiation at 3, 9, and 15 kGy. The color of Kraft paper was clarified, and amate paper increased in yellowness. Perceptions of chromatic differences due to gamma radiation were smaller than those observed with UV radiation; however, they are still important, especially for kraft paper.

Keywords: UV radiation, bond, amate, rice, kraft, Whatman#1.

INTRODUCTION

Paper has played a prominent role over time, and its permanence and durability are important requirements for librarians, archivists, the electric industry, and conservation of cultural heritage. Permanence of paper was defined [1] as the degree to which it resists chemical action from agents, such as light, air, pollution, high-energy radiation, and microorganisms, over time. Ultraviolet (UV) radiation from both artificial and

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natural light sources are particularly harmful for paper, and that damage is cumulative [2]. Therefore, the studies regarding these effects are useful for cultural heritage preservation and for paper manufacturing techniques, among other areas. Because cellulose is the main component of paper, studies have been devoted to the chemical effects of several agents on this material. Air temperature and relative humidity [2], heat/UV radiation exposure [3], gamma radiation [4], Near-UV and visible pulsed laser [5], thermal oxidation in air at constant temperature and photo-oxidation under Xenon arc lamp [6], and museum environments [7] are among the conditions of these studies. Reduction of the degree of cellulose polymerization and the deterioration of the optical and mechanical properties of papers are among the consequences of aging, and both natural and accelerated processes cause the same effects in cellulose [8]. The processes of aging leads to irreversible changes, usually slowly under environmental conditions [1]; therefore, interest in accelerating those processes, such as by exposition to UV radiation, remains constant.

Wood-derived papers may contain hemicelluloses and lignin in addition to cellulose; on the other hand, some papers also include inorganic and/or organic additives, which may complicate studies on those types of paper [9]. Another aspect to take into consideration among the aging processes is the possibility of color changes in paper [10].

Amate paper is manufactured in a region of Puebla, Mexico, from the bark of trees from the *Moracea* family [11]; today, it is used for handcrafted designs, but pre-Hispanic people used amate for making their codices. Rice paper has been used in China since prehistory for painting and calligraphy [12]; it is usually manufactured out of the *Tetrapanax papyrifer* tree. Bond paper is commonly used for writing and printing, and it is usually made of cotton, linen, or wood. Kraft paper is a recovered/recycled paper, commonly used for packaging; it is also used in the electrical industry as insulator for winding conductors [13]. As far as we know, amate, rice, and kraft papers have not been studied with regard to the possible effects of UV radiation on them; with respect to cellulose, many studies have been conducted, as mentioned above.

The aim of the present study was to characterize the papers (bond, rice, amate, kraft, and Whatman#1) in their original conditions and after the exposition to UV radiation, in order to evaluate possible changes in their physicochemical characteristics. A study was reported about the physicochemical effects of gamma radiation on several kinds of papers (virtually the same as the present research), not including kraft. A comparison may be made with those data [14].

MATERIALS AND METHODS

The papers were bond, rice, amate, kraft, and Whatman#1 (Sigma-Aldrich), using the last as a reference for the others because it contains virtually only alpha cellulose.

UV irradiations were carried out inside a wooden box 80 cm long, 60 cm wide, and 35 cm high lined inside with aluminum foil. A UVC lamp (Philips TUV 8W G8 T5, 254 nm), a luxometer (UNI-T, UT382), and a thermometer/hygrometer with a probe (Cole-Parmer Traceable) were placed inside the box. Luminescence (Lux), temperature (°C), and relative humidity (%) were measured multiple times throughout the irradiation. The paper specimens, rectangles of 250 mm x 20 mm in polyethylene bags were placed 25 cm away from the lamp. These experimental conditions are based on a referenced norm [15], in which an accelerated aging of papers by UV radiation is proposed. The samples were analyzed before and after 120, 240, 360, and 480 h of UV radiation exposure.

The experimental conditions during the exposure of paper specimens to UV radiation were the following: lamp intensity of 226 ± 53 Lx, $49 \pm 3\%$ relative humidity, and 17.8 ± 0.2 °C. Luminous intensity ($\text{kLx} \cdot \text{h}$) was calculated as the mean value of intensity and the exposure time in hours. This parameter was converted to rates of energy transfer (RET) in Watts (= Joule/s) with Equation 1:

$$\text{RET (W)} = \frac{\text{Luminous intensity} * \text{Dimension of the paper}}{\text{Conversion factor}} \quad (1)$$

where the dimension of the papers is 0.005 m^2 and the conversion factor for a fluorescent lamp is 60 lm/W . Therefore, the rates of energy transfer were 2.25, 4.5, 6.75, and 9 W for each experimental condition.

2 g of each paper in small pieces (before and after exposure to UV radiation) were gently shaken (wrist stirrer Lab Line Instr., Model 3587) with 0.1 dm³ of distilled water for 6 days. Subsequently, parts of these suspensions were kept at 40 °C until the de-fibrated papers were completely dried. Samples of de-fibrated paper were placed in an aluminum sample holder, and a gold coating was applied. The specimens were observed with a scanning electron microscope (SEM) (JSM-6610LV with an OXFORD probe, coupled with an EDAX microanalysis system) at 50X and 200X to measure the length and width of fibers, respectively. The chemical compositions of papers were determined by energy dispersive X-ray spectrometry (EDS) analysis. At least five measurements were done for length, width, and chemical composition at the different conditions.

A sample of each paper (before and after exposure to UV radiation) were milled (FRITSCH-Pulverisette Spartan) into fine powder, which was stored in polyethylene bags.

The pH was measured with 0.2 g of each powdered paper and 0.1 dm³ of distilled water in polyethylene flasks. After 15 minutes of shaking the mixture and 10 minutes of centrifugation, the pH of supernatants was measured with a combined electrode coupled with a potentiometer (Orion VersaStar Pro, previously calibrated).

X-ray diffractogram (XRD) of the powdered papers were obtained using a Discover model D8 equipment attached to an X-ray tube with a copper anode. The spectra were compared with data from the Joint Committee on Powder Diffraction Standard Files (JCPDF).

The thermogravimetric spectra of powdered papers were obtained using a differential scanning calorimetry/thermogravimetric analysis (DSC-TGA) equipment (STD Q600 TA Instruments) under the following experimental conditions: temperature between 15 and 800 °C, rate of 10 °C/min, and a helium flow of 0.1 dm³/min.

Fourier transform infrared (FTIR) analysis was conducted with a VARIAN® model 640-IR. For these analyses, a piece of each paper was placed on a quartz sample holder. The absorbance spectra were obtained by rationing the single-beam spectrum against that of the background from 4000 to 400 cm⁻¹, with 40 scans and a resolution of 4 cm⁻¹. The total number of data points was 1869 for each spectrum.

Ultraviolet/visible (UV-Vis) spectra were obtained with integrating sphere equipment (Perkin Elmer Lambda 35). Measurements were made directly with pieces of paper 225 – 325 mm wide and 400 – 800 mm long.

Color was evaluated with the Commission Internationale d'Eclairage System (CIE L*a*b*) using a spectrophotometer PCE-CSM 8 (PCE Instruments) and 3 X 3 cm samples of each paper. The instrument was calibrated using a white standard reflectance plate (L* = 96.37, a* = 0.19, b* = 1.68). The non-irradiated papers were used as control samples to determine changes in color.

Some tests were performed to establish a comparison between UV and gamma radiation. Samples of amate and kraft paper were exposed to gamma radiation at doses of 3, 9, and 15 kGy using a Transelektro LGI-01 irradiator (0.9 kGy/h, Sept. 2016), periodically calibrated with alanine dosimeters. The colors of these samples were evaluated as described above.

RESULTS AND DISCUSSION

Figure 1 shows SEM images of some de-fibrated papers and their EDS spectra. No appreciable changes in the morphology, were observed in the SEM images from the original and UV-irradiated specimens, nor of length, or width of the fibers (Table I). Such changes of the fibers would be an indicator of possible damages, related to the degradation of cellulose [16].

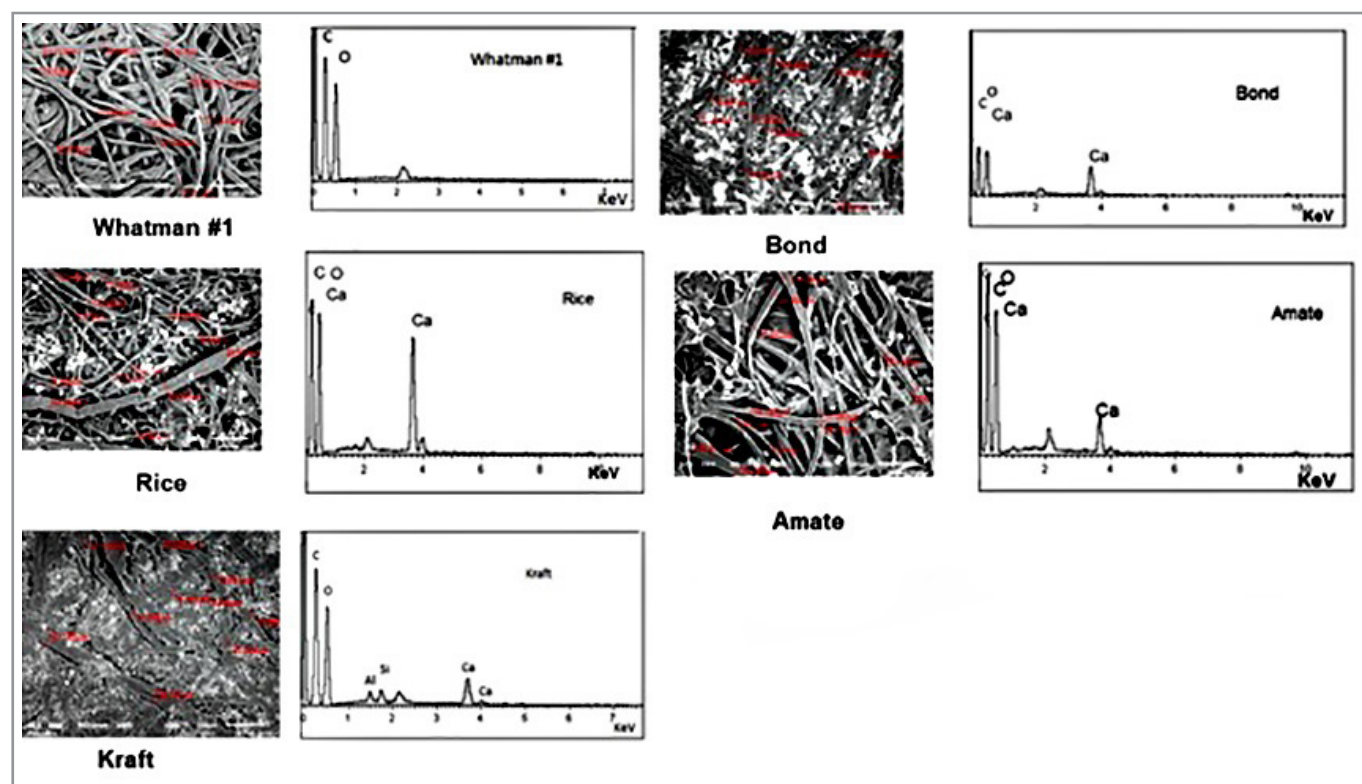


Figure 1. Images of de-fibrated papers (SEM, x200) and EDS spectra.

Table IA. Length (mm) of the fibers of the papers before and after the exposition to UV radiation

Paper	Rate of energy transfer, W				
	0	2.25	4.5	6.5	9
Whatman#1	1±0.7	0.8±0.2	0.9±0.4	0.9±0.4	0.9 ±0.2
Bond	0.4±0.1	0.5±0.1	0.7±0.2	0.9±0.4	0.7±0.1
Rice	1.4±0.7	1.3±0.2	0.9±0.5	1±0.5	0.8±0.2
Amate	1.1±0.5	0.8±0.2	0.8±0.2	1±0.3	0.8±0.3
Kraft	0.8±0.2	0.6±0.2	0.7±0.2	0.7±0.3	0.7±0.2

Table IB. Width* (μm) of the fibers of the papers before and after the exposition to UV radiation

Paper	Rate of energy transfer, W				
	0	2.25	4.5	6.5	9
Whatman#1	20±6	16±9	16±9	19±6	12±4
Bond	15±2	18±12	16±13	18±14	21±16
Rice	20±18	22±18	21±17	13±9	18±15
Amate	23±10	16±8	21±10	20±8	15±9
Kraft	22±17	22±11	22±20	23±18	20±18

The elemental composition of the papers was analyzed using the EDS spectra (Figure 1), in which the peaks associated with C, O, Ca, Si, and Al are observed, depending on the type of paper. The peaks between 2 and 3 keV correspond the $M\alpha$ X-ray emission of gold due to the coating applied to the defibrated papers. Table II shows the mean values and standard deviations of elemental concentrations. As no noticeable differences were found between natural and irradiated papers, this table presents the average values obtained under all experimental conditions. The small standard deviations show little change in the chemical compositions attributable to exposure to UV radiation. C and O were quantified in all papers. Calcium is present in bond, rice, amate, and kraft papers, and this last contains in addition small amounts of silicon and aluminum.

Table II. Elemental concentrations of the papers (percentages). Mean values \pm s.d. obtained from data before and after the exposition to UV radiation, at 2.25, 4.5, 6.75, and 9 W.

Paper	C	O	Ca	Si	Al
Whatman#1	45 \pm 0.3	55 \pm 0.3	0	0	0
Bond	37 \pm 0.4	54 \pm 0.3	9 \pm 0.4	0	0
Rice	35 \pm 1	54 \pm 0.3	10 \pm 1	0	0
Amate	42 \pm 2	54 \pm 0.9	4 \pm 1.5	0	0
Kraft	41 \pm 2	52 \pm 0.8	5 \pm 0.9	1 \pm 0.2	1 \pm 0.2

The pH measurements of each paper, exposed to UV radiation, do not differ of the initial conditions of the papers. Therefore, global results are given in Table III. All papers are alkaline, except for Whatman#1, which is neutral. A slight acidification was observed for kraft paper; however, it is still alkaline after UV exposure. Paper is preferably alkaline to avoid degradation [9].

Table III. Mean values of pH measurements of the papers before and after the exposition to UV radiation, at 2.25, 4.5, 6.75, and 9 W.

Paper	0 W	2.25, 4.5, 6.75, and 9 W
Whatman#1	6.9 \pm 0.1	7 \pm 0.1
Bond	9.4 \pm 0.0	9.4 \pm 0.0
Rice	9.6 \pm 0.2	9.4 \pm 0.3
Amate	8.4 \pm 0.4	8.2 \pm 0.4
Kraft	8.2 \pm 0.1	8 \pm 0.1

According to the XRD spectra, the cellulose is semi-crystalline, and the other components are crystalline. No changes occurred due to UV radiation exposure. The diffractogram of Whatman #1 only presented the characteristic peaks of cellulose, which occurred at 14.9°, 16.5°, and 22.6° 2 θ ; these peaks were present in the spectra of all other papers (Figure 2). Rice, bond, and kraft papers contain calcite (CaCO_3), whose main peaks occur at 23.1°, 24.4°, 36°, 39.4°, 43.2°, 47.5°, 48.5°, and 57.4° 2 θ . Calcium carbonate gives paper favorable physical and mechanical properties; this compound can be added to the pulp or be formed during the process with calcium hydroxide [9]. The bond paper may contain calcium sulfate (peak at 23.1° 2 θ), which is added to improve printing and writing rigidity, whiteness, and retention of paper [17]. This peak is not seen in the spectrum because it overlaps with one of cellulose. The spectra of Kraft paper also showed small peaks due to kaolinite (12.4° and 24.9° 2 θ), which sometimes coats this kind of paper [18].

The presence of whewellite (calcium oxalate monohydrate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) was identified on amate paper spectra (15° , 24.5° , 30.2° , 36° , and 38.3° 2θ). This compound is generated by the metabolism of the plant as a defensive measure against external agents, such as insects [19].

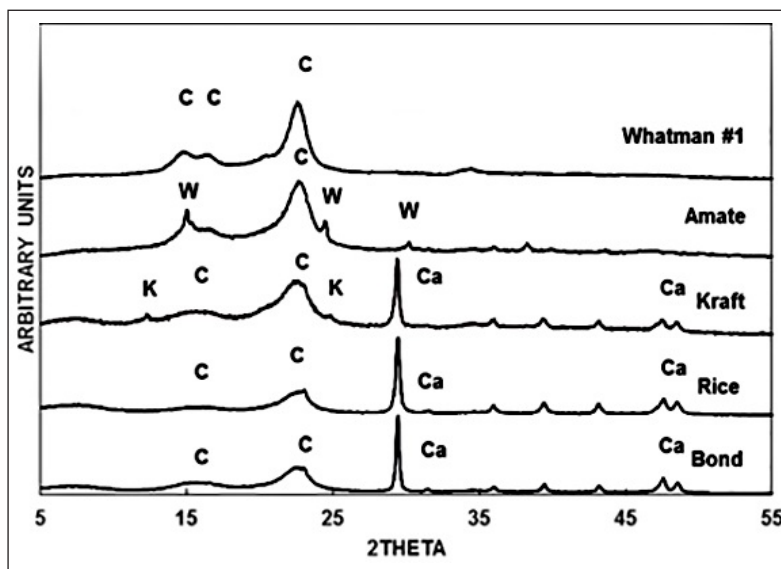


Figure 2. X-ray diffraction patterns of the papers. C: Cellulose, Ca: Calcite (CaCO_3), W: Whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), K: Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$).

Few differences were found in the FTIR band intensity and none in their wave numbers due to the UV exposures regarding the original specimens. The bands at 1160 , 1107 , 1055 , and 1031 cm^{-1} corresponding to cellulose [20-22] were present in spectra of all papers. Bands of calcite (C-O stretching and O-C-O bending: 1420 , 880 , and 712 cm^{-1}) were present in the bond, rice, and kraft spectra, and the stretching vibration of $-\text{COOH}$ due to whewellite (1620 and 1350 cm^{-1}) was observed in the amate spectrum. The FTIR spectra of bond, rice, and kraft papers were remarkably similar among them; whereas those of amate paper were like to that reported for soft wood of Southern pine [23].

Some FTIR bands of cellulose, hemicellulose, and lignin occurred in the region between 900 and 1200 cm^{-1} . Other characteristic bands of hemicellulose and lignin are found in the region between 1700 and 1800 cm^{-1} ; however, no bands were observed in this region for any paper. The absence of lignin in handmade papers, amate and rice, both of tree barks, is due to the alkaline manufacturing process because lignin is soluble in this medium. Disappearance of spectral bands in the mentioned region after the lignocellulosic fibers were cooked and bleached was reported [24]. On the other hand, a band around 1730 cm^{-1} was observed when Whatman #1 paper was aged under a xenon light source, suggesting a photo-degradation process [6]. This effect was not observed under the conditions of the present study. Common laser-printer paper, newspaper, and thermal fax paper were exposed to UV radiation and analyzed by ATR-FTIR spectroscopy; only the last one was sensitive to UV radiation and scarce effect was observed for the two first [25]. FTIR spectrum of thermally aged Whatman paper was virtually the same that the natural paper spectrum [6]. This scarce effect was observed in the present research for the papers exposed to UV radiation.

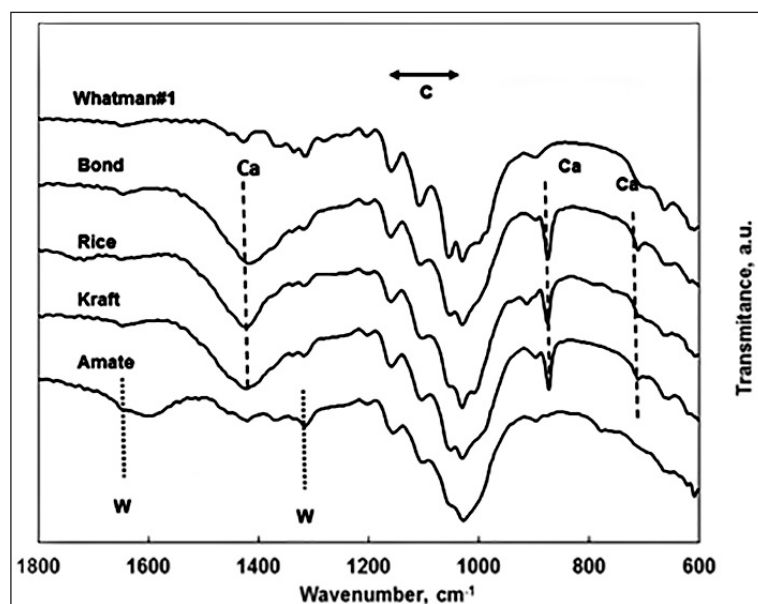


Figure 3. Infrared spectra of the papers exposed at 9 W. C: Cellulose, Ca: Calcite, W: Whewellite.

Deconvolution procedures were applied to the DTC diagrams of the papers to calculate the percentage of each pyrolysis process. The processes observed for all papers were dehydration (20 – 200 °C) and decarboxilation of cellulose (250 – 400 °C). Cellulose decomposes between 277 and 427 °C, with maximum decomposition occurring at 355 °C [20,26,27]. Calcium oxalate monohydrate in amate paper decomposes to calcium carbonate at 400 - 500 °C, creating calcium oxide. Decomposition of this last compound was observed for amate, bond, rice, and kraft papers at 600 - 800 °C. Carbon and calcium oxide, as a residue at >800 °C, represented a large percentage of these four papers, whereas Whatman #1 left a small residue of carbon. Data regarding the exposure (or not) of the papers to UV radiation were virtually identical, as showed by the small standard deviation values of the pyrolysis percentages of the compounds. Therefore, Table IV includes mean values and standard deviations of data obtained in all experimental conditions. Similar results were found with thermally aged Whatman paper, no changes were observed in TGA analysis before and after the thermal treatment [6].

Table IV. Percentages of the compound pyrolysis by TGA/DTA, at different intervals of temperature. Mean values \pm s.d. obtained from data before and after the exposition to UV radiation, at 0, 2.25, 4.5, 6.75, and 9 W.

Temperature (°C)	Compound	Whatman#1	Bond	Rice	Amate	Kraft
20 - 200	Humidity	3 \pm 1	2.5 \pm 1	3 \pm 0.4	4 \pm 0.3	3 \pm 1
250 - 400	Cellulose	92 \pm 1	66 \pm 1	63 \pm 1	64 \pm 3	75 \pm 1
450 - 500	Ca(COO) ₂				6 \pm 1	
600 - 700	CaCO ₃		10 \pm 0.2	13.5 \pm 1	6 \pm 1	5.4 \pm 0.4
450 - >800	C	2 \pm 0.3				
700 - >800	C + CaO		21 \pm 1	20 \pm 1	21 \pm 3	14 \pm 4

No peaks were observed in the UV spectra obtained with integrating sphere equipment between 225 and 325 nm for Whatman#1, rice, amate, or kraft paper, and no changes were evident in these papers after exposure to UV radiation between 0 and 9 W (figure not included). Brightness of Whatman paper virtually remained constant when it was exposed to near-UV and visible pulsed laser [5]. On the contrary, due to the brightness of bond paper, a specular effect rather than diffuse reflectance was observed at 276 ± 1 nm (Figure 4A). This effect was particularly noticeable in the original paper and was progressively reduced as a function of the UV rate of energy transfer, being almost imperceptible at >6.75 W (Figure 4B). Then, exposure with UV radiation induced in bond paper the effect known as brightness reversion [8], which can be interpreted as an accelerated aging effect. Absorbance spectral changes below 300 nm were observed using Fabriano paper exposed to ambient solar radiation [2], like was observed for bond paper exposed to UV radiation in the present work. A similar effect was caused by surfactants on photocopy paper; the reflectance of this paper increased but not that of the filter paper [28]. The coatings of the bond, photocopy and Fabriano papers are maybe the responsible of these effects.

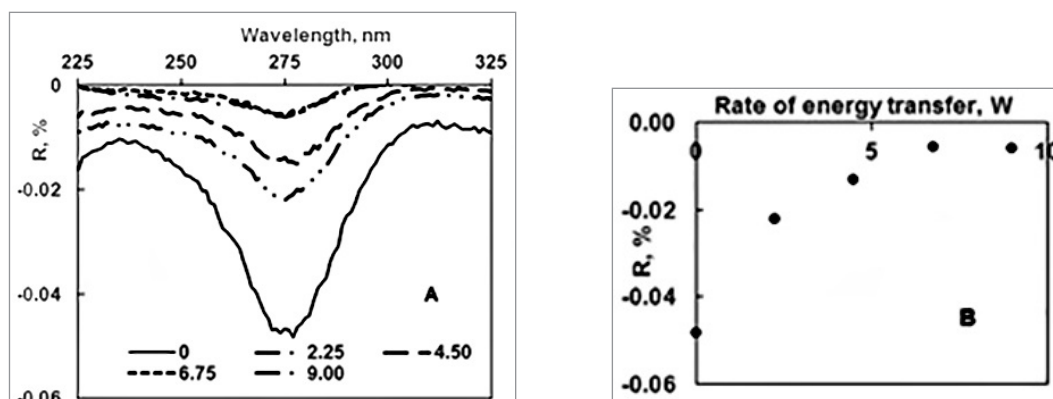


Figure 4. A: UV diffuse reflectance spectra of bond paper, exposed from 0 to 9W.
B: Behavior of R % (at 275 nm) as a function of the rate of energy transfer.

Regarding the diffuse reflectance spectra in the visible region of white papers (Whatman #1, bond, and rice), non-irradiated and irradiated up to 9 W, none presented maximum of diffuse reflectance between 400 and 800 nm (figure not included). Amate paper spectra were very intense, whereas those of kraft paper were less intense.

Figure 5A shows the deconvolution of amate paper visible spectrum of diffuse reflectance. Several maxima were revealed, specifically at 425, 481, 590, and 670 nm, which correspond to the plant's pigments, β carotenoids (400 - 525 nm) and chlorophylls (400 - 500 nm and 575 - 700 nm) [29]. That figure shows the spectrum of non-irradiated amate paper, but deconvolution of all the spectra generated the same results. The visible spectrum of amate was sensitive to the rate of energy transfer (Figure 5B). The natural logarithm of the diffuse reflectance at 481 and 670 nm showed a good fit with the first-order kinetic model (Figure 5C). This effect corresponds to degradation of β carotenoids and chlorophylls due to UV radiation exposition. Thermal degradation of β carotenoids, induced a similar behavior [30].

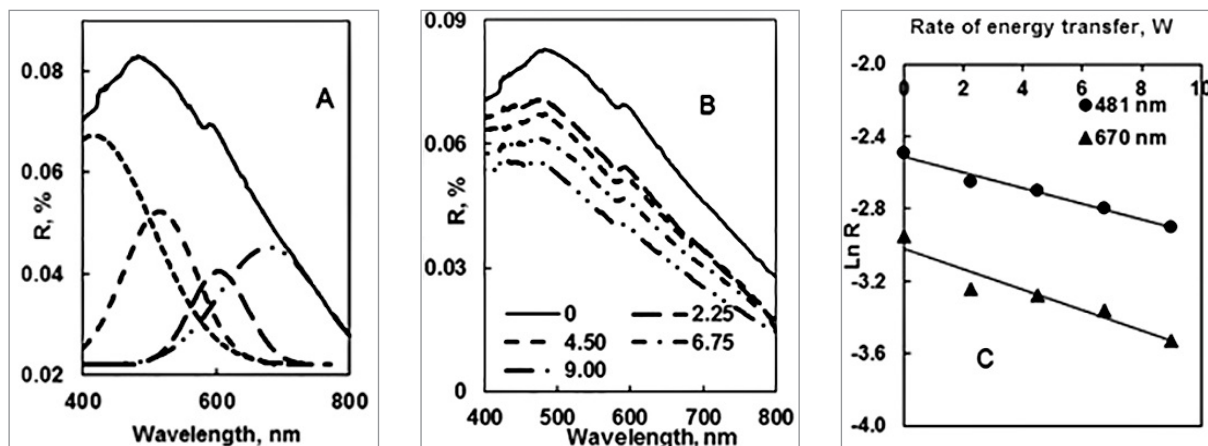


Figure 5. A: Deconvolution of Visible diffuse reflectance spectrum of amate paper. B: Visible diffuse reflectance spectra of amate paper, exposed from 0 to 9 W. C: Behavior of the Ln R as a function the rate of energy transfer at 481 nm (circles), $\text{Ln R} = -0.005 \text{ RET} - 2.5$ ($R^2 = 0.99$) and 670 nm (triangles), $\text{Ln R} = -0.006 \text{ RET} - 3$ ($R^2 = 0.96$).

The original kraft paper visible spectrum of diffuse reflectance changed when it was exposed to 2.25 W of UV radiation, mainly between 400 and 570 nm (region of green color) and less notably between 700 and 750 nm (region of red color) (Figure 6A). This effect may be explained by a color reversion of cellulose and the resulting increase in yellowness due to accelerated aging [8,31,32] and/or the presence of some additives. Above 2.25 W and up to 9 W, the spectra's intensity decreased (Figure 6A), possibly due to the degradation of dyes present in the kraft paper. These dyes were not identified; however, industrial coloring materials that are used for kraft paper and carton may be suggested [33]. Deconvolution of all the kraft paper visible spectra of diffuse reflectance revealed several maximum regions, specifically at 481, 527, and 718 nm; Figure 6B shows the spectrum corresponding to 2.25 W. The natural logarithm of the diffuse reflectance between 2.25 and 9 W showed a good fit with the first-order kinetic model (Figure 6C).

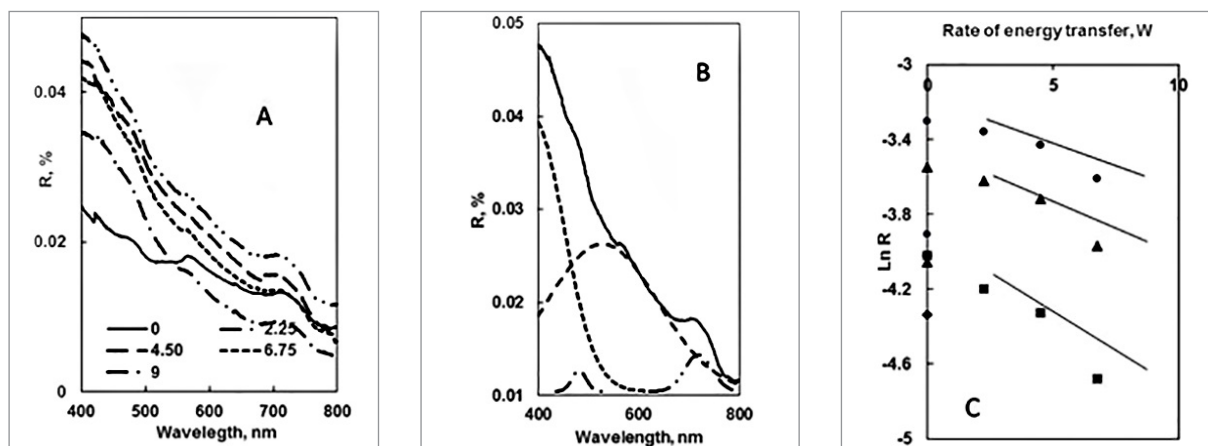


Figure 6. A: Visible diffuse reflectance spectra of kraft paper, exposed from 0 to 9 W. B: Deconvolution of the visible diffuse reflectance spectrum of kraft paper (exposed at 2.25 W). C: Behavior of Ln R as a function rate of energy transfer at 481 nm (circles): $\text{Ln R} = -0.004 \text{ RET} - 3.1$ ($R^2=0.92$), 527nm (triangles): $\text{Ln R} = -0.005 \text{ RET} - 3.4$ ($R^2=0.91$), and 718 nm (squares): $\text{Ln R} = -0.008 \text{ RET} - 3.8$ ($R^2=0.95$).

The results regarding color evaluation are found in Table V. The L^* parameter refers to lightness [100 = white, 0 = black]; according to this parameter, the order of non-irradiated papers is Whatman #1 = Bond > rice > kraft >> amate. The parameter a^* corresponds to the greenness-redness axis (a positive value indicates redness, and a negative one indicates greenness). The values for Whatman #1, rice, and kraft papers are slightly negative, that of bond paper slightly positive, and amate clearly tends toward the red direction ($a^* = 6$). The parameter b^* corresponds to the yellowness-blueness axis (negative values for blue and positive values for yellow). The b^* values for Whatman #1, bond, and rice paper are small. Kraft paper is yellow ($b^* = 8$), and the value of the brown amate paper is even higher ($b^* = 16$). In a study about Whatman paper, this sample was treated by washing, deacidification, immersion in methylcellulose and the CIEL a^*b^* color system showed lightness and yellowness due to these treatments [34]. None of these effects was observed for Whatman paper exposed to UV radiation in the present research.

$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$ expresses the colorimetric difference between the irradiated and original papers. Regarding the effect of UV irradiation, the parameters ΔL^* , Δa^* , Δb^* , and ΔE^* of white papers (Whatman #1, bond, and rice) were small and virtually did not change when the luminous intensity was increased to 9 W.

The kraft paper darkened slightly (negative values of ΔL^*) throughout the exposure to UV radiation, with a 2.25 W increase in yellowness ($\Delta b^* = 9.4$), and thereafter gradually decreased when the rate of energy transfer was increased to $\Delta b^* = 7.8$ with 9 W. The perception of this color difference is appreciated with the values of ΔE^* (Table V).

Table V. Results of colorimetric measurements of papers, originals and exposed to UV radiation.

Paper	Parameters	Rate of energy transfer, W					Mean values or intervals
		0	2.25	4.5	6.75	9	
Whatman #1	L^*	92					
	a^*	-0.04					
	b^*	1.1					
	ΔL^*		0.3	-0.1	0.3	1.1	0.4 ± 0.5
	Δa^*		0.004	-0.002	-0.04	-0.02	-0.01 ± 0.02
	Δb^*		0.5	0.4	0.7	0.6	0.6 ± 0.2
	ΔE^*		0.6	0.4	0.8	1.3	0.8 ± 0.4
Bond	L^*	92					
	a^*	0.3					
	b^*	0.6					
	ΔL^*		0.5	0.5	0.2	0.6	0.4 ± 0.2
	Δa^*		-0.5	-0.6	-0.6	-0.6	-0.6 ± 0.02
	Δb^*		1.7	1.7	1.7	1.5	1.7 ± 0.1
	ΔE^*		1.8	1.9	1.8	1.7	1.8 ± 0.1
Rice	L^*	87					
	a^*	-0.22					
	b^*	1.6					
	ΔL^*		1.6	1.9	2.1	2.5	2 ± 0.4
	Δa^*		-0.1	-0.1	-0.1	-0.1	-0.1
	Δb^*		1.3	1.0	0.5	0.8	0.9 ± 0.3
	ΔE^*		2.0	2.1	2.2	2.6	2.2 ± 0.2

Table V. Results of colorimetric measurements of papers, originals and exposed to UV radiation. (Continuation)

Paper	Parameters	Rate of energy transfer, W					Mean values or intervals
		0	2.25	4.5	6.75	9	
Kraft	L*	82					
	a*	-0.5					
	b*	8					
	ΔL^*		-2	-2	-2	-2	-2
	Δa^*		-0.07	0.00	0.10	0.10	0.03
	Δb^*		9.4	8.6	8.4	7.6	9.4 to 7.6
	ΔE^*		9.6	8.8	8.6	7.8	9.6 to 7.8
Amate	L*	61					
	a*	6					
	b*	16					
	ΔL^*		7.1	9.3	12.0	16.0	7.1 to 16
	Δa^*		-2.3	-1.5	-2.6	-3.7	-3 \pm 1
	Δb^*		1.4	5.3	2.0	-1.7	2 \pm 3
	ΔE^*		7.6	10.8	12.4	16.5	7.6 to 16.5

UV radiation gradually increased the amate paper lightness (ΔL^*), clarifying its color, and although no significant changes were observed in the values of the greenness-redness (Δa^*) and yellowness-blueness (Δb^*) axis (between 2.25 and 9 W), the colorimetric (ΔE^*) difference is important.

The colorimetric differences (ΔE^*) in kraft and amate paper were plotted as a function of the rate of energy transfer. Figure 7 shows that these colorimetric differences behave linearly with this parameter, negatively for the kraft paper, and positively for the amate paper.

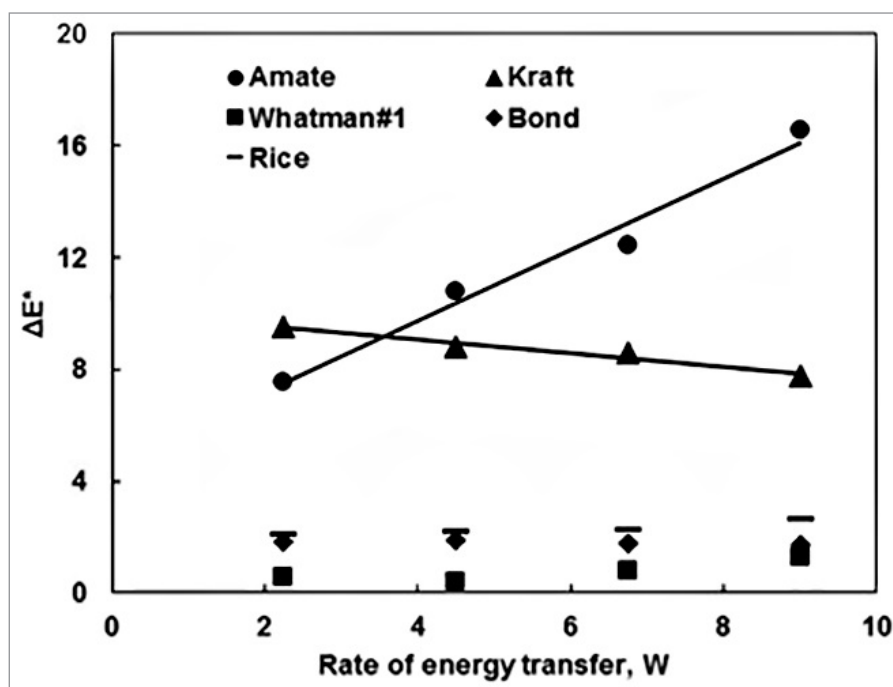


Figure 7. Colorimetric difference (ΔE^*) of the papers as a function the rate of energy transfer. For kraft: $\Delta E^* = -0.25 W + 10.1$ ($R^2 = 0.95$) and for amate: $\Delta E^* = 1.3 + 4.7$ ($R^2 = 0.98$).

As mentioned earlier, color was evaluated with the formula in the CIE Lab System, which is similar to NBS standardization. According to that standardization, the perception of chromatic difference is quite important for values of ΔE^* > 6, which was the case for amate and kraft paper. These results agree with those obtained by means of spectrometric measurements in the visible light region. The chromatic difference of amate paper emerged due to the degradation of the pigments (β carotenes and α chlorophyll), whereas chromatic differences in kraft paper appeared due to its non-identified dyes or the cellulose itself.

A study was conducted on color and degradation of kraft papers of various compositions and degrees of grinding [10]. When the paper was heated at 200 °C for 40 – 60 minutes, ΔE^* values were of the same order of magnitude as those found in the present study with UV radiation. Under these conditions, these authors obtained a ΔE^* close to 5 for Whatman#1. The value of this parameter for Whatman #1 in the present research was quite smaller (0.8 ± 0.4), which might mean that cellulose is virtually not affected by UV radiation of up to 9 W.

The colorimetric results of amate and kraft paper exposed to gamma radiation (see Table VI) were the following: A) The color of kraft paper with 3 kGy was clarified ($\Delta L^* = 7.1$) and this parameter had virtually the same value for 3, 9, and 15 kGy; on the contrary, changes in coloration (Δa^* and Δb^*) were virtually not observed. ΔE^* was equal to 7.2 ± 0.2 for the interval of gamma doses between 3 and 15 kGy. Even though the values of the perception of chromatic difference (ΔE^*) were smaller than those observed with UV radiation, they should be considered especially important. B) The amate paper increased in yellowness ($\Delta b^* = 4.9$) at 3 kGy, but the values of this parameter remained virtually the same for 3, 9, and 15 kGy, and no changes were observed for ΔL^* and Δa^* . ΔE^* was equal to 5.2 ± 0.5 . Even if it is lesser than ΔE^* for the UV radiation and < 6, it should be considered of medium importance.

Table VI. Results of colorimetric measurements of papers, non-irradiated and exposed to gamma radiation

Paper	Parameters	Dose, KGy				Mean values
		0	3	9	15	
Kraft	L^*	82				
	a^*	-0.5				
	b^*	8				
	ΔL^*		7.1	7.4	7.0	7.1 ± 0.2
	Δa^*		-0.2	-0.1	-0.1	-0.1
	Δb^*		0.9	1.0	1.1	1 ± 0.1
	ΔE^*		7.1	7.4	7.1	7.2 ± 0.2
Amate	L^*	61				
	a^*	6				
	b^*	16				
	ΔL^*		1.8	0.4	1.8	1.3 ± 0.8
	Δa^*		1.1	1.6	0.9	1.2 ± 0.4
	Δb^*		4.9	5.4	4.2	4.8 ± 0.6
	ΔE^*		5.3	5.7	4.6	5.2 ± 0.5

CONCLUSIONS

Neither the structure of the fibers, pH, nor the elemental chemical composition seemed to be affected by the exposure of the studied papers to up to 9 W of UV radiation. Cellulose (all papers), calcite (bond, rice, and kraft), whewellite (amate), and kaolinite (kraft) were the main components. These compounds remained unaltered after exposure to UV radiation. The FTIR spectra of the studied papers (irradiated and non-irradiated) did not show peaks corresponding to lignin, so they all lacked it. These results were like those found for papers irradiated with ≤ 15 KGy of gamma radiation [14].

The UV diffuse reflectance spectra of Whatman #1, rice, amate, and kraft paper (irradiated and non-irradiated) did not show any peaks. Only non-irradiated bond paper showed a specular effect in its UV spectra that was progressively reduced with exposure at > 6.75 W to be almost imperceptible. This effect is known as brightness reversion and may be considered as an effect of accelerated aging.

Only colored papers presented visible diffuse reflectance spectra. The spectra of amate paper showed peaks of β carotenoids and chlorophylls, which degraded by UV exposition, according to a first-order kinetic model. The kraft paper spectra changed greatly when the paper was irradiated at 2.25 W, showing a color reversion. This effect progressively diminished as a function of the rate of energy transfer, according to a first-order kinetic model. Spectra deconvolved into several peaks of unknown identity. Degradation of pigments may be interpreted as accelerated aging effects.

Colorimetric differences due to exposure to UV radiation were detectable in Kraft and amate papers. Non-irradiated kraft paper is yellow, it darkened slightly with 2.25 W but this effect gradually decreased at higher rate energy transfer. The non-irradiated amate paper is brown and gradually increased its lightness by UV exposition. Colorimetric differences of kraft and amate paper behaved linearly with the rate energy transfer.

When kraft and amate paper were exposed to gamma radiation between 3 and 15 kGy, the color of the kraft paper was clarified, and amate paper increased in yellowness. The perception of chromatic difference (ΔE^*) was smaller than that observed with UV radiation; however, they are still important, especially for kraft paper.

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Conflicts of interest

The authors declare that they have no conflicts of interest.

REFERENCES

1. Gurnagul, N.; Howard, R. C.; Zou, X.; Uesaka, T.; Page, D. H. *J. Pulp Paper Sc.*, **1993**, *19*, pp 160-160.
2. Casale, G. R.; Siani, A. M.; Palmieri, S.; Campanella, L. Spectral Changes of Paper Exposed to Ambient Solar Radiation. In: Panero, F. S.; Silva, H. E. B. (Eds) *Abstract book of 1st International Meeting on Chemometrics and Multivariate Analysis Applied to Cultural Heritage and Environment*. Nemi (RM), Italy, **2006**, pp 61-62.
3. Yatagai, M.; Zeronian, S. H. *Cellulose*, **1994**, *1* (3), pp 205-214.
4. Adamo, A. M.; Giovannotti, M.; Magaudo, G.; Plossi Zappalà, M.; Rocchetti, F.; Rossi, G. *Restaurator*, **1998**, *19* (1), pp 41-59.
5. Kolar, J.; Strlic, M.; Müller-Hess, D.; Gruber, A.; Troschke, K.; Pentzien, S.; Kautek, W. *Journal of Cultural Heritage*, **2000**, *1*, S221-S224 ([https://doi.org/10.1016/S1296-2074\(00\)00149-7](https://doi.org/10.1016/S1296-2074(00)00149-7)).
6. Cocca, M.; D'Arienzo, L.; D'Orazio, L. *Int. Scholarly Res. Not. Materials Science*, Volume **2011**, Article ID 863083, 7 pages (<https://doi.org/10.5402/2011/863083>).
7. Zervos, S.; Choulis, K.; Panagiaris, G. *Procedia-Social and Behavioral Sciences*, **2014**, *147*, pp 39-46 (<https://doi.org/10.1016/j.sbspro.2014.07.100>).
8. Zervos, S. Natural and accelerated ageing of cellulose and paper: A literature review. In: A. Lejeune; T. Deprez (Eds.). *Cellulose: Structure and properties, derivatives, and industrial uses*. Nova Science Publishers, Inc., New York. **2010**, Chapter 5, pp 155-203.
9. Area, M. C.; Cheradame, H. *BioResources*, **2011**, *6* (4), pp 5307-5337.

10. Urreaga, J. M.; Villar, J. C.; de la Orden, M. U. *O Papel* [ISSN:00311057], **2005**, 66 (2), pp 19-26 [Available at [ResearchGate](#)].
11. Binnqüist, C. L.; Quintanar-Isaías, A.; Vander Meeren, M. *Econ. Bot.*, **2012**, 66 (2), pp 138-148 (<https://doi.org/10.1007/s12231-012-9196-1>).
12. Na, N.; Ouyang, Q.; Ma, H.; Ouyang, J.; Li, Y. *Talanta*, **2004**, 64 (4), pp 1000–1008 (<https://doi.org/10.1016/j.talanta.2004.04.025>).
13. Fernández, I.; Delgado, F.; Ortiz, F.; Ortiz, A.; Fernández, C.; Renedo, C. J.; Santisteban, A. *Appl. Therm. Eng.*, **2016**, 104, pp 129-138 (<https://doi.org/10.1016/j.applthermaleng.2016.05.020>).
14. Jiménez-Reyes, M.; Tenorio, D.; Rojas-Robles, M.; García-Rosales, G. *Radiat. Phys. Chem.*, **2018**, 148, pp 13-18 (<https://doi.org/10.1016/j.radphyschem.2018.02.021>).
15. Asociación de técnicos de la industria papelera y celulósica. Argentina. *NOM IRAM-ATIPCA P3 118*, **1983**. Personal communication.
16. Sawoszczuk, T.; Wandelt, P.; Baranski, A.; Lagan, J. M.; Lojewski, T.; Perlinska-Sipa, K. Degradation of paper as studied by fiber length measurements after hydrodynamical treatment. In: Kolar, J.; Strlic, M.; Havermans, J. B. G. A. (Eds.). *Proceedings of the International Conference. Durability of Paper and Writing*, Ljubljana, Slovenia, **2004**, pp 78-80.
17. Silva, R.; González, J. *Ciencias Forestales*, **1998**, 12-13, pp 43-52.
18. Torres, J.; de Gutiérrez, R. M.; Castello, R.; Viscayno, C. *Rev. Lat. Metalurgia y Materiales*, **2010**, 31 (1), pp 35-43.
19. Korth, K. L.; Doege, S. J.; Park, S. H.; Goggin, F. L.; Wang, Q.; Gomez, S. K.; Liu, G.; Jia, L.; Nakata, P. A. *Plant Physiology*, **2006**, 141 (1), pp 188-195 (<https://doi.org/10.1104/pp.106.076737>).
20. Yang, H.; Yan, R.; Chen, H.; Lee, D. H.; Zheng, C. *Fuel*, **2007**, 86 (12-13), pp 1781-1788 (<https://doi.org/10.1016/j.fuel.2006.12.013>).
21. Morán, J. I.; Álvarez, V. A.; Cyras, V. P.; Vázquez, A. *Cellulose*, **2008**, 15 (1), pp 149-159 (<https://doi.org/10.1007/s10570-007-9145-9>).
22. Causin, V.; Marega, C.; Marigo, A.; Casamassima, R.; Peluso, G.; Ripani, L. *Forensic Sc. Int.*, **2010**, 197 (1-3), pp 70-74 (<https://doi.org/10.1016/j.forsciint.2009.12.056>).
23. Kline, L. M.; Hayes, D. G.; Womac, A. R.; Labbe, N. *BioResources*, **2010**, 5 (3), pp 1366-1383.
24. Pavithra, R.; Gunasekaran, S.; Sailatha, E.; Kamatchi, S. *Int. J. Curr. Res. Aca. Rev.*, **2015**, 3 (11), pp 42-59.
25. Robotti, E.; Bobba, M.; Panepinto, A.; Marengo, E. *Anal. Bioanal. Chem.*, **2007**, 388 (5-6), pp 1249-1263 (<https://doi.org/10.1007/s00216-007-1370-4>).
26. Lopez-Capel, E.; Sohi, S. P.; Gaunt, J. L.; Manning, D. A. *Soil Sc. Soc. of America J.*, **2005**, 69 (1), pp 136-140. (<https://doi.org/10.2136/sssaj2005.0930>).
27. Soto, N. A.; Machado, W. R.; López, D. L. *Quim. Nova*, **2010**, 33 (7), pp 1500–1505.
28. Dermanovic, I.; Mikocevic, Z. B.; Malcic, V. D.; Cosic, K. Surfactants influence on the paper optical characteristics exposed to ageing. *Annals of DAAAM & Proceedings*, **2008**, pp 375-377.
29. Lichtenthaler, H. K.; Buschmann, C. *Current Protocols in Food Analytical Chemistry*, **2001**, 1 (1), F4.3 (<https://doi.org/10.1002/0471142913.faf0403s01>).
30. Henry, L. K.; Catignani, G. L.; Schwartz, S. J. *J. Am. Oil Chemists' Soc.*, **1998**, 75 (7), pp 823-829 (<https://doi.org/10.1007/s11746-998-0232-3>).
31. Bukovský, V. *Restaurator*, **2000**, 21 (2), pp 55-76 (<https://doi.org/10.1515/REST.2000.55>).
32. Karlovits, M.; Gregor-Svetec, D. *Acta Polytechnica Hungarica*, **2012**, 9 (6), pp 81-100.
33. BTC-Europe. <https://www.btc-europe.com/es/ES/solution-finder/industria/industria-del-papel/papel-y-carton/materias-colorantes/pigments-and-dyes-for-speciality-colouration-in-paper-and-board/> [Accessed March **2020**].
34. Zervos, S. *Restaurator*, **2007**, 28 (1), pp 55-69 (<https://doi.org/10.1515/REST.2007.55>).