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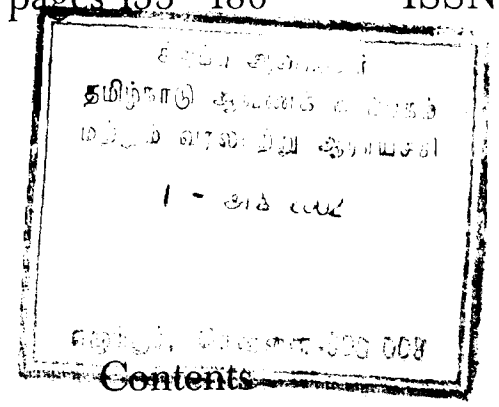

Contents

133: JOSÉ LUIZ PEDERSOLI JÚNIOR & FRANK J. LIGTERINK:
Spectroscopic Characterization of the Fluorescence of Paper at the Wet-Dry Interface

146: A. MOROPOULOU, S. ZERVOS & P. MAVRANTONIS:
Quality Control and Optimization of the Conservation Treatments Applied to the Material of the Archives of the Greek Communist Party

164: SIMONA MARGUTTI, GIUSEPPINA CONIO, SILVIA VICINI & ENRICO PEDEMONTE:
Paper Conservation Part II: Consolidation by Grafting of Acrylic Monomers

181: SVETLANA GURKINA & NATALIA REBRIKOVA:
Treatment of Parchment Fragments of a Hebrew Bible

Indexed in:
Chemical Abstracts
Current Contents
IBR (Internationale Bibliographie der Rezensionen wissenschaftlicher Literatur)
Information Science Abstracts
Library Literature
Library Science
Social and Educational Science Citation Index

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Spectroscopic Characterization of the Fluorescence of Paper at the Wet-Dry Interface

by JOSÉ LUIZ PEDERSOLI JÚNIOR & FRANK J. LIGTERINK

INTRODUCTION: THE PROBLEM

The development of brown stains on the surface of paper due to the local action of water is a well-known problem to those concerned with the preservation of paper-based objects. Cellulose-water interactions, leading to brown discoloration of the substrate, have been the subject of several investigations by the textile industry and the paper conservation field[1–5]. The formation of brown lines where wet-dry interfaces occur has been attributed to a combination of the transport and concentration of coloured cellulose degradation products, and chemical changes at the sites where water evaporates from the cellulose surface. Studies based on methylene blue absorption have indicated that cellulose undergoes oxidative reactions at the wet-dry interface[1]. The generation of free radicals due to mechanical stresses arising from humidity changes[6], the relatively higher concentration of peroxides and mono- and disaccharides detected at the interface[4,7], the increased mobility of those species in solution compared to solid-phase reactions and the greater accessibility to oxygen due to the swelling of the cellulosic fibres can be seen as possible factors promoting chemical changes at the wet-dry interface.

The effect of artificial ageing on the colour intensity, the solubility and the susceptibility of brown lines formed at the wet-dry interface to reducing bleaching has been assessed[5]. Whereas freshly formed lines display a lighter brown colour, are soluble in water and bleach relatively easily, aged lines are darker in colour, insoluble and do not bleach completely. This behaviour suggests the occurrence of condensation reactions yielding polymerised, insoluble brown substances.

The formation of brown lines at the wet-dry interface created with purified liquids and fibrous substrates in different combinations in the presence of oxygen has been observed[8]. Based on those observations it was concluded that the chemical changes taking place at the wet-dry interface in the cellulose-water system are an example of a more general phenomenon.

FLUORESCENCE

Similar to other browning phenomena such as foxing[9–12] and iron-gall ink corrosion[13,14], discoloration of paper at the wet-dry interface is accompanied by UV-fluorescence[4,5]. An apparently common occurrence observed with these phenomena is that fluorescence appears before discoloration. As the paper browns the fluorescence increases in intensity changing from white-blue to green-yellow. At a later stage, when discoloration has developed into dark brown stains, fluorescence can no longer be observed. It has been suggested that the formation of fluorescent species is an intermediate stage in the degradation process of paper that culminates in brown discoloration[15].

Examination under UV illumination is the common method used in conservation practice to assess changes in the fluorescence of paper. Interpretation and comparison of results are based on the perceived colour and intensity of fluorescence patterns seen under the UV-illumination, both of which depend on a subjective judgement, on the spectral characteristics of the UV source, and on various aspects of the surroundings that can affect colour judgement. A more accurate interpretation of the fluorescence of paper is possible by using spectroscopic analysis, where excitation and emission spectra can provide information on the chemical nature of the fluorescent species, as well as on the changes in intensity and spectral distribution occurring as degradation proceeds. The use of spectroscopic analysis to compare the fluorescence of paper observed in association to different phenomena (wet-dry interfaces, iron-gall ink-corrosion, foxing) also makes it possible to verify if the perceived fluorescence arises from a common fluorescent species or if there are different fluorescent species associated to each particular phenomenon.

Fluorescence spectroscopy has already been used to investigate foxing[9] and to track the degradation of paper submitted to artificial ageing[16]. The results reported in both cases showed a single emission maximum within the range of 420–450 nm (λ_{Ex} = 365 nm). The intensity of fluorescence increased in the course of artificial ageing, and the formation of new fluorescent species re-emitting in the green-yellow region of the visible spectrum was observed for an additive-free, bleached, chemical pulp paper.

The intention of this study is to characterise the fluorescence of paper at the wet-dry interface by using spectroscopy and to compare it to other types of degradation-related fluorescence reported in the literature. The nature of the fluorescent species is addressed in relation to identifying the mechanism responsible for the formation of a fluorescent tide line at the wet-dry interface.

Investigation into the molecular structure of fluorescent species in paper is currently under way. It is expected that this information will contribute to a bet-

ter understanding of the degradation processes of paper, in particular the development of brown discoloration accompanied by fluorescence, which may provide a basis for more comprehensive preservation actions.

MATERIALS AND METHODS

Wet-dry interface

A 12x12 cm piece of Whatman No.1 filter paper that had been acquired approximately three years ago, was suspended vertically and immersed in distilled water under room conditions to a depth of ca. 2 cm. The apparatus was left undisturbed for approximately 10 minutes, after which the water had risen by capillary action up the paper to a height of ca. 9 cm (Fig. 1). The paper was then removed from

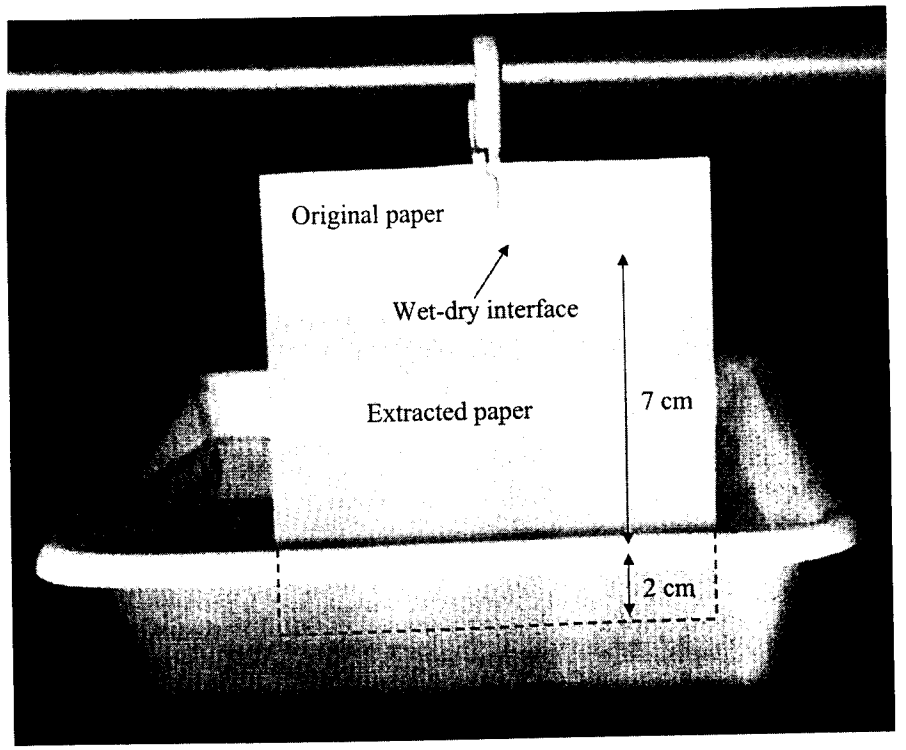

Fig: 1. Photograph showing a 12x12 cm piece of Whatman No.1 filter paper suspended vertically and immersed to a depth of ca. 2 cm in distilled water. The wet-dry interface and the areas, both below (extracted paper) and above (original paper) it, are indicated.

the water and allowed to dry. Drying was accomplished by leaving the paper suspended vertically in air under room conditions. Visible examination of the dried paper in daylight showed a faint brown discoloration of the surface at the wet-dry interface. Examination under UV illumination at 365 nm using a Spectroline® Super High Intensity black light lamp model SB-100/F (Spectronics Corporation, USA) revealed a distinct white-bluish, narrow fluorescent line across the paper coinciding with the tide line.

Under UV illumination the paper was then cut into three parts in the direction of the fluorescent line. The area above the fluorescent line provided a sample of original paper and the area below it provided a sample of extracted paper, the extract being in the middle strip, that containing the tide line. In order to prevent any oxygen induced changes on the fluorescent species present at the wet-dry interface, the strip of paper containing the tide line was sealed in a polyethylene bag in a nitrogen atmosphere, prior to analysis.

The same procedure was used to create fluorescent lines in 16 similar pieces of the same type of filter paper. Narrow paper strips (0.5–1.0 cm wide) containing the fluorescent lines were cut and soaked in 10 mL HPLC-grade water (Acros Organics) at room conditions for 30 minutes. The extract was filtered through a Millipore Millex-SR 0.5 µm filter unit prior to the analysis.

*Fluorescence spectroscopy**

Surface fluorescence measurements were carried out using a Perkin Elmer LS50 Luminescence Spectrometer. Paper samples were mounted onto a Front Surface Accessory, and the measurement geometry consisted of excitation at an angle of 60° and detection at an angle of 150° to the sample surface. Filters were used both directly after the light source and between the sample and the detector in order to remove stray light in the exciting radiation (Schott UG5 filter) and scattered light from the sample surface (built-in 390 nm filter). Excitation and emission slits were fixed at 2.5 nm, and the photomultiplier operated with an applied voltage of 900 V.

Measurements of the aqueous extract were performed with the same equipment using a Hellma 10 mm fluorescence cuvette and the standard 90° geometry.

* Fluorescent species have two characteristic spectra: the excitation spectrum and the emission spectrum. The former reflects the relative efficiency of different wavelengths of radiation shone on the fluorescent compound to cause fluorescence. The latter consists of the relative intensity of radiation re-emitted at various wavelengths by that compound. Fluorescence spectroscopy is based on the measurement of both excitation and emission spectra. For more details the reader is referred to reference 20.

Experimental conditions were identical to those used for the surface measurements.

Excitation spectra

Since the analysis of foxing on paper, as well as studies using artificially aged paper and photo-irradiated cellulose samples[17], have shown increased degradation-related fluorescence with emission maximum within the range of 440–525 nm, acquisition of excitation spectra on the surface of paper was performed by measuring the emission at 500 nm. The excitation spectrum of the aqueous extract produced from the fluorescent tide line was recorded with emission at 450 nm.

Emission spectra

Emission spectra were recorded using excitation radiation at wavelengths corresponding to the maxima observed in the excitation spectra.

The intensity of all spectra is expressed in arbitrary units.

RESULTS AND DISCUSSION

The excitation spectra recorded on the fluorescent tide line, as well as on the original and extracted paper, are shown in Fig. 2. Excitation maxima occurring at 260 nm, 340 nm, and 385 nm can be observed in all three spectra. Although the spectra exhibited practically the same spectral distribution of energy, the intensity of the spectrum recorded on the fluorescent tide line exceeded that of the other

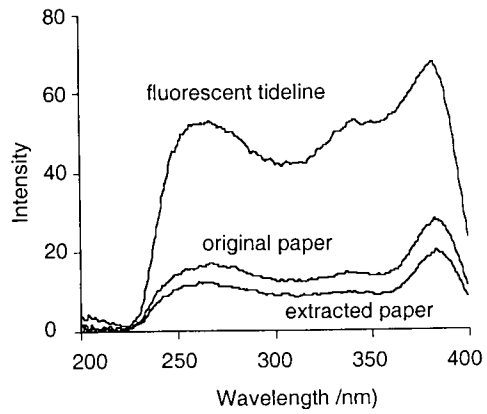

Fig. 2. Excitation spectra of original and extracted Whatman No.1 filter paper and of the fluorescent tide line formed at the wet-dry interface (λ_{Em} = 500 nm).

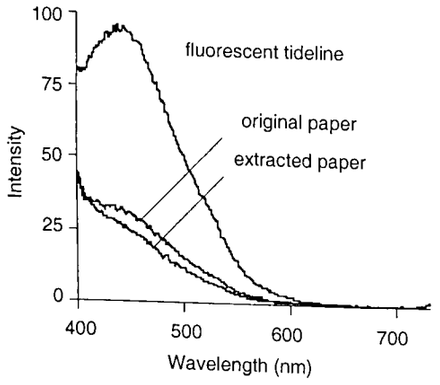

Fig. 3. Emission spectra of original and extracted Whatman No.1 filter paper and of the fluorescent tide line formed at the wet-dry interface (λ_{Ex} = 254 nm).

two spectra by a factor of approximately 3. Additionally, the intensity of the spectrum recorded on the area below the tide line, that is the extracted paper, was lower than that of the spectrum recorded on the original paper. These excitation spectra showed a close similarity to a typical fluorescence excitation spectrum recorded on foxing stains by Choisy et al.[9] within the wavelength range of 275–425 nm, which displayed a maximum at 395 nm and a shoulder at 340 nm.

Figs. 3 and 4 show the series of emission spectra recorded on the fluorescent tide line and on the original and extracted paper excited at 254 nm and 340 nm, respectively. Measurements taken at a wavelength of 380 nm were complicated by excessive stray light. A single maximum at 440 nm is observed in all six spectra in Figs. 3 and 4. The increase in intensity, displayed at the lower wavelength side of the spectra, can be attributed to the fact that the filter used to remove scattered light from the sample surface allowed some of the light in the range of ca. 400–430 nm to pass through it. Excitation at 254 nm and at 340 nm yielded emission spectra with virtually the same spectral distribution, the intensity of which was higher for the longer excitation wavelength. The absence of spectral changes when excitation was performed at different wavelengths and the relative purity of the spectra suggest that fluorescence was caused by light absorption and re-emission by a single chemical species. The existence of different fluorescent structures would have been revealed by changes in the spectral distribution of the emission spectrum depending on the excitation wavelength. The fluorescence exhibited by the original paper may be attributed to oxidative changes in the cellulose molecule as a result of processing and/or natural ageing[18]. The transportation of liquid water through the paper caused a decrease in fluorescence,

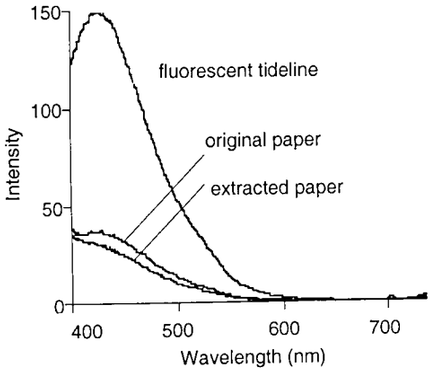

Fig. 4. Emission spectra of original and extracted Whatman No.1 filter paper and of the fluorescent tide line formed at the wet-dry interface (λ_{Ex} = 340 nm).

which indicated the existence of a water-soluble fluorescent compound that migrated as the water moved within the paper. Transport and concentration of this compound at the wet-dry interface is evident from the spectrum of the fluorescent tide line, which is very similar to that of the original paper – including the single maximum at 440 nm – but whose intensity is 3–4 times higher. The residual fluorescence observed from the extracted paper indicated that the concentration of the fluorescent species had decreased, but that it had not been completely removed. This could be a result of low solubility in water and of the different regions of the cellulosic fiber having varying accessibility to the water. It is also possible that the same fluorescent structure may be present in both low-molecular weight and water-soluble fragments of depolymerised cellulose as well as in the main cellulosic backbone. The latter would account for the residual fluorescence of the extracted paper.

Assuming that the increased fluorescence intensity (I_t) at the tide line is the result of a transport mechanism only and that the fluorescence efficiency remains constant, it should be expected that the ratio between the intensity increase at the tide line ($I_t - I_0$), where I_0 indicates the fluorescence intensity recorded on the original paper, and the intensity decrease below the tide line ($I_0 - I_b$), where I_b indicates the fluorescence intensity recorded on the extracted paper, is equal to the ratio between the length of the area below the tide line L_b (approx. 7 cm) and the length of the tide line area L_t (approx. 0.2 cm). The values of both ratios are listed in Table 1 for the two series of emission spectra. It can be seen that prediction and measurement have the same order of magnitude. It is therefore likely that the observed changes in fluorescence intensity were simply due to the trans-

Table 1. Comparison of theoretically expected and experimentally observed ratios for differences in fluorescent emission intensities recorded at the tide line and on the area below it. Ratios for both series of fluorescence spectra with excitation at 254 nm and 340 nm are shown.

λEx	Theoretical ratio (Lb:Lt)	Measured ratio (It - I0):(I0 - Ib)
254 nm	35	15.3
340 nm	35	17.3

port of a water-soluble fluorescent compound. Despite the correct order of magnitude, the measured intensity difference ratios are consistently a factor of two below the values predicted by the length ratio calculation. Within the scope of this simple experiment such a difference cannot be attributed to a single cause.

The development of fluorescence at the wet-dry interface of highly purified cellulose has been observed by Bone and Turner[1] and was attributed to chemical changes undergone by the polymer due to the increased activity of the cellulose-water-air system at that area. Since the present experiment was performed with Whatman No.1 filter paper that had not been subjected to any further purification treatment, and given the relatively short time during which the wet-dry interface occurred, our results can neither confirm nor reject the hypothesis of cellulose degradation caused by the action of water at the wet-dry interface. However, our results do indicate that even in the case of a recently produced additive-free paper, made of purest commercially available cotton linters, the formation of fluorescent tide lines can be explained by a simple transport mechanism.

The emission spectrum measured on the tide line shows a significant similarity to that observed for paper submitted to artificial ageing[16], as well as to the fluorescence associated to foxing stains on different papers[9]. Such results suggest that fluorescence arises from a major fluorescent species and that a common degradation mechanism mayoccur in the course of both natural and artificial ageing of paper, as well as in the development of foxing.

The excitation and emission spectra of the aqueous extract of the fluorescent tide line are shown in Figs. 5 and 6, respectively. Whereas the emission spectrum is equal to that recorded for the fluorescent tide line on the paper, the excitation spectrum only exhibited maxima at 255 nm and 325 nm. By simply comparing the excitation spectra recorded on the tide line and in solution it would seem correct to conclude that the reason for such a difference is the presence of a fluorescent species that is insoluble in water and therefore was not extracted from the paper. This is not true, however, since it is obvious from the comparison of the excitation spectra recorded on the tide line and on the original paper that the intensity of absorption at 385 nm increased by the same ratio as the other two

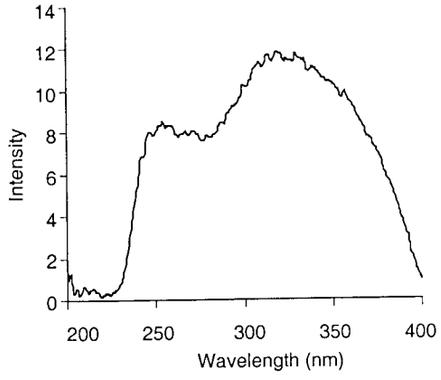

Fig. 5. Excitation spectrum of the aqueous extract of the fluorescent tide line formed at the wet-dry interface of Whatman No.1 filter paper (λ_{Em} = 450 nm).

maxima (at 254 and 340 nm), which indicates that the species giving rise to fluorescence due to light absorption at that wavelength has been transported by water to the tide line. The fact that the ratio of the intensities of excitation maxima remained the same for the different spectra also indicates the absence of instrumental artefacts such as the presence of stray light. A possible explanation for the difference between the excitation spectra recorded in solution and on the paper matrix, would be the presence of a water-insoluble, non-fluorescent chromophore that absorbs light at 385 nm and then excites the fluorescent species within the paper matrix by energy transfer (e.g. carbonyl groups bonded to the cellulose molecule).

The emission spectrum shown in Fig. 6 confirms that the enhanced fluorescence observed at the wet-dry interface is at least partially due to the presence of a water-soluble, fluorescent compound within the paper, which is transported to that area by water. The lower fluorescence intensity observed in solution could be ascribed to a number of factors including a lower concentration in the extract and different molecular environments. The sensitivity of fluorescence to the environment of the chromophore arises from the relatively long lifetime of the excited singlet state of the fluorescent species before de-excitation. Whereas the energy absorption process is of the order of magnitude of 10^{-15} second, during which the fluorescent species and its environment remain effectively static, the lifetime of a singlet state is considerably longer, within the order of magnitude of 10^{-9} to 10^{-8} second. Several processes may occur during this time, including local conformational changes, solvent-cage relaxation, protonation or deprotonation and bimolecular collisional quenching, which will significantly affect the fluores-

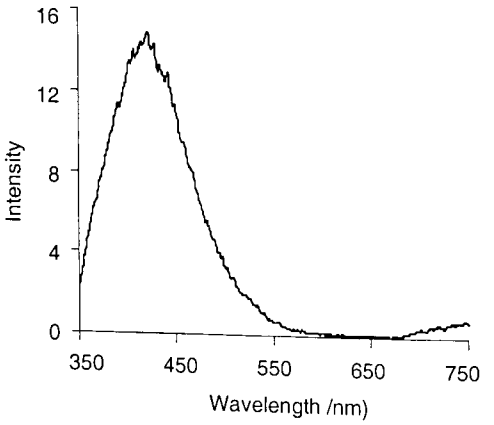

Fig. 6. Emission spectrum of the aqueous extract of the fluorescent tide line formed at the wet-dry interface of Whatman No.1 filter paper (λ_{Ex} = 310 nm).

cence spectrum. For example, a number of fluorescent molecules are known to have their fluorescence very strongly quenched in aqueous solutions, whereas in a rigid environment a striking enhancement is observed[19].

Conclusion

The spectroscopic characterisation of fluorescence at the wet-dry interface in Whatman No.1 filter paper showed excitation maxima at 260, 340, and 385 nm (λ_{Em} = 500 nm), and a single emission maximum at 440 nm (λ_{Ex} = 254 and 340 nm). Transport and concentration of a water-soluble, fluorescent compound contributed to the formation of a fluorescent tide line at the wet-dry interface. Because Whatman No.1 is an additive-free paper, made of purified cotton linters, the fluorescent species is likely to be a cellulose degradation product formed in the course of manufacturing and/or during natural ageing of the paper.

The results also indicated that if oxidative degradation of cellulose at the wet-dry interface, yielding fluorescent species, did occur within the time-scale of the experiment, the chromophoric structure of the reaction products should be equivalent to that of the already existing fluorescent compound.

The spectral similarity between the degradation-related fluorescence of paper observed in relation to the wet-dry interface, foxing stains and artificial ageing, suggests a common degradation mechanism at some level. It is possible that the fluorescent species is a product of hydrolytic and/or oxidative reactions of cellulose, which invariably take place in the course of degradation promoted by different factors. Subsequent oxidation and condensation reactions undergone by that fluorescent species may contribute to the discoloration of paper.

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Summaries

Spectroscopic Characterization of the Fluorescence of Paper at the Wet-Dry-Interface

Changes in the fluorescence of an additive-free cotton cellulose paper in which a wet-dry interface has been created by capillary action using distilled water under static air have been characterised spectroscopically. Fluorescence was measured on the surface of the paper at the wet-dry interface, where a fluorescent tide line developed. Measurements were also carried out on the areas both above (original paper) and below (extracted paper) the wet-dry boundary. The fluorescence spectra recorded on the three different areas showed the same spectral distribution with excitation maxima at 260, 340, and 385 nm (λ_{Em} = 500 nm), and a single emission maximum at 440 nm (λ_{Ex} = 254 and 340 nm). The intensities of the spectra recorded at the wet-dry boundary were approximately three times higher than those recorded on the original paper. Furthermore, a decrease in fluorescence intensity was observed for the extracted paper in comparison to the original paper. These results show that the migration and concentration of a fluorescent compound already present within the paper contributed to the enhanced fluorescence observed at the wet-dry interface. Spectroscopic analysis of the aqueous extract of the fluorescent tide line confirmed the presence of a water-soluble fluorescent compound. The results of this study are discussed in relation to the more general phenomenon of fluorescence accompanying the discoloration of paper.

Description spectroscopique de la fluorescence du papier observée à l'interface entre le sec et l'humide

Du papier en cellulose pure a été plongé verticalement à une profondeur de 1 cm dans de l'eau distillée de façon à ce qu'une montée capillaire de l'eau se produise dans le papier avec formation d'une interface entre le sec et l'humide. Une analyse spectroscopique a démontré des changements de fluorescence à la ligne de démarcation entre le sec et l'humide. L'analyse a porté également sur la surface du papier située au-dessus (papier original) et au-dessous (papier plongé dans l'eau) de cette ligne frontière sec/humide. Les spectres de fluorescence enregistrés sur les trois endroits indiquent la même distribution spectrale avec une intensité maximale à 260, 340 et 385 nm (λ_{Em} = 500 nm), et une autre émission maximum à 440 nm (λ_{Ex} = 254 et 340 nm. L'intensité des spectres mesurés à l'interface sec/humide est environ trois fois plus forte que celle obtenue sur le

papier original, celle du papier plongé dans l'eau distillée est inférieure à celle du papier original. Ces résultats démontrent que des substances fluorescentes qui étaient contenues dans le papier ont migré vers l'interface entre le sec et l'humide et s'y sont concentrées, contribuant ainsi à augmenter l'intensité de la fluorescence à cet endroit. Une analyse spectroscopique de l'extrait aqueux prélevé à cette ligne d'interface a confirmé la présence de substances fluorescentes solubles dans l'eau. Les résultats de cette étude font l'objet de discussions dans le domaine plus général de la fluorescence observée dans le jaunissement du papier.

Spektroskopische Beschreibung der in Papier an der Grenzfläche zwischen Naß und Trocken zu beobachtenden Fluorescence

Reines Baumwollpapier wurde senkrecht hängend bei Raumatmosphäre 2 cm tief in destilliertes Wasser getaucht, so daß Wasser kapillarisch in das Papier aufstieg und daß sich eine Naß-Trocken-Grenzfläche ausbildete. Die spektroskopische Untersuchung ergab Fluoreszenz an der Linie, die den Übergang von Naß zu Trocken markierte. Auch der Bereich darüber (= unverändertes Papier) und darunter (= von Wasser durchzogenes Papier) wurde untersucht. Die Fluoreszenzspektren der drei Bereiche zeigen eine gleiche spektrale Verteilung mit Anregungsmaxima bei 260, 340, and 385 nm (λ_{Em} = 500 nm), und ein einziges Emissionsmaximum bei 440 nm (λ_{Ex} = 254 and 340 nm). Die Intensität der an der Naß-Trocken-Grenzfläche gemessenen Spektren ist rund dreifach höher als die des unveränderten Papiers: die des wasserdurchzogenen Papiers ist geringer als die des unveränderten. Daran ist zu erkennen, daß in dem Papier fluorenzierende Substanzen vorhanden waren, die von dem Wasser an die Naß-Trocken-Grenzfläche transportiert wurden und sich dort in hoher Konzentration ansammelten. Eine spektroskopische Analyse des diesem Bereich entnommenen Extraktes bestätigte das Vorhandensein von wasserlöslichen fluoreszierenden Substanzen. Die berichteten Ergebnisse werden in Zusammenhang gestellt mit der allgemein zu beobachtenden Fluoreszenz im Bereich von braunen Verfärbungen in Papier.

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Quality Control and Optimization of the Conservation Treatments Applied to the Material of the Archives of the Greek Communist Party*

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INTRODUCTION

This study presents the quality control of the conservation treatment applied to the paper of the Archives of The Greek Communist Party (KKE), mainly of the deacidification treatment with calcium hydroxide solution in water after it had suffered a serious flood. It also aims to suggest a reliable, simple and relatively inexpensive procedure for the quality control of interventional conservation treatments in general, which can be carried out in a more or less well organized archival institution or library.

The methodology and the methods used for the evaluation of conservation treatments on paper originate from the paper industry[1]. Table 1 presents the most common tests. In the majority of such studies, a large number of time consuming and expensive tests are carried out. Folding endurance and tensile properties in both machine and cross direction, together with bursting strength, are very often used for the evaluation of the mechanical properties of paper. The results are often contradictory and confusing.

It has been suggested[2] that a limited number of tests in one direction only of a paper sample should be applied. For the purposes of this study therefore, only one mechanical, one chemical and one optical fundamental property was investigated. Complementary to these, a fibre optic microscope was used to examine the structural properties of the paper and the precipitation pattern of the chosen deacidification agent.

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Table 1: The most common tests used for the evaluation of paper conservation treatments.

	Method	ISO	Other related standards
1	Tearing Resistance	1974	CPPA D. 9; TAPPI T 414 m-49
2	Folding endurance	5626	CPPA D. 17P; TAPPI: T511 423 su-68
3	Tensile Properties:	1924-1	CPPA D. 34; DIN 63112; TAPPI T494
	1 Constant load,	1924-2	
	2 Constant elongation		
4	Bursting strength	2758	TAPPI T403 m-55
5	Tensile post fold		
6	Zero span tensile strength		
7	ISO Brightness	2470	CPPA E. 1
8	Colorimetry (CIE Lab)		ASTM D 2244 - 93
9	Water absorption	5637	
10	pH of aqueous extracts cold or warm extraction	6588	CPPA G. 25P; TAPPI: T435 om 88, T509, T-428; ASTM D-542; DIN 53124; NEN 2151
11	Alkali reserve	10716	TAPPI T 428; ASTM: D 548, D 4988 – 89; ANSI PH 1.53 - 1978
12	Kappa number	302	
13	Intrinsic viscosity of cellulose (DP)		ASTM 1795 – 90 Afnor NFT 12-005
14	SEM (Scanning Electron Microscope) EDX (X-Ray Microanalysis)		
15	FTIR (Fourier Transformation Infra Red Spectroscopy)		
16	Water soluble Cl^- (Potentiometric titration)	9197-1	
17	TLC (Thin Layer Chromatography)		
18	Fibre furnish analysis Staining guide optical microscopy	9184,1-7	TAPPI: T401om-88;T263 om-82, T259 om-33; ASTM D1030
19	Carboxyl content		ASTM 1926 - 89
20	Copper number (i cu)		Afnor NFT 12-004; TAPPI T 430; ASTM D919
21	Lignin content		TAPPI T 222
22	α-cellulose content		TAPPI: T 203 os-74, T-429; ASTM D-588
23	Accelerated ageing	5630, 1-4	TAPPI T 453 ts-63; ASTM D 776
24	Conditioning (23°, 50%)	187	ASTM D685-87; TAPPI T 402
25	Grammage determination	536	
26	Dry matter determination	287	
27	Moisture content		ASTM D1348-89
28	Thickness		TAPPI T411

THE KKE ARCHIVES

The Historical Archives of The KKE (The Greek Communist Party) are housed in the headquarters of the party at Perisos, Athens. They consist of about 30,000,000 pages and include every kind of written and printed material: books, newspapers, periodicals, pamphlets, propaganda sheets, posters, manuscripts, mimeograph prints, letters, ledger books etc, spanning from the beginning of the 20th century to the present day.

In October 1994, as the result of a heavy rainstorm, the basement of the headquarters of The KKE, where the Archives were kept, was flooded. Mud and refuse, washed by the rain, covered the material of the Archives threatening to completely destroy the whole collection.

Six years have passed since then and the situation today is completely different. Conservation treatments and preservation measures have been implemented, triggered by the flood, in order to save the Archives. The Sector of Material Science and Engineering (SMSE) of the Chemical Engineering Faculty of the National Technical University of Athens undertook the planning. Recognizing that the most important internal factor accelerating the ageing of paper is its acidity, deacidification was proposed as the main paper conservation treatment intended to stabilize it.

It should be remembered that there were no specialized personnel available and that any treatment would rely on volunteers. Therefore, the chosen method had to be easy to apply, not implementing sophisticated chemicals and equipment. To this end, the most feasible deacidification method, with its simple application and low cost, appeared to be treatment with calcium hydroxide solution in water.

Directly after the flood, the wet and soiled material was placed in freezers (-10°C) to avoid fungi growth. When decisions had been made and everything was ready for coping with the situation, material was taken out of the freezers in batches, washed to remove the worst of the mud, air-dried and disinfected with T-gas (ethylene oxide 90%, carbon dioxide 10%). Microbiological examination confirmed that after disinfecting any fungi present had been destroyed. All the material of the Archives has been subjected to these stages and is now securely stored in a specially designed room (600 m^2), which is air conditioned (RH = 50–60%, T = 16–18°C) and ventilated. A significant part of it has already been deacidified (over 15%).

The treatment procedure[3] is as follows:

- Prewashing in lukewarm (up to 40°) running tap water, for at least 45 min, until the water stops becoming yellow.
- Immersion in a saturated calcium hydroxide ($Ca(OH)_2$) solution in water for 20 min.

- Air-drying.
- Random pH testing (cold extract; desired pH between 8–8.5).
- The treated paper is then stored in archival quality envelopes and kept in the specially designed room.

This procedure is applied to batches of paper in large stainless steel (inox) vats. A plastic grid is used to support the fragile wet paper during wet treatment and drying.

EXPERIMENTAL

Samples

It was decided that blank historic paper should be used as sample material. Paper with text can be weaker at the places where it has been printed or written, resulting in unreliable strength measurements. This problem was encountered by Green[4]. Initially, 72 leaves of paper (size A4 or equivalent quantity) were requested from the KKE, to be taken from three different time periods. This request was not met, because it was not possible to find sets of eight sheets of paper of identical quality as samples in all the periods. Finally, the Archives of The KKE provided 30 leaves of paper. They comprised four sample sets from four different decades (A (1935), B (1940), C (1950) and D (1965) series). The quality of the paper of each series was identical. This was ensured by taking the eight leaves of a series from the same archival file and verified by macroscopic observation. Unfortunately, not all of the paper provided by The KKE could be used as samples. There was also not enough paper for the number of samples needed. The paper from the margins of three books, contemporary to the Archives of The KKE was therefore used as additional samples (E (1909), F (1944), and G (1956) series). The paper of the sample series A, B, C and D was of poor quality and in poor condition, not uniformly coloured, badly stained, creased and discoloured. In contrast, the paper of series E, F and G was uniformly coloured, of medium quality and in better condition. Some samples in good condition were necessary to measure folding endurance. Mechanical properties could not be reliably measured by non-uniform samples.

TECHNIQUES AND METHODOLOGY

The basic concept behind every work attempting to evaluate the efficacy of methods and materials used in paper conservation is the comparison of the degradation

rate of the mechanical, chemical and optical properties of treated and untreated paper over the course of time[2]. In order to make this comparison possible and extract conclusions without having to wait for many years so that the properties of the treated and untreated paper can be assessed, a method of accelerating the ageing of the paper is necessary.

In this study, dry accelerated ageing at 105°C was chosen (ISO 5630-01)[5], mainly because of the convenience of its application[2]. A simple desiccator was adjusted at 105±2°C and the paper samples were hung from wires, leaving a space of at least 1 cm between them for the air to circulate evenly. According to the literature three days of accelerated ageing is the minimum length of time to produce measurable changes in the properties of most kinds of papers[5]. A period of three days accelerated ageing seemed to be an appropriate choice for this study. However, as the colorimetry test showed, the treated and untreated samples had not differentiated sufficiently after that period. It was decided, therefore to continue the ageing process for another three days, after which time the colorimetry results were satisfactory. Colorimetry was used as an indicator of the efficacy of accelerated ageing because it was the only non-destructive method available that could give information about the chemical degradation of the samples.

Three paper properties were selected for comparison before and after accelerated ageing[6]:

- Mechanical properties: Folding Endurance (ISO 5626)[7]. FE was selected because it represents paper usability better than other mechanical properties. Furthermore, it is very sensitive to accelerated ageing[5]. A Köhler-Molin instrument made by Lorentzen & Wettres was used. The samples were left to acclimatize for 24 h in the testing room before measurements were taken. The load was 7.85 N (800 gr). 10 strips (10 x 80 mm) were cut in whichever direction of the paper sheets (machine direction or cross direction) that could give the most strips. A significant quantity of paper of some sheets (from sample series A, B, C and D) had to be rejected, as it was unusable because of holes, creases and rust stains. All the measurements of the same series were taken in the same direction.
- Chemical Properties: pH of cold aqueous extract (ISO 6588)[8]. pH was selected since it is the chemical property that mostly influences the ageing stability of paper. The paper strips used in the previous test were reused for measuring the pH. 2 gr (oven dry basis) of paper were cut into small pieces (5x5 mm), weighed (0.01 gr precision) and extracted for an hour with 100 ml of twice distilled water (Merck).
- Optical Properties: L* and b* coordinates of the CIE L*a*b* (1976) colour system[9].

Table 2: The samples according to their processing.

Process Leaves	1st group R: Reference 1 & 2	2nd group A: Aged 3 & 4	3rd group T: Treated 5 & 6	4th group TA: Treated and aged 7 & 8	Pulp type
A (1935)	AR	AA	AT	ATA	MP mechanical pulp
B (1940)	BR	BA	BT	BTA	MP: mechanical pulp
C (1950)	CR	CA	CT	CTA	CP: Chemical pulp
D (1965)	DR	DA	DT	DTA	MP: mechanical pulp
E (1909)	ER	EA	ET	ETA	CP: Chemical pulp
F (1944)	FR	FA	FT	FTA	CP: Chemical pulp
G (1956)	GR	GA	GT	GTA	CP: Chemical pulp

Aqueous treatments of paper result in the washing and removing of coloured degradation products, thus increasing the brightness and reducing the yellowness (cleaning). On the other hand, alkaline catalyzed lignin oxidation – occurring in the highly alkaline deacidification bath (pH ≈ 12) – produces coloured compounds (such as stilbenes and quinones[10]) that absorb blue light, thus giving paper a yellow hue and reducing brightness. Ageing too, natural or accelerated, produces yellow-brown compounds (by direct oxidation of the paper components or by oxidation of the cellulose, lignin and hemicelluloses degradation products), which also contribute to an increase in yellowness and reduction in the brightness of paper. For these reasons, L* (luminance or lightness, equivalent to brightness) and b* (position on the blue-yellow axis, indicating the degree of yellowness) coordinates of the CIE L*a*b* colour system are considered of major importance because they quantify the above-mentioned trends.

A Dr. Lange Colour Pen LMG 159/160 colorimeter with precision ±0.1 was used. For the uniformly coloured samples (E, F, G series), the average of 5 measurements from specific book pages is presented. For the non-uniformly coloured samples (A, B, C and D series), 5 measurements were taken in two specific spots of every paper leaf (α and β). In order to specify accurately the spots, masks were cut from plain photocopy paper and applied to the samples. The tip of the colorimeter was traced with pencil on the masks .

Phloroglucinol spot test (Ref.1 p. 377) was carried out to categorize the samples according to the kind of the pulp used in their manufacture (Table 2). A positive test (a red colour) indicated the presence of lignin, which is a major constituent of mechanical pulps. A negative test indicated no detectable quantities of lignin, and meant that the paper was made of chemical pulp.

In order to determine how the deacidification agent was deposited, a fibre optics microscope (FOM) was used. FOM is a small, portable video camera. Lenses of various magnifications (from x10 to x600) can be used with it. It can be con-

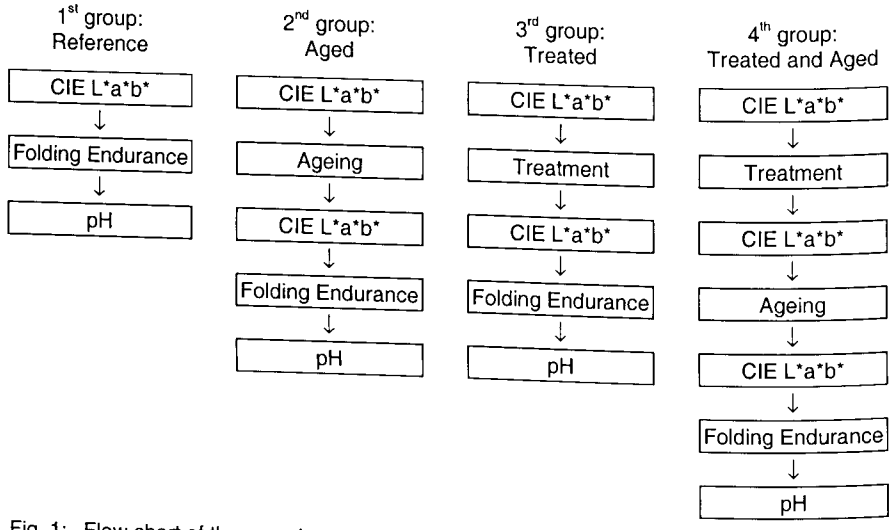

Fig. 1: Flow chart of the experimental procedure.

nected to a P/C via a video capture interface and the pictures taken can be saved as a compressed *jpg image file*, enabling further processing[11, 12]. FOM has been used in the laboratory of the Sector of Material Science and Engineering (SMSE) to evaluate cleaning treatments and consolidation of architectural surfaces. This was the first time it had been used to evaluate paper conservation treatments.

Each series of samples was divided into four groups:

- Reference = untreated;
- Aged;
- Treated;
- Treated and Aged.

Because the paper available was scarce, the same sample was used for several measurement. Details are given in Fig. 1. The treatment, i.e. deacidification procedure as described previously was done at the conservation laboratory of the Archives of KKE.

Results

Fiber optic microscope

The fibre optic microscope has been proved to be a very efficient tool for the structural examination of paper, offering sufficient magnification and convenience of use since it is portable and samples need no preparation.

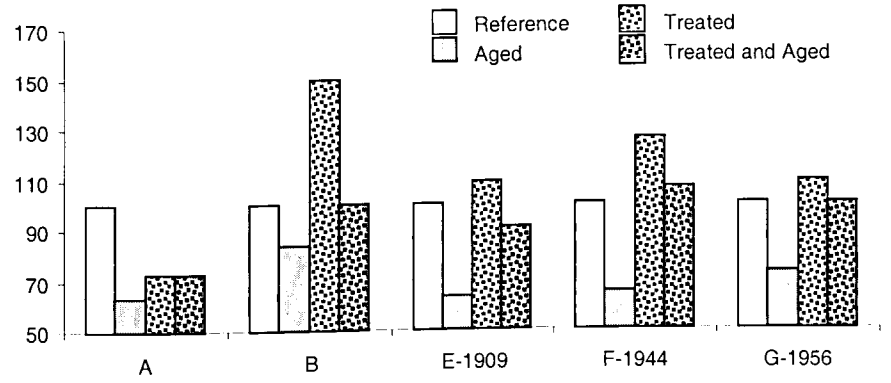

Fig. 2: Number of double folds, normalized (Reference = 100).

All FOM pictures showed that a part of the alkaline reserve was deposited unevenly as large crystals on the surface of the paper. This was considered to be a disadvantage since it meant that the deacidification agent had not been uniformly distributed, and there was a danger that the large crystals could cause abrasion on the surface. An uneven distribution of the deacidification agent could create areas that would be more vulnerable to acid hydrolysis in the future. Thus, differences in colour and strength could develop.

Folding endurance

Loss of strength due to ageing was found to be greater for the untreated samples. Four out of five samples exhibited increased strength, compared to the reference samples as a direct result of the treatment. This most probably happens because of the rearrangement of the cellulose chains and the regeneration of the broken hydrogen bonds among them[13].

The sensitivity of the method towards accelerating ageing was reconfirmed. According to Fig. 2, the behavior of the samples exhibited satisfactory differentiation and therefore conclusions could be drawn.

pH

Deacidification increased the pH of the samples from 1.5 to 3.5 units (Fig. 3). The pH values measured after deacidification did not exceed 8.5. pH 8.5–9 was considered to be the threshold where the alkaline catalyzed autoxidation of cellulose starts[14]. Ageing caused only a slight decrease in pH, leaving it in the alkaline region.

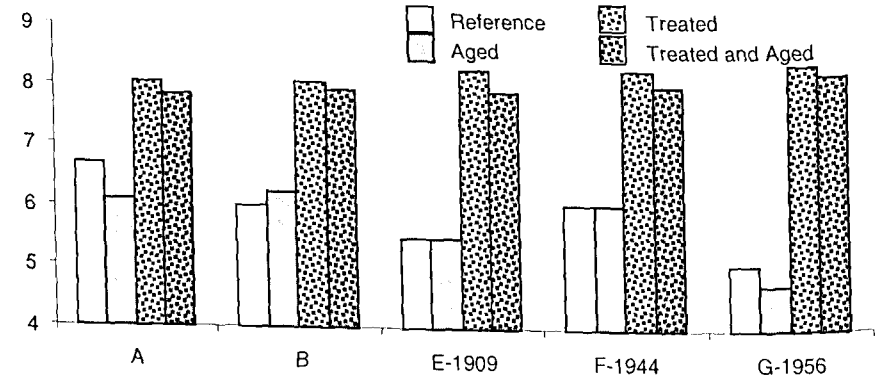

Fig. 3: pH.

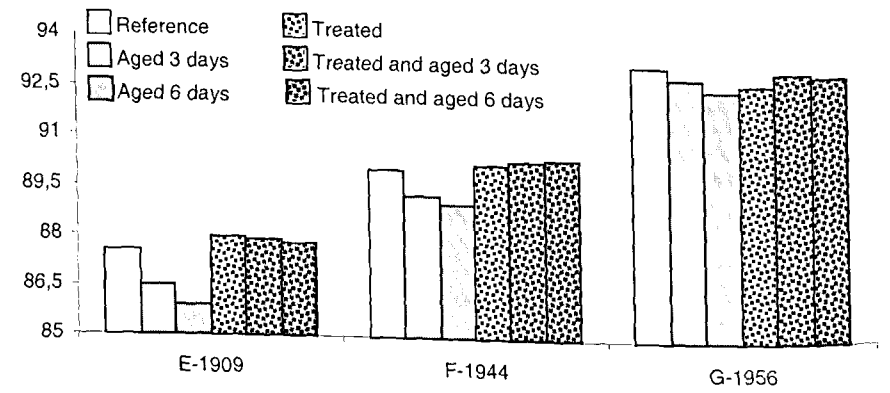

Fig. 4: Lightness (CIE L* value) of samples E, F and G (chemical pulp).

Colorimetry (CIEL*a*b*)

The rate of the decrease in lightness (L*) and the increase in yellowness (increase of b*) – ageing rate – was less for the deacidified samples (Figs. 4, 5, 6, 7).

Comparison of L* and b* between "Reference" and "Treated" in Figs. 4 and 5, which show the immediate results of the deacidification on the colour of the samples made of chemical pulp, indicates that as far as L* is concerned there was no significant change. On the other hand, the decrease of b* indicates that coloured degradation compounds have been removed (cleaning).

Fig. 8 shows the lightness of sample B (made of mechanical pulp) before and after deacidification. It indicates that lightness increased at places where rust stains were evident, since water removes coloured substances and that lightness decreased elsewhere because of the oxidation of lignin in the highly alkaline de-

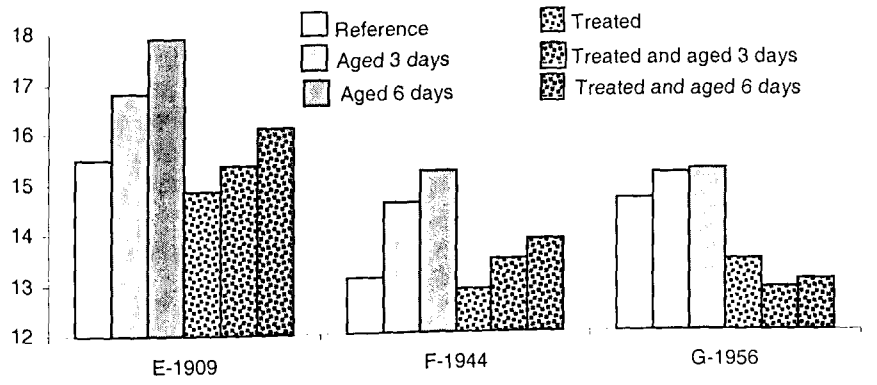

Fig. 5: CIE b* coordinate of samples E, F and G (chemical pulp).

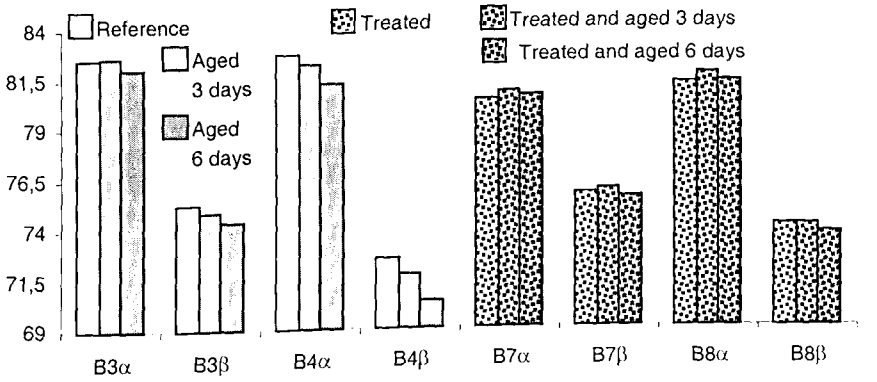

Fig. 6: Ageing rate of sample B (mechanical pulp) as indicated by the reduction of CIE L*. For α and β cf. p. 151.

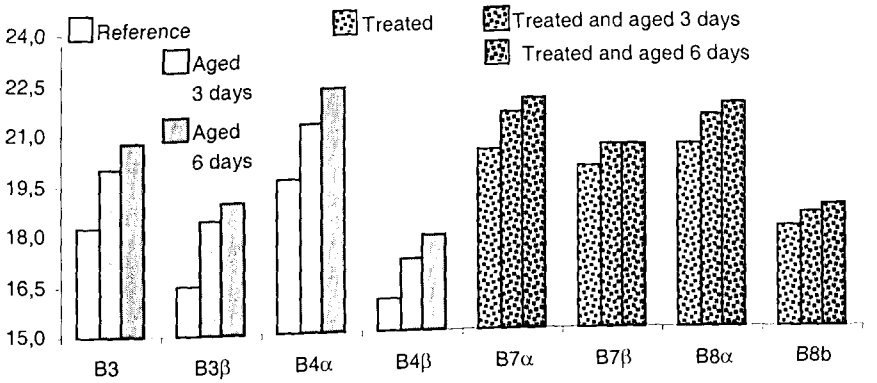

Fig. 7: Ageing rate of sample B (mechanical pulp) as indicated by the increase of CIE b*. For α and β cf. p. 151

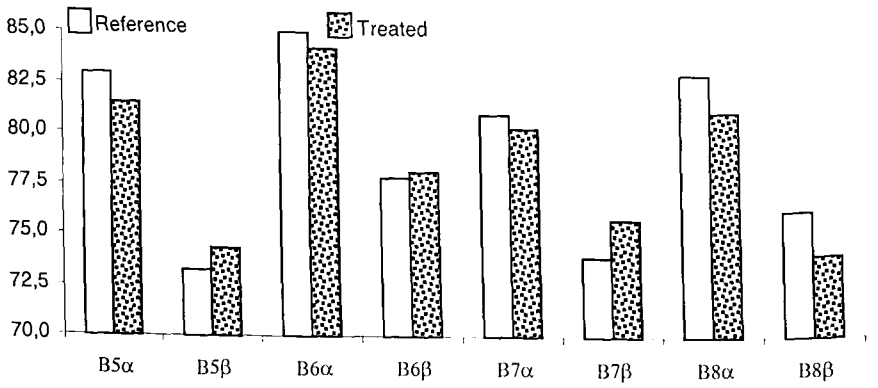

Fig. 8: Effect of deacidification on the lightness (CIE L* value) of sample B (mechanical pulp). B5β, B6β and B7β represent rust stains.

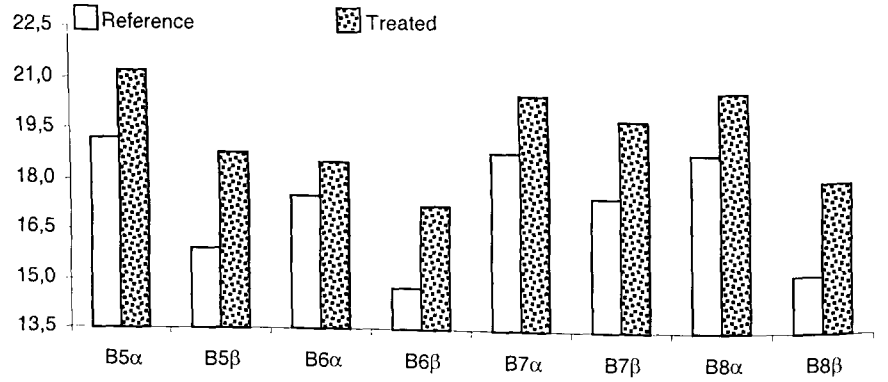

Fig. 9: Effect of deacidification on the CIE b* coordinate of the sample B (mechanical pulp). B5β, B6β and B7β represent rust stains.

acidification bath. The oxidation of lignin was responsible for the overall yellowing of the sample (increase of b*, Fig. 9). The samples A and D (not presented) displayed the same behaviour as sample B.

ELABORATION OF RESULTS BY PRINCIPAL COMPONENT ANALYSIS

Principal Component Analysis (PCA)[15] was used in order to examine if the variables measured in this study were statistically correlated. The computer program STATGRAPHICS PLUS for Windows (version 2.1) was used for the extraction of the Principal Components. The same program was used for the calculation of the correlation coefficient. Although not a routine method for data statistical analy-

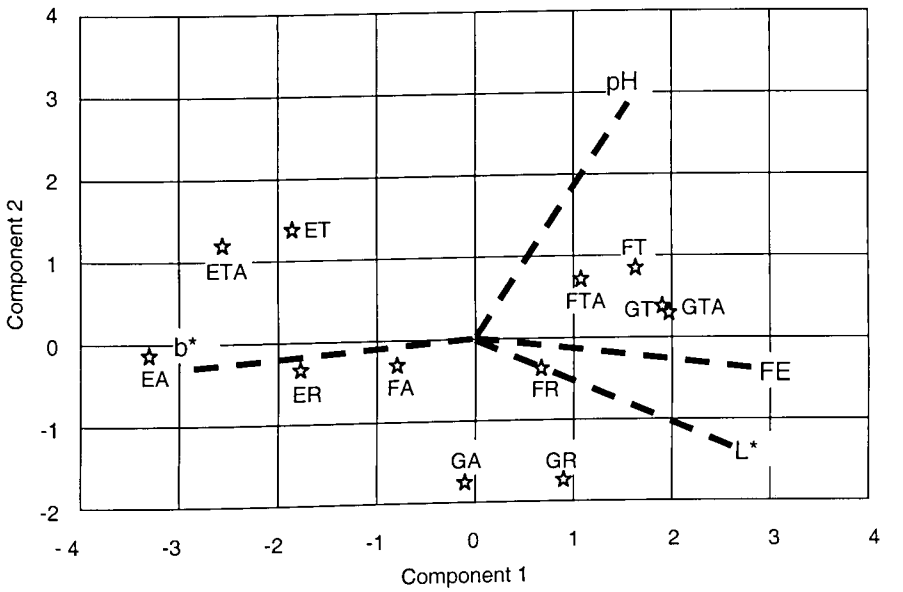

Fig. 10: Component weights and plots of the variables pH, CIE L*, CIE b* and Folding endurance (FE). For the letters EA, ET, ETA etc. representing paper samples and treatments cf. Table 2.

sis, PCA has been used successfully in many fields. It has been utilized in the laboratory of the SMSE for the examination of the correlation between crusts and degradation products of architectural surfaces and their causes[16, 17]. This is the first time it has been used for the investigation of the correlation among paper properties.

PCA could only be applied to the data pertaining to the sample series E, F and G, because every sample had one, definite value attributed to each variable. This was not the case for the samples of the A, B, C, and D series, where the samples were not uniformly coloured and where there was no definite value for the colour coordinates L* and b*. This did not reflect a shortcoming of either PCA or the experimental procedure but merely an inherent attribute of historic paper.

It is possible to see from the plot of the principal components (Fig. 10), that there is a significant relation between L* and folding endurance (FE) and a significant inverse relation between b* and FE. pH is not correlated significantly to any other variable. The correlation coefficient between FE and b* was calculated and was found to be equal to –0.88 (P-value = 0.0001). Since the P-value is less than 0.01, there is a statistically significant relationship between FE and b* at the 99% confidence level. This relationship was found for the non-lignin containing samples.

Discussion

Quality control of conservation treatments

It is believed that the experimental procedure followed in this study can be implemented for routine quality control of conservation treatments undertaken in a fairly well-organized institution, since it is relatively quick, convenient and inexpensive and can give clear-cut results:

- Six days of dry accelerated ageing can cause a sufficiently noticeable difference between treated and untreated samples and can be done easily and inexpensively.
- Fibre Optic Microscopy can provide information for the precipitation pattern of the deacidification agent and for structural changes. It is non-destructive and can be applied in situ.
- Folding Endurance is very sensitive to accelerated ageing; treated and untreated samples differentiate significantly.
- pH measurements exhibit significant differences between treated and untreated samples.
- Colorimetry can be used as an indicator of the efficiency of accelerated ageing before applying destructive tests on the samples. It gives valuable results concerning the aesthetics and the degree of chemical deterioration of the samples.

A deceleration of the deterioration of the paper properties after conservation was the general criterion for declaring whether a treatment had been successful. Other minor criteria were:

- Improvement of the measured property after treatment,
- Uniformity of precipitation of the deacidification agent,
- Small sized crystals of the deacidification agent on the paper,
- pH after deacidification between 7 and 8.5,
- pH after deacidification and ageing in the alkaline region,
- Increase in lightness (higher L*) and decrease in yellowness (lower b*),
- No alterations in the appearance of the treated samples.

Suitability of the conservation treatment

Quality control showed a significant improvement of the ageing rate of the treated samples. The mechanical properties were improved and the pH of the treated samples was well in the alkaline region and remained there after accelerating

ageing. The overall assessment of the conservation treatment was positive with two exceptions concerning the aesthetics:

1. The colour of the lignin containing samples deteriorated. The yellowing of these samples is attributed to the highly alkaline deacidification bath that caused lignin oxidation with the subsequent production of yellow substances that were insoluble in water and could not be removed in the deacidification bath. For colour difference between the treated and the untreated sample the formula of the CIE L*a*b* colour system was used[9]:

$$\Delta E = \sqrt{((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)}$$ where:

- ΔE : total colour difference,
- ΔL^*: difference in lightness,
- Δa^*: difference in the red-green axis
- Δb^*: difference in the yellow-blue axis.

ΔE was found to be between 1.3 and 5.7, exceeding in many cases the limit value of 2, above which the colour differences are distinctly discernible by the human eye[18]. To see the yellowing, the samples had to be put side by side. If not seen together, the difference is not noticeable. The colour deterioration was not, therefore, considered to be a major problem.

2. The deacidified papers were air-dried on a plastic grid. This is common practice at the KKE Archives. Observation of the treated samples revealed that the marks of the plastic grid were imprinted on many of the paper sheets. The places where the grid was in contact with the paper dried last, forming dark lines. This fact is considered to be of major importance, not only as an aesthetics concern. It is suspected that the gridline marks consist of degradation products of cellulose, which has been oxidized at the boundary of the wet-dry interface as the paper dried[19].

The results of the PCA indicate that for rag made paper or chemical pulp (with no lignin component), the colour coordinates L* and especially b* was strongly related to folding endurance. This implied that the more yellow a paper is, the less usable it is, which is what common sense suggests. This fact, if confirmed by further investigation, could be exploited in paper condition surveys, as the measurement of b* is very easy and quick and, most importantly, non destructive.

Suggestions for optimizing the treatment

Even if we considered the colour deterioration not to be a major problem, we modified the deacidification procedure in order to improve this property. For these tests as well untreated samples as those previously treated according to the

standard KKE described above were used: Samples were sprayed with a 50% ethanol solution prior to washing. They were washed for half an hour at a time in a bath of tap water at an ambient temperature with four changes of water. Colorimetry confirmed[13] that this resulted in better removal of coloured compounds. It has been thus recommended that papers are:

- sprayed with a 50% ethanol solution with water before washing,
- washed for longer, washing water changed several times,
- Pressed from time to time as they lie in batches in the basins during prewashing, in order to stir the water of the bath, treated in smaller quantities.

Moreover, we recommend that the papers are

- supported by Holytex or another non-woven, polyester tissue instead of the plastic grid currently used for support during the washing and drying of the paper. This would increase the cost of the treatment but it would reduce the possibility of accidents during washing and would definitely improve the appearance (and probably the life expectancy and durability) of the paper, since there would be no grid marks,
- dried under slight pressure to avoid cockling. It has been recommended that 4 weights of between 0.5–1 kg at each of the 4 corners of a board be used to press the drying papers and that it is necessary for the paper to be interleaved with Holytex tissue and blotting paper. This would allow 20 to 30 leaves of paper to be dried in a pile.
- Finally, KKE should consider replacing the deacidification agent (calcium hydroxide) with calcium bicarbonate[6]. The pH of the saturated calcium bicarbonate in water is about 6, which is closer to neutral than the pH of the saturated calcium hydroxide solution (pH • 12). The low pH value denotes that there will be no lignin oxidation problem, so there will be no or at least less paper discoloration. Moreover, that would result in a higher alkaline reserve, since calcium bicarbonate is more soluble in water (3.8 g/l at 20°C) than calcium hydroxide (1.63 g/l. at 20°C).

Conclusions

The results of this study show that the techniques, criteria and methodology used have been proved to be suitable for routine quality control of conservation treatments. Six days of accelerated ageing can effectively differentiate treated and untreated paper. Folding endurance, lightness (L*) and yellowness (b*) and pH represent fundamental mechanical, optical and chemical properties of paper and are sufficiently sensitive to accelerated ageing. A fibre optic microscope (FOM)

can be used instead of optical microscope for the structural examination of paper with good results. The main criterion for declaring a treatment as being successful was the decrease of the deterioration rate of the named paper properties due to the conservation treatment.

The conservation interventions applied to the material of the KKE Archives were successful, as the quality control indicated. The application of minor alterations (spraying with alcohol solution before prewashing and the use of non-woven polyester tissue) could optimize the deacidification procedure.

Summaries

Quality Control and Optimization of the Conservation Treatments Applied to the Material of the Archives of the Greek Communist Party

This study presents the quality control of the conservation treatment (deacidification with calcium hydroxide solution) applied to the paper of the Historical Archives of KKE (Greek Communist Party) after the flood of 1994.

Fundamental chemical, mechanical and optical properties of paper were examined (pH, folding endurance and the colour coordinates L* and b* of the CIE L*a*b* system), along with structural properties by fiber optics microscopy. The decrease of the deterioration rate of these properties of paper is one of the aims of conservation. The results showed deceleration of the deterioration of the measured properties due to the conservation treatment after 6 days of accelerated ageing at 105°C. Only the optical properties of the samples containing lignin degraded as a result of lignin oxidation in the highly alkaline environment of the deacidification bath. The principal component analysis revealed a strong relation between the colour coordinates and the mechanical strength of the samples without a lignin component. It is believed that the experimental procedure followed in this study can be utilized for routine quality control of the conservation treatments in a well-organized archival institution.

Contrôle de qualité et optimalisation des traitements de conservation appliqués aux documents des Archives du Parti Communiste Grec

Cette étude décrit le contrôle de qualité du traitement de conservation (désacidification au moyen d'une solution d'hydroxyde de calcium) appliqué au papier des Archives historiques du KKE (Parti Communiste Grec) après l'inondation de 1994.

Les propriétés essentielles du papier : chimiques, mécaniques et optiques ont été examinées (le pH, la résistance au pliage, les coordonnées des couleurs L* et b* du système CIE L*a*b*) ainsi que les propriétés structurales à l'aide de la méthode de microscopie des fibres optiques. Un des objectifs poursuivis par la conservation consiste à réduire le taux de dégradation des propriétés du papier. Les résultats ont mis en évidence que la dégradation des propriétés mesurées, obtenue après 6 jours de vieillissement accéléré à 105°C, ralentissait grâce au traitement de conservation. Seules les propriétés optiques des échantillons contenant de la lignine se sont dégradées suite à

l'oxydation de la lignine dans le milieu fortement alcalin du bain de désacidification. L'analyse des constituants principaux a révélé qu'il existe une forte corrélation entre les coordonnées des couleurs et la résistance mécanique des échantillons ne contenant pas de lignine. Il semble que l'utilisation de la méthode expérimentale appliquée dans cette étude puise être recommandée aux institutions d'archives bien organisées pour les tests de routine dans le contrôle de qualité des traitements de conservation.

Qualitätskontrolle und Optimierung der konservatorischen Behandlung des Archivgutes der Griechischen Kommunistischen Partei.

Es wird die Qualitätskontrolle nach konservatorischer Behandlung von Beständen des Historischen Archivs der Griechischen Kommunistischen Partei nach der Überschwemmung von 1994 beschrieben, d.h. nach Neutralisierung mit Calciumhydroxid-Lösung.

Es wurden die wesentlichen chemischen, mechanischen und optischen Papiereigenschaften (pH, Falzfestigkeit und die (Farbkoordinaten des CIE L*a*b* Systems) gemessen, und ebenso wurde die Faserstruktur unter dem Mikroskop untersucht. Den Rückgang solcher Qualitätsmerkmale zu verlangsamen ist das Ziel der Konservierung: Die Ergebnisse zeigen, daß die negative Veränderung der gemessenen Eigenschaften nach beschleunigter Alterung (105°C 6 Tage) als Folge der konservatorischen Behandlung verlangsamt wurde. Allerdings verschlechterten sich die optischen Eigenschaften der ligninhaltigen Proben: eine Folge der Oxidation des Lignins in dem hochalkalischen Neutralisierungsbad. Bei den ligninfreien Proben zeigte sich eine deutliche Korrelation zwischen den Farbmeßwerten und der mechanischen Festigkeit, Es wird die Meinung vertreten, daß die hier berichtete Vorgehensweise sich eignet zur routinemäßigen Qualitätskontrolle nach konservatorischen Behandlungen in gut organisierten Archiven.

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Paper Conservation Part II:

Consolidation by Grafting of Acrylic Monomers

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INTRODUCTION

The chemical structure of cellulose can be modified in different ways[1]:

- By replacement of the hydroxy groups with other functional groups: usually esterification or ether formation reactions are employed. This type of treatment reduces some of the less desirable characteristics of the material such as flammability and susceptibility to microbial attack.
- By reaction with bi- or polyfunctional compounds: these reactions afford cross-linking products and the global effect is the increase of the mechanical resistance of the material.
- By grafting reaction: this process combines synthetic polymers with cellulose and improves the characteristics of both the materials.

The synthesis of grafted copolymers seems to be the best approach for the consolidation of paper. In fact, if the appropriate co-monomer is chosen, it is possible to reduce the amount of water the cellulose-based material can absorb increasing its mechanical strength and making it less susceptible to chemical and biological attack.

Such a process has been researched and proposed by The British Library[2]. A grafting reaction is carried out on cellulose using mixtures of acrylic monomers: Ethylacrylate (EA) and methylmetacrylate (MMA). The two monomers are mixed as vapours and condensed on the paper. Copolymerisation is started by irradiating the system with gamma radiation from a Co-60 source for about 18 hours. The gamma radiation creates radical sites on the cellulose by extraction of hydrogen radicals. It can also create radicals originating from the monomers with the formation of EA/MMA non-grafted copolymers. This is an undesired effect, which reduces the effect of the grafting process to only about 10–20%. The insertion does not alter the aesthetic appearance of the treated paper and, at the same time, it improves both the paper's and the monomers' mechanical properties.

The main limitation of the The British Library's method is the Need to use high energy radiation for long periods to initiate the reaction, which causes considerable depolymerisation of the cellulose chains of the exposed samples. Although this method is being marketed, investigation into reducing these drawbacks is being undertaken.

The present work aims to improve the method proposed by The British Library by grafting vaporised acrylic monomers on cellulose and exposing the samples to ultraviolet (UV) radiation for a very short time[3,4,5]. UV is a low energy radiation and in contrast to gamma rays, does not induce the depolymerisation on cellulose[6]. It is a method based on physical initiation in which the presence of photosensitive agents is required. These can, but do not necessarily have to be linked to cellulose, they can be activated by UV radiation, and subsequently activate the cellulose.

The main idea of this method is to use, as linked photosensitive agents, the oxidised functional groups that are present in ancient documents and that derive from the action of oxygen in the air. The carboxyl and carbonyl groups are transformed into active sites on the cellulose that can then be employed for a grafting reaction. Along with the grafting reaction, a competitive homopolymerisation reaction is observed and should be minimised.

MATERIALS AND METHODS

The photo-initiated grafting reaction was carried out on Whatman No. 1 filter paper samples, which had been artificially oxidised by sodium metaperiodate and sodium hypochlorite, as described in Part I of this study[7]. The reaction was also transferred to a real sample of paper in order to verify the suitability of the method to impure cellulose samples.

- The oxidation conditions, common to the two oxidising systems, were:
- two hours of oxidation,
- T = 25°C,
- cellulose / oxidising system ratio: 1g/100 ml.
- The oxidation time was fixed at two hours because this is the time necessary for the complete depolymerisation of the cellulose molecule.

Since acrylic polymers are sufficiently transparent and form good films, we decided to employ their monomers. Methylmetacrylate, (MMA), ethylacrylate, (EA) and methylacrylate, (MA) from Aldrich were used as starting materials and were purified from the inhibitor (hydroquinone monomethylether) with an Inhibitor Remover column.

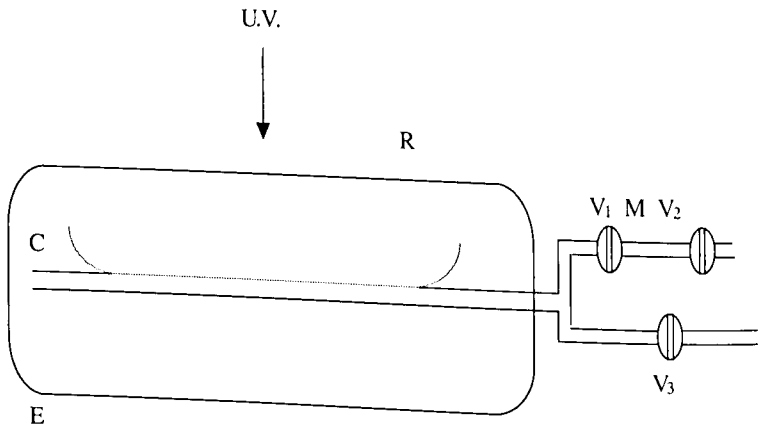

Fig. 1: Polymerisation unit. R: quartz reaction vessel; C: sample lodging area; M: monomer lodging area; E: vacuum connection; V_1, V_2, V_3: cocks. Reactor volume: 415 cm^3.

The polymerisation was carried out on samples "swollen" by treatment with deionised water. After the absorption of water the fibres were more accessible to the vaporised monomer, and were therefore more reactive. The cellulose samples were oven dried and weighed; then brought up to 150% of their original weight by soaking in deionised water. Before the swelling process, some of the samples were pre-treated with UV radiation. Three different radiation processing methods were used:

- under air;
- under vacuum;
- under a nitrogen atmosphere.

The grafting reactions were carried out by using the unit shown in Fig. 1. The cellulose sample was introduced into the reaction vessel (R) and the liquid monomer was loaded at M between V_1 and V_2. The reactor was connected, via E, to a vacuum pump and was evacuated; once the pressure of 0.1 mm Hg was reached, V_3 awas closed and the monomer vaporised and diffused into the reactor by opening V_1. The unit was then exposed to UV deriving from a metal iodide lamp: (150 W, colour temperature 3200°K) at a distance of 60 cm from the reactor surface. No cooling system was required since a low power lamp was used. All of the polymerisations were carried out at 28°C.

The polymerization reaction was stopped by bringing up the reactor to room pressure. The unreacted monomer was isolated by washing the fibers with methanol, a solvent for acrylic monomers only, not for the reacted polymers, and with water. After that procedure, the sample containing grafted cellulose and homo-

polymers was filtered on a tared gooch crucible (G3) and heated up to a constant weight. It was deemed better not to use soxhlet extraction of the homopolymer from the fibers as this system is not thoroughly efficient. Instead, extraction was performed using acetone in a closed vessel[8] under the following conditions:

- Sample: acetone ratio = 1 g / 100 ml;
- temperature: 38°C
- duration: 50 hours.

After the homopolymer had been extracted, the sample was filtered on a tarred gooch crucible and brought up to a constant weight.

The quantity of grafted monomer was evaluated as the weight increase of the sample after the extraction of the homopolymer; it is expressed as the percentage increase of weight.

$$\frac{\text{Sample weight after grafting - sample weight before grafting}}{\text{Sample weight before grafting}} \times 100$$

The grafting efficiency is defined as the ratio between the quantity of grafted monomer and the total polymerised monomer:

$$\frac{\text{Sample weight after grafting - sample weight before grafting}}{\text{Sample weight before extraction - sample weight before grafting}} \times 100$$

The grafted samples were submitted to FTIR analysis using a Brucker spectrophotometer IFS 66 with Globar source (silicon carbide rod brought up to incandescence) with a water cooling system and the OPUS data processing program. The samples were analysed with transmission measurements, i.e. by registering their absorbance. The sampling procedures are described above (Ref. 7 p. 79).

RESULTS

Grafting of samples oxidised by sodium metaperiodate

Results presented here concentrate on the grafting data of the Whatman No. 1 paper samples oxidised by sodium metaperiodate. The results enabled us to evaluate the role of the aldehyde groups as linked photosensitising agents and to optimise the insertion result.

As previously demonstrated, oxidation with sodium metaperiodate is specific and leads to the formation of one product only, that is aldehydic cellulose. Therefore, the grafting reaction carried out on this type of sample enabled us to evalu-

Table 1: Result of grafting in special conditions with several variables.

General conditions:
Polymerisation time = 60 min — Relation monomer:cellulose = 1.35 mmol / 100 g
Monomer: MMA — Polymerisation pressure = 0.1 mmHg
Sample: Whatman paper no. 1

Row	Special conditions	Variables	Influence on Grafting (%)	Efficiency of Grafting (%)	MMA conversion (%)
1	Oxidation with $NaIO_4$ for 2 h:	0	0	0	
2	mol/l	0.01	0.36	77.0	
3		0.1	11.00	81.5	
4	Oxidation with NaClO 3%	5	6	82	5
5	for 2 h:	8	9	88	8
6	pH	12	3	80	3
7	Pre-irridiation:	0	11	81	
8	min	15	33	83	
9		30	65	87	
10		45	57	87	
11		60	39	83	
12	Pre-irradiation on paper oxidised with	air	65	88	
13	$NaIO_4$ 0.1 mol/l:	vacuum	27	83	
14	Type	N_2	24	83	
15	Pre-irradiation on non-oxidised paper:	none	0	0	
16	Type	air	20	66	
17		vacuum	2	18	
18		N_2	3	18	

ate the ability of the aldehydic groups to act as photosensitising agents. This type of reaction also enabled us to reduce the number of variables of the system to a minimum. Unfortunately, it reproduced less accurately the natural ageing process when compared to oxidation with hypochlorite (a non-specific oxidising agent); oxidation produced by oxygen in the atmosphere is non-specific. Oxidation with hypochlorite leads to the formation of carboxyl and carbonyl groups, i.e. to three types of linked photosensitive agents. If only one of these functional groups were responsible for the activation, it would be impossible to identify it by working on this type of sample.

Effect of the oxidation grade of the samples

To evaluate the dependence of the grafting yield on the concentration of sodium metaperiodate, i.e. on the oxidation grade of the samples, the reaction was carried out on samples oxidised by $NaIO_4$ 0.01 M and 0.1 M. At the same time, the polymerisation reaction was also carried out on an untreated Whatman sample, i.e. on a sample that had not been oxidised. The results are given in Table 1 Row 1–3. From the data it can be seen that on the non-treated Whatman paper no insertion occurs; this confirms the role of the oxidised functional groups on the photosensitising process.

The data of the polymerisations carried out on the oxidised samples, show that the grafting percentages were very different, nevertheless the efficiency of grafting was acceptable even for the samples oxidised by 0.01 M metaperiodate. Finally, it can be concluded that:

- the grafting reaction prevails on the homopolymerisation reaction,
- by increasing the concentration of the oxidising agent by ten times, the grafting percentage was about thirty times higher.

The study of the grafting reaction and its optimisation were therefore carried out on Whatman No. 1 paper samples oxidised by sodium metaperiodate for two hours.

Effect of the polymerisation time

Table 2 Rows 1–6 and Fig. 2 show the results of the dependence of the yields against the polymerisation time. The reproducibility of the reaction was evaluated: the error is ± 1%. As predicted, by raising the polymerisation time, the yields increased until a constant value was reached after about ten hours. The reaction terminated once 80–85 % of the conversion of the monomer was reached; The reaction can be considered to be complete after ten hours.

The most important parameter to study in the grafting reaction is the percentage grafting efficiency. It describes the percentage of monomer that is converted into homopolymer. The two values are related by the following relationship:

$$\% \text{ homopolymer} = 100 - \% \text{ Efficiency of Grafting}$$

Analysing the data given in Table 2 Rows 1–6 it can be observed that, raising the reaction time, caused the ratio between the inserted monomer and the monomer converted into homopolymer to remain practically constant: the average

Table 2: Result of grafting in various conditions.

General conditions (if not given otherwise below):
Polymerisation time = 60 min
Monomer: MMA — Relation monomer:cellulose = 1.35 mmol / 100 g
Sample: Whatman paper no. 1 — Polymerisation pressure = 0.1 mmHg

Row	Conditions	Variables	Influence on Grafting (%)	Efficiency of Grafting (%)	Monomere conversion (%)
1	Polymerisation time: min				
2		60	11	82	
3		120	21	82	
4		180	32	84	
5		300	54	84.3	
6		480	86	84	
		600	96	88	
7	Polymerisation time				
8	after 30 min pre-radiation: min	30	18	89	
9		60	65	87	
10		90	66	81	
		120	67	80	
11	Pressure during 2 h: mmHg				
12		0.1	21	82	16
		0.3	15	73	16
13	Relation monomer:cellulose: mmol:100g				
14		0.80	7.64	84.4	24.0
15		1.35	65.0	87.4	56.5
		2.31	48.6	42.2	22.6
16	Type of monomer				
17		MMA	65	88	57
18		MA	28	93	23
		EA	14.5	85	12
19	Historic paper (1750)		18.5	87	16.3

percentage grafting efficiency is 84 %. This result is very good and demonstrates that the grafting reaction predominated the homopolymerisation reaction: the reaction conditions are not favourable to the formation of PMMA. To confirm this result, the reactor was loaded with MMA without the presence of the cellulose sample, brought up to the pressure of 0.1 mmHg and exposed to UV: no formation of PMMA was observed under these conditions.

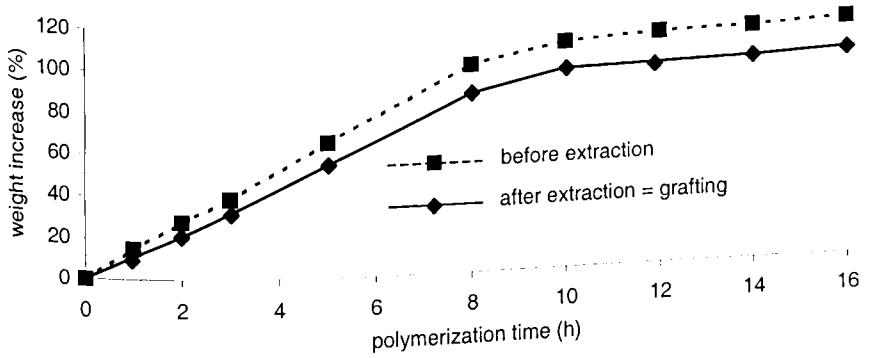

Fig. 2: Increase in weight during polymerisation time.

Effect of the pressure

The grafting efficiency was also influenced by the pressure at which the reaction was carried out. If the other variables remained constant, the grafting efficiency increased with the lower pressure. From Table 2 Rows 11 and 12 it can be seen that increasing the pressure by three times, the total conversion of the monomer was not changed, but the ratio between the grafted monomer and the homopolymer decreased, together with the percentage grafted monomer. For this reason, all of the tests were carried out at a pressure of 0.1 mmHg, which was the minimum experimental value of our unit. The experimental results obtained up to now demonstrated the effectiveness of this grafting method: only small quantities of homopolymer being formed.

In order to increase the grafting yields even more, some experiments of photoinitiated polymerisation were performed using Whatman paper samples previously oxidised by metaperiodate and irradiated with UV. This treatment aimed at bringing the monomer in contact with cellulose chains, the aldehyde groups of which were already "activated". This causes the reaction time to be shorter and the homopolymerisation reaction to be reduced. Table 1 Rows 7–11 and Fig. 3 give the results obtained after pre-irradiation in air. The two curves are characterised by a maximum that corresponds to a pre-irradiation time of 30 minutes; at longer pre-irradiation the activation of the samples and the yields decreased. It can therefore be concluded that the ideal pre-irradiation time is 30 minutes. The grafting percentage that was obtained by submitting the oxidised Whatman paper to pre-irradiation and to one hour polymerisation (Fig. 4) was higher than that obtained after five hour grafting carried out on non-irradiated oxidised samples (Fig. 2). These results are very good: pre-irradiation reduced the formation of the

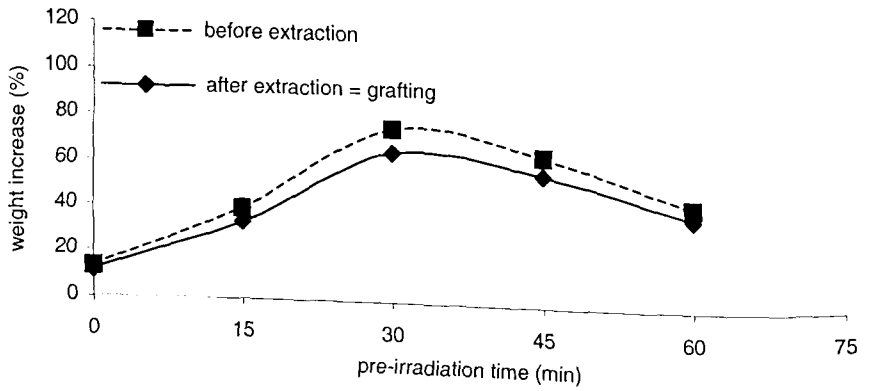

Fig. 3: Increase and decrease of weight as result of increased pre-irradiation time.

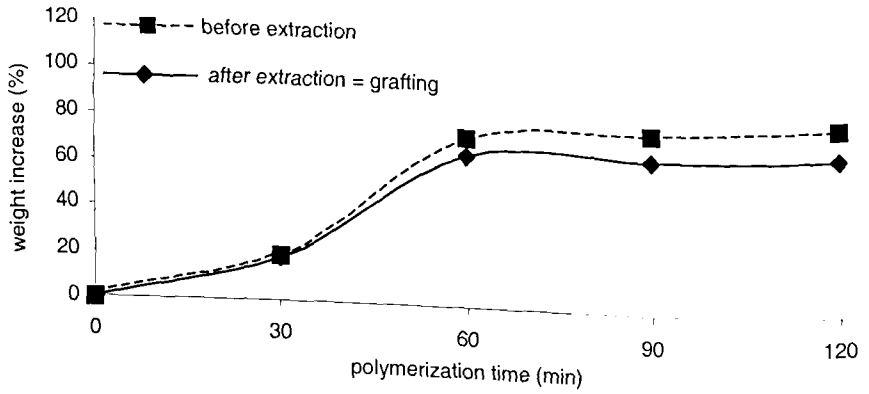

Fig. 4: Increase in weight during polymerisation time of samples submitted to the ideal pre-radiation time.

homopolymer without affecting the grafting yields. Furthermore, the reaction time was 20% of that necessary for non pre-irradiated samples.

As for the samples submitted to the ideal pre-radiation time of 30 minutes, we have studied the grafting yields vs. the polymerisation time, Table 2 Rows 7–10 and Fig. 4 give the results. The activation time was chosen on consideration of the previous results. Analysing the data, it became evident that it was more convenient to carry out the polymerisation on pre-irradiated samples rather than on simply oxidised samples. The polymerisation time was much less: in one hour the percentage of grafting of a pre-irradiated sample was comparable to that obtained in five hours on a non pre-irradiated one.

From Fig. 4 it becomes evident that the percentage of grafted sample can be considered as being constant after 60 minutes, whereas the percentage of mono-

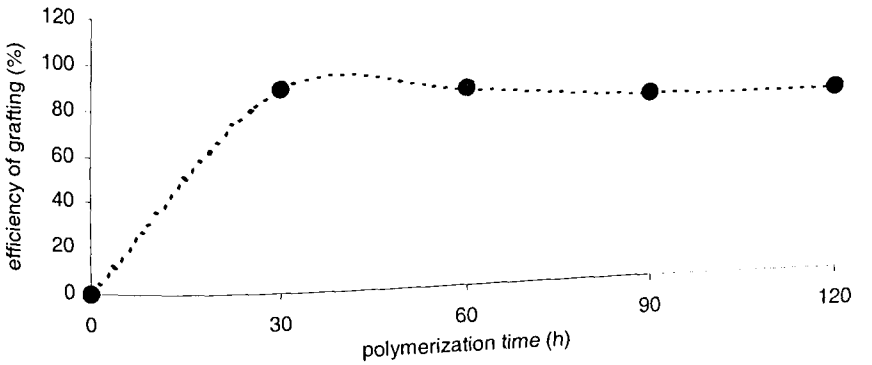

Fig. 5: Dependence of grafting efficiency on polymerization time.

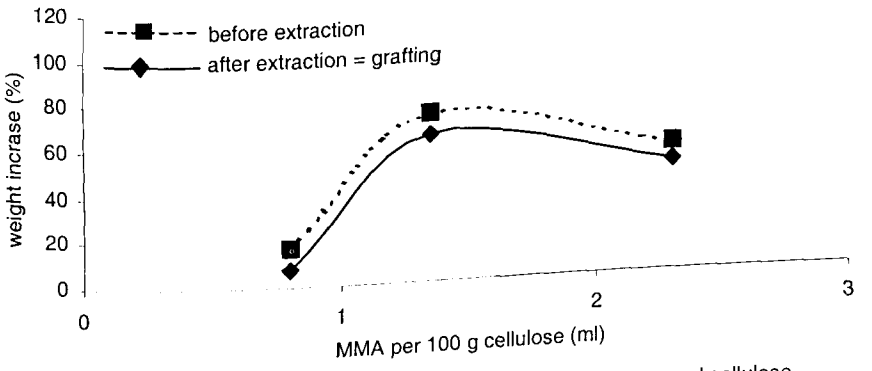

Fig. 6: Increase in weight depending on the relation between monomer and cellulose.

mer added to the fibres is slightly higher. This means that the maximum percentage of grafting is obtained after one hour of polymerisation and that afterwards the monomer is converted only into homopolymer. The data of the efficiency of grafting (Fig. 5) confirm this result. The grafting efficiency initially increased and for polymerisations between 30 and 60 minutes the percentages were higher compared to those of the reactions carried out on simply oxidised samples (84%: Table 2 Row 1–6).

Effect of the monomer/polymer ratio

In order to evaluate the possibility of controlling the quantity of inserted monomer, we carried out polymerisation reactions with different percentages of mono-

mer/cellulose, i.e. the quantity of monomer employed per 100 g of cellulose sample submitted to grafting reaction. The data are given in Table 2 Rows 13–15 and in Fig. 6.

The weighed gain of the samples, as predicted, was influenced by the ratio between the employed monomer and the quantity of sample submitted to the grafting reaction. The ideal monomer/cellulose ratio is 1.35 mmol MMA/100g of sample; for this value the grafting percentage was high and the grafting efficiency showed that the insertion reaction significantly prevails over the homopolymerisation. Furthermore, the conversion of the monomer (depending on the monomer/sample ratio) reaches the optimal values.

Effect of the type of pre-irradiation

The experimental data show that it was appropriate to submit the oxidised cellulose sample to UV in air since, the insertion yields were high, the reaction time was reduced and the quantity of homopolymer was minimised. In order to obtain some information on the type of activation produced by the pre-irradiation, the grafting reactions were carried out on samples submitted to pre-irradiation under vacuum (P = 0.1 mmHg) and under a nitrogen atmosphere. The pre-irradiation time (30 minutes) and the polymerisation time (1h) were maintained as constants in all of the experiments.

Table 1 Rows 12–14 lists the data relative to the oxidised samples and the following four rows 15–18 those of the insertion on non-oxidised Whatman paper.

The results of the oxidised samples show that the activation was higher in the presence of oxygen: under these conditions the grafting percentage was more than double that obtained under vacuum and under a nitrogen atmosphere. This result seems to indicate that the activation of the sample occured with a photo-oxidative mechanism. The grafting efficiency was very good for all of the experiments: the UV activation of the samples, in all of the cases, favoured the grafting reaction vs. the homopolymerisation.

A confirmation of the synergetic action of the pre-irradiation and the presence of oxygen in the activation of the samples is obtained by the data of the non oxidised Whatman paper. For the untreated paper neither grafting reaction nor homopolymerisation reactions were observed; in the samples submitted to pre-irradiation under vacuum and under a nitrogen atmosphere the grafting percentage was very low (at the limit of the experimental error on the measurements) and the grafting efficiency was below 50%: the homopolymerisation reaction prevailing on the insertion. For the pre-irradiated, non oxidised paper under an oxygen atmosphere the grafting percentage was 20% and the grafting efficiency

reached 66%: the insertion reaction prevailing on the homopolymerisation. Therefore, the synergetic action of UV and of oxygen activated a substrate, such as non-treated paper, in which the only oxidised functions were the hydroxy groups of the pyranose ring and the terminal aldehyde functions. This demonstrates that not only the aldehyde functions but also the others (produced by a random oxidation) are able to induce the insertion reaction. It should also be taken into account that under these conditions the depolymerisation reaction was limited to 7% and the insertion reaction cannot be attributed to the cleavage of the glucosidic bond.

Grafting of samples oxidised by sodium hypochlorite

Another confirmation of the fact that the reaction does not depend on the nature of the oxidised functional groups becomes evident from the results of the grafting reaction carried out on Whatman paper samples oxidised by hypochlorite. In fact, the products of this reaction were heterogeneous and depended on the pH. Under very alkaline conditions, carboxyl groups were preferentially formed, while under slightly alkaline or acid conditions, carbonyl groups predominated.

In the previous study the grafting and UV activation method was optimised, having considered the results of experiments carried out on Whatman paper samples oxidised by metaperiodate. In a follow-up experiment this method was used for samples oxidised by hypochlorite at different pH values (5, 8, 12). The data of these experiments are listed in Table 1 Rows 4–6. The data show that, even if the conversion of monomer was low, the efficiency of grafting reaches values only slightly smaller than those obtained with the grafting reaction on samples oxidised by $NaIO_4$: the grafting reaction prevailing over the homopolymerisation.

Grafting on a naturally oxidised paper sample

The grafting reaction on Whatman No. 1 paper samples, artificially oxidised, enabled us to study the influence of different variables on the insertion reaction on pure cellulose, i.e. on a sample without "interferences" due to the presence of lignin, hemicelluloses, glues and inks. But "real" paper is not only made out of pure cellulose. It is, in fact, a heterogeneous material made out of a mixture of fibrous pulps of vegetable origin, of minerals and chemical additives of different natures. It might therefore be possible that the presence of these other materials could interfere with the grafting reaction. The oxidising action of oxygen in the air has been proved to be non-specific; i.e. none of the positions of the pyranose ring are

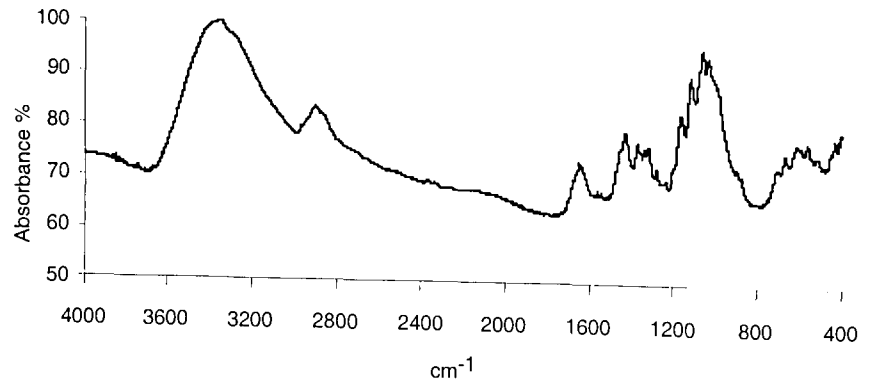

Fig. 7: FTIR-spectrum of a real paper sample produced ca. 1750.

preferentially attacked. It is might be possible that the optimal insertion and activation conditions of the Whatman paper samples are not directly applicable to real paper. In order to evaluate this possibility, the method was applied to a naturally aged paper sample dated 1750 from a private collection.

The FTIR spectrum of the sample submitted to thermic treatment under vacuum is given in Fig. 7. It shows the following absorption typical for cellulose or paper respectively:

- OH stretch: 3400 cm^{-1};
- CH_2 and CH stretch between 2999 and 2800 cm^{-1};
- peak of the water absorbed by the fibres: 1652 cm^{-1};
- non-symmetric stretch of the oxygen bond 1162 cm^{-1};
- beta oxygen bond: 895 cm^{-1};
- the absorption of gelatine: 1535 and 1652 cm^{-1};
- the absorption typical of the hemicelluloses as "shoulders" at the peak of the absorbed water.

The analysis also revealed the absence of lignin, unsurprisingly, as a paper from 1750 would be made of rag. The appearance of the shoulder around 900 cm^{-1} shows that that the sample was not submitted to a strong alkaline treatment. Most relevant for the study of the nature of the oxidised functional groups is the absence of the absorption of C=O in the carbonyl group region. This would lead us to exclude the presence of keto or aldehyde groups. Though, we cannot exclude the presence of carboxyl groups, as their absorption is covered by the peak for water.

The sample was activated by pre-irradiation in air (30 min) and then submitted to grafting (1h). The results, listed in Table 2 Row 19, show that the reaction can be extended to real samples; the efficiency of grafting proves that even if the process is carried out on an impure cellulose sample, the grafting reaction prevails over the homopolymerisation: the percentage of homopolymer is in fact low: only 13%. The grafted sample is less yellow compared to the initial sample: this is probably a consequence of the exposure to UV. Furthermore, even if the inserted monomer is methylmetacrylate, the sample did not assume a sticky consistency.

The grafting reaction on samples oxidised by sodium metaperiodate and activated with pre-irradiation can be extended also to other acrylic monomers. Some experiments have been carried out by employing methylacrylate and ethylacrylate (Table 2 Rows 16–18) and using the same oxidation, activation and grafting conditions previously optimised.

The higher percentage of grafting was obtained with methylmetacrylate (MMA): the quantity of grafted copolymer was higher than that with methylacrylate (MA) and ethylacrylate (EA). However, in the case of MA the formation of homopolymer was practically negligible. The efficiency of grafting was the highest. Less satisfactory results were obtained with EA. In all cases the grafting reaction prevailed significantly over the homopolymerisation and the percentages of homopolymer were considerably low; they varied between 15 and 7%.

FTIR ANALYSIS

Both the Whatman paper samples and the grafted copolymers were submitted to FTIR analysis. The analyses were carried out after the extraction of the homopolymer from the fibres.

The presence of inserted polymer chains is indicated by the peak of the synthetic polymer around 1670 cm^{-1}. Figs. 8 and 9 are relative to the most significant FTIR spectra. Fig. 10 is the spectrum of PMMA; here the peak of COOCH is observed around 1700 cm^{-1}.

CONCLUSIONS

The results obtained in this work demonstrate that it is possible to carry out a photo-initiated grafting reaction of vaporized acrylic chains on the oxidised cellulose macromolecule and the grafting yields are remarkable even for relatively short reaction times. This is especially true if the oxidized cellulose is previously submitted to UV irradiation.

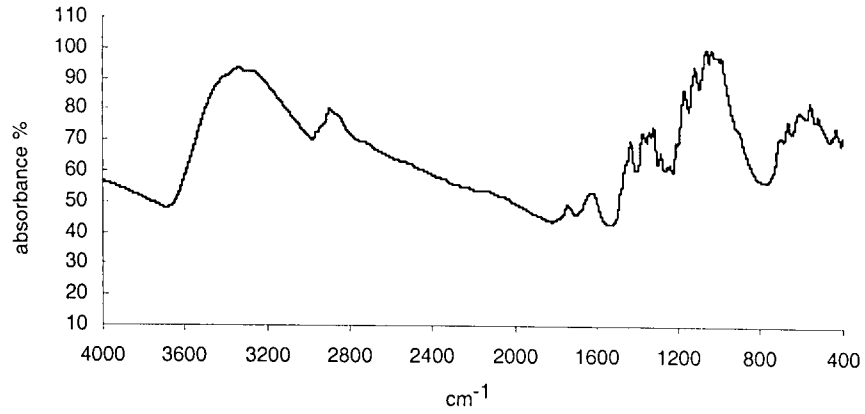

Fig. 8: FTIR-spectrum of a Whatman paper oxidized by $NaIO_4$ 0.1 M (t_{ox} = 2h)

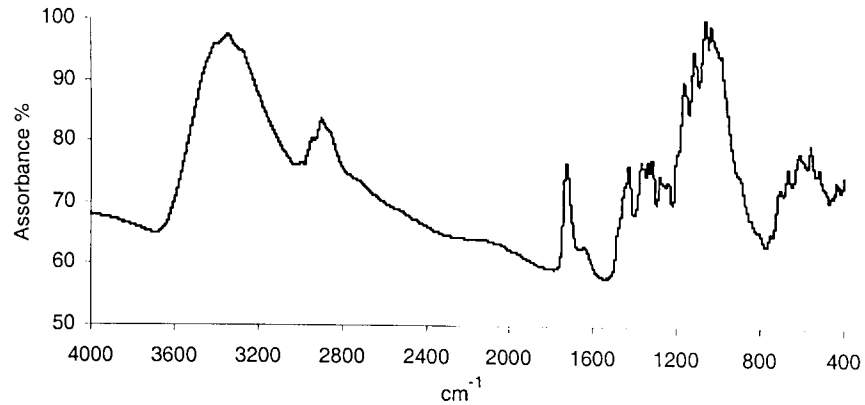

Fig. 9: FTIR-spectrum of a Whatman paper oxidized for 2 h by $NaIO_4$ and grafted with MMA.

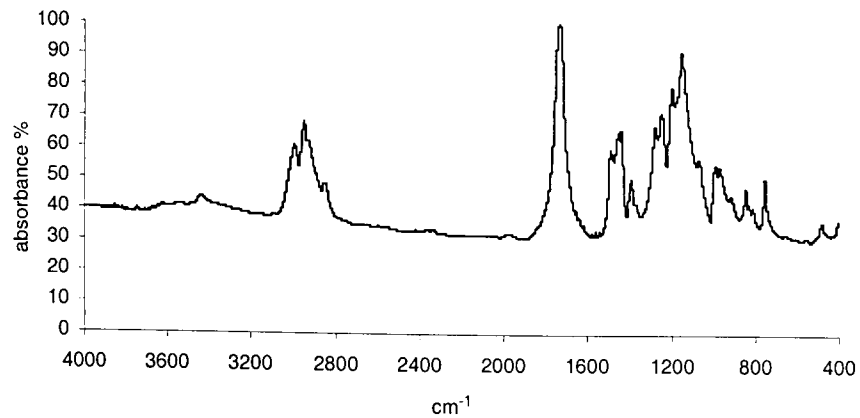

Fig. 10: FTIR spectrum of PMMA. (KBr disk).

Furthermore, it has been demonstrated that it is particularly convenient to work with vaporized monomers since all the problems related to the use of liquid or monomers in solution are avoided. Using vaporized monomers represents a non-conventional system. Another advantage is that the quantity of homopolymer extracted from the fibres is drastically reduced (7–20%) and the access to the fibres is facilitated by employing samples "swollen" with deionised water. Finally, the absence of the solvent avoids also all the problems related to the solubility of the monomer.

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The authors thank professor B. Focher from the *Stazione Sperimentale per Carta, Cellulosa e Fibre Naturali* (experimental Centre for Paper, Cellulose and Natural Fibres) in Milan for the useful suggestions given during the development of this research work.

SUMMARIES

Paper Conservation Part II: Consolidation by Grafting of Acrylic Monomers

In the present work a consolidation method for cellulose or paper is proposed, based on the insertion of an acrylic monomer on the cellulose macromolecule, exploiting its active sites deriving from oxidation. The acrylic monomers used are: methylmetacrylate, ethylacrylate and methylacrylate in the form of vapour and the copolymerisation reaction photo-induced by UV. Some parameters of the reaction have been studied and in particular the ratio of monomer conversion to the polymerisation time. Furthermore, this research focuses on the importance of the pre irradiation of the samples. The work has been carried out on pure cellulose, artificially oxidised with the purpose of applying the method to naturally aged paper documents.

Conservation du papier 2ème partie: Consolidation au moyen de greffe de monomères acryliques

Dans la présente étude on propose une méthode de consolidation de la cellulose ou du papier qui est basée sur l'insertion d'un monomère acrylique dans la macromolécule de cellulose en exploitant ses groupes réactifs dérivant de l'oxydation. Les monomères acryliques utilisés sont : le méthacrylate de méthyle, l'acrylate d'éthyle et l'acrylate de méthyle sous forme gazeuse et la copolymérisation est induite par l'action des rayons ultra-violets. Différents paramètres de cette réaction ont été étudiés et en particulier le rapport entre le degré de la conversion monomère et la durée de la polymérisation. En outre, cette recherche se concentre sur l'importance de l'irradiation préalable des échantillons. L'étude a été réalisée sur de la cellulose pure oxydée artificiellement dans le but d'appliquer cette méthode aux documents en papier vieillis naturellement.

Papierkonservierung Teil II: Festigen durch Aufpfropfen monomerer Acrylate

Es wird eine Methode zum Festigen von Cellulose bzw. Papier vorgeschlagen, die auf dem Einbringen monomerer Acrylate in das Cellulose-Mamromolekül basiert, wobei dessen durch natürliche Oxidation entstandenen reaktiven Gruppen eine Rolle spielen. Die monomeren Acrylate sind gasformges Methylmetacrylate, Ethylacrylate and Methylacrylate, und die Copolymrisation wird durch UV-Bestrahlung initiiert. Es wurden verschiedene Parameter dieser Reaktion untersucht, insbesondere das Verhältnis des Ausmaßes zur Dauer der Polymerisation. Sodann wird die Bedeutung einer der Polymerisation vorgeschalteten Bestrahlung des zu festigenden Papiers betont. Die Versuche wurden an reiner Cellulose durchgeführt, die jedoch künstlich oxidiert worden war, um zu zeigen, daß die Methode auch auf natürlich gealtertes, d.h. in jedem Falle oxidierte Gruppen enthaltendes Papier angewandt werden kann.

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Treatment of Parchment Fragments of a Hebrew Bible

by SVETLANA GURKINA & NATALIA REBRIKOVA

Introduction: The Object

The Department of Manuscripts of The Russian National (ex-Public) Library in St. Petersburg includes more than 15,000 Hebrew manuscripts and fragments. A large number of them come from the famous collection of Abraham Firkovich. Some of the codices from this collections have suffered in the past and are in a particularly poor state of preservation. Two fragments from the Firkovich collection entered the State Research Institute for Restoration in Moscow in 1992. One of them, dating from the fifteenth century (RNB, Ist collection of Firkovich, N 92), was of special interest because of the nature of its damage and because of the treatment decided on for its repair[1,2].

Damage

The fragment in question is part of The Book of Prophets (the end of the 22nd and beginning of 23rd chapter of Jeremiah). It had been originally a large parchment bifolio with text written in two columns of 31 lines. Now, part of the text and all the margins have been cut off. The velvety surface of the parchment was severely deformed and soiled. There were many vertical and horizontal ruptures with losses. Thinning and decaying of the parchment was observed in the ruptured areas. The edges of tears were creased.

The iron gall ink had been applied in a thick, heavy layer, which was probably the reason why the parchment had deformed. The surface of the ink appeared to be covered by tiny craquelure. In the upper part of the bifolium, which had suffered considerable losses of parchment, a brown, horny stain pierced with small holes had formed. This rigid stain appears to have created associated cockling.

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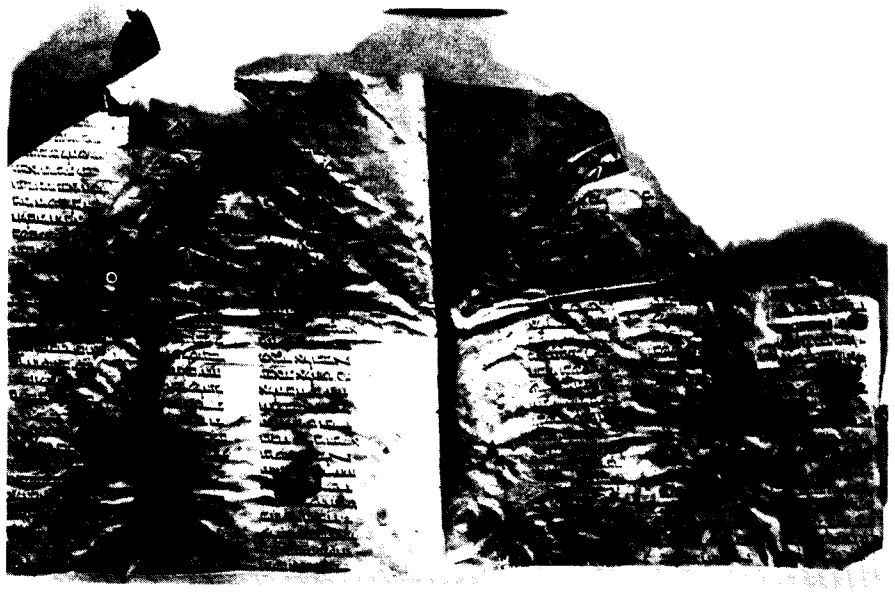

Fig. 1. The bifolio before treatment. The parchment was cockled; the margins and part of the leaf had been cut off; in the damaged sections the parchment was very thin and fragile; light and dark blood stains were distinguishable on the surface; in the upper left part of the folio a rigid, horny stain with small holes was evident; the ink was flaking away.

All surfaces were marked by extensive, dark brown stains many of which have penetrated to both sides of the parchment (Figs. 1 and 2).

Blood stains

Preliminary microscopic examination gave reason to suppose that the stains were caused by blood. This supposition was confirmed by The Republican Center of Forensic Investigation. It was impossible to determine whether the blood was that of a human being or of an animal. The dark brown colour of the stains can be considered to be the result of a reaction between blood and partly dissolved ink. Blood stains are rarely seen in documents requiring treatment and are not usually considered the type of dirt that should be removed. On the contrary, conservator-restorers will try to preserve such stains, because they could be considered as having important historical evidence. In this particular case, however, it was decided that the text should be made more visible and the deformation of the parchment eliminated and so an attempt was made to remove the blood stains as far as possible.

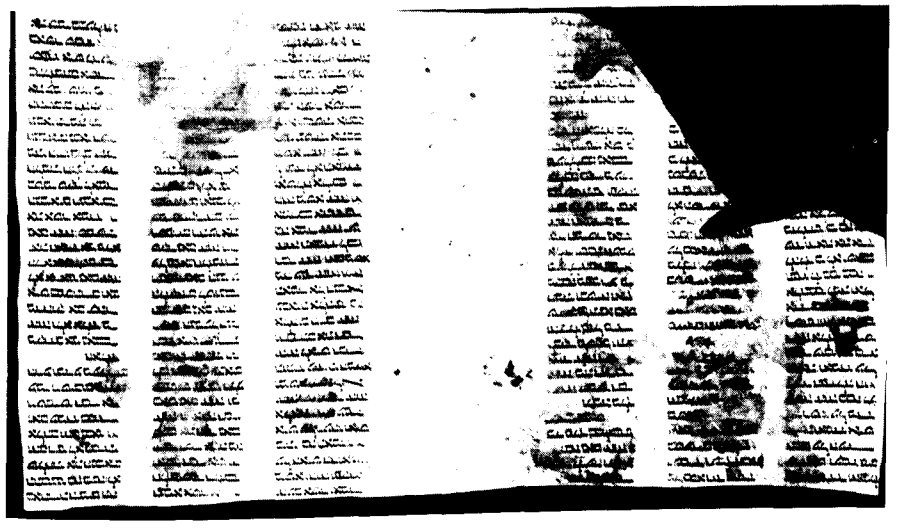

Fig. 2. The bifolio after treatment. The parchment has been flattened; the dirt from the surface has been eliminated as much as possible; the blood stains have been removed and the brownish hue of the stains has lessened; the tears and losses have been repaired using new parchment.

Treatment

Initially, surface dirt was removed from those sections of parchment, which were free of text by applying a soft eraser. Fragile layers of ink were then consolidated by an application of a 2% solution of the copolymer ethylene with vinylacetate (CEV) [3, 4]. After treating the flaking ink on the text, the surface of the parchment was cleaned more thoroughly than before, especially between the text lines and between separate words and letters. This process was carried out using small cotton-wool swabs moistened in a solution of distilled water and ethyl-alcohol (1:1).

Removing blood stains using enzymes

The most challenging problem was the choice of the right method to reduce the intense dark brown colour of the blood stains. Usual compounds applied for this kind of treatment, such as a 2% aqueous-alcohol solution of peroxide, or mixtures of benzene and ethyl-alcohol in different concentrations, appeared not to be effective. As the basic part of these stains includes globular proteins – haemoglobin, albumen of blood serum, etc. – it was decided to apply a proteolytic enzyme,

which would facilitate the removal of inveterate protein strata (clots) at room temperature and at a neutral pH. Use of such substances has had a long medical history, particularly in the application of burn and wound treatment to eliminate necrotic tissue and blood clots. We chose the proteolytic preparation, chemotripsin, that contains two proteinases compounds (trypsin and chemotripsin) with optimal action at a mildly alkaline pH. The choice of a suitable mixture was also determined by the knowledge that proteinases are used in dressing leather and fur to soften the hides. The advantages of using enzymes includes their high activity and selectivity. Thus, the destruction of proteins in the interfibrillar matrix facilitate their removal and in this case proteinases do not have a damaging effect on a basic component of the parchment support itself, the fibrillar protein, collagen. Collagen is a substratum of specific proteinases of microbic origin, that are known as collagenases.

Precautions

The application of enzymes for the removal of protein strata from parchment should be carried out with caution, as partially denaturated collagen in heavily damaged sections may be hydrolized by an unspecific proteolytic substance. In medical practice chemopsin is employed as a 0.05% solution in tris-HCI buffer pH 7.2–7.4[5].

For the treatment undertaken on the parchment fragment we used the same solution applied with the help of slightly moistened cotton-wool swabs. The blood stained section under treatment was covered by polyethylene film with a light weight placed on top. After 10–15 minutes the compress was removed. The action of the compound on the hardened sections of parchment resulted in an improvement of its texture causing it to become softer and more elastic. The treated section was then immediately swabbed by the buffer. A few layers of blotting paper were placed beneath and on top of the treated stains; with the help of a slight stroke of the fingers the blotting paper absorbed the softened dirt. This process was repeated a few times until No further discolouration residues were noticeable on the blotting paper. A layer of brown dirt was noticeable in the area of the stain. This dirt was easily removed by using a scalpel The remnants of dirt were collected with the help of cotton-wool swabs moistened by a solution of distilled water and ethyl alcohol. The procedure took some time and may continue for several days. The treatment of the horny-textured stains was stopped as soon as traces of ink appeared, i.e. when text, that had not been visible before appeared. The layers of ink were treated with 2% aqueous-alcohol solution of CEV[3].

CONCLUSION

The conservation treatment as described resulted in considerable lessening of the dark brown discolouration of the blood stains. The damaged parchment, after this treatment, had lost its rigidity and deformations and had to a large extent regained its original, soft velvety texture. The method of applying enzymes in this particular case appeared to be more effective and perhaps more inoffensive than other traditional methods of softening parchment (urea treatment, PEG), which sometimes make it transparent and fragile.

As already said, it was impossible to determine the origin of blood stains, although, it is likely that they reflect the turbulent and difficult history of the manuscript. Because their history was unknown however it was felt that their removal would be more beneficial. Therefore, our work can be considered not only as a proposal for a different method of conserving a mediaeval manuscript but also as making a modest contribution towards helping make available a Hebrew manuscript, which was previously unreadable.

SUMMARIES

Treatment of Parchment Fragments of a Hebrew Bible

A method is described for eliminating blood stains from the fragments of a fifteenth-century Hebrew manuscript, using the proteolytic enzymes tripsin and chemotripsin.

Traitement de fragments de parchemin d'une Bible hébraïque

On décrit comment des vieilles taches de sang ont été éliminées des fragments d'un manuscrit hébraïque datant du 15ème Siècle à l'aide d'enzymes protéolytiques, la trypsine et la chemotrypsine.

Behandlung von Pergamentfragmenten einer hebräischen Bibel

Es wird beschrieben, wie gealterte Flecken und Klumpen von Blut aus den Fragmenten einer hebräischen Bibel aus dem 15. Jh. mit Hilfe von proteolytischen Fermenten, Trypsin Chemotrysin, entfernt wurden.

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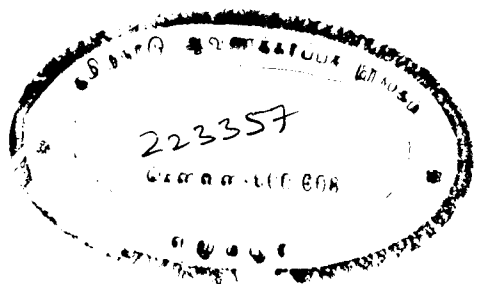

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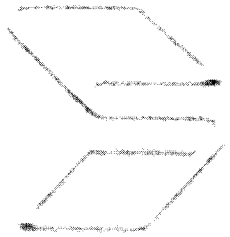

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